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Vijay P. Singh
Shalini Yadav
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Water Quality Management

Select Proceedings of ICWEES-2016

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Preface

Fundamental to sustainable economic development, functioning of healthy ecosystems, reliable agricultural productivity, dependable power generation, maintenance of desirable environmental quality, continuing industrial growth, enjoyment of quality lifestyle, and renewal of land and air resources is water. With growing population, demands for water for agriculture and industry are skyrocketing. On the other hand, freshwater resources per capita are decreasing. There is therefore a need for effective water resources management strategies. These strategies must also consider the nexus between water, energy, environment, food, and society. With these considerations in mind, the International Conference on Water, Environment, Energy and Society (WEES-2016) was organized at AISECT University, Bhopal, Madhya Pradesh, India, from March 15 to 18, 2016. The conference was fifth in the series and had several objectives.

The first objective was to provide a forum to not only engineers, scientists, and researchers, but also practitioners, planners, managers, administrators, and policy makers from around the world for discussion of problems pertaining to water, environment, and energy that are vital for the sustenance and development of society.

Second, the Government of India has embarked upon two large projects one on cleaning of River Ganga and the other on cleaning River Yamuna. Further, it is allocating large funds for irrigation projects with the aim to bring sufficient good quality water to all farmers. These are huge ambitious projects and require consideration of all aspects of water, environment, and energy as well as society, including economics, culture, religion, politics, administration, law.

Third, when water resources projects are developed, it is important to ensure that these projects achieve their intended objectives without causing deleterious environmental consequences, such as waterlogging, salinization, loss of wetlands, sedimentation of reservoirs, loss of biodiversity.

Fourth, the combination of rising demand for water and increasing concern for environmental quality compels that water resources projects are planned, designed, executed, and managed, keeping changing conditions in mind, especially climate change and social and economic changes.

Fifth, water resources projects are investment-intensive, and it is therefore important to take a stock of how the built projects have fared and the lessons that can be learnt so that future projects are even better. This requires an open and frank discussion among all sectors and stakeholders.

Sixth, we wanted to reinforce that water, environment, energy, and society constitute a continuum and water is central to this continuum. Water resources projects are therefore inherently interdisciplinary and must be so dealt with.

Seventh, a conference like this offers an opportunity to renew old friendships and make new ones, exchange ideas and experiences, develop collaborations, and enrich ourselves both socially and intellectually. We have much to learn from each other.

Now the question may be: Why India and why Bhopal? India has had a long tradition of excellence spanning several millennia in the construction of water resources projects. Because of her vast size, high climatic variability encompassing six seasons, extreme landscape variability from flat plains to the highest mountains in the world, and large river systems, India offers a rich natural laboratory for water resources investigations.

India is a vast country, full of contrasts. She is diverse yet harmonious, mysterious yet charming, old yet beautiful, ancient yet modern. Nowhere can we find as high mountains as snowcapped Himalayas in the north, the confluence of three seas and large temples in the south, long and fine sand beaches in the east as well as architectural gems in the west. The entire country is dotted with unsurpassable monuments, temples, mosques, palaces, and forts and fortresses that offer a glimpse of India's past and present.

Bhopal is located in almost the center of India and is situated between Narmada River and Betwa River. It is a capital of Madhya Pradesh and has a rich, several century-long history. It is a fascinating amalgam of scenic beauty, old historic city, and modern urban planning. All things considered, the venue of the conference could not have been better.

We received an overwhelming response to our call for papers. The number of abstracts received exceeded 450. Each abstract was reviewed, and about two-thirds of them, deemed appropriate to the theme of the conference, were selected. This led to the submission of about 300 full-length papers. The subject matter of the papers was divided into more than 40 topics, encompassing virtually all major aspects of water and environment as well energy. Each topic comprised a number of contributed papers and in some cases state-of-the-art papers. These papers provided a natural blend to reflect a coherent body of knowledge on that topic.

The papers contained in this volume, "Hydrologic Modelling," represent one part of the conference proceedings. The other parts are embodied in six companion volumes entitled, "Energy and Environment," "Groundwater," "Environmental Pollution," "Water Quality Management," "Climate Change Impacts," and "Water Resources Management." Arrangement of contributions in these seven books was a natural consequence of the diversity of papers presented at the conference and the topics covered. These books can be treated almost independently, although significant interconnectedness exists among them.

This volume contains seven parts. The first part deals with some aspects of rainfall analysis, including rainfall probability distribution, local rainfall interception, and analysis for reservoir release. Part 2 is on evapotranspiration and discusses development of neural network models, errors, and sensitivity. Part 3 focuses on various aspects of urban runoff, including hydrologic impacts, storm water management, and drainage systems. Part 4 deals with soil erosion and sediment, covering mineralogical composition, geostatistical analysis, land use impacts, and land use mapping. Part 5 treats remote sensing and GIS applications to different hydrologic problems. Watershed runoff and floods are discussed in Part 6, encompassing hydraulic, experimental, and theoretical aspects. Water modeling constitutes the concluding Part 7. SWAT, Xinanjiang, and SCS-CN models are discussed.

The book will be of interest to researchers and practitioners in the field of water resources, hydrology, environmental resources, agricultural engineering, watershed management, earth sciences, as well as those engaged in natural resources planning and management. Graduate students and those wishing to conduct further research in water and environment and their development and management may find the book to be of value.

WEES-16 attracted a large number of nationally and internationally well-known people who have long been at the forefront of environmental and water resources education, research, teaching, planning, development, management, and practice. It is hoped that long and productive personal associations and friendships will be developed as a result of this conference.

College Station, USA
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Conference Chair

Bhopal, India
Shalini Yadav
Conference Organizing Secretary

Hazaribagh, India
Ram Narayan Yadava
Conference Co-Chair

Sponsors and Co-Sponsors

The International Conference on Water, Environment, Energy and Society was jointly organized by the AISECT University, Bhopal (M.P.), India, and Texas A&M University, Texas, USA, in association with ICE WaRM, Adelaide, Australia. It was partially supported by the International Atomic Energy Agency (IAEA), Vienna, Austria; AISECT University, Bhopal; M.P. Council of Science and Technology (MPCOST); Environmental Planning and Coordination Organization (EPCO), Government of Madhya Pradesh; National Bank for Agriculture and Rural Development (NABARD), Mumbai; Maulana Azad National Institute of Technology (MANIT), Bhopal; and National Thermal Power Corporation (NTPC), Noida, India. We are grateful to all these sponsors for their cooperation and providing partial financial support that led to the grand success to the ICWEES-2016.

Acknowledgements

We express our sincere gratitude to Shri Santosh Choubey, Chancellor, and Dr. V. K. Verma, Vice Chancellor, Board of Governing Body, and Board of Management of the AISECT University, Bhopal, India, for providing their continuous guidance and full organizational support in successfully organizing this International Conference on Water, Environment, Energy and Society on the AISECT University campus in Bhopal, India.

We are also grateful to the Department of Biological and Agricultural Engineering and Zachry Department of Civil Engineering, Texas A&M University, College Station, Texas, USA, and International Centre of Excellence in Water Management (ICE WaRM), Australia, for their institutional cooperation and support in organizing the ICWEES-2016.

We wish to take this opportunity to express our sincere appreciation to all the members of the Local Organization Committee for helping with transportation, lodging, food, and a whole host of other logistics. We must express our appreciation to the Members of Advisory Committee, Members of the National and International Technical Committees for sharing their pearls of wisdom with us during the course of the conference.

Numerous other people contributed to the conference in one way or another, and lack of space does not allow us to list all of them here. We are also immensely grateful to all the invited keynote speakers and directors/heads of institutions for supporting and permitting research scholars, scientists and faculty members from their organizations for delivering keynote lectures and participating in the conference, submitting and presenting technical papers. The success of the conference is the direct result of their collective efforts. The session chairmen and co-chairmen administered the sessions in a positive, constructive, and professional manner. We owe our deep gratitude to all of these individuals and their organizations.

We are thankful to Shri Amitabh Saxena, Pro-Vice Chancellor, Dr. Vijay Singh, Registrar, and Dr. Basant Singh, School of Engineering and Technology, AISECT University, who provided expertise that greatly helped with the conference organization. We are also thankful to all the heads of other schools, faculty member and staff of the AISECT University for the highly appreciable assistance in different organizing committees of the conference. We also express our sincere thanks to all the reviewers at national and international levels who reviewed and moderated the papers submitted to the conference. Their constructive evaluation and suggestions improved the manuscripts significantly.

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About the Editors

Prof. Vijay P. Singh is a Distinguished Professor, Regents Professor, Caroline and William N. Lehrer Distinguished Chair in Water Engineering, Department of Biological and Agricultural Engineering & Zachry Department of Civil Engineering, Texas A&M University, USA. He received his B.S., M.S., Ph.D., and D.Sc. degrees in engineering. He is a registered professional engineer, a registered professional hydrologist, and an Honorary Diplomate of American Academy of Water Resources Engineers.

Professor Singh has extensively published the results of an extraordinary range of his scientific pursuits. He has published more than 900 journal articles; 25 textbooks; 60 edited reference books, including the massive Encyclopedia of Snow, Ice and Glaciers and Handbook of Applied Hydrology; 104 book chapters; 314 conference papers; and 72 technical reports in the areas of hydrology, ground water, hydraulics, irrigation engineering, environmental engineering, and water resources.

For his scientific contributions to the development and management of water resources and promoting the cause of their conservation and sustainable use, he has received more than 90 national and international awards and numerous honors, including the Arid Lands Hydraulic Engineering Award, Ven Te Chow Award, Richard R. Torrens Award, Norman Medal, and EWRI Lifetime Achievement Award, all given by American Society of Civil Engineers; Ray K. Linsley Award and Founder's Award, given by American Institute of Hydrology; Crystal Drop Award, given by International Water Resources Association; and Outstanding Distinguished Scientist Award, given by Sigma Xi, among others. He has received three honorary doctorates. He is a Distinguished Member of ASCE and a fellow of EWRI, AWRA, IWRS, ISAE, IASWC, and IE and holds membership in 16 additional professional associations. He is a fellow/member of 10 international science/engineering academies. He has served as President and Senior Vice President of the American Institute of Hydrology (AIH). Currently, he is editor-in-chief of two book series and three journals and serves on editorial boards of 20 other journals.

Professor Singh has visited and delivered invited lectures in almost all parts of the world but just a sample: Switzerland, the Czech Republic, Hungary, Austria, India, Italy, France, England, China, Singapore, Brazil, and Australia.

Prof. Shalini Yadav is a Professor and Head of the Department of Civil Engineering, AISECT University, Bhopal, India. Her research interests include solid and hazardous waste management, construction management, environmental quality, and water resources. She has executed a variety of research projects/consultancy in environmental and water science and technology and has got rich experience in planning, formulating, organizing, executing, and management of R&D programs, seminars, and conferences at national and international levels. She has got to her credit guiding an appreciable number of M.Tech. and Ph.D. students. She has published more than 10 journal articles and 30 technical reports. Dr. Shalini has also visited and delivered invited lectures at different institutes/universities in India and abroad, such as Australia, South Korea, and Kenya.

Professor Shalini Yadav graduated with a B.Sc. in Science from the Bhopal University. She earned her M.Sc. in Applied Chemistry with specialization in Environmental Science from Bhopal University, and M.Tech. in Civil Engineering with specialization in Environmental Engineering from Malaviya National Institute of Technology, Jaipur, India, in 2000. Then she pursued the degree of Ph.D. in Civil Engineering from Rajiv Gandhi Technical University, Bhopal, India, in 2011. Also, she is a recipient of national fellowships and awards. She is a reviewer for many international journals. She has been recognized for one and half decades of leadership in research, teaching, and service to the Environmental Engineering Profession.

Dr. Ram Narayan Yadava holds position of Vice Chancellor of the AISECT University, Hazaribagh, Jharkhand. His research interests include solid mechanics, environmental quality and water resources, hydrologic modelling, environmental sciences, and R&D planning and management. Yadava has executed a variety of research/consultancy projects in the area of water resources planning and management, environment, remote sensing, mathematical modelling, technology forecasting, etc.

He has got adequate experience in establishing institutes/organizations, planning, formulating, organizing, executing, and management of R&D programs, seminars, symposia, conferences at national and international levels. He has got to his credit guiding a number of M.Tech. and Ph.D. students in the area of Mathematical Sciences and Earth Sciences. Dr. Yadava has visited and delivered invited lectures at different institutes/universities in India and abroad, such as USA, Canada, United Kingdom, Thailand, Germany, South Korea, Malaysia, Singapore, South Africa, Costa Rica, and Australia.

He earned an M.Sc. in Mathematics with specialization in Special Functions and Relativity from Banaras Hindu University, India, in 1970 and a Ph.D. in Mathematics with specialization in Fracture Mechanics from Indian Institute of Technology, Bombay, India, in 1975. Also, he is the recipient of Raman Research Fellowship and other awards. Dr. Yadava has been recognized for three and half decades of leadership in research and service to the hydrologic and water resources profession. Dr. Yadava's contribution to the state of the art has been significant in many different specialty areas, including water resources management, environmental sciences, irrigation science, soil and water conservation engineering, and mathematical modelling. He has published more than 90 journal articles; 4 textbooks; and 7 edited reference books.

Part I
Wastewater Treatment

Investigation on the Treatment of Combined Effluent Treatment Plant Wastewater and Its Safe Use in Agriculture—A Green Technology Concept

Malairajan Singanan

Abstract Recent reports reveal that growing water scarcity and misuse of freshwater pose serious and growing threats to sustainable economic development, food security and protection of the environment. In developing countries, industrial sectors consuming most of the available freshwater for their productions. At the same time, it releases some wastewater into the environment and causes ecosystem damages. In the concept of environmental and economic sustainability, a proper wastewater management and water reuse system can help to a greater extent in development of national economy. Existing conventional water treatment technologies are costlier, and some are not eco-friendly in nature and consumes large amount of energy and produces secondary effluent. In this context, a new search for cheap and low-cost water purification technology is essential. The biocarbon material is generated using a novel medicinal plant, Garland daisy (*Glebionis coronia*—Asteraceae). The characteristics of the biocarbon are unique and having good potential for the removal of salts and organic components in water. As a model trial, a grey water system having heavy metal ions (Pb, Cr, Cu, Ni and Cd) of average concentration of 8.73 and 1800 mg/L of organic load was introduced in the reactor system; after equilibrium time of 3 h, the average concentration of heavy metal ions in outlet water is 0.57 mg/L, and the organic load of 360 mg/L is achieved at the biocarbon dose of 2.5 g/100 mL. The treated wastewater was introduced in the pilot agricultural system, where, *Setaria glauca,* a fodder grass and Sorghum crop were grown well. These results suggest that new biocarbon technology is a promising option for wastewater treatment. The treated water can be reused for various purposes in industries as well as in agricultural development and help to prevent the misuse of available freshwater resources.

Keywords Garland daisy · *Glebionis coronia* (L) · Biocarbon
Wastewater reuse · Agriculture practices

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Introduction

Water is a critical component in the functioning of the earth and of all living forms of life. Raising human population and industrialization has increased tremendous pressures on global freshwater resources and resulting growing water consumption and pollution, in combination with the impacts of climate change. In many arid and semi-arid regions of the world, the availability of freshwater is very much limited. In such situations, wastewater reuse has become an acceptable part of the water supply system in many parts of the world. While water reuse has the potential to improve water usage and protect and preserve global freshwater resources, also it should be taken into the account of possible environmental and health risk facts associated with the wastewater reuse (Mapanda et al. 2005; Oghenerobor et al. 2014).

There are several contaminants in wastewater, with organic pollutants playing the major role. Toxic organic pollutants cause several problems to the environment. The most common organic pollutants are persistent organic pollutants (POPs). POPs are compounds of great concern due to their toxicity, persistence, long-range transport ability (Harrad 2001) and bioaccumulation in animals (Burkhard and Lukazewycz 2008). The presence of colour and colour-causing compounds has always been undesirable in water for any use. It, therefore, need to be treated before discharge (George et al. 2013; Ali et al. 2012; Abdel-Ghani et al. 2016).

In addition, the toxic heavy metals are also the major contaminant in industrial wastewater. The metals commonly include cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), nickel (Ni) and chromium (Cr). These metals enter into human bodies either through direct intake or through food chains (Argun and Dursun 2008; Ghanbari and Shahram 2016). Due to toxicity and cumulative effects, these pollutants impose destructive effects on environment and ultimately human into the threat of toxicity, cancer and long-term and short-term genetic effects (Gholamreza and Mehrzad 2016). The aim of water reuse for agriculture is to promote ecologically sustainable development, protection of environment by pollution and protection of public and community health. Reusing the treated wastewater is becoming more valuable resources for industrial, agriculture practices and other domestic uses.

The greater environmental awareness among public in recent years and the demand for clean environment have necessitated the treatment of industrial effluent. As such there has been a great deal of research into finding cost-effective methods for the removal of contaminants from wastewater. In recent years, considerable attention has been devoted to the study of removal of heavy metal ions from solution by adsorption (Bohli et al. 2012; Abdul et al. 2014; Taik-Nam and Choong 2013).

Many physico-chemical methods have been proposed for their removal from industrial effluents. Adsorption is an effective purification and separation technique used in industry especially in water and wastewater treatments (Guixia et al. 2011; Bernard et al. 2013). Sorption technique is a commonly used method for the treatment of various industrial effluents (Naseem 2012; Hala 2013). Numbers of cheaper materials, including soil, silica, activated carbon, green coconut shell and others, have been used to remove different pollutants from industrial effluents for their safe disposal into the biosphere (Mahmoodi et al. 2011; Kumar and Meikap 2014). Biosorption is a relatively new process that has been proven very promising in the removal of contaminants from aqueous effluents using low-cost adsorbents derived from agricultural materials (Nomanbhay and Palanisamy 2005).

In this study, an attempt was made to use the leaves of Garland daisy *(Glebionis coronia*—Asteraceae) for the preparation of biocarbon for the potential removal of colour and toxic heavy metals from industrial wastewater. The treated industrial wastewater is applied in pilot scale for cultivation of Sorghum crop and *Setaria glauca,* a fodder grass for livestock applications. The selected medicinal herb is found in agricultural fields in Tamil Nadu, India, throughout the seasons. The present work investigates the potential use of biocarbon of Garland daisy *(Glebionis coronia*—Asteraceae) for biosorption of organic and inorganic pollutants from a combined effluent treatment plant (CETP) wastewater. The factors that influence biosorption capacity such as pH, contact time, metal ion concentration and biocarbon dosage were evaluated.

Materials and Methods

Preparation of Biocarbon

Garland daisy *(Glebionis coronia*—Asteraceae) is an important medicinal plant widely distributed in agricultural fields. The plant leaves were collected and air-dried for 48 h. The dried leaves were grounded in ball mills, and the screened homogeneous powder was used for the preparation of biocarbon. The activated biocarbon was prepared by treating the leaves powder with the concentrated sulphuric acid (Sp. gr. 1.84) in a weight ratio of 1:1.8 (biomaterial: acid). The resulting black product was kept in an air-free oven, maintained at 160 ± 5 °C for 6 h followed by washing with distilled water until free of excess acid, then dried at 105 ± 5 °C. The particle size of activated carbon between 100 and 120 µm was used (Singanan 2015).

Collection and Analysis Grey Water

The grey water samples were collected from a combined effluent treatment plant (CETP) of metal plating and distillery effluents from an industrial area located in

Tamil Nadu, India. The important physico-chemical characteristics such as pH, EC, alkalinity, SS, TDS, EC, DO, BOD, COD and heavy metals mainly for Pb, Cr, Cu, Ni and Cd were performed by using standard methods outlined in APHA manual (APHA 1985). The level of metal ions content in grey water was analysed using Shimadzu AAS 6200 instrument with air–acetylene flame system.

Treatment of Grey Water: Biosorption Process

The grey waters collected from CETP plant were passed through the specific screening system for the removal any dirt materials. A dirt-free grey water samples were collected in clean polythene containers and subjected to batch biosorption process with pre-defined equilibrium data. The biosorption process was carried out at the room temperature of 28 ± 2 °C in a series of six 250 mL capacity Erlenmeyer flask. Each flask is loaded with 100 mL of wastewater and subjected to equilibrium process. The wastewater treatment process and reuse for cultivation operation were illustrated in Fig. 1.

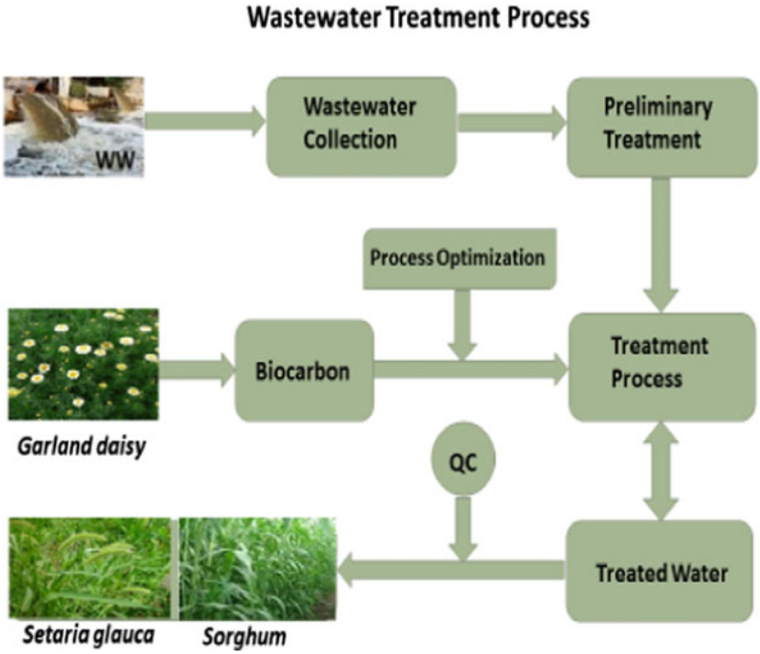

Fig. 1 Wastewater treatment and reuse for cultivation process

Evaluation of Capacity of Biocarbon

The evaluation of treatment capacity of biocarbon was carried out as follows: 100 mL of grey water sample was used in each biosorption flask containing 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 g biocarbon dose. All the flasks were equilibrated using Remi orbital shaker system at 250 rpm for the contact time of 150 min. At the end of equilibrium time, samples were collected, and respective concentration of heavy metal ions present in the wastewater is determined using AAS. The pH of the test solution was monitored by using a Hanna pH Instruments (Italy). The experiments were carried out in triplicates, and the average values are obtained and used for the discussion of findings.

Data Analysis

Biosorption values were determined as the difference between the initial heavy metal ion concentration in raw wastewater and that in the treated wastewater. The amount of heavy metal ions adsorbed per unit mass of the biosorbent was evaluated by using the following equation:

$$q_e = \left(\frac{C_o - C_e}{w}\right) \times V \tag{1}$$

where q_e, amount of heavy metal ions adsorbed (mg/g); V, volume of heavy metal ions in solution (mL); w, mass of biocarbon (g); C_o, initial heavy metal ion concentration (mg/L); C_e, heavy metal ion concentration at equilibrium (mg/L). The percent removal of heavy metal ions was evaluated from the equation:

$$\%\ \text{Removal} = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \tag{2}$$

The analytical data were analysed, and standard deviations of the statistical tests were carried out using the programme of analysis of variance (ANOVA) by using SPSS program.

Results and Discussion

Characteristics of Biocarbon (BC)

The nature and the characteristics of the biocarbon are essential to understand the adsorptive behaviour on the surface of the biocarbon. The detailed characteristics of the biocarbon of Garland daisy *(Glebionis coronia)* are reported in Table 1. It is observed that the surface and particle size are relatively high and are responsible for potential removal of metal ions and organic molecules from grey water system. The result indicates that the biocarbon has high capacity for metal ion adsorption, and it is regenerative in nature.

Surface Analysis

Information on the morphological features of the adsorbents in wastewater treatment system is very much important. It mainly reveals the possible mode of biosorption process and its regenerative nature of adsorbents. To investigate surface condition for before and after adsorption of metal ions and organic pollutants, SEM photograph and EDX spectrum were used. The SEM picture shows the presence of number of microcavities and canal-like structures. As shown in Fig. 2a, b, electron dense part which is thought to be metal ion present in the effluent was appeared at the SEM (b) as compared with SEM (a).

Characteristics of Grey Water and Treated Water

The analytical results of physico-chemical characteristics of raw grey water and treated grey water have been evaluated and presented in the Table 2. It indicates that the grey water is highly contaminated with heavy metals and organic pollutants which accelerate the higher level of COD in the grey water system. Higher organic load is mainly contributing the rise in biological oxygen demand (BOD) of the wastewater.

Table 1 Characteristics of the biocarbon

S. No.	Parameters	Values for BC
1	Moisture content	0.40%
2	Ash content	8.75%
3	Total carbon	92.5%
4	Bulk density	1.35/mL
5	Matter soluble in water	0.60%
6	Matter soluble in acid	1.5%
7	pH	7.30
8	Ion exchange capacity	0.95 meq/mg
9	Methylene blue value	35
10	Phenol number	48.5
11	Decolourizing power	1.50 mg/g
12	Iron	0.82%
13	Surface area	385 m^2/g

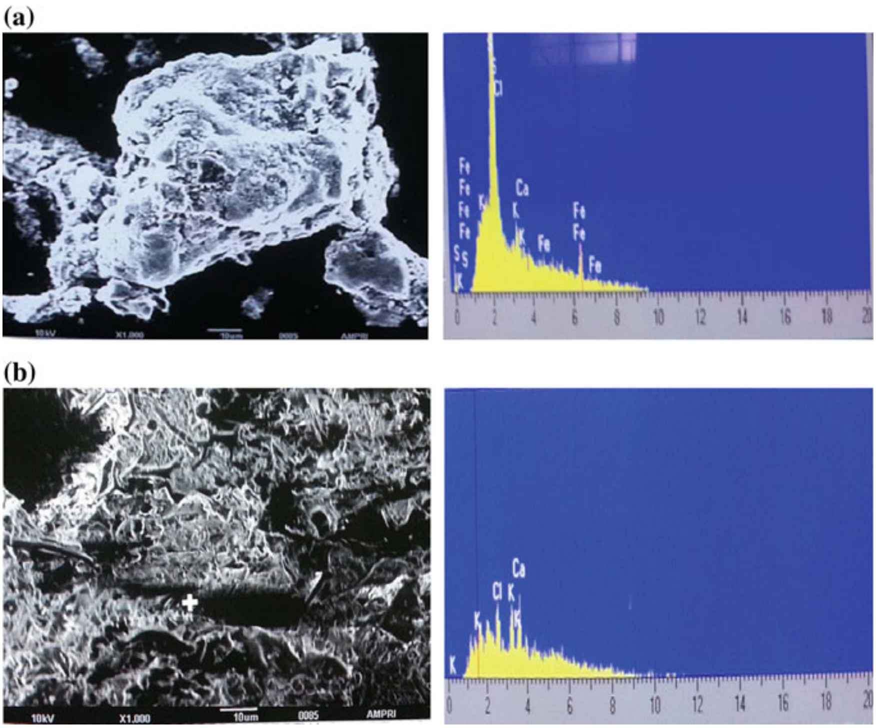

Fig. 2 **a** SEM photograph and EDX spectrum of biocarbon—before adsorption. **b** SEM photograph and EDX spectrum of biocarbon—after adsorption

Table 2 Characteristics of CETP grey water

S. No.	Characteristics of grey water	Quality of grey water (mg/L)		Percent reduction
		Before treatment	After treatment	
1	pH	8.5	6.7	21.17
2	EC (µmhos/cm)	2080	485	76.68
3	Alkalinity	955	275	71.20
4	Suspended solids	1125	220	80.44
5	Total dissolved solids	1350	315	76.66
6	Dissolved oxygen	4.2	5.8	–
7	Total nitrogen	145	35	75.86
8	Total phosphorous	120	30	75.00
9	BOD	640	120	81.25
10	COD	1800	360	80.00
11	Pb	10.5	0.75	92.85
12	Cr	12.5	0.65	94.80
13	Ni	8.55	0.58	93.21
14	Cu	6.40	0.35	94.53
15	Cd	5.70	0.50	91.22

The results indicate that the biocarbon technology works well, and all the parameters are significantly reduced. The dark colour of grey water was well reduced to almost colourless. The main pollution parameter such as COD and BOD is reduced to 80–81.25%, respectively. Alkalinity of the wastewater is 71.20% reduced making the water suitable for crop irrigation. Relatively, the level of TDS is good in treated wastewater. The level of heavy metals such as Cr and Pb is high in the grey water. It will definitely cause toxic effects in humans and animals when using this grey water for any irrigation purpose. After the treatment process, the concentration of heavy metals is well reduced as Pb (92.85%), Cr (94.80%), Ni (93.21%), Cu (94.53%) and Cd (91.22%) and is within the agricultural quality of wastewater. The analytical results support that the biocarbon has excellent biosorption capacity to the removal of heavy metals and the organic pollutants in grey water system.

Effect of Biocarbon Dose on Heavy Metals Removal

The amount of biocarbon dose was a key parameter to control both availability and accessibility of adsorption sites in the sorption process of heavy metal ions present in the wastewater (Rafeah et al. 2009). The effect of biocarbon dosage on the removal of Pb(II) and Cr(VI) ions as representative species in the wastewater is presented in Fig. 3. The per cent removal of metal ions has reached up to 92.5 and 94.8 for both Pb(II) and Cr(VI), respectively, at the biocarbon dose of 2.5 g/100 mL. The results indicate that the higher dosage of adsorbent will increase the adsorption due to more surfaces, and functional groups are available on the biocarbon matrix.

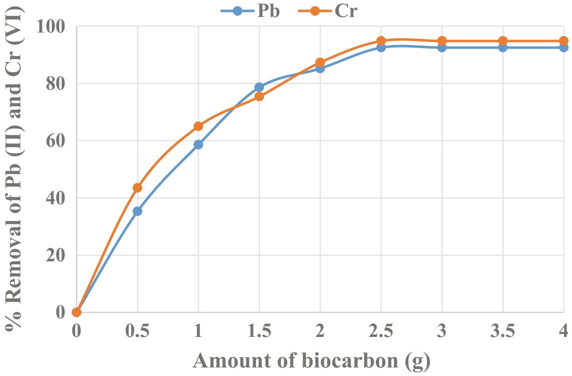

Fig. 3 Effect of biocarbon dose on the removal of Pb(II) and Cr(VI)

Removal of Colour from a Grey Water

The removal of colour from grey water was performed with the initial concentration of 800 mg/L (100%) with optimum biocarbon dose of 2.5 g/100 mL. An excellent result (95.0%) of colour removal is achieved in 150 min (Fig. 4). These results suggest that new biocarbon technology is a promising option for water and wastewater treatment.

Water Reuse in Agriculture Practice

The treated industrial wastewater is applied in pilot scale for cultivation of Setaria glauca, a fodder grass for livestock applications, and Sorghum for small-scale irrigation shown in Fig. 5. The productive results are presented in Table 3. The results demonstrated that the treated grey water has good nutrient capacity and hence, the species is steadily grown well and produced good yield.

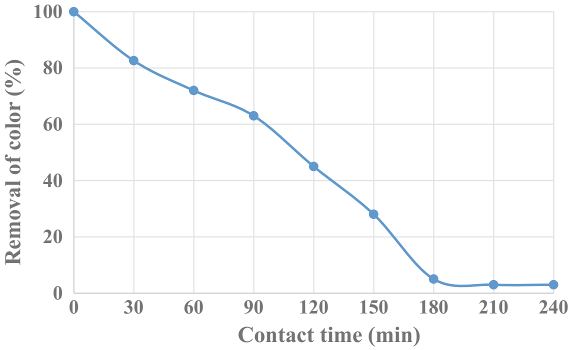

Fig. 4 Effect of contact time on colour removal

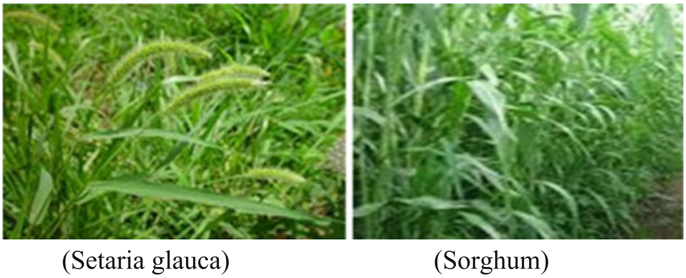

Fig. 5 Cultivation of *Setaria glauca* and Sorghum

Table 3 Growth characteristics of *Setaria glauca* and Sorghum

S. No.	Parameters	*Setaria glauca*	Sorghum
1	Field size	12 × 12 sq. ft.	12 × 12 sq. ft.
2	Growth period	120 days	120 days
3	Total biomass	3.0–4.0 kg/sq. ft.	3.5–4.5 kg/sq. ft.

Conclusion

The toxic inorganic and organic pollutants (POPs) in the ecosystem are of the most important environmental concerns in the world. An eco-friendly and most efficient technologies for the removal of highly toxic contaminants from wastewater have drawn significant interest in recent times. Biosorption is recognized as an effective and low-cost technique for the removal of industrial pollutants from water and wastewater and produces high-quality treated wastewater. It is also found that there is a certain limit for increasing the biosorbent doses for given amount of wastewater. This has to be carefully controlled. An excess use can lead to uneconomical process. The initial concentration plays an important role throughout the biosorption. With the experimental data obtained in this study, it is possible to design and optimize an economical treatment process for the removal of various pollutants from industrial wastewater. The biocarbon technology is an efficient and economically sound technology for the treatment of industrial grey water and does not produce any major secondary effluent and sludge. The treated water can be reused for various purposes in industries as well as in agricultural development. In the present pilot scale study, the yield of fodder grass *Setaria glauca* and *Sorghum* is confirmed as good, and also further revealed that the biocarbon-treated wastewater is much useful for irrigation for cultivation of plants by reuse technology and imposes to save the environment from pollution-causing agents.

References

Abdel-Ghani NT, Rawash ESA, El-Chaghaby GA (2016) Equilibrium and kinetic study for the adsorption of p-nitrophenol from wastewater using olive cake based activated carbon. Global J Environ Sci Manage 2(1):11–18

Abdul G, Azhar M, Naveed I (2014) A novel material for removal of organochlorine pesticides from aqueous environment: Kinetics and thermodynamics investigations. Cur Env Eng 1:100–110

Ali I, Asim M, Khan TA (2012) Low cost adsorbents for the removal of organic pollutants from wastewater. J Environ Manage 113:170–183

APHA (1985) Standard methods for the examination of water and wastewater. American Public Health Association, Washington, D.C

Argun ME, Dursun S (2008) A new approach to modification of natural adsorbent for heavy metal adsorption. Bioresour Technol 99:2516–2527

Bernard E, Jimoh A, Odigure JO (2013) Heavy metals removal from industrial wastewater by activated carbon prepared from coconut shell. Res J Chem Sci 3(8):3–9

Bohli T, Ouederni A, Fiol N, Villaescusa I (2012) Uptake of Cd^{2+} and Ni^{2+} metal ions from aqueous solutions by activated carbons derived from waste olive stones. Int J Chem Eng App 3 (4):232–236

Burkhard LP, Lukazewycz MT (2008) Toxicity equivalency values for polychlorinated biphenyl mixtures. Environ Toxicol Chem 27:529–534

George Z, Kyzas Jie Fu, Kostas AM (2013) The change from past to future for adsorbent materials in treatment of dyeing wastewaters—review. Materials 6:5131–5158

Shahram GP (2016) Adsorptive removal of Al, Zn, Fe, Cr and Pb from hydrogen peroxide solution by IR-120 cation exchange resin. Iran J Chem Chem Eng 35(1):75–84

Gholamreza M, Mehrzad M (2016) Examination of the level of heavy metals in wastewater of bandar abbas wastewater treatment plant. Open J Ecol 6:55–61

Guixia Z, Xilin W, Xiaoli T, Xiangke W (2011) Sorption of heavy metal ions from aqueous solutions: a review. Open Coll Sci J 4:19–31

Hala AH (2013) Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. HBRC J 9:276–282

Harrad S (2001) Persistent organic pollutants environmental behaivour and pathways for human exposure. Kluwer Academic Publishers, Norwell

Kumar S, Meikap BC (2014) Removal of Chromium (VI) from waste water by using adsorbent prepared from green coconut shell. Desal Water Treat 52(16–18):3122–3132

Mahmoodi NM, Hayati B, Arami M, Lan C (2011) Adsorption of textile dyes on pine cone from colored wastewater: kinetic, equilibrium and thermodynamic studies. Desalination 268(1–3):117–125

Mapanda F, Mangwayana EN, Nyamangara J, Giller KE (2005) The effect of long-term irrigation using wastewater on heavy metal content of soil under vegetable in Harara. Zimbabwe Agri Ecosys Env 107:151–165

Naseem Z (2012) Lead removal from water by low cost adsorbents: a review. Pak J Anal Env Chem 13(1):01–08

Nomanbhay S, Palanisamy K (2005) Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. Ele J Biotech 8(1):43–53

Oghenerobor BA, Gladys OO, Tomilola DO (2014) Heavy metal pollutants in wastewater effluents: sources, effects and remediation. Adv Biosci Bioeng 2(4):37–43

Rafeah W, Zainab N, Veronica UJ (2009) Removal of mercury, lead and copper from aqueous solution by activated carbon of Palm oil empty fruit bunch. World Appl Sci J 5:84–91

Singanan M (2015) Biosorption of Hg(II) ions from synthetic wastewater using a novel biocarbon technology. Env Eng Res 20(1):33–39

Taik-Nam K, Choong J (2013) Adsorption characteristics of sericite for nickel ions from industrial waste water. J Ind Eng Chem 19:68–72

Evaluation of Treatment Technologies for Arsenic-Free Drinking Water Supply, Disposal of Backwash Water and Exhausted Media in Bihar, India

Astha Kumari and N. S. Maurya

Abstract Drinking water supply in Bihar is mainly dependent upon groundwater. The toxicology and health hazard due to presence of arsenic in drinking water also has been reported for many years. Dimension of the problem may be experienced by the fact that fifty-seven blocks, in 15 districts, located on the banks of river Ganga are affected from arsenic. Due to the knowledge of the fact that arsenic at even low concentrations in drinking water causes severe health effects, Public Health Engineering Department, Government of Bihar, has taken several initiatives of providing arsenic removal units at the water source in order to provide access to safe drinking water to each and every one. Efficiency of supplying arsenic-free water by treatment of polluted groundwater using arsenic removal units based on adsorption/ion-exchange/reverse osmosis/membrane filtration process has proved more contradictory mainly due to the problem with handling of large quantities of arsenic-rich sludge produced from the treatment units. Thus, in order to provide arsenic-free water from alternate sources, piped water supply scheme, based on surface sources in feasible locations and where surface water is not available tapping of water from deep aquifers, has been put in place. This paper aims to review briefly arsenic contaminated areas in Bihar and the mitigation techniques available that have been reported in arsenic removal. Disposal of backwash water and exhausted media will also be discussed.

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and Technology Library 79, https://doi.org/10.1007/978-981-10-5795-3_2

Introduction

Arsenic is a metalloid. It is found as 20th most common element in the earth's crust, 14th in sea water and 12th in human body (Woolson 1975; Sharma and Sohn 2009). A number of natural and anthropogenic activities are responsible for its appearance in the water environment. Natural activities include weathering of rocks, mineral ores formation process, volcanic eruptions, geothermal activities etc. (Goldberg and Johnston 2001). Anthropogenic activities like mineral ores processing, combustion of arsenic-enriched coals, and manufacturing of semiconductors, glass and some pharmaceuticals also lead to arsenic contamination in nature (Chen et al. 1995).

Arsenic is widely distributed in nature. It occurs in the both inorganic and organic forms in four oxidation states namely arsenate (+5), arsenite (+3), elemental arsenic (0) and arsine (−3) (Das and Sengupta 2008). However, natural water mostly contains inorganic arsenic either as arsenite As (+3) or arsenate As (+5). Arsenite is more toxic than arsenate (Petrick et al. 2000). The organic arsenic/methylated arsenic is considered least toxic (Kumar 2015).

The presence of arsenic in drinking water is considered one of the most alarming challenges to be solved in order to assure the human right to access of potable water (UNDP 2011). According to the World Health Organization (WHO), consumption of water contaminated with arsenic levels over 0.05 mg/L may cause skin lesions and cancer (WHO 1993). Until 2009, India the acceptable limit for Arsenic in drinking water was 0.05 mg/L (BIS 2009). After the year 2009, Bureau of Indian Standards (BIS) has set the desirable limit of Arsenic in drinking water as 0.01 mg/L (BIS 2012).

Arsenic has dual characteristics. It can be a medicine to cure several diseases for example acute leukemia in humans, if consumed in proper way or can be a toxic element and threat to human health (Miller et al. 2002). Arsenic contamination in drinking water may have several damaging effects on health ranging from skin ailments to serious and dangerous diseases such as cancer (Mandal and Suzuki 2002). Long-term exposure to arsenic can damage cardiovascular, gastrointestinal, dermal, hepatic, pulmonary, renal, neurological systems (ATSDR 2000) since it also possesses genetic, mutagenic and carcinogenic properties, thus categorized as Group I carcinogenic element (IARC 2004) (Figs. 1 and 2).

Fig. 1 Keratosis (*left*, *middle*) and Melanosis (*right*). *Source* Matthijs et al. 2013

Fig. 2 Patients from arsenic-affected districts of Bihar. *Source* SOES 2012

Arsenic Pollution in Bihar

Presence of arsenic in drinking water source is now a well-recognized problem worldwide. Bihar, the third largest populated state of India, is also severely affected by arsenic contamination in groundwater, the only source of drinking water (PHED, Govt. of Bihar). Dimension of the problem may be experienced by the fact that fifty-seven blocks, in 15 districts, mostly located on the either side of river Ganga are arsenic affected (Saha et al. 2009).

Singh and Ghosh (2012) have specified high health-risk area in Patna, Bhojpur, Samastipur, and Bhagalpur districts of Bihar, are severely affected by arsenic where as high as 1000 µg/L and even more concentration was observed. In Vaishali, Saran, Begusarai, Khagaria, Munger, and Katihar districts, more than 50 µg/L arsenic were detected. The other districts namely Siwan, Lakhisarai, Darbhanga, Supaul, and Kishanganj are also experiencing arsenic contamination, but concentration is generally lower than 50 µg/L (CGWB and BARC 2009).

Arsenic contamination in ground water was first observed in Simariya Ojhapatti village of Bhojpur district in October 2002. After this PHED department tested more than 80,000 water sources from 10 km section bordering river Ganga which is distributed over sixty-five blocks of 11 districts. The results indicated that at least 892 habitations were consuming arsenic contaminated water. The department

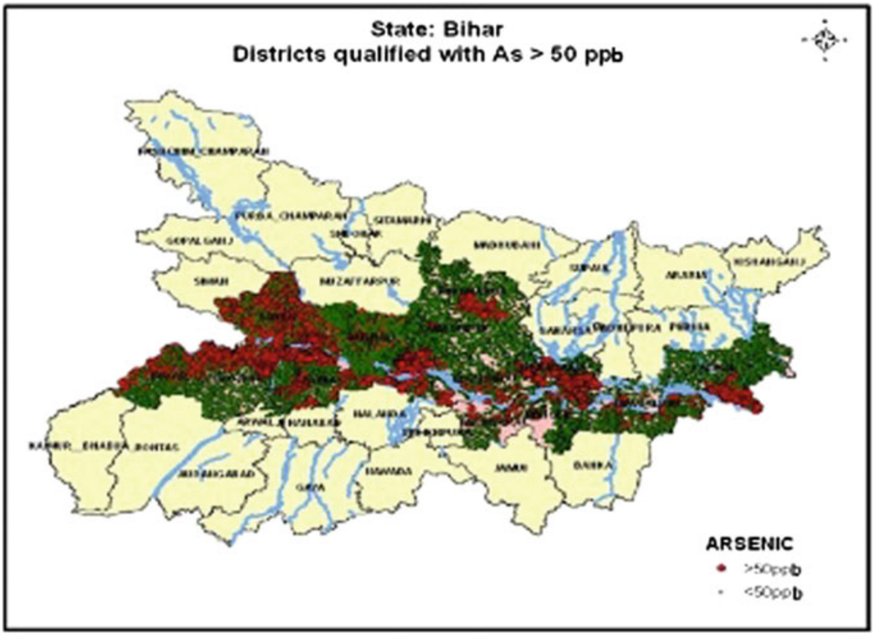

Fig. 3 Arsenic-affected area in Bihar. *Source* PHED

further planned extensive water testing of 270,318 water sources from all districts of Bihar in year 2007–08 (PHED 2008). Fig. 3 shows extent/distribution of arsenic pollution in groundwater of Bihar.

The green and red areas indicate arsenic concentration more than 50 µg/L and less than 50 µg/L, respectively. Blockwise total number of habitations affected due to arsenic contamination are presented in Table 1.

Table 1 Blockwise arsenic-affected habitations in Bihar

S. No.	District	Block	Maximum concentration of arsenic (mg/L)	Number of habitations
1	Begusarai	Bachwara	>0.05	84
		Balia		
		Barauni		
		Begusarai		
		Matihani		
		Sahebpurkamal		
2	Bhagalpur	Jagdishpur	>0.05	159
		Nathnagar		
		Sultanganj		

(continued)

Table 1 (continued)

S. No.	District	Block	Maximum concentration of arsenic (mg/L)	Number of habitations
3	Bhojpur	Ara	0.426	31
		Barhara	0.42	
		Behea	0.8	
		Koilwar	0.306	
		Shahpur	1.63	
		Udwant Nagar	0.051	
4	Buxar	Brahmpur	1.22	385
		Buxar	0.94	
		Chakki	>0.05	
		Semary	1.4	
5	Darbhanga	Biraul	>0.05	5
6	Katihar	Amdabad	>0.05	26
		Barai		
		Kursela		
		Manihari		
		Mansahi		
		Sameli		
7	Khagaria	Gogri	>0.05	246
		Khagaria		
		Mansi		
		Parbatta		
8	Kisanganj	Bahadurgarh	0.085	204
		Kisanganj	0.058	
9	Lakhisarai	Lakhisarai	0.23	118
		Piparia	0.024	
10	Munger	Bariarpur	>0.05	65
		Dharahra		
		Jamalpur		
		Munger		
11	Patna	Bakhtiyarpur	>0.05	154
		Barh	0.584	
		Danapur	>0.05	
		Maner	1.81	
12	Purnea	Kasba	0.067	14
		Purnea East	0.097	
13	Samastipur	Mohanpur	0.626	53
		Mohinuddin nagar	0.37	
		Patori	>0.05	
		Vidyapati Nagar	>0.05	

(continued)

Table 1 (continued)

S. No.	District	Block	Maximum concentration of arsenic (mg/L)	Number of habitations
14	Saran	Chapra Sadar	0.205	37
		Dighwara	>0.05	
		Revelganj	>0.05	
		Sonepur	0.23	
15	Vaishali	Bidupur	>0.05	76
		Desri		
		Hajipur		
		Raghopur		
		Sahdei Bujurg		

Source CGWB and PHED 2005

Mitigation Techniques Adopted

For the supply of arsenic-free water in the above-mentioned areas, mainly two approaches are adopted. The initial approach is to supply surface/groundwater from arsenic-free sources after employing conventional treatment. In the second approach, arsenic contaminated groundwater (from contaminated source) is supplied after providing suitable treatment mainly based on adsorption/ion-exchange process and RO/MF techniques.

Since last few years, PHED has proposed/started various arsenic mitigation projects. They may be broadly categorized in two groups namely (i) short-term measures and (ii) long-term measures. The projects included in short-term as well as long-term measures are listed as follows:

- Short-term measures:
  1. Replacement of tube wells by India Mark-II hand pumps with more than 100 m depth.
  2. Construction of new sanitary wells fitted with solar pumps and
  3. Construction of hand pumps with arsenic removal units.
- Long-term measures:
  1. Construction of deeper hand pumps with proper sealing;
  2. Surface water-based multi-village piped water supply schemes;
  3. Rainwater harvesting and
  4. Mini water supply schemes attached with Arsenic treatment units earmarked to the specialized technical agencies for operation and maintenance.

Presently, seven projects are under implementation stage namely at Patna (E), Sambalpur, Begusarai, Vaishali, Bhagalpur (E), Bhagalpur (W) and Buxur divisions to provide safe drinking water in 1296 villages. The estimated cost of the projects is Rs. 986.26 crores. An action plan has been prepared by the Government of Bihar to provide safe drinking water in arsenic-affected areas through mini piped water supply scheme employing solar power and withdrawing water from deep aquifer with an estimated cost of Rs. 430.80 crores. The projects are funded by NRDWP (National Rural Drinking Water Supply Programme) (MoWR 2015).

Approximately, 62 projects are funded by NRDWP (National Rural Drinking Water Supply Programme). Twenty-three arsenic removal units were installed in two districts by Envirotech East Pvt. Ltd. Kolkata. The removal technique employed is reverse osmosis/membrane filtration etc./other innovative treatment unit. M/s D.N.A Infrastructure, Noida, had installed 39 ARU's in 13 districts out of which two are non-functioning. Another arsenic treatment unit which is also functioning under National Rural Drinking Water Programme aims to provide proper treatment units with solar water based pumps in arsenic-affected areas is installed by M/s Punj Lloyd Ltd., Gurgaon. Total no. of proposed ARU's in this scheme is 150 among 13 districts, but the current status of installation of these ARU's is numerically very low as 57 in numbers showing delay and improper functioning of schemes. (Personal communication with Joint Secretary PHED, Er. D.S. Mishra). Status of these arsenic treatment units are presented in Table 2 and Fig. 4.

Table 2 Arsenic removal projects in Bihar

S. No.	Funding organization	M/s D.N.A infrastructure, Noida		M/s Punj Lloyd Ltd., Gurgaon	
	PHED division	No. of ARU projects proposed	Current project status	No. of ARU projects proposed	Current project status
1	Bhagalpur West	4	4	8	4
2	Lakhisarai	11	11	9	0
3	Patna	2	2	15	5
4	Bhojpur	2	0	5	1
5	Buxar	3	3	5	0
6	Vaishali	2	2	10	3
7	Darbhanga	2	2	15	5
8	Samastipur	3	3	8	8
9	Begusarai	9	9	8	0
10	Saran	1	1	20	7
11	Munger	1	1	9	1
12	Katihar	8	8	15	10
13	Khagaria	4	4	15	5

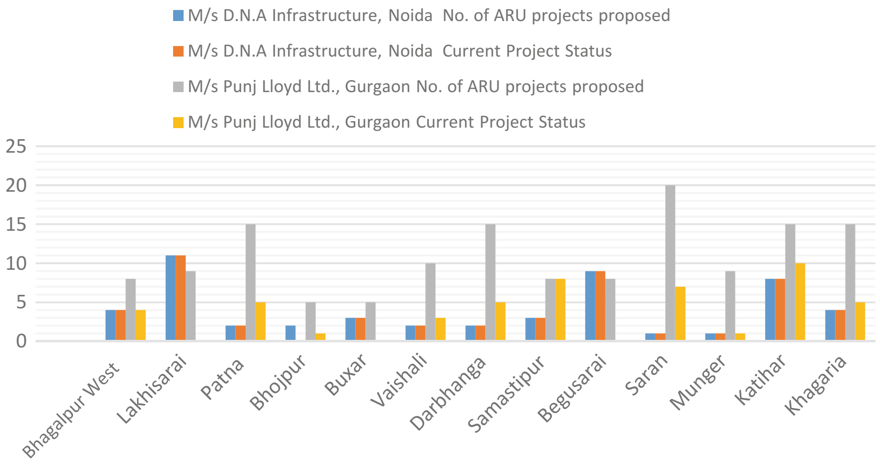

Fig. 4 Status of districts covered under NRDWP with solar water based pumps and their status of functioning. *Source* PHED Department

Probable Waste Disposal Strategies

Waste disposal is an important factor in the selection of treatment processes. Arsenic removal units produce different types of highly contaminated waste, including backwash water, spent media, water rejects, discarded membrane filter etc. depending on technology employed. These wastes have the characteristics for being classified as hazardous and lead to disposal problems. Therefore, the above-mentioned wastes may be disposed as per methods suggested by NIH and CGWB (2010) as given below:

- Disposal in on-site sanitation pits,
- Mixing with concrete,
- Mixing with clay for brick manufacturing.

Liquid wastes must have lower concentrations than the toxicity level in order to be classified as non-hazardous. The highest level of arsenic toxicity is 5.0 mg/L., and the wastes having arsenic concentration more than 5.0 mg/L would, therefore, be classified as a hazardous waste (NIH and CGWB 2010).

Status of Waste Disposal in Bihar

During maintenance of adsorption filters, sludge and backwash water are being with a high concentration of arsenic is produced. There is no any standard methods/procedure adopted to dispose the arsenic containing materials. The sludge (spent media) and backwash water are just dumped in ditch or are just spread over the area adjacent to the filter unit. Indiscriminate disposal of these materials may further increase the concentration of arsenic in groundwater and soil.

Keeping in view safe disposal of arsenic containing wastes, treatment-based safe drinking water supply scheme is now of least choice. All future schemes are planned to be either based on surface or deep aquifer water (Personal communication with Executive Engineer (Monitoring) PHED, S.N. Mishra). Multi-village piped water supply schemes will have their intake from the River Ganga.

The schemes are at:

(a) Mauzanpur, Bhojpur district, covering 39 villages
(b) Bidupur in Vaishali
(c) Simri block in Buxar district
(d) Mohiuddinnagar and Mohanpur blocks in Samastipur
(e) Kahalgaon and Pirpainti blocks in Bhagalpur
(f) Sultanagalganj and Nathnagar blocks in Bhagalpur
(g) Matihani and Barauni blocks in Begusarai.

Conclusions

This review is an attempt to summarize the harmful effects of arsenic along with incidents of arsenic contamination in groundwater in various districts of Bihar. In several places, arsenic contaminate in groundwater, the only source of drinking water, is significant. It possesses a significant risk to public health. Therefore, the first priority to deal with this crisis should be pre-identification of the affected sources. Several mitigation techniques are adopted by the Bihar State Govt. and Public Health Engineering Department Patna to cope up with this situation. The measures thus adopted are providing Arsenic removal units at sources. These ARU's are based on RO/MF/Adsorption treatment methods. Despite huge investments made on water supply, many schemes are non-functional due to lack of social awareness, improper handling and maintenance activities.

But due to the issues related with arsenic filtering units, such as sludge and backwash disposal and management of the filter media, this treatment option was only viable as a last resort. Therefore, use of non-contaminated surface water sources as mini water supply schemes and driving water from deep aquifers is Governments new policy of tackling with the situation. But second option cannot be much efficient in providing safe water if large quantities of water are being subtracted, then the only solution to get arsenic-free water is surface water. Therefore, river Ganga is a suitable option for supplying safe drinking water. In order to supply a large portion of residents with drinking water, large-scale surface water treatment plants have to be built which supply the treated water to the villages using pipes. In the long run, these treatment plants can also provide household connections.

Acknowledgements The authors take this opportunity to thanks S.N. Mishra (Executive Engineer, Monitoring Dept.) PHED, Bihar, for his kind support and inspiration. Thanks are due to D.S. Mishra Sir (Joint Secretary) for taking keen interest in arsenic studies and being a constant source of inspiration during the initial phases of arsenic study.

References

ATSDR (2000) Toxicological profile for arsenic. Public Health Service Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services

BIS (2009) Drinking water—specification (IS-10500:2009)

BIS (2012) Drinking water—specification (second revision) IS-10500:2012

CGWB and BARC (2009) Studies on arsenic pollution of groundwater using isotopic and geochemical methods in arsenic Bhojpur District of Bihar, India. Patna, CGWB-Mid Eastern Region, p 49

CGWB and PHED (2005) A report on status of arsenic contamination in groundwater in the state of Bihar and action plan to mitigate it. Central Ground Water Board, Govt. of India and Public Health Engineering Dept, Govt. of Bihar

Chen SL, Yeh SJ, Yang MH, Lin TH (1995) Trace element concentration and arsenic speciation in the well water of a Taiwan area with endemic blackfoot disease. Biol Trace Elem Res 48:263–274

Das N, Sengupta S (2008) Arsenicosis: diagnosis and treatment. Indian J Dermatol Venereol Leprol 74:571–581

Goldberg S, Johnston CT (2001) Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modelling. J Colloid Interface Sci 234:204–216

IARC (2004) International Agency for Research on Cancer, Some drinking-water disinfectants and contaminants, including arsenic, vol. 84. IARC, Monographs, Lyon

Kumar C (2015) Status and mitigation of arsenic contamination in groundwater in India. Int J Earth Environ Sci 1:1–10

Mandal BK, Suzuki KT (2002) Arsenic round the world: a review. Talanta 58:201–235

Matthijs B, Merijn J, Andrew W (2013) Dealing with arsenic in rural Bihar, India. Evaluating the successes and failures of mitigation projects and providing a long-term mitigation strategy

Miller WH, Schipper HM, Lee JS, Singer J, Waxman S (2002) Mechanisms of action of arsenic trioxide. Cancer Res 62:893–903

MoWR (Ministry of Water Resources) (2015) Report of the inter-ministerial group (IMG) for 'Arsenic Mitigation' river development and Ganga rejuvenation government of India

NIH & CGWB (2010) Mitigation and remedy of groundwater arsenic menace in india: a vision document

Petrick JS, Ayala-Fierro F, Cullen WR, Carter DE, Vasken AH (2000) Monomethylarsonous acid (MMAIII) is more toxic than arsenite in chang human hepatocytes. Toxicol Appl Pharmacol 163:203–207

PHED (2008) Arsenic pollution in groundwater in Bihar, report

PHED Department Bihar, personal communication with executive engineer S.N. Mishra and Joint Secretary D.S. Mishra

Saha D, Dwivedi SN, Sahu S (2009) Arsenic in ground water in parts of middle Ganga Plain in Bihar—an appraisal. Bhu—Jal News 24:82

Sharma VK, Sohn M (2009) Aquatic arsenic: toxicity, speciation, transformations, and remediation. Environ Int 35:743–759

Singh SK, Ghosh AK (2012) Health risk assessment due to groundwater arsenic contamination: children are at high risk. Hum Ecol Risk Assess Int J 18:751–766

SOES (2012) Groundwater arsenic contamination in middle Ganga plain, Bihar, India: a future danger?. Jadavpur University, Kolkata, India, School of Environmental Science

UNDP, United Nations Development Programme, human development report (2011) A better future for all, united nations development programme. New York, Sustainability and Equity

WHO, World health Organization (1993) Guidelines for drinking-water quality. World Health Organization, Geneva

Woolson EA (1975) Arsenical pesticides. ACS symposium series vol. 7. American Chemical Society, Atlantic City

Simultaneous Removal of Arsenic and Nitrate in Anaerobic Batch Reactors

A. K. Shakya and P. K. Ghosh

Abstract Arsenic contamination of drinking water is a severe problem around the world. Arsenic consumptions in low or high concentrations either through contaminated drinking water or food may cause arsenicosis in humans. Nitrate is often found as co-contaminant with arsenic in groundwater of many rural and urban areas throughout the world. This project investigates the simultaneous removal of arsenic and nitrate by means of terminal electron-accepting process (TEAP) in suspended growth batch bioreactors. Arsenic and nitrate were effectively removed in batch reactors from an initial concentration of 550 µg/L and 150 mg/L, respectively and comply with the WHO as well as BIS guidelines for drinking water. Mineralogical analyses using field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDS) analyses indicated that biogenic arsenic sulfide mineral phases are the likely mechanisms for arsenic removal in the bioreactors.

Keywords Co-contaminant · Biogenic sulfide · TEAP

Introduction

Arsenic and nitrate are the most common pollutants in groundwater. Simultaneous occurrence of nitrate and arsenic from groundwater is reported from various locations around the world (Fytianos and Christophoridis 2004; Tellez et al. 2005). After pathogenic contamination, arsenic poisoning happens to be second most important health hazard in the world related to drinking water. Arsenic poisoning in humans may cause melanosis, keratosis, hyperkeratosis, gangrene, and skin cancer (Singh et al. 2015). More than 150 millions people all over the world, including nearly 110 millions of South and South-east Asian countries, are at risk of arsenicosis due to drinking water arsenic contamination (Ravenscroft et al. 2009).

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The World Health Organization's maximum contaminant level (MCL) of arsenic is 10 μg/L. Arsenic pollution is caused by geogenic as well as anthropogenic activities which includes volcanic emissions, mining wastes, smelting operations and landfilling (Singh et al. 2015). If we consider the cases of nitrates, the major nitrate pollution sources include agricultural runoff and unsafe domestic/industrial effluent discharge etc. (Bhatnagar and Sillanpaa 2011).

In the past several decades, a number of technologies, including oxidation, coagulation–flocculation, adsorption, ion exchange, phytoremediation, and biological methods, have been developed to remove arsenic from contaminated groundwater (Ng et al. 2004). Similarly, nitrate remains another common toxic pollutant that is linked with diverse kinds of cancers, adverse reproductive problems, infectious diseases, and diabetes in humans including "blue baby syndrome" in infants (Majumdar and Gupta 2000; Ward et al. 2005). Keeping in mind the link between serious health problems and excessive concentration of nitrate in drinking water, WHO recommended nitrate concentration limit of 50 mg NO_3^-/L (WHO 2011). Further, the high nitrate values in groundwater has become a significant environmental problem in Australia, Canada, China, Europe, India, Japan, USA, and many other parts of the world (Kapoor and Viraraghavan 1997). It has been frequently detected at hundreds of mg/L in groundwater in many rural areas in India (Kakar 1981). Nitrate is most commonly removed from drinking water using ion exchange or reverse osmosis (Pintar and Batista 2006). Biological nitrate removal from drinking water has been widely studied and is commonly applied at the full-scale level in the world (Mateju et al. 1992). Although nitrate and arsenic have been frequently co-exist in groundwater, there are biotechnologies that can only remove arsenic or nitrate separately. There are no technologies that can simultaneously remove nitrate and arsenic in a single treatment step. Accordingly, it is urgently necessary to seek cost-effective biological methods that can simultaneously remove nitrate and arsenic from contaminated groundwater. In this context, it has been reported that bacteria have the ample ability to take nitrate, arsenic, sulfate, etc., as the terminal electron acceptors in presence of an electron donor for respiration (Lovley and Chapelle 1995). The terminal electron-accepting process (TEAPs) enable microorganisms to use a number of suitable electron acceptors present in a system for their energy generation process sequentially. The ability of sulfate-reducing bacteria to reduce arsenic as well as other metals and metalloids has been well documented (Jong and Parry 2003). Many sulfate-reducing bacteria are reported that can reduce sulfate to sulfide as well as As(V) to As(III), so that arsenic can be effectively removed as sulfide insoluble precipitate (Luo et al. 2008). Anaerobic nitrate-reducing bacteria reduce nitrate to dinitrogen gas and sulfate-reducing bacteria reduce arsenic, sulfate and produce sulfides; these types of systems provide a novel and promising solution for simultaneous arsenic and nitrate removal from contaminated groundwater. Therefore, this cost-effective and efficient bioremediation method can be used in the poverty-stricken arsenic-poisoning areas.

In the present study, authors have investigated the potential of simultaneous removal of nitrate and arsenic from groundwater by acclimated sludge under anaerobic conditions. The biogenic precipitate was characterized by field emission scanning electron microscopy (FESEM). This study showed that mixed microbial consortia successfully removed nitrate and arsenite from polluted groundwater by means of terminal electron-accepting process (TEAP) in suspended growth batch bioreactors.

Materials and Methods

Experimental Setup

High-density polyethylene conical flasks with the effective volume of 250 mL were used as the reactors. The cap was butyl synthetic rubber, with air tightness, and the solution volume was 100 mL, including feed medium and inoculation sludge. Simulated groundwater was added into the reactor with a sterile syringe. Residual air in the reactor was expelled by purging nitrogen gas. The reactors were covered with aluminum foil and incubated in a shaking incubator at 120 rpm.

Inoculum and Starting up

Anerobic sludge was collected from the anoxic pond of IIT Guwahati Sewage Treatment Plant (Guwahati, India). Seed culture for inoculation of reactors was obtained by mixing sludge collected from IIT Guwahati sewage treatment plant, a bench-scale perchlorate and nitrate-reducing anoxic bioreactor, and a bench-scale sulfate removal anoxic bioreactor. Acclimatized sludge (100 mg/L as MLVSS) was added as inoculum in the experiments. Based on carbon required for complete removal of all electron acceptors (i.e., residual DO, nitrate, arsenate, and sulfate) and average net yield of 0.4 g biomass/g COD acetate, 39 mg/L acetic acid as carbon was supplemented in synthetic groundwater with a safety factor of 1.5. The composition of simulated groundwater is given in Table 1. All the chemicals used were of analytical grade. To investigate the potential for bio-reduction of nitrate and arsenic (V), a test group and two control groups were examined. The test group was investigated with three replications, with starting As(V) concentrations 250 µg/L, nitrate 50 mg/L and sulfate 25 mg/L, to ensure the reliability of results. One control group was investigated without inoculum, while other control group was inoculated but without sulfate, keeping arsenic and nitrate concentrations same. All groups were examined at pH 6.8 and 35 °C for 7 days. The medium pH was set as 6.8 because groundwater pH is neutral in most cases. The batch reactors were also evaluated for arsenic removal capacity at different initial concentrations of arsenic, i.e., 250, 350, 450, and 550 µg/L. The effect of initial nitrate concentration, i.e., 50, 100, and 150 mg/L, on nitrate removal capacity and its effect on arsenic removal were also evaluated.

Table 1 Composition of the simulated groundwater

Components	Concentration	Components	Concentration
$NaNO_3$ (mg/L as NO_3^-)	50*	$CaCl_2$ (mg/L as Cl^-)	13.0
Na_2SO_4 (mg/L as SO_4^{2-})	25	$MgCl_2.6H_2O$ (mg/L as Cl^-)	13.0
$Na_2HAsO_4.7H_2O$ (mg/L as As)	0.25*	NaCl (mg/L as Cl^-)	13.0
$NaHCO_3$ (mg/L as HCO_3^-)	40	CH_3COOH (mg/L as C)	39
K_2CO_3 (mg/L as CO_3^{2-})	1.5	H_3PO_4 (mg/L as P)	0.5

*Variable concentration were used

Analytical Methods

Samples for pH, nitrate, sulfate, and residual COD were analyzed promptly on the same day. Liquid samples were centrifuged at 8000 rpm for 10 min (R-24 REMI) and then filtered prior to nitrate, sulfate, COD, and arsenic measurements. The pH of the medium from reactor was measured using pH meter (Thermo Scientific). Nitrate was measured using an UV-visible spectrophotometer (Varian, Cary 50 Bio) at 220 and 275 nm. Sulfate analysis was done using digital nephelo-turbidity meter (132, Systronics). Residual COD was measured by using closed reflux titrimetric method (Hach DRB 200). In general, standard techniques as given in Standard Methods for the Examination of Water and Wastewater (APHA 2005) have been followed unless otherwise stated. Samples for total arsenic were acidified to a final concentration of 0.02 N HCl to solubilize any precipitates and stored at 4 °C after filtering through 0.2-mm filters. Total arsenic samples were analyzed within 48 h by using an atomic absorption spectrometer (Varian, Spectr AAnalyst 800). A continuous flow hydride generation system was used for detection of arsenic concentration with detection limits of 1 μg/L As (T). Biogenic precipitates were analyzed using field emission scanning electron microscope–energy-dispersive X-ray spectroscopy (FESEM-EDS). After centrifugation, the pellets were collected and frozen at –20 °C for 12 h and then freeze-dried C for 48 h. The freeze-dried samples were examined using a FESEM (Sigma, Carl Zeiss, Germany). The elemental composition of precipitate was analyzed using EDS (Oxford instruments, Germany).

Results

Nitrate and Arsenic Removal

The increase in MLVSS suggests that mixed microbial consortia grew well using nitrate, sulfate, and arsenate as the terminal electron acceptor under anoxic condition in the presence of acetate as electron donor (Fig. 1e). This increase in MLVSS also suggests that the mixed culture not only utilized various electron acceptors but also showed resistance to toxicity of arsenite. In the uninoculated control group, the removal percentage of nitrate and arsenic removal was not observed. When there were no mixed culture present, the nitrate and arsenic concentration remained unchanged which demonstrated that nitrate and arsenic removal was a biochemical process. In inoculated control group without sulfate, complete nitrate removal and nearly 1% arsenic was observed which showed that physical adsorption on biomass contributed a small amount of arsenic removal. This means arsenic removal is associated with sulfate reduction. The mixed culture almost completely reduces the 50 mg/L nitrate present in the medium with in 24 h (Fig. 1a). As shown in Fig. 1d, the total soluble As concentration dropped to 10.0 ± 2.0 µg/L from an initial arsenic concentration of 250 µg/L. Furthermore, with respect to the effect of initial arsenic concentration on arsenic removal, arsenic removal was always in accordance with drinking water permissible limits (Fig. 1d). Arsenic removal percentages by the mixed microbial consortia were not affected by high arsenic concentration, also indicating that the mixed culture viability was not inhibited by arsenite toxicity in the experimental concentration range. The high

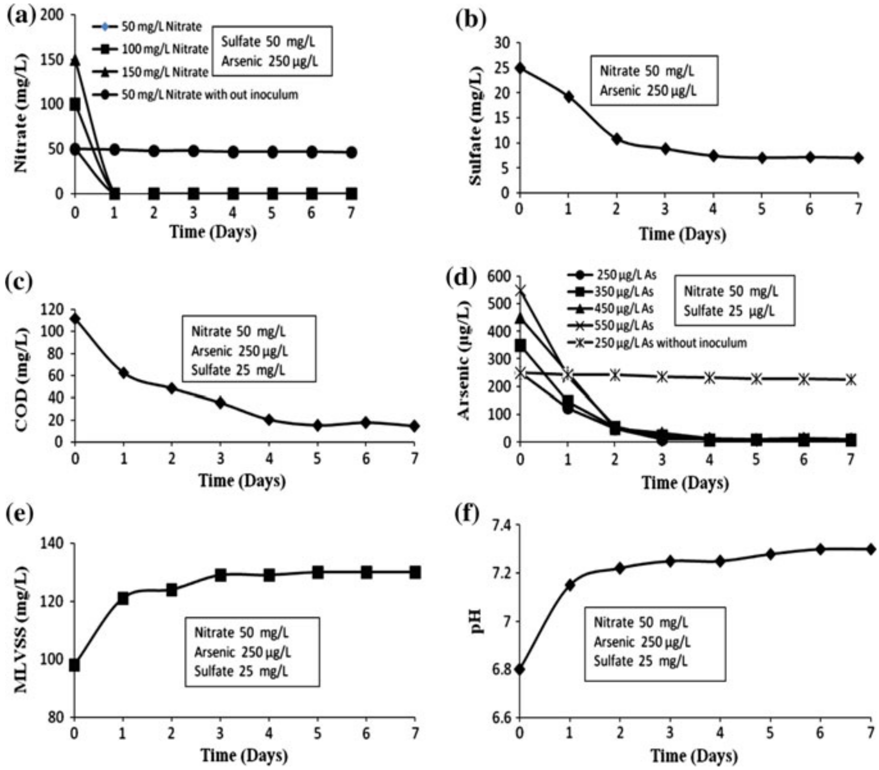

Fig. 1 Change of nitrate (**a**), sulfate (**b**), and arsenic (**d**) concentrations in the medium inoculated or uninoculated with mixed culture as a function of incubation time in presence of various concentrations of arsenic and nitrate. The COD profile (**c**) MLVSS concentration (**e**) and pH profile (**f**)

arsenic concentration had no impact on the reduction rate of nitrate. The results also confirmed that high nitrate concentration of 100 and 150 mg/L had negligible impact on the arsenic removal and provided almost complete nitrate removal (Fig. 1a). In the inoculated medium with an initial sulfate concentration of 25 mg/L, 70.0% ± 2% sulfate reduction was seen in first 4 days, and no considerable sulfate removal was observed in next 3 days (Fig. 1b). The decrease in arsenic concentration started after sulfate reduction and decreased in a stepwise manner along with sulfate reduction. As most of the arsenic was removed during sulfate reduction period which confirmed the precipitation of reduced arsenic with the sulfide formed as a result of sulfate reduction. In summary, mixed culture and sulfate were essential. Once these conditions were met, the arsenic removal was possible.

COD removal was rapid on the first day, and about 70.0% ± 2% COD was removed (Fig. 1c). This is in compliance with the complete nitrate removal. COD removal became slow during 2–6 d as sulfate reduction occurred slowly. In the uninoculated control, almost no COD removal were observed, confirming that the biological removal of nitrate and arsenic was the dominant process. The final pH of the synthetic ground water was in range of 7.2 ± 0.2 (Fig. 1e).

Characterization of Precipitates

The FESEM image of precipitates formed in inoculated medium is shown in Fig. 2a. EDS analysis showed that the precipitates were mainly composed of As (35.40%), and S (64.60%) (Fig. 2b). The results indicated that reduced arsenic was probably precipitated with sulfide or by adsorption on to biomass.

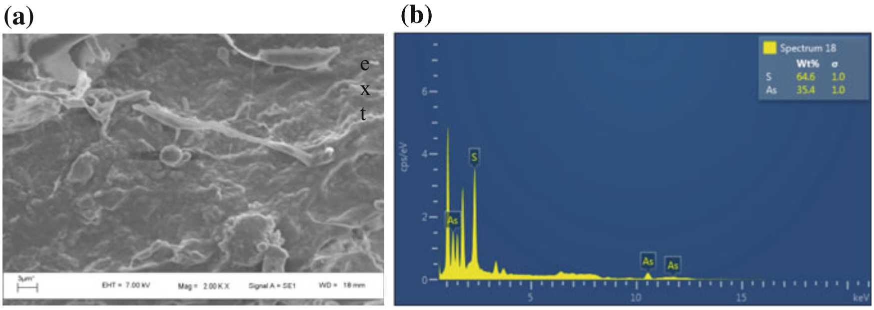

Fig. 2 FESEM image (**a**) and EDS analysis of precipitate (**b**) formed in the batch reactor

Discussion

The batch reactor employed in this study relies on terminal electron-accepting processes (TEAPs) which involves coupling the oxidation of an electron donor to the reduction of electron acceptors (DO, nitrate, sulfate, and arsenate). This is similar to the terminal electron-accepting processes (TEAPs) observed in natural environments (Lovley and Chapelle 1995). The acetic acid was selected as carbon source as it has been approved for drinking water treatment. In addition, many nitrate and sulfate-reducing bacteria can utilize acetic acid as their electron donor (Calderer et al. 2010; Rabus et al. 2013). Anaerobic nitrate- and sulfate-reducing bacteria have been found in habitats such as activated sludge (Nielsen and Nielsen 1998). Nitrate removal followed by arsenate and sulfate removal was observed in the reactors, which is following the thermodynamic favorability of electron acceptors (Macy et al. 1996). In chemical analyses of the liquid samples, sulfate reduction corresponded with arsenic removal, and arsenite (As^{+3}) can react with sulfide (S^{2-}) and result in the formation of arsenic sulfides; it is possible that arsenic was removed through the precipitation of arsenic sulfides. The EDS results were consistent with results found by other investigators. They reported arsenic precipitation as orpiment (As_2S_3) (Newman et al. 1997) and realgar (AsS) (O'Day et al. 2004), and confirmed the formation of arsenic sulfides by extensive X-ray absorption near edge structure and thermodynamic modeling (Kirk et al. 2004; Onstott et al. 2011, Battaglia-Brunet et al. 2012). Some amount of arsenic may also get adsorbed on to biomass as reported by Teclu et al. (2008). In present study, although the exact arsenic removal processes are not clear, it is evident that when compared to the control group containing no mixed culture, sulfate reduction can greatly enhance the arsenic removal efficiency.

Conclusion

The present article investigated the simultaneous bioremoval of arsenic and nitrate by acclimatized mixed microbial consortia. The microbes utilized nitrate, sulfate, and arsenate as the electron acceptors in a sequential manner in the presence of the electron donor (acetic acid). Nitrate was reduced to nitrogen gas, while arsenic was removed by biogenic sulfides through the formation of arsenosulfides, and/or surface precipitation and adsorption on to the biomass. Total soluble As removal was consistent with the trend of sulfate reduction. This work demonstrates the feasibility of anaeroic biological treatment systems for achieving simultaneous removal of arsenic and nitrate from contaminated groundwater. Nitrate was found below detection limits even at increased influent nitrate concentration of 150 mg/L, and this did not affect arsenic removal. When the synthetic feed was supplemented with

550 μg/L, 98% arsenic removal was achieved. Although the influent pH was 6.8, the effluent pH averaged 7.2 throughout the study. The findings of this study can be applied in column reactors in order to check the viability of the process in treating drinking water.

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References

APHA (2005) Standard methods for the examination of water and wastewater. 21st edition

Battaglia-Brunet F, Crouzet C, Burnol A, Coulon S, Morin D, Joulian C (2012) Precipitation of arsenic sulphide from acidic water in a fixed-film bioreactor. Water Res 46:3923–3933

Bhatnagar A, Sillanpaa M (2011) A review of emerging adsorbents for nitrate removal from water. Chem Eng J 168:493–504

Calderer M, Gibert O, Marti V et al (2010) Denitrification in presence of acetate and glucose for bioremediation of nitrate-contaminated groundwater. Environ Technol 31:799–814

Fytianos K, Christophoridis C (2004) Nitrate, arsenic and chloride pollution of drinking water in Northern Greece. Elaboration by applying GIS. Environ Monit Assess 93:55–67

Jong T, Parry DL (2003) Removal of sulfate and heavy metals by sulfate reducing bacteria in short-term bench scale upflow anaerobic packed bed reactor runs. Water Res 37:3379–3389

Kakar YP (1981) Nitrate pollution of ground water in Southern and South-Western Haryana, India. In: van Duijvenbooden PG, Lelyveld H (eds) Studies in environmental science, vol 17, Elsevier, pp 125–129

Kapoor A, Viraraghavan T (1997) Nitrate removal from drinking water—review. J Environ Eng 123:371–380

Kirk MF, Holm TR, Park J, Jin Q, Sanford RA, Fouke BW, Bethke CM (2004) Bacterial sulfate reduction limits natural arsenic contamination in groundwater. Geology 32:953–956

Lovley DR, Chapelle FH (1995) Deep subsurface microbial processes. Rev Geophys 33:365–381

Luo Q, Tsukamoto T, Zamzow K, Miller G (2008) Arsenic, selenium, and sulfate removal using an ethanol-enhanced sulfate-reducing bioreactor. Mine Water Environ 27:100–108

Macy JM, Nunan K, Hagen KD, Dixon DR, Harbour PJ, Cahill M, Sly LI (1996) *Chrysiogenes arsenatis* gen. nov., sp. nov., a new arsenate-respiring bacterium isolated from gold mine wastewater. Int J Syst Bacteriol 46:1153–1157

Majumdar D, Gupta N (2000) Nitrate pollution of groundwater and associated human health disorders. National Environmental Engineering Research Institute, Nagpur, India

Mateju V, Cizinska S, Krejci J, Janoch T (1992) Biological water denitrification—a review. Enzyme Microb Technol 14:170–183

Newman DK, Kennedy EK, Coates JD, Ahmann D, Ellis DJ, Lovley DR, Morel FM (1997) Dissimilatory arsenate and sulfate reduction in *Desulfotomaculum auripigmentum* sp. nov. Arch Microbiol 168:380–388

Ng K-S, Ujang Z, Le-Clech P (2004) Arsenic removal technologies for drinking water treatment. Rev Environ Sci Biotechnol 3:43–53

Nielsen JL, Nielsen PH (1998) Microbial nitrate-dependent oxidation of ferrous iron in activated sludge. Environ Sci Technol 32:3556–3561

O'Day PA, Vlassopoulos D, Root R, Rivera N (2004) The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. Proc Natl Acad Sci USA 101:13703–13708

Onstott TC, Chan E, Polizzotto ML, Lanzon J, DeFlaun MF (2011) Precipitation of arsenic under sulfate reducing conditions and subsequent leaching under aerobic conditions. Appl Geochem 26:269–285

Pintar A, Batista J (2006) Improvement of an integrated ion-exchange/catalytic process for nitrate removal by introducing a two-stage denitrification step. Appl Catal B: Environ 63:150–159

Rabus R, Hansen TA, Widdel F (2013) Dissimilatory sulfate-and sulfur-reducing prokaryotes. In: The Prokaryotes. Springer, Berlin, pp. 309–404

Ravenscroft P, Brammer H, Richards K (2009) Arsenic pollution: a global synthesis. Wiley, New York

Singh R, Singh S, Parihar P, Singh VP, Prasad SM (2015) Arsenic contamination, consequences and remediation techniques: a review. Ecotoxicol Environ Saf 112:247–270

Teclu D, Tivchev G, Laing M, Wallis M (2008) Bioremoval of arsenic species from contaminated waters by sulphate-reducing bacteria. Water Res 42:4885–4893

Tellez RT, Chacon PM, Abarca CR, Blount BC, Landingham CBV, Crump KS, Gibbs JP (2005) Long-term environmental exposure to perchlorate through drinking water and thyroid function during pregnancy and the neonatal period. Thyroid 15:963–975

Ward MH, DeKok TM, Levallois P, Brender J, Gulis G, Nolan BT, VanDerslice J (2005) Workgroup report: drinking-water nitrate and health-recent findings and research needs. Environ Health Perspect, pp 1607–1614

WHO (2011) Guidelines for drinking-water quality. World Health Organisation, Geneva, vol 4, pp 315–318

Oxyanions Removal by Biological Processes: A Review

Ranjeeta Bhande and Pranab Kumar Ghosh

Abstract Major toxins of drinking water are oxyanions such as perchlorate, nitrate, sulfate, arsenic (arsenate and arsenite), iodate, uraninites, bromate, chromates and selenite, which affects the human health with numerous diseases such as thyroidal disorder, diarrhea and cancer. It is imperative to understand the effects of various parameters that affect the bioreduction of oxyanions removal. Sometimes it helps in reduction in treatment cost in terms of amount of carbon requirement while simultaneous bioreduction of multiple number of oxyanions. As for example, simultaneous bioreduction of sulfate and nitrate will generate innocuous nitrogen and elemental sulfur as an end product. Formation of nitrogen gas and elemental sulfur is due to chemical reaction between the highly reactive nitrite (an intermediate of denitrification process) and sulfides (an unacceptable end product of sulfate bioreduction). The oxyanions, perchlorate, nitrate and sulfate can play a major role in removal of arsenic in the form of solid arseno-sulfide from aqueous phase. However, the efficiency will greatly depend upon the feeding and operating conditions of the reactor such as COD/oxyanion ratio, oxyanions loading rate, and hydraulic retention time (HRT). In this paper, effect of various factors on bioreduction of different oxyanions is discussed.

Keywords Arsenic · Bioreduction · Nitrate · Oxyanions · Perchlorate · Sulfate

Introduction

Rapidly growing population in the world causes intense industrialization leading to contaminate fresh water bodies. Hence, it will be undoubtedly a major challenge to provide safe drinking water to all in the coming century. The major toxins of drinking water are oxyanions [perchlorate, nitrate, sulfate, arsenic (arsenate and

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arsenite), iodate, uraninite, bromate, chromate, selenate, etc.] composed with oxygen and central element and are of great concern among researchers and environmentalists due to their particular toxicity. In this review article, the effect of these oxyanions, treatment policies and safe limit for human consumption has been dealt with briefly. Oxyanions affect human body in the form of numerous diseases and disorder due to high concentration in drinking water. As for example, thyroidal disorder, diarrhea and cancer (lung, bladder and skin) may occur due to high concentration of perchlorate (>24.5 μg/L), sulfate (>250 mg/L), arsenate (>0.01 mg/L) and nitrate (>50 mg/l), respectively. In the past few years, physio-chemical and biological processes have been proposed to remove oxyanions from drinking water. Among different treatment options, biological treatment is gaining more attention due to its low cost and higher efficiency. However, it is imperative to understand the effects of various parameters that affect the biological process of oxyanions removal. Although simultaneous bioreduction of multiple number of oxyanion is a more complicated process, proper operation of bioreactor may help in further reduction in treatment cost in terms of the amount of carbon source requirement. As for example, simultaneous bioreduction of sulfate and nitrate will generate innocuous nitrogen and elemental sulfur as the end products. Formation of nitrogen gas and elemental sulfur is due to chemical reaction between the highly reactive nitrite (an intermediate of denitrification process) and sulfides (an unacceptable end product of sulfate bioreduction). The oxyanions, perchlorate, nitrate and sulfate can play a major role in removal of arsenic in the form of solid arseno-sulfide from aqueous phase. However, the efficiency will greatly depend upon the feeding and operating conditions of the reactor (COD/oxyanion ratio, oxyanion loading rate, hydraulic retention time, etc.).

The use of biological treatment, either in situ or ex situ, has recently gaining more importance due to certain advantages offered in comparison with conventional physico-chemical treatment methods. Biological treatment does not require chemical reagents rather using microorganisms to reduce, oxidize or eliminate groundwater contaminants, either as the sole treatment technique or combined with other conventional physico-chemical processes, such as sorption and filtration. Bacteria are widespread, abundant, geochemically reactive components of aquatic environments. A basic decision must be taken about the need for removal of single oxyanion versus multiple oxyanion. It is necessary to determine whether it is desirable to remove only one or two oxyanion using selective physico-chemical process or to remove multiple oxyanion via biological treatment. However, the size of the system is another factor to be considered in process selection. Ground water serves as a sole source of drinking water in the rural communities and urban areas, in many parts of the world. However, over the past few decades, the ever-growing population, industrialization, urbanization, agricultural activities and unskilled utilization of water resources have led to degradation of water quality of surface and ground water as well as generation of toxic contaminants such as inorganic anions, metal ions, synthetic organic chemicals which have increased public concern about the quality of drinking waters. Toxicity of inorganic oxyanions leads to harmful effect to humans at a very low concentration; thus, these are gaining more attention.

Some of these toxic oxyanions remain undetected due to the presence of them at a trace amount, and there are no visible and organoleptic changes in drinking water, thereby increasing health possible risk (Velizarov et al. 2004). Inorganic anions have a property to react with environmental oxygen and form an oxyanion. These oxidized contaminants are considered as serious drinking water pollutants. Several number of hazardous oxyanion persists in the environment such as sulfate, nitrite, nitrate, chlorate, perchlorate, arsenate found in potential harmful concentration in numerous drinking water sources (DeZuane 1997).

Presence of these toxins in underground water has been reported from different parts of India (Liu et al. 2005). The majority of them can be considered as micropollutants because maximum allowed concentration of these compounds is set by drinking water quality regulatory standards in relative range from µg/L to mg/L. Thus, there is a need to focus greater attention on the future impact of oxyanion on drinking water quality and its health issues as well as planning and development of treatment processes.

Occurrence and Sources of Oxyanions

Sulfate

Sulfate is major contaminants among all oxyanions which is found in natural water and industrial effluents, such as inorganic chemical industry wastewater and acid mine drainage. Natural source of sulfate is biological oxidation of sulfur and sulfide ores like pyrite and chemical weathering of sulfur-containing minerals. Industrial wastewaters are responsible for most anthropogenic emissions from paper, board, paint, plastic and rubber industries, molasses-based fermentation industries and edible oil refineries. Certain industrial effluents may contain several thousands of milligrams per liter, while domestic sewage contains typically less than 500 mg/L. The damage caused by sulfate emissions is not direct, since sulfate is a non-toxic compound. Laxative effect may occur due to consumption of drinking water containing sulfate concentrations in excess of 600 mg/L (WHO 2004). The natural sulfur cycle can be unbalanced due to high sulfate concentrations (Silva et al. 2002) which increase risk in human health (Rinzema 1988). Apart from this, corrosive effect of sulfate toward concrete is becoming a major water quality problem. The taste threshold limit for the most prevalent sulfate salts varies from 250 to 500 mg/L (Haghsheno et al. 2009).

Nitrate

The primary source of nitrate is surface runoff from agricultural land areas where excess amount of fertilizer and pesticides has been applied. The production of plastics, fuel additives, nitric acid and explosive production plant contribute nitrate contamination on water (Wakida and Lerner 2005). Nitrate concentration greater than 50 mg/L can be fatal for infants (WHO 2011). In infants, reduction of nitrate into nitrite occurs, which combines with hemoglobin in blood known as methemoglobin causing blue baby syndrome. Several diseases causing nitrate ingestion in drinking water have been reported such as infant mortality (Super et al. 1981) and central nervous system birth defects (Dorsch et al. 1984). High levels of nitrate are responsible for eutrophication in surface water, resulting water anoxia and dead zones. Moreover, nitrate forms a component of total dissolved solids, which is widely used as an indicator of water quality. After high level of nitrate ingestion in drinking water sources can lead to a potential risk to environment and public health, acute poisoning may occur.

Perchlorate

Environmental contamination with oxyanions of chlorine (perchlorate, chlorate, chlorite) mostly perchlorate is controversial issue, which is constantly growing problem over a last couple of years (Charnley 2008; Carrasco 1993). Perchlorate is a most oxidized form of chlorine which came into prominence as a pollutant in the late 1990s. It has been found that both naturally and as a manmade manufactured substance which originates as a contaminant in ground and surface waters from the dissolution of perchloric acid and its salts including ammonium, potassium, magnesium or sodium perchlorate (Schilt 1979; Hogue 2003). Manmade source of perchlorate is manufacture and disposal of ammonium perchlorate, a highly reduced compound used as the oxidizer in solid rocket propellant and also has been found in fertilizers derived from Chilean caliche (Urbansky et al. 2001). Perchlorate is found in groundwater throughout the USA (USEPA 2004), and it interferes with iodide uptake into the thyroid gland, disrupting thyroid function (Capen and Martin 1989; Wolff 1998) and making it an endocrine disruptor on humans. Thus, perchlorate is listed by the USEPA in the drinking water contaminant candidate list (USEPA 2005). EPA has established an official reference dose (RFD) of 0.0007 mg/kg/day of perchlorate for human uptake, while notification level set by California is 6 μg/L for drinking water (CDHS 2006), and also EPA is following the same standards.

Arsenate

The common source of arsenic in environment is the manufacturing of pesticides (including wood preservatives), desiccants, glass, alloys, electronic components (semiconductors), pigments and pharmaceuticals. The elements occur in environment in different oxidation states and form various species, e.g., arsenics as As(V), As(III) and As(0). Arsenic can be converted into different form or transformed into insoluble compounds in combination with other elements, such as iron hydroxides, which further can be removed by precipitation with sulfide (Rittle et al. 1995). Arsenic contamination in natural water is an important issue and a worldwide public health problem which challenge for the engineers, scientists and even the policy makers, due to its hazardous acute toxicity (Shemirani et al. 2005). Arsenic toxicity was reported up to 2 mg/L in drinking water. Based on earlier published reports, arsenic in drinking water causes 200,000–270,000 deaths from cancer in Bangladesh alone (Chowdhury et al. 1997). A heavier natural contamination in groundwater due to the presence of arsenic and selenium has been recorded in southeast Argentine. The arsenic content of nearly 50% of the water samples from this area ranged from 100 to 316 μg/L with a maximum value of 3810 μg/L (Nicolli et al. 1989). Inorganic arsenic is considered a cause of human carcinogen, associated with increased risk of cancer of the skin, lungs, urinary bladder, liver and kidney. Chronic toxicity due to drinking arsenic-contaminated water had been one of the worst environmental health hazards in India (West Bengal) in which 6 districts were effected (RoyáChowdhury 1995).

Conventional Treatment Strategies for Oxyanions

Several treatment technologies are available for removal of oxyanions. Conventional water treatment process is used for removal of inorganic pollutants through physical, chemical and biological processes. Physical and chemical treatment process involves coagulation and precipitation, adsorption, ion exchange etc. Membrane separation processes such as, reverse osmosis (RO), nano-filtration (NF), ultra-filtration (UF), microfiltration (MF), dialysis (D), Donnan dialysis (DD) and electro dialysis (ED), foam flotation and solvent extraction are also practiced. Conventional water treatment processes, such as coagulation and precipitation, are very effective, but limiting due to ferric or alum dose applications and requirement of frequent backwashes when high coagulant doses are used. In chemical oxidation and adsorption process, efficient control of the pH, temperature and oxidation step is required. Similarly in physical membrane processes, inorganic anions cannot be destroyed and have been argument as costly solution. Recently, reverse osmosis and ion exchange have been demonstrated simultaneous removal of multiple contaminants (Matos et al. 2006). However, high energy input and post-treatment demand make it unreliable solution to be used as scale-up solution

(Nerenberg and Rittmann 2004). Biological reduction is most appreciable due to its low capital cost, and it offers selective removal of the target anion from water using anoxic bacteria. These microorganisms grow under appropriate microenvironmental conditions (pH, oxidation–reduction potential, temperature, etc.) by utilizing anions as an electron acceptors and organic (heterotrophic microorganisms) or inorganic (autotrophic microorganisms) compounds as electron donors.

Overview of Biological Oxyanion Removal

Different oxyanions have a unique characteristic based on their persistence in water, taste and odor thresholds, health risk, transport and fate, current laboratory analytical methods, remediation techniques and regulatory issues. These points must be considered to proceed for detailed remediation efforts or developing public policy. The use of biological treatment, either in situ or ex situ, has recently gaining importance due to certain advantages over conventional physico-chemical treatment methods. Biological treatment does not require chemical reagents or intensive energy source and can achieve more than 90% removal efficiency. In the progressive sections, treatment of various oxyanion such as sulfate, arsenate, perchlorate and nitrate using biological process has been dealt deeply.

Sulfate

Biological removal of sulfate from wastewater proceeds in two steps: Firstly, sulfate or sulfite reduces to sulfide, and second sulfide partially re-oxidizes into elemental sulfur, which can be recovered as by-product (Buisman 1989). Sulfate-reducing bacteria play a major role in sulfur reduction, which fall into three major categories (1) the δ-subclass of proteobacteria (more than 25 genera), (2) the gram-positive bacteria (*Desulfotomaculum*, *Desulfosporosinus*), (3) this class formed by *Thermodesulfobacterium* and *Thermodesulfovibrio*. These major categories can be further subdivided as psychrophilic, mesophilic and thermophilic for categories 1, 2 and 3, respectively (Rabus et al. 2006). Under anaerobic conditions, sulfate reduces to sulfide in the presence of sulfate-reducing bacteria (SRB) and finally sulfide can precipitate with heavy metals (Tichý et al. 1998). In anaerobic sulfur reduction, hydrogen and acetate are intermediate and precursors to methane formation in the presence of SRBs. Sulfate-reducing microorganisms are very diverse as compared to methanogens in terms of their metabolic possibilities (Stams and Elferink 1997). Methanogens can grow using countless organic compounds as sources of energy for their metabolism, but SRBs were mainly found to be relied on hydrogen as key electron source (Mizuno et al. 1998). Competition between SRB and methanogens is a major failure for treatment of sulfate-rich wastewater. Under anaerobic conditions, SRB competes with methane-producing bacteria (MPB) for electron sources such as acetate and hydrogen, which reduces sulfur removal efficiency from wastewater. Hence, proper pre-treatment of inoculums is required to inhibit methanogens.

Nitrate

Biological methods provide most promising option for treatment of nitrate pollution from wastewater and drinking water. Aerobic and denitrification have been widely reported in earlier studies (Joo et al. 2005; van Rijn et al. 2006). Biological denitrification is a mechanism by which denitrifying bacteria use nitrate as a terminal electron acceptor in their respiratory process in the absence of oxygen and converts nitrite and nitrate into harmless elemental nitrogen gas (Prosnansky et al. 2002). Denitrifying bacteria are ubiquitous in nature which can be cultivated from wastewater treatment plants as seeds (Gamble et al. 1977). It is to be noted that biological denitrification is a slow process which requires long time to achieve sufficient treatment efficiency for industrial wastewater containing high concentrations of nitrate. Denitrification can be carried out by both heterotrophic and autotrophic bacteria. Nitrate reduction to nitrogen gas under anoxic condition proceeds as follows $NO_3 \rightarrow NO_2 \rightarrow NO \rightarrow N_2O \rightarrow N_2$ under two types of major reactions: In the first reaction, nitrate is reduced to nitrite which is further reduced to gaseous products such as nitrogen or nitrous oxide, a process called nitrate respiration or denitrification. The second reaction involves the reduction of nitrate to ammonia via nitrite, a process known as ammonification. Nitrate reduction under anaerobic conditions is known as dissimilation process, in which bacteria utilize nitrate instead of oxygen as a terminal electron acceptor. Oxygen concentrations ranging from 0.1 to 0.2 mg have been found to have inhibitory effects on denitrification (Rittmann et al. 1989). *Thiobacillusdenitrificans* and *Thiomicrospiradenitrificans* are two known obligatory chemolithotrophic sulfur bacteria with the ability of reducing nitrate to nitrogen in which *Thiobacillusdenitrificans* can grow under either of aerobic or anaerobic conditions, whereas *Thiomicrospiradenitrificans* grows well under anaerobic condition or only under extremely low oxygen concentrations (Gevertz et al. 2000).

Perchlorate

Microbial reduction of perchlorate to chloride by dissimilatory perchlorate-reducing bacteria (DPRB) is considered as an effective treatment strategy for perchlorate remediation (Dudley et al. 2008). DPRB are known to reduce perchlorate (ClO_4^-) to chlorate (ClO_3^-) and then to chlorite (ClO_2^-) using a single enzyme (per) chlorate reductase (PCR) (Bender et al. 2005). Chlorite then converts into chloride and molecular oxygen by chlorite dismutase (Giblin and Frankenberger 2001). Owing to its solubility and non-reactivity, bioremediation has been targeted as the most promising method for reduction of perchlorate contamination. Evidences/researches have shown that perchlorate can be easily metabolized by perchlorate-reducing bacteria (PCRB) and biological approaches using perchlorate as an electron acceptor can completely reduce perchlorate without any waste disposal production; this has been proven to be the most effective and economically attractive approach for treating perchlorate-contaminated waters. Recent studies have reported wide variety of organic (e.g., acetate, lactate, pyruvate, fumarate, succinate, methanol, ethanol) and inorganic (H_2, reduced iron, elemental sulfur, H_2S and $S_2O_3^{2-}$) substances which can serve as electron donors for biological perchlorate reduction (Son et al. 2011). Autotrophic PCRB use inorganic compounds as electron donors for perchlorate reduction (Shrout et al. 2005), and conversely, heterotrophic PCRB use organic electron donors for perchlorate reduction (Okeke and Frankenberger 2005).

Many denitrifying bacteria found to have capability to reduce chlorate. However, under denitrifying conditions, gas formation occurred but chloride production was not observed, implying that nitrate inhibited chlorate respiration (Logan 1998). Sodium chlorate decomposition was observed in water-saturated soil in the presence of *Penicillium*, *Aspergillus* and *Fusarium* (Åslander 1928). Moreover, microbes known to respire both chlorate and perchlorate are *Vibrio dechloraticans* Cuznesove B-1168 (Korenkov et al. 1976); *Acinetobacter thermotoleranticus* (Stepanyuk et al. 1993); *Ideonelladechloratans* (Malmqvist et al. 1994); Proteobacteria GR-1 (Rikken et al. 1996).

Arsenate

Arsenate removal was achieved by bioaccumulation process in which microbial biomass acts as a biosorbent for biosorption. The physiological uptake of arsenic by microorganisms occurring active and passive processes involves several process including As(V) reduction, As(III) oxidation and the various methylation reactions. The relative proportions of the various arsenic oxidation states in a given environment are governed by bioprocesses involved in the metabolism by microorganisms (Macur et al. 2004). These reactions enhance the resistance mechanisms to protect the bacteria from the toxic effects of arsenic. Two major mechanisms of reduction were reported in literature for As. The first one is related to the detoxification of the cells, in which arsenate ions enter the cells via phosphate transporters, due to structural homologies with phosphate ions (Mukhopadhyay and Rosen 2002). This transformation process followed by the excretion of arsenic is a common occurrence in the environment and is widespread in bacteria (Páez-Espino et al. 2009). A second reduction process, known as dissimilatory reduction, in this case, bacterial cells utilize As(V) as an electron acceptor and gain metabolic energy by "breathing" arsenic (Ahmann 1994). For heterotrophic bacteria and chemoautotrophic bacteria, As(III) serves as an electron donor and reduces oxygen or nitrate. The energy produced in this process fixes CO_2, which provide a carbon source to bacteria for growth. In abundance of both heterotrophic and chemoautotrophic bacteria, heterotrophic As(III)-oxidizing bacteria can develop using organic substances synthesized by chemoautotrophic bacteria (Battaglia-Brunet et al. 2002).

Factors Affecting Oxyanion Removal

Temperature

Temperature is a main controlling factor for the growth of sulfate-reducing bacteria and also has distinguished effect on hydrogen sulfide solubility in water organic substrate decomposition (Neculita et al. 2008). Sulfate removal via biological process can be achieved under wide range of temperature from mesophilic (25–35 °C) to thermophilic range of 35–70 °C (Austin 1984). However, the optimum temperature for mixed culture of sulfate-reducing bacteria using lactate as a carbon source was found at 37 °C (Singh et al. 2011). Temperature shifting from mesophilic to thermophilic at a rate of 1 °C per day could produce promising removal efficiency of sulfur from wastewater (Rudd et al. 1985). Rintala and Lettinga 1992 suggested an increment of 1–3 °C/d up to 48 °C for complete cessation of sulfate conversion in UASB reactors.

The hot and high loading rate of sulfate-rich industrial wastewater, thermophilic temperature as much as 55 °C was found to be an attractive alternative with sulfur conversion rate of up to 7.5 g SO_4^{2-}/L d. The process produced less sludge which is an additional advantage of this process (Zinder 1986). Waste sludge mixture (WS) and anaerobic digester effluent (ADS) containing sulfate of 6700 and 5300 mg SS l^{-1}, respectively, were subjected to treat at low temperature (8 °C) in which a 7 mmol and 1.6 mmol of sulfate were reduced, respectively (Sahinkaya 2009). The protection of the biofilm and extracellular polymer on bacteria is highly necessary for steady performance of reactors (Jianping et al. 2003). Low temperature can inhibit the activity of intracellular enzyme and result in a low-level metabolism. Too high temperature can lead to protein denaturation. The optimum temperature for treating nitrate–nitrogen wastewater ranges from 20 to 35 °C. However, some researchers reported that denitrification ceases below 5 °C (Stanford et al. 1975). Chlorate removal at concentrations of 83 to 1250 mg/L (1 to 15 mM) was found to be almost 100% with stoichiometric conversion of chlorate to chloride at 37 °C (Malmqvist et al. 1991). Wu et al. (2008) reported 40 °C as an efficient temperature condition for chlorate to chloride conversion under which 41 mg l^{-1} perchlorate was reduced with 82% efficiency within 12 h, whereas only 32.8% perchlorate was removed in the same time frame at 30 °C. One hundred percent perchlorate reduction needed 24 h at 40 °C which was 2 times lesser than 30 °C temperature condition (48 h).

PH

SRB and methanogens are syntrophs. The inhibition of SRB was found to be correlated with the sulfide concentration and MPB with the free H_2S concentration (Hilton and Oleszkiewicz 1988). SRB are usually inhibited at pH values lower than 6 or higher than 9 (Widdel 1988). O'Flaherty (1998) have studied the effect of pH and sulfide concentration on the growth of SRB and MPB, in pure culture and anaerobic digester sludge. It was observed that propionate and hydrogen-utilizing SRB have higher sulfate affinities than acetate-, butyrate- or ethanol-degrading SRB. Moreover, between pH 7.0 and 7.5, the growth rates of the SRB and MPB were similar. Sulfide inhibition of all of the groups of bacteria was related to the un-dissociated H_2S concentration between pH 6.8 and 7.2, while above pH 7.2 the inhibition was related to the total sulfide concentration. The production of sulfide is the major problem associated with the anaerobic treatment of sulfate-rich wastewater. The critical value for sulfide concentration in anaerobic reactor was found to be 150 mg/L for optimum growth of SRB (Rinzema 1988).

Higher concentration of hydrogen sulfide (>150 mg/l) was affected methane production due to increase in volatile acids (Lawrence 1966). Hence, to reduce the inhibitory effect of sulfide (H_2S, pKa = 7), reactor should be operated at slightly alkaline condition 7.9 ± 0.1 for optimum growth of acetotrophic sulfate-reducing bacteria (Dries et al. 1998). Furthermore, in a long-term study, the optimum pH was found to be 7 for biological sulfate removal in anaerobic two-stage pilot plant (Genschow et al. 1996). In a gas–liquid–solid fluidized bed bioreactor, the maximum removal of 96% was observed at pH value of 7.0, and in the pH range of 6.5–7.5, the reactor was demonstrated optimum performance wherein removal efficiency was found in the range of 92–96% (Jianping et al. 2003). Therefore, it was believed that the condition becomes non-ideal in the reactor for treatment under pH value higher than 8.0 or lower than 6.0 due to inhibitory effect of super-acidity or super-alkalinity on the activity of intracellular enzyme of bacteria. Moreover, at pH higher than 8, NO_2–N accumulation occurs which may inhibit the NO_2–N reductase enzyme. The rate of denitrification depends on pH and temperature of the system. Above pH 9.0 and below 5.5, denitrification rate proceeds with slow kinetics (Valera and Alexander 1961).

The optimum pH range for excellent growth of denitrifying bacteria was reported to be 6.5–7 (Matsubara and Mori 1968). However, in pure culture systems, optimum pH for denitrification was found to be varied with the electron donor substrate such as hydrogen, acetate and lactate (Sacks and Barker 1952). During treatment of perchlorate-rich wastewater containing 500 mg/L perchlorate using heterotrophic perchlorate-reducing bacterium (*Azospira* sp.), optimum perchlorate reduction of 100% in 60 h with reduction rate of 11.2 mg/L h was observed in pH range of 7.8–8 (Xu et al. 2015). Furthermore, at pH below 6, the removal rate of perchlorate was found to be reduced drastically. In this line, Wu et al. (2008) also reported similar kind of results in which perchlorate reduction from the wastewater was found to be inhibited under pH of 6, whereas at pH 8, maximum perchlorate removal efficiency of 96.5% was recorded in 12 h of reactor operation.

Hydraulic Retention Time (HRT)

The effect of hydraulic retention time on oxyanion removal has been documented widely. Many researchers have been reported profound effect of HRT in terms of oxyanion removal. The effect of HRT was observed on sulfate removal; sulfate removal efficiency increased with the increase in HRT. At HRT of 8 h, more than 90% sulfate removal was obtained when initial sulfate concentrations were of 600 and 1200 mg/L (Mizuno et al. 1998). Van Houten et al. (1994) investigated the potential of synthesis gas utilization by feeding CO (up to 20%) to H_2/CO_2-fed mesophilic gas lift reactors. With 20% of CO in the H_2 feed gas, sulfate reduction rates as high as 100 mmol $L^{-1}d^{-1}$ were achieved. However, the removal rate was decreased after 2 days of operation due to competition between CO-derived H_2 between thermophilic sulfate reducers and methanogens (Sipma et al. 2006).

The selection of HRT is an important parameter for biological reactor since in many cases, the HRT between 6 and 14 h found suitable for substrate consumption competition between thermophilic sulfate reducers and methanogens (Vallero et al. 2005). Moreover, the methanogens had a generation time of 4.5 h (Sipma et al. 2007). Hence, reducing the HRT below 4 h could achieve more than 95% sulfate removal (Sipma et al. 2006, 2007). On contrary, studies on up-flow anaerobic suspended growth reactor operated in continuous, suggested that the higher retention time significantly decreased sulfide concentration in effluent and had less chance of biomass washout which is a great concern in case of biological reactor (Polo-Christy 2001). Very few studies are available on nitrate and perchlorate removal concerning HRT. However, Zhao et al. 2011 reported 100% removal of nitrate at HRT of 8 h. HRT of 1.5 h was found sufficient to remove 99.8% of nitrate in earlier study (Hanaki and Polprasert 1989). In case of perchlorate, a HRT of 0.6 h could achieve 100% removal of perchlorate from wastewater under pH of 7 and at temperature of 37 °C.

COD/Oxyanion Ratio

COD/Sulfate

During oxyanion treatment, the COD/oxyanion ratio should be optimized to get reliable results. However, the bacteria present in inoculums require organic carbon for proper maintenance in metabolism. Therefore, COD is an important parameter. The theoretical COD/sulfate ratio is 0.67 for the sulfate-reducing biomass to completely remove the organic matter (COD) (Rinzema 1988). However, for wastewaters in which COD/sulfate ratios exceed 0.67, the complete removal of organic matter can only be achieved when sulfate reduction and methanogenesis occur, simultaneously. It was observed that at COD/sulfate ratio of 1.7–2.7, there was an active competition between the MPB and SRB (Choi and Rim 1991). However, SRB were found to be dominant at lower COD/sulfate ratio (<1.5) and the MPB were dominated at higher ratios (>1) (Jeong et al. 2008). On the other hand, at COD/sulfate ratios >3 and <1.5, benzoate was found to be consumed by the SRB, converting the sulfate into sulfide, which suppressed methane production (Li et al. 1996). It was reported that the COD/sulfate ratio >10 can ensure complete sulfate removal (Mendez et al. 1989). When COD/sulfate ratio was below 6 in ethanol-fed expanded granular sludge blanket (EGSB), the sulfate removal efficiency decreased due to healthy competition between SRB and MPB (de Smul et al. 1999). In addition, at COD/sulfate ratio of 7, maximum sulfate removal rate of 4 g S/L d could be achieved with 80–90% removal efficiency. In conclusion, in order to obtain complete sulfate reduction, theoretically COD/sulfate ratio of 0.67 will be required. If the ratio is lower, extra electron donor (i.e., methanol, ethanol, H_2 or synthesis gas) has to be dosed. Moreover, partial oxidation of sulfide to elemental sulfur requires dissolved oxygen concentrations about 0.1 mg L^{-1} in the sulfide-oxidizing reactor, which has to add externally (Pol et al. 1998).

COD/Nitrate

The influence of different types and magnitudes of carbon sources to achieve the optimum removal of nitrate has been investigated widely. The C/N ratio should be balanced for proper denitrification. C/N ratio lower than theoretical demand leads to improper denitrification, while a high C/N ratio can cause accumulation of nitrite other than nitrogen gas (Kim et al. 2002; Chiu and Chung 2003). A C/N ratio of about 1.45 was found to be optimal when acetic acid was used as the carbon source (Dahab and Lee 1988). The optimum ratio of methanol, ethanol and acetic acid to nitrate–nitrogen ratios was found to be 2.9, 2.35 and 4.3, respectively, in a pilot scale rotating biological contactor (RBC) (Mohseni-Bandpi and Elliott 1998).

A recent batch study revealed that COD/NO_3^-–N ratio of 7–8 is critical ratio for simultaneous occurrence of denitrification and methanogenesis in the anaerobic effluent of cassava stillage (CS) and glucose-fed culture at pH 7.8 and temperature 35 °C rotated at 110 rpm (Xie et al. 2012). In addition, incomplete denitrification was observed at COD/NO_3^-–N ratio below 7 in both the anaerobic effluent of CS and glucose-fed cultures due to the insufficient availability of organic carbon. Laboratory-scale completely stirred anaerobic digesters were fed with synthetic wastewaters containing nitrate and nitrite in which glucose was used as source of organic carbon. Denitrification percentage was found to be decreased as the COD/nitrate and nitrite ratio decreased from 8.86 to 6.65, respectively (Akunna et al. 1992). Therefore, upon various studies it can be concluded that C/N ratio has an important role while treating nitrogen-rich wastewater. Overdose of carbon source can bring toxic effect to the denitrifiers, a higher concentration of nitrogen can inhibit assimilation of nitrogen in the cell wall.

COD/Perchlorate

The optimal acetate/perchlorate ratio of 1.2 mg COD/mg $ClO_4^-$was suggested to achieve 100% removal efficiency of perchlorate and lactate from wastewater (Shrout and Parkin 2006). In another study, the optional ratio of acetate/perchlorate was found to be 1.3, which was equivalent to 1.45 mg-COD per mg—perchlorate (Nor et al. 2011). This ratio was comparable to the theoretical ratio of 1.32 mg-COD mg-perchlorate^{-1}, which can be calculated using the thermodynamic approach (Rittmann and McCarty 2001). Moreover, in this line, Kim and Logan (2001) obtained slightly higher ratio value of 2.1 mg-COD/mg ClO_4^- with acetate-fed packed-bed bioreactor.

Simultaneous Removal of Multiple Oxyanion

Some SRB gain energy by the fermentation of glucose. However, in the absence of favorable electron acceptor, SRB can utilize O_2 and nitrate as an electron acceptor (Dar et al. 2008). Hence, in a single reactor or single biological system two or more oxyanions can be reduced, but the efficiency may be less as compared to single oxyanion. As for example, wastewater containing 4000 mg/L of lactate and 200 mg/L of sulfate, at stable performance of reactors, the sulfate reduction efficiency of 80% with reduction rate of 3.84 g/L/d was observed (Dar et al. 2008). After replacing the electron acceptor with nitrate, the efficiency of reactor was reduced from 85 to 65%. Addition of nitrate stimulate the activity of NR-SOB (Nitrate reducing sulfide oxidizing bacteria), resulting in oxidation of sulfide to sulfate (García de Lomas et al. 2006). Hence, the capture of electron flow by SRB stimulated growth of DB (denitrifying bacteria), which resulted in higher removal efficiency of nitrate (combined effect). Moreover, in the presence of many electron acceptors the utilization of hydrogen is sequenced in the following manner: oxygen, nitrate, nitrite and then perchlorate. The maximum surface loading nitrate and perchlorate at ratio of 0.21 mg NO_3-N/cm^2-d: 3.4 µg ClO_4/cm^2-d was found to achieve more than 99.5% reduction efficiency (Ziv-El and Rittmann 2009). This multioxyanion concept can reduce simultaneously more than one oxyanion, but it has some limitations such as high amount of hydrogen requirement and requires pH control and temperature control, etc.

Conclusion

In this manuscript, the factor affecting the removal rate or efficiency of oxyanions under biological treatment process was dealt extensively. A number of research works have been reported in the last decade with stress to remove sulfides through oxidation by nitrate and/or nitrite. Recent work on groundwater treatment on arsenate removal in the presence of iron, sulfate and nitrate highlights the potential use of multiple oxyanions for water treatment by biological process. While the microorganisms get energy through denitrification process, sulfides (formed due to sulfate bioreduction) react with iron to form iron sulfide that helps in arresting arsenic through adsorption. The results obtained by various researchers are very informative for removal of oxyanions from wastewater as well as drinking water. Several convenient designs are available for such treatment; however, due to complexity of system, these are not adequate to meet the demand. Hence, more intensive and intelligent design will be required to get highly efficient systems at a low price.

References

Ahmann D (1994) Microbe grows by reducing arsenic. Nature 371:750

Akunna JC, Bizeau C, Moletta R (1992) Denitrification in anaerobic digesters: possibilities and influence of wastewater COD/N-NOX ratio. Environ Technol 13(9):825–836

Åslander A (1928) Experiments on the eradication of Canada thistle: *Cirsium arvense*, with chlorates and other herbicides. US Government Printing Office

Austin GT (1984) Shreve's chemical process industries. pp 136–138

Battaglia-Brunet F, Dictor MC, Garrido F, Crouzet C, Morin D, Dekeyser K, Clarens M, Baranger P (2002) An arsenic (III)-oxidizing bacterial population: selection, characterization, and performance in reactors. J Appl Microb 93(4):656–667

Bender KS, Shang C, Chakraborty R, Belchik SM, Coates JD, Achenbach LA (2005) Identification, characterization, and classification of genes encoding perchlorate reductase. J Bacteriol 187(15):5090–5096

Buisman CJ (1989) Biotechnological sulphide removal with oxygen

Capen CC, Martin SL (1989) The effects of xenobiotics on the structure and function of thyroid follicular and C-cells. Toxicol Pathol 17(2):266–293

Carrasco N (1993) Iodide transport in the thyroid gland. BBA—Rev Biomembr 1154(1):65–82

CDHS (2006) Perchlorate in California drinking water. Overview and links Department of Health Services, Sacramento, California

Charnley G (2008) Perchlorate: overview of risks and regulation. Food Chem Toxicol 46(7):2307–2315

Chiu YC, Chung M-S (2003) Determination of optimal COD/nitrate ratio for biological denitrification. Int Biodet Biodegrad 51(1):43–49

Choi E, Rim JM (1991) Competition and inhibition of sulfate reducers and methane producers in anaerobic treatment. Water Sci Technol 23(7):1259–1264

Chowdhury TR, Mandal BK, Samanta G, Basu GK, Chowdhury P, Chanda C, Karan NK, Lodh D, Dhar RK, Das D (1997) Arsenic in groundwater in six districts of West Bengal, India: the biggest arsenic calamity in the world: the status report up to August, 1995. Springer, Berlin, pp 93–111

Dahab MF, Lee YW (1988) Nitrate removal from water supplies using biological denitrification. J Water Pollut Control Fed, 1670–1674

Dar SA, Kleerebezem R, Stams AJ, Kuenen JG, Muyzer G (2008) Competition and coexistence of sulfate-reducing bacteria, acetogens and methanogens in a lab-scale anaerobic bioreactor as affected by changing substrate to sulfate ratio. Appl Microbiol Biotechnol 78(6):1045–1055

de Smul A, Goethals L, Verstraete W (1999) Effect of COD to sulphate ratio and temperature in expanded-granular-sludge-blanket reactors for sulphate reduction. Process Biochem 34 (4):407–416

DeZuane J (1997) Handbook of drinking water quality. Wiley, New York

Dorsch MM, Scragg RK, McMichael AJ, Baghurst PA, Dyer KF (1984) Congenital malformations and maternal drinking water supply in rural South Australia: a case-control study. Am J Epidemiol 119(4):473–486

De Smul A, Goethals L, Grootaerd H, Verstraete W (1998) High rate biological treatment of sulfate-rich wastewater in an acetate-fed EGSB reactor. Biodegradation 9(2):103–111

Dudley M, Salamone A, Nerenberg R (2008) Kinetics of a chlorate-accumulating perchlorate-reducing bacterium. Water Res 42(10):2403–2410

Gamble TN, Betlach MR, Tiedje JM (1977) Numerically dominant denitrifying bacteria from world soils. Appl Environ Microbiol 33(4):926–939

García de Lomas J, Corzo A, Gonzalez JM, Andrades JA, Iglesias E, Montero MJ (2006) Nitrate promotes biological oxidation of sulfide in wastewaters: experiment at plant-scale. Biotechnol Bioeng 93(4):801–811

Genschow E, Hegemann W, Maschke C (1996) Biological sulfate removal from tannery wastewater in a two-stage anaerobic treatment. Water Res 30(9):2072–2078

Gevertz D, Telang AJ, Voordouw G, Jenneman GE (2000) Isolation and characterization of strains CVO and FWKO B, two novel nitrate-reducing, sulfide-oxidizing bacteria isolated from oil field brine. Appl Environ Microbiol 66(6):2491–2501

Giblin T, Frankenberger W (2001) Perchlorate and nitrate reductase activity in the perchlorate-respiring bacterium perclace. Microbiol Res 156(4):311–315

Haghsheno R, Mohebbi A, Hashemipour H, Sarrafi A (2009) Study of kinetic and fixed bed operation of removal of sulfate anions from an industrial wastewater by an anion exchange resin. J Hazard Mater 166(2–3):961–966

Hanaki K, Polprasert C (1989) Contribution of methanogenesis to denitrification with an upflow filter. Res J Water Pollution Control Federation, 1604–1611

Hilton BL, Oleszkiewicz JA (1988) Sulfide-induced inhibition of anaerobic digestion. J Environ Eng 114(6):1377–1391

Hogue C (2003) Rocket-fueled river. Chem Eng News 81(33):37–46

Jeong T-Y, Cha G-C, Seo Y-C, Jeon C, Choi SS (2008) Effect of COD/sulfate ratios on batch anaerobic digestion using waste activated sludge. J Indust. Eng Chem 14(5):693–697

Jianping W, Lei P, Liping D, Guozhu M (2003) The denitrification treatment of low C/N ratio nitrate-nitrogen wastewater in a gas–liquid–solid fluidized bed bioreactor. Chem Eng J 94 (2):155–159

Joo H-S, Hirai M, Shoda M (2005) Characteristics of ammonium removal by heterotrophic nitrification-aerobic denitrification by Alcaligenes faecalis No. 4. J Biosci Bioeng 100(2):184–191

Kim K, Logan BE (2001) Microbial reduction of perchlorate in pure and mixed culture packed-bed bioreactors. Water Res 35(13):3071–3076

Kim Y-S, Nakano K, Lee T-J, Kanchanatawee S, Matsumura M (2002) On-site nitrate removal of groundwater by an immobilized psychrophilic denitrifier using soluble starch as a carbon source. J Biosci Bioeng 93(3):303–308

Korenkov VN, Romanenko VI, Kuznetsov SI, Voronov JV (1976) Process for purification of industrial waste waters from perchlorates and chlorates. Google Patents

Lawrence AW (1996) The effects of sulfide on anaerobic treatment. Air Wat Pollut Int J 10:207–221

Li Y-Y, Lam S, Fang HH (1996) Interactions between methanogenic, sulfate-reducing and syntrophic acetogenic bacteria in the anaerobic degradation of benzoate. Water Res 30 (7):1555–1562

Liu A, Ming J, Ankumah RO (2005) Nitrate contamination in private wells in rural Alabama, United States. Sci Total Environ 346(1):112–120

Logan BE (1998) A review of chlorate-and perchlorate-respiring microorganisms. Bioremed J 2 (2):69–79

Macur RE, Jackson CR, Botero LM, Mcdermott TR, Inskeep WP (2004) Bacterial populations associated with the oxidation and reduction of arsenic in an unsaturated soil. Environ Sci Technol 38(1):104–111

Malmqvist Å, Welander T, Gunnarsson L (1991) Anaerobic growth of microorganisms with chlorate as an electron acceptor. Appl Environ Microb 57(8):2229–2232

Malmqvist Å, Welander T, Moore E, Ternström A, Molin G, Stenström I-M (1994) *Ideonella dechloratans* gen. nov., sp. nov., a new bacterium capable of growing anaerobically with chlorate as an electron acceptor. Syst Appl Microbiol 17(1):58–64

Matos CT, Velizarov S, Crespo JG, Reis MA (2006) Simultaneous removal of perchlorate and nitrate from drinking water using the ion exchange membrane bioreactor concept. Water Res 40(2):231–240

Matsubara T, Mori T (1968) Studies on denitrification IX. Nitrous oxide, its production and reduction to nitrogen. J Biochem 64(6):863–871

Mendez R, Ten Brummeler E, Pol LH (1989) Start up of UASB reactors treating sucrose-containing substrates with a low cod/sulfate ratio. Environ Technol 10(1):83–90

Mizuno O, Li YY, Noike T (1998) The behavior of sulfate-reducing bacteria in acidogenic phase of anaerobic digestion. Water Res 32(5):1626–1634

Mohseni-Bandpi A, Elliott DJ (1998) Groundwater denitrification with alternative carbon sources. Water Sci Technol 38(6):237–243

Mukhopadhyay R, Rosen BP (2002) Arsenate reductases in prokaryotes and eukaryotes. Environ Health Persp 110(Suppl 5):745

Neculita C-M, Zagury GJ, Bussière B (2008) Effectiveness of sulfate-reducing passive bioreactors for treating highly contaminated acid mine drainage: I. Effect of hydraulic retention time. Appl Geochem 23(12):3442–3451

Nerenberg R, Rittmann B (2004) Hydrogen-based, hollow-fiber membrane biofilm reactor for reduction of perchlorate and other oxidized contaminants. Water Sci Technol 49(11–12):223–230

Nicolli HB, Suriano JM, Peral MAG, Ferpozzi LH, Baleani OA (1989) Groundwater contamination with arsenic and other trace elements in an area of the Pampa, Province of Córdoba, Argentina. Environ. Geol Water S 14(1):3–16

Nor SJ, Lee SH, Cho K-S, Cha DK, Lee KI, Ryu HW (2011) Microbial treatment of high-strength perchlorate wastewater. Bioresource Technol. 102(2):835–841

O'Flaherty V (1998) Effect of pH on growth kinetics and sulphide toxicity thresholds of a range of methanogenic, syntrophic and sulphate-reducing bacteria. Process Biochem 33(5):555–569

Okeke BC, Frankenberger WT (2005) Use of starch and potato peel waste for perchlorate bioreduction in water. Sci Total Environ 347(1):35–45

Páez-Espino D, Tamames J, de Lorenzo V, Cánovas D (2009) Microbial responses to environmental arsenic. Biometals 22(1):117–130

Pol LWH, Lens PN, Stams AJ, Lettinga G (1998) Anaerobic treatment of sulphate-rich wastewaters. Biodegradation 9(3–4):213–224

Polo-Christy BC (2001) Effect of hydraulic retention time and attachment media on sulfide production by sulfate-reducing bacteria. Electronic thesis and dissertations

Prosnansky M, Sakakibara Y, Kuroda M (2002) High-rate denitrification and SS rejection by biofilm-electrode reactor (BER) combined with microfiltration. Water Res 36(19):4801–4810

Rabus R, Hansen TA, Widdel F (2006) The prokaryotes. Springer, Berlin, pp 659–768

Rikken G, Kroon A, Van Ginkel C (1996) Transformation of (per) chlorate into chloride by a newly isolated bacterium: reduction and dismutation. Appl Microbiol Biotechnol 45(3):420–426

Rintala J, Lettinga G (1992) Effects of temperature elevation from 37 to 55 °C on anaerobic treatment of sulphate rich acidified wastewaters. Environ Technol 13(9):801–812

Rinzema A (1988) Anaerobic treatment of wastewater with high concentrations of lipids or sulfate

Rittle KA, Drever JI, Colberg PJ (1995) Precipitation of arsenic during bacterial sulfate reduction. Geomicrobiol J 13(1):1–11

Rittmann BE, McCarty PL (2001) Environmental Biotechnology: principles and applications. McGraw Hill

Rittmann BE, Huck PM, Bouwer EJ (1989) Biological treatment of public water supplies. Crit Rev Envron Sci Tec 19(2):119–184

RoyáChowdhury T (1995) Arsenic in ground water in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part I. Arsenic species in drinking water and urine of the affected people. Analyst 120(3):643–650

Rudd T, Hicks SJ, Lester JN (1985) Comparison of the treatment of a synthetic meat waste by mesophilic and thermophilic anaerobic fluidized bed reactors. Environ Technol 6(1–11):209–224

Sacks L, Barker H (1952) Substrate oxidation and nitrous oxide utilization in denitrification. J Bacteriol 64(2):247

Sahinkaya E (2009) Microbial sulfate reduction at low (8 °C) temperature using waste sludge as a carbon and seed source. Int Biodeter Biodegr 63(3):245–251

Schilt AA (1979) Perchloric acid and perchlorates

Shemirani F, Baghdadi M, Ramezani M (2005) Preconcentration and determination of ultra trace amounts of arsenic (III) and arsenic (V) in tap water and total arsenic in biological samples by cloud point extraction and electrothermal atomic absorption spectrometry. Talanta 65(4):882–887

Shrout JD, Scheetz TE, Casavant TL, Parkin GF (2005) Isolation and characterization of autotrophic, hydrogen-utilizing, perchlorate-reducing bacteria. Appl Microbiol Biotechnol 67 (2):261–268

Shrout JD, Parkin GF (2006) Influence of electron donor, oxygen, and redox potential on bacterial perchlorate degradation. Water Res 40(6):1191–1199

Silva AJ, Varesche MB, Foresti E, Zaiat M (2002) Sulphate removal from industrial wastewater using a packed-bed anaerobic reactor. Process Biochem 37(9):927–935

Singh R, Kumar A, Kirrolia A, Kumar R, Yadav N, Bishnoi NR, Lohchab RK (2011) Removal of sulphate, COD and Cr(VI) in simulated and real wastewater by sulphate reducing bacteria enrichment in small bioreactor and FTIR study. Bioresource Technol 102(2):677–682

Sipma J, Lettinga G, Stams AJ, Lens PN (2006) Hydrogenogenic CO conversion in a moderately thermophilic (55 °C) sulfate-fed gas lift reactor: competition for CO-derived H2. Biotechnol Progr 22(5):1327–1334

Sipma J, Osuna MB, Lettinga G, Stams AJ, Lens PN (2007) Effect of hydraulic retention time on sulfate reduction in a carbon monoxide fed thermophilic gas lift reactor. Water Res 41 (9):1995–2003

Son A, Schmidt CJ, Shin H, Cha DK (2011) Microbial community analysis of perchlorate-reducing cultures growing on zero-valent iron. J Hazard Mater 185(2):669–676

Stams AJ, Elferink SJO (1997) Understanding and advancing wastewater treatment. Curr Opin Biotech 8(3):328–334

Stanford G, Stanislaw D, Roger A, Vander P (1975) Effect of temperature on denitrification rate in soils. Soil Sci Soc Am J 39(5):867–870

Super M, Heese HV, MacKenzie D, Dempster W, Du Plessis J, Ferreira J (1981) An epidemiological study of well-water nitrates in a group of South West African/Namibian infants. Water Res 15(11):1265–1270

Tichý R, Lens P, Grotenhuis J, Bos P (1998) Solid-state reduced sulfur compounds: environmental aspects and bio-remediation. Crit Rev Environ Sci Tec 28(1):1–40

Urbansky ET, Brown SK, Magnuson ML, Kelty CA (2001) Perchlorate levels in samples of sodium nitrate fertilizer derived from Chilean caliche. Environ Pollut 112(3):299–302

USEPA (2004) Known perchlorate releases in the US

USEPA (2005) State perchlorate advisory levels as of 4/20/05

Valera CL, Alexander M (1961) Nutrition and physiology of denitrifying bacteria. Plant Soil 15 (3):268–280

Vallero MV, Lettinga G, Lens PN (2005) High rate sulfate reduction in a submerged anaerobic membrane bioreactor (SAMBaR) at high salinity. J Membrane Sci 253(1):217–232

Van Houten RT, Pol LWH, Lettinga G (1994) Biological sulphate reduction using gas-lift reactors fed with hydrogen and carbon dioxide as energy and carbon source. Biotechnol Bioeng 44 (5):586–594

van Rijn J, Tal Y, Schreier HJ (2006) Denitrification in recirculating systems: theory and applications. Aquacult Eng 34(3):364–376

Velizarov S, Crespo JG, Reis MA (2004) Removal of inorganic anions from drinking water supplies by membrane bio/processes. Rev Environ Sci Bio Technol 3(4):361–380

Wakida FT, Lerner DN (2005) Non-agricultural sources of groundwater nitrate: a review and case study. Water Res 39(1):3–16

WHO (2004) Sulfate in drinking-water

WHO (2011) Nitrate and nitrite in drinking-water

Widdel F (1988) Microbiology and ecology of sulfate-and sulfur-reducing bacteria. Biol Anaerobic Microorgan, pp 469–585

Wolff J (1998) Perchlorate and the thyroid gland. Pharmacol Rev 50(1):89–106

Wu D, He P, Xu X, Zhou M, Zhang Z, Houda Z (2008) The effect of various reaction parameters on bioremediation of perchlorate-contaminated water. J Hazard Mater 150(2):419–423

Xie L, Chen J, Wang R, Zhou Q (2012) Effect of carbon source and COD/NO3 − –N ratio on anaerobic simultaneous denitrification and methanogenesis for high-strength wastewater treatment. J Biosci Bioeng 113(6):759–764

Xu X, Gao B, Jin B, Zhen H, Wang X, Dai M (2015) Study of microbial perchlorate reduction: considering of multiple pH, electron acceptors and donors. J Hazard Mater 285:228–235

Zhao Y, Feng C, Wang Q, Yang Y, Zhang Z, Sugiura N (2011) Nitrate removal from groundwater by cooperating heterotrophic with autotrophic denitrification in a biofilm-electrode reactor. J Hazard Mater 192(3):1033–1039

Zinder SH (1986) Thermophilic waste treatment systems. Thermophiles: general, molecular and applied biology, pp 257–277

Ziv-El MC, Rittmann BE (2009) Systematic evaluation of nitrate and perchlorate bioreduction kinetics in groundwater using a hydrogen-based membrane biofilm reactor. Water Res 43 (1):173–181

Factors Influencing Electrocoagulation Treatment of UASB Reactor Effluent

Abhipsa R. Makwana

Abstract Upflow anaerobic sludge blanket reactor (UASBR) works best in the hot climatic condition. In India, UASB process has been used in almost 23 sewage treatment plants. However, when UASB process is applied for sewage treatment (where the undiluted BOD is between 200–300 mg/L), the cumulative experience has shown need for post-treatment of UASB effluent. During last two decades, more efforts have been put on use of electrocoagulation (EC) process for treatment of various effluents. Literature has reported promising results also. Study undertaken focuses to evaluate applicability of EC process for post-treatment of UASB reactor-treated municipal wastewater. Understanding the significance of various process variables is initial step to be achieved before optimizing any process. EC has many process variables like current density (CD), electrolysis time, influent waste strength, initial pH, electrolyte dose (NaCl dose), interelectrode distance etc. Here, significance of CD, time and NaCl dose were studied. Response surface methodology (RSM) was used as statistical tool for experimental design and data analysis with Design Expert software version 8.0. It is understood from the results that CD and time are significant variables, while NaCl dose was not found significant variable. Thus, it is reported from the study that process efficiency of electrocoagulation of sewage pretreated with UASBR will be affected with change in current density and electrolysis time but electrolyte variation found insignificant.

Keywords Electrocoagulation · UASBR · Sewage · NaCl dose

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Introduction

Anaerobic technology presents a high potential in most developing countries for domestic wastewater treatment and thus is a suitable and economical solution (Foresti 2002). Within the spectrum of anaerobic sewage treatment technologies, the upflow anaerobic sludge blanket (UASB) reactor offers great promise, especially in developing countries that usually have hot climates (Foresti 2002). India is one of the leading countries in terms of the amount of sewage volume treated by the UASB process (Sato et al. 2006). At present, about 23 number of sewage treatment plants with total installed capacity of 985 MLD (MoEF 2005–2006) based on the UASB are in operation and about 20 number are in pipeline which are likely to be commissioned within next 3–4 years.

UASB technology has been found to be very effective for treatment of high strength industrial effluents particularly from distilleries, pulp and paper, tanneries, and food processing industries. However, when applied for sewage treatment (where the undiluted BOD is between 200–300 mg/L), the cumulative experience has shown that these "unique" features are not convincing for a variety of reasons. Some of the disadvantages are: UASB reactor is able to bring down BOD of sewage only to 70–100 mg/L (Khan et al. 2011). Nutrient removal (nitrogen and phosphorus) is also low during anaerobic treatment. Due to anaerobic conditions, removal of total and faecal coliforms in UASB is about 1–2 on log scale and it entails tertiary treatment for disinfection. Different post-treatment techniques based on physico-chemical and biological processes have been used/attempted for this. These include coagulation-flocculation, aeration, sand filtration, biological processes such as polishing pond, activated sludge process, tricking filter, constructed wetlands, rotating biological contactor, sequence batch reactor and membrane bioreactor.

Electrocoagulation reported to be used widely in treatment of many industrial effluents. A few attempts have been made to assess the applicability of EC as a possible post-treatment for UASB reactor effluent treating poultry manure wastewater (Yetilmezsoy et al. 2009) and unbleached Kraft pulp mill effluent (Buzzini et al. 2007) and gave promising results. Use of EC for post-treatment of UASBR-treated sewage has not yet reported in literature; hence, this study was undertaken to thoroughly understand the applicability of EC as a post-treatment of UASBR-treated sewage. This paper reports basic understanding of significance of process variables like current density, electrolysis time and NaCl dose on EC efficiency. Electrocoagulation is a process consisting of creating metallic hydroxide flocs within the wastewater by electro-dissolution of soluble anodes, usually made of iron or aluminium (Irdemez et al. 2006). The difference between electrocoagulation and chemical coagulation is mainly in the way aluminium ions are delivered (Irdemez et al. 2006). In electrocoagulation, coagulation and precipitation are not conducted by delivering chemicals—called coagulants—to the system but via electrodes in the reactor (Kopral 2002). Suitable electrode choice is very important in electrocoagulation. Most common electrode materials are iron and aluminium. Both of these are cheap, easily found and effective materials (Irdemez et al. 2006).

There are several variables or factors which influence performance of electrocoagulation treatment process. These variables include current density, reaction time, electrolyte concentration (NaCl dose), initial pH, initial effluent concentration, type of electrode connection (monopolar, bipolar etc.), sludge formation, interelectrode distance and temperature. In the present study effect of CD, time and NaCl dose has been studied to understand their effect on COD and turbidity removal using response surface methodology as a statistical tool for process optimization.

Materials and Methods

Experimental

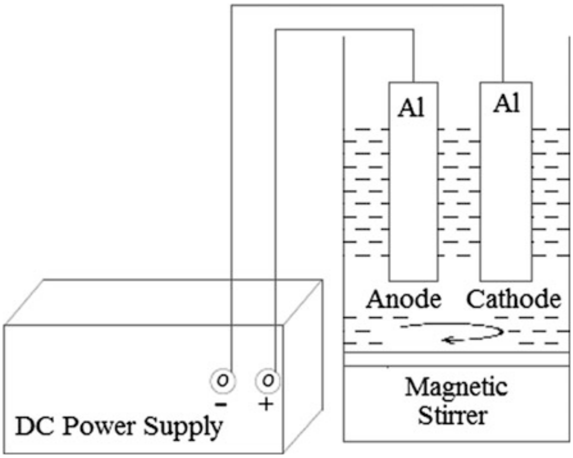
In the experimental study, UASB effluent from Bamroli STP, Surat, was used to carry optimization of EC process. The characteristics of the UASB effluent were analysed, and average values were given in Table 1. The experimental set-up is shown in Fig. 1 for process optimization. The electrocoagulator was made up of Plexiglas with the dimensions of 200 mm × 85 mm × 85 mm. Two electrodes were used, (one anode–one cathode) for RSM study. Both anode and cathodes were made from aluminium plates with dimension of 185 mm × 75 mm × 5 mm, and the effective electrode area was 51 cm^2 per sacrificial anode with interelectrode spacing of 15 mm. The electrodes were dipped into the cell containing UASB effluent with a 0.5 L working volume. The electrodes were connected to the digital DC power supply (30.0 V, 0.0–5.0 A). All laboratory runs were performed at room temperature of 27 ± 3 °C. To increase mass and heat transfer, constant magnetic stirring was applied at 100 rpm. The current density was adjusted to a required value, and the EC process was performed. At the end of each operating time, the treated UASB effluent was collected from 2 cm above the electrocoagulator inner base and then was analysed. Before starting of each run, electrodes were washed with tap water to remove impurities present on the electrode surface. The sacrificial anodes were oven dried and weighed before starting the first run and after completion of each run.

Table 1 Characteristics of UASB effluent

Parameter	Value* Bamroli, STP
COD (mg/L)	210
Turbidity (NTU)	157
Phosphate (mg/L)	3.58
Initial pH	7.51
SS (mg/L)	161
BOD (mg/L)	90
Total coliforms (MPN/100 mL)	31×10^7

*Average value based on analysis of 3 samples

Fig. 1 Experimental set-up for process optimization study



Experimental Design and Data Analysis

The Box-Behnken design (BBD) is an economical, efficient and rotatable quadratic design where factor combinations are at the midpoints of the edges and at the centre (Bezerra et al. 2008; Ferreira et al. 2007). The central points are used to estimate the experimental error and to perform the model adequacy check.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k=1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{1}$$

where y represents the predicted response; x_i and x_j are the independent variables, b_0, b_i, b_{ii} and b_{ij} are regression coefficients for intercept, linear, quadratic and interaction coefficients respectively, ε is the error, and k is the number of variables studied.

Table 2 shows the independent variables used for RSM along with their coded values. The BBD factorial design with five replicates at central point is presented in Table 3. To evaluate the contribution of the three variables, experimental data were analysed and fitted to the following second-order polynomial model using Design Expert 8.0 software.

Table 2 Experimental range and levels of the independent variables

Variable	Factors	Coded factor level		
		−1	0	1
CD (mA/cm^2)	x_1	1	5.5	10
Time (min)	x_2	1	5.5	10
NaCl dose (mg/L)	x_3	0	250	500

Table 3 Design matrix along with observed and predicted response values

Std. run	Influent COD mg/L	Current density mA/cm^2	Contact time min	COD removal (%)		Turbidity removal (%)	
				Actual	Predicted	Actual	Predicted
1	−1	−1	0	26.73	18.45	27.39	12.21
2	1	−1	0	39.60	45.43	40.38	42.94
3	−1	1	0	57.43	57.56	68.92	67.23
4	1	1	0	81.19	84.54	95.86	97.96
5	−1	0	−1	48.51	48.50	52.93	57.77
6	1	0	−1	77.23	75.48	91.72	88.51
7	−1	0	1	41.58	49.74	47.64	59.66
8	1	0	1	84.16	76.72	91.85	90.40
9	0	−1	−1	40.59	42.19	27.39	39.03
10	0	1	−1	82.18	81.30	95.11	94.05
11	0	−1	1	42.57	43.43	39.94	40.92
12	0	1	1	85.15	82.54	95.29	95.94
13	0	0	0	70.30	73.48	87.07	86.48
14	0	0	0	72.28	73.48	89.24	86.48
15	0	0	0	74.26	73.48	89.81	86.48
16	0	0	0	74.26	73.48	89.49	86.48
17	0	0	0	75.25	73.48	88.98	86.48

Results and Discussion

Current density (CD) is the most important factor which has effect on the performance of EC process. Normally, it was observed that increase in CD increases removal efficiency because when the current density increases, the efficiency of ion production on the anode and cathode increases. Therefore, there is an increase in floc production in the solution and hence an improvement in the efficiency of process, but it will increase the cost of the process also, so it is advisable to optimize it to obtain required degree of treatment.

It has been observed that higher electrolysis time increases the removal efficiency; this is so because EC process involves two stages which are destabilization and aggregation. The first stage is usually short, whereas the second stage is relatively long (Kobya et al. 2016). Complete or satisfactory removal can be achieved only when both the stages are completed, which can be possible only when more electrolysis time is given. Hence, lesser time shows lesser removal.

Table salt is usually employed to increase the conductivity of the water or wastewater to be treated. Besides its ionic contribution in carrying the electric charge, it was found that chloride ions could significantly reduce the adverse effect of other anions such as HCO^{3-}, SO_4^{2-}. The existence of the carbonate or sulphate ions would lead to the precipitation of Ca^{2+} or Mg^{2+} ions that forms an insulating layer on the surface of the electrodes. This insulating layer would sharply increase the potential between electrodes and result in a significant decrease in the current efficiency. It is therefore recommended that among the anions present there should be 20% Cl^- to ensure a normal operation of electrocoagulation in water treatment. The addition of NaCl would also lead to the decrease in power consumption because of the increase in conductivity. Moreover, the electrochemically generated chlorine was found to be effective in water disinfections.

Model Development and Validation

Obtained results of effluent COD removal (%) and turbidity removal (%) are presented in Table 3. Observed removal percentages were used to develop the model using second-order polynomial as shown in Eq. (1). Equations (2) and (3) represent model for % COD removal and % turbidity removal in terms of coded factors.

$$\%\text{COD removal} = +73.48 + 13.49x_1 + 19.55x_2 + 0.62x_3 - 10.87x_1^2 - 11.11x_2^2 \tag{2}$$

$$\begin{aligned}\%\text{Turbidity removal} = &+86.48 + 15.37x_1 + 27.51x_2 + 0.95x_3 \\ &- 12.39x_1^2 - 19.00x_2^2\end{aligned} \tag{3}$$

ANOVA test has given quadratic models for % COD and % turbidity removal. ANOVA results for both the removal are represented in Tables 4 and 5. Fisher test

Table 4 Analysis of variance (ANOVA) test for effluent COD concentration

Model term	Source	Sum of squares	d*f*	Mean square	*F* value	*p* value Prob. > *F*	
	Model	5676.71	9	630.75	23.67	0.0002	Significant
1	x_1-current density	1455.86	1	1455.86	54.64	0.0002	
2	x_2-time	3059.01	1	3059.01	114.81	<0.0001	
3	x_3-NaCl dose	3.06	1	3.06	0.11	0.7445	
4	x_1 x_2	29.65	1	29.65	1.11	0.3265	
5	x_1 x_3	48.03	1	48.03	1.80	0.2213	
6	x_2 x_3	0.25	1	0.25	0.01	0.9263	
7	x_1^2	499.44	1	499.44	18.75	0.0034	
8	x_2^2	522.39	1	522.39	19.61	0.0031	
9	x_3^2	1.03	1	1.03	0.04	0.8496	
	Residual	186.50	7	26.64			
	Lack of fit	170.82	3	56.94	14.52	0.0129	Significant

All model term—R^2 = 0.9682, R^2_{adjusted} = 0.9273, $R^2_{\text{predicted}}$ = 0.5297
Model term 1, 2, 3, 7, 8—R^2 = 0.954723, R^2_{adjusted} = 0.934143, $R^2_{\text{predicted}}$ = 0.86321

Table 5 Analysis of variance (ANOVA) test for effluent turbidity

Model term	Source	Sum of squares	d*f*	Mean square	*F* value	*p* value Prob. > *F*	
	Model	10476.01	9	1164.00	22.55	0.0002	Significant
1	x_1-current density	1888.97	1	1888.97	36.60	0.0005	
2	x_2-time	6054.55	1	6054.55	117.31	<0.0001	
3	x_3-NaCl dose	7.15	1	7.15	0.14	0.7208	
4	$x_1\ x_2$	48.64	1	48.64	0.94	0.3640	
5	$x_1\ x_3$	7.33	1	7.33	0.14	0.7175	
6	$x_2\ x_3$	38.29	1	38.29	0.74	0.4176	
7	x_1^2	615.28	1	615.28	11.92	0.0107	
8	x_2^2	1471.10	1	1471.10	28.50	0.0011	
9	x_3^2	141.34	1	141.34	2.74	0.1419	
	Residual	361.30	7	51.61			
	Lack of fit	356.65	3	118.88	102.46	0.0003	Significant

All model term—$R^2 = 0.9667$, $R^2_{\text{adjusted}} = 0.9238$, $R^2_{\text{predicted}} = 0.4728$
Model term 1, 2, 3, 7, 8—$R^2 = 0.9449$, $R^2_{\text{adjusted}} = 0.9199$, $R^2_{\text{predicted}} = 0.8334$

was used to evaluate the significance of each factor and their interaction with each other. Values of "Prob. > *F*" less than 0.0500 indicate model terms are significant (Montgomery 2010; Nair et al. 2014). Coefficients with *p* value greater than 0.1 were considered statistically insignificant and were eliminated from the quadratic equations (Montgomery 2010; Nair et al. 2014). Equations (2) and (3) were developed after eliminating statistically insignificant terms based on *p* value of coefficient for those terms. The *p* value for all the models was less than 0.05 means models for % COD removal and % turbidity removal found to be significant with 5% confidence interval. The "Lack of Fit *p*-value" $\gg 0.1$ for both the removals represent it to be significant. Significant Lack of Fit is bad for model to be fit. NaCl dose being one of the process variable out of the three variables, which is insignificant as the *p* values for both the models for this variable are more than 0.1, which in turn makes the "Lack of Fit" test significant. R^2 being the coefficient of determination, determines overall efficiency of model prediction. In this study, R^2 and R^2_{adjusted} ensures good correlation with each other. On the other hand, $R^2_{\text{predicted}}$ is less than 0.8 for both the models, due to inclusion of insignificant process variable NaCl dose. NaCl dose being the main process variable, its exclusion is not possible. Figure 2a and b represents comparison of actual and predicted values of % COD and % turbidity removal with lesser agreement due to inclusion of NaCl dose which seems to be insignificant as per the ANOVA TEST.

Figure 3a shows interaction effect of NaCl dose and current density on COD removal (%), while Fig. 3b depicts interaction effect of NaCl dose and time on turbidity removal (%). *P values* of interaction effect coefficients of NaCl dose and

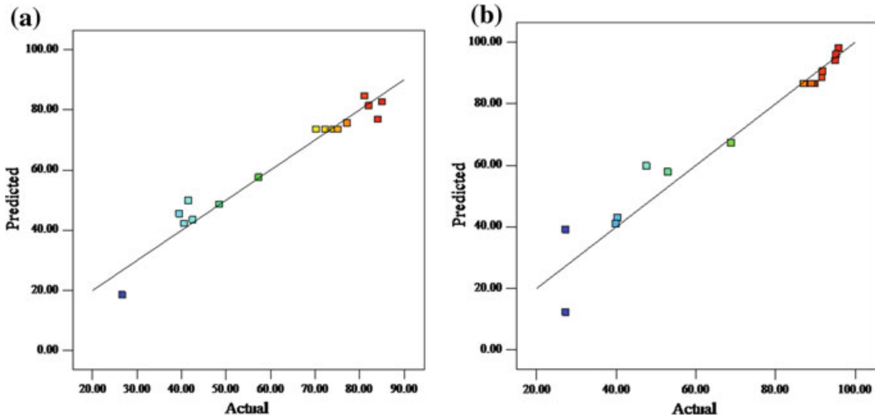


Fig. 2 Predicted versus actual values for **a** % COD removal and **b** % turbidity removal

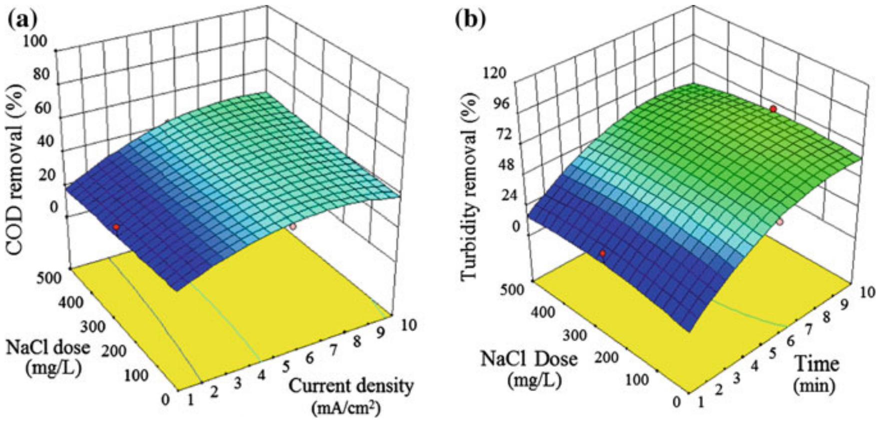


Fig. 3 Response surface plots and contour plot for **a** COD removal (%) as a function of current density and NaCl dose at 1 min residence time, **b** turbidity removal (%) as a function of NaCl dose and time at 1 mA/cm^2 current density

current density on COD removal (%) and of NaCl dose and time on turbidity removal (%) equal to 0.2213 and 0.4176 respectively. Montgomery (2010) suggests, term to be insignificant when *P value* is greater than 0.1. Surface plot (Fig. 3a) supports this result, increase in COD removal % has been observed with increase in current density, but no significance of NaCl dose increment has been observed. Similarly, increase in time of electrocoagulation increases turbidity removal (Fig. 3b), but NaCl addition remains ineffective at the same time. It is reported in literature that EC is two stage process of comprises of destabilization followed by aggregation. More time ensure satisfactory completion of both the stages hence longer time will always give good result when EC is studied process (Makwana and Ahammed 2016; Kobya et al. 2007). Increase in current density increases sacrificial electrode dissolution and also enhances H_2 bubble concentration with reduction in its diameter (Makwana and Ahammed 2016; Chen 2004). Aluminium-based EC removes pollutant through coagulation only, due to entrapment of pollutant in freshly formed aluminium hydro-complexes and their floatation with hydrogen bubble, hence increment in CD, increases removal efficiency.

Conclusion

The objective of this study is to understand the effects of CD, time and addition of NaCl dose on EC as a post-treatment of UASB reactor-treated municipal wastewater. RSM is used as a statistical tool to understand the significance of the process variables. As per the statistical test, CD and electrolysis time were found significant variables for EC process but addition of NaCl to increase the electrolyte concentration was found insignificant for post-treatment of UASB reactor-treated urban wastewater. This is so because NaCl was proven effective in EC process as and when the wastewater to be treated contains higher concentration of Ca^{2+} and Mg^{2+} ions that forms an insulating layer on the surface of the electrodes. This insulating layer would sharply increase the potential between electrodes and result in a significant decrease in the current efficiency. It is therefore recommended that among the anions present, there should be 20% Cl^{-} to ensure a normal operation of electrocoagulation in water treatment. UASB effluent treating urban wastewater contains lesser or negligible amount of these ions and thus NaCl as major process variable found insignificant.

References

Bezerra MA, Santelli RE, Oliveiraa EP, Villar LS, Escaleira LA (2008) Response surface methodology (RSM) as a tool for optimization in analytical chemistry. Talanta 76:965–977

Buzzini AP, Patrizzi LJ, Motheo AJ, Pires EC (2007) Preliminary evaluation of the electrochemical and chemical coagulation processes in the post-treatment of effluent from an upflow anaerobic sludge blanket (UASB) reactor. J Environ Manag 85:847–857

Chen G (2004) Electrochemical technologies in wastewater treatment. Sep Purif Technol 38:11–41

Ferreira SLC, Bruns RE, Ferreira HS, Matos GD, David JM, Brandao GC, da Silva EGP, Portugal LA, dos Reis PS, Souza AS, dos Santos WNL (2007) Box Behnken design: an alternative for the optimization of analytical methods. Anal Chim Acta 597:179–186

Foresti L (2002) Anaerobic treatment of domestic sewage: established technologies and perspectives. Water Sci Technol 45(10):181–186

Irdemez S, Demircioglu N, Yildiz YS, Bingul Z (2006) The effect of current density and phosphate concentration on phosphate removal from wastewater by electrocoagulation using aluminium and iron plate electrodes. Sep Purif Technol 52:218–223

Khan AA, Gaur RZ, Tyagia VK, Khursheed A, Lew B, Mehrotraa I, Kazmi AA (2011) Sustainable options of post treatment of UASB effluent treating sewage: a review. Resour Conserv Recycl 55:1232–1251

Kobya M, Gengec E, Demirbas E (2016) Operating parameters and costs assessments of a real dyehouse wastewater effluent treated by a continuous electrocoagulation process. Chem Eng Process 101:87–100

Kobya M, Bayramoglu M, Eyvaz M (2007) Techno-economical evaluation of electrocoagulation for the textile wastewater using different electrode connections. J Hazar Mater 148:311–318

Kopral AS (2002) The removal of salinity from produced formation by conventional and electrochemical methods. Fresenius Environ Bull 11(12a):1071–1077

Makwana AR, Ahammed MM (2016) Continuous electrocoagulation process for the post-treatment of anaerobically treated municipal wastewater. Process Saf Environ Prot 102:724–733

MoEF (2005 and 2006) Management information system, technical report, National River Conservation Directorate. New Delhi, India: Ministry of Environment and Forests

Montgomery DC (2010) Design and analysis of experiments, 7th edn. Wiley India Pvt. Ltd., New Delhi

Nair AT, Makwana AR, Ahammed MM (2014) The use of response surface methodology for modelling and analysis of water and wastewater treatment processes: a review. Water Sci Technol 69:464–478

Sato N, Okubo T, Onodera T, Ohashi A, Harada H (2006) Prospects for a self-sustainable sewage treatment system—a case study on full-scale UASB system in India's Yamuna river basin. J Environ Manage 80:198–207

Yetilmezsoy K, Ilhan F, Sapci-Zengin Z, Sakar S, Gonullu MT (2009) Decolorization and COD reduction of UASB pretreated poultry manure wastewater by electrocoagulation process: a post-treatment study. J Hazar Mater 162:120–132

Performance Evaluation of Filters for Sedimentation Particle Filtration

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Abstract This study was undertaken for performance evaluation of filters for separation of sediments at different loads of sedimentation. These observations are conducted at Plasticulture Farm, CTAE, Udaipur, Rajasthan. For this study, three types of filters were used, i.e. sand filter, screen filter and disc filter. Water with different sediment loads was feeded and samples of filtrate were analysed for removal efficiency of these particles. During the study of particle size distribution, it was found that sand filter was able to retain 100% particles larger than 0.05 mm size, whereas disc and screen filters were able to retain only 92.73 and 86.33%, respectively. The main difference in the removal of particles of different diameters was found that sand filter is most efficient (i.e. 82.35%) in removing particles of all diameters and achieved the total retention of particles with diameters greater than 0.05 mm.

Keywords Micro-irrigation · Filtration · Clogging · Sediment load

Introduction

Population of India is increasing day by day, but land holding and water resources are remaining the same. Water is a prime natural resource, a basic human need and precious asset of nation. Therefore, it is necessary for efficient utilization of water. Water is a basic entity for all agricultural practices. It plays a vital role in progress of agriculture in the form of irrigation.

Clogging is one of the serious problems associated with the maintenance of micro-irrigation system and is directly associated with irrigation water, and a small number of clogged emitters can affect distribution uniformity and may ultimately reduce crop yield. Filtration to retain particle and regulate emitter clogging therefore remains a vital issue for irrigation sector (Oron et al. 1979; McDonald et al.

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1984). Such clogging of emitter in micro-irrigation system using treated wastewater effluent is primarily attributable to suspended matter in the water (Capra and Scicolone 2004). Suspended solids cause rapid pressure drops and flow disturbances in screen filters commonly used for the protection of sensitive appurtenances (Adin and Alon 1986).

By determining the particle volume distribution, the volumes of each of the main particle sizes that are captured by filter can be established (Adin and Elimelech 1989). The sediment particle size distribution is followed by a potential law (Puig-Bargues et al. 2005). The aim of the present study is to be characteristic of the sedimentation particle size and volume distribution of different sediment load concentrations as used in micro-irrigation and assess the filtration efficiency of various filters. All the three types of filters, i.e. sand, screen and disc filters, are used in the present study, keeping in view the fact that determining the sedimentation particle size distribution helps in the assessment of the efficiency of filtration systems that can easily identify the problems, which is impossible for any other method (Kobler and Boller 1997; Hatukai et al. 1997). However, Boller et al. (1997) indicated that sedimentation particle size distribution analysis is not representative of particle transport because of the mixing and formation of preferential channels; they accept its validity for assessing the differences between small- and large-particle retention. The effect of filtration on outflow sedimentation particle distribution is rarely studied with the commonly used filters in micro-irrigation systems. Moreover, only a few studies with screen, disc and sand filters done on this aspect revealed the need of more accuracy for better results (Adin and Alon 1986; Adin and Elimelech 1989; Tajrishy et al. 1994).

Materials and Methods

The observations are conducted at Plasticulture Farm in College of Technology and Engineering, Maharana Pratap University of Agriculture and Technology, Udaipur, Rajasthan. The study area is situated at 24° 35′ north latitude and 73° 44′ east longitude and at an altitude of 582.17 m above the sea level. Sieve analysis was performed and the particle passing through a 400 μm size sieve was used to prepare the impure water with different sediment load concentrations of 100, 200, 300 and 400 mg/L for the study. The test assembly was specially fabricated and installed for the study. The entire unit consists of bore well, HDPE tank, 5 HP pump with bypass arrangement, water meter, control valve, pressure gauges, sand filter, screen filter, disc filter, stop watch and PVC pipe fittings. A pump was operated at a constant flow rate of 1.38 lps. The purpose of this study was to regulate pressure drop across the filters and filtrate volume at regular time interval until the pressure drop reached a value of 5 m of water. At this mark, the screen filter was cleaned by using suitable brush and disc filter cleaned by rinsing with water hose, i.e. cleaned manually by washing it under strong flow of water.

Particle Size Distribution

The particle size distribution analysis performed during sedimentation analysis was evaluated in the laboratory by adopting hydrometer method (Plate 1). The percentage of various sizes of particle in the source water as well as filtered water was found through particle size distribution analysis. The observed particle diameter was determined in the range of >0.05 to <0.002 mm.

Particles Filtration Efficiency

The filtration efficiency was calculated by using the following formula (Gideon and Yoel 1982):

$$\mathrm{Fe} = 100 \times \left\{1 - \frac{S_\mathrm{o}}{S_\mathrm{i}}\right\}$$

where

Fe filtration efficiency (%)
S_o component concentration of filter outlet (mg/L)
S_i component concentration of filter inlet (mg/L)

Plate 1 Sedimentation analysis by hydrometer method

The time required for the different ranges of particle was calculated by,

$$t = \frac{18 \times h \times \pi}{d^2 \times \left(\rho_s - \rho_f\right) \times g}$$

where

t	time
h	settling depth (cm)
d	diameter of particle (mm)
ρ_s	density of the soil solids (2.65 g/cm^3)
ρ_f	density of the distilled water (1.00 g/cm^3)
G	acceleration due to gravity (981 cm/s^2)

The particle size distribution was calculated by the formula,

$$X_1 = \frac{100}{\text{wt. of sample}} \times \frac{\rho_s}{\rho_s - \rho_f} \times 100 \times \left(R_\mathrm{h} + T_\mathrm{c} - \mathrm{C.D}\right)$$

$$X_1 = \text{ silt + clay in } (\%)$$

where

X_1	particle size diameter (%)
ρ_s	density of the soil solids (2.65 g/cm^3)
ρ_f	density of the distilled water (1.00 g/cm^3)
R_h	hydrometer reading at 1 min
T_C	temperature correction factor
C.D	density correction factor

The particle size distribution percentage was calculated from above equation such that

$$\begin{aligned} > 0.05 &= 100 - X_1 \\ 0.05\text{-}0.02 &= 100 - X_2 \\ 0.02\text{-}0.002 &= 100 - X_3 \\ < 0.002 &= X_4 \end{aligned}$$

where

X_1	for >0.05 mm at 1 min reading
X_2	for >0.05–0.02 mm at 7 min reading
X_3	for >0.02–0.002 mm at 4 h reading
X_4	for <0.002 mm at 7 h reading

Results

Particle Size Distribution

The particle size distribution of sand, screen and disc filters was studied for sediment load concentration. The particle size distribution was determined considering filtration efficiency and particle size percentage present before and after filtration. The ranges of the particle size were determined in four different classes, i.e. >0.05 mm, 0.05–0.02 mm, 0.02–0.002 and <0.002 mm for 1 min, 7 min, 4 h and 7 h, respectively (Figs. 1 and 2). The fraction of particle in before filtration was remained as 10.47, 13.67, 23.26 and 52.04%. The particle size distribution for sediment load range of particle greater than 0.05 mm was 100, 86.33 and 92.73% of sand filter; screen filter and disc filter respectively. The finest particle ranges for less than 0.002 mm was 44.76, 6.3 and 22.38% of sand, screen and disc filters respectively (Table 1).

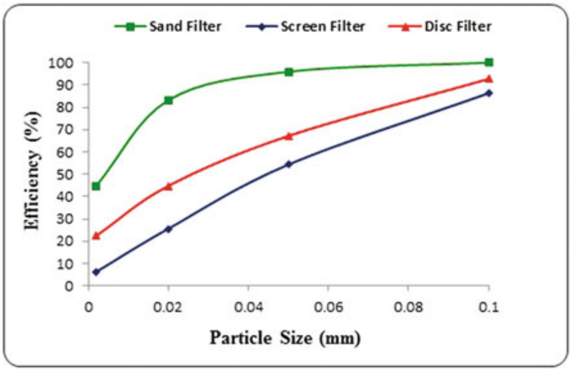

Fig. 1 Efficiency of sand, screen and disc filters at removing different particle sizes

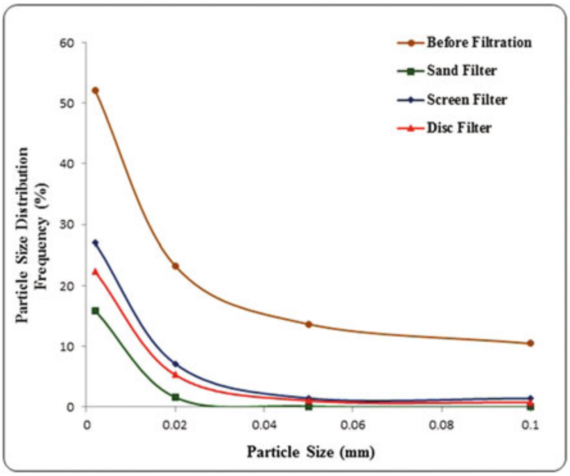

Fig. 2 Mean particle volume distribution of sediment load concentration before and after filtration

Table 1 Sedimentation particle size distribution after filtration efficiency of filters

Diameter range (mm)	Filtration efficiency		
	Sand filter (%)	Screen filter (%)	Disc filter (%)
>0.05	100	86.33	92.73
0.05–0.02	95.92	54.35	67.14
0.02–0.002	83.13	25.58	44.76
<0.002	44.76	6.3	22.38

Results revealed that sand filter was found most efficient in removing particles of all diameters and achieved the total retention of particles with diameters greater than 0.05 mm, and it was accomplished the entire elimination of particle greater than 0.05 mm diameter in sediment load concentration.

Different Particle Sizes

The particle volume distribution is very slightly attenuated by only screen and disc filters. The 125 μm size of screen and disc filters retained particle size distribution, i.e. 6.3 and 22.38%. The filtration efficiency of screen and disc filters was increased in sedimentation particle size distribution.

Particle Volume Distribution

The particle volume distribution of both before and after filtrates is shown in Fig. 2.

The particle volume distribution for sand filter was found that the particles size larger than the filter pores appeared in the filtrate of the sediment. The particle volume distribution of the sedimentation was observed in the range of >0.05, 0.05–0.02, 0.02–0.002 and <0.002 mm diameter in the sediment that the particles present in before filtration large than filtrate particle of sand, screen and disc filters.

Conclusions

Filtration efficiency of the sand, screen and disc filters decreased with the increase in the level of sediment load concentration with elapsed time. The particle size distribution of suspension and filtrate of filters show that the sand filter is very efficient to remove all sizes of particles of all diameters and it can achieve the total retention of particles of all diameters greater than 0.05 mm, respectively. The screen and disc filters are very alike in function but the disc filter can retain more solids than that of the screen filter and hence, it shows the better performance than screen filter.

References

Adin A, Alon G (1986) Mechanism and process parameters of filter screen. J Irrig Drainage 112 (4):293–304

Adin A, Elimelech M (1989) Particle filtration for waste water irrigation. J Irrig Drainage 115:274–287

Boller M, Kobler D, Koch G (1997) Particle separation, solids budgets and headloss development in different biofilters. Water Sci Technol 36(4):239–247

Capra A, Scicolone B (2004) Emitter and filter tests for wastewater reuse by drip irrigation. J Agric Water Manag 68(2):135–149

Gideon JA, Yoel D (1982) Effluent in trickle irrigation of cotton in arid zones. J Irrig Drainage 108:115–125

Hatukai S, Ben-Tzur Y, Rebhun M (1997) Particle counts and size distribution in system design for removal of turbidity by granular deep bed iteration. Water Sci Technol 36(4):217–224

Kobler D, Boller M (1997) Particle removal in different filtration system for tertiary wastewater treatment a compression. Water Sci Technol 36(4):15–23

McDonald DR, Lau LS, Wu IP, Gee HK, Young SCH (1984) Improved emitter and network system design for wastewater reuse in drip irrigation. Technical Report No. 163, vol 87. Water Resources Research Center, Honolulu, Hawaii

Oron G, Shelef G, Truzynski B (1979) Trickle irrigation using treated wastewaters. J Irrig Drainage 105:175–186

Puig-Bargues J, Baragan J, Ramirez de Cartagena F (2005) Effluents particles removed by micro irrigation filters. Spanish J Agric Res 3(2):182–191

Tajrishy MA, Hill DJ, Tchobanoglous G (1994) Pretreatment of secondary effluent for drip irrigation. J Irrig Drainage E-ASCE 120(4):716–731

Magnetic Extracellular Polymer Composite for the Effective Removal of Microcystin

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Abstract Microcystin is heterocyclic toxin released from dead cyanobacterial cells, and their potential occurrence in drinking water sources prompted investigations into remedial water treatments for their removal. The present investigation employed the magnetic iron oxide extracellular polymer (ECP–Fe_3O_4) composite for the effective removal of microcystin from treated wastewater. The extracellular polymer produced from bacterial cell was impregnated with magnetite to develop ECP–Fe_3O_4 composite. The ECP–Fe_3O_4 matrix was characterized by optical microscope, FTIR, XRD. The ECP–Fe_3O_4 matrix was used for the removal of microcystin in aqueous solution. ECP–Fe_2O_3 matrix removed microcystin about 96% after treated water. ECP–Fe_3O_4 effectively removed the microcystin as the ECP and Fe ion-integrated matrix is an effective complex with special functional groups such as carboxylic and amide groups to sequester microcystin in aqueous solution. The matrix was separated by the application of magnetic field. The separated matrix was reused for the microcystin removal, and the efficiency of recovered ECP–Fe_3O_4 was consistent even after several cycles for the removal of microcystin. The microcystin removal was confirmed by UV–visible spectral analysis.

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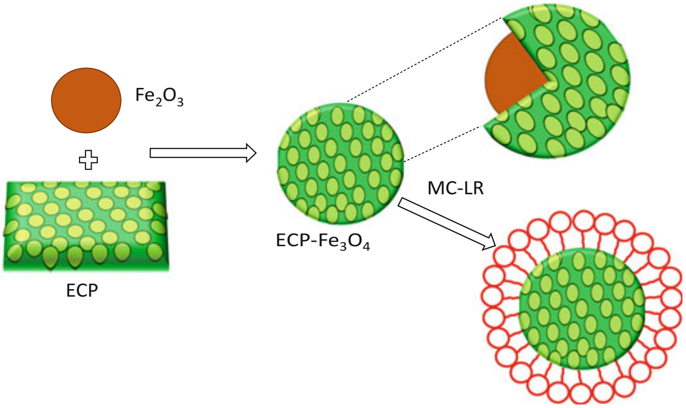
Graphical Abstract



Keywords Microcystin · Magnetic nanoparticle · Extracellular polymer
Cyanobacteria

Introduction

Microcystin is the secondary metabolite produced from algae–cyanobacteria species and many genera such as Anabaena, Nostoc, Oscillatoria and Planktothrix (Nishiwaki et al. 1992; Sivonen and Jones 1999). The microcystin is released in the condition of cell death wherein the cell wall bursts, releasing the toxin into the water. The cells are usually lysed in the presence of chemicals [e.g., Reglone A, NaCl, $KMnO_4$, Simazine and $CuSO_4$] that inhibit new cell wall synthesis, enzymatic reactions or photosynthesis (Kenefick et al. 1993; Kotak et al. 1995). A sudden release of microcystins into the surrounding water body could be hazardous to the animals drinking the water (Lam et al. 1995). Chemically, they are monocyclic heptapeptides and are produced through nonribosomal peptides synthases. Microcystins can be produced in large quantities during algal blooms and pose a major threat to drinking and irrigation water supplies, as well as the environment at large. After bloom decomposition, large amounts of microcystins are dissolved in water (Sedmak and Gorazd 1998). Toxins act as growth stimulators for other species like *S. quadricauda* commonly present in cyanobacterial blooms and appearing in large numbers specifically after hepatotoxic blooms (Bucka and Wilk 1999). Ingestion of microcystins can lead to liver damage and may initiate liver tumor-promoting activity (Malbrouck and Patrick 2006). The World Health Organization (WHO) established a provisional concentration limit of 1 µg/L for microcystin-LR in drinking water (Falconer et al. 1999). A number of approaches have been investigated for the removal of microcystins from drinking water.

Conventional treatment technologies such as coagulation, flocculation and sand filtration are for the removal of particulate cyanobacterial cells but not for the dissolved toxins (James and Fawell 1991; Rositano and Nicholson 1994; Mouchet and Bonnelye 1998). Moreover, filtration systems have a relatively low removal capacity (below 50%), even when they include activated carbon and ion-exchange-resin filtration systems (Lawton et al. 1998). In general, procedures that are based on ultra and nanofiltration can remove microcystins at rates greater than 95%, which makes them a good option for the treatment of small-to-medium volumes of water (Gijsbertsen-Abrahamse et al. 2006). Chemical processes that use oxidizing agents such as ozone (Brooke et al. 2006), potassium permanganate (Rodríguez et al. 2007) and chlorine (Deblois et al. 2008) can remove microcystins completely within short reaction times. Many metals were used for microcystin removal such as TiO_2, $CuSo_4$ and ZnO (Liu et al. 2008; Pradhan et al. 2007). However, the low selectivity and mineralization capacity of these chemicals can lead to the formation of degradation intermediates, which creates biologically unstable environments in water systems. That degraded intermediate again creates hazardous conditions to the environment. So, this present study focused on preparation of matrix for the degradation of microcystin and removal (adsorption) of their intermediates from the water using extracellular polymer (ECP). ECP is the effective matrix for adsorbing the organic and inorganic molecules. These properties give the possibility to bind with iron oxide and adsorb the degraded intermediates. Bacterial ECP has a high binding capacity with iron because of the carboxyl group sites present in the ECP (Linchuan Fang 2014).

Methodology

Chemical and Reagent

MC-LR (standard sample), protein phosphatase, ferrous sulfate, diethanolamine and ammonia solution were purchased from Merk and kept at 22 °C. The microbiological ingredients were purchased from HiMedia.

Screening and Culturing of Polymer-Producing Microorganisms

Biopolymer-producing was isolated from tannery sludge samples. Isolates were obtained by serial dilution plating on Tryptic-Soy Agar media. The isolated strains were grown in 100-ml basal medium in 500-ml flasks on a rotary shaker at 37 °C for 3 days; the resultant fully grown bacteria were examined for their flocculating activity. Batch fermentations of the isolate were carried out in a 5-L stirred tank bioreactor at a controlled temperature of 37 °C for 48 h with an agitation rate of

200 rpm without control of pH during the operation. The fermented medium was clarified using a refrigerated centrifuge at 5000 rpm, 4 °C, for 20 min, and the cell-free supernatant was used as the source of ECP extraction using ethanol.

Preparation of Magnetic-Induced ECP

In 500-mL conical flask, 100 mL ECP suspensions (5 g/L) and a known volume of 0.5 g of magnetic iron oxide was mixed. The solution was kept in stirring at 60 °C for 30 min. The final concentration of Fe_2O_3 in the suspensions ranged from 0 to 200 mg/L. The initial pH was controlled to 5.0 by adding 0.1 M NaOH or 0.1 M HCL. The kinetic experiments showed that adsorption reached equilibrium within 2 h. Free ECP concentrations were measured by carbohydrate estimation. The difference between the initial ECP concentration and the final ECP concentration was assumed to be adsorbed by the Fe_2O_3. The ECP adsorbed magnetic iron oxide (ECP–Fe_3O_4).

Removal of Microcystin-LR

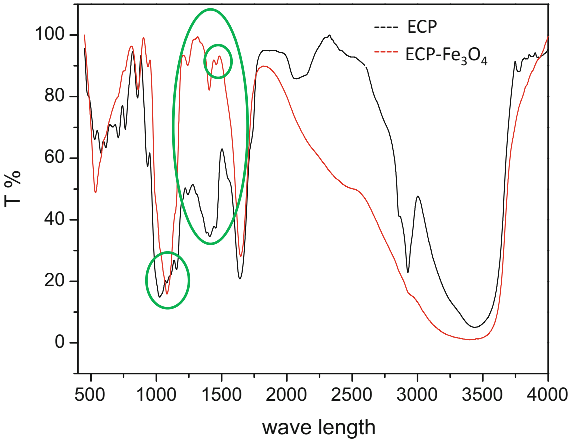
A stock solution of microcystin-LR about 500 µg/mL concentration was prepared by dissolving in methanol and water (1:9 v/v) solution. In a separate vial, stock solutions of Fe_2O_3 was prepared. Next, solution of Fe_2O_3 was mixed with solution of microcystin-LR for different concentrations. The typical concentrations of Fe_2O_3 were found to be 0.05 and 1.0 mg/mL, respectively, and the final volume of water was 1.0 mL. The whole solution was stirred for 2 h, and then, particles were separated by laboratory-based bar magnet. The supernatant solution was used for estimation of the remaining microcystin-LR by UV–visible spectroscopy.

Results and Discussion

Characterization of Matrices

The synthesized matrices were characterized by FTIR and are presented in Fig. 1. The free COOH stretching frequency occurs at 1241, its correspondence to ECP. Functional groups that absorb in the energy region 1200–1400 cm^{-1} have been assigned to the broad symmetric stretching vibration of COO^- in the presence Fe_2O_3 in ECP. Because the carboxyl group was deproteinization due to the attachment of Fe_2O_4. The peak at 1409 cm^{-1} shifted to 1405 cm^{-1}, and the peak at 1480 cm^{-1} disappeared after the addition of Fe_2O_4. Therefore, the above changes of the specific IR assignments for the COO^- stretching vibration suggest that Fe_2O_4 is

Fig. 1 Characterization of ECP and ECP–Fe_2O_3 by FTIR spectrum



directly complex with carboxylic groups. It was also observed that the peak at 1080 cm^{-1} (C–O–C, C–C) in the EPS spectrum disappeared after exposure to Fe_2O_4.

Separation of Microcystin-LR by ECP–Fe_2O_3

Advantage of ECP-immobilized nanocomposites toward separation of microcystin-LR from water has been investigated in detail. The separation approach and removal efficiency of microcystin-LR by different nanocomposites. Typically, ECP–Fe_2O_3 nanocomposite is mixed with the aqueous solution of microcystin-LR, and then, the nanocomposite is removed by magnet. This property of the material helps easier separation of adsorbed materials. We have determined removal efficiency for ECP–Fe_2O_3, keeping the fixed concentration of microcystin-LR (10 µg/mL), and then selected an optimum concentration of each material for microcystin-LR separation. The results indicate that ECP is less efficient than ECP–Fe_2O_3 and so more Fe_2O_3 is needed for separation of a similar amount of microcystin-LR separation. Thus, we have selected some optimum concentration of each material for microcystin-LR separation. It shows that UV absorbance of microcystin-LR decreases remarkably after treatment with nanocomposites. The results summarize the separation efficiencies due to different functionalizations.

Microcystin-LR separation efficiencies by ECP, Fe_2O_3 and ECP–Fe_2O_3 have been compared, and it is observed that ECP–Fe_2O_3 offers better performance as compared to Fe_2O_3 at different pHs (Fig. 2). Removal capacity has been summarized for different nanocomposites. The values that are in the range of 4, 7 and 9 µg were ECP, Fe_2O_3 and ECP–Fe_2O_3. In particular, the ECP that are bound inside the pores is easy accessible to microcystin-LR. So the high performance of microcystin-LR separation by ECP–Fe_2O_3 is mainly due to high immobilization of ECP on Fe_2O_3. One of the most important aspects for practical application is the

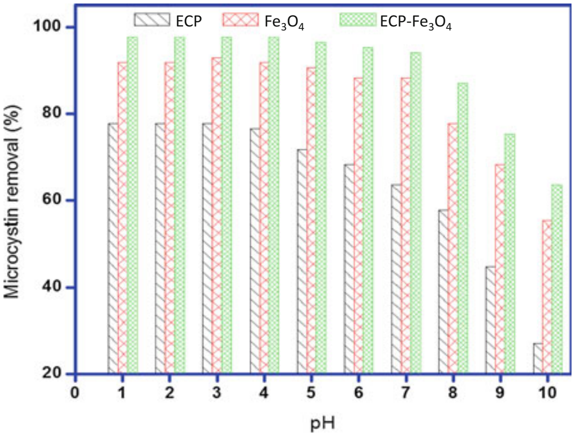


Fig. 2 Effect of pH on the removal of microcystin by ECP, Fe_2O_3 and ECP–Fe_2O_3

materials that can be regenerated and reused. This has been tested for removal of microcystin-LR using ECP–Fe_2O_3 as representative material. Detailed procedures of ECP–Fe_2O_3-based microcystin-LR separation. Regeneration of ECP–Fe_2O_3 involves magnetic separation followed by repeated washing with ethanol to extract the adsorbed microcystin-LR. Results show that ECP–Fe_2O_3 can be used several times with little loss of removal efficiency. The loss of removal efficiency can be due to aggregation of ECP–Fe_2O_3. It is also important that the materials should be environmentally friendly or nontoxic so that it does not introduce any secondary pollutant during the removal of microcystin-LR.

Characterization of MC-LR

UV–visible spectrum for MC-LR: The UV–visible absorption spectrum of the MC-LR evaluated in the present study is shown in Fig. 3. The results indicated that

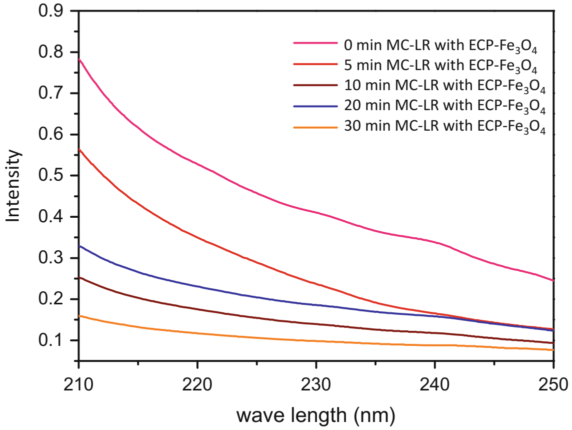


Fig. 3 Characterization of microcystin removal by UV spectrum

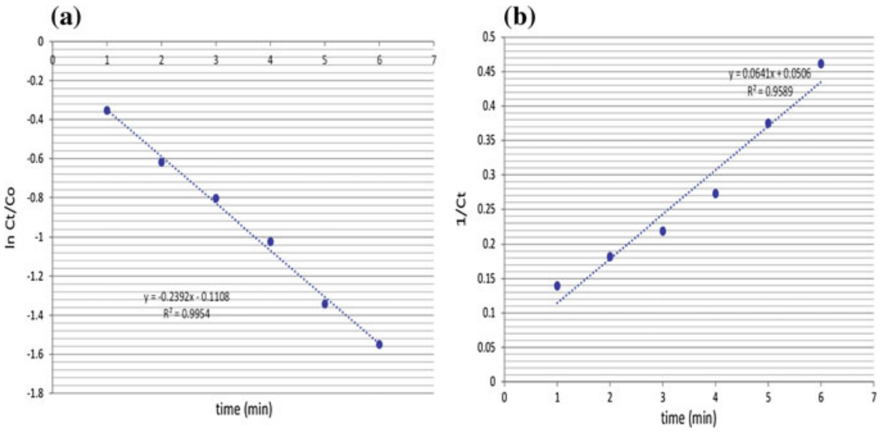


Fig. 4 Kinetic studies of microcystin removal by **a** pseudo-first order and **b** pseudo-second order

there was a significant absorption in the UV region at $\lambda_{220\text{–}240\ \text{nm}}$. The strong absorption in the range of MC-LR may be due to the presence of conjugate bond of ADDA moiety of MC-LR. The MC-LR has strong absorption at $\lambda_{238\ \text{nm}}$, which may be due to peptide bonds in protein moiety. The absorption in the wavelength range $\lambda_{200\text{–}300\ \text{nm}}$ often results from $n - \sigma^*$ and/or $\pi - \pi^*$ transitions, which are found in amine, carboxyl and carbonyl functional groups. The kinetic models such as pseudo-first order and pseudo-second order were performed for the removal of microcystin (Fig. 4). The kinetic model was selected based on the regression coefficiency, the pseudo-first order showed 0.99 and pseudo-second order showed 0.95. The removal of microcystin process obeys the pseudo-first-order kinetic model.

Conclusion

In summary, we have synthesized magnetic nanocomposites which are impregnated functionalized with ECP. These ECP nanocomposites have been used for separation of microcystin-LR from contaminated water via host–guest interaction between microcystin-LR and ECP. Resultant ECP nanocomposites are dispersible in water but separable by external magnet. Microcystin-LR separation efficiency is significantly enhanced after ECP impregnated with iron oxide. The proposed ECP nanocomposite is environmentally friendly and can be reused. Developed ECP nanomaterials can be used for advanced water purification applications.

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References

Brooke S, Gayle N, Brenton N, Gunter K (2006) Decrease in toxicity of microcystins LA and LR in drinking water by ozonation. Toxicon 48:1054–1059

Bucka H, Wilk W (1999) Cyanobacteria responsible for planktic water blooms in reservoirs in southern Poland. Algol Stud 94:105–113

Deblois CP, Aranda-Rodriguez R, Giani A, Bird DF (2008) Microcystin accumulation in liver and muscle of tilapia in two large Brazilian hydroelectric reservoirs. Toxicon 51(3):435–448

Falconer I, Barteam J, Chorus I, Kuiper-Goodman T, Utkilen H, Burch M, Codd GA (1999) Safe levels and safe practices. In: Toxic cyanobacteria in water: a guide to their public health consequences, monitoring, and management. E&F Spon., London

Gijsbertsen-Abrahamse AJ, Schmidt W, Chorus I, Heijman SGJ (2006) Removal of cyanotoxins by ultrafiltration and nanofiltration. J Membran Sci 276:252–259

James H, Fawell J (1991) Detection and removal of cyanobacterial toxins from freshwaters FR 0211. Foundation for Water Research, Murlow

Kenefick SL, Hrudey SE, Peterson HG, Prepas EE (1993) Toxin release from microcystis aeruginosa after chemical treatment. Water Sci Technol 27(3–4):433–440

Kotak BG, Lam AKY, Prepas EE, Kenefick SL, Hrudey SE (1995) Variability of the hepatotoxin microcystin-lr in hypereutrophic drinking water lakes1. J Phycol 31(2):248–263

Lam AKY, Fedorak PM, Prepas EE (1995) Biotransformation of the cyanobacterial hepatotoxin microcystin-LR, as determined by HPLC and protein phosphatase bioassay. Environ Sci Technol 29(1):242–246

Liu X, Hu Q, Fang Z, Zhang X, Zhang B (2008) Magnetic chitosan nanocomposites: a useful recyclable tool for heavy metal ion removal. Langmuir 25(1):3–8

Malbrouck C, Patrick K (2006) Effects of microcystins on fish. Environ Toxicol Chem 25:72–86

Mouchet P, Bonnelye V (1998) Solving algae problems: French expertise and world-wide applications. J Water SRT-Aqua 47:125–141

Nishiwaki R, Ohta T, Nishiwaki S, Suganuma M, Kohyama K, Ishikawa T, Fujiki H (1992) Liver tumor promotion by the cyanobacterial cyclic peptide toxin microcystin-LR. J Cancer Res Clin Oncol 118(6):420–424

Pradhan S, Singh S, Rai LC (2007) Characterization of various functional groups present in the capsule of Microcystis and study of their role in biosorption of Fe, Ni and Cr. Biores Technol 98(3):595–601

Rodríguez E, Majado ME, Meriluoto J, Acero JL (2007) Oxidation of microcystins by permanganate: reaction kinetics and implications for water treatment. Water Res 41(1):102–110

Rositano J, Nicholson B (1994) Water treatment techniques for the removal of cyanobacterial toxins from water 2/94. Australian Centre for Water Quality Research

Sedmak B, Gorazd K (1998) The role of microcystins in heavy cyanobacterial bloom formation. J Plankton Res 4:691–708

Sivonen K, Jones G (1999) Cyanobacterial toxins. In: Chorus I, Bartram J (eds) Toxic cyanobacteria in water. E and FN Spon, London, pp 41–111

Wei X, Linchuan F, Peng C, Qiaoyun H, Hao C, Wei L, Xinming R (2011) Influence of extracellular polymeric substances (EPS) on Cd adsorption by bacteria. Environ Pollut 159:1369–1374

Bioremediation of Chromium Complex Dye by Growing *Aspergillus flavus*

Arpita Ghosh, Manisha Ghosh Dastidar and T. R. Sreekrishnan

Abstract A chromium complex dye (Acid brown 45) was chosen to explore the feasibility of color and chromium removal using growing *Aspergillus flavus* in a batch bioreactor. The chromium concentration was observed to be 1.006 mg/L in 100 mg/L dye concentration. Removal of color and chromium was studied for a dye concentration range of 50–750 mg/L for up to 50 h and showed a reduction of 78–9% and 81–21% for color and chromium, respectively, at an optimized pH 4.5. The biomass concentration was reduced from 3.8 to 0.7 g/L with increasing dye concentration from 50 to 750 mg/L. Further, optimization of parameters for color removal was studied using a statistical approach response surface methodology (RSM). The ranges of the parameters were initial dye concentration: 100–300 mg/L, pH: 3.5–4.5 and time: 35–50 h. Maximum color removal (75.25%) was observed at dye concentration: 100 mg/L, pH: 4.84, and time: 50 h. The desirability of the RSM model was found to be 0.967.

Keywords *Aspergillus flavus* · Color removal · Chromium removal
Chromium complex dye · Batch bioreactor

Introduction

Huge amount of various synthetic dyes are generally used in textile industry for production of cottons, woolen, nylon, etc. Metal complex dyes are used for coloring woolen and nylon (Aksu and Balibek 2010; Li and Guthrie 2010). The effluents of these industries are very toxic due to the presence of both heavy metals and dyes.

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and Technology Library 79, https://doi.org/10.1007/978-981-10-5795-3_8

These effluents need to be treated before disposal to surface or aquatic systems. There are various techniques available for treatment of such effluents (Sheng et al. 2004; Banerjee and Dastidar 2005). In recent years, microorganisms are effectively used for removal of different pollutants from aqueous solution (Wang and Chen 2006; Bishnoi et al. 2007). A lot of studies are available on removal of dyes and metals separately from synthetic solutions using different microorganisms (Plaza Caźon et al. 2013; Prithviraj et al. 2014). However, very little information is available on simultaneous removal of metal and dye from synthetic solution of metal complex dye. The fungal strains, among all other microorganisms, are more efficient to remove pollutants due to their highly porous surface (Kalpana et al. 2011; Ghosh et al. 2015).

In the present study, simultaneous removal of both color and chromium from synthetic solution of chromium complex dye (Acid brown 45) was attempted in batch bioreactor using growing *Aspergillus flavus*. To optimize the parameters for removal process, the conventional batch methods require many experimental runs and hence more time. The optimization of parameters for color removal was studied using a statistical approach response surface methodology (RSM).

Experimental

Dye: Acid Brown 45 was procured from Indian dyestuff limited (India). The anionic dye was water soluble and was used without any purification (Web site: http://www.dyescolours.com/acid-dyes.html). The molecular structure of the dye was not reported anywhere. The dye was complexed with chromium, and atomic absorption spectroscopy (AAS) was used to determine the chromium concentration of the dye.

Fungal strain and growth media: *A. flavus* were isolated previously in the laboratory from effluent of an electroplating industry and reported separately to remove heavy metals as well as dyes (Ranjusha et al. 2010; Pundir and Dastidar 2015). The growth media (Ghosh et al. 2014) was prepared in distilled water, and 100 mL media was taken in 250-mL conical flask. The media was autoclaved, inoculated with the fungal strain and preserved in refrigerator for further study. Media containing dye (Acid Brown 45) was prepared using different quantities of dye required to prepare solutions of different concentrations.

Removal of chromium and dye: Media containing dye was inoculated with the strain and was kept in Orbitek incubator up to 50 h at 27 °C. The liquid samples were collected from the flask after different time intervals and centrifuged at 4000 rpm. For chromium and color estimation, AAS and UV–visible spectrophotometer were used, respectively. Batch studies were carried out to determine the color and chromium removal from initial dye concentrations 50–750 mg/L. The RSM was applied to optimize the dye concentration, pH and time for maximum removal of color. The ranges of the parameters were dye concentration: 100–300 mg/L, pH: 3.5–4.5 and time: 35–50 h (Table 1). A confirmatory experiment in batch mode was conducted at optimum conditions as suggested by the RSM model.

Table 1 Experimental range and levels of independent process variables

Independent variables	Range and levels (coded)				
	−α	−1	0	+1	+α
Dye concentration, mg/L (*A*)	31.8207	100	200	300	368.179
pH (*B*)	2.81821	3.5	4.5	5.5	6.18179
Time, hours (*C*)	29.8866	35	42.50	50	55.1134

SEM and EDX Analyses

To investigate the changes in surface morphology of the biomass after dye removal, scanning electron microscopic (SEM) analysis was performed *using* ZEISS EVO series scanning electron microscope model EVO 50. To determine the presence of Cr in the biomass after dye removal, energy-dispersive X-ray (EDX) analysis was performed using Bruker-AXS energy-dispersive X-ray system.

Results and Discussion

Dye: In 100 mg/L Acid brown 45 dye solution, chromium (Cr) was determined to be 1.006 mg/L through AAS. The UV–visible spectroscopic analysis of acid brown 45 dye in the wavelength range of 200–900 nm before bioremediation indicated maximum absorbance at 474.4 nm. The energy-dispersive X-ray analysis (EDX) micrograph (Fig. 1) of dye shows the presence of Cr, Cu, and Fe in the dye molecule.

Bioremediation Study in Batch Mode

The tolerance and ability to remove color and chromium during the growth of the fungi at initial dye concentrations up to 1000 mg/L were studied. No growth of the fungi was observed at 1000 mg/L initial dye concentration. The fungi were able to grow and remove color and chromium studied up to 750 mg/L.

Figure 2 shows the color and chromium removal and biomass concentration at different concentrations of dye. Removal of color and chromium up to 50 h was reduced from 78 to 19% and from 81 to 21%, respectively, with increasing dye concentration from 50 to 750 mg/L at pH 4.5 which is optimum for maximum growth of the organism. The biomass concentration was reduced from 3.8 to 0.7 g/L with increasing dye concentration from 50 to 750 mg/L. At higher initial dye concentration, decrease in biomass concentration and color and chromium removal was observed, indicating the toxicity of dye as well as chromium to the fungi cells at higher concentrations. Table 2 shows the comparison between color

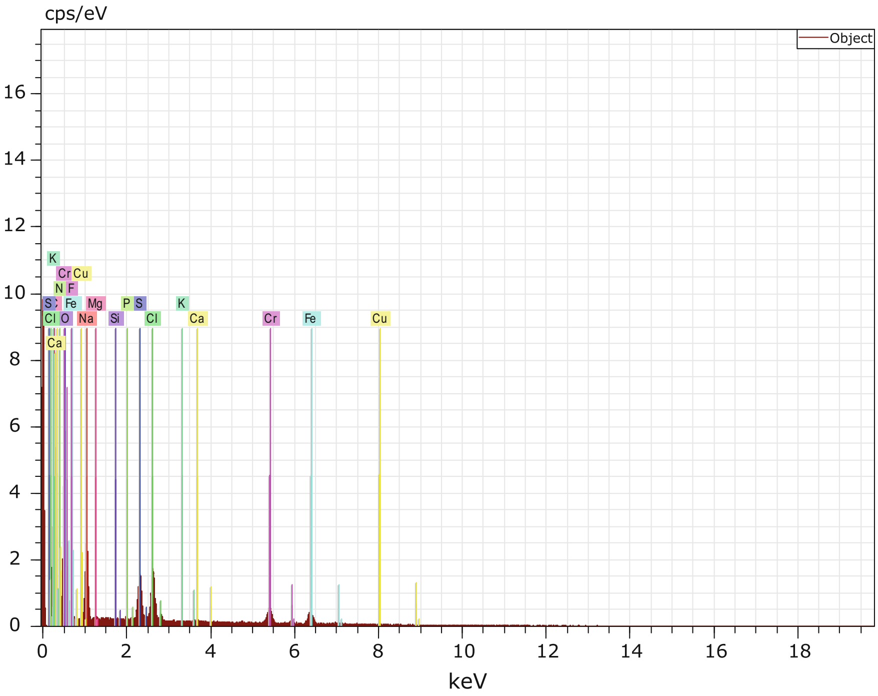


Fig. 1 EDX analysis of acid brown 45 dye

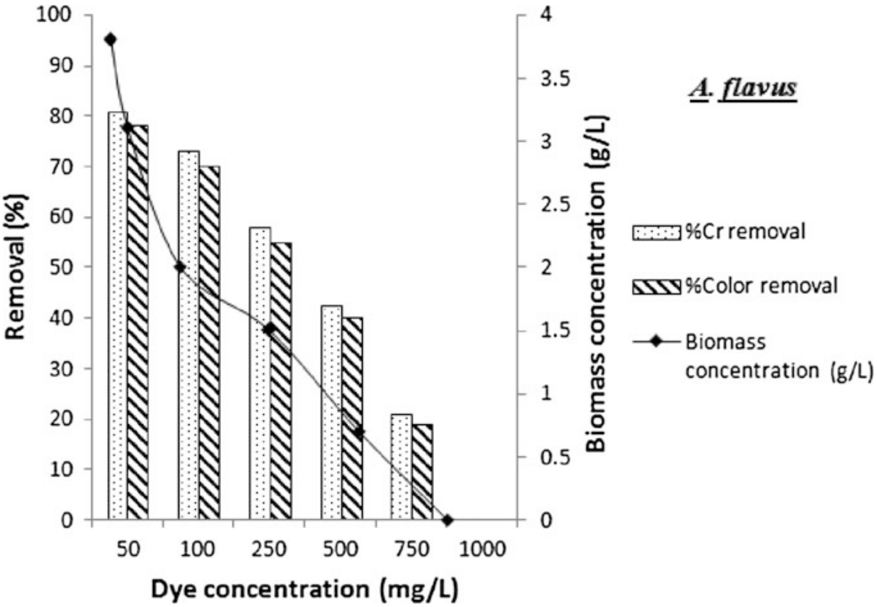


Fig. 2 Color and chromium removal and biomass concentrations at different dye concentrations

Table 2 Color and chromium removal by different *Aspergillus* sp. during growth

Microorganisms	Chromium/dye	Initial concentration (mg/L)	Removal (%)	References
Aspergillus lentulus	Chromium	100	Chromium: 99.8%	Sharma et al. (2009)
Aspergillus versicolor	Chromium	50	Chromium: 99.89%	Taştan et al. (2010)
Aspergillus versicolor	Remazol blue dye	100	Color: 95%	Taştan et al. (2010)
Aspergillus flavus	Remazol black b dye	100	Color: 89%	Ranjusha et al. (2010)
Aspergillus flavus	Acid brown 45 dye	100	Chromium: 73%; Color: 70%	Present study
Aspergillus flavus	Acid brown 45 dye	50	Chromium: 81%; Color: 78%	Present study

and chromium removal using growing *Aspergillus* sp. It shows higher color removal from remazol black b dye (azo dye) than acid brown 45 dye (chromium complex dye) using the same fungal strain (*A. flavus*), which indicates more toxic effect of acid brown 45. It is expected that the complexity of dye structure along with chromium as a whole was responsible for the lower removal obtained in the present study.

SEM and EDX Analyses

In the previous study, the surface of *A. flavus* was observed to be smooth through *SEM analysis* (Ranjusha et al. 2010). Figure 3 shows SEM analysis *of fungal biomass* after color and chromium removal from acid brown 45 dye solution (100 mg/L). The cell shape appears to be distorted after color and chromium removal. The EDX micrograph (Fig. 4) shows the presence of Cr in the fungal biomass after dye removal which implies the uptake of chromium complex dye by the fungi.

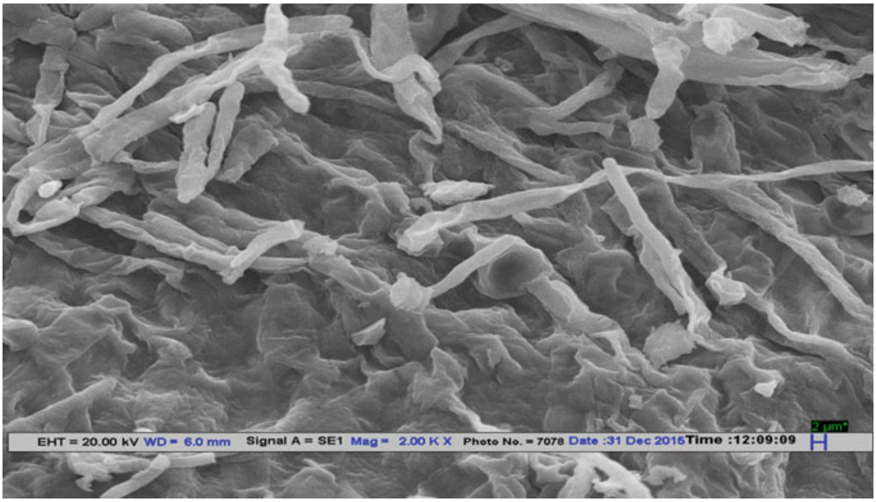


Fig. 3 SEM picture of fungal biomass after color and chromium removal

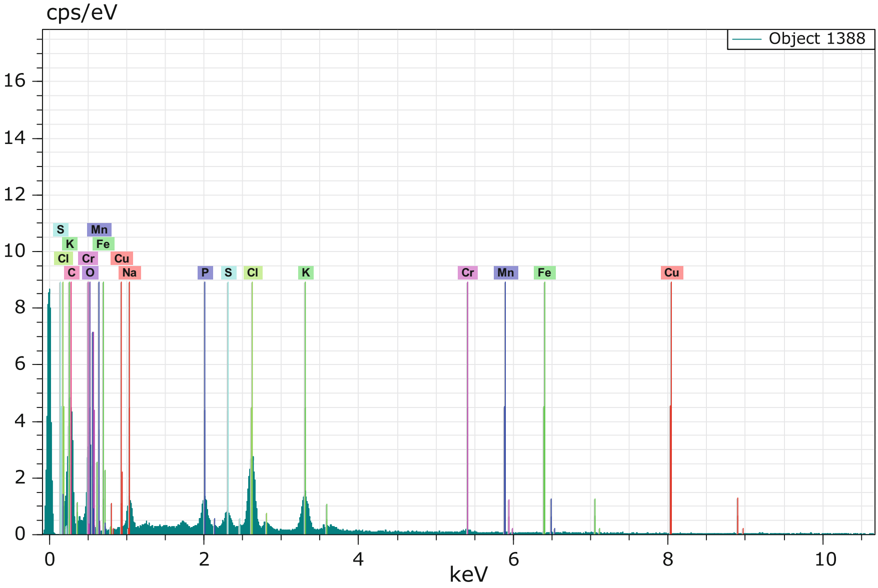


Fig. 4 EDX picture of fungal biomass after color and chromium removal

Table 3 2^3 factorial experimental setup and percentage color removal

Run	Dye concentration, mg/L (A)	pH (B)	Time, hours (C)	Experimental responses of % color removal
1	100.00	5.50	35.00	63.00 ± 0.01
2	200.00	4.50	42.50	60.00 ± 0.03
3	300.00	5.50	50.00	48.50 ± 0.01
4	200.00	4.50	42.50	60.50 ± 0.01
5	31.82	4.50	42.50	80.00 ± 0.01
6	100.00	3.50	35.00	44.00 ± 0.02
7	300.00	5.50	35.00	41.00 ± 0.02
8	200.00	4.50	42.50	59.50 ± 0.02
9	300.00	3.50	50.00	33.00 ± 0.02
10	100.00	3.50	50.00	50.60 ± 0.01
11	368.18	4.50	42.50	44.70 ± 0.01
12	200.00	4.50	29.89	50.70 ± 0.01
13	200.00	2.82	42.50	5.80 ± 0.02
14	200.00	4.50	42.50	60.00 ± 0.03
15	200.00	6.18	42.50	37.50 ± 0.02
16	200.00	4.50	55.11	65.00 ± 0.02
17	200.00	4.50	42.50	59.70 ± 0.01
18	200.00	4.50	42.50	60.00 ± 0.03
19	300.00	3.50	35.00	23.00 ± 0.03
20	100.00	5.50	50.00	69.00 ± 0.03

Response Surface Optimization

The results of the 20 experimental runs under different combinations (dye concentration, pH, and time) as designed by RSM for optimization study are shown in Table 3. A mathematical relationship between the color removal and independent parameters such as dye concentration (*A*), pH (*B*), and time (*C*) has been expressed by the following Eq. (1):

$$\begin{aligned}\%\text{Color removal} = {} & -284.88693 - 0.14955A + 134.14065B + 1.72057C \\ & - 0.004875AB + 0.000816667AC - 0.051667BC \\ & + 0.0000848007A^2 - 13.54162B^2 - 0.013209C^2\end{aligned} \tag{1}$$

The 2D plots of response surface were drawn for the results obtained from experiments carried out to study the effect of different parameters on the percentage color removal of acid brown 45 dye. The analysis of variance (ANOVA) is shown in Table 4. The nonsignificant “Lack-of-fit *F* value” of 4.72 explains that the model is fit for the study (Ghosh and Saha 2012). The value of R^2 (0.9994) implies that more than 99% of the data deviation can be explained by the model. The model

Table 4 Analysis of variance (ANOVA)

Source	Sum of squares	Degree of freedom (df)	Mean square	F value	Probability value (P value)
Model	5510.37	9	612.26	1862.23	<0.0001
Lack of fit	2.71	5	0.54	4.72	0.0569

$R^2 = 0.9994$

Table 5 Regression analysis by using central composite design

Model term	Coefficient estimate	Standard error	F value	P value	Remarks
A	−10.29	0.16	*121.12*	<0.0001	Significant
B	9.10	0.16	*1267.58*	<0.0001	Significant
C	3.97	0.16	*693.09*	<0.0001	Significant
AB	−0.49	0.20	*5.22*	0.0370	Significant
AC	0.61	0.20	*5.77*	0.0129	Significant
BC	−0.39	0.20	*5.77*	0.0850	
A^2	0.85	0.15	*22.80*	0.0002	Significant
B^2	−13.54	0.15	*4757.57*	<0.0001	Significant
C^2	−0.74	0.15	*264.04*	0.0006	Significant

F value (1862.23) with a low probability value ($P < 0.0001$) implies high significance of the model. In this model, the P values of A, B, C, AB, AC, A^2, B^2, and C^2 denote that the terms are significant (Table 5).

Combined Effect of Different Parameters on Color Removal

Figure 5 shows the combined effect of dye concentration and pH on color removal at 50 h time. With increasing pH up to 4.84, color removal was increased. Above pH 4.84, decolorization was observed to be decreased. Maximum decolorization was observed at pH 4.84. The solution pH affects the charge of the functional groups on the fungal cell wall. Concentration of hydrogen ions decreases in the solution with increasing pH, which favors binding of dye molecules to the free functional groups. The decolorization is decreased with increasing dye concentration above 100 mg/L. Maximum color removal (75.25%) was observed at dye concentration: 100 mg/L, pH: 4.84, and time: 50 h.

Figure 6 shows the combined effect of initial solution pH and time on decolorization at initial dye concentration 100 mg/L. Initially with increase in time, color removal increased. Maximum decolorization is observed in 50 h of time. Increase in time after 50 h does not show any improvement in decolorization. Maximum decolorization (75.25%) is observed at pH 4.84 and 50 h time. Figure 7 shows the combined effect of initial dye concentration and time on color removal at pH 4.84.

Fig. 5 Combined effect of dye concentration (*A*) and pH (*B*) on color removal

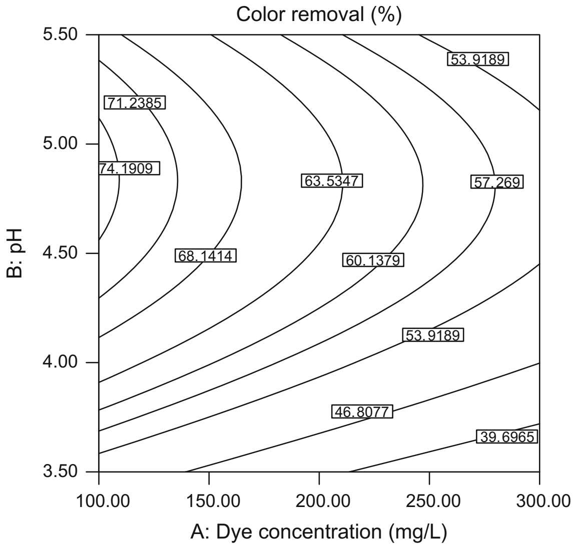
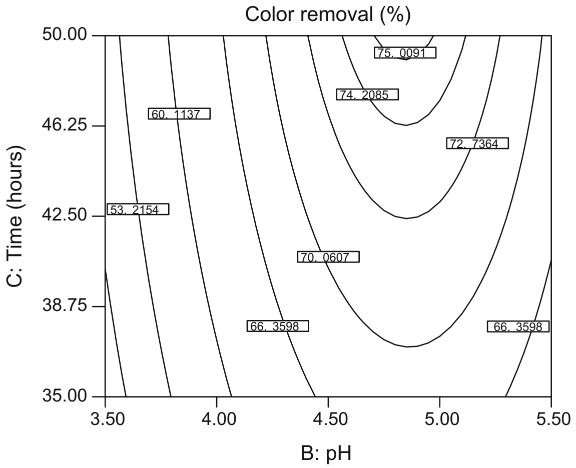


Fig. 6 Combined effect of pH (*B*) and time (*C*) on color removal



At 50 h maximum, decolorization is observed at different concentrations of acid brown 45. It is evident from the 2D plots that all the independent process parameters (dye concentration, pH and time) have strong effect on color removal. Growth of the fungal strain and corresponding color removal are strongly influenced by dye concentration, pH, and time.

Figure 8 shows a ramp of desirability (0.967) that was generated via numerical optimization. The optimum conditions for maximum decolorization (75.25%) are found at dye concentration 100 mg/L, pH 4.84, and time 50 h.

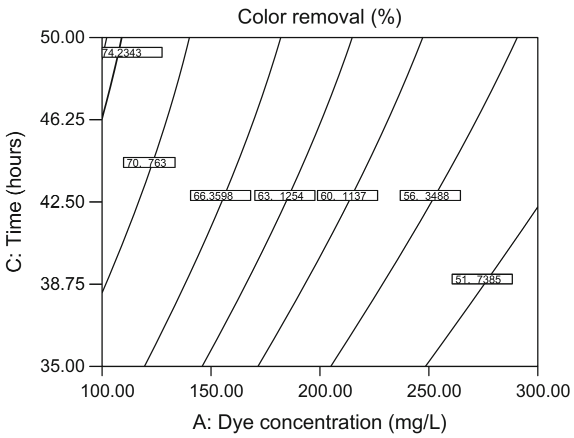


Fig. 7 Combined effect of dye concentration (*A*) and time (*C*) on color removal

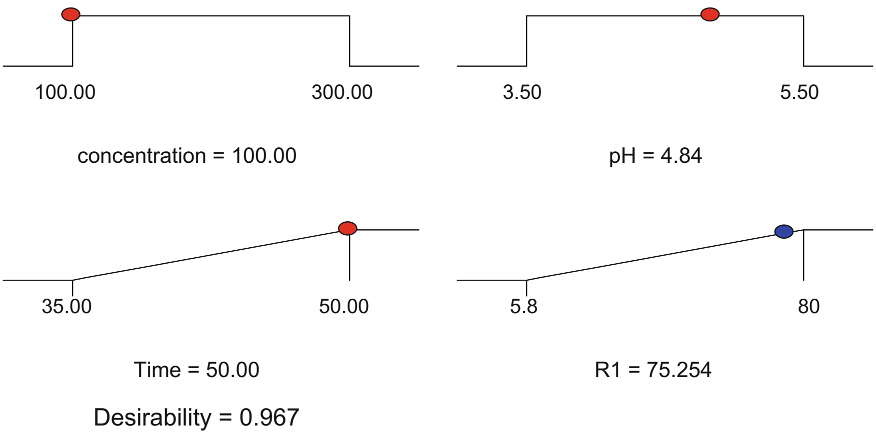


Fig. 8 Desirability ramp for optimized color removal

Confirmatory Experiment

The confirmatory experiment was conducted under optimum conditions (dye concentration 100 mg/L, pH 4.84, and time 50 h) as suggested by the model. Under optimum conditions, maximum decolorization (75.25%) generated by RSM software is in close agreement with the maximum decolorization (73%) obtained in the confirmatory experiment.

Conclusion

This study shows *A. flavus* can be used to remove color and chromium from aqueous solution of high concentration of chromium complex dye. The SEM and EDX analyses indicated color and Cr removal by the fungi. Based on the statistical analysis using response surface methodology, the optimum conditions for 75.25% decolorization are found as: pH 4.84, initial dye concentration 100 mg/L, and time 50 h. It was revealed that color removal was influenced by dye concentration, pH, and time. On the basis of present study, it can be concluded that *A. flavus* has the potential for treatment of industrial wastewater contaminated with both dye and chromium.

References

Aksu Z, Balibek E (2010) Effect of salinity on metal-complex dye biosorption by *Rhizopus arrhizus*. J Environ Manage 91(7):1546–1555

Banerjee S, Dastidar MG (2005) Use of jute processing wastes for treatment of wastewater contaminated with dye and other organics. Bioresour Technol 96(17):1919–1928

Bishnoi NR, Kumar R, Kumar S, Rani S (2007) Biosorption of Cr (III) from aqueous solution using algal biomass *spirogyra* spp. J Hazard Mater 145(1):142–147

Ghosh A, Saha PD (2012) Optimization of copper adsorption by chemically modified fly ash using response surface methodology modeling. Desalin Water Treat 49:218–226

Ghosh A, Dastidar MG, Sreekrishnan TR (2014) Biosorption and biodegradation of chromium complex dye using *Aspergillus* species. J Hazard Toxic Radioactive Waste, ASCE 18(4):1–9

Ghosh A, Ghosh Dastidar M, Sreekrishnan TR (2015) Recent advances in bioremediation of heavy metals and metal complex dyes: review. J Environ Eng, ASCE, C4015003

Kalpana D, Shim JH, Oh BT, Senthil K, Lee YS (2011) Bioremediation of the heavy metal complex dye isolan dark blue 2SGL-01 by white rot fungus *Irpexlacteus*. J Hazard Mater 198:198–205

Li T, Guthrie JT (2010) Colour removal from aqueous solutions of metal-complex azo dyes using bacterial cells of *Shewanella* strain J18 143. Bioresour Technol 101(12):4291–4295

Plaza Caźon J, Viera M, Donati E, Guibal E (2013) Zinc and cadmium removal by biosorption on *Undaria pinnatifida* in batch and continuous processes. J Environ Manage 129:423–434

Prithviraj D, Deboleena K, Neelu N, Noor N, Aminur R, Balasaheb K, Abul M (2014) Biosorption of nickel by *Lysinibacillus* sp. BA2 native to bauxite mine. Ecotoxicol Environ Saf 107:260–268

Pundir R, Dastidar MG (2015) Feasibility of cheese whey as an energy source for the growth of *Aspergillus* sp. and for the removal of heavy metals in batch reactor. Desalin Water Treat 1–8

Ranjusha VP, Pundir R, Kumar K, Dastidar MG, Sreekrishnan TR (2010) Biosorption of remazol black B dye (Azo dye) by the growing *Aspergillus flavus*. J Environ Sci Health Part A 45 (10):1256–1263

Sharma S, Malik A, Satya S (2009) Application of response surface methodology (RSM) for optimization of nutrient supplementation for Cr (VI) removal by *Aspergillus lentulus* AML05. J Hazard Mater 164(2):1198–1204

Sheng PX, Ting YP, Chen JP, Hong L (2004) Sorption of lead, copper, cadmium, zinc and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. J Colloid Interface Sci 275(1):131–141

Taştan BE, Ertuğrul S, Dönmez G (2010) Effective bioremoval of reactive dye and heavy metals by *Aspergillus versicolor*. Biores Technol 101(3):870–876

Wang J, Chen C (2006) Biosorption of heavy metals by *Saccharomyces cerevisiae*: a review. Biotechnol Adv 24(5):427–451

Biosorption as a Novel Approach for Removing Aluminium from Water Treatment Plant Residual—A Review

Mansi Mishra and M. S. Chauhan

Abstract The processes of coagulation and flocculation that are frequently being employed in water treatment plants involve the use of substances known as coagulants. Commonly used coagulants include alum, PAC (Poly Aluminium Chloride) and iron salts ($Fe_2(SO_4)_3$). These processes of coagulation and flocculation, in turn, lead to the generation of water treatment plant residuals (WTRs) having high concentrations of aluminium. Management of water treatment plant residuals therefore is extremely important since aluminium is found to have toxic impacts on plant growth and animal reproduction systems and has been identified as a causative agent for Alzheimer's disease and autism spectrum disorder in human beings. The paper focuses on potential applicability of biosorption for rendering the WTRs aluminium free by virtue of various available biosorbents.

Keywords Water treatment plant residuals · Aluminium · Alzheimer's disease Biosorption

Introduction

Treatment of water so as to render it safe and potable for drinking purposes is one of the major concerns of the environmentalists around the globe. Even though new and better technologies for achieving higher water quality are emerging every day, the issue of disposal of by-products generated in these processes still remains the same. Water treatment technologies aim at removing various impurities, such as suspended and dissolved solids, natural organic matter, present in the raw water by means of processes such as sedimentation, coagulation, filtration, disinfection.

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Throughout the process of water treatment, the by-products so generated as a result of water purification are collectively termed as water treatment plant residuals (WTR).

The two major categories of waste streams generated are:

1. Sludges from sedimentation and coagulation operations
2. Filter backwash water (FBW)

The quantity and characteristics of the waste so generated in the process of water treatment depend chiefly on the quality of raw water, type of treatment methodology adopted, amount of various chemicals used, drinking water production rate and the efficiency of treatment systems (Verlichhi and Masotti 2000).

These wastes have been found to contain high solids content as well as mineralogical and bacteriological impurities exceeding the general disposal standards. Generally, the coagulant used in sedimentation–coagulation process is aluminium sulphate (Alum), and hence, the residual sludge contains higher amounts of aluminium hydroxide which if discharged directly in a water body can inhibit the biological activity of the receiving stream due to the release of aluminium. Not only in the streams and other water bodies, aluminium has also been found to affect plant growth and soil chemistry and in turn soil microfauna. Even though aluminium has not been found to be acutely toxic in insects and animals, however, the continuous exposure for a long period of time can cause adverse impacts on their reproduction capabilities (Ippopolito et al. 2011). Aluminium is also highly reactive with both carbon and oxygen and hence proves to be toxic for human health as it has been identified as one of the major causative factor for Alzheimer’s disease, autism spectrum disorders and in neurotoxicity of central nervous system (Shaw and Tomljenovic 2013). Also the backwash water is believed to have high bacteriological contamination due to the presence of cryptosporidium and Giardia cysts (Subramani and Thomas 2012). Discharging the WTRs without any prior treatment in the water bodies is therefore highly undesirable and hence should be avoided.

However, currently no measures are being adopted for proper handling and treatment of WTRs in India. Most of the water treatment plants are simply disposing off the WTRs in nearby streams, rivers or drains without any prior treatment (Sadashiv et al. 2007). Even though certain water treatment plants such as Asifnagar WTP in Hyderabad, Indira Gandhi WTP in Kolkata, Balaganj water works in Lucknow and a few others have adopted certain measures for recycling the sludge from clarifier and backwash water generated from filter, still most of the plants are still disposing the rejects without any treatment (CPCB 2008). In view of the above-mentioned concerns, this paper focuses on biosorption as a suitable method for eliminating aluminium present in WTP rejects with the help of various available biosorbents.

Biosorption as a Promising Alternative

Biosorption is a process in which the removal of a particular dissolved species (sorbate, metal ions) in liquid phase is achieved by sorption on a solid phase (biosorbent material) (Das et al. 2007). Like all other processes, biosorption too has its own advantages and disadvantages. The major advantages that make this process a preferred choice over other existing technologies of chemical precipitation, electrochemical treatment and membrane technologies include its low cost, reduced sludge generation, high efficiency, the fact that the biosorbent can be regenerated and the adsorbed metal ions can be recovered. The process has certain limitations as well, such as, the early exhaustion of adsorption capacity of the biosorbent due to the active sites being occupied by the metal ions giving rise to the need for desorption (Ahalya et al. 2003).

The literature has reported successful use of different algae, fungi, yeast, parts of certain plants and agricultural wastes as potential biosorbents that can be employed for removing a wide range of metals (such as nickel, copper, cadmium) present as contaminants in wastewaters. Das et al., have reported the use of various algal biomass for removal of copper ions by *Sargassum sp*—a brown seaweed, application of *Eclonia* biomass and *Lyngbya Putealis* for removal of Cr (VI) and *Chlorella Vulgaris* for removing lead (Pb) from wastewaters through biosorption. Algal biosorbents are gaining use worldwide due to their low cost, low nutrient requirements and algae being autotrophic in nature produce large amounts of biomass. Algal biosorbents have an added advantage that it does not produce any toxic substances such as bacteria and fungi (Volesky and Holan 1995). However, fungi and bacterial biomass are also being employed as biosorbents due to their excellent metal binding capacities (Mullen et al. 1989), and the fact that the anti-biotic and food industries are the biggest source of fungal biomass makes it an eco-friendly alternative. *Vienna* et al. used *Aspergillus niger* as biosorbent for removal of cadmium and copper, and the role of various functional groups present in its cell wall was also studied (Vianna et al. 2000). Apart from this, Volesky et al., reported removal of zinc ions in a batch reactor by *Rhizopusarrhizus*, application of pretreated fungal biomasses *Metarrhiziumanisopliae* and *Penicilliumverrucosum* for lead (Pb) uptake and effective bioextraction of mercury (Hg) and cadmium (Cd) by *Agaricusmacrospores*. Though, both algae and fungi have depicted good metal removing capacities as biosorbents, but bacterial biomass has depicted significantly high removal capacity. Therefore, bacterial biomass has gained applicability in biosorbent production at commercial level (Das et al. 2007). Hussein et al. reported the use of different species of *Pseudomonas* for removal of nickel, copper, chromium and cadmium and evaluated the applicability of Freundlich and Langmuir adsorption isotherms. Besides there are reports of *Bacillus sp, Zoogloearamigera* and *Streptomyces sp* having high metal-removal capacities (Das et al. 2007).

Agricultural by-products form another major category of biosorbents. These biosorbents have their own characteristic advantages of easy and economic availability, being nonhazardous and inexhaustible. There is a wide range of agricultural waste biosorbents that have been employed effectively for metal removal. The most important in this category are rich husk, coconut and soybean husk, sawdust, tea waste, banana pith, wood, wool, wheat bran, corn cobs, etc. (Bailey et al. 1999). Sciban and Klasnja depicted the applicability of wood sawdust for removal of Cu (II) ions in single and multistage batch adsorption process and studied the variations in efficiency of removal with respect to contact time and pH (Sciban and Klasnja 2003). Naiya et al. have also shown high removal efficiencies for Zn (II) and Cd (II) through adsorption on sawdust of teakwood origin and neem bark. The results showed that pseudosecond-order model describes the kinetics of adsorption in the best possible manner (Naiya et al. 2009). Amarsinghe and Williams performed batch and fixed-bed column studies for evaluating adsorption of Cu and Pb on tea waste derived from black tea leaves. Biosorption thus provides an economical, sustainable and eco-friendly pathway for removing toxic metal contaminants from aqueous solutions and holds the potential for application in wide variety of fields (Amarsinghe and Williams 2007). Therefore, biosorption as a means for aluminium removal from filter backwash water can also be explored. The next section of paper focuses on suitability of various biosorbents for adsorption of aluminium.

Aluminium Removal Through Biosorption

Developing techniques for management of water treatment plant residuals have always been a matter of concern for researchers across the globe due to its high aluminium concentrations that could be potentially toxic to human beings, animals, plants and insects as explained in earlier sections of this paper. Adsorption, being a cost-effective method of metal ion removal from aqueous solutions is therefore consistently being explored in this regard. Takassi et al. employed activated carbon for adsorption of aluminium ions in aqueous solution and monitored the variations in pH, temperature, contact time and dose of adsorbent in batch experiments. The results of the study revealed that when activated carbon is used for adsorbing aluminium the entire process is endothermic in nature (Takassi et al. 2015). Even though the adsorption of aluminium using activated carbon as adsorbent proved to be successful but is not a cost-effective and economical option. Therefore, the use of biosorbents for aluminium removal needs to be explored. Lee et al. studied aluminium sorption on a biosorbent *Laminaria Japonica* derived from a brown marine alga through batch experiments (Lee et al. 2004). Similar studies were also conducted by Sari and Tuzen on a biomass *Padina Pavonica* which was also obtained from brown algae. The effects of pH, temperature, contact time and adsorbent dose on the biosorption process were monitored and found that *P. Pavonica* is a suitable biosorbent for aluminium removal with capacity of removal being 77.3 mg/g (Sari and Tuzen 2009). Not only algae, but also bacterial biomass has also been employed for biosorption of aluminium. Tassist et al. utilized the biosorbent derived from *Streptomyces rimosus*, a gram +ve mycelial bacteria belonging to actinomycetes family (Tassist et al. 2010), whereas Cayllahua and Torem employed *Rhodococcus opacus* strains for aluminium removal. The maximum capacity of biosorption with *S. rimosus* was 11.76 mg/g, whereas with *R. opacus* it was as high as 49.59 mg/g with biosorption being a spontaneous and endothermic process as found in other studies as well (Cayllahua and Torem 2010).

Agricultural by-products have also been investigated for their suitability as biosorbents for aluminium removal due to their easy availability, cost-effectiveness and nonhazardous nature. Kumari and Ravindranath employed the powder of leaves of plants—*Achiranthus aspera* and *Cassia occidentalis* as biosorbents for aluminium removal from aqueous solutions. The plants of *Achiranthus aspera* and *Cassia occidentalis* have been found to have great affinity for aluminium ions. The results of the study showed maximum aluminium removal at a pH of 6–8 with an equilibrium time of 120 min (Kumari and Ravindranath 2012). Tony Sarvinder Singh, on the other hand, employed rice husk and rice husk char as biosorbents and showed that rice husk char has better sorption capacities as compared to plain rice husk. Abdel-Ghani et al. performed a similar study using rice husk activated carbon on real wastewater samples collected from various locations and obtained a maximum removal capacity of 34.48 mg/g (Abdel-Ghani et al. 2015). Muhtaseb et al., utilized locally prepared date-pit-activated carbon and achieved sorption capacities of 0.305 mg/g at a pH of 4 (Al-Muhtaseb et al. 2008). Coconut shells form another major category of agricultural by-products. Ghazali et al. studied biosorption of aluminium on activated carbon derived from coconut shell through batch adsorption experiments. The parameters considered were pH and initial concentration of metal ion. The maximum observed adsorption capacity was approximately 0.957 mg/g (Ghazali et al. 2012). Shameem Rani compared the removal efficiencies of various biosorbents—sawdust, coconut husk, rice husk and tea waste—for aluminium sorption and found biosorption to be a novel technique for aluminium removal from aqueous solutions (ShameemRani 2015).

Conclusion

Research has shown that biosorption is an economical and efficient way of removing metal ions from polluted wastewaters, and satisfactory high efficiencies can be achieved. There is a wide variety of materials to be used as biosorbents ranging from algal, fungal and bacterial biomass to agricultural by-products. Biosorption is also capable of removing aluminium ions from aqueous solutions with fairly good removal capacities. Thus, it provides a novel, cost-effective, cheap and eco-friendly way of removing aluminium from water treatment plant residuals. Further studies are required regarding application of biosorption particulary for aluminium removal from filter backwash water so that the performance of the entire process can be predicted with respect to different operating parameters. Mathematical modelling can be helpful in this regard, and further strategies regarding processing of biosorbents need to be developed so as to achieve higher removal efficiencies.

References

Abdel-Ghani NT, El-Chaghaby GA, Zahran EM (2015) Cost effective adsorption of aluminium and iron from synthetic and real wastewater by rice hull activated carbon. Am J Anal Chem 6:71–83

Ahalya N, Ramchandra TV, Kanmadi RD (2003) Biosorption of heavy metals. Res J Chem Environ 7(4):71–79

AL-Muhtaseb AS, El-Naas MH, Abdallah S (2008) Removal of aluminium from aqueous solutions by adsorption on date-pit and BDH activated carbons. J Hazard Mater 158:300–307

Amarsinghe BMWPK, Williams RA (2007) Tea waste as a low cost adsorbent for removal of Cu and Pb from wastewater. Chem Eng J 132:299–309

Bailey SE, Olin TJ, Bricka RM, Adrian DD (1999) A review of potentially low cost sorbents for heavy metals. Water Res 33:2469–2479

Cayllahua JEB, Torem ML (2010) Biosorption of aluminium ions onto rhodococcusopacus from wastewaters. Chem Eng J 161:1–8

Central Pollution Control Board (CPCB) (2008) Status of water treatment plants in India

Das N, Vimala R, Ksarthika P (2007) Biosorption of heavy metals—an overview. Ind J Biotechnol 7:159–169

Ghazali Z, Othaman R, Abdullah MP (2012) Preparation of activated carbon from coconut shell to remove aluminium and manganese from drinking water. Adv Nat Appl Sci 6(8):1307–1312

Ippopolito JA, Barbarick KA, Eliott HA (2011) Drinking water treatment residuals—a review of recent uses. J Environ Qual 40:1–12

Kumari AA, Ravindranath K (2012) Removal of aluminium (III) ions from polluted waters using biosorbents derived from achiranthusaspera and cassia occidentalis. Int J Water Res Environ Sci 1(1):8–19

Lee HS, Suh JH, Kim IB, Yoon T (2004) Effect of aluminium in two-metal biosorption by an algal biosorbent. Miner Eng 17:487–493

Mullen LD, Wolfe DC, Ferris FG, Beveridge TJ, Flamming CA (1989) Bacterial sorption of heavy metal. Appl Environ Microbial 55:3143–3149

Naiya TK, Chowdhary P, Bhattacharya AK, Das SK (2009) Saw dust and neem bark as low cost biosorbents for adsorptive removal of Zn and Cd ions from aqueous solutions. Chem Eng J 148:68–79

Sadashiv Murthy BM, Swaminathan P, Madhu SM (2007) Reclamation and reuse of filter backwash water—a case study of the Kalliseri water treatment plant in Kerala state. J Water Wastewater Asia 23:48–51

Sari A, Tuzen M (2009) Equilibrium, thermodynamic and kinetic studies on aluminium biosorption from aqueous solution by brown algae (PadinaPavonica) biomass. J Hazard Mater 171:973–979

Sciban M, Klasnja M (2003) Optimization of usage of wood sawdust as adsorbent of heavy metal ions from water ISIRR 3:51–56

ShameemRani K (2015) Removal of aluminium from metal plating industrial wastewater by different column chromatography technique. Int J Sci Res 4(2):1701–1704

Shaw CA, Tomljenovic L (2013) Aluminium in the central nervous system (CNS)—toxicity in humans and animals, vaccine adjuvants and autoimmunity. Immunol Res 13:1–14

Subramani T, Thomas S (2012) Experiments on tube settler for treatment of FBW and optimization of plant operation for residual reduction. Int J Eng Appl Res 2:190–203

Tassist A, Lounici H, Abdi N, Mameri N (2010) Equilibrium, kinetic and thermodynamic studies on aluminium biosorption by a mycelia biomass (Streptomycesrisomus). J Hazard Mater 183:35–43

Takassi MA, Pour PG, Farhadi A, Hamule T (2015) Thermodynamic study of isothermal adsorption of aluminium ion from water using activated carbon as adsorbent. J Water Res Hydraul Eng 4:76–82

Verlichhi P, Masotti L (2000) Reuse of drinking water treatment plant sludges in agriculture—problems, perspectives and limitations. 19–25 (Lo smaltimentodeifanghidipotabilizzazione in Europa e negliStatiUniti)

Vianna LNL, Andrade MC, Nicole JR (2000) Screening of waste biomass from *Saccharomycescerevisiae*, *Aspergillusniger* and *Bacillus lentus* fermentations for removal of Cu, Zn, Cd by biosorption. World J Microbiol Biotechnol 16:437–440

Volesky B, Holan ZR (1995) Biosorption of heavy metals- a review. Biotechnol Prog 11:25–235

Catalytic Oxidation of Sulphide Laden Tannery Wastewater Without Sludge Production

N. Prabhakaran, S. Swarnalatha and G. Sekaran

Abstract The beam house operations in tanning process of hides/skins comprise of soaking, liming, fleshing and deliming operations. The removal of animal hair and flesh from skin is facilitated by the liming operation. About 5 m^3/ton of wastewater containing a credible concentration of sulphide and dissolved proteins are discharged in tannery process. It is highly alkaline and having high BOD/COD ratio. The biological treatment of wastewater occurs at neutral pH requires neutralization of the wastewater using acidic stream. This results in the emission of hydrogen sulphide which is considered to be highly toxic gas. The present investigation employed Heterogeneous Peroxide Oxidation process (HPO) for the oxidation of sulphide in the lime sulphide liquor without sludge production with simultaneous removal of COD from wastewater. The screened effluent was adjusted to pH 9.7 using conc. sulphuric acid, and it is catalytically oxidized with hydrogen peroxide 3.921 mM/L and nanoporous activated carbon (NPAC), 30 g/L at HRT 24 h. The dosage of hydrogen peroxide, mass of NPAC and HRT were optimized. The integrated catalytic and biological oxidation in Fluidized Immobilized Carbon Catalytic Oxidation (FICCO) reactor eliminated COD, sulphide, total Kjeldahl nitrogen, protein, amino acids and TOC by 66.66, 98.95, 75.67, 44.21, 48.98 and 62.18%, respectively. The sulphide present in the wastewater was catalytically oxidized to sulphate, and ammonia content was increased about 78.05% by cleaving protein molecules.

Keywords HPO · NPAC · FICCO · COD · BOD

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Introduction

Leather industry is the significant contributor to the Indian economy and provides large-scale employment opportunity. The total processing capacity of the world tanning industry is more than 10 million tons of hides and skins per year. Totally, 2500 tanneries are located in India including Tamil Nadu 50%, West Bengal 20% and Uttar Pradesh 15% (CPCB 2009). The beam house operations such as soaking, liming, fleshing, deliming in the process of hides/skins are common irrespective of the types of tanning process. The preservation and processing of raw hides and skins for tanning process cause severe pollution problem towards environment and mankind (Aravindhan et al. 2004). In fleshing and liming process, unhairing is done by chemical dissolution of the hair and epidermis with an alkaline medium of sulphide and lime. After skinning at the slaughterhouse, the hide appears to contain excessive meat, fleshing usually precedes unhairing and liming. Liming and unhairing produce the effluent stream with the highest COD value. The removal of hair and flesh from skin is facilitated during the liming operation. Conventional process employs 10% lime (calcium hydroxide) and 2% sodium sulphide on hide/skin weight basis for loosening the hair. About 5 m^3 of spent lime liquor is discharged per ton of raw hides/skins processed. Sodium sulphide being a good reducing agent interferes in the oxidation of organic wastes and contributes significantly to the BOD and COD concentrations in the wastewater. Lime sulphide is most environmental harmful chemical in tanning process (Schraederet et al. 1998; Huber and De 1990). The spent lime liquor is highly alkaline (pH 10–12) and 100% toxicity (Taylor et al. 1987; Marsal et al. 1999). The major amount of pollution in terms of BOD (5000–10,000 mg/L), COD (10,000–25,000 mg/L), sulphide (500–800 mg/L), total solids (24000–48000 mg/L), suspended solids (6000–18,000 mg/L), chloride (4000–8000 mg/L) and sulphate (600–1200 mg/L) is contributed by sulphide-liming process. This sulphide containing wastewater has extensive hazardous to environment and treatment plant (Davies 1997).

Problems Associated with Presence of Sulphide in Effluent

Under alkali conditions sulphide largely remain in solution. When the pH of the effluent falls below 9.5, hydrogen sulphide may evolve from the effluent. The rate of evolution of hydrogen sulphide increases with decrease in aqueous pH and is characterized by severe odour problem. This gas is toxic similar to hydrogen cyanide and even low-level exposure will cause headaches and nausea, and there is a danger of attack to the surface of the eye. At higher levels, death can rapidly result and there are many deaths recorded from sulphide build up in sewage systems. Hydrogen sulphide gas is also fairly soluble, and when dissolved by condensation weak acids can be formed with resultant corrosion (Obuka et al. 2012). This typically weakens metal roofing, girders and metal building supports. In sewers, major problems can result by corrosion of metal fitting, reinforcement and pipe work. If discharged to surface water, there are toxicological dangers even at low concentrations. Sulphide can also be oxidized into non-toxic compounds by certain bacteria in rivers, but this creates an oxygen demand and if excessive there is damage to aquatic life. It also inhibits the methanogenesis process. Soluble sulphide ranging from 50 to 100 mg/L can be tolerated in anaerobic treatment with little or no acclimation. Sulphide has high oxygen demand of 2 mol O_2/mol sulphide and thus causes depletion of oxygen concentration in water.

Treatment of Lime Sulphide Liquor

The presence of sulphide in wastewaters may dramatically interfere with microbial activities and consequently disturb the function of the system (Mesdaghinia and Yousefi 1991). Biological processes can be carried out only when concentration of sulphide is not exceeding 50 mg/L (Valeika 2006). Aerobic treatment was not effective method for treatment of high sulphide containing tannery effluent (Sekaran et al. 1996; Ganesh and Ramanujam 2009). Sekaran et al. (1996) have reported that anaerobic treatment of tannery wastewater in high rate close type reactors leaves sulphides in the range 31–795 mg/L, COD 395–1886 mg/L, BOD 65–450 mg/L and TOC 65–605 mg/L. So high sulphide concentration present in treated wastewater may not be suitable for aerobic biological treatment. In order to remove sulphide from wastewater streams, a number of physico-chemical methods like direct air stripping, chemical precipitation and oxidation are in common method of treatment. Many of the metals such as iron, zinc, copper could be used to precipitate the sulphide into insoluble metal sulphide. Oxidation processes used for sulphide removal are aeration (catalysed and un-catalysed), chlorination, ozonation and hydrogen peroxide treatment (Valeika et al. 2006; Anglada et al. 2009). During the sulphide oxidation by aeration, there is noticeable loss of sulphide directly into the atmosphere. Sulphide consumes the oxygen in aerator reaction and thus reduces the efficiency of the treatment (Lacorte et al. 2003). In chlorination, chlorine reacts with certain metals and organic matter in the water to form hazardous chlorinated organic chemicals. Catalytic chemical oxidation of the sulphide with air removes the sulphide quantitatively, but it is a time-consuming and expensive process. (Valeika et al. 2006) proposed the use of manganese oxide to oxidize sulphide in tannery effluent by oxidation of Na_2S in two stage treatment method. In the first stage, Na_2S reacts with MnO_2 to give manganese hydroxide and in second stage, the catalysis reaction between Na_2S and air O_2 is taking part. (Sekaran et al. 1995) also reported the removal of sulphide in lime yard wastewater by wet air oxidation in the presence of manganese sulphate as a catalyst. During the oxidation of sulphide, 92% of the total oxygen demand and 90% of the dissolved protein were also removed in lime yard wastewater. But manganese sulphate results in formation of Manganese hydroxide sludge and also when the level exceeds 0.01 g/100 g of water, it gets solubilized (solubility of manganese hydroxide at pH 9.5 = 5.9×10^{-4} g/L), thus increase in

Mn^{2+} concentration in wastewater also contributing to metal pollution load. Hence, there has been a constant research on the development of methods for the removal of sulphide from lime sulphide liquor without sludge formation. The focal theme of the present investigation was to employ HPO process and fluidized immobilized cell carbon oxidation reactor (FICCO) for the oxidation of sulphide in the lime sulphide liquor without sludge production.

Materials and Methods

Source and Collection of Lime Sulphide Liquor and Methods

The lime sulphide liquor was collected from tannery lime processing wastewater in CSIR-CLRI, Chennai. The wastewater was screened to remove the floating solids such as hair, flesh, trimmings. The screened effluent was adjusted to pH 9.7 using con. sulphuric acid under mixing by magnetic stirrer then the solution was allowed to remove grit in imhoff cone gravity settling equipment for two hours. Then supernatant liquor was siphoned off without disturbing the settled grits. The Hetero Peroxide oxidation (HPO) process was performed for the above solution using 0.4 ml/L of 30% hydrogen peroxide and 30 g/L of nanoporous activated carbon (NPAC) for 24 h. The consumption of hydrogen peroxide and time were optimized and then neutralized using lime for the second stage processing in fluidized immobilized carbon catalytic oxidation (FICCO) using mixed microorganism cultivated from sewage sludge with NPAC 30 g/L.

Materials

All the reagents were purchased from Merck, India, and nanoporous carbon was prepared in laboratory using two stage processes.

Preparation and Characterization of Nanoporous Activated Carbon (NPAC)

The nanoporous activated carbon was prepared by two step activation process. First step, rice husk was pre-carbonized at 400 °C and in the second step activated using phosphoric acid at 800 °C. It was washed with hot distilled water several times and dried at 110 °C for 1 h in a hot air oven and stored over dehydrating agent in the desiccators (Swarnalatha et al. 2009). The prepared nanoporous activated carbon (NPAC) was used as base catalyst for the removal of sulphide and COD simultaneously.

Physico-Chemical Analysis of the Wastewater

The wastewater samples were analysed for pH, BOD_5 (biochemical oxygen demand), COD (chemical oxygen demand), sulphide, sulphate, TOC and total dissolved solids, in accordance with standard methods of analysis of wastewater (American Public Health Association 1998). TOC analyser used to measure presence of TOC and TN. The instrumental analyses of UV/Visible spectroscopy and FT-IR spectroscopy were performed for the identification of treatment of wastewater. The sample was completely dried at 100–120 °C and analysed using Thermogravimetric analysis (TGA). Total Kjeldahl Nitrogen (TKN) and Ammoniacal Nitrogen were measured using Buchi TKN and amoniacal nitrogen analyser.

Treatment Methods for Lime Sulphide Liquor

The lime sulphide liquor was taken for the heterogeneous Fenton oxidation using NPAC/H_2O_2 at specific concentration in FBR at required pH.

Results and Discussion

The characteristics of initial sulphide laden tannery wastewater samples are presented in Table 1.

Table 1 Characteristics of initial effluent

Parameters	Values
pH	12.59 ± 0.523
ORP	−524.8 ± 11.682
COD (mg/L)	11523 ± 1657.88
BOD (mg/L)	6975 ± 1372
TOC (mg/L)	1644 ± 1155
NH_3 (mg/L)	96.55 ± 76.076
TKN (mg/L)	624.1 ± 393.69
Total solids (mg/L)	66,626 ± 69,248
Total dissolved solids (mg/L)	25,513 ± 14,082
Total suspended solids (mg/L)	41,113 ± 55,166
Sulphide (mg/L)	1211 ± 402.43
Sulphate (mg/L)	958.4 ± 962.19
BOD: COD	0.339 ± 0.0906
Protein (mg/L)	7331 ± 1262.9
Aminoacid	52,702 ± 72022

Characteristics of NPAC

The NPAC samples were characterized by surface area 291.15 (m^2/g), average pore diameter 25.91 (Å), carbon 48.45 (%) and free electron density 16.052×10^{18} (spins/g) (John Kennedy et al. 2004; Swarnalatha et al. 2009).

Fluidized Bed Reactor (FBR)

The fluidized bed reactor for the oxidation of sulphide in lime sulphide liquor is presented in Fig. 1, which consists of three zones. The first zone is known as "reactive zone" which contains catalyst (either $MnSO_4$ or NPAC) which can be fluidized by compressed air and wastewater at upflow velocity of 5 ml/min. The quantity of compressed air required for the oxidation of organics in wastewater is decided on the rate of organics oxidation in wastewater. The compressed air required for the fluidization and oxidation of organics is supplied through the perforated pipe lines provided at the bottom of the reactor for uniform distribution. The pressure of air required is a function of upflow velocity, viscosity of medium, total solids content of the medium, temperature and height of the reactor. The second zone is fluid separation zone, the compressed unspent air is seperated by triangular septum provided at top of the reactor and recirculated inside it. Then it is passed through the perforated scrubbing chamber. The third zone is the settling zone. The treated wastewater was allowed to pass through inclined baffled zone for the separation of suspended solids. The angle of the inclined plate was decided based on zone of settling of the suspended solids. The settling tendency of the suspended solids was enhanced by providing the extended surface area to capture

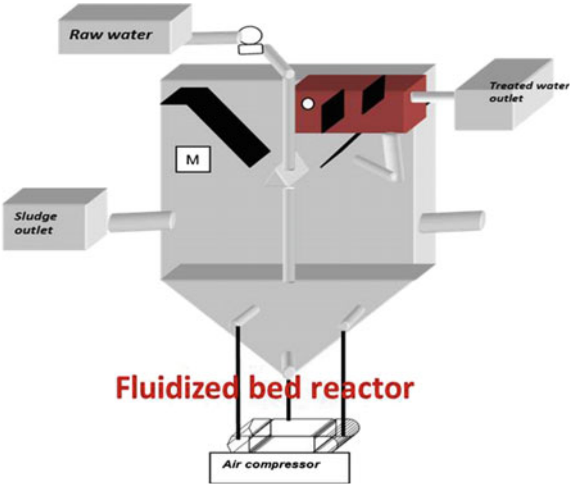


Fig. 1 Fluidized bed reactor

the particles. The media used to increase the surface area for interception of the suspended particles are by poly propylene plastic media of defined geometry. The screened suspended solids are sloughed off from the media on exceeding a critical thickness. The sloughed suspended solids slides back into the reactor through the aperture. The sludge accumulated in the reactor is withdrawn daily through sludge withdrawal pipe line provided in the reactor.

Optimization of pH

Hetero Peroxide oxidation process was optimized by batch process for 24 h with 0.4 ml/L of 30% for the optimization of pH by varying solution pH of 12, 11, 9.7, 8 and 7, respectively. The removal of COD for the studied solution pH was represented in Fig. 2. Initial COD value was 11040 mg/L and the residual COD after treatment at pH 12, 11, 9.7, 8.0 and 7.0 were found to be 6760, 7520, 5500, 6080, 5600 mg/L, respectively. It clearly indicates that the removal of COD at pH 7.0 and 9.7 is greater than any other pH, but at the pH 7.0, the liberation of hydrogen sulphide is greater, thus we fixed at optimum pH of 9.7. Figure 2b indicates the removal of BOD and the removal was better in pH 7.0 and 9.7. In order to avoid the liberation of sulphide, optimum pH was fixed at pH 9.7. The BOD: COD of initial sample was 0.25 and it increased during the process at different pH (Fig. 3a), and NH_3 formation was also increased by varying the pH (Fig. 3b).

Figure 4a, b represents the removal of TN and TOC at various pH. The removal of TOC and TN were decreased for all the studied pH of the wastewater on treatment as given below. Sulphide removal is considered to be one of the important criteria in pH optimization for the treatment of sulphide containing wastewater. Though it decreases drastically in pH 7 and pH 8 (Fig. 5), pH 9.7 was considered as optimum in order to avoid the evolution of H_2S gas (results in rotten egg smell) by decreasing the pH.

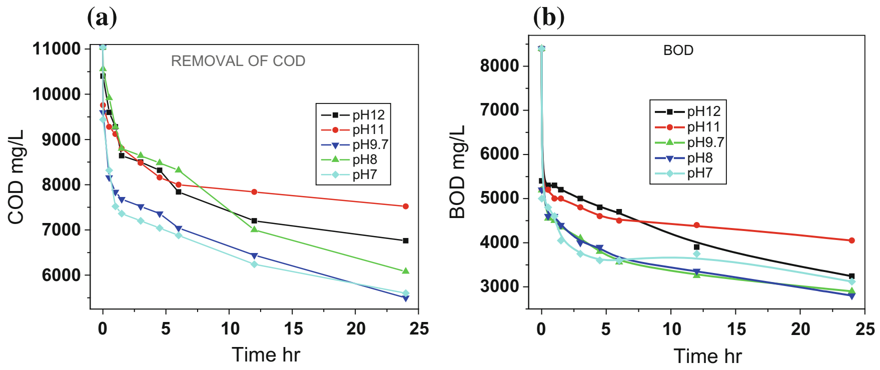


Fig. 2 Optimization of pH for the removal of **a** COD and **b** BOD on HPO process

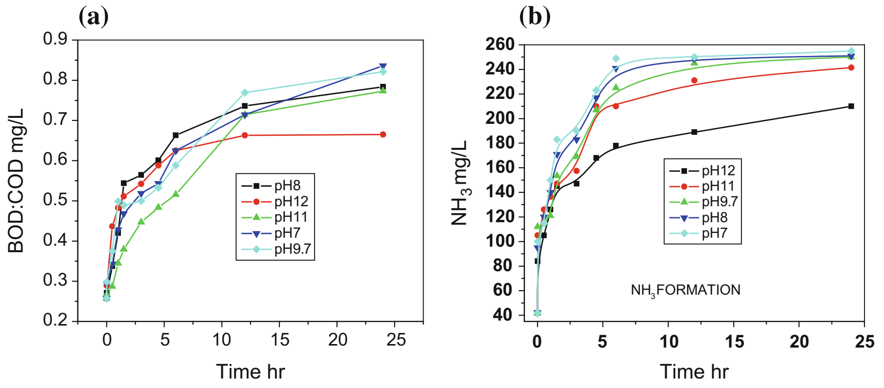


Fig. 3 Optimization of pH on the values of **a** BOD: COD and **b** NH_3 formation in HPO process

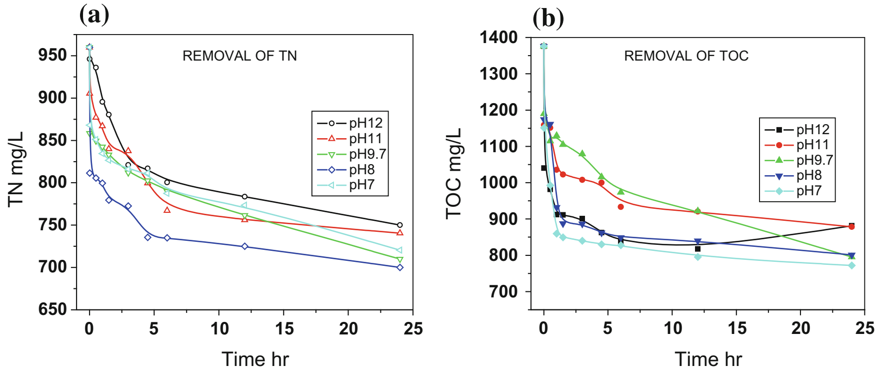


Fig. 4 Optimization of pH for the removal of **a** TN and **b** TOC in HPO process

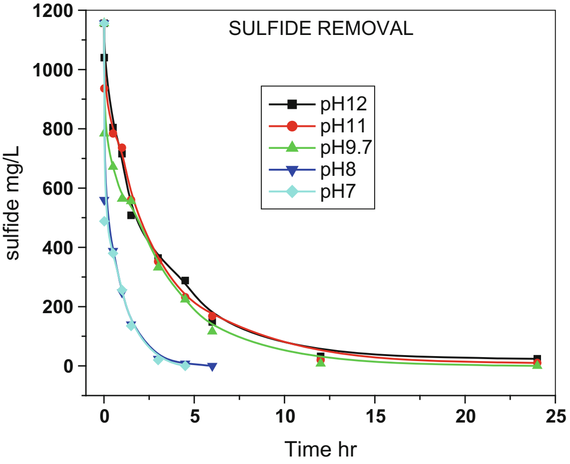


Fig. 5 Optimization of pH for the removal of sulphide on HPO process

Optimization of H_2O_2

Optimization concentration of peroxide (0.2, 0.4, 0.6 and 0.8 ml of 30% hydrogen peroxide/L) was carried, put at optimum pH (pH 9.7). The result confirmed that the optimum concentration of H_2O_2 was found to be 0.4 ml. Though sulphide removal was high at 0.8 ml of 30% hydrogen peroxide/L, there is no considerable removal of COD at this dosage than the other studied peroxide concentration (Fig. 6a). The removal of sulfide was also studied using different peroxide dosage in which it has been found that 0.4 and 0.6 ml of H_2O_2 yielded the same results (Fig. 6b). With respect to COD removal, 0.4 ml peroxide dose was fixed as optimum.

Optimization of NPAC (Nanoporous Activated Carbon)

Optimization of NPAC dose was optimized by varying the mass of NPAC addition into the reactor such as 20 g, 25 g, 30 g and 40 g/L of NPAC per litre of treatment. Figure 7a, b shows that the higher reduction of COD and BOD was observed for

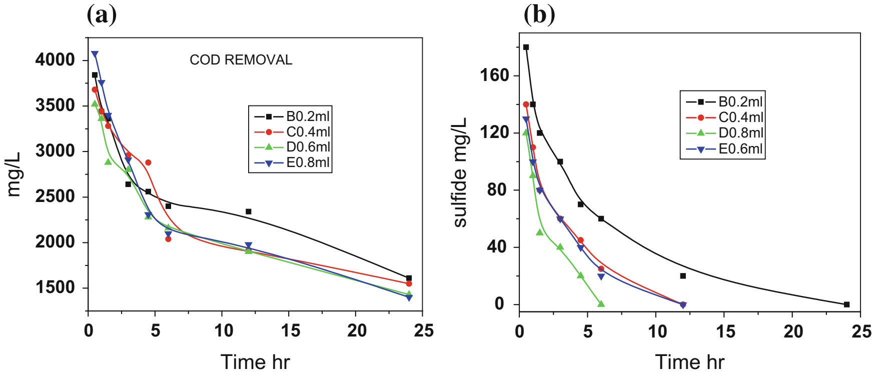


Fig. 6 Optimization of H_2O_2 for the removal of **a** COD and **b** Sulphide

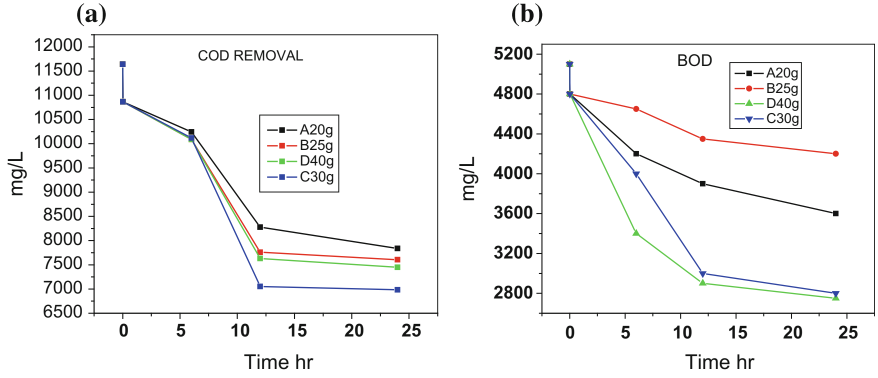


Fig. 7 Optimization of NPAC for the removal of **a** COD and **b** BOD

40 g of NPAC/L. However, the optimum mass was taken as 30 g/L based on the comparison with respect to cost of treatment.

Overall Processes

HPO process was carried out at an optimum pH, peroxide and NPAC concentration to achieve the maximum sulphide and COD reduction. It has been observed that the removal of sulphide in the proposed method maybe due to the formation of sulphoxides (Patai et al. 1988), sulphenic and sulphinic compounds due to homolytic and heterolytic cleavage of peroxide (Bach et al. 1996). The peroxide can oxidize sulphide and thiols present in the system via nucleophilic substitution reaction. Equation (1) shows the oxidation of organic sulphide molecule reacting with peroxide at room temperature to form sulphoxides. Equation (2) shows thiols undergoing oxidation to form sulphenic acid and water; it further oxidized to form sulphinic acid compound Eq. (3). sulphinic is a more stable species when compared to sulphenic acid (Burkhard et al. 1959). Sulphinic acids can be also generated by disproportionation of sulphenic acid (Abraham et al. 1983).

$$\mathrm{R{-}S{-}R + HO{-}OH \rightarrow R{-}SO{-}R} \tag{1}$$

$$\mathrm{R{-}SH + HO{-}OH \rightarrow R{-}S{-}OH + H_2O} \tag{2}$$

$$\mathrm{2R{-}S{-}OH \rightarrow R{-}SH + RS_2OH} \tag{3}$$

The above-mentioned reaction is supported by the reduction of solution pH throughout the process (Fig. 8a) for the formation of acid compounds in the system. Then the resulting solution was passed through FICCO reactor for further treatment after correcting the pH to 7.0. HPO process oxidizes the chemically oxidizable compounds present in water confirmed by ORP analysis (Fig. 8b) and also enhance the BOD: COD to oxidize by microorganisms which feed in the FICCO process, because of having NPAC in this process the microbes can accumulate on other words immobilize inside and outer sphere pore of the matrix to oxidize biologically degradable compounds (Kumara Sashidara et al. 2013). Regular period of interval solution ORP was checked; the initial sample was observed to be −524 mV and it was reduced to −100 mV at the end of the treatment, which indicates the oxidation on treatment process (Fig. 8b). The initial solution COD was calculated to be (19,200 mg/L) reduced to 6400 mg/L (66.66%) after the various treatment processes with the removal of TOC by oxidation process (Fig. 10b). Similarly BOD was reduced from 7200 to 4500 mg/L after treatment (Fig. 9a, b). Figure 10a shows that BOD: COD ratio was 0.33 for the initial wastewater (Dahl 1999; Lacorte et al. 2003); it was increased to 0.66 after the treatment process.

Further, the concentration of amino acid of the sample was analysed for all the processes for the confirmation of degradation of free amino acid in the waste water

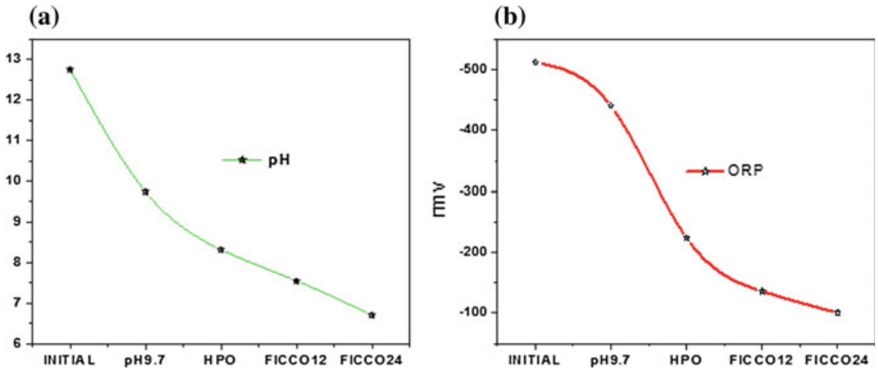


Fig. 8 The values of **a** pH and **b** ORP during the all treated processes

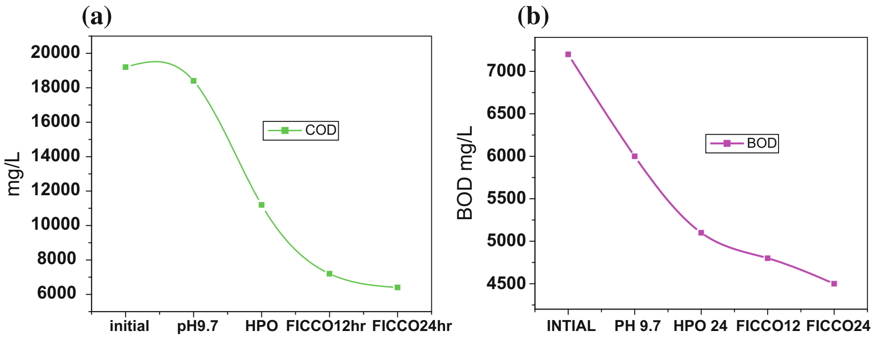


Fig. 9 The values of removal of **a** COD and **b** BOD during the treatment process

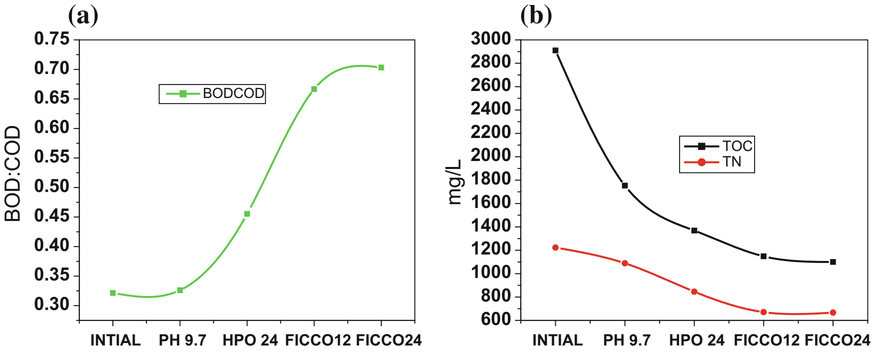


Fig. 10 The values of **a** BOD: COD and **b** TOC and TN during treatment processes

with the help of Ammonia and Total Nitrogen analysis (Fig. 10b). The decrease of Amino acids observed with the decrease in TKN (Fig. 11a), TN (Fig. 10b) and Ammonia (Fig. 11b) because of break down of large protein molecule and the removal of nitrogen due to the oxidation of Amino groups present in the protein molecules. Further, the increase in concentration of amino acid after FICCO also confirms the degradation of higher molecular weight protein to amino acids. The concentration of initial protein was 8228 mg/L which is decreased to 4590 mg/L after FICCO treatment (Fig. 12). The complete removal of Sulfide (Fig. 11a) observed. The residual COD present at end of the treatment process may be due to the non-degraded protein molecules.

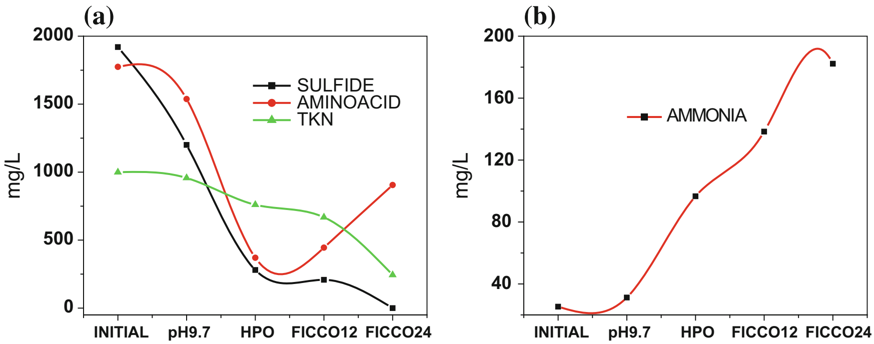
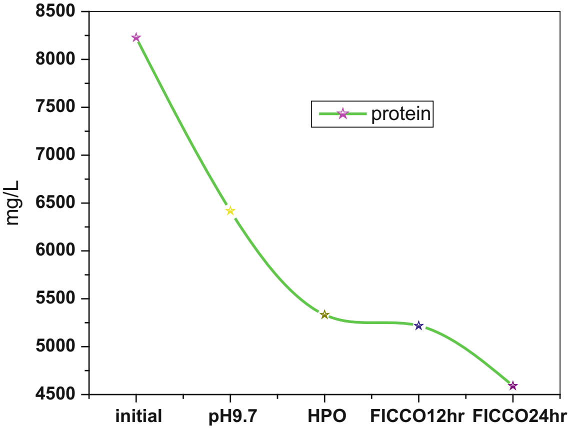


Fig. 11 The values of **a** sulphide, amino acid and total Kjeldahl nitrogen and **b** ammonia during treatment process

Fig. 12 Removal of protein during treatment processes



Instrumental Analyses

Thermo-Gravimetric Analysis (TGA) and UV-Visible Spectroscopic Studies

The TGA analysis of initial wastewater was carried out after complete water dry using nitrogen evaporator at 80 °C (Model: Rapid 25 mini EC system) using nitrogen gas. The TGA was performed for the temperature range from 30 to 800 °C at 5 °C/min. The results showed a final residue of 28.45% which confirms the wastewater has higher concentration of organic molecules (Fig. 13a).

UV-Visible spectrum of initial solution and after treatment for the verification of organic removal is done. The intensity was found to be decreased with respect to the treatment process at a wavelength observed at 300 nm. The decrease in intensity confirmed the removal of organic molecules (Fig. 13b).

FT-IR Spectroscopic Studies

FT-IR spectrum of the initial sample and final sample were taken as shown in Fig. 14. The sample was dried using nitrogen evaporator at 80 °C then analysed FT-IR spectroscopy. The initial wastewater with abroad peak at 3460 cm^{-1} conforms the presence of –OH stretch, then at 1638 cm^{-1} sharp peak due to the sec. amide stretch, at 1450 cm^{-1} due to the presence of aromatic C–C stretching, at 1122 cm^{-1} due to the hydronium sulphonate salts, at 673 cm^{-1} by C–S stretching frequency, at 1453 cm^{-1} due to the stretching frequency of sulphate salt, at 999 cm^{-1} due to the stretching frequency of S–O–C molecule. When compare from initial to final some of the peaks shift was observed the above figure shows a broad peak at 3460 cm^{-1} due to –OH stretch, at 1638 cm^{-1} sharp peak due to sec. amide

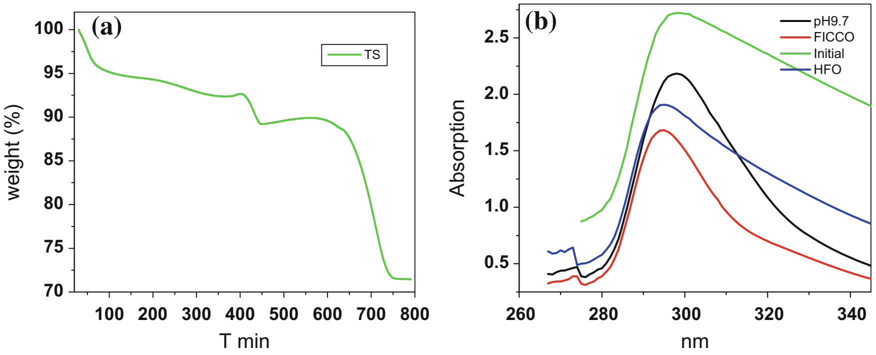


Fig. 13 **a** TGA spectrum for total solids and **b** UV–visible spectrum for the treatment system

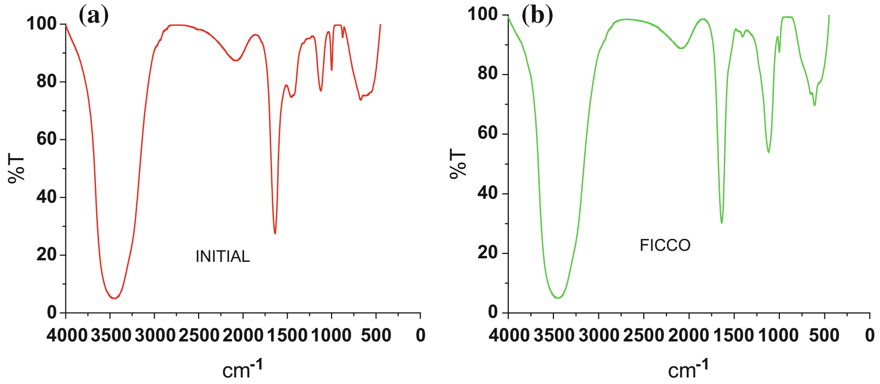


Fig. 14 FT-IR spectrum of **a** initial and **b** final treated lime sulphide water sample

stretch, at 1405 cm^{-1} due to—Aromatic C−C stretching, at 1120 cm^{-1} due to hydronium sulphonate salts, at 673 cm^{-1} C–S stretching, at 1453 cm^{-1} stretching frequency of sulphate, at 1000 cm^{-1} due to the –S–O–C were observed.

Conclusion

Treatment of sulphide laden wastewater processed using HPO process followed by FICCO was performed for the organic removal. In HPO, the sample was catalytically oxidized using 0.4 ml of 30% H_2O_2/L (optimized) and 30 g/L NPAC. The oxidation process successfully removed the protein content significantly. The maximum percentage of COD removal was found to be 66.66% and sulphide removal percentage of 98.95% with considerable removal of TOC, TKN and increasing of NH_3.

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References

Abraham RT, Benson LM, Jardine I (1983) Synthesis and pH-dependent stability of purine-6-sulfenic acid, a putative reactive metabolite of 6-thiopurine. J Med Chem 26:1523–1526

Aravindhan R, Madhan B, Rao JR, Nair BU, Ramasami T (2004) Bioaccumulation of chromium from tannery wastewater: an approach for chrome recovery and reuse. Environ Sci Technol 38 (1):300–306. doi:10.1021/es034427s

Anglada A, Urtiaga A, Ortiz I (2009) Contributions of electrochemical oxidation to waste-water treatment: fundamentals and review of applications. J Chem Technol Biotechnol 84:1747

Bach RB, Ayala PY, Schlegel HB (1996) A reassessment of the bond dissociation energies of peroxides. an ab initio study. J Am Chem Soc 118:12758–12765

Burkhard RK, Sellers DE, DeCou F, Lambert JL (1959) The pKa's of aromatic sulfinic acids. J Org Chem 24:767–769

Control of Urban Pollution Series: Cups (2009–10) Central Pollution Control Board Ministry of Environment & Forests, Jan 2009

Dahl O (1999) Evaporation of acidic effluent from kraft pulp bleaching, reuse of the condensate and further processing of the concentrate. Oulu University, Oulu

Davies RM (1997) Setting of consent limits for tanning industry trade effluents. J Soc Leather Tech Ch 81:32–36

Ganesh R, Ramanujam RA (2009) Biological waste management of leather tannery effluents in India current options and future research needs. Int J Environ Eng 1:165–186. doi:10.1504/IJEE.2009.027313

Huber CV, De SM (1990) Toxicity of tannery effluent —the next concern. J Am Leather Chem Assoc 85(8):276–286

John Kennedy L, Mohan das K, Sekaran G (2004) Integrated biological and catalytic oxidation of organics/inorganics in tannery wastewater by rice husk based mesoporous activated carbon department of environmental technology. CSIR-CLRI Carbon 42:2399–2407

Kumara Sashidara P, Sharmila J, Karthikeyan S, Sekaran G (2013) Treatment of domestic sewage through immobilized cell reactor with minimum sludge production. Res J Eng Tecnol 4(4):8

Lacorte S, Latorre A, Barceló D, Rigol A, Malmqvist A, Welander T (2003) Organic compounds in paper-mill process waters and effluents. Trends Anal Chem 22(10):725–737

Marsal A, Cot J, Boza EG, Celma PJ, Manich AM (1999) Oxidizing unhairing process with hair recovery. Part I. experiments on the prior hair immunization. J Soc Leather Tech Ch 83:310–315

Mesdaghinia AR, Yousefi Z (1991) The use of oxygen in catalytic oxidation of sulfide in tannery wastewater. Iranian J Publ Health 20(1–4):17–26

Obuka NSP, Celestine ON, Ikwu, Gracefield Reuben O, Chukwumuanya, Okechukwu E (2012), Review of corrosion kinetics and thermodynamics of CO2 and H_2S corrosion effects and associated prediction/evaluation on oil and gas pipeline system. Int J Sci Tecnol Res 1(4) (ISSN 2277–8616)

Patai S, Rappoport L, Stirling CJM (1988) The chemistry of sulfoxides and sulfones. Wiley, New York, p 120231206

Schraeder CE, Ervin RT, Eberspacher JL (1998) Economic analysis of the feasibility of using enzymes in the unhairing process. J Am Leather Chem Assoc 93(9):265–271

Sekaran G, Chitra K, Mariappan, M (1995) Removal of sulphide in tannery effluent by wet oxidation. J Sci Leather Techno Chemists 79:123–126

Sekaran G, Chitra K, Mariappan M, Raghavan KV (1996) Removal of sulfide in anaerobically treated tannery wastewater by wet air oxidation. J Environ Sci Heal A 31(3):579–598

Swarnalatha S, Kumar AG, Sekaran G (2009) Electron rich porous carbon/silica matrix from rice husk and its characterization. J Porous Mater 16(3):239–245

Taylor MM, Bailey DG, Feairheller SH (1987) A review of the uses of enzymes in tannery. J Am Leather Chem Assoc 82:153–165

Valeika V, Beleška K, Valeikienė V (2006) Oxidation of sulphides in tannery wastewater by use of manganese (IV) oxide kaunas. Chem Technol Fac Polish J Environ. Stud 15(4):623–629

Treatment of Dye Wastewater from Textile Industry by Electrocoagulation and Fenton Oxidation: A Review

Sandeep Thakur and M. S. Chauhan

Abstract Textile and dyeing industry are the essential industries in the present scenario and have become one of the major sources of water pollution. This industry generates huge quantity of wastewaters containing high concentrations of dyes, surfactants, suspended solids and organic matter. The major classes of dyes according to their dyeing process in textile finishing are acid dyes, basic dyes, direct dyes, reactive dyes, disperse dyes, mordant dyes, solvent dyes, sulfur dyes and vat dyes. These dyes are very stable in the environment and persist under oxidation and reduction conditions, light exposure and biodegradation. Dyes consist of many toxic materials and can cause some serious harmful impacts in environment. From previous studies, it has been observed few conventional and biological methods are inadequate and insufficient for the treatment of wastewater from dye industries. Advance treatment processes such as electrocoagulation and Fenton oxidation process or combination of these processes can be a better option for treatment of such wastewater. This paper reviews the application of electrocoagulation and Fenton oxidation processes for the treatment of dye wastewater.

Introduction

Globally, the textile industry and its dye-containing wastewaters are the major source of serious water pollution. This industry consists of around 10,000 different textile dyes with an estimated yearly production of 7.10^5 metric tonnes worldwide on commercial level (Robinson et al. 2001). The textile industries discharge a huge quantity of dyes as an effluent into water bodies that cause a serious problem to environment. Besides color, many of these dyes are persistent and recalcitrant in

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environment and their breakdown products are noxious, carcinogenic or mutagenic to life forms generally because of carcinogenic aromatic compounds such as benzidine and naphthalene (Hashmi and Saleem 2013). According to one of the estimated up to 10–25% of the dyes may directly lost into the wastewater (Zaharia and Suteu 2012). The coloration of water by the presence of dyes even in small concentration is easily noticeable and may have effect on the process of photosynthesis, thus affecting the aquatic ecosystem. Therefore, it is necessary to treat dye wastewater before discharged into water. The removal of dyes from colored effluent particularly from textile industries is one of the major environmental concerns these days (Tyagi et al. 2015).

Numerous wastewater treatment units are employed around the world, each having its advantages and disadvantages (Hirzallah 2011). The conventional treatment methods of dyeing wastewater are physico-chemical and biological methods (Carneiro et al. 2005). The majority of these conventional methods is becoming inadequate and inefficient, because the dye effluent contains mainly complex aromatic molecular structures. Dye compounds are usually made to resist fading on exposure to soap; water, light and this make them more stable against biodegradation. The treatment of industrial wastewater involves many challenges that are not limited to the technical objectives of good water quality and solid/liquid separation. In developing a treatment method, its overall environmental impact, usefulness in various industrial applications, ease of installation and operation, energy efficiency, and cost-effectiveness must be considered (Hirzallah 2011).

Dyes

The synthetic dyes were firstly discovered in 1856, beginning with, mauve dye (aniline), a brilliant fuchsia color synthesized by W.H. Perkin (UK), and some azo dyes synthesized by diazotization reaction discovered in 1958 by P. Gries (Germany). These dyes are aromatic compounds produced by chemical synthesis, having aromatic rings into their structure that contain different functional groups and delocated electrons. Their color is due to the chromogene–chromophore structure which is electrons acceptor, and the dyeing capacity is due to electron donor auxochrome groups (Zaharia and Suteu 2012). The unsaturated fraction of the molecule which is responsible for the color is called as chromophore. The chromophore generally consists of aromatic rings (anthraquinone and triphenylmethane) or azo groups (azo benzene) in textile dyes (Khandegar and Saroha Anil 2012).

Classification of Dyes

Classification of the entire commercial textile dyes by their generic name and chemical constitution has been done by the color index (C.I.), a journal published by the Society of Dyers and Colourists (UK) in association with the American Association of Textile Chemists and Colorists (AATC). Textile dyestuffs can be categorized into the following group (Types of Dyes 2015).

Classification Based on the Source of Materials

A very common classification of the dyestuff is based on the source from which it is prepared

1. **Natural dyes**: Natural dyes are the dyes which are produced naturally from different plant sources like roots, leaves, bark, berries and fungi wood lichens, very beginning of the dyeing history man started dyeing their material by natural dyes. Indigo, saffron and madder are the plant-based dyes which is popular in Asia.
2. **Synthetic dyes**: Synthetic dyes occupied the marked of dyes. Now a most of the dyeing operation is done by synthetic dyes. Synthetic dyes are made from the reaction of two or more chemicals (Dyes: Classifications 2015).

Classification Based on Industrial Use of the Dyes

Dyes can also be classified according to how they are used in the dyeing process. Majority of the dyestuff is primarily consumed by the textile industry. Following are the major classes of dyes in textile finishing.

1. **Acid dyes**: These are anionic water-soluble dyes applicable in nylon, wool, silk and modified acrylics fabrics. They are also used in paper, leather, ink-jet printing, food and cosmetics.
2. **Basic dyes**: These are cationic dyes applied to paper, modified nylons and polyesters. The actual use of these dyes was for wool, silk and tannin-mordanted cotton when brightness of shade was more important than fastness to light and washing. The principal chemical classes are oxazine, thiazine, cyanine, diazahemicyanine, hemicyanine, triarylmethane and acridine. Some basic dyes have biological activity and are used in medicine as antiseptics.
3. **Direct dyes**: These water-soluble anionic dyes, when dyed from aqueous solution in the presence of electrolytes, are substantive to, i.e., has high affinity for, cellulosic fibers. Their principal use is the dyeing of cotton and regenerated cellulose, paper, leather and, to a lesser extent, nylon.

4. **Reactive dyes**: These dyes form a covalent bond with the fiber, usually cotton, although they are used to a small extent on wool and nylon. These dyes achieve extremely high wash fastness properties by relatively simple dyeing methods. The principal chemical classes of reactive dyes are azo including metallized azo, triphendioxazine, phthalocyanine, formazan and anthraquinone.
5. **Disperse dyes**: Disperse dyes are substantially water-insoluble nonionic dyes for application to hydrophobic fibers from aqueous dispersion. These dyes are mostly used on polyester as compared to nylon, cellulose, cellulose acetate and acrylic fibers on which their application is less (Hunger 2003).
6. **Mordant dyes**: These are water-soluble dyes and have affinity for silk, wool and polyamides. Mordant dyes require a mordant in their application and these dyes upon combination with the mordant deposit on the fiber in the form of insoluble color. Usually, dyes are negatively charged and have hydroxyl or carboxyl groups. There are very few synthetic dyestuffs that require a separate mordant. Some dyes are for wool, where mordant dyes are still in trend. Chrome dye has become very popular mordant dye because chromium is extensively used as the mordant on wool. Numerous natural dyes (plant extracts, etc.) need a mordant. The tone produced with a particular dyestuff can be significantly influenced by the mordant used. Mordant dyes are particular acid dyes in which certain metal atom can be introduced during dyeing process (Dyes: Classifications 2015).
7. **Solvent dyes**: These dyes are water-insoluble but solvent-soluble that belong to the polar solubilizing groups such as carboxylic acid, sulfonic acid or quaternary ammonium. They are used for coloring plastics, gasoline, oils and waxes. The dyes are predominantly azo and anthraquinone, but phthalocyanine and triarylmethane dyes are also used.
8. **Sulfur dyes**: These dyes are applicable in cotton fiber from an alkaline-reducing bath with sodium sulfide as the reducing agent. Comparatively, this is numerically small group of dyes. From an economic point of view, the low cost and good wash fastness properties of the dyeing make this class important. However, these dyes are under pressure from an ecological viewpoint.
9. **Vat dyes**: These are water-insoluble dyes mainly applied to cellulosic fibers as soluble leuco salts after reduction in an alkaline bath, usually with sodium hydrogen sulfite. Subsequently exhausted onto the fiber, the leuco forms are reoxidized to the insoluble keto forms and later treated, generally by soaping, to reform the crystal structure. Anthraquinone and indigoid are the major chemical classes of vat dyes (Hunger 2003).

Usage of Various Dyes in Textile Industries

The textile industry is classified into three main categories:

1. Cellulose fibers (cotton, rayon, linen, ramie, hemp and lyocell)
2. Protein fibers (wool, angora, mohair, cashmere and silk)

3. Synthetic fibers (polyester, nylon, spandex, acetate, acrylic, ingeo and polypropylene)

The type of dyes and chemicals used in the textile industry is found to differ depending on the fabrics manufactured. Reactive dyes, direct dye, naphthol dyes and indigo dyes are some of the dyes used to dye cellulose fibers. Reactive dyes are most common dyes used in dyeing protein fibers and cellulose fiber dye. In most common fibers, cotton is dyed mostly using reactive dyes. The worldwide use of reactive dyes increased from 60,000 tonnes to 178,000 tonnes since year 1988 till 2004. Acid dyes (azo dyes, triarylmethane dyes and anthraquinone dyes) are used to dye protein fibers. High pH affects proteins; thus, acid dyes are the most commonly used in dyeing protein fibers. The chemical reactions between the acid dye and the fibers form an insoluble dye molecule on the fiber. Acid dyes contain azo groups (–N = N–) in the center. It is estimated that the global import and export market for acid dye was 680,000 tonnes in 2011.

Other dyes, like dispersed dyes, basic dyes and direct dyes, are applied on synthetic fibers. Dispersed dyes are mostly used synthetic fabrics dye used to dye polyester, nylon or acetates. Manufacture and the global business for dispersed dyes was increased from 150,000 tonnes in 1998 to 570 000 metric tonnes in 2011. Basic dyes are proved as a powerful coloring agent for acrylic fibers. Nylon fibers are found to be effective when dyed with direct dyes. Cotton could also be dyed using direct dyes, indigo dyes and naphthol dyes. The export and import world market for direct dyes and their preparations increased from 53,848 tonnes in 1992 to 181,998 tonnes in 2011. The annual world production of indigo dye is 80,000 tonnes, while the global import and export market for naphthol dye was about 112, 000 tonnes per year. There are some fabrics such as linen, ramie, hemp, rayon and lyocell which show good dyeing effect with several varieties of dyes and could be dyed using both reactive dyes and direct dyes. Also silk angora, mohair, cashmere and Wool can be dyed by reactive dyes or acid dyes (Ghaly et al 2014).

Dyeing Wastewater from Textile Industry

Dyeing and finishing are the two chief processes usually applied in most of the textile industries. These two processes generate huge quantity of wastewater, which may contain strong color, suspended particles, high pH and high chemical oxygen demand (COD) concentration. The disposal of these dye wastewaters poses a major problem for the industry as well as a threat to the environment. The majority of synthetic dyes are noxious substances to human and aquatic life. In textile industries, because of the low efficiency (60–90%) of dye fixing on textile fibers, considerable amounts of unfixed dyes are released in wastewaters. It is estimated that 1–15% of the dye is lost during dyeing and finishing processes and is released into wastewaters (Daneshvar et al 2006).

At present, about 700,000 tonnes and 10,000 different varieties of dyes and pigments are being produced yearly across the world and it has been reported that up to 15% of the dyes used are released into wastewaters. Taking into account, both volume and composition effluent from the textile industry were declared as one of the main sources of wastewater in ASEAN (Association of South East Asian Nations) countries. Not only they have coloring impact but also dyes are responsible for the destruction of ecological balance of the aquatic system; therefore, removal of dyes from textile wastewater is of great concern. They cause the depletion of the dissolved oxygen and a great harm on the food chain by interfering with the transmission of sunlight and inhibit the photosynthesis process. Also, many reactive dyes produce carcinogen compounds upon dissociation which not only destroying the aquatic life but also entering and causing the serious health risk to human beings including causing many serious diseases in many provision of the globe, especially in developing countries via the action of food chain (Deb and Majumdar 2013). Dye-containing effluent is toxic to the environment since dyes are stable compounds, with low biodegradability, and can be carcinogenic. In general, dyes are very large aromatic molecules consisting of numerous linked rings (Phalakornkule et al. 2010).

The sensitivity of biological treatment processes and secondary pollution caused by conventional chemical methods make advance treatment processes more popular. Electrocoagulation and Fenton oxidation are suitable methods for the treatment of such complex wastewater.

Electrocoagulation

Electrocoagulation (EC) is a versatile method for water and wastewater treatment that relies upon the electrochemical dissolution of sacrificial metal electrodes (usually iron or aluminum) into soluble or insoluble species that enhance the coagulation, the adsorption or the precipitation of soluble or colloidal pollutants (Holt et al. 2005). In an electrocoagulation process, the coagulating ions are produced ‘in situ’ and it involves three consecutive steps:

(i) Coagulant formation by electrolytic oxidation of the sacrificial electrode.
(ii) Destabilization of the pollutants, particulate suspension and emulsion breaking
(iii) Aggregation of the destabilized phases to form flocs.

The destabilization mechanisms of the pollutants, particulate suspension and emulsion breaking have been summarized as follows:

1. The diffuse double layer compression around the charged species by the interactions of ions generated by oxidation of the sacrificial anode.
2. Neutralization of charge of the ionic species present in wastewater by counter ions produced by the electrochemical dissolution of the sacrificial anode. These

counter ions decrease the electrostatic interparticle repulsion to such level that the Van der Waals attraction predominates, and as a result cause coagulation in the solution. Outcome of the process is a zero net charge.

3. Formation of floc as a result of coagulation creates a blanket of sludge that entraps and bridges colloidal particles still remaining in the solution. The hydroxides, oxyhydroxides and solid oxides give active surfaces for the adsorption of the polluting species (Mollaha Mohammad et al. 2004).

Mechanism of Electrocoagulation

A direct current supply is applied to metal electrodes immersed in wastewater. The flow of electrical current helps in the dissolution of metal electrodes into the solution. The dissolved metal ion forms wide ranges of coagulated species and metal hydroxides at appropriate pH. It helps to destabilize and aggregate the suspended particles or adsorb and precipitate dissolved contaminants (Arslan-Alaton et al. 2009; Murthy and Parmar 2011; Mollaha Mohammad et al. 2004, El-Ashtoukhy and Amin 2010). The diverse reactions occurring at anode, cathode and solution are prescribed below (Irdemez et al. 2006); (Sevki et al. 2007); (Wei et al. 2012):

- At the cathode:

$$3H_2O + 3e^- \rightarrow 1.5H_2(g) + 3OH^- \qquad (1)$$

- At the anode:

$$4Fe(s) \rightarrow 4Fe_2^+(aq) + 8e^- \qquad (2)$$

- And with dissolved oxygen in solution:

$$4Fe_2^+(aq) + 10H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3 + 8H^+(aq) \qquad (3)$$

- Overall reaction:

$$4Fe(s) + 10H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s) + 4H_2(g) \qquad (4)$$

During electrocoagulation due to the change in pH various kinds of monomeric and polymeric iron species formed are mentioned as follows:

$Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5OH^{2+}$, $Fe(H_2O)_4(OH)_2^{+}$, $Fe_2(H_2O)_8(OH)_2^{4+}$, $Fe_2(H_2O)_6(OH)_4^{2+}$ and $Fe(OH)^{4-}$ (Sengil and Ozacar 2009).

Application of Electrocoagulation in the Treatment of Dye Wastewater

Electrocoagulation (EC) is reported by many authors in the field of treatment of dye-containing wastewater. In year 2003 Kobya et al. have made the comparative study of treatment of textile wastewaters by electrocoagulation using iron and of aluminum electrode materials. The effects of wastewater characteristics such as pH and conductivity, and process variables such as current density and reaction time on the COD and turbidity removal efficiencies have been investigated. Moreover, the electrode and energy consumptions for each electrode have been calculated. The results show that iron is better than aluminum as sacrificial electrode material, with respect to COD removal efficiency and energy consumption. The use of iron and aluminum electrode materials has been found to be pH dependent in the treatment of textile wastewater by electrocoagulation. According to the results, in acidic medium, $pH < 6$, COD and turbidity removal efficiencies of aluminum are higher than those of iron, while in neutral and alkaline medium iron is preferable. High conductivity favors high process performances. On the other hand, for the same turbidity or COD removal efficiencies, iron requires a current density of 80–100 A/m^2, while aluminum requires 150 A/m^2 for a operating times of 10 min.

Lambert et al. 2013 investigated the feasibility of two decontaminating processes, ozonation and electrocoagulation, to decolorize wastewater generated by humid finishing leather manufacture. Bench-scale experiments were conducted with three different colorants, representative of the main dye groups: diazo (CI Direct Blue 1), anthraquinone (CI Green G) and aniline (CI Fast Red B base). Two methods were compared on the basis of electrical energy consumption. In this study, it has been found that electrocoagulation achieves removal efficiency near 99% of decolorization for two colorants, CI Direct Blue 1 and CI Fast Red B base among three which has been studied. On the other hand in the case of the third dye, CI Green G, higher decolorization, up to 89% has been achieved by ozonation.

Chafi et al (2011) investigated the decolorization of a synthetic textile wastewater was using electrocoagulation (EC) in a batch electrochemical cell. A monoazo acid dye Orange II was used for experiments. Comparison of aluminum and iron electrodes has been made. The effects of operational parameters like initial dye concentration, current density, electrolysis time and wastewater properties such as initial pH and conductivity were investigated on the basis of color removal, energy and electrode consumption and sludge produced. A comparison of EC with chemical coagulation (CC) using the same amount of metal cations was also made. Results showed that EC maximized decolorization up to 98% in comparison with CC which is limited to 53% of color removal. For EC, iron electrodes show the highest decolorization and decrease the simultaneous energy requirements, the amount of floc and operation costs in comparison with aluminum.

Phalakornkule et al. (2010) studied an application of the optimal parameters in operating a continuous upflow electrocoagulation reactor in removing Direct red 23 (azo-based dye). Initially, experiments have been done on a batch mode to optimize the design parameters electrode material, current density, electrode distance and operation time. In result, optimal parameters were iron anode, electrodes distance of 8 mm and current density of 30 A/m^2 with contact time of 5 min. The continuous upflow reactor with these parameters showed a good efficiency, with >95% color removal and energy consumption in the order of 0.6–0.7 kW/hm^3.

Kabdasl et al. (2009) investigated the application of electrocoagulation to a simulated reactive dyebath effluent using aluminum and stainless steel as electrode materials. A mixture of dyes and auxiliary chemicals was employed instead of a single dyestuff to reflect actual reactive dyeing conditions. The study was based on the effect of color and COD removal rates and efficiencies by electrocoagulation on individual reactive dyebath components. Results showed that electrocoagulation using stainless steel electrodes was found to be more effective for color removal. Sequestering agent and Na_2CO_3 significantly reduced the process efficiency in terms of both color and COD removals, whereas increasing the NaCl concentration not only enhanced color and COD removal efficiencies but also compensated the adverse effects of Na_2CO_3 and sequestering agent on the electrocoagulation process.

Zaroual et al (2006) in this study investigated the electrocoagulation method with iron electrode to treat the industrial textile wastewater in batch reactor. The effects of operating parameters such as time and potential electrolysis on the decolorization and COD removal efficiency have been examined. It has been observed that the effluent wastewater was very clear and its quality was near direct discharge standard. The results indicate that electrocoagulation is very efficient, around 100% color and 84% COD removal in 3 min at potential 600 mV.

El-Ashtoukhy and Amin (2010) have done a comparative study for deduction of acid green dye 50 by electrocoagulation and anodic oxidation using a self-gas stirred electrochemical cell. The effect of operating parameters such as current density, initial dye concentration, NaCl concentration and pH on color removal has been investigated. The chemical oxygen demand (COD) removal was found to be 68 and 87% in case of electrochemical oxidation and electrocoagulation, respectively. The results show that electrocoagulation is more economic than anodic oxidation, energy consumption ranged from 2.8 to 12.8 kWh/kg dye removed in case of electrocoagulation, while in case of anodic oxidation it ranged from 3.31 to 16.97 kWh/kg dye removed.

Fenton Oxidation Process (H_2O_2/Fe^{2+})

The Fenton process was reported by Fenton already over a hundred years ago for maleic acid oxidation:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH$$

The rate constant for the reaction of ferrous ion with hydrogen peroxide is high, and Fe(II) oxidizes to Fe(III) in a few seconds to minutes in the presence of excess amounts of hydrogen peroxide. Hydrogen peroxide decomposes catalytically by Fe (III) and generates again hydroxyl radicals according to the reactions:

$$\begin{aligned}&Fe^{3+} + H_2O_2 \leftrightarrow H^+ + Fe{-}OOH^{2+}\\&Fe{-}OOH^{2+} \Rightarrow HO_2 + Fe^{2+}\\&Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\end{aligned}$$

For this reason, it is believed that most waste destruction catalyzed by Fenton's reagent is simply a Fe(III)–H_2O_2 system-catalyzed destruction process, and Fenton's reagent with an excess of hydrogen peroxide is essentially a Fe(III)–H_2O_2 process (known as a Fenton-like reagent). Thus, the ferrous ion in Fenton's reagent can be replaced with the ferric ion. Iron salts act as a catalyst for hydrogen peroxide decomposition; further, reactions regenerate iron (II). It has been demonstrated that Fenton's reagent is able to destroy different phenols, nitrobenzene and herbicides in water media as well as to reduce COD in municipal wastewater. The usefulness of the Fe(II)/H_2O_2 system as a potential oxidant for soil contaminants has also been investigated. It has been shown that PCP and trifluralin are extensively degraded, while hexadecane and dieldrin are partially transformed in a soil suspension at acidic pH. The use of Fe(II)/H_2O_2 as an oxidant for wastewater treatment is attractive due to the facts that:

1. Iron is a highly abundant and nontoxic element, and
2. Hydrogen peroxide is easy to handle and environmental friendly.

Thus, the Fenton process is very effective for Fe(III)–H_2O_2 OH radicals generation; however, it involves consumption of one molecule of Fe^{2+} for each OH radical produced, demanding a high concentration of Fe(II) (Munter 2001).

Application of Fenton and Electro-Fenton Methods in the Treatment of Dye Wastewater

Fenton and electro-Fenton methods were also employed by some researchers for the treatment of dye-containing wastewater and reported good results. Lin Sheng and Lo Cho (1997) have investigated the treatment of synthetic desizing wastewater by the Fenton process along with chemical coagulation. The wastewater contained a direct dye Blue G or a reactive dye Black B and less than 0.2% polyvinyl alcohol (PVA). Experiments were conducted to study the effects of operating variables such as pH, temperature and the treatment time, on the COD removal. The most favorable operating conditions were determined experimentally. Chemical coagulation using polyaluminum chloride and polymer was found to enhance the Fenton treatment process in reducing the settling time of floc, increasing the color removal and reducing Fe ion concentration. In the results, it has been observed that the two-step Fenton treatment process applied separately the chemical coagulation and chemical oxidation was observed to be only slightly better than the single-step one.

Shyh-Fang et al. (2002) in this paper examined the removal of COD and color from synthetic textile wastewater containing polyvinyl alcohol and a reactive dye R94H by the Fenton process. The variable parameter dosages of iron salts and hydrogen peroxide, oxidation time, mixing speed and organic content were studied. The results show color removal of maximum 90% at a reaction time of 5 min under low dosages of H_2O_2 and Fe^{2+}. On the other hand, the COD removal was primarily achieved by Fenton coagulation instead of Fenton oxidation. The ratio of removal efficiency between Fenton process and ferric coagulation was 5.6 for color removal and 1.2 for COD removal. This study concludes that for the treatment of textile wastewater Fenton process favors the removal of color rather than COD.

Wang et al. (2008a, b) have investigated the performance of a full-scale combined treatment plant for jean-wash wastewater (JWW). The combined process consisted of chemical coagulation, hydrolysis/acidification and Fenton oxidation. Chemical coagulation treatment with polymeric ferric sulfate (PFS)/lime alone proved to be effective in eliminating the COD (>70%) and part of the color (>50%) from the JWW. Fenton oxidation combined with hydrolysis/acidification as pretreatment offered a noticeable BOD removal efficiency. The average removal efficiencies for COD, BOD, SS, color and aromatic compounds of the combined process were about 95, 94, 97, 95 and 90%, respectively, with the average effluent quality of COD 58, BOD 19, SS 4 mg/L and color 15. The result indicated that the combined procedure can be an effective solution for JWW treatment.

In this study, Djafarzadeh and Khataee (2011) used the electro-Fenton (EF) process for decolorization of an anthraquinone dye, Reactive Blue 69 (RB69). Hydrogen peroxide was electrogenerated by reduction of dissolved oxygen in acidic solution. The effect of operational parameters such as initial pH, applied current, electrolyte type and reaction time was studied in an attempt to reach the higher dye removal efficiency. The degradation of RB69 was followed by chemical oxygen demand (COD) analysis. The results showed that electro-Fenton with carbon paper modified with carbon nanotubes allowed 70% degradation of COD after 5 h of electrolysis.

Conclusion

An observation in the earlier studies says that there are various treatment processes employed in the treatment of dyeing wastewater. Based on that study, it is observed that the electrocoagulation and advance oxidation are very efficient in the treatment of dye in wastewater. For the treatment of dye wastewater, the application of electrocoagulation and hydrogen peroxide individually or hybrid system could result in a more powerful method of generating hydroxyl radicals, thus improving the rate of organic/inorganic content degradation in wastewater.

References

Arslan-Alaton I, Kabdasl I, Sahin Y (2008) Effect of operating parameters on the electrocoagulation of simulated acid dye bath effluent. Open Environ Biol Monit J 1:1–7

Arslan-Alaton I, Kabdasl I, Vardar B, Tunay O (2009) Electrocoagulation of simulated reactive dyebath effluent with aluminum and stainless steel electrodes. J Hazard Mater 164:1586–1594

Carneiro PA, Osugi ME, Fugivar CS, Boralle N., Furlan M, Zanoni MV (2005) Evaluation of different electrochemical methods on the oxidation and degradation of reactive blue 4 in aqueous solution. Chemosphere 59(3):431–439

Chafi M, Gourich B, Essadki AH, Vial C, Fabregat A (2011) Comparison of electrocoagulation using iron and aluminium electrodes with chemical coagulation for the removal of a highly soluble acid dye. Desalination 281:285–292

Daneshvar N, Oladegaragoze A, Djafarzadeh N (2006) Decolorization of basic dye solutions by electrocoagulation: an investigation of the effect of operational parameters. J Hazard Mater (B 129) 116–122

Deb TK, Majumdar S (2013) Removal of reactive dyes from textile wastewater by electrocoagulation process: an effective and clean approach. Int J Environ Bioenergy 6(2):96–116

Djafarzadeh N, Khataee A (2011) Treatment of reactive blue 69 solution by electro-Fenton process using carbon nanotubes based cathode. In International conference on biology environment and chemistry IPCBEE, vol (24). IACSIT Press, Singapore

Dyes: Classifications (2015) http://textilefashionstudy.com/dyes-classification-of-dyes/

El-Ashtoukhy E-SZ, Amin NK (2010) Removal of acid green dye 50 from wastewater by anodic oxidation and electrocoagulation—a comparative study. J Hazard Mater 179:113–119

Ghaly AE, Ananthashankar R, Alhattab M, Ramakrishnan VV (2014) Production, characterization and treatment of textile effluents: a critical review. J Chem Eng Process Technol 5:1

Hashmi S, Saleem Q (2013) Original research article potential role of *Pleurotus ostreatus* in the decolorization and detoxification of the dye Synozol Red. Int J Curr Microbiol Appl Sci 2 (6):106–112

Hirzallah W (2011) Effectiveness of electrochemical treatment of municipal sewage, department of building, civil and environmental engineering. Concordia University Montreal, Quebec, Canada

Holt PK, Barton GW, Mitchell CA (2005) The future for electrocoagulation as a localised water treatment technology. Chemosphere 59:355–367

Hunger K (2003) Industrial dyes, chemistry, properties, application. WILEY-VCH Verlag GmbH & CoKGaA, Weinheim

Introduction of mordant dye, properties of mordant dyes/mechanism of mordant dyeing, application of mordant dyes, URL: http://textilelearner.blogspot.in/2011/03/defination-properties-working-procedure_4365.html

Irdemez S, Demircioğlu N, Yildiz YŞ (2006) The effects of pH on phosphate removal from wastewater by electrocoagulation with iron plate electrodes. J Hazard Mater (B) 137:1231–1235

Kabdasl I, Vardar B, Arslan-Alaton I, Tünay O (2009) Effect of dye auxiliaries on color and COD removal from simulated reactive dyebath effluent by electrocoagulation. Chem Eng J 148:89–96

Khandegar V, Saroha Anil K (2012) Electrochemical treatment of distillery spent wash using aluminum and iron electrodes. Chin J Chem Eng 20(3):439–443

Kobya M, Can OT, Bayramoglu M (2003) Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes. J Hazard Mater (B) 100:163–178

Lambert J, Vega MM, Isarain-Chavez E, Peralta-Hernandez Juan M (2013) Ozone and electrocoagulation processes for treatment of dye in leather industry wastewater: a comparative study. Int J Emerg Technol and Adv Eng 3(7):1–9

Lin Sheng H, Lo Cho C (1997) Fenton process for treatment of desizing wastewater. Water Resour 31(8):2051–2056

Mollaha Mohammad YA, Morkovskyb P, Gomesc Jewel AG, Kesmezc M, Pargad J, Cockec DL (2004) Fundamentals, present and future perspectives of electrocoagulation. Elsevier, Netherlands

Munter R (2001) Advanced Oxidation processes—current status and prospects. Proc Estonian Acad Sci Chem 50(2):59–80

Murthy ZVP, Parmar S (2011) Removal of strontium by electrocoagulation using stainless steel and aluminum electrodes. Desalination 282:63–67

Phalakornkule C, Polgumhang S, Tongdaung W (2009) Performance of an electrocoagulation process in treating direct dye: batch and continuous upflow processes. World Acad Sci Eng Technol 33

Phalakornkule C, Polgumhang S, Tongdaung W, Karakat B, Nuyut T (2010) Electrocoagulation of blue reactive, red disperse and mixed dyes, and application in treating textile effluent. J Environ Manage 91:918–926

Robinson T, McMullan G, Marchant R, Nigam P (2001) Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Biores Technol 77(12):247–255

Sengil AI, Ozacar M (2009) The de-colorization of C.I. reactive black 5 in aqueous solution by electrocoagulation using sacrificial iron electrodes. J Hazard Mater 161:1369–1376

Sevki YS, Koparal AS, Irdemez S, Keskinler B (2007) Electrocoagulation of synthetically prepared waters containing high concentration of NOM using iron cast electrodes. J Hazard Mater B139:373–380

Shyh-Fang K, Chih-Hsaing L, Mon-Chun C (2002) Pre-oxidation and coagulation of textile wastewater by the Fenton process. Chemosphere 46:923–928

Tyagi N, Mathur S, Kumar D (2015) Electrocoagulation for textile wastewater treatment in continuous upflow reactor. J Sci Ind Res 73:195–198

Types of Dyes (2015) http://www.dyespigments.net/types-of-dyes.html

Wang X, Zenga G, Zhua J (2008a) Treatment of jean-wash wastewater by combined coagulation, hydrolysis/acidification and Fenton oxidation. J Hazard Mater 153:810–816

Wang CT, Hu JL, Chou WL, Kuo YM (2008b) Removal of color from real dyeing wastewater by electro-fenton technology using a three-dimensional graphite cathode. J Hazard Mater 152:601–606

Wei MC, Wang KS, Huang CL, Chiang CW, Chang TJ, Lee SS, Chang SH (2012) Improvement of textile dye removal by electrocoagulation with low-cost steel wool cathode reactor. Chem Eng J 192:37–44

Zaharia C, Suteu D (2012) Textile Organic Dyes—characteristics, polluting effects and separation/elimination procedures from industrial effluents—a critical overview. Organic pollutants ten years after the stockholm convention—environmental and analytical update

Zaroual Z, Azzi M, Saib N, Chainet E (2006) Contribution to the study of electrocoagulation mechanism in basic textile effluent. J Hazard Mater B131:73–78

Impact of Hydrocarbon Pollutants on Partially Saturated Soil Media in Batch System: Morphological Analysis Using SEM Techniques

Pankaj Kumar Gupta, Abhishek and Brijesh Kumar Yadav

Abstract Soil surface morphology is an important functional parameter in fate and transport of pollutants in subsurface. Therefore, the aim of present study is to investigate the soil morphological changes using batch experiments having different concentration of a hydrocarbon pollutant, toluene. A series of six batch sets containing 20 g of oven-dried sand with particle size of 0.5–1.0 mm and 40% porosity were prepared at room temperature under partially saturated condition. Various concentrations of dissolved toluene varying from 5 to 100 ppm were considered in the designed batches. After 24 h of the incubation, when the soil water concentration reached to equilibrium, the temporary slides of respective soil samples were prepared. To capture the high magnification at pore scale, scanning electron microscopy (SEM) analysis was conducted at magnification of 10×, 20×, 30× and 40×. The results showed that the level of soil surface losses and the number of cavities on soil surface were increased with increasing hydrocarbon concentration. Furthermore, attenuation in the brightness of the sand particles was observed with increment in hydrocarbon concentration indicating the more adsorption capacity of toluene at high concentration levels. Results of this study are helpful in investigating the geochemical stability of soil, remediation strategy and for upscaling of fate and transport of pollutants in subsurface environment.

Keywords Hydrocarbon pollutants · Subsurface · Soil morphology
SEM analysis · Batch experiment

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Introduction

Solute fate and transport in the subsurface are controlled by a series of physical, chemical and biological processes that merit further exploration in order to understand the full complexity and interactions of the process-based conceptual model (Yadav and Hassanizadeh 2011; Yadav et al. 2013; Jahangeer et al. 2017). Fate of hydrocarbon is influenced by the flow of air, water and hydrocarbon phases in porous media(Gupta and Yadav, 2017), as well as by the hydraulic properties of the porous media (Shachi and Yadav 2015; Gupta et al. 2013; Gupta and Yadav 2015). Furthermore, mass transfer governs the partitioning of contaminants between these phases; finally, reactive processes occur within these phases, especially including fate of residual hydrocarbon and adsorption on the soil surface as shown in Fig. 1 (Soga et al. 2004; Lee and Chrysikopoulos 1995; Dobson et al. 2007). This reactive process causes the soil surface changes due to soil loess and origin of cavities on surface (Kumar et al. 2015). Therefore, the soil morphological changes are important physical parameters to determine the impact of pollutant on adsorption capacities. The most of the peer reviewed literature strongly recommended the soil morphological studies to determine the adsorption scenarios under prevailing environmental conditions.

The objective of this study is to investigate the impact of different hydrocarbon concentration on soil morphological changes using batch experiments. This will help to the geochemical stability of soil, remediation strategy and for upscaling of fate and transport of pollutants in subsurface environment.

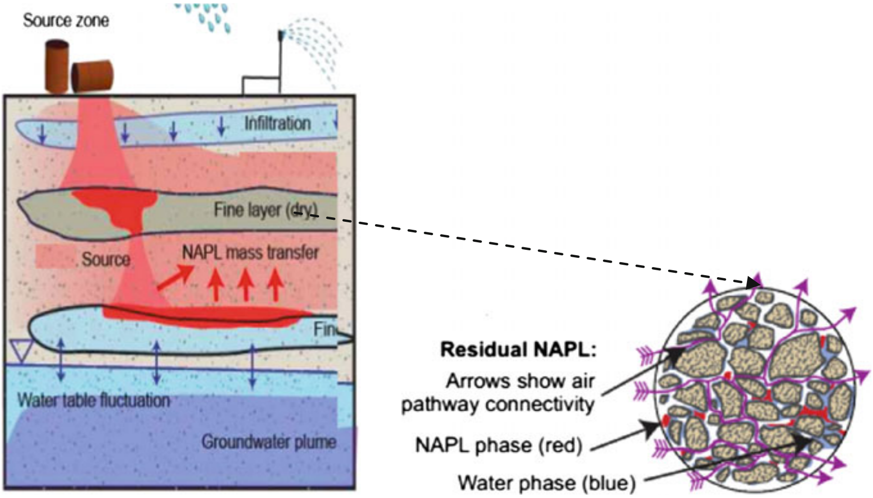

Fig. 1 Conceptual model hydrocarbon configurations under varying subsurface conditions

Methodology

In this study, a series of six batch sets containing 20 g of oven-dried sand with particle size of 0.5–1.0 mm and 40% porosity were prepared under partially saturated condition. The detail of soil types and texture is listed in Table 1. Various concentrations of dissolved toluene varying from 5 to 100 ppm were considered in the designed batches (Fig. 2). To maintain the level of saturation the 0.002 L dissolved phase groundwater was added (Table 2). The batch experiments were performed at room temperature (21.6 ± 0.3 °C) by maintaining the initial substrate concentration. The detailed experimental setup is listed in Table 3. To prevent any other microbiological degradation, the effective concentration of $HgCl_2$ was used for maintaining sterile conditions. The continuous hourly gas phase samples were analyzed using GC-MS to compute equilibrium breakthrough curve. The 2 µL gas phase air from different microcosm was analyzed using GCMS.

Table 1 Physio-chemical properties of porous media

Porous media	Sand ($g\ hg^{-1}$)	Silt ($g\ hg^{-1}$)	pH	EC	OM	Bulk density (g/cm^3)	Size	Types
Sand	92.8	4.2	5.5	4.9	0%	1.65	0.5–1 mm	Indian Standard Sand Grade II

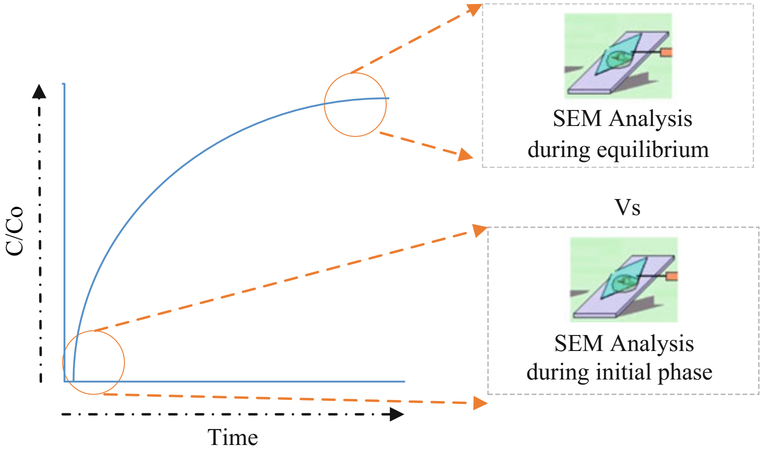

Fig. 2 Schematic diagram shows the phase of batch system when soil morphology was analyzed using SEM for comparative study

Table 2 Other microcosm setup to maintain the level of 100% saturation

Total batch volume [L]	Soil volume [L]	Remain headspace [L]	Total pore volume [L]	LNAPL dissolved groundwater [L]	Batch moisture %
0.12	0.02	0.11	0.008	0.002	100

Table 3 Summery of the combination of batches having different substrate concentration

Total batch volume [L]	Soil volume [L]	Remain headspace [L]	Total pore volume [L]	Groundwater [L]	Toluene Stock [L]	Total liquid volume [L]	Air-filled pore volume [L]	Total batch gas volume [L]	Toluene concentration [ppm]
0.12	0.02	0.11	0.008	0.002	0.002	0.004	0.004	0.114	100
									80
									60
									40
									20
									05

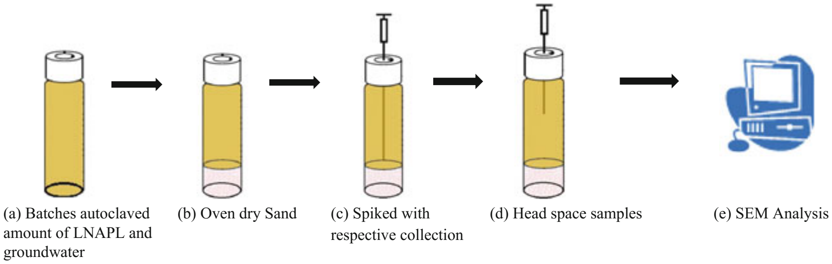

Fig. 3 Schematic diagram of adopted methodology for batch experiment investigating the impact of hydrocarbon pollutants on partially saturated soil media

SEM Analysis: To capture the high magnification at pore scale, SEM (scanning electron microscopy) (model no. LEO 435 VP) analysis was conducted at 10×, 20×, 30× and 40×. Initially, the soil samples were collected before spiking the toluene in batch system and then after 24 h of the incubation, when the soil water concentration reached to equilibrium, the temporary slides of respective soil samples were prepared. The comparative study of the soil morphology of the initial phase and equilibrium phase samples indicates the difference and or impact of the hydrocarbon on the adsorption capacity. In Fig. 1, the general concept of the BTCs is having increasing concentration and finally reached to equilibrium. Further, the red circular lines on BTCs show the phase of the samples taken for SEM analysis (Fig. 3).

Result and Discussion

The obtained breakthrough curves (BTCs) showed the increasing concentration with time finally reaching to the equilibrium. The relative concentration of the obtained curves shows the equilibrium phase after 20 h. The concentration and relative concentration are tabulated in Table 4. Therefore, the two sets of the SEM slides of each set of batches were prepared: first samples taken during the initial phase and second after 24 h during equilibrium.

The SEM-analyzed images of both the initial and equilibrium phase samples show the varying soil surface. More number of cavities are shown on the soil surface of equilibrium phase samples in comparison with the initial phase samples shown in Fig. 4. Similarly, the number of cavities is increasing with increasing concentration. The results showed that the level of soil surface losses and the number of cavities on soil surface were increased with increasing hydrocarbon concentration. Furthermore, attenuation in the brightness of the sand particles was observed with increment in hydrocarbon concentration indicating the more adsorption capacity of toluene at high concentration levels. In Fig. 4, the left-hand side single SEM image is of the initial phase soil samples, whereas the right-hand side SEM images are of different concentration batches. The lower most images of high concentration show the high level of residual hydrocarbon in cavities (Fig. 5).

Table 4 Measured LNAPL concentration in microcosm setups

Hours	Relative concentration [ppm/ppm]
0	0
1	0
2	0.084
3	0.24
4	0.32
5	0.36
6	0.4
7	0.43
8	0.45
9	0.492
10	0.52
11	0.54
12	0.57
13	0.59
14	0.6
15	0.62
16	0.64
17	0.65
18	0.66
19	0.666
20	0.678
21	0.67
22	0.68
23	0.69
24	0.69
25	0.7
26	0.71
27	0.71
28	0.71
29	0.71
30	0.71

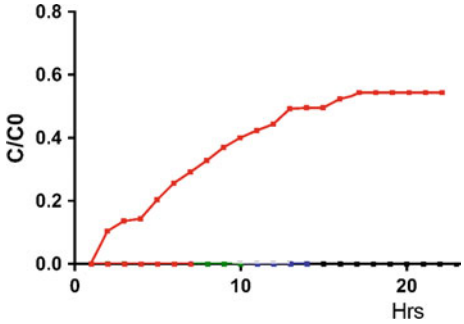

Fig. 4 Obtained BTCs of the batches showing the increasing relative concentration in soil-water system

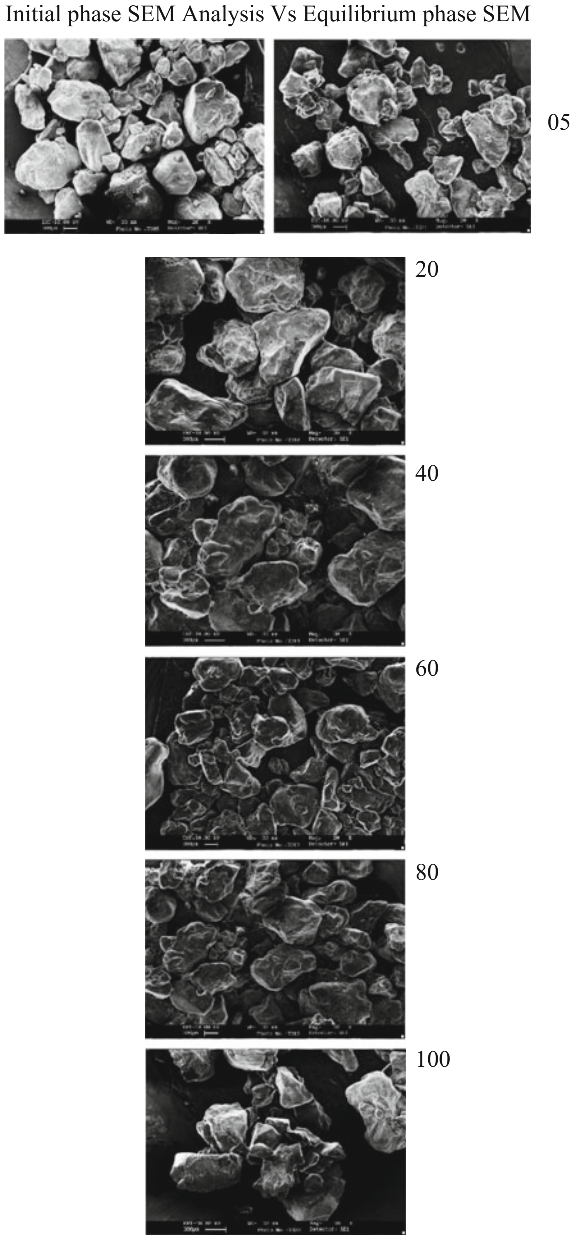

Fig. 5 SEM images of the initial phase and equilibrium phase samples collected from different concentrations batches

Conclusion

The aim of present study is to investigate the impact of different substrates concentration of a hydrocarbon pollutant, toluene on soil morphology using batch experiments. Thus, a series of microcosm experiments were performed at prevailing environmental condition having the different six concentration ranges from 05 to 100 ppm. The BTCs of each batch were analyzed using gas phase concentration analysis by GCMS. To see the soil morphology at the initial phase and equilibrium phase, the SEM slide was prepared for each batch. The SEM-analyzed images show the residual LNAPL on soil cavities as well as in pore spaces. The level of soil surface losses and the number of cavities on soil surface were increased with increasing hydrocarbon concentration. Furthermore, attenuation in the brightness of the sand particles was observed with increment in hydrocarbon concentration indicating the more adsorption capacity of toluene at high concentration levels. Results of this study are helpful in investigating the geochemical stability of soil, remediation strategy and for upscaling of fate and transport of pollutants in subsurface environment.

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References

Dobson R, Schroth MH, Zeyer J (2007) Effect of water-table fluctuation on dissolution and biodegradation of a multi-component, light nonaqueous-phase liquid. J Contam Hydrol 94:235–248

Gupta PK, Ranjan S, Yadav BK (2013) BTEX biodegradation in soil-water system having different substrate concentrations. Int J Eng Res Technol (IJERT) 2(12):1765–1772. ISSN: 2278-0181

Gupta PK, Yadav BK (2015) Large scale laboratory investigation and simulation of fate and transport of LNAPL plume in variably saturated subsurface. In: HYDRO-2015, 20th international conference on hydraulics, water resources and river engineering. IIT Roorkee, 17–19 Dec 2015. (Manuscript no HYD-330)

Gupta PK, Yadav BK (2017) Bioremediation of non-aqueous phase liquids (NAPLS) polluted soil and water resources. In: Bhargava RN (eds) Environmental pollutants and their bioremediation approaches. Taylor and Francis Group, Florida, USA CRC Press. ISBN 9781138628892

Jahangeer GPK, Yadav BK (2017) Transient water flow and nitrate movement simulation in partially saturated zone. J Irrig Drain Eng (ASCE). doi:10.1061/(ASCE)IR.1943-4774.0001238

Kumar D, Tomar J, Gupta PK, Yadav BK (2015) Engineered in situ bioremediation: an emerging technology for contaminated groundwater remediation. In: Fifth international conference on plants & environmental pollution (ICPEP-5). CSIR-National Botanical Research Institute, Lucknow, 24–27 Feb 2015, p 184 (Book-of-Abstracts)

Lee KY, Chrysikopoulos CV (1995) Numerical modelling of three-dimensional contaminant migration from dissolution of multicomponent NAPL pools in saturated porous media. Environ Geol 26(3):157–165. doi:10.1007/BF00768737

Shachi, Yadav BK (2015) Modelling transport of a non-aqueous phase liquid's (NAPL) vapor in variably saturated zone. In: International conference on hydraulics, water resources and river engineering. Roorkee, India, p 151

Soga K, Page JWE, Illangasekare TH (2004) A review of NAPL source zone remediation efficiency and the mass flux approach. J Hazard Mater 110(1–3):13–27. doi:10.1016/j.jhazmat.2004.02.034

Yadav BK, Hassanizadeh SM (2011) An overview of biodegradation of LNAPLs in coastal (semi)-arid environment. Water Air Soil Pollut. doi:10.1007/s11270-011-0749-1

Yadav BK, Ansari FA, Basu S, Mathur A (2013) Remediation of LNAPL contaminated groundwater using plant-assisted biostimulation and bioaugmentation methods. Water Air Soil Pollut 225(1):1793. doi:10.1007/s11270-013-1793-9

Kitchen Greywater Treatment in a Constructed Wetland Microcosm Using Aquatic Macrophytes

Abhik Gupta and Jyoti Rani Nath

Abstract Greywater or sullage is wastewater generated from households, commercial establishments and other sources that has not come into contact with faecal matter. In this study, greywater from a canteen kitchen was treated in microcosm-scale constructed wetlands which were designed as scaled-down models of free water surface (FWS) and vertical sub-surface flow (VSF) systems. Canteen greywater was made to flow through the microcosms planted with *Phragmites australis* or *Phragmites karka* or *Ipomoea aquatica* at an average hydraulic retention time (HRT) of 24 h. The kitchen wastewater was characterized by pH ranging from 2.48 to 6.25, phosphate (1.87–19.75 mg L^{-1}), chloride (55–500 mg L^{-1}) and sulphate (39.54–208.87 mg L^{-1}). *P. australis* and *I. aquatica* were efficient in neutralizing pH and reducing phosphate, electrical conductivity, total dissolved solids and chloride contents in VSF model. Moderate sulphate reduction was observed in FWS model with *P. australis* and *P. karka*, with no reduction in VSF. Reuse of this greywater for gardening or toilet flushing could contribute towards recycling and conservation of water and protection of natural water quality in educational institutions, multi-storey housing, office and commercial complexes.

Introduction

Wastewater is commonly classified into 'greywater' and 'blackwater', the former comprising wastewater generated from households, commercial establishments and other sources that has not come into contact with faecal matter. On the contrary, wastewater from septic tanks is termed as blackwater and is much more difficult and hazardous to treat. Although wastewater from kitchen is generally classed as greywater, it is considered more cumbersome to treat because of its high organic

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load, chloride (from salts), presence of oil and grease, and high fluctuations in pH due to the presence of lemon peels and waste, vinegar, etc. Detergents used to clean utensils can contribute to the phosphate load of this class of greywater, which is, therefore, included in a distinct subclass of 'darkwater' by many. Greywater reuse and recycling after proper treatment can contribute significantly towards water resource conservation and management. While a number of treatment systems are in use for greywater treatment, constructed wetlands (CW) can provide simple, low-cost yet effective solutions to greywater management based on the property of phytoremediation. Generally speaking, CWs have very low operation and maintenance costs, capitalizing on natural environmental energies of sun, wind, soil, plants, animals, micro-organisms and the like. They can also be designed as dual- or multi-purpose ecosystems providing additional ecosystem services such as flood control, carbon sequestration and wildlife habitats (Vymazal 2010). Vymazal (2007) classified CWs as horizontal sub-surface flow (HSF), vertical sub-surface flow (VSF), free water (or surface) flow (FWS) or hybrid types. O'Hogain (2003) reported COD and BOD5 removals of 88 and 89% in VF-HF constructed wetland in Ireland with final COD and BOD5 outflow concentrations of 47 and 27 mg/L, respectively. Oovel et al. (2007) reported BOD7 removal of 90.8% with the final concentration of 5.5 mg/L in a VF-HF constructed wetland in Estonia.

Relatively few studies have been conducted in India on the efficacy of CWs (Vipat et al. 2008; Yadav et al. 2010, 2012). Similarly, the suitability of employing CWs has been assessed in other developing countries such as Tanzania (Kaseva 2004) and in the tsunami-affected areas of Thailand (Brix et al. 2007). It has also been suggested that CWs could serve as stand-alone wastewater treatment systems in small villages (Solano et al. 2004). The rich aquatic and semi-aquatic plant biodiversity of North East India has remained relatively unexplored for their applied value in pollution biomonitoring and bioremediation. However, a few studies have revealed the phytoremediation potential of aquatic macrophytes that could be exploited for wastewater treatment (Khumanleima Chanu and Gupta 2014; Nimisha and Gupta 2015). A microcosm model has also been tested in an earlier study for treatment of laboratory greywater (Gupta et al. 2015).

Materials and Methods

Collection of Experimental Plants

Three species of aquatic/semi-aquatic macrophytes were used in the present experiment. These were:

(a) *Phragmites australis* Cav. Trin. Ex Steud;
(b) *Phragmites karka Trin. Fund. Ex Steud*;
(c) *Ipomoea aquatica* Forskk.

These were collected from wetland margins and marshy areas in and around the Assam University Campus at Dargakona, Cachar, Assam. The plants were brought to the laboratory and acclimatized for 15 days before the start of the experiment. The macrophytes were placed in separate PVC containers filled with water for acclimatization.

Experimental Set-up for Greywater Treatment

The dimensions of the microcosms used in the present study are provided in Table 1. The 'grey' wastewater generated from the canteen near the Department of Ecology & Environmental Science, Assam University, Silchar, was collected and stored for 24 h in a PVC container which also served as the sedimentation tank. The storage-cum-sedimentation tank as well as the microcosms comprised cylindrical PVC containers (32 cm height; 28.5 cm in diameter; *c*20 L capacity) with a bottom outlet fitted with a stopcock. The microcosms were filled with a 15-cm layer of gravel of 1.5–2 cm thickness approximately. Each microcosm was planted with either *P. australis* or *P. karka* or *I. aquatica*. A control microcosm was also set up, which contained only a 15-cm layer of gravel without any plant. Ten litres of collected greywater was poured into the control microcosm and each of the three PVC microcosms containing the plants at the same time. Thus the microcosms could either serve as free water surface (FWS) or vertical sub-surface flow (VSF) wetlands depending on whether the treated greywater was collected after each experiment from the surface (FWS) or drained out from the bottom (VSF). The schematic design of the experimental set-up is shown in Fig. 1. Both FWS and VSF experiments were done in three replicates and repeated thrice. The mean hydraulic retention time (HRT) was 24 h. The microcosms were thoroughly washed and cleaned after each experiment.

Table 1 Dimensions and operating conditions of wetland microcosms

Diameter	28.5 cm
Height	32 cm
Substrate type	Gravel (1.5–2 cm diameter)
Bed depth	15 cm
Gross capacity of reservoir and microcosm	20 L
Gross capacity of collecting container	20 L
Plant species	*Phragmites australis*; *P. karka*; *Ipomoea aquatica*
Type of wastewater	Kitchen greywater
Mode of operation	Batch
Mean hydraulic retention time (HRT)	24 h

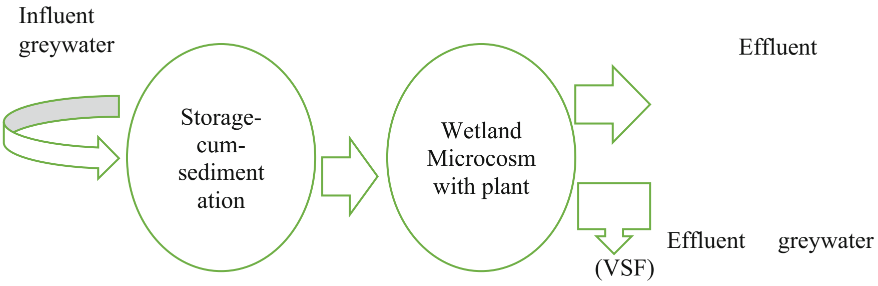

Fig. 1 Schematic representation of kitchen greywater treatment with *P. australis*, *P. karka* and *I. aquatica* in a wetland microcosm

Removal efficiency for the different variables was calculated as:

$$R = \frac{\mathrm{IC} - \mathrm{EC}}{\mathrm{IC}} 100 \qquad (1)$$

where R = removal efficiency; IC = influent concentration; and EC = effluent concentration (Gruyer et al. 2013).

Statistical Analysis

The data collected were compiled and computed using MS Excel 2010 and SPSS 20 for Windows.

Results

The physico-chemical characteristics of the greywater produced from a canteen in the Assam University Campus at Silchar, Assam, during the FWS and VSF experiments are shown in Table 2. Differences in physico-chemical properties could be observed between the two sets, which reflect the natural variability in kitchen waste that occurs due to the variations in the composition of the ingredients used in the preparation of the food items. For instance, the highly acidic pH of the VSF dataset was due to the presence of higher amounts of lemon peels, vinegar and sour sauces, which were used in larger quantities during that period. The VSF dataset also showed a higher chloride, sulphate, EC and TDS values when compared to the greywater used in the FWS experiment. Thus, there was considerable variability in the composition of the greywater treated in this study.

Table 2 Physico-chemical characteristics of Assam University canteen wastewater

Variable	Mean ± standard error (range of values)	
	FWS	VSF
pH	5.85 ± 0.15 (5.32–6.25)	3.99 ± 0.58 (2.48–5.9)
Electrical conductivity (EC) mS cm^{-1}	0.585 ± 0.05 (0.367–0.751)	1.68 ± 0.57 (0.36–3.68)
Total dissolved solids (TDS) ppt	0.38 ± 0.03 (0.24–0.485)	1.14 ± 0.4 (0.239–2.49)
Nitrate mg L^{-1}	BDL	0.137 ± 0.08 (BDL–0.41)
Phosphate mg L^{-1}	9.43 ± 1.52 (9.375–13.8)	12 ± 2.4 (5.5–19.75)
Total alkalinity mg L^{-1}	203.01 ± 11.54 (146.4–234.24)	49.33 ± 28.48 (BDL–148)
Chloride mg L^{-1}	92.36 ± 8.51 (55.97–127.94)	353.32 ± 84.7 (59.97–500)
Sulphate mg L^{-1}	79.82 ± 9.85 (39.54–113.39)	113.39 ± 28.2 (47.74–208.87)

BDL—Below detection limit

Greywater Quality in FWS Microcosm

Table 3 shows the physico-chemical properties of the greywater after treatment in a free water surface (FWS) wetland microcosm planted with either *P. australis* or *P. karka* or *I. aquatica* for a mean hydraulic retention time (HRT) of 24 h. The

Table 3 Physico-chemical characteristics of kitchen greywater in control (only gravel) and in FWS microcosms planted with *Phragmites australis*, *P. karka* and *Ipomoea aquatica*, with per cent change from raw greywater in parentheses

Variable	Control (gravel)	*P. australis*	*P. karka*	*I. aquatica*
pH	4.54 ± 0.39 (−22.93)	6.14 ± 0.14 (+4.96)	6.19 ± 0.44 (+5.81)	6.02 ± 0.12 (+2.91)
Electrical conductivity (EC) mS cm^{-1}	0.955 ± 0.1 (+63.25)	0.59 ± 0.04 (+1.03)	0.59 ± 0.11 (+1.03)	1.33 ± 0.07 (+127.35)
Total dissolved solids (TDS) ppt	0.626 ± 0.07 (+64.74)	0.39 ± 0.03 (+1.32)	0.38 ± 0.07 (+1.05)	0.86 ± 0.04 (+127.11)
Nitrate mg L^{-1}	BDL	BDL	0.008 ± 0.01	BDL
Phosphate mg L^{-1}	13.56 ± 0.8 (+43.74)	4.1 ± 1.35 (−56.54)	3.94 ± 1.27 (−53.23)	8.13 ± 0.52 (−13.79)
Total alkalinity mg L^{-1}	176 ± 6.57 (−13.31)	178.79 ± 17.64 (−11.93)	185 ± 14.52 (−8.87)	189.1 ± 6.28 (−6.85)
Chloride mg L^{-1}	389.49 ± 24.56 (+321.7)	91.23 ± 5.59 (−1.22)	94.68 ± 6.22 (+ 2.51)	78.54 ± 0.81 (−14.96)
Sulphate mg L^{-1}	132.23 ± 3.8 (+65.66)	58.93 ± 5.63 (−26.17)	62.25 ± 6.5 (−22.01)	101.82 ± 1.63 (+27.56)

+ denotes increase; − denotes reduction

slightly acidic pH of the greywater is somewhat neutralized in all the three plant treatments, while it turns more acidic when passed through the control containing gravel bed without plants. EC and TDS increased in control and in *I. aquatica* treatment, while it was slightly augmented in *P. australis* and *P. karka*. Phosphate was reduced by over 50% in *P. australis* and *P. karka* treatment, and by about 14% in *I. aquatica*, while its concentration increased in the control. Total alkalinity decreased in the control and the plant treatments. Chloride and sulphate increased in the control. Chloride increased and decreased marginally in *P. australis* and *P. karka*, respectively, while its reduction was about 14% from the untreated greywater in *I. aquatica*. Sulphate was reduced by *c*26 and 22% in *P. karka* and *P. australis*, respectively, while it increased by about 27% in *I. aquatica*.

Greywater Quality in VSF Microcosm

The physico-chemical properties of greywater in VSF control (water passed through gravel bed only) and in the three plant treatments are shown in Table 4. The highly acidic pH of the untreated greywater showed considerable recovery in gravel, *P. australis* and *I. aquatica* (36.83, 47.12 and 50.13%, respectively), while the increase was only 12.53% in *P. karka*. Total alkalinity also recorded a 486.52 and 351.39% increase, respectively, in *P. australis* and *I. aquatica*, which were also highly efficient in reducing EC, TDS, phosphate and chloride. In contrast, none of the treatments was effective in reducing sulphate.

Table 4 Physico-chemical characteristics of kitchen greywater in control (only gravel) and in VSF microcosms planted with *Phragmites australis*, *P. karka* and *Ipomoea aquatica*, with per cent change from raw greywater in parentheses

Variable	Control (gravel)	*P. australis*	*P. karka*	*I. aquatica*
pH	5.46 ± 0.55 (+36.83)	5.87 ± 0.22 (+47.12)	4.49 ± 0.69 (+12.53)	5.99 ± 0.31 (+50.13)
Electrical conductivity (EC) mS cm^{-1}	1.13 ± 0.43 (−46.92)	0.73 ± 0.15 (−56.67)	1.53 ± 0.48 (−8.93)	0.73 ± 0.14 (−56.55)
Total dissolved solids (TDS) ppt	0.74 ± 0.28 (−35.2)	0.47 ± 0.09 (−58.49)	0.99 ± 0.31 (−13.49)	0.47 ± 0.09 (−58.58)
Nitrate mg L^{-1}	BDL	BDL	0.143 ± 0.082	BDL
Phosphate mg L^{-1}	6.76 ± 3.83 (−43.67)	6.25 ± 2.05 (−47.92)	8.75 ± 2.72 (−27.08)	6.54 ± 2.11 (−45.5)
Total alkalinity mg L^{-1}	132.8 ± 25.32 (+169.21)	289.33 ± 65.79 (+486.52)	36 ± 20.78 (−27.02)	222.67 ± 35.93 (+351.39)
Chloride mg L^{-1}	187.17 ± 61.39 (−47.03)	102.61 ± 22.18 (−70.96)	344.66 ± 89.69 (−2.45)	148.46 ± 41.08 (−57.98)
Sulphate mg L^{-1}	127.56 ± 17.36 (+12.5)	114.38 ± 21.73 (+0.87)	149.69 ± 34.46 (+32.01)	125.32 ± 17.35 (+10.52)

+ denotes increase; − denotes reduction

Discussion

The results showed that the control with only gravel bed was not efficient in improving greywater quality in the FWS microcosm. The pH turned more acidic, while EC, TDS, phosphate, chloride and sulphate recorded increase after being retained for 24 h in the FWS microcosm. On the contrary, pH and total alkalinity recorded increase, and all the other variables except sulphate were reduced in the VSF gravel treatment. It is to be noted that the greywater did not pass through the gravel bed and the root zone of the plants in FWS, but was collected from the surface, while in the VSF system it percolated through the gravel and the root zone, which appears to improve its quality. The quality improvement in terms of pH, EC, TDS, total alkalinity, phosphate and chloride was more pronounced under gravel coupled with *P. australis* and *I. aquatica* treatments. *P. karka* had a relatively poor performance, while none of the treatments was found capable of effectively reducing sulphate levels in the greywater. In the present study, EC and TDS reductions ranged from 46.92 and 35.2, 56.67 and 58.49, and 56.55 and 58.58% under control gravel, *P. australis* and *I. aquatica* treatments, respectively. On the contrary, these were only 8.93 and 13.49%, respectively, under *P. karka* treatment. Baskar et al. (2009) recorded a TDS removal of only 4% from kitchen wastewater using *P. australis*. In the same study, nitrogen and phosphorus reductions were 76 and 77%, respectively. Phosphate reduction was 43.67% in gravel, 47.92% in *P. australis*, 45.5% in *I. aquatica* and 27.08% in *P. karka* treatment in our study, indicating that percolation through gravel resulted in possible adsorption and resultant reduction of phosphate, which was further supplemented by phytoabsorption. Physical substrates such as dewatered alum sludge have been shown to be effective in phosphorus removal (Wu et al. 2011). Phosphate removal ranged from 31.2 to 81.3% in a constructed reed-bed system for treating domestic greywater in Costa Rica (Dallas et al. 2004). Vymazal and Kröpfelová (2011) also found that the removal of total phosphorus varied between 40 and 60% in constructed wetlands depending on CW type and inflow loading. Chloride concentrations were found to increase in a surface flow wetland (Vidales-Contreras et al. 2010). On the other hand, chloride reduction in the VSF wetland in our study was about 70% in *P. australis* and 57% in *I. aquatica*, although *P. karka* was not at all effective. Reductions in chloride from 7 to 68%; that in PO_4^{3-} from 27 to 87%; and that in SO_4^2 from 5 to 83% were observed in a recent study on treatment of laboratory wastewater (Gupta et al. 2015). Thus, it appears that the compositional matrix of greywater influences the efficiency of the CW system.

Conclusions

The present study based on microcosm models shows that constructed wetlands, especially the vertical sub-surface flow type, have the potential to treat kitchen greywater which in turn could be used for gardening and/or for toilet flushing. It is, therefore, necessary to scale up the model and test the efficacy of the system under field conditions. A few additional variables such as BOD, COD and coliform counts along with sodium and selected trace elements also need to be investigated for a comprehensive assessment.

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References

Baskar G, Deeptha VT, Rahman AA (2009) Treatment of wastewater from kitchen in an institution hostel mess using constructed wetland. Int J Recent Trends Eng 1(6):54–58

Brix H, Koottatep T, Laugesen CH (2007) Wastewater treatment in tsunami affected areas of Thailand by constructed wetlands. Water Sci Technol 56(3): 69–74

Dallas S, Scheffe B, Ho G (2004) Reedbeds for greywater treatment—case study in Santa Elena-Montverde, Costa Rica, Central America. Ecol Eng 23:55–61

Gruyer N, Dorais M, Alsanius BW, Zagury GJ (2013) Simultaneous removal of nitrate and sulfate from greenhouse wastewater by constructed wetlands. J Environ Qual 42:1256–1266

Gupta A, Barman M, Naiding S (2015) Laboratory greywater treatment in a constructed wetland microcosm using aquatic macrophytes. In: Rana S (ed.) Reviving traditional water & environment conservation techniques, pp 116–126. Proceedings Aqua Foundation, IX World Aqua Congress, 26–27 Nov, New Delhi, India

Kaseva ME (2004) Performance of a sub-surface flow constructed wetland in polishing pre-treated wastewater—a tropical case study. Water Res 38:681–687

Khumanleima Chanu H, Gupta A (2014) Necrosis as an adaptive response to copper toxicity in *Ipomoea aquatica* Forsk. and its possible application in phytoremediation. Acta Physiol Plantarum 36:3275–3281

Nimisha, Gupta A (2015) Uptake and accumulation of Cd from wastewater by *Alternanthera philoxeroides* (Mart.) Griseb. Indian J Appl Res 5(5):19–20

O'Hogain S (2003) The design, operation and performance of a municipal hybrid reed bed treatment system. Water Sci Technol 48(5):119–126

Oovel M, Tooming A, Mauring T, Mander U (2007) Schoolhouse wastewater purification in a LWA-filled hybrid constructed wetland in Estonia. Ecol Eng 29:17–26

Solano ML, Soriano P, Ciria MP (2004) Constructed wetlands as a sustainable solution for wastewater treatment in small villages. Biosyst Eng 87(1):109–118

Vidales-Contreras JA, Gerba CP, Karpiscak MM, Fuentes HR, Escareño JJH, Chaidez-Quiroz C (2010) Performance of a surface flow constructed wetland system used to treat secondary effluent and filter backwash water. Int J Agric Biol 12:821–827

Vipat V, Singh UR, Billore SK (2008) Efficacy of rootzone technology for treatment of domestic wastewater: field scale study of a pilot project in Bhopal (M.P), India. In: Sengupta M, Dalwani R (eds) Proceedings of taal 2007: the 12th world lake conference, pp 995–1003. Jaipur, India, 29 Oct–2 Nov 2007

Vymazal J (2007) Removal of nutrients in various types of constructed wetlands. Sci Total Environ 380:48–65

Vymazal J (2010) Constructed wetlands for wastewater treatment. Water 2:530–549

Vymazal J, Kröpfelová L (2011) A three-stage experimental constructed wetland for treatment of domestic sewage: first two years of operation. Ecol Eng 37:90–98

Wu S, Austin D, Liu L, Dong R (2011) Performance of integrated household constructed wetland for domestic wastewater treatment in rural areas. Ecol Eng 37:948–954

Yadav AK, Kumar N, Sreekrishnan TR, Satya S, Bishnoi NR (2010) Removal of chromium and nickel from aqueous solution in constructed wetland: mass balance, adsorption-desorption and FTIR study. Chem Eng J 160:122–128

Yadav AK, Jena S, Acharya BC, Mishra BK (2012) Removal of azo dye in innovative constructed wetlands: influence of iron scrap and sulfate reducing bacterial enrichment. Ecol Eng 49:53–58

Assessment of Aerobic Biodegradability for Vegetable Tanning Process Wastewater Generated from Leather Industry

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Abstract The most important process in the making of leather is converting raw hides/skins into leather by chrome tanning using basic chromium sulfate or vegetable tanning using vegetable extracts like wattle, chestnut, myrobalan and valonea. Vegetable tanning extracts predominantly contain tannins which bind to the collagen. Vegetable tanning process is usually carried out in tanneries for the production of sole and heavy leathers. In this study, the vegetable tanning wastewater (VTW) was collected from the vegetable tanning bath and was characterized for all physicochemical parameters. The biodegradability assessment was performed using laboratory-scale batch aerobic reactors of 2 L capacity. The results indicated that the VTW had a BOD_5/COD ratio of 0.154 implying that it was not easily biodegradable and 80% of COD was found due to the presence of tannins. The biodegradability test showed an apparent removal of only 24 and 34% of COD, and tannins were observed over a residence time of 24 h. This shows that the efficiency of aerobic microorganisms is affected by the binding of tannins to their cell wall. Supporting data obtained with the help of FTIR is presented in this paper.

Introduction

In leather industries, tanning is the process of converting raw hides or skins into leather. Tannins are water-soluble complex organic compounds that are capable of combining with protein to convert it into a material. The wastewater from vegetable tanning process imparts color and consists of non-biodegradable matter like tannin which persists for long (Dhaneswar 1990). Tannins inhibit the growth of a number of microorganisms, resist microbial attack and are recalcitrant to biodegradation

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and Technology Library 79, https://doi.org/10.1007/978-981-10-5795-3_14

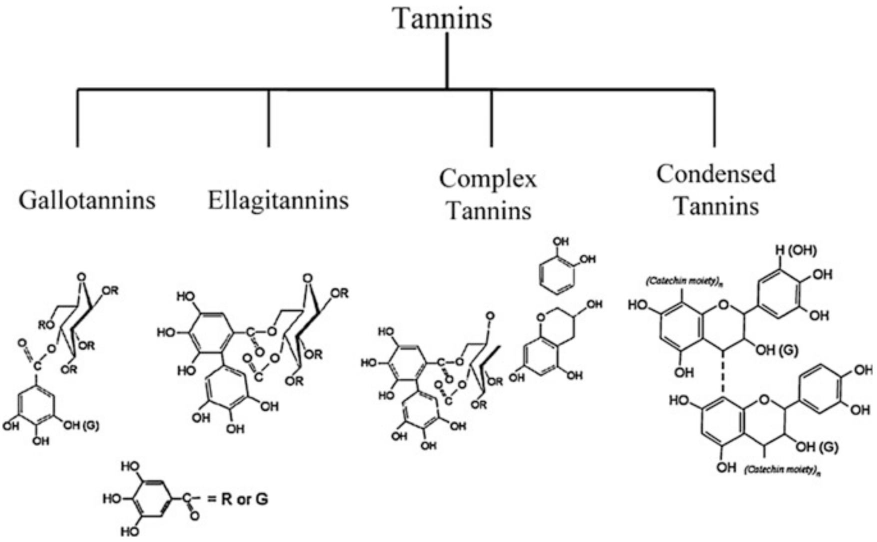

Fig. 1 Classification of tannins (*Source* Aquilar et al. 2007)

(Field and Lettinga 1992). There are two major types of tannins: condensed and hydrolyzable. The classification of tannins is presented in Fig. 1.

Hydrolyzable tannins are composed of esters of gallic acid (gallotannins) or ellagic acid (ellagitannins) with a sugar core which is usually glucose and are readily hydrolyzed by acids or enzymes into monomeric products. Condensed tannins, also known as polymeric proanthocyanidins, are composed of flavonoid units and are usually more abundant in tree barks and woods than their hydrolyzable counter parts (Bhat et al. 1998).

Shoe soles, brief cases, luggage and belts are made by vegetable tanning process. On the other hand, shoe uppers are tanned by chrome tanning process. However, most of these chrome-tanned products are later re-tanned with vegetable tannins.

Owing to the presence of tannins, the wastewater is usually highly colored, which is very difficult to be removed by conventional treatment methods (Etiegni et al. 1999). In addition, tannins can inhibit growth of microorganisms and inhibit the efficiency of the biological treatment process. This negative effect can be observed when tannin-containing wastewater is biologically treated in wastewater treatment plants (Ren 2004). Methods such as adsorption (Liao and Shi 2005; Marsal et al. 2003), photocatalytic and sonochemical process (Arana et al. 2001; Svitelska et al. 2004), membrane filtration (Cassano et al. 2003; Scholz and Lucas 2003) and Fenton and ozonation (Kalyanaraman et al. 2015) have been explored to treat tannin-containing wastewaters by various researchers.

Even though anaerobic digestion is a preferred process, problems of high toxicity and inhibition of biodegradation have been encountered (Beccari et al. 1996). This is because methanogens are sensitive to the organic compounds present, especially the phenolic compounds like tannin, thus limiting the performance of anaerobic digestion process (Hamdi 1992). A concentration of tannins higher than 0.2 g/L inhibits the anaerobic digestion process (Gupta and Haslam 1989), while 2 g/L of tannin will completely inhibit the process as reported by Munz et al. (2009).

Several studies were conducted to study the biodegradability of tannin wastewater (Routh 2000; Tramsek et al. 2006; Banu and Kaliappan 2007). In a study by He et al. (2007), when the tannin content of the wastewater was 4,900 mg/L, only 34.7% of biodegradation extent was reached in 14 days of incubation. On the other hand, when the tannin content was 490 mg/L, the COD and tannin removals reached 51.3 and 45.1% respectively in 6 days.

Aerobic biodegradation of VTW was performed to find out how tannin influences the conventional aerobic treatment process efficiency. The results of removal of COD and tannin after aerobic treatment were assessed, and validation of degradation through FTIR analysis was described in detail in this paper.

Materials and Methods

Analytical Methods

Characterization of Vegetable Tannin Wastewater

During vegetable tanning operation, a mixture of condensed tannins and hydrolyzable tannins were used based on the nature of the final product. Vegetable tanning process wastewater (VTW) was collected from a commercial tannery and characterized for physicochemical parameters, viz. pH (Part 4500-H + method B), chemical oxygen demand (COD; Part 5220 method C), biochemical oxygen demand (BOD as BOD_5 at 20 °C; Part 5210 method B), sulfates (SO_4^{2-}; Part 4500 method E) and suspended solids (total suspended solids dried at 103–105 °C; Part 2540 method D), and tannin content was measured by Folin–Ciocalteau phenol method (tannin and lignin; Part 5550 method B) as per standard methods 20th edition (APHA 1998). Samples were analyzed in triplicate, and the average values with standard deviation are reported. The aromaticity of the wastewater due to the presence of aromatic compounds in terms of UV_{280} measurements, before and after treatments, was determined by UV-2450 Shimadzu spectrophotometer using a 1-cm quartz cell.

Aerobic Biodegradation of Vegetable Tanning Wastewater

Batch experiments were conducted in 2 L reactors with working volume of 1.5 L. The initial biomass and COD were kept to maintain an F/M ratio of 0.15 as suggested in CPHEEO manual (1993) for extended aeration process. Aquarium air pumps and microporous air diffusers were adopted for aeration. Studies were carried out for a period of 72 h, and the samples were collected at intermittent time intervals for analysis.

Fourier Transform Infrared Spectrometry Analysis

Fourier transform infrared spectrometry (FTIR) analysis was carried out in order to assess the functional groups present in the VTW before and after aerobic treatment. The samples were filtered through 0.45-mm filter paper and dried and were pelletized with potassium bromide (KBr) in the ratio of 1:50. The pellets were subjected to FTIR analysis using transmission mode. The measurements were carried out in the mid-infrared range from 4000 to 500 cm^{-1}, with Thermo Scientific make Nicolet iS5 model FTIR.

Results

Characterization of Vegetable Tanning Process Wastewater

Vegetable tanning process wastewater (VTW) collected from a commercial tannery was characterized for pH, COD, BOD, tannin, sulfate, sulfide, suspended solids and dissolved solids as per the procedures given in standard methods (APHA 1998). The results are presented in Table 1.

Vegetable tannin wastewater was acidic in nature. The pH was always found to be around 3.5 because of the acids used in pre-tanning process like in pickling of hides. The BOD_5/COD ratio was 0.154, indicating that the VTW is not easily biodegradable. It was observed that almost 80% of the COD was found due to the presence of tannins. The BOD was always found to be about 15–20% of COD of the VTW. This is because of the polyphenolic nature of the tannin, which is

Table 1 Characteristics of vegetable tanning process wastewater

S. No.	Parameter	Average value ± standard deviation
1	pH	3.3–4.2
2	Chemical oxygen demand (COD), (mg/L)	23,140 ± 250
3	Biochemical oxygen demand (BOD_5), (mg/L)	3577 ± 150
4	Total tannin content (mg/L)	19,640 ± 300
5	Sulfates (mg/L)	7526 ± 100
6	Suspended solids (mg/L)	3670 ± 50
7	BOD_5/COD ratio	0.154

composed of complex organic constituents. This contributes to the non-biodegradable nature of VTW. The presence of sulfates can be attributed due to the addition of sodium sulfate salts during the pre-tanning process of liming. Spectrophotometric analysis at 700 nm for the presence of tannins and for identification of functional groups FTIR analysis was carried out. UV–visible and FTIR spectra are presented in Figs. 2 and 3.

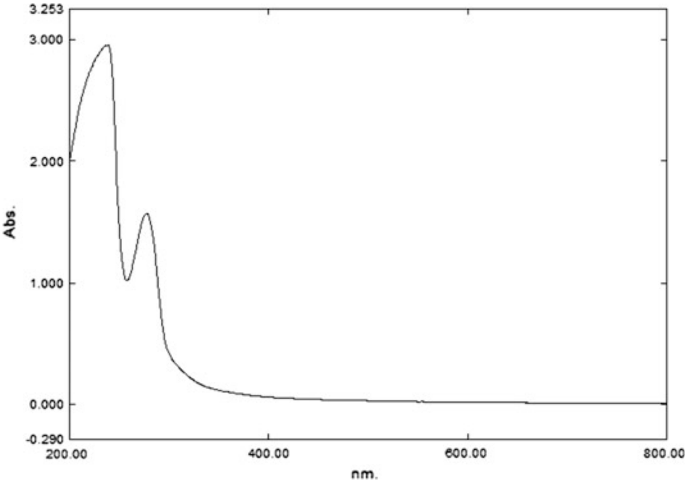

Fig. 2 UV visible spectrum of vegetable tannin wastewater

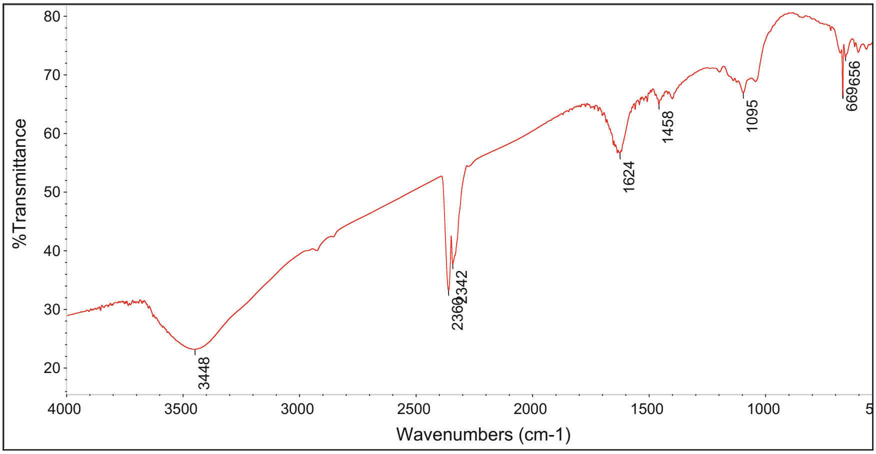

Fig. 3 FTIR spectrum of vegetable tanning wastewater

The UV–visible spectra of VTW showed two peaks at around 220 and 280 nm. The 280-nm peak corresponds to aromatic ring groups which are the predominant groups present in tannin. The 220-nm peak corresponds to amino groups. The presence of aromatic rings in tannin makes it resistant to biodegradation.

In the FTIR spectrum of VTW, the broad absorption band around 3400 cm^{-1} was due to O–H stretching and C–H stretching vibrations. The FTIR spectrum of VTW shows the peaks at 1624 and 1457 cm^{-1} which denotes C=C stretching vibrations present in alkenes and aromatics. CO stretching of carboxylic acid was observed at 1624 cm^{-1}. Peak due to O–H stretching was observed at 3448 cm^{-1}. Peak at 1095 cm^{-1} showed the stretching of C–O–H bond. Peak observed in the region of 2342 cm^{-1} was characterized by dissolved CO_2.

Aerobic Treatment of Vegetable Tanning Wastewater

The seed sludge used for aerobic process contained 7500 mg/L of mixed liquor suspended solids. Based on this, an F/M ratio, i.e., BOD/MLSS = 1125/7500 = 0.15, was maintained. Before adding to the sludge, the initial COD and tannin content of VTW were found to be 5000 and 3000 mg/L, respectively. The contribution of COD and tannin by the sludge was detected by using a control reactor with only the seed sludge. The efficiency of the aerobic treatment was monitored. The percentage removal of tannin and COD is presented in Fig. 4.

From the removal efficiency graph, it was seen that only 8 and 14% of tannin and COD removal occurred at the end of 4 h. After 24 h, it increased to 24 and 35% reduction in tannin and COD. It did not decrease to any significant level even after 72 h aeration. This is due to the binding of tannin to the cell wall of sludge microbe. Tannins cannot be removed through biodegradation since they are recalcitrant to microbial action. Generally, a residence time of 24 h is maintained in the aerobic

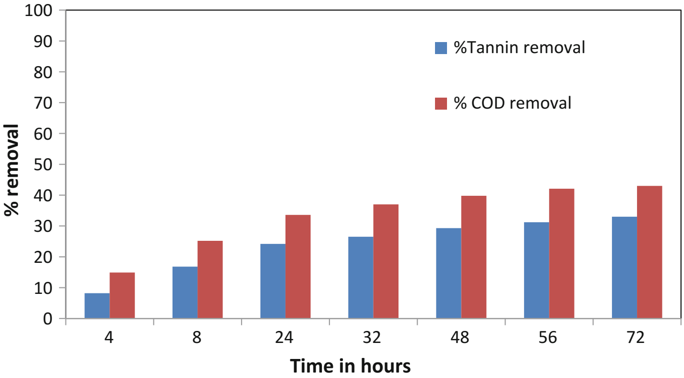

Fig. 4 Removal efficiency of tannin and COD

treatment units for the tannery wastewater in CETPs and ETPs. But in this case of non-biodegradable nature of wastewater, only 24 and 34% removal of tannins and COD was observed for 24 h. By further increasing the contact time, no substantial increase in the removal of tannins and COD was observed. Tannins present in VTW are composed of flavonoid units and are difficult to degrade by the aerobic microorganisms (Danhong et al. 2008). Tannins form strong cross-link with the cell membranes of microorganisms during their biodegradation process, which is responsible for their low biodegradability.

FTIR Analysis of VTW Before and After Aerobic Treatment

FTIR spectrum of VTW before and after aerobic treatment is shown in Figs. 5 and 6. The FTIR spectra of tannins showed transmittance in the range 1500–800 cm^{-1}, known as the “finger print” region. There was a prominent absorption band around 3400 cm^{-1} in all the spectrum of VTW. It can be associated with O–H stretching of intra-molecularly hydrogen bonded polymeric compound (Mistry 2009). The peaks around 1635 and 1400 cm^{-1}, in the fingerprint zone, could be due to C=C–C aromatic ring stretching.

After aerobic treatment, VTW showed that almost all the compounds present in it were not degraded effectively. The presence of aromatic ring stretching was still observed in the fingerprint region. In particular, the intensity of both the peaks 1635 and 1400 cm^{-1} due to aromatic ring remained the same in the treated effluent, indicating that the degradation was not efficient. These results clearly indicated that tannins should be made biodegradable so that the aerobic microorganisms are not hindered to carry out efficient biodegradation.

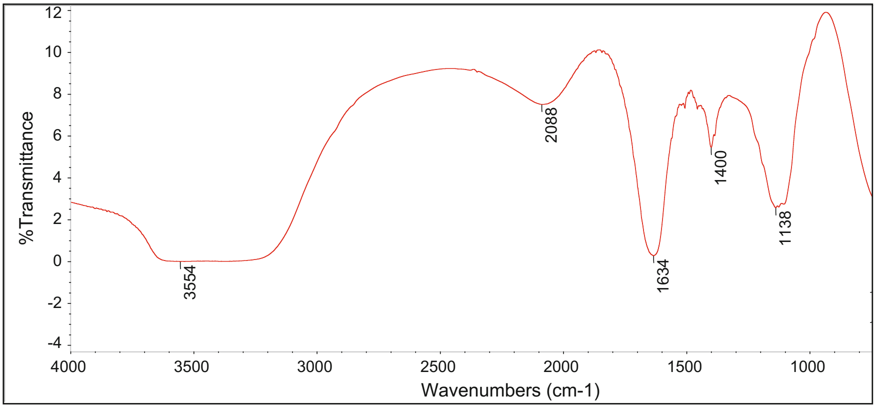

Fig. 5 FTIR spectrum before aerobic biodegradation

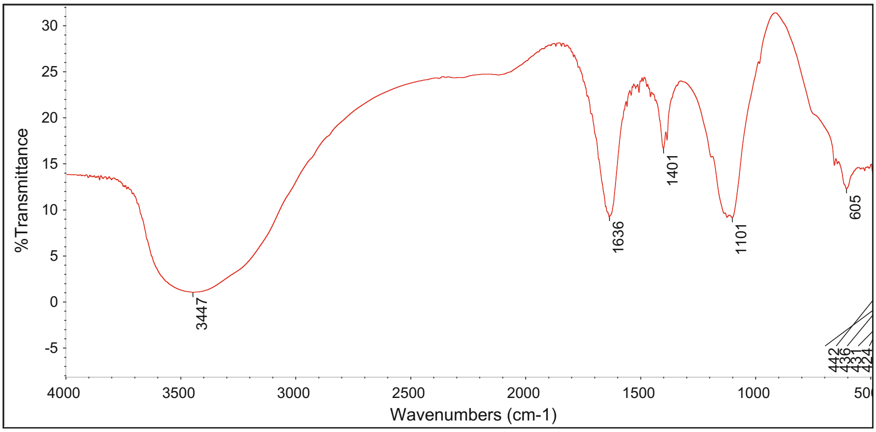

Fig. 6 FTIR spectrum after 24 h of aerobic biodegradation

Owing to the aromaticity/polyphenolic nature of tannin, the aerobic microorganisms are inefficient to degrade tannin completely. In order to change the nature of the compound, appropriate pre-treatment is necessary to increase the biodegradability of VTW.

Conclusion

Vegetable tannin wastewater (VTW) predominantly contains tannins which are recalcitrant to biodegradation. This VTW is characterized by high COD and color. Almost 80% of COD is due to the presence of tannins. The aerobic treatment studies show that the COD and tannin removal is not very significant even after 72 h of treatment. Only 24 and 34% removal of tannin and COD, respectively, was observed. The low removal efficiencies of COD and tannins are mainly due to binding of tannins over the cell wall of the aerobic microorganisms. The FTIR spectrum also revealed that there was no change in the 1635 and 1400 cm^{-1} aromatic stretch peaks before and after aerobic treatment.

It is therefore necessary to treat the VTW before aerobic biodegradation, using appropriate pre-treatment technologies such as application of advanced oxidation process or enzyme application, in order to increase the biodegradability. From this study, it is evident that there is no significant removal of COD and tannin by aerobic biodegradation process. This was attributed to the toxic effect of tannin toward the aerobic microorganisms.

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References

Aguilar CN, Rodríguez R, Gutiérrez-Sánchez G, Augur C, Favela-Torres E, Prado-Barragan LA, Ramírez-Coronel A, Contreras-Esquivel JC (2007) Microbial tannases: advances and perspectives. Appl Microbiol Biotechnol 76:47–59

APHA, AWWA, WEF (1998) Standard methods for the examination of water and wastewater, 20th edn. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA

Arana J, Tello RE, Dona RJM, Herrera MJA, Gonzalez DO, Perez PJ (2001) High concentrated phenolic wastewater treatment by the Photo-Fenton reaction—mechanism study by FTIR-ATR. Chemosphere 44:1017–1023

Banu JR, Kaliappan S (2007) Treatment of tannery wastewater using hybrid upflow anaerobic sludge blanket reactor. J Environ Eng Sci 6:415–421

Beccari M, Bonemazzi F, Majone Mand Riccardi C (1996). Interaction between acidogenesis and methanogenesis in the anaerobic treatment of olive oil mill effluents. Water Res 30:183–189

Bhat TK, Singh B, Sharma OP (1998) Microbial degradation of tannins—a current perspective. Biodegradation 9:343–357

Cassano A, Adzet J, Molinari R, Buonomenna MG, Roig J, Drioli E (2003) Membrane treatment by nanofiltration of exhausted vegetable tannin liquids from the leather industry. Water Res 37:2426–2434

CPHEEO (1993) Manual of sewerage and sewage treatment, 2nd edn. Central Public Health and Environmental Engineering Organization, Ministry of Urban Development

Danhong S, Qiang H, Wenjun Z, Yulu W, Bi S (2008) Evaluation of environmental impact of typical leather chemicals. Part II. Biodegradability of organic tanning agents by activated sludge. J Soc Leather Technol Chem 92(2):59–64

Dhaneswar RS (1990) Tannery wastewater treatment and disposal—state of art. J Ind Environ Prot 10:134–141

Etiegni L, Wakoli M, Ofosu AK (1999) Design of an efficient tannin extract effluent treatment system. Water Sci Technol 39:321–324

Field JA, Lettinga G (1992) Toxicity of tannic compounds to microorganisms. In: Hemingway RW, Laks E (eds) Plant Polyphenols: synthesis, properties, significance. Plenum Press, New York, pp 673–692

Gupta RK, Haslam E (1989) Vegetable tannin structure and biosynthesis in polyphenol in cereals and legumes-report. International Development Research Center, Ottawa, Canada

Hamdi M (1992) Toxicity and biodegradability of olive mill wastewaters in batch anaerobic digestion. Appl Biochem Biotechnol 37:155–163

He Q, Yao K, Sun D, Shi B (2007) Biodegradability of tannin containing wastewater from leather industry. Biodegradation 18:465–472

Kalyanaraman C, Kameswari KSB, Rao JR (2015) Studies on enhancing the biodegradation of tannins by ozonation and Fenton's oxidation process. J Ind Eng Chem 25:329–337

Liao XP, Shi B (2005) Selective removal of tannins from medicinal plant extracts using a collagen fiber adsorbent. J Sci Food Agric 85:1285–1291

Marsal A, Garcia EA, Ribosa I, Cot J, Manich A (2003) Removal of vegetable extracts by the use of activated clays. J Soc Leather Technol Chem 87:219–222

Mistry B (2009) A handbook of spectroscopic data chemistry: UV, IR, PMR, cNMR and mass spectroscopy. Oxford Book Company

Munz DG, De Angelis R, Gori G, Mori M, Casarci C Lubello (2009) The role of tannins in conventional and membrane treatment of tannery wastewater. J Hazard Mater 164(2–3):733–739

Ren S (2004) Assessing wastewater toxicity to activated sludge: recent research and developments. Environ Int 30:1151–1164

Routh T (2000) Anaerobic treatment of vegetable tannery wastewater by UASB process. Indian J Environ Health 20:15–123

Scholz W, Lucas M (2003) Techno-economic evaluation of membrane filtration for the recovery and re-use of tanning chemicals. Water Res 37:1859–1867

Svitelska GV, Gallios GP, Zouboulis AI (2004) Sonochemical decomposition of natural polyphenolic compound. Chemosphere 56:981–987

Tramsek M, Gorsek A, Glavic P (2006) The aerobic biodegradation kinetics of plant tannins in industrial wastewater. Chem Biochem Eng 20:285–291

Biodegradability of Syntans Using Ozonation as a Pretreatment Process

N. Dhivya Priya, K. Sri Bala Kameswari and Kalyanaraman Chitra

Abstract Syntans are high molecular weight synthetic organic compounds that are used for rendering hides and skins into a non-putrifiable substance called leather. Biodegradability of syntans, phenol and sulfone based, used for tanning process was studied to arrive at their biodegradability index (BI). The BOD/COD ratio of 0.087 and 0.033 of these two syntans clearly indicates that they resist microbial attack and are recalcitrant to biodegradation. In order to increase the BI, as pretreatment, ozonation studies were carried out as one of the Advanced Oxidation Processes. These studies were carried out with a dosage of 0.54 g/L at pH 4.0 and 8.0 to see whether it was acting as molecular ozone or through release of $^{\cdot}$OH radicals produced by decomposition; the contact time was optimized. An increase in BI to 0.1006 and 0.1088, respectively, was observed at acidic and alkaline pH for 15-min contact time for sulfone-based syntan. Whereas for the same contact time, in the case of phenol-based syntan, BI increased to 0.170 and 0.197, respectively, at acidic and alkaline pH. Further, efficacy of biological treatment of wastewater containing syntans was evaluated, with and without application of ozonation as pretreatment. During aerobic biological treatment, i.e., without pretreatment, only 25% of COD removal was observed whereas with application of ozone as pretreatment 50% removal of COD was observed for both the syntans for a residence time of 48 h. Even after application of ozonation, recalcitrant COD contributed by syntans was still persistent in the wastewater and the syntans can be classified as persistent organic pollutants.

Keywords Biodegradability index · Chemical oxygen demand
Ozonation · Syntan

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Introduction

Tanning is the process of converting raw hides to non-putrifiable material called leather which is resistant against decomposition. Syntans are used in pre-tanning and re-tanning processes; some are used as auxiliary chemicals also. These process effluents carry a high load of COD and show a low biodegradability (European Commission 2003). The raw materials selected in the manufacture of syntans vary according to the property that they are expected to impart in the tanning process (Phaniendra et al. 2011). Chrome-tanned leathers are mostly re-tanned to modify the properties of the finished leather to suit modern demand. Generally, organic compounds with several phenolic hydroxyl groups like natural tannins and syntans are preferred in re-tanning operations (Kalyanaraman et al. 2015). The effluent from the leather industry contains a wide range of organic and inorganic impurities like sulfide, chromium, tannin and biocides which contribute to a very higher amount of organic and inorganic pollutants (Rema and Ramanujam 2012). In addition to these, recalcitrant pollutants, namely synthetic tanning agents, are also present. Syntans are mainly based on formaldehyde; sulfone and phenol based are almost non-biodegradable and are present in the wastewater as persistent organic pollutants (POPs). When the treated effluent is discharged into water bodies, they combine with cell walls of the microbes and cause toxicity.

Biodegradation of such synthetic tanning agents may not be effective as they are composed of extended set of chemicals such as phenol, naphthalene and melamine which make the compound complex for breakdown by microbial action (Giusy et al. 2005). Prior to biological treatment, physicochemical treatment of the wastewater is necessary, and owing to increase the biodegradability index (BI), Advanced Oxidation Processes (AOPs) are being adopted to improve the BI of these compounds (Giusy et al. 2013). It is widely accepted that ozone reacts in aqueous solution with various organic and inorganic compounds, either by a direct reaction of molecular ozone in acidic $\mathrm{pH} < 6$, or through the hydroxyl radical produced by the ozone decomposition in water at alkaline pH (Soares et al. 2006).

Ozonation of POPs results in the formation of simpler compounds with lesser molecular weight and simple structure that can be easily degraded by activated sludge process (Munoz et al. 2005). In the present study, ozonation studies were carried out as an AOP in pretreatment. Further, efficacy of biological treatment of wastewater containing syntans was evaluated with and without application of ozonation as pretreatment.

Materials and Methods

Characteristics of Syntan Containing Wastewater

Sulfone- and phenol-based syntans were procured from a commercial tannery. Syntan containing wastewater was prepared by dissolving 5 g of syntan in 1 L distilled water separately. Syntan containing wastewater was characterized for physicochemical parameters like pH, chemical oxygen demand (COD), biological oxygen demand (BOD), sulfates and phenol according to standard methods (APHA 1998). Samples were analyzed in triplicate and the average values are reported.

Ozonation Studies

Ozone is an extremely strong oxidant ($E^\circ = 2.07$ V) and reacts rapidly with most of the organic pollutants. The degree of reactivity with ozone depends on the nature of compounds present in the wastewater. Functional groups containing aromatic rings, unsaturated hydrocarbons are prone to cleave during ozonation, and compounds such as saturated hydrocarbons, alcohols and aldehydes are resistant to ozonation (Beltran 2003). pH of the wastewater would determine whether the applied ozone will acts as a molecular ozone or release of $^{\cdot}$OH radicals. In general, syntans are used in tanneries in the tanning and re-tanning processes where the pH of the water will be adjusted to 3.5–4.0, using formic acid. Considering the real application in the tanning process, ozonation studies were carried out at acidic pH. Apart from that, ozonation studies were also carried out at alkaline pH in order to increase the BI. Ozonation studies were carried out in bubble column glass reactor using laboratory ozone generator Model No L6G from Faraday Instruments, India, with pure oxygen as the feed inlet gas to produce 0.54 g/L of ozone. Ozonation studies were carried out for 30 min, and the samples were collected at regular intervals of time and analyzed.

Experiment Setup for Biodegradation of Syntans Under Aerobic Conditions

Studies were carried out in batch reactors of 2.0 L capacity with working volume of 1.5 L. In order to maintain aerobic conditions throughout the experimentations, air was supplied through diffusers fitted to an aquarium-type pump and dissolved oxygen (DO) concentration of 2–2.5 mg/L was maintained. pH plays an important role in biological treatment of wastewater. Hence, pH of syntan containing wastewater was adjusted to 7.0 prior to aerobic biological treatment. The COD: N: P ratio of 100:5:1 was maintained in the reactors with the addition of necessary macronutrients (Heredia et al. 2000; Fadila et al. 2003) along with supplementary trace minerals (Chipasa and Medrzycka 2008). The activated sludge used as inoculum in the experiment was collected from the aeration tank of a Common Effluent Treatment Plant (CETP) situated in Chennai, India, exclusively operating for treatment of tannery wastewater. Food to microbial (F/M) ratio plays an important role in aerobic studies as it would provide a congenial environment to the aerobic microorganisms. The F/M ratio maintained during the study was 0.15, which is the ratio maintained in aerobic treatment units of CETPs and ETPs for tannery wastewater treatment (Durai et al. 2011). The samples were collected at regular intervals of time and filtered through 0.45-µm filter, and the filtered samples were analyzed for soluble BOD, COD, sulfates and phenol content.

Results and Discussion

Characteristics of Syntan Containing Wastewater—Sulfone and Phenol Based

It was observed from the studies that the pH of the phenol- and sulfone-based syntan containing wastewater was acidic in nature. From Table 1, it can be observed that the BOD_5/COD ratio of phenol- and sulfone-based syntan containing wastewater is 0.087 and 0.033, respectively. This suggests that both the syntans have very low BI. Phenols of varying concentration were present in both the syntans. However, sulfate concentration was very low in case of phenol-based syntan containing wastewater. Also, it was observed from the results that the COD concentration was higher in the case of phenol-based syntan containing wastewater which may be attributed to the presence of phenols in the wastewater. The characteristics of sulfone- and phenol-based syntan containing wastewater are presented in Table 1.

Table 1 Characteristics of phenol- and sulfone-based syntan

Parameters	Phenol-based syntan	Sulfone-based syntan
pH	4.2	5.4
COD (mg/L)	4200.00	2300.00
$BOD_{5@20°C}$ (mg/L)	366.80	76.60
Phenol (mg/L)	807.00	107.50
Sulfates (mg/L)	4.50	685.30
BOD_5/COD ratio	0.087	0.033

Ozonation Studies

Optimization of Contact Time for Phenol-Based Syntan Containing Wastewater

Ozonation studies were carried out for a contact period of 30 min, and samples were collected at regular intervals of time. Ozonation studies were carried out at pH 4.0 and 8.0. Initially, for phenol-based syntan containing wastewater, the BI was only 0.087. Ozonation studies were carried out at pH 4.0 and pH 8.0 for a contact period of 30 min, and the results are presented in Fig. 1.

Direct ozonation at acidic pH mainly attacks the aromatic rings and results in cleaving of the molecules. The results indicated that increasing the contact time up to 15 min increased the BI to 0.170 and further increasing the contact time did not substantially increase the BI. Ozonation at alkaline pH resulted in generation of hydroxyl radicals for the treatment of phenol-based syntan containing wastewater. BI increased to 0.197 in 15-min contact time and further increasing the contact time did not improve the BI. Hence, 15-min contact time was selected as optimum contact time for phenol-based syntan containing wastewater both in acidic and alkaline pH conditions.

Ozonation was used as a pretreatment to eliminate toxic compounds such as polyphenols present in the wine distillery wastewater. Organic compounds present in the wastewater are partially oxidized to low molecular weight intermediates, which could eventually act as a substrate for microorganisms in subsequent aerobic treatment (Lucas et al. 2010). Similar observations were found in the present study also and resulted in increase in BI of phenol-based syntan containing wastewater.

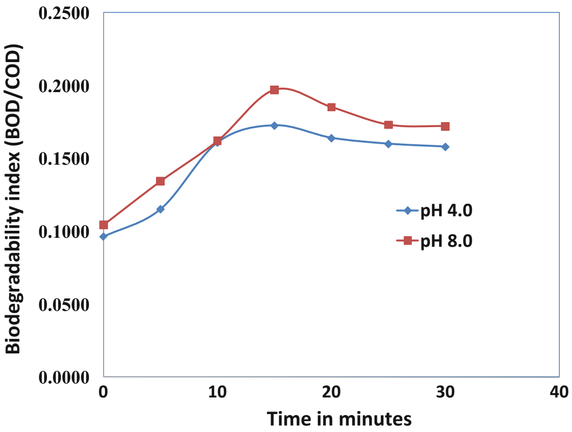


Fig. 1 Optimization of ozonation contact time for phenol-based syntan

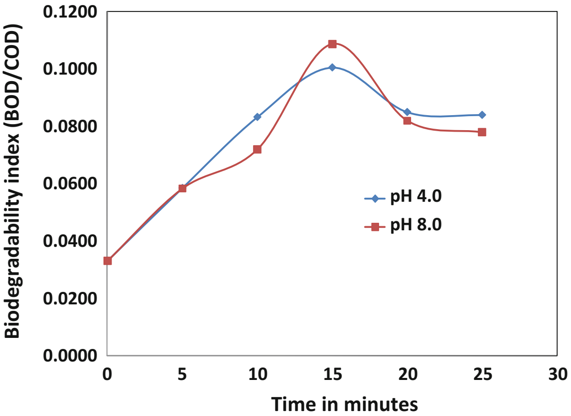
Optimization of Contact Time for Sulfone-Based Syntan Containing Wastewater

Ozonation studies were carried out for a contact period of 30 min, and samples were collected at regular intervals of time. Ozonation studies were carried out at pH 4.0 and 8.0. Initially, for sulfone-based syntan containing wastewater, the BI was 0.033. After ozonation at pH 4.0 for a contact period of 15 min, the BI increased to 0.1006 and the results are presented in Fig. 2. At pH 8.0, the BI increased from 0.033 to 0.1088 for contact period of 15 min. Further increasing the contact time did not substantially increase the BI. Hence, 15-min contact time was selected as optimum contact time for sulfone-based syntan containing wastewater both in acidic and alkaline pH conditions.

Assessment of Biological Treatment of Phenol- and Sulfone-Based Syntan Containing Wastewater Before and After Ozonation

The efficacy of biological treatment of wastewater containing phenol- and sulfone-based syntan containing wastewater was evaluated separately, with and without application of ozonation as pretreatment. The initial COD of phenol-based syntan containing wastewater was 4200 mg/L, and after ozonation for a contact period of 15 min it was 3600 and 4000 mg/L at pH 8.0 and 4.0, respectively. The COD removal efficiencies of the phenol-based syntan with and without ozonation are depicted in Fig. 3. For phenol-based syntan containing wastewater without any pretreatment, the percent removal of COD obtained was 1.36, 13.89 and 26.7 only after 3 h of aeration period in aerobic rectors. During 24 h of aeration period, COD removal efficiencies gradually increased and reached up to 16.36, 36.04 and 44.2%, respectively, for rectors operated without pretreatment and with pretreatment using ozonation at pH 4.0 and pH 8.0. Further, increasing the aeration period to 48 h resulted in COD removal of 23.68, 39.16 and 49.2%, respectively.

Fig. 2 Optimization of ozonation contact time for sulfone-based syntan



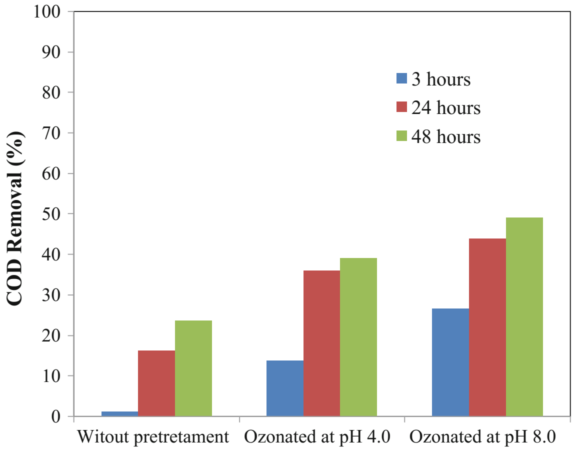


Fig. 3 Biological treatment of phenol-based syntan without and with pretreatment

When compared with aerobic studies of pre-ozonated samples at pH 4.0, ozonated samples at pH 8.0 indicated cleaving of the molecules by the hydroxyl radicals and resulted in generation of more biodegradable compounds when compared with molecular ozonation. For the raw sample, the mechanism for the reduction was mainly due to the binding of the syntan with the cell wall of the microbes. John Kennedy and Sekaran (2004) reported that the synthetic organic chemicals such as sulfonated mono-, di- and tri-nuclear aromatics, sulfonated azo aromatic compounds, sulfated or sulfited long-chain fatty acids present in tannery wastewater after biological treatment indicated their resistance toward biodegradation.

Assessment of Biodegradability Before and After Ozonation of Sulfone-Based Syntan

The initial COD of sulfone-based syntan containing wastewater was 2300 mg/L, and COD after ozonation for a contact period of 15 min was 1600 and 1800 mg/L at pH 4.0 and pH 8.0, respectively. For sulfone-based syntan containing wastewater without any pretreatment, the percent removal of COD obtained was 1.75, 12.29 and 15.45 only after 3 h of contact time in aerobic rectors. During 24 h of aeration period, COD removal efficiencies gradually increased and reached up to 3.20, 19.345 and 44.02%, respectively, for rectors operated without pretreatment and with pretreatment using ozonation at pH 4.0 and pH 8.0. Further, increasing the aeration period to 48 h resulted in percentage COD removal of 19.95, 29.85 and 49.91%, respectively. The results are presented in Fig. 4.

The biodegrading properties of aromatic syntans tested are closely associated with their chemical composition and molecular structure. Among the synthetic tannins, the sulfonated syntans and their formaldehyde condensates play a primary role and appear in tannery wastewater in significant concentrations after biological

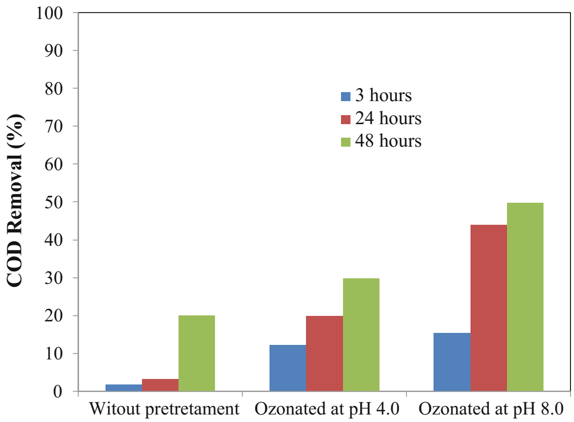


Fig. 4 Biological treatment of sulfone-based syntan without and with pretreatment

treatment and have been found to be persistent pollutants in surface waters (Munz et al. 2009).

The difficulty in biodegradation was due to the fact that syntans are inhibitors to microorganisms. The usage of syntans in tanneries cannot be avoided, and the effluent containing syntans cannot be treated effectively in the existing aerobic treatment unit without pretreatment. Even though pre-ozonation improves the biodegradability of syntans, some residual organics are still carried over in the treated effluent indicating that some of the compounds formed during ozonation resist biodegradation.

Conclusion

The study results clearly indicated that syntans containing wastewater cannot effectively be degraded in the aerobic biological system operated for tannery wastewater at F/M ratio of 0.15 without any pretreatment. The hydrogen bonding reactions with proteins cause toxicity to bacteria and interfere with the functioning of enzymes and resulted in lesser removal of COD of 3.2 and 16.36% for sulfone- and phenol-based syntans. Pre-ozonation improved the BI of the syntans which resulted in improved removal efficiencies of COD for both the syntans, i.e., phenol and sulfone based. Even though pre-ozonation improves the biodegradability of syntans, about 50% of COD are still carried over in the treated wastewater indicating that even after application of ozone; recalcitrant COD contributed by syntans was still persistent in the wastewater and can be classified as persistent organic pollutants.

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References

APHA, AWWA, WEF (1998) Standard methods for the examination of water and wastewater, 20th edn. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA

Beltran FJ (2003) Ozone reaction kinetics for water and wastewater systems. CRC Press

Chipasa KB, Medrzycka K (2008) Characterization of the fate of lipids in activated sludge. J Environ Sci 20:536–542

Durai G, Rajasimman M, Rajamohan N (2011) Kinetic studies on biodegradation of tannery wastewater in a sequential batch bioreactor. J Biotech Res 1:19–26

European Commission (2003) Integrated Pollution Prevention and Control (IPPC) reference document on best available techniques for the tanning of hides and skins. Accessible via http://eippcb.jrc.es/reference/tan.html

Fadila K, Chahlaouia A, Ouahbib A, Zaida A, Borja R (2003) Aerobic biodegradation and detoxification of wastewaters from the olive oil industry. Int Biodeterior Biodegradation 51:37–41

Lofrano G, Meric S, Belgiorno V, Napoli RMA (2005) Fenton's oxidation of different based synthetic tannins. In: Proceedings of the 9th international conference on environmental science and technology, Phodes Island, Greece, 1–3 Sept 2005

Lofrano G, Meric S, Zengin GE, Orhon D (2013) Chemical and biological treatment technologies for leather tannery chemicals and waste waters—a review. Sci Total Environ 265–281

Heredia JB, Torregrosa J, Dominguez JR, Garciam J (2000) Treatment of black-olive wastewaters by ozonation and aerobic biological degradation. Water Res 34:3515–3522

Kalyanaraman C, Kameswari KSB, Rao JR (2015) Studies on enhancing the biodegradation of tannins by ozonation and Fenton's oxidation process. J Ind Eng Chem 25:329–337

John Kennedy L, Sekaran G (2004) Integrated biological and catalytic oxidation of organics/inorganics in tannery wastewater by rice husk based mesoporous activated carbon - *Bacillus* sp. Carbon 42(12):2399–2407

Lucas MS, Peres JA, Li Puma G (2010) Treatment of winery wastewater by ozone-based advanced oxidation processes (O_3, O_3/UV and O_3/UV/H_2O_2) in a pilot-scale bubble column reactor and process economics. Sep Purif Technol 72(3):235–241

Munoz I, Rieradevall J, Torrades F, Peral J, Domènech X (2005) Environmental assessment of different solar driven advanced oxidation processes. Sol Energy 79(4):369–375

Munz G, De Angelis D, Gori R, Mori G, Casarci M, Lubello C (2009) The role of tannins in conventional and membrane treatment of tannery wastewater. J Hazard Mater 164(2):733–739

Phaniendra A, Ramachandra Rao CSV, Satish Babu R, Rema T (2011) Assessment of biodegradability of synthetic tanning agents used in leather tanning process. Int J Eng Technol. 3(5):302–308

Rema T, Ramanujam RA (2012) Decomposition of aromatic sulphonic syntan in aqueous solution using ozone. Int J Eng Technol 3(5):302–308

Soares OSG, Orfao JJ, Portela D, Vieira A, Pereira MFR (2006) Ozonation of textile effluents and dye solutions under continuous operation: influence of operating parameters. J Hazard Mater 137(3):1664–1673

Treatment of Synthetic Petroleum Refinery Wastewater in Anoxic Reactors at Varied Feed Phenol

Subrat Kumar Mallick and Saswati Chakraborty

Abstract Present study was carried out using simulated refinery wastewater of varying concentrations of phenol in feed along with diesel, sulphide, ammonia–nitrogen (NH_4^+–N) and nitrate–nitrogen (NO_3^-–N). Four reactors were maintained in anoxic environment with heterogeneous microorganisms grown on sponge cubes. Hydraulic retention time was constant of one day in all reactors. Degradations of phenol, diesel and organic COD were inhibited with increase in feed phenol concentrations. Denitrification increased as more amount of NO_3^-–N was consumed for phenol removal in anoxic environment. With increase in feed phenol, sulphide degradation was favoured and higher amount of feed sulphide was converted to elemental sulphur (S^0). Batch kinetics studies revealed complete degradation of all pollutants in anoxic condition, and time required for complete removal increased with increase in feed phenol concentration.

Keywords Denitrification · Refinery wastewater · Sulphide · Diesel
Phenol · Organic COD

Introduction

Increased demand of fossil fuel in both quantity and quality has raised the manufacture of petroleum products and generation of refinery effluents. Petroleum refineries are complex systems of multiple operations that depend on the type of crude refined and the desired products, which differentiate refineries from each other. The process of refining crude oil consumes large amounts of water. Consequently, significant volumes of wastewater are generated. It is reported that the volume of wastewater generated during crude oil processing is 0.4–1.6 times the oil processed (Coelho et al. 2006). Contamination in the liquid effluent is caused not

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only from the undesirable crude oil constituents, but also by various compounds introduced in the course of crude refining and product finishing operations (MoEF 2010). Aqueous effluents from petroleum refineries generated by different intra-industrial processes contain a diverse range of pollutants including oil, phenolics, sulphides, ammonia, dissolved solids, suspended solids, toxic metals and BOD exerting biodegradable organics (Chen et al. 2014). The pollutants released from petroleum refineries possess serious effects on the surrounding environment as well as can cause life-threatening diseases in living beings. Dissolved oxygen depletion in aquatic bodies, effect of sticky oily substances on aquatic animals, methemoglobinemia, cancer in various organs, decrease in fertility, heart disease in living beings and foul smell in respective areas are some of the adverse effects caused by these pollutants (Bakke et al. 2013).

Various physicochemical processes have been reported for the treatment of petroleum refinery wastewater which include coagulation (Santo et al. 2012), electrocoagulation (Wei et al. 2010), adsorption (Chen et al. 2014), chemical oxidation (Altas and Buyukgungor 2008), advance oxidation processes (Shahrezaei et al. 2012), membrane separation (Santos et al. 2016) and microwave-assisted catalytic wet air oxidation (Sun et al. 2008). Physicochemical operations generally comply with transfer of pollutants from one medium to other or precipitation through chemical reaction. Requirement of high amount of chemicals, generation of less disposable toxic sludge and fragile properties of membrane limit their application for the treatment of large volume of wastewater and increase the overall operational cost.

Biological treatment is the most inexpensive one to convert several toxic pollutants from toxic form to non-toxic form by microbial action. However, refinery wastewater is a complex mixture of diverse type of pollutants and treatment by biological methods making the whole treatment process very difficult and challenging. Aerobic reactors can be employed for the treatment of organic compounds in a very efficient way, but the volatile properties of the compounds (sulphide, BTEX, diesel) in refinery wastewater lead to their escape prior to biodegradation and hence polluting the surrounding air (Ghorbanian et al. 2014). Anaerobic reactors are not able to treat the petroleum hydrocarbon to the desired discharge limits. They need longer hydraulic retention time, and anaerobic biomass is highly sensitive to sulphide toxicity (Khong et al. 2012).

Recently, anoxic biodegradation of crude oil was studied in anoxic fixed film reactor by several researchers (Ghorbanian et al. 2014; Moussavi and Ghorbanian 2015). Oxidation of sulphide in anoxic reactor in the presence of nitrate is a relatively new technology (Cardoso et al. 2009). Literatures on simultaneous biodegradation of sulphide, oil and phenol in anoxic reactors are very scanty. The objective of the present study was to investigate the simultaneous biodegradation of sulphide, phenol, diesel, ammonia–nitrogen in anoxic reactor and to estimate reactor performance at varied feed phenol concentration.

Materials and Methods

Materials

Chemicals and Reagents

All the chemicals used were of either analytical grade (AR) or laboratory grade (LR). Phenol (C_6H_5OH), sodium sulphide ($Na_2S.xH_2O$), ammonium chloride (NH_4Cl), potassium nitrate (KNO_3) used as feed in the study were of analytical grade and obtained from Merck, India. Potassium dihydrogen phosphate (KH_2PO_4) and dipotassium hydrogen phosphate (K_2HPO_4) are taken for phosphate buffer. $MgSO_4.7H_2O$, $CaCl_2.2H_2O$, $FeCl_3.6H_2O$, $CuCl_2$, $ZnCl_2$, $NiCl_2.6H_2O$ and $CoCl_2$ used for trace metal solution were analytical grade and purchased from Merck, India. Yeast extract used as nutrient in feed was purchased from CDH, India. Potassium dichromate ($K_2Cr_2O_7$), ferrous ammonium sulphate, ferroin solution, ammonium hydroxide, 4-aminoantipyrene, potassium ferric-cyanate ($K_3Fe(CN)_6$), ethanol, trisodium citrate, sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$) used for various analysis were of analytical grade. Diesel was purchased from the nearby Indian Oil petrol pump. For preparation of feed to the reactors, tap water was used, whereas for reagent preparation, stock/standard solution preparation and analysis of samples, deionized water ($pH = 7 \pm 0.05$) or Millipore water ($pH = 5.6 \pm 0.1$) was used wherever applicable.

Biomass Support Material

Sponge sheet (polyurethane foam) was procured from local market and cut into cube sizes of approximately 1 cm × 1 cm × 1 cm, washed with tap water and dried overnight at 70 °C in a hot air oven before being used as biomass support material in the reactors. Sponge cubes had porosity 0.81, density 0.051 g/cm^3 and specific surface area 600 m^2/m^3. About 60 g (1550 Nos.) of oven-dried sponge cubes were placed in each 5-L reactors manually.

Experimental Methodologies

In this section, description of various experimental setups, reactor specification, feeding and operating conditions are given in detail. The reactor system was maintained at a constant temperature (30 ± 3 °C) using a temperature controlled blower in a closed room.

Seed Sludge

For anoxic reactors, initial inoculums were collected from anaerobic storage tank of Indian Oil Corporation Limited (IOCL), Noonmati, Assam. The collected inoculum had total solids 7.5 g/L and volatile solids 5 g/L. Three-litre sludge was used as inoculum in each reactor of working volume five litres, and remain was filled up with synthetic feed added in tap water.

Synthetic Feed

This study was conducted with synthetic feed consisting of phenol (0–300 mg/L as C_6H_5OH), sulphide (750 mg/L S^{2-} as $Na_2S x H_2O$), diesel (300 mg/L), ammonia–nitrogen (200 mg/L NH_4^+–N as NH_4Cl) and nitrate–nitrogen (1000 mg/L NO_3^-–N as KNO_3). Freshly prepared feed without the addition of sodium sulphide was purged with N_2 gas. Later required amount of $Na_2S x H_2O$ was added to the deoxygenated feed to avoid volatilization. Feed pH was maintained at 7.8–8.7 ± 0.2 by using 1 mL/L of phosphate buffer (using KH_2PO_4 72.3 g/L and K_2HPO_4 104.5 g/L). This also worked as a phosphorus source to the microorganisms. Yeast extract (10–20 mg/L) and trace metals solution (1 mL/L) were added as nutrients. The composition of stock trace metal solution was: $MgSO_4.7H_2O$: 10,000 mg/L, $CaCl_2.2H_2O$: 10,000 mg/L, $FeCl_3.6H_2O$: 5000 mg/L, $CuCl_2$: 1000 mg/L, $ZnCl_2$: 1000 mg/L, $NiCl_2.6H_2O$: 500 mg/L, $CoCl_2$: 500 mg/L (Chakraborty and Veeramani 2006).

Acclimatization of the Anoxic Reactors

The collected heterogeneous bacterial culture was fed with predetermined concentrations of phenol, sulphide, diesel and ammonia–nitrogen in anoxic condition for an acclimatization period of 145 days in four reactors named from R1 to R4. Acclimatization of all the reactors was similar and done simultaneously. Initially reactors were operated with phenol as the sole carbon source. Ammonia-N and nitrate-N were provided as nitrogen source where nitrate-N served as electron acceptor. Concentrations of phenol, ammonia-N and nitrate-N were increased at each 5-day interval up to 45 days. Sulphide was introduced on day 46 and gradually increased at each 5-day interval up to day 70 along with phenol, ammonia-N and nitrate-N. Diesel was introduced on day 71 and gradually increased at each 5-day interval along with sulphide, phenol, ammonia-N and nitrate-N. Before the study of varied phenol feed was initiated, the reactors were operated till the heterogeneous culture was completely acclimatized to the provided environment.

Reactor Operations with Varying Phenol

Phenol concentration was varied at four levels in four anoxic reactors. R1 was operated in the absence of phenol, whereas R2, R3 and R4 were operated with 100, 200 and 300 mg/L phenol, respectively. At each parameter variation, steady-state data were characterized by consistency of effluent quality of the reactors after a transient period of 10–12 days. Steady-state data were collected for 10–12 days and considered to analyse the performance of each reactor. The operational conditions of the anoxic reactors are summarized in Table 1.

Kinetics Study

Kinetics study was done in 250-mL plastic conical flasks with screw cap. Effective volume of each flask was 100 mL. For attached biomass, 31 (of the same proportion of anoxic reactors) biomass-loaded sponge cubes (10 from top, 10 from middle and 11 from bottom) were collected from the anoxic reactors (R1 to R4). For suspended biomass, 100 mL of suspended biomass was collected from anoxic reactors and centrifuged at 8500 RPM for 10 min. Both 31 biomass-loaded cubes and 100 mL centrifuged biomass were added in each flask. The conical flasks were placed in shaking incubator at 30 °C and 150 RPM. They were taken out one by one at predetermined interval of time, and the effluent was analysed for various parameters.

Analytical Methods

Standard techniques according to APHA (2005) have been followed for influent and effluent sample analysis. Samples of reactor effluents were collected and centrifuged at 8500 RPM for 10 min prior to analysis as per respective methods. Influent and effluent pH was measured using a digital pH meter with a sensitivity of 0.01 with temperature correction facility. The instrument was calibrated periodically with standard buffer solutions. Temperature was measured with thermometer.

Table 1 Operational conditions of anoxic reactors during varying phenol feed

Reactors	Feed (mg/L)					HRT (d)
	Sulphide	Phenol	Diesel	NH_4^+–N	NO_3^-–N	
R1	750	0	300	200	1000	↑ 1 ↓
R2	750	100	300	200	1000	
R3	750	200	300	200	1000	
R4	750	300	300	200	1000	

Analysis of phenol, sulphide, sulphate, ammonia-N, nitrate-N, nitrite-N and COD_T was done as per APHA (2005).

Due to the presence of diesel, COD digestion required longer time of 8 h instead of usual 2 h. All COD analyses were carried out for 8 h of digestion time at 150 °C. Sulphide is an inorganic compound, but also contributes to the total COD of the system. To determine the COD due to sulphide, different concentrations of sulphide were analysed for COD and observed that the COD of 1 mg/L sulphide is equal to 3.43 mg O_2/L. Therefore, organic COD was calculated by the following formula. Similarly COD due to 1 mg/L of thiosulphate was found to be 0.82 mg O_2/L experimentally and COD due to 1 mg/L nitrite –N was obtained to be 1.1 mg O_2/L (APHA 2005).

$$\mathrm{COD}_{\mathrm{Organic}} = \mathrm{COD}_{\mathrm{Total}} - (3.43 \times C_{\mathrm{S}}) - (1.1 \times C_{\mathrm{n}}) - (0.82 \times C_{\mathrm{T}}) \tag{1}$$

$\mathrm{COD}_{\mathrm{Organic}}$	COD due to phenol and diesel (mg O_2/L)
$\mathrm{COD}_{\mathrm{Total}}$	COD due to sulphide, phenol and diesel (mg O_2/L)
C_{S}	Residual concentration of sulphide (mg/L)
C_{n}	Concentration of nitrite –N (mg/L)
C_{T}	Concentration of thiosulphate (mg/L)

Diesel was analysed by solvent extraction method described by Evdokimov and Losev (2007) by using *n*-hexane as solvent and corrected for interference of phenol.

For the analysis of thiosulphate, the sulphide in the effluent was precipitated by the addition of 4 drops of 1 M zinc acetate solution. The solution was filtered and used as titrant. Standard iodine solution was prepared by adding 10 mL each of 0.02 N $K_2Cr_2O_7$, 10% KI solution and 1 M H_2SO_4 in a stoppered bottle and kept in dark for 10 min. The iodine produced was titrated against the sulphide-free effluent solution till pale yellow colour. Starch indicator (5 drops) was added, and titration was continued till the disappearance of blue colour. The normality of thiosulphate was calculated by the following formula.

$$N_{\mathrm{PD}} \times V_{\mathrm{PD}} = N_{\mathrm{ST}} \times V_{\mathrm{ST}} \tag{2}$$

where

N_{PD}	Normality of potassium dichromate (0.02 N)
V_{PD}	volume of potassium dichromate
N_{ST}	normality of sodium thiosulphate
V_{ST}	volume of sodium thiosulphate

Generation of elemental sulphur during the study was calculated by the mass balance of the sulphur compounds which was calculated by the following formula.

$$\mathrm{S}^0 = \mathrm{Sulphide}_{\mathrm{inf}} - \left[\mathrm{Sulphide}_{\mathrm{eff}} + (0.57 \times \mathrm{Thiosulphate}_{\mathrm{eff}}) + \left(\frac{\mathrm{Sulphate}_{\mathrm{eff}}}{3}\right)\right] \tag{3}$$

where

S^0	elemental sulphur (mg/L),
$\text{Sulphide}_{\text{inf}}$	influent sulphide (mg/L),
$\text{Thiosulphate}_{\text{eff}}$	effluent thiosulphate (mg/L) and
$\text{Sulphate}_{\text{eff}}$	effluent sulphate (mg/L)

Microscopic Images

For the scanning electron microscope (SEM) photograph, fragments of sponge cube containing the microbial biofilm were sampled from the reactors, dried and cut into small thin pieces. The sample was mounted on aluminium stubs and then coated with gold using sputter coater. The stubs were then introduced into the specimen chamber of the microscope for scanning.

Results and Discussion

Steady-State Performance of the Anoxic Reactors During Varying Feed Phenol Concentration

Growth of biomass in the reactors was observed as change in the colour of the sponge cubes from yellow to brown and then to dark brown. Pollutants were utilized when the solution containing feed seeped through the pores of the sponge cubes already impregnated by the growth of biomass. Microscopic view of the reveal pores and growth of biomass inside the sponge cubes is shown in Fig. 1. Average steady-state performance of the reactors is summarized in Tables 2 and 3. Maximum 91% phenol removal was observed in R2 (influent phenol 100 mg/L) and gradually decreased to 74 and 63% in R3 and R4, respectively, with increase in

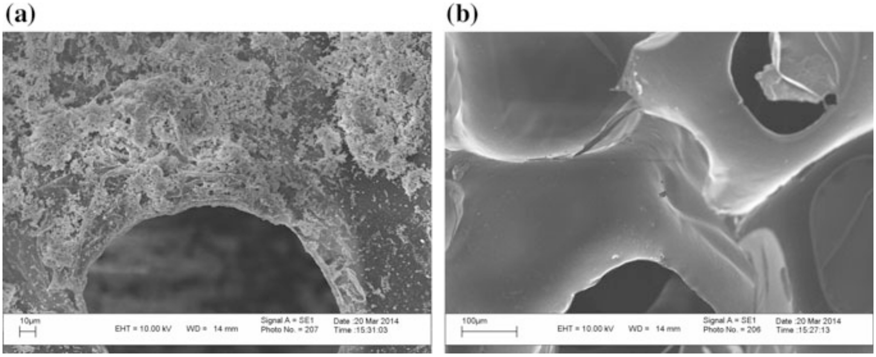

Fig. 1 **a** SEM image of PUF without biofilm, **b** SEM image of PUF with biofilm

Table 2 Influent and effluent concentrations of organic COD, phenol and diesel during varying phenol feed at 24-h HRT

Reactor	Organic COD (mg/L)		Phenol (mg/L)		Diesel (mg/L)	
	Initial	Final	Initial	Final	Initial	Final
R1	476.19 ± 58.89	313.57 ± 47.75	–	–	305.74 ± 2.03	115.59 ± 2.67
R2	770.25 ± 60.76	500.03 ± 54.55	101.20 ± 0.71	8.82 ± 1.82	306.67 ± 2.94	136.69 ± 3.35
R3	1095.03 ± 28.93	612.14 ± 35.03	201.85 ± 1.19	52.12 ± 0.41	307.14 ± 1.98	149.21 ± 3.22
R4	1351.17 ± 42.76	787.62 ± 43.90	305.35 ± 2.22	114.46 ± 1.56	307.87 ± 1.93	166.42 ± 3.59

*Represented data are the average of 15 days of steady-state condition

*Data are in the form of value ± standard deviation

Table 3 Influent and effluent concentrations of sulphide, thiosulphate, sulphate and nitrate-N during varying phenol feed at 24-h HRT

Reactor	Sulphide (mg/L)		Thiosulphate (mg/L)	Sulphate (mg/L)	Nitrate-N (mg/L)		Nitrite-N (mg/L)	Gas (mL)
	Initial	Final	Final	Final	Initial	Final	Final	Final
R1	753.07 ± 4.05	350.24 ± 9.49	2.73 ± 0.56	840.56 ± 50.88	1046.82 ± 4.45	609.51 ± 6.43	134.17 ± 4.74	190 ± 15
R2	759.54 ± 5.00	315.70 ± 5.11	11.61 ± 0.96	776.49 ± 19.60	1043.46 ± 6.29	505.39 ± 5.34	124.67 ± 4.41	230 ± 10
R3	754.18 ± 3.97	293.07 ± 7.94	16.22 ± 1.11	776.02 ± 19.59	1045.78 ± 11.47	416.68 ± 8.68	121.96 ± 4.31	250 ± 10
R4	754.18 ± 3.05	267.02 ± 0.48	10.34 ± 0.69	745.88 ± 18.83	1049.52 ± 8.44	315.13 ± 5.64	119.25 ± 4.21	270 ± 10

*Represented data are the average of 15 days of steady-state condition

*Data are in the form of value ± standard deviation the influent phenol concentration (Fig. 2a). In the literature, it has been reported that degradation of phenol (sole electron donor) inhibited beyond the concentration of 300 at 20 mg/L nitrate-N concentration (Vasiliadou et al. 2008). In the present case, removal was significant even in the presence of two other electron donors (sulphide and diesel).

Diesel degradation was maximum in the absence of phenol and decreased with increase in the influent phenol (Fig. 2a). Maximum 62% diesel removal was observed in R1 and decreased to 46% in R4. Diesel removal decreased because of its immiscible nature, and therefore, soluble phenol was preferred by the biomass as main carbon source. Also increased toxicity to the diesel degrading microorganisms due to increased phenol could be a possible reason for the decline in the diesel removal. Increase in the influent phenol increased the influent organic COD from 476 mg O_2/L to 1351 mg O_2/L (Table 2) due to contribution of phenol to organic COD. Removal of organic COD remained from 35 to 44% during the study (Fig. 2a).

Sulphide removal slightly increased with increase in the influent phenol. In R1, 53% sulphide removal was observed in the absence of phenol. Sulphide removal of 58, 61 and 65% was observed in R2, R3 and R4, respectively (Fig. 2b). The final product of the degradation of sulphide was sulphate, and its concentration decreased with increase in the phenol from 840 to 627 mg/L and elemental sulphur formation increased from 16 to 45%. Thiosulphate concentration was asymptotic and ranged between 2 and 16 mg/L.

Nitrate-N was the sole electron acceptor in the systems (phenol, diesel, sulphide as electron donors), and competition increased with increase in the influent phenol. Although removal of sulphide slightly increased with increase in phenol concentration, partial degradation dominated the total degradation of sulphide. Therefore, there were less formation of the final product (sulphate) and more formation of the intermediate products (elemental sulphur and thiosulphate). Nitrate-N removal increased with increase in the initial phenol concentration from 42 to 70% (Fig. 2b) as more nitrate-N was utilized for the degradation of phenol as well as sulphide.

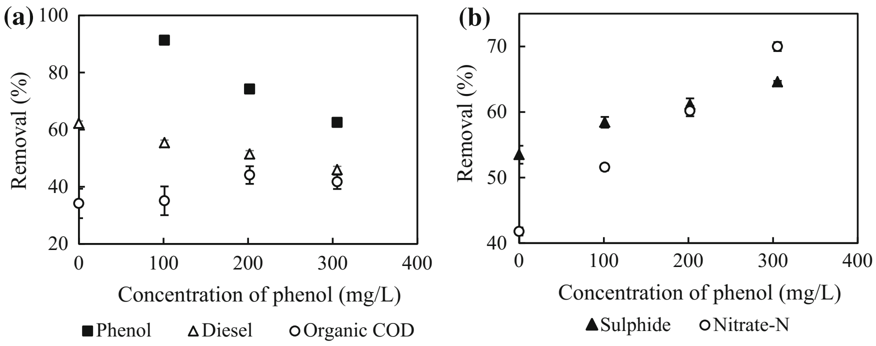

Fig. 2 Effect of initial phenol feed on the removals of **a** phenol, diesel and organic COD, **b** sulphide and nitrate-N

Nitrite-N (NO_2^--N) production in the reactors decreased from 134 to 119 mg/L, and gas production increased from 190 to 270 mL (Table 3).

Removal Kinetics of Phenol, Sulphide, Nitrate, Organic COD During Varying Feed Phenol Concentration

The kinetics of pollutants removal at varied phenol feed is shown in Fig. 3. Complete degradation of all the pollutants was observed, but there was increase in the total degradation time with increase in the influent phenol feed. Phenol degradation started instantly at initial concentration of 100 mg/L. Lag time for initiation of phenol removal increased to 3 and 4 h when the concentration was increased to 200 and 300 mg/L, respectively. Increased toxicity due to higher phenol led to the late start and slower degradation. Similarly, complete removal of

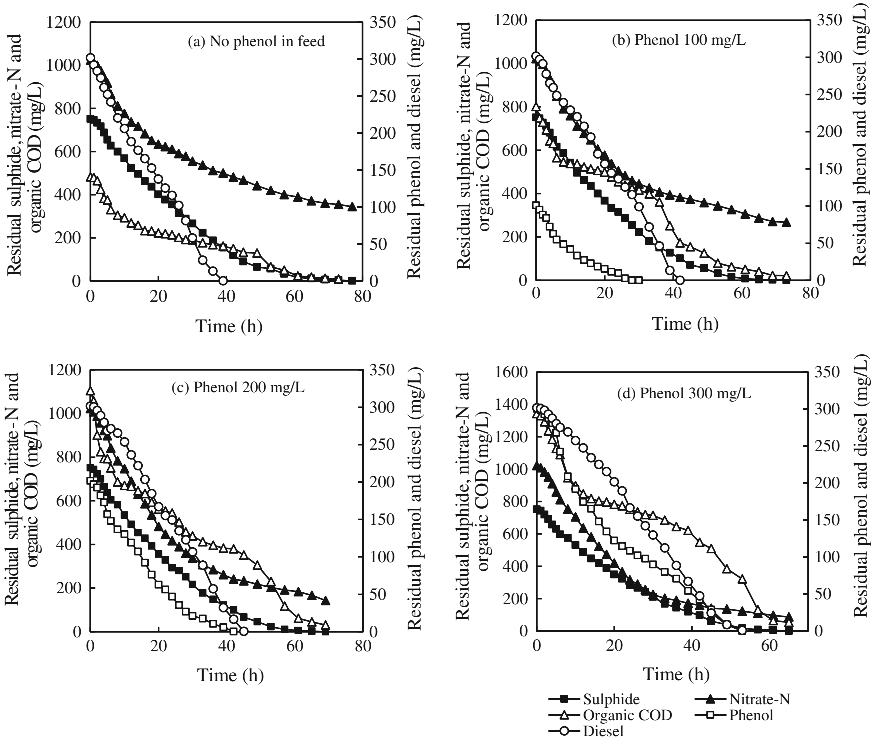

Fig. 3 Removal kinetics of phenol, sulphide, diesel, organic COD and nitrate-N at various influent phenol loading

diesel was achieved but there was increase in the degradation time as influent phenol concentration increased. With increase in phenol feed, the initial lag time for diesel degradation increased. Diesel degradation started at 2 h in the absence of phenol, which increased to 10 h at influent phenol 300 mg/L. Hence, there was increase in the complete degradation time of diesel from 39 to 53 h at constant in feed (300 mg/L). Mukherji et al. (2004) reported 80% diesel (200 mg/L) degradation in denitrifying condition in 50 days which was higher than the present study. Organic COD was removed faster at the initial stages but later became slower due to simultaneous slow degradation of phenol and diesel. At the end of the degradation study, organic COD was always less than 100 mg/L.

Sulphide degradation became faster with increase in the phenol concentration and took comparatively less time with each increase in the phenol concentration. Degradation of sulphide occurred simultaneously with phenol and diesel. No lag time was observed for the degradation of sulphide as it was observed in case of phenol and diesel degradation. Self-inhibition of phenol degrading organisms and toxicity towards diesel degradation led to faster thrive of the sulphide degrading organisms at alkaline pH. Thus, sulphide degradation became faster with each increase in phenol feed. It can be observed that at constant influent sulphide (750 mg/L) total degradation time decreased from 77 to 65 h with increase in the phenol concentration from 0 to 300 mg/L. Initially phenol removal was slow as long as there was high sulphide in the reactor. Degradation of phenol and diesel became faster with decrease in the sulphide concentration. Although simultaneous removals of phenol, sulphide and diesel occurred during the study, the degradation of sulphide was faster than both phenol and diesel. Hsien and Lin (2005) found complete degradation of phenol (70 mg/L) at 50 h in denitrifying condition and increase in biomass along with decrease in phenol. The literature supports the generation of biomass by phenol degradation, but degradation time was much high compared to the present study (30 h for 100 mg/L).

Removal of nitrate-N increased with initial phenol and became faster with increase in the influent phenol. Effluent nitrate-N after the removal of phenol, diesel and sulphide was 340, 270, 140 and 85 mg/L, respectively, for initial phenols of 0 to 300 mg/L. Therefore, complete removal of nitrate was never observed during the study, suggesting complete anoxic condition prevailed during the total degradation kinetics study. No lag time for nitrate-N degradation was observed as phenol, diesel and sulphide were degraded simultaneously which consumed nitrate-N from the systems.

Conclusions

Degradations of phenol and diesel were negatively affected by increase in the influent phenol due to self-inhibition and toxicity, respectively. Decrease in the degradation of diesel was due to preference of soluble carbon source over immiscible carbon source. Sulphide oxidation increased with increase in phenol, but led to partial degradation as more elemental sulphur and thiosulphate production at higher initial phenol concentrations. Generation of sulphate decreased with increase in feed phenol concentration. Nitrate-N degradation increased as more electron acceptor was utilized in the degradation of phenol. Complete degradation of nitrate-N was enhanced as there was less formation of nitrite-N and more generation of N_2 gas. Batch kinetics study revealed that degradation of both phenol and diesel started with a lag time which increased with each level of phenol feed. No lag time was observed for sulphide and nitrate-N degradation, and the degradation rate got faster with each increase in the influent phenol feed. Complete degradation of all the pollutants was achieved with increase in the complete degradation time. Complete nitrate-N degradation was never achieved ensuring anoxic condition throughout the study. Further studies are needed to analyse the effect of higher concentrations of phenol (more than 300 mg/L) on the degradation of sulphide and diesel.

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References

Altas A, Buyukgungor H (2008) Sulphide removal in petroleum refinery wastewater by chemical precipitation. J Hazard Mat 153:462–469

APHA, AWWA, WPCF (2005) Standard methods for the examination of water and wastewater, 21st edn. American Public Health Association, Washington, DC

Bakke T, Klungsøyr J, Sanni S (2013) Environmental impacts of produced water and drilling waste discharges from the Norwegian offshore petroleum industry. Marine Environ Res 92 (1):154–169

Cardoso RB, Texier AC, Alvarez RS, Flores ER, Field JA, Gomez J (2009) Effect of initial sulphide concentration on sulphide and phenol oxidation under denitrifying conditions. Chemosphere 74(1):200–205

Chakraborty S, Veeramani H (2006) Effect of HRT and recycle ratio on removal of cyanide, phenol, thiocyanate and ammonia in an anaerobic–anoxic–aerobic continuous system. Process Biochem 41:96–105

Chen C, Wei L, Guo X, Guo S, Yan G (2014) Investigation of heavy oil refinery wastewater treatment by integrated ozone and activated carbon supported manganese oxides. Fuel Process Technol 124(1):165–173

Coelho A, Castro VA, Dezotti M, Sant'Anna GL Jr (2006) Treatment of petroleum refinery wastewater by advanced oxidation processes. J Hazard Mat B137:178–184

Evdokimov IN, Losev AP (2007) Potential of UV-visible absorption spectroscopy for characterizing crude petroleum oils. Oil and Gas Business

Ghorbanian M, Moussavi G, Farzadkia M (2014) Investigating the performance of an up-flow anoxic fixed-bed bioreactor and a sequencing anoxic batch reactor for the biodegradation of hydrocarbons in petroleum-contaminated saline water. Int Biodeterior Biodegradation 90 (1):106–114

Hsien TY, Lin YH (2005) Biodegradation of phenolic wastewater in a fixed biofilm reactor. Biochem Eng J 27:95–103

Khong FC, Isa MH, Kutty SRM, Farhan SA (2012) Anaerobic treatment of produced water. World Acad Sci Eng Technol 62(1):798–802

Moussavi G, Ghorbanian M (2015) The biodegradation of petroleum hydrocarbons in an upflow sludge blanket/fixed-film hybrid bioreactor under nitrate-reducing conditions: performance evaluation and microbial identification. Chem Eng J 280(1):121–131

Mukherji S, Jagadevan S, Mohapatra G, Vijay A (2004) Biodegradation of diesel oil by an arabean sea sediment culture isolated from the vicinity of an oil field. Bioresour Technol 95(1):281–286

Santo CE, Vilar VJP, Botelho CMS, Bhatnagar A, Kumar E, Boaventura RAR (2012) Optimization of coagulation-flocculation and floatation parameters for the treatment of a petroleum refinery effluent from a Portuguese plant. Chem Eng J 183:117–123

Santos B, Crespo JG, Santos MA, Velizarov S (2016) Oil refinery hazardous effluents minimization by membrane filtration: an on-site pilot plant study. J Environ Manag 1–8

Shahrezaei F, Mansouri Y, Zinatizadeh AAL, Akhbari A (2012) Process modelling and kinetic evaluation of petroleum refinery wastewater treatment in a photocatalytic reactor using TiO_2 nanoparticles. Powder Technol 221:203–212

Sun Y, Zhang Y, Quan X (2008) Treatment of petroleum refinery wastewater by microwave-assisted catalytic wet air oxidation under low temperature and low pressure. Sep Purif Technol 62(3):565–570

Technical EIA Guidance Manual for Petroleum Refining Industry (2010) The Ministry of Environment and Forests, Government of India

Vasiliadou IA, Tziotzios G, Vayenas DV (2008) A kinetic study of combined aerobic biological phenol and nitrate removal in batch suspended growth cultures. Int Biodeterior Biodegradation 61:261–271

Wei L, Guo S, Yan G, Chen C, Jiang X (2010) Electrochemical pretreatment of heavy oil refinery wastewater using a three-dimensional electrode reactor. Electrochimia Acta 55:8615–8620

Fluoride Pollution Abatement

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Abstract In the present research article, earlier research studies on the impact of fluoride on human health have been reviewed as well. Further, an experimental study has been carried out in order to evaluate the efficiency of alumina to absorb fluoride, for it is widely used as de-fluoridation filter material. The study focuses on the task of finding governing factors that optimize the efficiency of absorption process and thus learn how this technique might be enhanced. Alumina are a complex process in which differences in surface morphology, pH, temperature, fluoride concentration, and the presence of other major ions such as sulfates and bicarbonates interact to produce a wide range of reported specific sorption values. This method would be more economic as well as effective if the water would be allowed to flow through some common and easily available materials such as cement granules, cement-sand granules, pipel leaves, bone charcoal, and some industrial wastes before the using of alumina.

Keywords Filtration process of drinking water · Fluoride contamination
Dental fluorosis · Skeletal fluorosis · Water treatment · Fluoride absorbents

Introduction

Fluoride contamination in drinking water is a major water pollutant in many areas around the world nowadays. Fluoride is known to cause diseases like dental fluorosis, Alzheimer's disease, dementia, skeletal fluorosis, and other hormonal

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disturbances. Excessive fluoride concentrations have been reported in groundwater of more than 20 developed and developing countries including India where 19 states are facing acute fluorosis problems. In addition to the fluoride-affected Indian states like Andhra Pradesh and Punjab, the specified regions of Birbhum district of West Bengal have already been declared to be fluoride-polluted by the Public Health Engineering Department. Various technologies are being used to remove fluoride from water, but the problem has not been rooted out yet. There are several methods for fluoride removal, and here, we discuss mainly the absorption method that has recently received attention as a suitable option. Before devising an appropriate filtering process to find the solution for fluoride contamination, it is well again to have a better understanding about its origin and physiochemical characteristics. Fluorine is the lightest member of the halogen group and is one of the most reactive of all chemical elements. In the environment, it is not found as fluorine. It is the most electronegative of all the elements which means that it has a strong tendency to acquire a negative charge and in the solution forms F^- ions. Fluoride ions have the same charge and nearly the same radius as hydroxide ions and may replace each other in mineral structures (Hem 1989). Fluoride thus forms mineral complexes with a number of cations, and some fairly common mineral species of low solubility contain fluoride. Other oxidation states are not found in natural systems, although uncharged complexes may be.

Fluoride in environment is therefore found as fluorides which together represent about 0.06–0.09% of the earth's crust. The average crustal abundance is 300 mg/kg. Fluoride is found at significant levels in a wide variety of minerals including fluorspar, rock phosphate, cryolite, apatite, mica, and others. Fluorspar contains the highest percentage of fluoride by weight of the minerals mentioned. Table 1 shows the permissible limit of fluoride of drinking water as defined by different organization.

Table 1 Permissible limit of fluoride of drinking water

Name of organization	Desirable limit (mg/L)	Sources
Bureau of Indian Standards	0.6–1.2	IS 10500: 2012
Indian Council of Medical Research	1.0	Kumar and Puri (2012)
The Committee on Public Health Engineering Manual and Code of Practice, Government of India	1.0	Bhagan et al. (1996)
World Health Organization (International Standards for Drinking Water)	1.5	Fawell et al. (2006)

Sources of Fluoride

Different sources of Fluoride include:

1. Groundwater
2. Air
3. Dental products: There are so many products for the children to reduce dental decay contains fluoride. This includes

Toothpaste	1.0–1.5 g kg^{-1} fluoride,
Fluoride Solutions and Gels	0.25–24.0 mg kg^{-1} fluoride,
Fluoride Tablet	0.25, 0.50, or 1.00 mg.

These products contribute to total fluoride exposure, albeit to different degrees. It is estimated that the swallowing of tooth paste by some children may contribute about 0.50 or 0.75 mg fluoride per child per day.

Food and Beverages: In Barley and rice (e.g. about 2 mg kg^{-1}) and taro, yams and cassava been found to contain relatively high fluoride levels. In general, the levels of fluoride in meat (0.2–1.0 mg kg^{-1}) and fish (2–5 mg kg^{-1}) are relatively low. Fish-protein concentrates may contain up to 370 mg kg^{-1} fluoride. However, Even with a relatively high fish consumption in a mixed diet, the fluoride intake from fish alone would seldom exceed 0.2 mg F^- per day. Milk typically contains low levels of fluoride, e.g. 0.02 mg L^{-1} in human breast milk and 0.02–0.05 mg L^{-1} in cow's milk. Tea leaves contain high levels of fluoride (up to 400 mg kg^{-1} dry weight). Fluoride exposure due to the ingestion of tea has been reported to range from 0.04 to 2.7 mg per person per day.

Effects of Fluoride

Fluoride has a significant mitigating effect on dental caries if the concentration is approximately 1 mg/L. However, continuing consumption of higher concentrations can cause dental fluorosis and in extreme cases even skeletal fluorosis. According to WHO guideline, the value for fluoride in drinking water is 1.5 mg/L (WHO 1984; Fawell et al. 2006). The effects of fluoride on humans when consumed in excess are briefly outlined below.

Effects on Humans

The effects of long-term exposure to naturally occurring fluoride from drinking water and other environmental sources are the major concern with regard to human health. A large number of epidemiological studies have been conducted in many countries concerning the effects of long-term exposure to fluoride. The effects on human can be seen in as effects on teeth, skeletal effects, and cancer.

Effects on Teeth

The first reports of the occurrence of dental fluorosis date back to 1888, when a family from Durango, Mexico, was described a shaving “blackteeth.” Dental fluorosis is caused by an elevated fluoride level in, or adjacent to, the developing enamel. High levels of fluoride present in concentrations up to 10 mg/L were associated with dental fluorosis (yellowish or brownish striations or mottling of the enamel), while low levels of fluoride, less than 0.1 mg L^{-1}, were associated with high levels of dental decay. Figure 1 shows the dental fluorosis ranging from very mild condition to severe condition.

Skeletal Effects

Crippling skeletal fluorosis can result from osteosclerosis, ligamentous, and calcification and extreme bone deformity. Evidence from occupational exposure also indicates that exposure to elevated concentrations of fluoride in the air may also be a cause of skeletal fluorosis. Figure 2 shows the skeletal fluorosis.

Fig. 1 Dental fluorosis

Fig. 2 Skeletal fluorosis

Cancer

There have been a significant number of epidemiological studies examining the possible association between various cancers and exposure to fluoride in drinking water. However, in spite of a large number of studies, there is no consistent evidence to demonstrate any association between the consumption of controlled fluoridated drinking water and cancer.

According to Central Pollution Control Board (PCB), the effects of fluoride levels in drinking water on human health are tabulated in Table 2.

Table 2 Different fluoride level affecting on human body

Fluoride (mg/L)	Effects on human body
Less than 0.5	Dental cavities
0.5–1.0	Protection against dental cavities. Care of bone and teeth
1.5–3.0	Dental fluorosis
3.0–10	Skeletal fluorosis (adverse changes in bone structure)
10 or more	Crippling skeletal fluorosis and severe osteosclerosis

Source Meenakshi and Maheshwari (2006)

Status of Fluoride Contamination Around the Globe

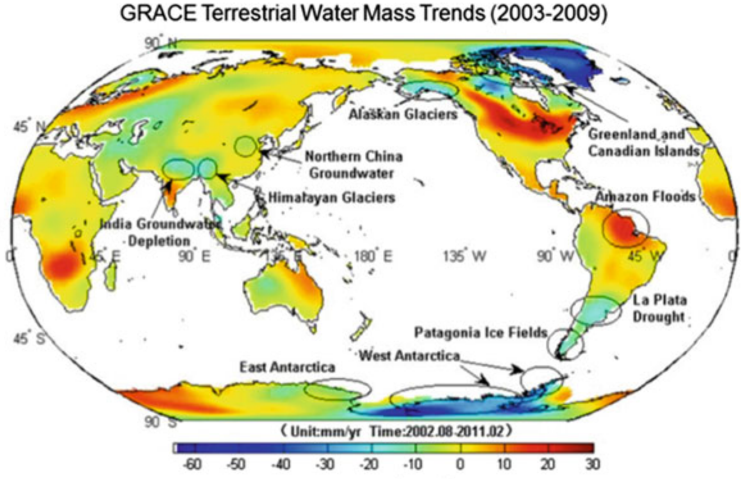
The World Scenario

In 1984, WHO estimated that more than 260 million people living all over the world consume water with fluoride concentration above 1 mg/L. UNICEF estimates that “fluorosis is endemic in at least 25 countries” and around 200 million people from 25 nations have health risks because of high fluoride in groundwater, and in India, around 25 million people of 150 districts are affected by fluorosis disease. Figure 3 shows the global scenario of fluoride contamination.

Indian Scenario

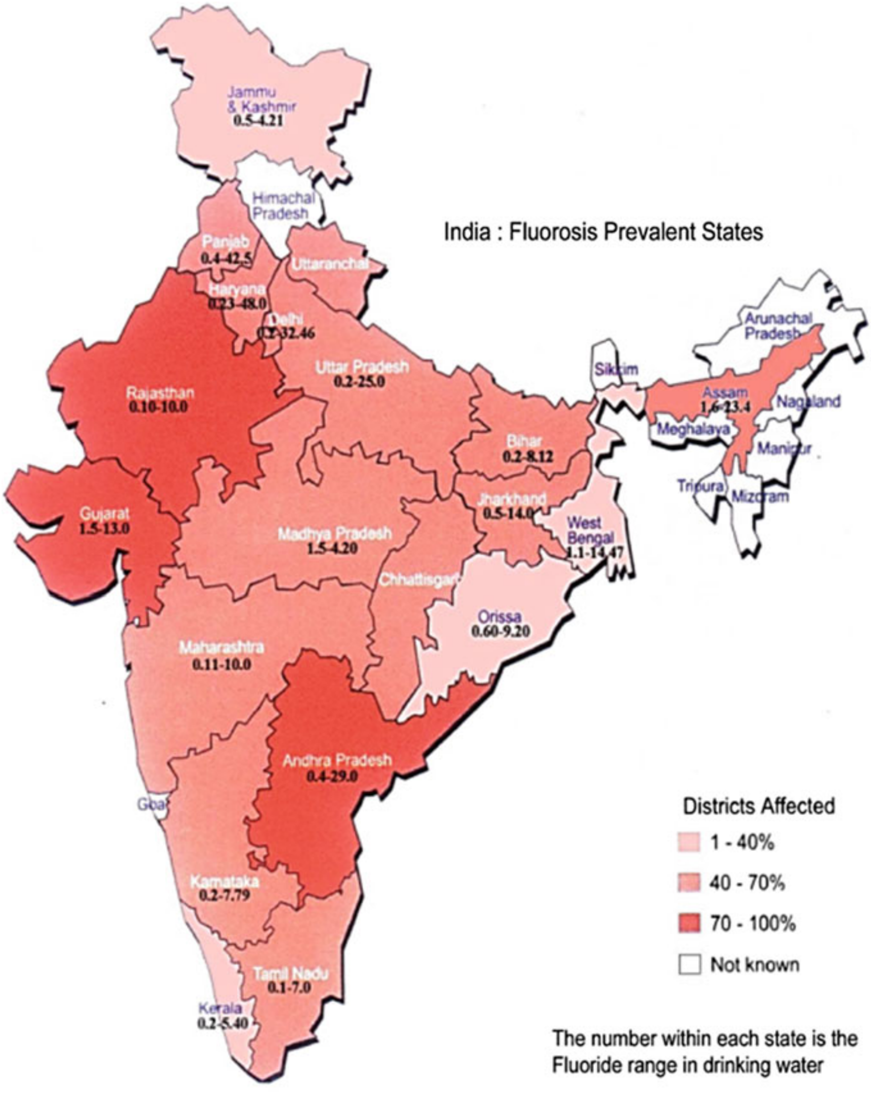
In the year 1991, 13 of India’s 32 states and union territories were reported to have naturally high concentrations of fluoride in water (Mangla 1991), but this had risen to 17 by 1999 (UNICEF). The most seriously affected areas are Punjab, Haryana, Andhra Pradesh, Rajasthan, Gujarat, Tamil Nadu, and Uttar Pradesh. The highest concentration observed to date in India is 48 mg L^{-1} in Rewari district of Haryana (UNICEF). Figure 4 shows the map with areas affected by fluoride contamination. Table 3 lists out the fluoride concentrations reported in groundwater in different parts of India.

Efforts to address the problem of fluoride in rural water supplies in India have been led by the Rajiv Gandhi National Drinking Water Mission. There have been



Source: Jin (2013)

Fig. 3 Global scenario of fluoride contamination



Source of information: 1) UNICEF State of Art Report, 1999
2) FR & RDF data bank

Fig. 4 Figure showing fluoride contaminations in India

no comprehensive health surveys for dental fluorosis from which the overall extent of the problem could be assessed. Nevertheless, in the most affected states listed above, half or more of the districts have some villages with groundwater supplies having high fluoride concentrations. In these states, 10–25% of the rural population has been estimated to be at risk.

Table 3 Fluoride concentrations reported in groundwater of India

Region/State	Fluoride concentration (mg L^{-1})	Maximum severity of fluorosis observed
Northwest India	0.4 –19	Severe
Central India	0.2–10	Moderate
South India	0.2–20	Severe
Deccan Province	0.4–8	Moderate

Sources Agarwal et al. (1997), Yadav et al. (1999)

Not all Indian states are equally affected, and the number of districts with endemic fluorosis within each state varies. Nine out of eighteen districts in West Bengal were recently identified as having fluoride-contaminated groundwater. It has been estimated that the total population consuming drinking water containing elevated levels of fluoride is over 66 million. In Rajasthan's Dungarpur district, activated alumina and Nalgonda de-fluoridation are practiced. De-fluoridation kits have been distributed at household level under the sponsorship of UNICEF. In Andhra Pradesh, the use of check dams has been investigated. The check dams, which are having rainwater harvesting structures, are designed to provide artificial recharge of groundwater.

Fluoride Contamination of Groundwater in West Bengal

In West Bengal, fluoride contamination of groundwater was first detected during 1997 at Nasipur area of Nalhati-I Block in Birbhum. Water supply arrangement based on riverbed tube wells (River Tripita) was provided as an alternative source of drinking water in the area. As a follow-up of the report on very high incidence of fluoride contamination of tube well waters of Nasipur area in Nalhati Block I of Birbhum district, GSI conducted one study covering an area of about 600 km^2 and observed that the fluoride-contaminated water occurs mostly within tube wells tapping groundwater within the basaltic rocks of Rajmahal trap. The dug wells, ponds, and tube wells tapping water from alluvium sediments are generally free from contamination beyond 1.50 mg/L. GSI also observed and reported that the Precambrian terrain with fractured/shear zones are possible locale for fluoride contamination in groundwater in parts of Purulia and Bankura districts. Habitation Survey 2003 conducted by PHED reveals the occurrence of fluoride in groundwater beyond 1.50 mg/L in 46 Blocks of 8 districts. Figure 5 shows the affected districts of West Bengal.

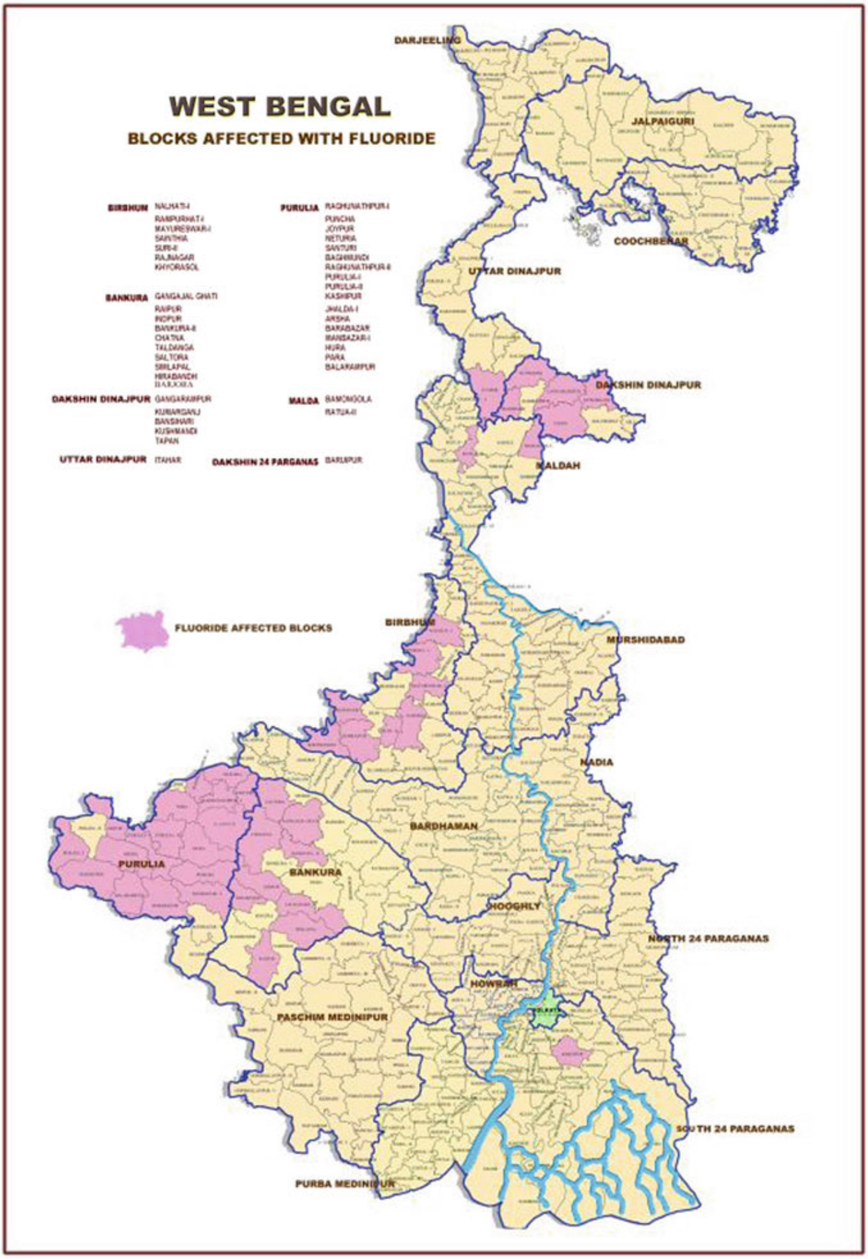


Fig. 5 Fluoride-affected districts in West Bengal

Water Supply Scheme by PHED, West Bengal

There are 166 Piped Water Supply Schemes (PWSS) in these Blocks as listed below.

1. Purandarpur Water Supply Scheme in Suri-II Block.
2. Agacha Water Supply Scheme in Kumarganj Block.
3. Matpalsa Water Supply Scheme in Sainthia Block of Birbhum District.
4. Dhiltail Water Supply Scheme in Bansihari Block of Dakshin Dinajpur District.

Objective of the Study

The objective of the study were as follows:

1. To study various methods of De-fluoridation,
2. To have an insight into the various materials that give much remedy to the problem of fluoride contamination and
3. To conduct comparative study of the following de-fluoridation methods as outlined below using fluoride-contaminated water collected from Nasipur, Lakshmikantapur, Nalhati, Rampurhat, Suri in Birbhum District, West Bengal. The de-fluoridation methods include (a) adsorption methods using activated alumina, cement granules, and cement-sand granules and (b) electro-coagulation method using alumina–alumina electrode combination.

Remedial Material

Here, we discuss some materials which give much remedy to the problem of fluoride contamination of groundwater.

Alumina and Aluminum

Among the adsorbents, activated alumina is one of the most important materials for de-fluoridation of water. For fluoride removal from water, acidic alumina, amorphous $Al(OH)_3$, gibbsite, or alumina (Al_2O_3) are used. It was found that this adsorbent react with fluoride at pH range 3–8 with fluoride concentration 1.9–19 mg/L. At pH 5–7, maximum fluoride removal was found to be 16.3 mg/g. At higher pH, fluoride adsorption on alum occurred due to electrostatic repulsion of fluoride ion to the negatively charged surface of alumina, competition for active sites by exclusive amount of hydroxide ion. At pH 7, adsorption capacity was obtained as 1450 mg/kg. De-fluoridation increased at pH 4–7 but decreased thereafter. At pH >7, silicates and hydroxyl ions were considered to compete with F^- ions for alumina exchange sites, but at pH <7, alumina fluoro complexes were formed in the presence of aluminum ions in the treated water. The proposed method is selective for aluminum fluoride complexes and Al(III) in the pH conditions of their occurrence.

Activated Alumina

Activated alumina is a granular, highly porous material consisting essentially of aluminum trihydrate. It is widely used as a commercial desiccant in many gas-drying processes. Activated alumina can be regenerated using HCl, H_2SO_4, Alum, or NaOH. The use of NaOH needs to be followed by a neutralization process to remove residual NaOH from the bed. Fluoride removal by activated alumina is strongly pH dependent. Batch adsorption data 14 showed very little removal at pH 11.0 and optimum removal at pH 5.0. Hence, raw water pH and regenerated bed pH need to be adjusted accordingly.

The ability of activated alumina to remove fluoride depends on hardness and presence of silica and boron, etc. If present in water, they interfere with fluoride removal and tend to reduce the efficiency of the system. The use of activated alumina in a continuous flow fluidized system is an economical and efficient method. The process has been found to bring down fluoride levels to 0.1 mg/L. The operational, control, and maintenance problems, mainly clogging of bed, may also be averted in this method.

The various advantages of using activated alumina are listed below:

- It requires minimum contact time for maximum de-fluoridation.
- It is readily available and cheap.
- Percentage of regeneration is considerably high.
- De-fluoridation capacity at neutral pH is appreciable, although it has greater de-fluoridation efficiency at low pH.
- Its de-fluoridation capacity is independent of temperature.

There other materials that are used for this purpose are as follows:

1. Modified activated alumina.
2. Iron-based adsorbents.
3. Calcium-based adsorbents.
4. Bio-adsorbents.

5. Carbon-based adsorbents
    - (a) Bone Charcoal
    - (b) Processed Bone
    - (c) Activated carbons.
6. Nano-adsorbents.
7. Building materials.
8. Apatite and hydroxyapatite.
9. Industrial waste adsorbent.
10. Tri-calcium Phosphate.

Various Removal Methods of Fluoride

A community with excess fluoride poisoning can be prevented or minimized to its exposure by

1. Using alternate water sources.
2. By improving the nutritional status of population at risk.
3. By removing excess fluoride (de-fluoridation).

Alternate Water Sources

Alternate water sources are a major remedy of fluoride contamination like surface water, rainwater, and low-fluoride groundwater. Surface water is non-usable for drinking purpose due to heavy contamination with biological and chemical pollutants. It is very necessary to treat all such water and disinfect it, but it is too expensive and complex for application in poor communities. So, rainwater is great remedy for cleaner water source and may provide a low-cost simple solution. The problem, however, is its uneven distribution and limited storage capacity in communities or households. Fluoride is unevenly distributed in groundwater, and its concentration varies both vertically and horizontally. This implies that every well has to be tested individually and regular monitoring has to be done. This is not possible always. Thus, the option of using alternate water sources has its own limitations.

Better Nutrition

This is another way of protecting oneself from the exposure of fluoride. Some researchers from their experience say that

- Adequate calcium intake is directly associated with a reduced risk of dental fluorosis.
- Vitamin C also safeguards against the risk.
- Improve the nutritional.

De-fluoridation of Water

This is yet another option to go for and minimize fluoride exposure. De-fluoridation is the only option to overcome the problem of excessive fluoride in drinking water, where alternate source is not available. During the years following the discovery of fluoride as the cause of fluorosis, extensive research has been done on various methods for removal of fluoride from water and wastewater. These methods are based on the principle of adsorption, ion exchange, precipitation–coagulation membrane separation process, electrolysis de-fluoridation, electro dialysis, etc. Each and every methods are discussed here along with their advantages and limitations.

Adsorption

In adsorption method, water is passed through a bed of de-fluoridation material. After a period of operation, the adsorbent gets saturated. Then, it needs regeneration. By certain pre-treatments like acid washing and calcinations, fluoride uptake capacity can be increased. As per the literature, the following are the materials used for the adsorption process activated alumina, calcite, magnesia, activated coconut shell carbon activated saw dust, activated carbon, activated alumina coated silica gel and activated fly ash, groundnut shell, coffee husk, rice husk, bone charcoal, activated soil sorbent, carbon, defluoron-1, defluoron-2, etc. The fluoride-removing efficiency of absorbent is mainly influenced by hardness of the water, pH, and surface loading (Fig. 6).

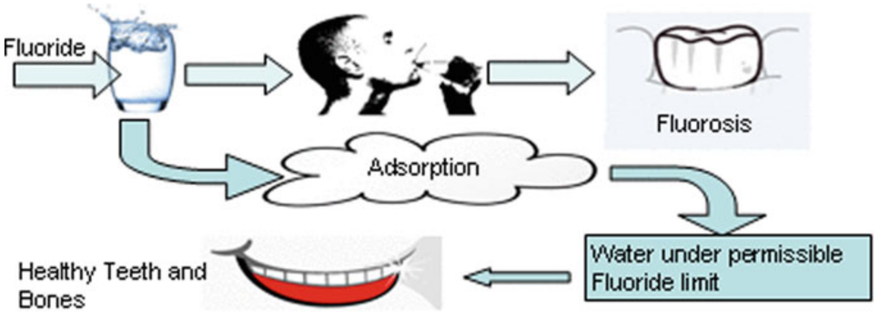


Fig. 6 Adsorption process

Advantages

- The adsorption is the most frequently employed method for fluoride removal.
- The process can remove fluoride up to 96%.
- All absorbents, i.e Activated Alumina, cement-sand granules, cement granules, used in this process are easily avalible and cost effective.
- Overall efficiency generally is higher as compared to other processes.
- Treatment is cost-effective.
- Electricity is not required.
- Unlike other processes, very less sludge is formed.

The whole process is very user friendly, cheap, and eco-friendly.

Limitations

- The regeneration is needed after every 5 months (approx).
- Presence of sulfate, carbonate, and phosphate results in ionic competition.
- Effectiveness of adsorbent reduces after each and every regeneration.
- Waste disposal of high concentrated fluoride sludge is a threat to the environment.

Ion Exchange

The fluoride removal takes place according to the following reaction:

$$\text{Matrix-NR3} + \text{Cl}^- + \text{F}^- \rightarrow \text{Matrix-NR3} + \text{F}^- + \text{Cl}^-.$$

Chloride ions of the resin are replaced by the F^- ions. This process continues until all the sites on the resin are occupied. The resin is then backwashed with water. Now, new chloride ions then replace the fluoride ions leading to recharge of the resin and starting the process again. Strong electro negativity of F^- Ions is the mail driving force in this process.

Limitations

- Cost of resin, pretreatment required to maintaining the pH, regeneration, and waste disposal increase the cost of the project.
- Other ions, like phosphate, sulfate, carbonate, and alkalinity reduce the overall efficiency of the system.
- Problem of disposals of high rich fluoride slacks.

Coagulation–Precipitation

Addition of lime leads to precipitation of fluoride as insoluble calcium fluoride and raises the pH value of water up to 11–12.

$$Ca(OH)_2 + 2F \rightarrow CaF_2 + 2OH^-$$

Lime leaves a residue of 8.0 mg F^-/L. It is used to ensure the level of proper fluoride removal. In this process lime reacts first followed by alum. In the first reaction, aluminum hydroxide [$Al(OH)_3$] is produced. In the second reaction, alum reacts with fluoride ions present. At pH range 5.5–7.5, the best fluoride removal is accomplished.

Advantages

- In this process lime and alum works seperately in two different stephis technique is most effective for fluoride removal and this is used in Nalgonda technique of De-fluoridation.
- In so many government projects, Nalgonda technique is successfully implemented.

Limitations

- Use of aluminum sulfate as coagulant causes the sulfate ion concentration increases; sometime it crosses the maximum permissible limit (400 mg/L), which causes cathartic effect in human beings.
- The process removes only a smaller portion of fluoride, i.e., 18–33% in the form of precipitates.
- Taste of the drinking water becomes pathetic.
- Correct doses of the chemicals need to be checked regularly, manually maintaining is tough.
- A plant of 10,000 L per day capacity requires Rs. 3000 every month. So the maintenance costs are very high.
- Temperature is also a factor for the de-fluoridation capacity.
- Large space is required for drying of sludge.

A Special Case of Co-precipitation is Nalgonda Technique Which is Briefly Described Below

Nalgonda Technique

In the year 1960, the Nalgonda technique was introduced by the National Environment Engineering Research Institute (NEERI) in Nagpur (India). The technique name taken after the village in India where the method was pioneered. The technique is a combination of several unit operations, and the process involves rapid mixing, chemical interaction, flocculation, sedimentation, filtration, and disinfection and sludge concentration. Alum (hydrated aluminum salts)—a coagulant commonly used for water treatment—is used to flocculate fluoride ions in the water under alkaline (lime added) conditions.

Advantages

- Adaptable to domestic use.
- Flexible up to several thousand m^3/d.
- Readily available chemicals used in conventional municipal water treatment are only required.
- High efficient removal of fluorides from 1.5 to 20 mg/L to desirable levels.
- Annual cost is very low.
- No need of high skills.
- Little wastage of water and least disposal problem.
- De-fluoridated water of uniform acceptable quality.
- Fluoride removal capacity is high.
- No energy except muscle power for domestic equipment.
- Simultaneous removal of color, odor, turbidity, bacteria, and organic contaminants.

Disadvantages

- Fluoride elimination rate is low (80–90%) compare to activated alum.
- Right amount of chemicals need to be added.
- Proper mixing of chemical in the water is essential.
- Rapid and slow mixing needs to be done properly.
- Residual aluminum in the water is a constant danger.
- High sulfate concentrations in the water make its taste salty.
- No regeneration of media (Fig. 7).

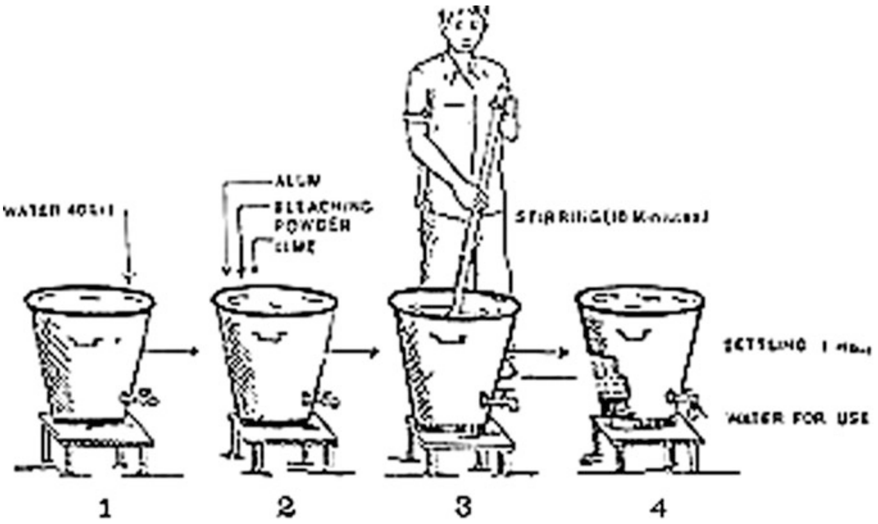


Fig. 7 Nalgonda technique

Membrane Process

Though having some drawbacks, in the recent years, RO membrane process has emerged as a preferred alternative to provide safe drinking water without. Reverse osmosis is a physical process in which high pressured water is passed through a semi permeable membrane. The membranes are selected on the basis of the following factors:

- Cost,
- Recovery,
- Rejection,
- Raw water characteristics, and
- Pretreatment. Efficiency of the process.

NF, as it is a low-pressure process, can remove primarily the larger dissolved solids as compared to RO. Conversely, fluoride removal efficiencies of RO are up to 98% by membrane processes. Moreover, the cost of the RO projects is going down day by day.

Advantages

- The process can remove fluoride up to 98%.
- Membranes also provide an effective barrier to suspended solids, all inorganic, inorganic micro pollutants, pesticides, and microorganisms.
- It ensures constant water quality.
- The process permits the treatment and disinfection of water in one step.

- As no chemicals are required, very little maintenance is required.
- Frequent regeneration is not required.
- pH range is not a vital factor.

Limitations

- It also removes some essential minerals from the water.
- The water becomes acidic and needs pH correction.
- Handsome amount of water gets wasted as brine.

Electro-Coagulation Process

In this process, the contaminants are dissolved/suspended by introducing an electrical current via parallel electrodes constructed of various metals generally selected to optimize the removal process into the medium. When the reactions start, then the elements approach to the most stable state. As it occurs, the contaminants of hydrophobic entities create phase separations, which can easily be removed by secondary separation techniques.

Iron (Fe) and aluminum (Al) are the two well-known materials used as electrode. As per the Faraday's law, metal ions generally split into the liquid medium. These metal ions tend to form metal oxide or hydroxide (nuclei) that are an electro-coagulation attractant to the contaminants, which have been destabilized. The quantity of electrical current required varies with the liquid to be treated. Thus, it is very essential to use perfect amount of current to run the process most efficiently (Fig. 8).

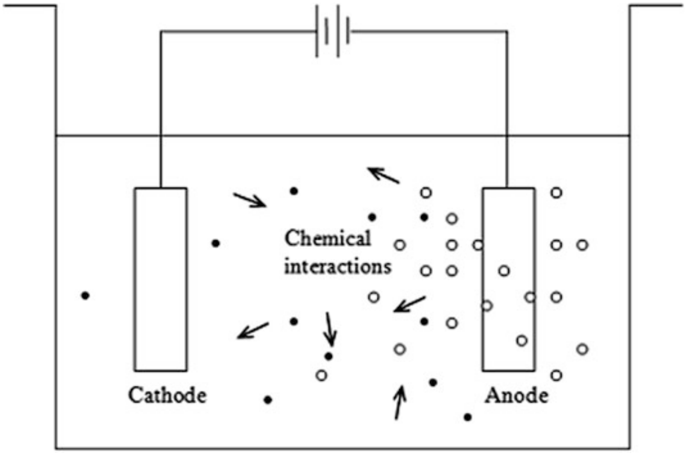


Fig. 8 Electro-coagulation process

An Experimental Data Collection From Some Fluoride-Affected Area of Birbhum

Background

Nasipur is the first place to report cases of fluorosis in the West Bengal. The village is located in Nalhati Block No. 1 (Bhavandapur mouza) of Birbhum district. It is 8 km northwest of Nalhati town and is connected by motorable road which is, however, not well maintained. The village is located very close to the heels of the Jharkhand border and is a part of Chota Nagpur Plateau. The groundwater contamination in the region may be an extension of the Jharkhand malice.

Nasipur area receives 1200-mm rainfall, bulk of which (90%) is lost due to quick runoff. The area is undulating, surface soil is thin, and the hard rock at the bottom does not allow rainwater to percolate downward except where some openings are created in the rocks through joints and cracks. In the village during summer months, sufficient surface water is not available for human consumption, and this forces people to use the groundwater. The climate and lack of alternate sources of water other than groundwater sources have been cited as the cause of high fluoride content in water.

The study of fluoride contamination in the drinking water at Nasipur village was undertaken in the year 2000 after it was reported in the daily newspaper. The history of fluoride of the problem sealed off all the three tube wells in the village and made necessary arrangement for supply of portable water in the village from nearby villages by tanker. This was a stop gap measure. Subsequently, a deep tube well was installed in the Tripita River (2 km north of the village) for supplying water to the village through pipes. Since then, this was the main sources of water supply in the village.

1. At Nasipur village, the rate of fluoride content in water was found very high (14 mg/L) as against the permissible limit 1–1.5 mg/L set by Bureau of Indian Standards. This was alarmingly high and was enough to paralyze one for life.
2. Every second, person in this village is the victim of fluoride. Survey identification 395 victims with visible manifestations of fluorosis in 1995, and about 6 people died due to this reason. There are many other people who are dying in this village till date.
3. The problem is further compounded as the people are poor and do not get sufficient meal. Low intake of protein also aggravates the situation.
4. At Nasipur, the salinity is low which indicate that the groundwater has high fluoride content.

The Study Area

1. NASIPUR, NALHATI BLOCK I.
    - 1 sample collected from the tube well (1.439 mg/L).
    - 1 sample collected from the tap water (1.013 mg/L).
    - 1 sample collected from the well (3.457 mg/L).
2. LAKSHMIKANTAPUR, NALHATI BLOCK I.
    - 1 sample collected from the tube well (8.590 mg/L).
3. 16 NO. WARD, RAMPURHUT BLOCK I.
    - 1 sample collected from the tube well (1.503 mg/L).
    - 1 sample collected from the tube well (2.045 mg/L).
4. SADHINPUR, NALHATI
    - 1 sample collected from the tube well (2.221 mg/L) (Fig. 9).

Primary Data Collection

The data related to the extent of the problem were collected through personal interaction with the people of the village. Through door-to-door survey, it was found that the people of the region were mostly suffering from the diseases like dental fluorosis and skeletal fluorosis. Few examples as shown in Fig. 10 are being cited below to show the diseases and the people who are suffering.

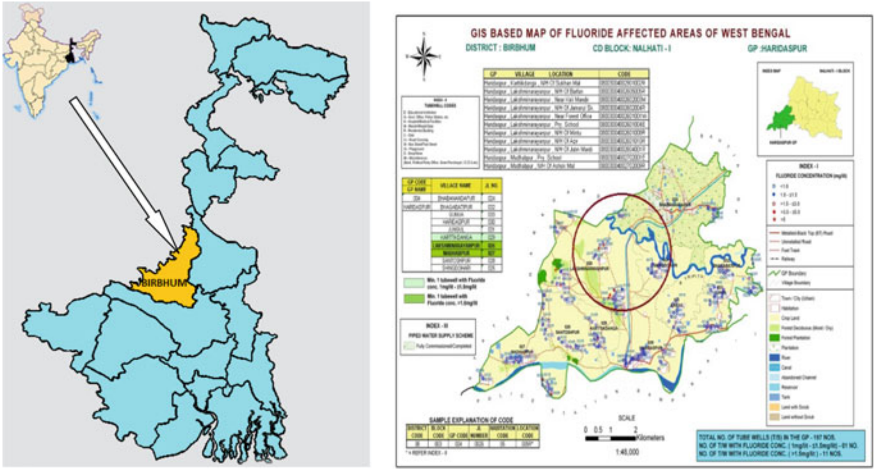


Fig. 9 Location of sampling points

Fig. 10 Skeletal and dental fluorosis patients in Nasipur village

Methodology

Aim

To carry out the test for removal of excess fluoride from drinking water following the permissible limit guideline of WHO.

Methodology

Fluoride is a major problem of our nation as on today. It has a very aggressive look nowadays. It would be dangerous in near future if we don't take immediate action. It is necessary to detect demands analytical grade chemicals and laboratory equipment and skills. Through management, the prevention of fluorosis of drinking water is a difficult task, which requires favorable conditions combining knowledge, motivation, prioritization, discipline, and technical and organizational support. There is de-fluoridation technique which is well known.

Here, we discuss the experimental characterization, detailing of filter unit followed by the most promising de-fluoridation methods like activated alumina adsorption method, cement granule filtration process, cement-sand granules absorption method, double filtration by both filter of activated alumina, electro-coagulation method, and double filtration by activated alumina and electro-coagulation.

Sample Preparation and Collection

Some solutions were prepared with distilled water in the laboratory of School of Water Resources Engineering, and some samples were collected from the fluoride-affected area of Birbhum district. Before collecting the samples, wood stick and plastic container and apparatus were acid-washed before use. Different concentration such as 5, 10, 15, 20, and 30 mg/L were used for the purpose. Fluoride solutions were freshly prepared for each experiment from concentrated primary stock solutions. Primary stock solution for fluoride, 1000 ppm was prepared by dissolving **2.20** g sodium fluoride (NaF) with 1000 mL distilled water in a 1-L volumetric flask and stored in a polyethylene bottle. All the containers used were washed with 1% H_2SO_4 acid. Before collecting the sample, container was rinsed three-five times with the water to be filled (Fig. 11).

Measurement of Fluoride

Fluoride level was measured by **Ion-Meter**. In Ion meter, a specific chemical is required for determination of fluoride level. If we take 2-mL raw water, then we need to take 2-mL chemical to determine the fluoride level. The following steps are followed to measure the fluoride level

- Prepared the solution.
- Calibration.
- Measuring (Fig. 12).

Fig. 11 Sample collection from Nasipur, Birbhum

Fig. 12 Picture of ion-meter and fluoride measuring chemical

De-fluoridation

(i) De-fluoridation Unit Detail of Activated Alumina

In order to pass the water sample through the de-fluoridation bed, an experimental setup with specification given in Table 4 was made for evaluating the efficiency of filtering process using activated alumina.

Mechanism

Activated alumina has high affinity toward fluoride because of aqueous environment at low pH, which is responsible for binding fluoride ions by the formation of inner-sphere complexes. The fluoride uptake by AA usually decreases with a

Table 4 Specification for de-fluoridation unit

Parameters of de-fluoridation unit	Specifications
Height of column	55.4 cm
Diameter of column	6.4 cm
Inlet and outlet diameter	0.508 cm
Area of base filter	0.003218 m^2
Volume of filter	0.001781 m^3
Volume of activated alumina	644 mL
Weight of activated alumina	515 g
Diameter of activated alumina	2 mm
Surface loading	30–45 mL/min (1.8–2.7 L/h)
Flow rate	2–3 L/h
Concentration	5 mg/L

decrease pH. Alumino-fluoro complexes are formed resulting in the presence of aluminum ions in the treated water and lowering of the active sites. At near neutral pH, the uptake of fluoride is maximum. The reaction can be represented by $Al–OH_2^+ + F^- \leftrightarrow AlF + H_2O$ $Al–OH + F^- \leftrightarrow Al–F + OH$.

Apparatus Required

Activated alumina column (with inlet and outlet), large plastic (20 L) bucket with a tap attached at the bottom, rubber pipe, stand with clamp, activated alumina as a filter media (515 g) column gravel sand packing, container, Ion Meter.

Solution Required

A primary stock solution for fluoride, having 1000 mg/L fluoride concentration, was mixed with raw water of JU (fluoride-spiked groundwater) to give samples having fluoride concentration of 5.0 mg/L. Some reagents are collected from Birbhum.

Development of De-fluoridation Filtration Unit

De-fluoridation filter unit fabricated in the laboratory consisted of GI sheet. **515 g** of AA was taken in the upper portion of gravel-sand bed (inside a **6.35 cm dia.** × **55.4 cm height** filter), which gave an AA bed depth of **20 cm**. A flow control device was fixed at the bottom of the filter so as to have a flow rate of **27–54 mL/min**, and the treated water was collected in a container. Size of the container was decided based on the volume of water (Fig. 13).

Preparation of the Filter Bed

The filter bed was prepared by using gravels (large, medium, and small diameter) at the bottom having a height of 8 cm from the bottom of the filter, sand at the middle having a height 8 cm above the gravel bottom of the filter to arrest the iron present in the raw water, and 547 g of activated alumina at the top as a medium for adsorbing fluoride having a height 20 cm above sand bed. After preparing the filter media, raw water was passed through the filter, and after filtration, the filtered water was collected and sent to the laboratory for testing the fluoride concentration.

Procedure: An experimental setup was prepared which is described below and represented by Fig. 14.

Details of the Process Are Described Below

- Sample water was taken in a plastic bucket and kept over parapet wall, and the filter was kept over the iron stand to provide it the necessary pressure head.
- The fluoride-concentrated raw water was passed through the pipe attached to the filter in a gravity flow manner.
- The treated water was collected from an outlet at the bottom of the filter.
- Treated water was analyzed using spectrophotometer to obtain the fluoride concentration; raw water was passed through the rubber pipe and passed through the filter in the downward direction. The treated water comes out of the filter with a flow rate of 1.5–2 L/h water. The filter was run up to the saturation level of activated alumina medium (Fig. 15).

Fig. 13 Activated alumina granules

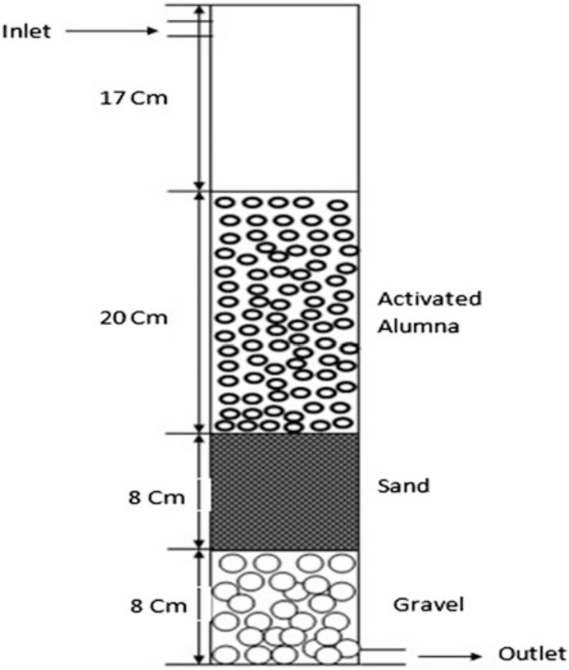


Fig. 14 Activated alumina filter column

Fig. 15 Activated alumina filter set up

(ii) De-fluoridation by Cement-Sand Granules

A primary stock solution for fluoride, having 1000 mg/L fluoride concentration, was mixed with raw water of JU (fluoride-spiked groundwater) to give samples having fluoride concentration of 5.0 mg/L. Some reagents are collected from Birbhum.

Apparatus Required

1. 1 L plastic beaker.
2. Glass rod.
3. Cement-Sand mortar (**190 g**).
4. Stock solution mixed with Jadavpur University groundwater (samples of **350 mL** each).
5. Polyethylene bottle for collecting samples and treated water.
6. Ion Meter for measuring fluoride content in water.

Stock Solution Preparation

Primary stock solution for fluoride, having 1000 mg/L fluoride concentration, was mixed with raw water of JU (fluoride-spiked groundwater) to give samples having fluoride concentration of 5.1 mg/L.

Preparation of the Adsorption Bed

The bed was prepared by using cement-sand mortar (having a volume of 100 mL) at the bottom of a 1-L plastic beaker filled with spiked sample.

Filtration Procedure

An experimental setup was prepared which is described below:

- The process started by taking of 2 L of sample with concentration of 5.1 mg/L.
- 400 mL of the sample was poured over the cement granules in the beaker and was mixed for 10 min by glass rod.
- The sample was kept in contact with the media for 20 min after mixing.
- Samples were collected at an interval of 15 min for the next 60 min and were sent to the laboratory to determine the fluoride concentration.

De-fluoridation by Cement Granule Filtration Process

Cement granule is a very good filter media for de-fluoridation. Its fluoride-removing capacity has been found to be satisfactory. It is produced by mixing cement and water. Cement granule is a good fluoride-removing filtering element (Fig. 16).

Apparatus Required

1. 1-L plastic beaker.
2. Glass rod.
3. Cement granule (200 g).
4. Stock solution mixed with Jadavpur University groundwater (samples of 400 mL each).
5. Polyethylene bottle for collecting samples and treated water.
6. Ion Meter for measuring fluoride content in water.

Reagents Required

A primary stock solution for fluoride, having 1000 mg/L fluoride concentration, was mixed with raw water of JU (fluoride-spiked groundwater) to give samples having fluoride concentration of 5.0 mg/L. Some reagents are collected from Birbhum.

Fig. 16 Cements granules

Preparation of the Adsorption Bed

The bed was prepared by using cement granules (having a volume of 110 mL) at the bottom of a 1-L plastic beaker filled with spiked sample.

Procedure

An experimental setup was prepared which is described below:

- The whole process was set up on a table.
- 400 mL of the sample was poured over the cement granules in the beaker and was mixed for 10 min by glass rod.
- The sample was kept in contact with the media for 20 min after mixing.
- First sample (60 mL) was collected after the first 30 min of contact, and after that, 4 samples were collected at an interval of 15 min for the next 60 min and were sent to the laboratory to determine the fluoride concentration.

Method of Electro-Coagulation

Apparatus Required

Bucket for preparing solution to be analyzed, measuring cylinder, electrocoagulation chamber ($l \times b \times h = 30 \times 15 \times 18\ \text{cm}^3$), electrodes (8 * 11 * 1) * 2, ammeter, voltmeter, 12 V, 7 Ah battery, glass rod, plastic beaker, glass beakers for collecting samples, and Ion-Meter.

Solution Use

A primary stock solution for fluoride, having 1000 mg/L fluoride concentration, was mixed with raw water of JU (fluoride-spiked groundwater) to give samples having fluoride concentration of 5.0 mg/L. Some reagents are collected from Birbhum.

Procedure

- 5 L of sample was prepared by mixing stock solution having 1000 ppm fluoride concentration with Jadavpur University groundwater to bring down the concentration of fluoride to 5 mg/L for carrying out electro-coagulation process.

- Electrodes were inserted into the chamber having a gap distance of 5 cm with the help of a glass rod.
- Ammeter was connected in series to record the current flow, and voltmeter was connected in parallel with the plates to record the voltage.
- Power supply was provided from a 12 V, 7 Ah batteries.
- Voltage and current readings were taken at an interval of 5 min.
- Treated samples were collected through the chamber outlet at an interval of 15 min for 120 min, and the contents were stirred occasionally to maintain even fluoride concentration using a glass rod.
- The treated water was taken in a glass beaker, and rapid mixing was done for 1 min, and slow mixing was done for 2 min. The sample was then allowed to settle for 1 h.
- The supernatant was collected by passing the treated water through Whatman filter paper, and the treated sample was sent to the laboratory for determining the fluoride concentration, and the concentration was measured by Ion-Meter.
- The supply was cut off after 120 min.
- The remaining water was allowed to remain in the chamber for 3–4 h for collecting the sludge formed for proper disposal later.
- Sometimes, after this period, samples were collected for further testing.

Double Filtration Unit

Here, we use two types of filter. One set of double filter is a set of activated alumina column, and the other is electro-coagulation with alumina-alumina combination (cathode-alumina, anode-alumina).

Activated Alumina Column

- Sample water was taken in a plastic bucket and kept over parapet wall, and the filter was kept over the iron stand to provide it the necessary pressure head.
- The fluoride-concentrated raw water was passed through the pipe attached to the filter in a gravity flow manner.
- The treated water was collected from an outlet at the bottom of the filter.
- Treated water was analyzed using spectrophotometer to obtain the fluoride concentration; raw water was passed through the rubber pipe and passed through the filter in the downward direction. The treated water comes out of the filter with a flow rate of 1.5–2 L/h water. The filter was run up to the saturation level of activated alumina medium.

Electro-Coagulation (Cathode-Alumina, Anode-Alumina)

- 5 L of sample was prepared by mixing stock solution having 1000 ppm fluoride concentration with Jadavpur University groundwater to bring down the concentration of fluoride to 5 mg/L for carrying out electro-coagulation process.
- Electrodes were inserted into the chamber having a gap distance of 5 cm with the help of a glass rod.
- Ammeter was connected in series to record the current flow, and voltmeter was connected in parallel with the plates to record the voltage.
- Power supply was provided from a 12 V, 7 Ah batteries.
- Voltage and current readings were taken at an interval of 5 min.
- Treated samples were collected through the chamber outlet at an interval of 15 min for 120 min, and the contents were stirred occasionally to maintain even fluoride concentration using a glass rod.
- The treated water was taken in a glass beaker, and rapid mixing was done for 1 min, and slow mixing was done for 2 min. The sample was then allowed to settle for 1 h.
- The supernatant was collected by passing the treated water through Whatman filter paper, and the treated sample was sent to the laboratory for determining the fluoride concentration.
- The supply was cut off after 120 min.
- The remaining water was allowed to remain in the chamber for 3–4 h for collecting the sludge formed for proper disposal later.
- Sometimes, after this period, samples were collected for further testing.

Results and Discussion

Double Filtration Methods by Activated Alumina

The concentration of fluoride and efficiency of filtration process using activated alumina has been listed in Table 5 for initial 5 mg/lit concentration sample and sample collected after 1st filtration. The quantity of water filtered with de-fluoridation process using activated alumina and its efficiency has been plotted for both the samples and presented in Fig. 17. It can be observed from Fig. 17 after double filtration by activated alumina we get almost fluoride free water because it observed that the efficency of fluoride removal decreases with increase of quantity of water which need to filter.

Table 5 Double filtration method by using Activated Alumina

Quantity of water filtered (L)	Initial sample		Sample collected after first filtration	
	Outflow fluoride concentration in mg/lit, When inflow concentration is 5.00 mg/L	Efficiency percentag	Outflow fluoride concentration in mg/lit, When inflow concentration is 0.018 mg/L	Efficiency percentage
4	0.003	99.94	0.001	99.98
8	0.006	99.88	0.001	99.98
12	0.011	99.78	0.002	99.96
16	0.021	99.58	0.003	99.94
20	0.043	99.18	0.003	99.94

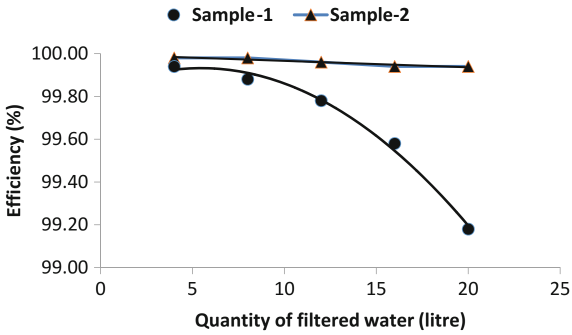


Fig. 17 Percentage removal of fluoride with quantity of filtered water

Discussion

1. Activated alumina is easily available.
2. Here, we observed that 515-g activated alumina can remove 945-mg fluoride.
3. 1-kg activated alumina can remove about 1700–1800-mg fluoride from water. Here, we give some calculation:
   Without recycling 1000 g activated alumina removed (Table 6).

Table 6 Comparative chart of water filtration of different concentration

Fluoride concentration (mg/L)	Quantity of filtered water when final concentration is 0.5 mg/L (L)	Quantity of filtered water when final concentration is 1 mg/L (L)
5	375–400	425–450
10	180–200	190–220
15	120–130	120–150
20	85–90	90–100
25	70–75	70–80
30	55–60	60–65

Fig. 18 Comparison of filtered water quantity when final concentration is 0.5 and 1mg/L

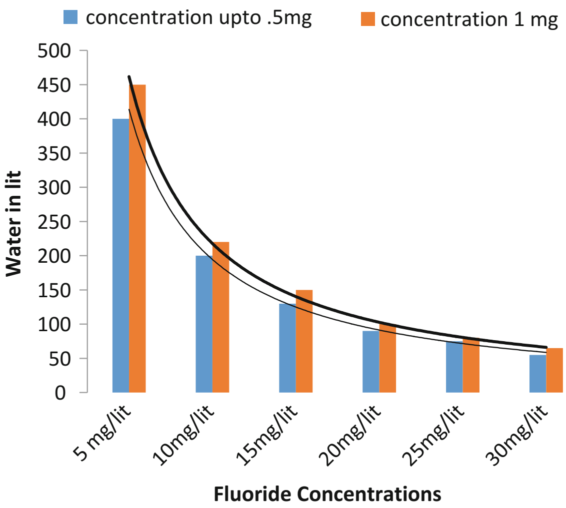


Table 7 Comparison result of different concentration

Concentration (mg/L)	Efficiency (No recycling)	Efficiency (After 100% recycling)	Remarks
5.00	99.94	99.98	No need of recycling
10.00	92.50	99.14	Some time need recycling
15.00	76.92	93.66	Need recycling
20.00	67.20	90.20	Need recycling
30.00	27.90	40.46	After recycling fluoride concentration are not satisfactory

1. If we use another filter before using activated alumina filter like cement-sand or cement granules filter, then the longevity is increased satisfactorily. This type of filter increases 30–40% filtration power also.
2. After double absorption process is done by activated alumina, increase filtration power about 10–20%.

Discussion

It is known that the fluoride removal capacity of all material as well as process is different. After carrying out the experimental studies on some of the materials, a clear picture can be drawn. Fig. 19 gives a comparison chart on efficiency of different de-fluoridation process.

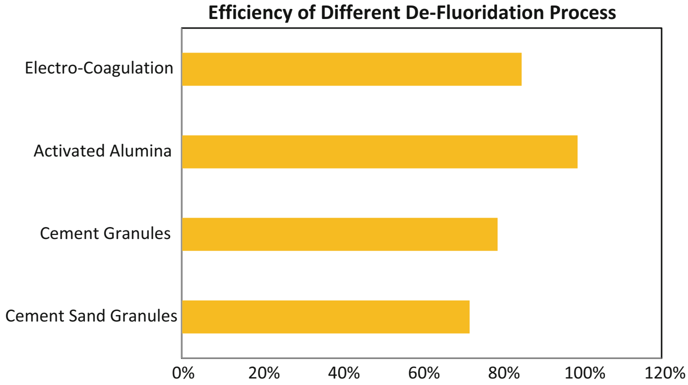


Fig. 19 Efficiency of different de-fluoridation process

So, from this graph, we found that activated alumina is most efficient absorbent for domestic use. Then, respectively, electro-coagulation, cement granules, and cement-sand granules. But activated alumina is costlier than other, so if we use two-stage filtration, then it will be very useful and economical as well as long-lasting also.

So, we can use a combination of:

1. De-fluoridation by using cement-sand granules—activated alumina.
2. De-fluoridation by using cement granules—activated alumina.
3. De-fluoridation by using activated alumina-electro-coagulation.
4. Electro-coagulation-de-fluoridation by using activated alumina.
5. De-fluoridation by using cement–sand granules-electro-coagulation.
6. De-fluoridation by using cement granules-electro-coagulation. etc.

Conclusion

From the above study, it can be concluded that the de-fluoridation of drinking water is the need of the hour and should be taken up seriously; otherwise, it will be a big problem in future. All the techniques discussed above are very much useful as well as very user friendly which one can easily apply in urban and rural areas. These processes are also very cost-effective. The raw materials are easily available in the market. So, we can use cement granules, activated alumina, cement-sand granules, electro-coagulation for de-fluoridation methods.

We can conclude that about 70–72% fluoride is removed by 220-g cement-sand granules and cement granules from 1000 mL water where the contact time is 2 h. If we use this absorbent before any other de-fluoridation technique, then it will be more helpful to the second de-fluoridation technique and it increase the longevity of the second filter. And most importantly, all these absorbents are very cheap also easily available, so we can use it in very remote area also.

The results reveal that activated alumina is a very efficient absorbent to remove fluoride from water. Here, we use different concentration fluoride contamination in water and removal of fluoride and its efficiency level in different rate of flow. And we show all the results before. It is the most efficient technique which we can do here. And it removes about 80–99% fluoride contamination.

Here, we use another technique electro-coagulation, which does not require any filters, daily maintenance, and additives. It also removes any size of suspended solids, oil, grease, heavy metals, and the smallest colloidal particles. It produces effluent with less TDS content as compared to chemical treatments. If this water is reused, the low TDS level contributes to a lower water recovery cost. The electrolytic processes in the electro-coagulation cell are controlled electrically and with no moving parts, thus requiring less maintenance. It avoids uses of chemicals, and so there is no problem of neutralizing excess chemicals and no possibility of secondary pollution caused by chemical substances added at high concentration as when chemical coagulation of wastewater is used. It removes about 70–80% fluoride from water.

It has been concluded that the selection of a treatment process should be site-specific as per local needs and prevailing conditions of pollutants in drinking water as each technology has its own limitations and no filtering process can serve in diverse conditions. The method comprising double filtration and multi-column candles may increase the efficiency of filtering process and decrease the frequency of replacing the candles.

References

Agarwal V, Vaish AK, Vaish P (1997) Groundwater quality focus on fluoride and fluorosis in Rajasthan. Curr Sci 73:743–746

Bhagan VU, Santhi D, Sri Renganathan P (1996) Study of fluorosis in Kavalkinaru Village of Nellai Kattabomman District of Tamilnadu, India. Asian J Chem 8(3):553–556. Retrieved from http://www.asianjournalofchemistry.co.in/User/ViewFreeArticle.aspx?ArticleID=8_3_39

Fawell J, Bailey K, Chilton J, Dahi E, Fewtrell L, Magara Y (2006) Fluoride in drinking water. Published on Behalf of World Health Organization. Retrieved from http://www.who.int/water_sanitation_health/publications/fluoride_drinking_water_full.pdf

Hem JD (1989) Study and interpretation of the chemical characteristics of natural water, 3rd edn. U.S Geological Survey Water-Supply Paper 2254, US Geological Survey, Washington, DCP, p 263

IS 10500 (2012) Drinking water-specification, Second Revision. Retrieved from http://cgwb.gov.in/Documents/WQ-standards.pdf

Kumar M, Puri A (2012) A review of permissible limits of drinking water. Retrieved from http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3482709/

Mangla B (1991) India's dentists squeeze fluoride warnings off tubes. New Sci 131:16

Meenakshi A, Maheshwari RC (2006) Fluoride in drinking water and its removal. J Hazard Mat 137(1):456–463

WHO (1984) Fluorine and fluorides. Environmental Health Criteria 36. World Health Organization, Geneva

Yadav S, Khan TI, Gupta S, Gupta AB, Yadav RN (1999) Fluorosis in India with special reference to Rajasthan. In: Proceedings of the international conference on water, environment, ecology, socioeconomics and health engineering (WEESHE), pp 3–10, Seoul National University, 18–21 Oct

Evaluation of Dolochar as a Filter Media in Slow Sand Filtration

Purushottam Das Vairagi and Rajesh Roshan Dash

Abstract The study was carried out to evaluate the feasibility of slow sand filter using dolochar, a solid waste generated from sponge iron industry, as a filter medium along with the sand to treat secondary treated wastewater effluent. Effectiveness of the slow sand filters were assessed using two laboratory-scale filter columns (0.10 m diameter and 0.50 m media depth), one consisting of sand media and the other with sand and dolochar (dual media filter). The effective size of sand and dolochar used were 0.41 and 0.53 mm to study the performance at a filtration rate of 0.10 m/h. For the 280 h of run period, dual media filter showed higher removal efficiencies in all respects, especially average chemical oxygen demand (COD) removal of up to 80.96% compared to 64.68% of sand media filter and turbidity removal of 91.13% compared to 82.27% of sand media filter. The phosphate and total suspended solids (TSS) removal efficiencies of dual media filter were 78.69 and 89.08%, whereas in case of sand media filter removal efficiencies were 66.17 and 82.48% respectively. Microbial removal efficiency observed was also more in the case of dual media filter. The only disadvantage in dual media filter observed for having more head loss which affects the filter run. Since the filter having dolochar exhibited to possess higher removal efficiencies, it supports the utility of dolochar as a low-cost and highly efficient filter media.

Keywords Dolochar · Slow sand filtration (SSF) · Biochemical oxygen demand (BOD) · Chemical oxygen demand (COD) · Coliforms · Moving bed biological reactor (MBBR)

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Introduction

Slow sand filters (SSFs) are probably the most effective, simplest and least expensive water treatment process for developing countries (Huisman and Wood 1974). They require few technical components and usually no chemicals. They are very efficient in removing bacteria, organics, cysts, ova and viruses. The performance of SSF is not controlled by any mechanical system. It is a controlled ecosystem of living organisms whose activities are affected by the raw water quality, and in particular temperature (Muhammad et al. 1996). As conventional SSFs can remove only coliforms and turbidity, modification techniques such as changing filter media can enhance efficiency in removing pollutants from wastewater (Abdolahnejad et al. 2014).

Dolochar is one such material produced as a by-product of direct reduction of iron (DRI) process for the production of sponge iron. Integrated instrumental (optical microscope, XRD, SEM) characterization studies done by Dwari et al. (2012), reveal that the dolochar samples consist of quartz (free as well as locked), free lime, aluminium silicate, Fe particles, and Ca or Mg and/or Ca+Mg+Fe oxide phases. Investigation by Sahoo et al. (2014), has been carried out on geotechnical properties of dolochar. Characterization study of dolochar revealed that the value of bulk density, maximum dry density, specific gravity, coefficient of uniformity, coefficient of curvature, pH was found to be 966 kg/m3, 1.15, 2.13, 13.33, 2.13, 10.5 respectively. Dolochar is a carbonaceous material and therefore, it is expected to have high surface area with requisite porosity which makes it ideal for adsorption. For the production of 100 tonnes of sponge iron the amount of iron ore and coal requirement is 154 and 120 tonnes, respectively, in which case the solid waste generated is around 45 tonnes and out of which 25 tonnes are char and widely known as dolochar (Panda et al. 2014). A negligible portion of generated dolochar is used as a domestic fuel, fuel in boilers and brick making industries, whereas the major portion is either dumped in the dump yards or is used in the land filling without considering their effect in adaphic and aquatic environments.

Till date, the application of various adept solid materials as sand filter media, involving synthetic materials, natural materials, agricultural by-products, industrial by-products, and other materials like zeolite as filter media had proved either expensive or having low removal efficiency. Thus, the main objective of this study was to determine the efficiency of removal of impurities from the wastewater by using low-cost material dolochar as a filter media.

Materials and Methods

Set-Up of the Experimental Column

The principal apparatus employed in this investigation consists of two 100 mm internal diameter vertical Perspex tubes of 120 cm (1.2 m) height as shown in

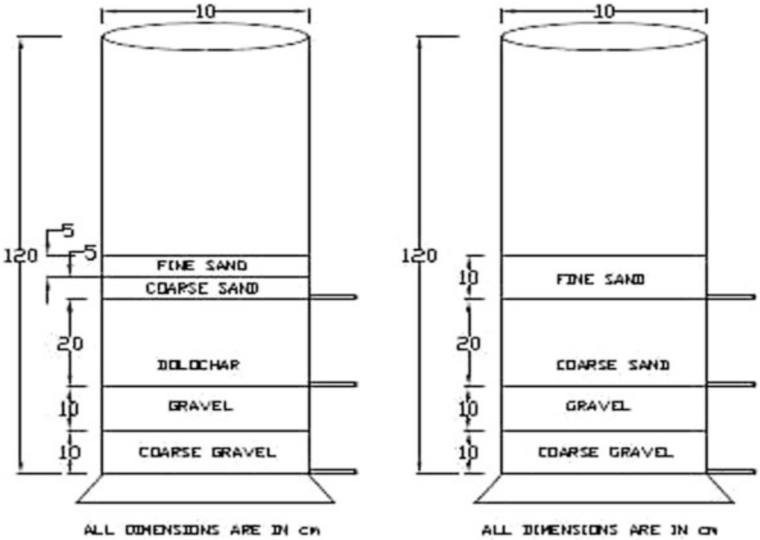


Fig. 1 Schematic diagram of laboratory-scale slow sand filter columns

Fig. 1. First filter is packed with single media of sand to a height of 50 cm. The column was filled with locally available natural sand. The quality of the treated water and maintenance requirements for the system also depend on the selected variables like sand size, flow rates and sand bed depth. The sand used is characterised by its effective size (ES or d10) and uniformity coefficient (UC or d60/d10). The recommendations for ES vary between 0.15 and 0.40 mm (Ellis and Wood 1985). The UC should be between 1.7 and 3.0, but preferably not greater than 2.7 (Ellis 1987). The 3370 g of sand was sieved mechanically on a set of sieves, and sieve fractions were weighed. The results of sieve analysis give the effective size and uniformity coefficient of sand used are 0.41 and 2.25 mm respectively, whereas dolochar has effective grain size of 0.53 mm of 20 cm and uniformity coefficient of 1.77. The sand size and filtration rate were decided on the basis of the published results for the optimisation of filtration process (Muhammad et al. 1996; Sadiq 2003).

Before filling into the column, the sand and dolochar were thoroughly washed with tap water to remove clay and other mineral contaminants from the sand particles and dried in an oven at 120 °C overnight. The lower section of the columns contains 10 cm depth of coarse gravel (4.75 mm), overlaid by 10 cm layer of 2 mm fine gravel, for sand media filter 20 cm of 1.18–4.75 mm coarse sand along with 10 cm of 0.15–1.18 mm fine sand at the top, whereas in dolochar media filter 20 cm of dolochar followed by 5 cm of 1.18–4.75 mm coarse sand along with 5 cm of 0.15–1.18 mm fine sand at the top.

The depth of the sand bed was so arranged that its top surface was at a level with the flanged joint in the filter tube. A layer of gravel of 4.75–10 mm size was provided on the top surface of the filter for homogenous distribution of wastewater on the surface of sand bed. A constant inflow of MBBR effluent at a hydraulic loading rate of 0.10 m/h was maintained by a peristaltic pump. The criterion applied for terminating the filter run was the attainment of head loss, i.e. clogging of filter. The filter was non-operational after 120 and 180 h of run for 5 days each. The top surface of the sand layer was scrapped of up to 1 cm for cleaning of deposited solids during these off periods.

Sample Collection

A MBBR (moving bed biological reactor)-based sewage treatment plant of 100 KLD capacity at the city of Bhubaneswar was selected for regular monitoring over a period of 3 months (October 2015–December 2015). Grab samples of wastewater were obtained at the outlet of MBBR. Effluent samples were collected from the effluent pipe provided to each filter column.

Sample Analysis

Samples were collected from the outlet of filter column at the different intervals for different parameters; generally, it is taken as 24 h. Samples were assayed for microbiological (total coliforms, faecal coliforms, faecal streptococci) and physico-chemical parameters (COD, BOD, phosphate, TSS and turbidity) as per standard methods (APHA 1998).

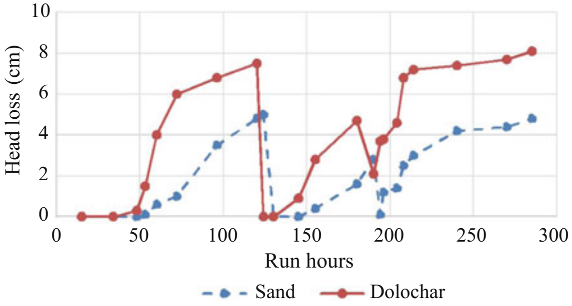
Results and Discussion

The range and average values of the physico-chemical characteristics of the MBBR effluent used as the influent to slow sand filters are reported in Table 1.

Table 1 Characteristics of MBBR reactor effluent

Parameters	Values (average)
pH	6.86–7.8 (7.12)
Turbidity (NTU)	16–59 (36.2)
TSS (mg/L)	172–424 (234.15)
COD (mg/L)	91–440 (195.6)
BOD (mg/L)	46–124 (77.9)
Phosphate	27.85–4.35 (12.31)

Fig. 2 Results of head loss development



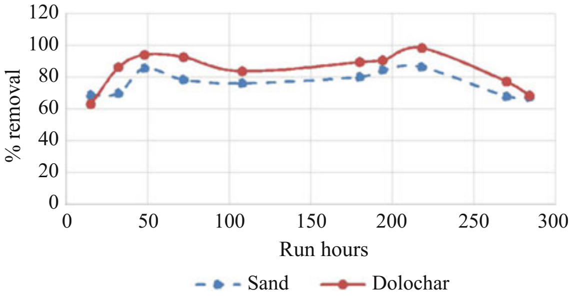
Head Loss

The head loss is measured by the piezometer placed at a certain height of filter column. The head loss profile for the run period of 280 h is shown in Fig. 2. It was observed that the head loss of both the filters was initially zero for 48 h and then gradually increased. It has been observed that in the dual media filter, head loss was more compared to the sand media filter. After 120 h of run period the filter columns were not operated for almost 5 days; due to this when the filter operated further, head loss did not appear and gradually increased, it may be due to the inactive biolayer on the surface of the filter (Arndt and Wagner 2004), and still filtrate quality was good. The head loss developed at the end of 240 h was 5.4 and 8.1 cm for sand and dolochar media, respectively.

Total Suspended Solids Removal

The total suspended solids removal efficiency of both the filters was observed to be almost same (Fig. 3). In this case initially the dual media filter has less TSS removal efficiency, and after 15 h of filter run the removal efficiency was high in the case of dual media filter. It is observed that due to the off period of filters, resulting in less removal efficiency of the total suspended solids which is supported by paper

Fig. 3 Results of TSS removal



of Marshall and Middlebrooks (1974). Overall, both filters showed good removal efficiency. For the 280 h of the run period, the removal efficiency of the dual media filter was about 89% which more compared to the 79% of the sand filter.

Turbidity Removal

Turbidity is one of the most important parameters for monitoring the performance of a filter. It is believed that turbidity serves as a carrier for nutrients and pathogens which can result in biological activity. The turbidity removal was observed to be significantly high and stable since the start of the experiment in the case of dual media filter (Fig. 4). The turbidity level in the filter influent ranged from 16 to 59 NTU (Avg. 36.2 NTU), whereas at a particular operational period, the effluent turbidity level of dual media filter lie in the range of 6 to 1 NTU (Avg. 2.6 NTU), and for sand media filter it is 13 to 2 NTU (Avg. 5.07 NTU) during the entire study. The average percentage turbidity removal was 91.24 and 82.65% for the dual media filter and sand media filter respectively, during the entire study period. This higher turbidity removal efficiency of the filter having dolochar might be attributed to the adsorption by biofilm and filter material or biodegradation in the filter by the microbial biomass, adding to this paper by Hatt et al. (2013) showed that the carbonaceous materials (dolochar) supports the removal of turbidity from wastewater.

Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) Removal

COD removal profile of both the filter columns is shown in Fig. 5. It was observed that the COD removal efficiency of the dual media filter was more than that of the sand media filter. The dual media filter is proved a good filter media as the average COD removal in this filter for the run period of 280 h achieved about 80.96% which is far more than the sand media filter of 66.45%. BOD removal efficiency of

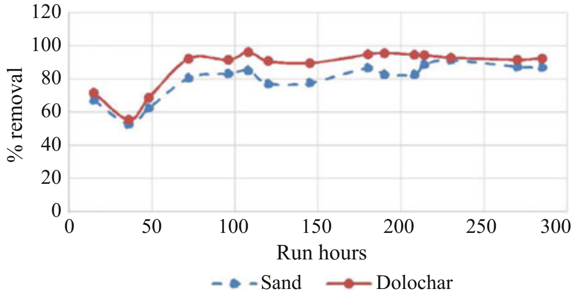


Fig. 4 Results of turbidity removal from the filter

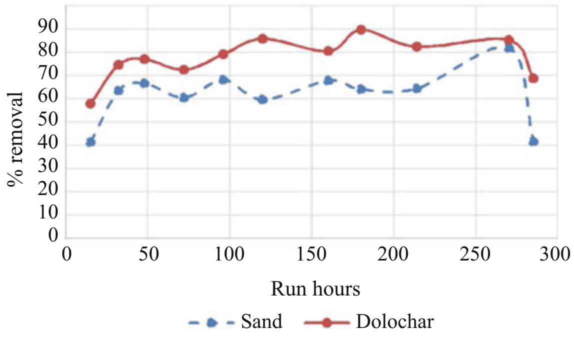


Fig. 5 Results of COD removal

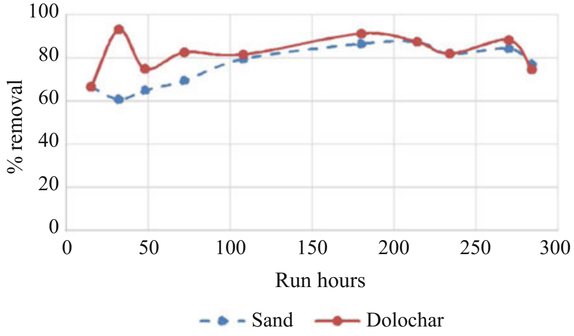


Fig. 6 Results of BOD removal

the dual media filter and sand media was 82.29 and 75.93% (Fig. 6). The influent BOD varied from 46 to 124.5 mg/L, and the average effluent BOD of sand filter and the dual media filter was 17.7 and 14.3 mg/L. The filtered BOD in the dual media filter was much lower than the permissible limit of 30 mg/L. Although the results of the experiments are lower than the results obtained in studies (Tyagi et al. 2009; Farooq and Al-Yousef 1993), the comparison will not be appropriate because of the poor development of surface layer in case of the sand media filter, and due to the off periods in filter run. Then also the results of the BOD and COD support the literature published (Fox et al. 1994; Huisman and Wood 1974).

Phosphate Removal

Phosphate removal from both the filters followed nearly same trend as shown in Fig. 7. In the case of dual media filter, it has higher removal efficiency than the sand media filter. It has been confirmed that the dual media filter is the highly effective media for the phosphate removal from the sample of wastewater, due to its high adsorbent capacity (Rout et al. 2015). The influent phosphate concentration was 7.43 and 27.85 mg/L. The average effluent concentration of sand and the dual

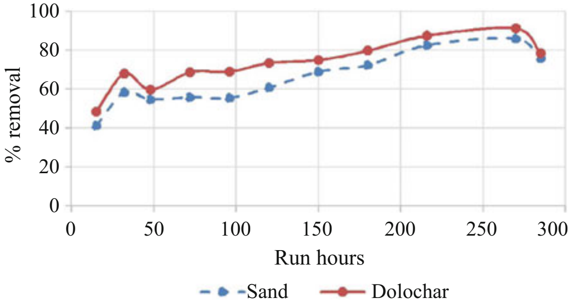


Fig. 7 Results of phosphate removal

media filter was 3.78 and 2.96 mg/L, which is below the permissible limit. There are well-documented studies suggesting that phosphate ions react with iron and aluminium oxides by ligand exchange forming inner sphere complexes, whereas the presence of magnesium and calcium ion facilitates phosphate removal via precipitation (Rout et al. 2015). Apart from eutrophication, the increasing loads of phosphates in water bodies stimulate the activity of a damaging microbe known as Pfisteria and speed up the production of microcystin, a toxin that poisons aquatic animals and can cause hepatocellular carcinoma in humans; thus, dolochar media filter proves to be effective in removing the phosphate from wastewater and lessen the potency of eutrophication. As the MBBR primarily removes the nitrogen compounds (by nitrification and denitrification), nitrate concentration in influent was very low. However, it is evaluated that dolochar also has efficiency in removing the nitrate, which contributes to the eutrophication (Rout et al. 2016).

Microbial Removal

The results of the total coliform, faecal coliform and streptococci removal efficiencies revealed that the filter with dolochar exhibited the highest microbial removal efficiency. The total coliform and faecal coliform removal efficiencies of sand media filter after the filter column run of 240 h were 98.75 and 98.11%; as expected, TC and FC removal efficiencies of the filter having dolochar are 99 and 98.44%. The influent TC and FC were 2.8×10^7 and 9×10^6 mpn/100 mL, the effluent TC and FC of sand media filter were 3.5×10^5 and 1.7×10^5 mpn/100 mL, and in the case of the dual media filter they were 2.8×10^5 and 1.4×10^5 mpn/100 mL. The streptococci measured by the MPN method gave the removal efficiency of 99% at the end of 240 h in the case of the dual media filter and 98.76% for sand media filter. The influent MPN was 1.7×10^6 mpn/100 mL, and the effluent MPN was 1.7×10^4 and 2.1×10^4 mpn/100 mL in the case of the dual media filter and sand media filter. Results of papers Busscher et al. (2006) and Stevik et al. (2004) showed that the bacterial removal can be due to the adsorption on the material, mainly on the carbon materials, adding to the straining action.

Conclusions

In this study, two filter media, sand and another cheap media, a sponge iron industry by-product, dolochar, were used in two laboratory-scale slow sand filters and compared. pH, turbidity, COD, BOD, phosphate, TSS, TC, FC, EC and streptococci removal efficiencies of these filter set-ups were measured. The quality of filter effluent in terms of BOD, SS and coliforms could be achieved for reuse purposes. The highest removal efficiency was related to filter having dolochar. Thus, it is concluded that the dolochar as a filter media can be a very good option for removal of impurities from wastewater in communities that have some problems with these parameters. For the run period of 280 h the removal of turbidity was above the 91%, and with the dual media filter it is up to 96%. In the filter run of 280 h the head loss developed is comparatively more in case of dual media filter which may be due to the unsettled influent. Roughing filters can be used to remove excessive turbidity prior to SSF treatment and by maintaining proper filter operation. As the gravel rock roughing filters have been used for decades as a pre-treatment method for source waters subject to high fluctuations in turbidity, filter having dolochar has comparatively more total coliform removal efficiency for the 280 h of run period. Although more study is required in this aspect to prove the effectiveness of the dolochar, tests such as X-ray detection (XRD) and scanning electron microscopy (SEM) can explain the higher removal efficiency in the case of filter having dolochar.

It is observed from the study that the 0.41 mm effective size of the sand and the filtration rate of 0.10 m/h are the optimum parameters for the slow sand filter to be effective in impurities removal as well as long filter run. Based on the quality of the effluent of the filtration process, reusability for recreational as well as irrigation purpose was suggested. The results of this study support dolochar as a low-cost and highly efficient adsorbent, it gave the hope that the dolochar can be most effectively utilised as filter media. Thus, the recommendation can be made on the basis of the results obtained from the study on the two laboratory-scale slow sand filters that the new filter media, dolochar, can be most effective in treating the impurities in the wastewater. However, more investigations are needed in this field with different types of industrial wastewater and different operating conditions before such conclusions can be generalised.

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References

Abdolahnejad A, Ebrahimi A, Jafari N (2014) Application of Iranian natural zeolite and blast furnace slag as slow sand filters media for water softening. Int J Environ Health Eng 3 (2):2277–9183

American Public Health Association, American Water Works Association, and Water Pollution Control Federation (APHA/AWWA/WPCF) (1998) Standard methods for the examination of water and wastewater, 20th edn. APHA, Washington, D.C.

Arndt RE, Wagner EJ (2004) Rapid and slow sand filtration techniques and their efficacy at filtering triactinomyxons of myxobolus cerebralis from contaminated water. North Am J Aquac 66:261–270

Busscher HJ, Dijkstra JB, Engels E, Langworthy DE, Collias DE, Bjorkquist DW, Mitchell MD, Vander HC (2006) Removal of two waterborne pathogenic bacterial strains by activated carbon particles prior to and after charge modification. Environ Sci Tech 40:6799–6804

Dwari RK, Rao DS, Swar AK, Reddy PSR, Mishra BK (2012) Characterization of dolochar wastes generated by the sponge iron industry. Int J Miner Metall Mat 19(11):992–1003

Ellis KV (1987) Slow sand filtration as technique for the tertiary treatment of municipal Sewages. Water Res 21(4):403–410

Ellis KV, Wood WE (1985) Slow sand filtration. Crit Rev Environ Control 15(4):315–354

Farooq S, Al-Yousef AK (1993) Slow sand filtration of secondary effluent. J Environ Eng Div ASCE 119(4):615–630

Fox KR, Graham NJD, Collins MR (1994) Slow sand filtration today: an introduction review. In: Slow sand filtration: an international compilation of recent scientific and operational development. AWWA, Denever, CO, USA, pp 1–8

Hatt JW, Germain E, Judd SJ (2013) Granular activated carbon for removal of organic matter and turbidity from secondary wastewater. Water Sci Technol 67(4):846–853

Huisman L, Wood W (1974) Slow sand filtration. World Health Organisation, Geneva, Chap. 3

Marshall GR, Middlebrooks EJ (1974) Intermittent sand filtration to upgrade existing wastewater treatment facilities. Utah Water Research Laboratory

Muhammad N, Ellis K, Parr J, Smith MD (1996) Optimization of slow sand filtration. In: 22nd WEDC conference on reaching the unreached: challenges for the 21st century

Panda H, Sahoo S, Tiadi N, Dash RR, Mohanty CR (2014) Sorption of hexavalent chromium from synthetic waste water using Dolochar. Recent Res Sci Technol 6(1):106–110

Rout P, Bhunia P, Dash RR (2015) Effective utilization of a sponge iron industry by-product for phosphate removal from aqueous solution: a statistical and kinetic modelling approach. J Taiwan Inst Chem Eng 46:98–108

Rout PR, Dash RR, Bhunia P (2016) Nutrient removal from binary aqueous phase by dolochar: highlighting optimization, single and binary adsorption isotherms and nutrient release. Process Safety Environ Prot. http://dx.doi.org/10.1016/j.psep.2016.01.01

Sadiq R (2003) Secondary effluent treatment by slow sand filters: performance and risk analysis. Water Air Soil Pollut 143:41–63

Sahoo S, Mohanty CR, Pradhan PK (2014) Utilisation of dolochar in road construction. J Civ Eng Res 4(2):37–41

Stevik TK, Aa K, Ausland G, Hanssen JF (2004) Retention and removal of pathogenic bacteria in wastewater percolating through porous media: a review. Water Res 38(6):1355–1367

Tyagi VK, Khan AA, Kazmi AA, Mehrotra I, Chopra I (2009) Slow sand filtration of UASB reactor effluent: a promising post treatment technique. Desalination 249:571–576

Removal and Recovery of Methyl Violet Dye from Industrial Wastewater by Liquid–Liquid Extraction

S. Elumalai and G. Muthuraman

Abstract In this study, cationic dye namely methyl violet (MV) from aqueous solution by liquid–liquid extraction (LLE) has been investigated. Toluic acid demonstrated to be a very effective extractant for selective extraction of methyl violet from aqueous solution. The various diluents used were benzene, xylene hexane, toluene, kerosene. Among them, xylene was found to be the most effective diluent for extraction of methyl violet dye. The maximum extraction efficiency (99.0%) was obtained at pH 12.0 ± 0.1. The other influencing parameters were also examined: effect of pH in feed phase, toluic acid concentration in organic phase, effect of diluents, acid concentration in strip phase and stripping phase ratio. The extracted dye has been successfully stripped by 0.5 N HCl. Real effluent was also extracted and found to give satisfactory result.

Keywords Methyl violet · Wastewater · Stripping · Extraction · Organic phase

Introduction

Dyes are of synthetic origins and complex of aromatic molecular structures having huge applications in our daily life. It is well known that dyes are widely used in various industries, such as food, paper, printing, leather, cosmetics, textiles, plastic and pharmaceutical industries, for coloring their final products (Zollinger 1987). They release colored wastewater which is a significant source of pollution, particularly the effluents released from textile dyeing processes. When these colored effluents enter the rivers or any other surface water systems, they upset biological activity. Color affects nature of water by inhibiting sunlight penetration, so it is essential to treat the textile wastewater prior to discharge into an environment

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(McKay et al. 1985a, b). Therefore, the color removal before discharging into the environment is necessary and accomplished via photocatalytic degradation, coagulation, liquid membrane, electro-Fenton's, chemical oxidation, ozone treatment, ultrafiltration and adsorption (Boucherit et al. 2013; Tong et al. 2011; Choi and Cho 1996; Muthuraman et al. 2013; Liu et al. 2011; Teng et al. 2014; Chu et al. 2008; Bouasla et al. 2010; Pi et al. 2014; Lei et al. 2010; Namasiwayam et al. 2007; Vaez et al. 2012).

The above-mentioned methods are only removing the colors and not recovering the dyes from wastewater. In recent years, much attention has been focused on a separation technique such as solvent extraction or liquid–liquid extraction (LLE). LLE has significant potential to remove the dyes from wastewater (Woo et al. 2000). LLE is based on the principle that a solute can distribute itself in a certain ratio between immiscible solvents (Muthuraman 2011). Therefore, the selection of both a diluent and an extractant determines the equilibrium for a given system and efficiency of the extraction process depends on its mass transfer rate (Muthuraman and Palanivelu 2005). LLE offers significant advantages in toxicological analysis such as preconcentration of toxic substances, simplicity, low cost, compatibility with analytical systems, high throughput, ease of automatic operation, high purification, enrichment, separation and analysis of various compounds in mixtures. The extraction and recovery of cationic dye from industrail wastewater by LLE using benzoic acid as an extractant has been reported. Methyl orange and congo red dyes were also extracted and recovered from aqueous solution by solvent extraction method.

In the present study, the LLE efficiency of cationic dye such as methyl violet (MV) from aqueous solutions using toluic acid in xylene and other important parameters were discussed and reported here.

Experiment and Methods

Reagents and Solutions

Sodium hydroxide (99.9%), benzene (99.0%), toluene (98.0%), hexane (>99.0%), hydrochloric acid (35%), xylene (98.5%), toluic acid (99.5%) and methyl violet (99.9%) were purchased from Merck, S D Fine and Fisher Scientific suppliers and used without any further purification.

Instrument

The absorbance of dye sample was determined using UV–visible spectrophotometer (Elico SL 159). A pH meter, Elico LI 120 pH meter, was used for the measuring pH values of the dye (feed) solution. Systronics Electrophoresis 606 was used to find out whether the dye is cationic or anionic.

Extraction Method

The organic solvent (toluic acid + xylene) was added to the prepared aqueous dye solution in a glass-stoppered bottle for extraction. The pH of the aqueous dye solution was adjusted using inorganic base such as 0.01 and 0.5 N sodium hydroxide. The glass-stoppered bottle was shaken at 100 rpm for few minutes. The solution mixture was then transferred into a separating funnel. Sample of aqueous solution at the bottom of the separating funnel was taken for absorbance (MV at $\lambda_{\max} = 582$ nm) measurement of the dye concentration. The dye concentration in the organic phase was calculated using mass balance.

Stripping Method

In stripping, the loaded organic phase and the aqueous strippant were added together into a glass-stoppered bottle and shaken at 100 rpm. After few minutes the content was transferred into a separating funnel. The aqueous strippant was taken for dye concentration measurement. All the experiments were run in duplicate, and analytical parameters were calculated in triplicate for each run.

$$E = 1 - [\mathrm{Feed}]_{\mathrm{eq}}/[\mathrm{Feed}]_0 \tag{1}$$

$$R = [\mathrm{Feed}]_s/[\mathrm{Feed}]_0 \tag{2}$$

where E is extraction efficiency, R is recovery efficiency and subscripts eq, 0 and s represent at equilibrium, initial and stripping, respectively.

Results and Discussion

Effect of PH of the Feed Phase

The extraction of MV from the aqueous solution was studied from pH 8 to 13 ± 0.1 of different dye concentrations. The pH of the dye solution was adjusted using 0.5 and 0.01 N NaOH. The results are shown in Fig. 1. It can be seen that the extraction efficiency of dye increased with increasing pH of the feed phase. The maximum extraction efficiency of dye obtained was as follows: 99% for 100 mg/L, 88% for 200 mg/L and 80% for 300 mg/L at pH 12 ± 0.1. At higher pH, OH^- ion concentration is higher and hence enhances the ion-pair complex formation. Therefore, the extraction efficiency increased. Hence, the pH 12 ± 0.1 was recommended for further studies.

Effect of Diluents

The extractant (toluic acid) was mixed with various diluents, and the extraction was carried out under optimum experimental conditions. Here two types of diluents were used: (i) aromatic hydrocarbons such as xylene, benzene and toluene and (ii) aliphatic hydrocarbons such as hexane, heptane and kerosene. Among them, xylene was found the best diluent compared with others as shown in Fig. 2. Compared with aliphatic hydrocarbons, aromatic hydrocarbons have high polarity and hence well interacted with extractant; therefore, the percentage of extraction is comparatively greater. So xylene was selected for the extraction of MV due to it is less toxicity compared to benzene and toluene. The previous researchers also examined xylene as diluent (Reddy et al. 1998; Adli et al. 2016).

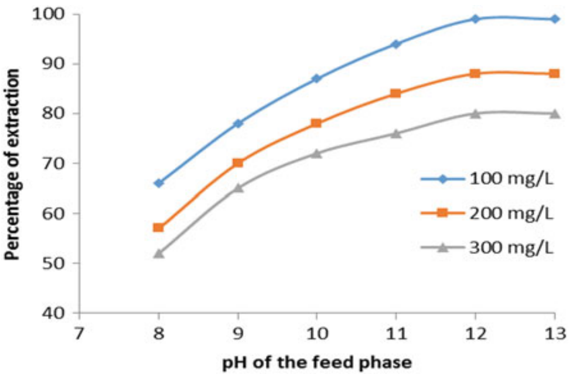

Fig. 1 Effect of pH of the feed phase (experimental conditions: volume of feed phase = 20 mL, volume of organic phase = 20 mL, toluic acid concentration = 1 × 10^{-3} mol/L, diluent = xylene)

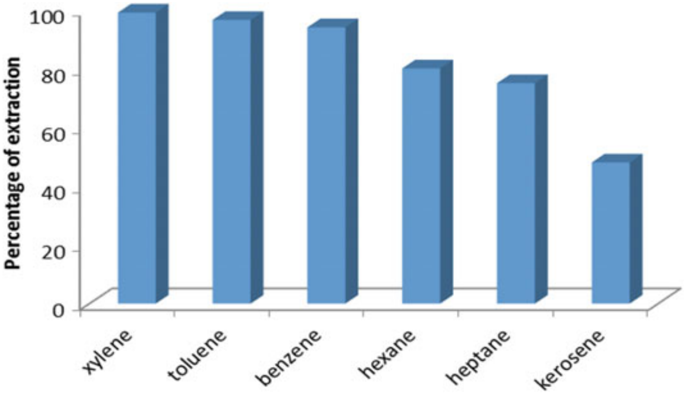

Fig. 2 Effect of diluent (experimental conditions: volume of feed phase = 20 mL, volume of organic phase = 20 mL, dye concentration = 100 mg/L, toluic acid concentration = 1 × 10^{-3} mol/L and pH = 12 ± 0.1)

Effect of Toluic Acid Concentration

The concentration of extractant is an important parameter influencing the extraction efficiency of target compounds. Therefore, the effect of concentration of toluic acid was varied in the range between 0.5 and 2.0 × 10^{-3} mol/L with optimized experimental conditions. Usually the extraction efficiency of dye increases with increasing carrier concentration. The experimental data for the percentage of extraction vs carrier concentration are plotted in Fig. 3. The maximum extraction efficiency of MV (99%) was obtained using 1.0 × 10^{-3} mol/L toluic acid in xylene. Further increase in toluic acid concentration did not improve the extraction

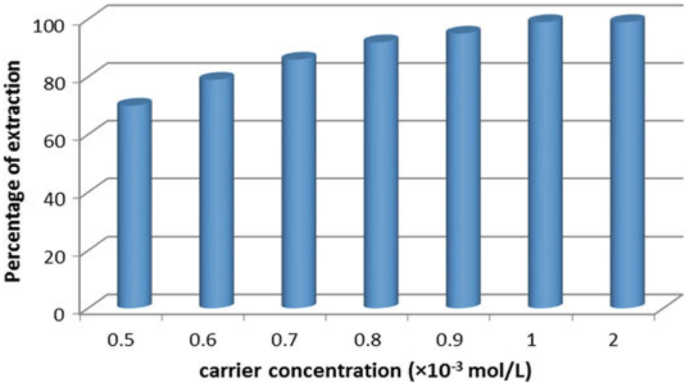

Fig. 3 Effect of carrier concentration (experimental conditions: volume of feed phase = 20 mL, volume of organic phase = 20 mL, dye concentration = 100 mg/L, diluent = xylene and pH = 12 ± 0.1)

efficiency. Therefore, toluic acid 2.0 × 10^{-3} mol/L has been recommended for further studies.

Effect of Dye Concentration

The effect of dye concentration was varied from 100 to 400 mg/L while other experimental conditions were kept constant, and the results are presented in Table 1. It shows that the extraction efficiency of MV decreased from 99 to 83% as dye concentration increases from 100 to 400 mg/L. At low dye concentration, most of the dye ions in solution will interact with extractant; as a result, higher efficiency of dye was obtained. At higher dye concentrations, the extractant has saturated and hence unable to extract the dye molecules from the aqueous phase; hence, dye remained in the aqueous phase; therefore, the removal efficiency of dye decreased (Othman et al. 2011). Hence, further studies were carried out using 100 mg/L of dye concentration.

Effect of Stripping Reagents and Its Concentration

In any extraction process, it is very important to strip the extracted dye from the organic phase and recovered organic solvent was reused several times without loss of extraction efficiency in liquid–liquid extraction system. Therefore, several acids such as sulfuric acid, hydrochloric acid and nitric acid have been tried as a stripping agent. Among them, hydrochloric acid (HCl) stripped the dye very well. Therefore, the acid concentration was varied from 0.1 to 0.6 mol/L and the results are shown in Fig. 4. It reveals that the stripping efficiency increases with increasing HCl concentration and tends to reach a maximum efficiency (98%) which was obtained at 0.5 mol/L HCl solutions. Further increasing acid concentration did not change in

Table 1 Effect of dye concentration (experimental conditions: volume of feed phase = 20 mL, volume of organic phase = 20 mL, toluic acid concentration = 1 × 10^{-3} mol/L, diluent = xylene and pH = 12 ± 0.1)

Dye concentration (mg/L)	$[\text{Dye}]_{\text{aq}}$	$[\text{Dye}]_{\text{org}}$	Percentage of extraction
100	1	99	99
200	10	190	95
300	33	267	89
400	68	344	83

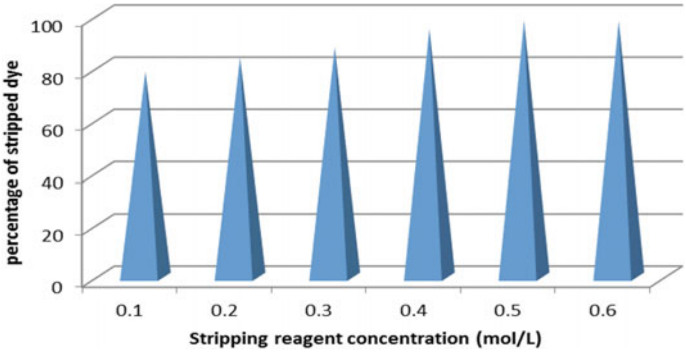

Fig. 4 Effect of stripping reagent concentration (experimental conditions: volume of organic phase = 20 mL, volume of strip phase = 20 mL and stripping agent concentration = 0.5 mol/L HCl)

stripping efficiency due to the saturation of the driving force for the stripping of dye from the carrier owing to sufficient proton concentration (Muthuraman et al. 2010). Hence, 0.5 mol/L HCl was recommended for further studies.

Mechanism of MV Extraction by LLE

The suggested mechanism of extraction and stripping of MV dye is shown in Fig. 5. In an extraction process, in an alkaline medium the toluic acid is converted into its anionic form such as toluic carboxylate ion which interacts with cationic dye. Hence, the ion-pair complex formation takes place between cationic dye and anionic toluic carboxylate ion. In stripping process, in an acidic medium the toluic carboxylate ion abstracts proton and the ion-pair complex is dissociated resulting in cationic dye being back-extracted into the aqueous phase and the carrier remaining in the organic phase which is used again extraction of MV from aqueous phase.

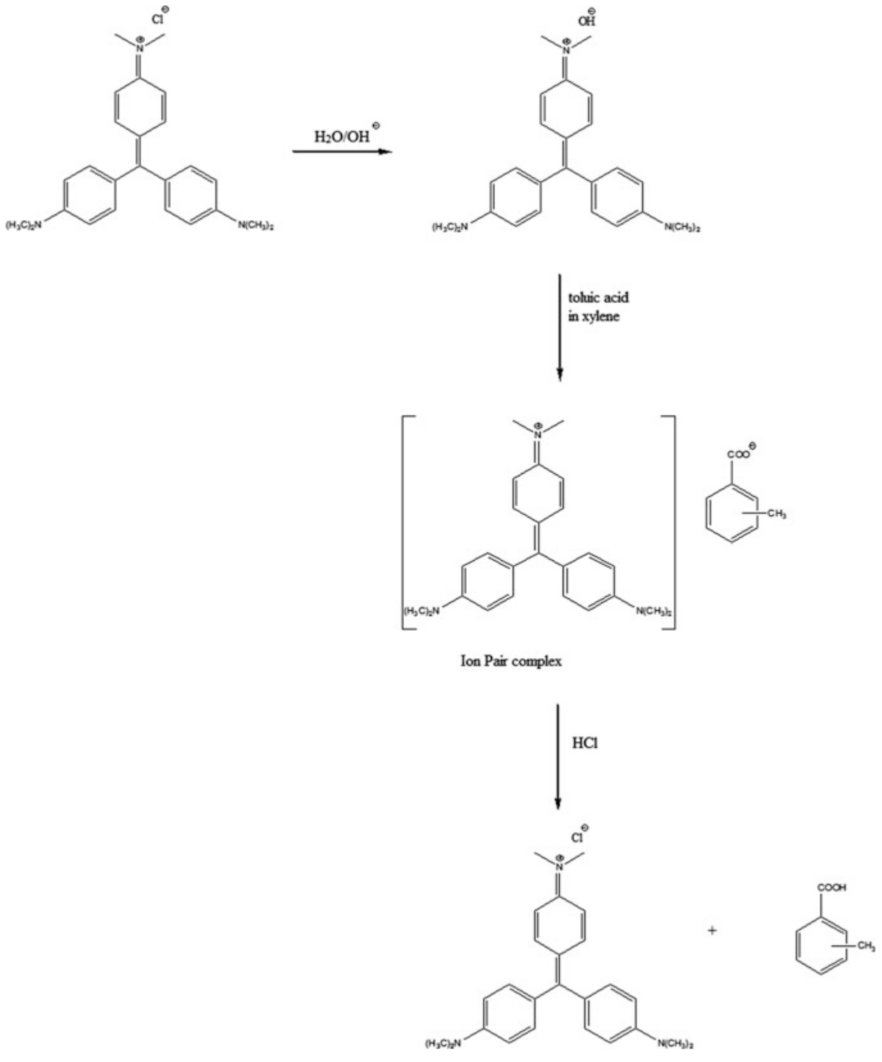

Fig. 5 Suggested mechanism of MV dye extraction

Conclusion

The removal and recovery of MV from aqueous solutions through liquid–liquid extraction containing toluic acid in xylene as carrier were studied. The extraction efficiency of MV dye decreases with increasing dye concentration. Under the optimized conditions (dye concentration = 100 mg/L, toluic acid concentration = 1×10^{-3} mol/L, diluent = xylene, pH = 12 ± 0.1, stripping reagent concentration = 0.5 mol/L HCl), the maximum percentage of extraction and stripping was obtained as 99 and 98%, respectively. The suggested mechanism was also studied. The optimized condition was applied for the removal of MV dye from industrial wastewater and found to be of satisfactory result.

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References

Adli N, Azimvand A, Sadr ZB, Moharamzadeh M, Amoli HS (2016) Rapid and continuous extraction of methyl red from wastewater using counter current chromatography. Mater Sci Appl 7:307–315

Bouasla C, Samar MEH, Ismail F (2010) Degradation of methyl violet 6B dye by the Fenton process. Desalination 254:35–41

Boucherit N, Abouseoud M, Adour L (2013) Effect of viscosity, basicity and organic content of composite flocculant on the decolorization of performance and mechanism for reactive dyeing wastewater. J Environ Sci 25:1235–1244

Choi YS, Cho JH (1996) Colour removal from dye wastewater using vermiculite. Environ Technol 17:1169–1180

Chu LB, Xing XH, Yu AF, Sun XL, Jurcik B (2008) Enhanced treatment of practical textile wastewater by microbubble ozonation. Process Saf Environ 86:389–393

Lei H, Li H, Li Z, Li Z, Chen K, Zhang X, Wang H (2010) Electro-Fenton degradation of cationic red X-GRL using activated carbon fiber cathode. Process Saf Environ 88:431–438

Liu Z, Wang F, Li Y, Xu T, Zhu S (2011) Continuous electrochemical oxidation of methyl orange wastewater using a three dimensional electrode reactor. J Environ Sci 23:50–573

McKay G, Otterburn MS, Aga JA (1985a) Fuller's earth and fired clay as adsorbents for dyestuffs. Water Air Soil Pollut 24:307

McKay G, Otterburn MS, Jamal Aga JA (1985b) Fullers earth and fired clay as adsorbents for dye stuffs. Equilibrium and rate studies. Water Air Soil Pollut 24:307–322

Muthuraman G (2011) Extractive removal of astacryl blue BG and astacryl golden yellow dyes from aqueous solution by liquid-liquid extraction. Desalination 277:308–312

Muthuraman G, Palanivelu K (2005) Selective extraction and separation of textile anionic dyes from aqueous solution by tetrabutyl ammonium bromide. Dyes Pigm 64:251–257

Muthuraman G, Palanivelu K, Teng TT (2010) Solvent extraction of methyl violet with salicylic acid from aqueous acidic solutions. Color Technol 126:97

Muthuraman G, Sathya M, Soniya M, Elumalai S (2013) Recovery of Levafix brilliant red E-4BA and Levafix brilliant red E-6BA from aqueous solution by supported liquid membrane. Membr Water Treat 4:277–300

Namasivayam C, Sangeetha D, Gunasekaran R (2007) Removal of anions, heavy metals, organics and dyes from water by adsorption onto a new activated carbon from jatrophas husk, an agro-industrial solid waste. Process Saf Environ 85:181–184

Othman N, Mili N, Wong YM (2011) Liquid-liquid extraction of black b dye from liquid waste solution using tridodecylamine. J Environ Sci Technol 4:324–331

Pi KW, Xiao Q, Zhang HQ, Xia M, Gerson AR (2014) Decolorization of synthetic methyl orange wastewater by electrocoagulation with periodic reversal of electrodes and optimization by RSM. Process Saf Environ 92:796–806

Reddy MLP, Varma RL, Ramamohan TR, Sahu SK, Chakravortty V (1998) Cyanex 923 as an extractant for trivalent lanthanides and yttrium. Solvent Extr Ion Exc 16:795–812

Teng TT, Elumalai S, Muthuraman G, Talebi A (2014) Wastewater engineering: advanced wastewater treatment systems. In: Bulk liquid membrane and its applications in wastewater treatment, pp 158–170

Tong S, Zhao S, Lan X, Ma C (2011) Degradation of reactive yellow 86 with photo-Fenton process driven by solar light. J Environ Sci 23:2087–2092

Vaez M, Moghaddam AZ, Mahmoodi NM, Alijani S (2012) Decolorization and degradation of acid dye with immobilized titania nanoparticles. Process Saf Environ 90:56–64

Woo LD, Hi HW, Yup HK (2000) Removal of an organic dye from water using a pre-dispersed solvent extraction. Sep Sci Technol 35:1951–1962

Zollinger H (1987) Color chemistry; synthesis, properties and applications of organic and pigments. Wiley-VCH, New York

Fenton's Treatment of Pulp and Paper Mill Effluent

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Abstract The pulp and paper industry produces large quantities of bleaching effluents that are highly colored and contain large concentrations of organic matter. Most of these contaminants mainly lignin and organic matter are difficult to eliminate by conventional wastewater treatment processes. Advanced oxidation processes (AOPs) are used to convert non-biodegradable organic matter to harmless substances. AOPs depend on the production of hydroxyl radicals (.OH) with a redox potential of 2.8 V. These radicals undergo various oxidation processes by reacting with oxygen and convert the organics to CO_2 and H_2O. The waste effluent for the present study was collected from bleaching process of pulp and paper industry located in Karnataka. Batch experiments were carried out on the effluent using Fenton's oxidation process. Various doses of $FeSO_4 \cdot 7H_2O$ and H_2O_2 30% W/V were used. All reactions were carried out in triplicate under atmospheric pressure in a dark place, to avoid direct attack of sunlight, with continuous shaking in a water bath maintained at 130 rpm at 30 °C. Lignin concentration was measured using spectrometric procedure at a wavelength of 700 nm. The optimum pH value of 4 was observed. The optimum condition for the maximum removal of COD and lignin was pH 4, H_2O_2 dosage 2 mg/mL, $FeSO_4.7H_2O$ 1.8 mg/mL and reaction time 30 min wherein COD removal efficiencies of up to 88% and lignin removal efficiencies of up to 92% were achieved. Hence, Fenton's oxidation seems to be an efficient and economical treatment technique for pulp and paper mill effluent.

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Introduction

The pulp and paper industry produces large quantities of bleaching effluents that are highly colored and contain large concentrations of organic matter (Bulskaya 2009). Most of these contaminants are difficult to eliminate by conventional wastewater treatment processes (Pokhrel and Viraraghavan 2004). Advanced oxidation process is used to convert non-biodegradable organic matter to harmless substances. AOPs depend on the production of hydroxyl radicals (.OH) with a redox potential of 2.8 V (Gogate and Pandit 2004). These radicals undergo various oxidation processes by reacting with oxygen and convert the organics to CO_2 and H_2O. Degradation of organic compound increases as the concentration of H_2O_2 increases until a critical value is reached. Acidic condition favors more for the production of hydroxyl radicals.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-}$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^{\cdot} + H^{+}$$

Major objective of the present study was to apply Fenton oxidation process on pulp and paper effluent. Integrated monitoring and analysis of the following parameters, viz. COD and lignin, were carried out to better understand the degradation mechanism.

Materials and Methods

Materials

The effluent for present study was collected from bleaching process of pulp and paper industry located in Karnataka. The grab effluent was collected after primary clarification where water from different streams was coming together, including bagasse plant, colored stream and non-colored stream. The main component of the effluent was lignin and its derivatives, fibers and inorganic materials. The wastewater characteristics mainly COD and lignin were analyzed using APHA standards.

Experimental Methods

Separate batch experiments were carried out on the effluent for the Fenton oxidation process. Effluent of 50 mL was taken in conical flask and brought to room temperature. pH of the effluent was adjusted using H_2SO_4 and NaOH. Various doses of $FeSO_4{\cdot}7H_2O$ and H_2O_2 30% W/V were added in the effluent. All reactions are

Table 1 Characteristics of the pulp and paper mill effluent

S. No.	Parameter	Value
1	pH	5.8
2	COD (mg/L)	732
3	Lignin (mg/L)	262
4	BOD (mg/L)	240

carried out in triplicate under atmospheric pressure in a dark place, to avoid direct attack of sunlight, with continuous shaking in a water bath maintained at 130 rpm at 30 °C. After certain reaction time, the experiment was stopped by adding 1 N NaOH and kept the system for 30 min for settling. The supernatants were taken, and COD concentration was found out by closed reflux method. Lignin concentration was measured using spectrometric procedure at a wavelength of 700 nm (Table 1).

Results and Discussion

Fenton oxidation process is carried out in paper and pulp industrial effluent. After Fenton's treatment, reduction in the color, lignin and COD occurred. The reaction parameters were optimized to obtain maximum COD and lignin removal. The reaction parameters included pH, H_2O_2 dosage, $FeSO_4 \cdot 7H_2O$ dosage and reaction time.

Effect of pH

In pH ranging from 2 to 4, the degradation is increasing and above 4 there is a decreasing trend as can be seen in Fig. 1. The maximum reduction in COD was 81.18% at pH 4 and lignin 88.45% at pH 3. The optimum value of pH was taken as 4 by this experiment.

Effect of H_2O_2

Highest removal of COD occurs at 2 mg/mL of 30% H_2O_2 and is 83.16% as can be seen from Fig. 2. Lignin removal is increasing with an increase in H_2O_2 dosage. The maximum removal of lignin is 91.16% at 4 mg/mL H_2O_2 and at 2 mg/mL H_2O_2 86.14%. 2 mg/mL of 30% H_2O_2 is taken as optimum dosage for the treatment of paper and pulp industrial effluent.

Fig. 1 Plot of pH versus % removal of COD and lignin

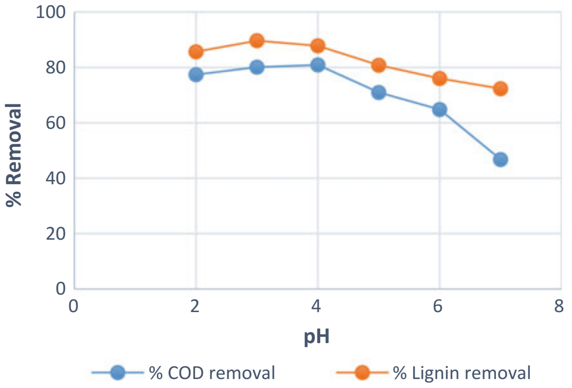
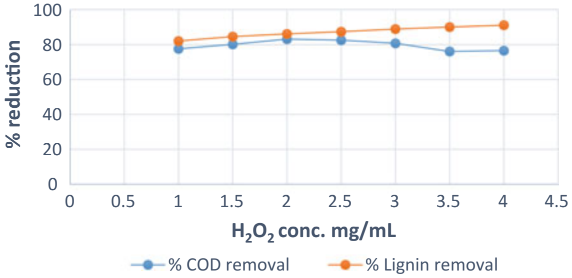


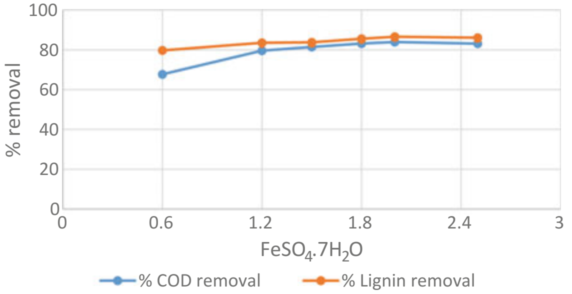
Fig. 2 Plot of H_2O_2 dosage versus % removal of COD and lignin



Effect of $FeSO_4{\cdot}7H_2O$

Experiments were carried out by adding different dosages of $FeSO_4{\cdot}7H_2O$ in each 50 ml effluent with a H_2O_2 dosage of 2 mg/mL in it. The rate of degradation increases with an increase in the concentration of ferrous ions. The removal of COD is maximum for the dosage of 2 mg/mL. Also for 1.8 mg/mL of $FeSO_4{\cdot}7H_2O$ dosage, the removal is almost high and about 83.2% as can be seen from Fig. 3. The removal of lignin for 1.8 mg/mL dosage is 85.62%, which is also high removal. Optimum dosage of 1.8 mg/mL $FeSO_4{\cdot}7H_2O$ was taken.

Fig. 3 Plot of $FeSO_4{\cdot}7H_2O$ dosage versus % removal of COD and lignin



Influence of H_2O_2/Fe^{2+} Ratio

Degradation efficiency by Fenton process is influenced by the concentration of Fe^{2+} ions. The optimal operating parameters for the degradation of COD and lignin by Fenton process were $H_2O_2:Fe^{2+}$ 5.6:1 with H_2O_2 dosage 2 mg/ml and Fe^{2+} dosage of 0.36 mg/mL as can be observed from Fig. 4.

Effect of Reaction Time

The COD and lignin removal efficiency increased with increased stirring time. COD removal efficiency exceeded 87% at a reaction time of 30 min and did not increase significantly when time was further increased. The lignin removal at 30 min is above 90% as can be observed from Fig. 5. Thirty minutes was selected as the optimal reaction time for the treatment of pulp and paper industrial effluent.

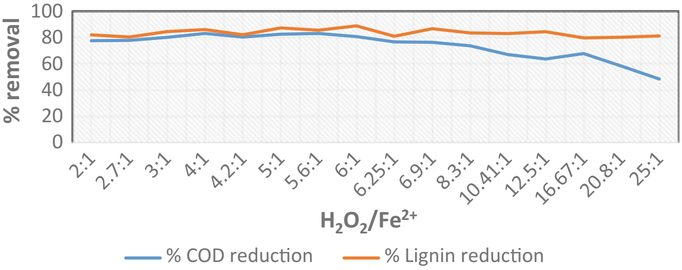


Fig. 4 Plot of H_2O_2/Fe^{2+} ratio versus % removal of COD and lignin

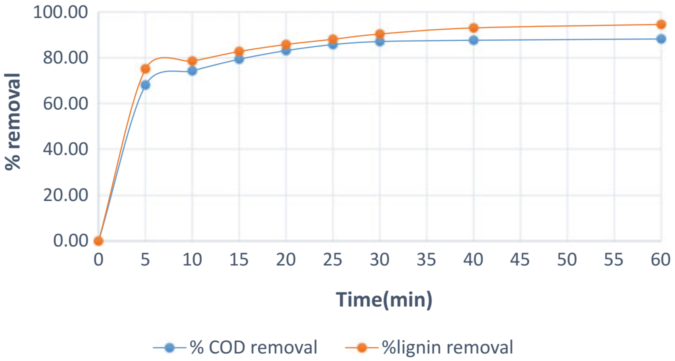


Fig. 5 Plot of reaction time % removal of COD and lignin

Summary

Fenton oxidation process on pulp and paper effluent was carried out and observed the reduction in COD and lignin concentrations. The optimum condition for the maximum removal of COD and lignin was pH 4, H_2O_2 dosage 2 mg/mL, $FeSO_4{\cdot}7H_2O$ 1.8 mg/mL and reaction time 30 min. COD removal was about 88%, and lignin removal 92% at optimum reaction conditions. Kumar et al. (2011) have reported 57.9% reduction in COD, the removal of BOD of up to 42.9%, and 89.2% color removal of the primary clarified pulp and paper mill effluent and for biotreated effluent 74.8% in COD, 52.7% in BOD, and 95.4% in color, in 4 h using UV/TiO_2/H_2O_2 process. Merayo et al. (2013) have reported 60% COD reduction of the effluent from the kraft pulp mill at an initial pH = 7 and 35% COD removal for the effluent of the recycled paper mill using 2.4 g O_3/L. During photocatalysis, a 20–30% reduction in the COD was observed for both types of effluents.

References

Bulskaya (2009) Oxidative treatment of paper mill effluent by TiO_2 photocatalysis or photo-fenton reagent. Thessaloniki, Greece

Gogate PR, Pandit AB (2004) A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. Adv Environ Res 8:501–551

Kumar P, Kumar S, Bhardwaj NK, Choudhary AK (2011) Advanced oxidation of pulp and paper industry effluent. In: 2011 IPCBEE, vol 15. IACSIT Press, Singapore

Merayo N, Hermosilla D, Blanco L, Cortijo L, Blanco Á (2013) Assessing the application of advanced oxidation processes, and their combination with biological treatment, to effluents from pulp and paper industry. J Hazard Mater 262:420–427

Pokhrel D, Viraraghavan T (2004) Treatment of pulp and paper mill wastewater—a review. Sci Total Environ 333:37–58

Treatment of Car Washing Unit Wastewater—A Review

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Abstract Rapidly growing population has resulted in exponential increase in the usage of the number of cars. As a practice of maintenance, the cars are washed periodically which draws enormous quantity of fresh water globally also the washing of cars bestows the pollutants like oil, grease, detergents, and dirt to the fresh water. This wastewater if untreated and directly mixes with the water stream, it causes pollution. World Health Organization reports that the quality of fresh water in earth is under constant pressure. This paper discloses importance of treatment of car wash wastewater by stating the environmental impacts of untreated car wash wastewater and also presents a global scenario which includes the quantity of water allocated to wash a car with the reclamation measures, regulations followed by them. This paper also states the quantity of water generally needed to wash a car, characteristics of water after washing, with a review on some of the works done so far to treat the car wash wastewater and also the challenges in reclamation of car wash wastewater.

Introduction

Day by day, the number of automobiles is getting increased on the roads due to the increase in population and also the economic status of people. This in turn increases the intake of water for car washing, which is to be done as maintenance. In European countries, the large car washing units and service stations are insisted upon by the respective pollution control boards to provide necessary treatment for the effluents (Janik and Kupieck 2007). Professional car wash systems create wastewater that can have a great impact on the environment, if not properly

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managed and discharged (Zaneti et al. 2012). Car washing installations producing detergent-rich sewage are usually located together with petrol stations (Perkowski et al. 2006). Oil and grease and detergents, including biodegradable detergents, can be poisonous to fish (Tony and Bedri 2014).

On the other hand, phosphates which are plant nutrients can cause excessive growth of nuisance plants in water bodies (Mazumder and Mukherjee 2011). So it is very necessary to treat the car wash wastewater. By 2025, nearly 2 billion people will be living in countries or regions with absolute water shortage, where water resources per person fall below the recommended level of 500 m^3 per year (WHO 2007). So treatment of fresh water which is utilized for the welfare of our human lives should be treated up to the desired level, to eliminate the pollutants so that it paves the path for sustainability.

In the past, people used to wash their cars in the backyards of their homes or other places of convenience, and nowadays, mechanical devices in designated areas mostly perform this task. Nevertheless, in every case the water used for cleaning the car gets polluted (Janik and Kupieck 2007). Car wash chemicals, road surface pollutants, traffic pollutants, oil and grease, and detergents together constitute the pollutants in the water coming from the car washing (Zaneti et al. 2012). The characteristics of car wash wastewater, different treatment systems adopted by researchers, and the challenges in reclamation are explained in this paper.

Quantity of Water Used to Wash a Car

Depending on the construction and water technology involved, professional car washes can be varied into different types:

a. Self-serve car washes—It is done by the customer itself in his home. It consumes about 440 L of water.
b. Bay automatic washes—This is mostly done at the fuel station that consumes about 114 L of water. The car wash machine moves back and forth over the car to wash while the car does not move.
c. Touchless washes—This is the most modern vehicle wash system. Only mild soap solutions and water touch the car. This method consumes of water about 270 L (Janik and Kupieck 2007).

The average water consumption for washing a car is 150–600 L (Lau et al. 2013). The fresh water requirement per vehicle for full service wash is listed in Table 1.

Table 1 Fresh water requirements per vehicle to wash

Type of vehicle	Range	Volume used (L/vehicle)
Small cars	Min–Max	114–217
	Mean	173
Vans and light trucks	Min–Max	269–388
	Mean	306

Fall et al. (2007)

Table 2 Car wash wastewater characteristics from various literatures

Parameters	References				
	Bossu et al. (2007)	Zaneti et al. (2012)	Zaneti et al. (2011)	Lau et al. (2013)	Rubi-Juarez et al. (2015)
pH	7.5–7.6	6.6–8.2	6.9–8.3	6.5–8.71	7.5
COD (mg/L)	208–382		217.5–264.5	75–738	488
BOD_5^{20} (mg/L)	63–140		72–194	20.5–11.9	150.96
Turbidity (NTU)		46–195	72.5–95.3	34–86	898
Total suspended solids (mg/L)	60–140	35–143	49–87		
Total dissolved solids (mg/L)		319.5–368.5	411.5–595.5		
Conductivity (mS/cm)	0.8–1.1		0.5–0.75	0.15–0.26	0.796

Characteristics of Car Wash Wastewater

Janik and Kupieck (2007) stated that the origin of pollutants in wastewater from car washing is from traffic pollutants, car exploitation pollutants, and car wash chemicals. The traffic pollutants include road surfacing pollutants and atmospheric fallout pollutants. The characteristics of car wash wastewater from some of the literatures are given in Table 2.

The two important parameters other than those mentioned in Table 2 are oil and grease and methylene blue active substances (MBAS). The MBAS method is useful for estimating the anionic surfactant content of waters and wastewaters. Anionic surfactants are among the most prominent of many substances, natural and synthetic, showing methylene blue activity. Soaps do not respond in the method. Nonsoap anionic surfactants commonly used in detergent formulations are strongly responsive to this method (APHA 1998). The range of MBAS in a typical car wash wastewater ranges from 3 to 68 mg/L (Lahti 2000; Fall et al. 2007; Rubi-Juarez et al. 2015). Oil and grease ranges between 10 and 386 mg/L (Lahti 2000; Rubi-Juarez et al. 2015). From the literature available, the researchers mainly concentrated with the parameters pH, conductivity, total dissolved solids, total suspended solids, oil and grease, chemical oxygen demand, turbidity, and methylene blue active substances. And they focused to reduce the concentration of chemical oxygen demand and turbidity while they adopted various treatment processes.

Regulations Around Worldwide

New car washing technologies must be employed, including reuse of water, in order to save natural resources and to provide a high-quality wash. By setting up rules and regulations and investing in strategic projects, some countries have made significant progress in reusing the wastewater, while other countries still lack adequate planning and regulations (Madwar and Tarazi 2003). Mainly, in European countries, the car wash industry appears today to be more conscious of the need for wastewater treatment and water reclamation. Worldwide environmental legislation and guidelines concerning this specific issue have been released. Switzerland, Germany, and the Netherlands no longer allow their citizens to wash cars at home (Janik and Kupieck 2007). In Germany, minimum there should be 80% of recycling of water should be done. In the Netherlands and Scandinavian countries, it is enforced that to consume the fresh water a maximum of 60–70 L per car (Bossu et al. 2007). In Queensland, Australia, it is mandatory that the use of 70 L of fresh water for a single car wash (Zaneti et al. 2011). In Europe, some countries restrict the water consumption to 60–70 L per car and/or impose a reclamation percentage (70–80%) (Zaneti et al 2011).

Reclaimed (reuse and recycling) water is defined as the wastewater that has gone through various treatment processes to meet specific water quality criteria the fit for purpose principle (Zaneti et al. 2012). Dunn and Bush (2001) stated that the increasing restrictive legislation and rising water prices are pushing the car wash industry to invest in process-integrated solutions, mainly in Europe, Australia and the USA, where this activity is one of the primary commercial uses of reclaimed water. The most studied technologies are membranes ultrafiltration and nanofiltration integrated with pretreatment. Although these technologies are extremely efficient, the associated costs with it like implementation, operation, and maintenance are very high (Zaneti et al. 2012). In Poland, Portugal, Italy, and many other countries, this issue is not strictly regulated (Janik and Kupieck 2007). In India, there are no such regulations and legislations for the fresh water consumption for washing cars.

Environmental Impacts Due to Untreated Car Wash Effluents

Professional car wash systems create wash wastewater that can have a great impact on the environment if not properly managed and discharged. Contaminants in wash wastewater can cause the worst environmental problems include the following:

- Phosphates which is plant nutrients and can cause excessive growth of nuisance plants in water bodies.

- Oil and grease, chemicals, and solvent-based solutions those are harmful to living organisms (IEPA 2002).
- Biodegradable soaps are also imparts the same, create a bacterial population increase, transmitting through the food chain to protozoa, which are more sensitive to car wash toxins than other aquatic organisms, such as fish.
- All detergents will destroy fish mucus membranes and gills to some degree. The gills may lose natural oils, interrupting oxygen transfer.
- Damaged mucus membranes leave fish susceptible to bacteria and parasites.
- Detergents are toxic to fish near 15 ppm, killing fish eggs at 5 ppm.
- A concentration of 2 ppm will lower the surface tension of water enough for fish to absorb double the amount of organic chemicals, such as pesticides and phenols (Oknich 2002).

Various Treatment Methods Approached in the Literatures

The researchers approached many treatment processes to bring down the concentration of some of the pollutants in the water caused due to the washing of cars. Some of them are summarized and given below.

Physical Treatment

Al-Odwani et al. (2007) designed a prototype car wash reclamation system which contained settling tank, oil/water separator and filters. They designed the tank with an inclined screen fixed in the middle to prevent all heavy particles with the sludge removal opening on the bottom of the tank and also an oil skimmer in the middle of the other half of the tank. They designed the filtration unit with the gravel, green sand, and carbon layers. They tested this system by passing the samples collected from car wash units, and they concluded that this setup had the oil removal efficiency of 73% and also had the total dissolved solids removal efficiency of 33.38%.

Flocculation, Activated Carbon Treatment and Ultrafiltration

Hamada and Miyazaki (2004) studied about the practical reuse system for car wash wastewater by employing cellulose acetate hollow fiber ultrafiltration membrane with the aid of flocculation and activated carbon treatments based on the results from a laboratory-scale experiment. They characterized the wastewater as follows pH 6.5–7.3, COD 7.7–41.7 mg/L, BOD 4.8–50 mg/L, turbidity 4.1–63.5 NTU, suspended solids 16–44 mg/L. They resulted the parameters after performing the above-mentioned treatment having the characteristics of pH 6.7–7.1, COD 3.7–15.7 mg/L, BOD 2.5–10 mg/L, turbidity 0.05 NTU, suspended solids 0.5 mg/L.

Chemical Coagulation and Activated Sludge Process

Mazumder and Mukherjee (2011) collected the samples from different automobile servicing garages and characterized the parameters. They found oil and grease and chemical oxygen demand (COD) were two major pollutant parameters concern. They tried to reduce the content of oil and grease in the effluent. They made composite sample based on the characterization of the collected samples in such a way it contains oil and grease concentration of 300 and 600 mg/L. They had given the coagulation using alum, alum with bentonite, $FeSO_4$, $CaCl_2$ with bentonite, and activated sludge process to the artificially made sample separately. They did with the different concentrations of coagulants and concluded that the 100% removal of oil and grease could be done with the coagulants. They concluded that with the very less concentration of coagulant (60 mg/L) and also without changing the pH, alum with bentonite removes 100% removal of oil and grease and activated sludge process has the removal efficiency of 18–68%, with the batch period of 18–30 h.

Flocculation Column-Flotation Technique

Flocculation Column-Flotation technique was adopted by Rubio and Zaneti (2009). They have reported that they have achieved 90% of turbidity removal and 75% of color removal in the car wash wastewater by this technique. The residual surfactant concentration in the wastewater also helped this process by the generation of microbubbles.

Combined Electrocoagulation—Electrooxidation Process

Rubi-Juarez et al. (2015) performed the treatment of wastewater from a carwash by electrocoagulation, electrooxidation and combined electrocoagulation and electrooxidation process. They stated that electrocoagulation with iron and aluminum produced similar results, but the iron electrode imparted color to the solution. They done the aluminum electrocoagulation at pH 7 with a current density of 150 A/m^2 for 60 min and achieved the reduction of turbidity by 98%, color by 96%, oils by 92%, chemical oxygen demand by 76%, biochemical oxygen demand by 74%, and methylene blue active substances by 56%. They performed the electrooxidation process with boron-doped diamond electrodes at 210 A/m^2 for 120 min and asserted it was effective in reducing chemical oxygen demand 82%, color 81%, methylene blue active substances 81%, biochemical oxygen demand 73%, and chlorides 72%. Finally, they performed combined process and mentioned it was very effective in reducing oils 100%, color 99.3%, turbidity 98.4%, chemical oxygen demand 96%, biochemical oxygen demand 93%, and methylene blue active substances 92%. They suggested the treated wash water could also be reused.

Membrane Filtration Techniques

Lau et al. (2013) employed ultrafiltration and nanofiltration membranes to treat car wash effluent. They learnt that nanofiltration exhibited greater flux stability also higher resistance against fouling when compared to ultrafiltration. They stated that COD removal was good in nanofiltration, turbidity removal was good enough in both ultrafiltration and nanofiltration, and both nanofiltration and ultrafiltration performance were ineffective in conductivity and total dissolved solids removal.

Challenges in Reclamation

Wiltrout (1973) described that suspended particles removed from the car wash wastewater are washed for rinsing the cars and further sent to remove soap, detergents, and other impurities to produce reusable clear water. This depicts the soap, detergents, suspended and colloidal particles; turbidity mainly stops the wash water to recycle. Zaneti et al. (2012) indicated that the water quality for vehicle washes must be sufficiently high such that vehicles and wash equipment are not damaged (corrosion, scaling, and spots chemical risk) and the aesthetic conditions are acceptable. The most studied technologies are ultrafiltration and nanofiltration integrated with pretreatment. Although these technologies are extremely efficient, the associated costs such as implementation, operation, and maintenance are very high. This indicates the cost of treatment is unaffordable also becomes a factor for not recycling the wash water (Koeller et al. 2006). The treatment of car wash wastewater could be carried out by sand filtration, adsorption, and biological process also. But they did not produce satisfactory results for reusing (Hamada and Miyazaki 2004).

Conclusions

Around 170 L of water is needed to wash a car. Definitely, water is to be conserved by all over the world, especially most populated country like India must do, in a very sensible manner. There are no sufficient basic resources for the current population. We are in a verge to take necessary steps to maintain sustainability. Treating and recycling the car washing unit wastewater certainly reduce the burden of intake of fresh water from the natural resources. The biological techniques so far tried by the researchers are not giving satisfactory results. Efficient membrane filtration techniques are extremely costly and not affordable to all the community of people. So a good efficient and economic treatment pattern is to be framed out and suggested to the washing units by considering the main parameters, which will in turn reduce their cost of payment of water from the municipal sources, through recycling. The literature available regarding the car wash wastewater treatments is very less which indicates enough attention is not paid globally except developed countries. The lack of strict regulations in India needs a better revision so that it paves for the better usage of water and its conservation.

References

Al-Odwani A, Ahmed M, Bou-Hamad S (2007) Carwash water reclamation in Kuwait. Desalination 206(1):17–28

APHA (1998) Standard methods for the examination of water and wastewater, vol 48, 20th edn, pp 5–47

Boussu K, Kindts C, Vandecasteele C, Van der Bruggen B (2007) Applicability of nanofiltration in the carwash industry. Sep Purif Technol 54(2):139–146

Dunn RF, Bush GE (2001) Using process integration technology for CLEANER production. J Clean Prod 9(1):1–23

Fall C, Lopez-Vazquez CM, Jimenez-Moleon MC, Ba KM, Diaz-Delgado C, Garcia-Pulido D, Lucero-Chavez M (2007) Carwash wastewaters: characteristics, volumes, and treatability by gravity oil separation. Revista Mexicana de Ingeniería Química 6(2):175–184

Hamada T, Miyazaki Y (2004) Reuse of carwash water with a cellulose acetate ultrafiltration membrane aided by flocculation and activated carbon treatments. Desalination 169:257–267

IEPA (2002) Illinois environmental protection agency. www.epa.state.il.us/small-business/car-wash/car-wash.pdf

Janik H, Kupiec A (2007) Trends in modern car washing. Pol J Environ Stud 16(6):927

Koeller J, Linda Y, Brown C (2006) Evaluation of potential best management practices, pp 1–17

Lahti WJ (2000) U.S. Patent No. 6,042,730. U.S. Patent and Trademark Office, Washington, DC

Lau WJ, Ismail AF, Firdaus S (2013) Car wash industry in Malaysia: treatment of car wash effluent using ultrafiltration and nanofiltration membranes. Sep Purif Technol 104:26–31

Madwar K, Tarazi H (2003) Desalination techniques for industrial wastewater reuse. Desalination 152(1):325–332

Mazumder D, Mukherjee S (2011) Treatment of automobile service station wastewater by coagulation and activated sludge process. Int J Environ Sci Dev 2:64–69

Oknich J (2002) The perceived environmental impact of car washing. Ramsey-Washington Metro Watershed District

Perkowski J, Bzdon S, Bulska A, Jozwiak WK (2006) Decomposition of detergents present in car-wash sewage by titania photo-assisted oxidation. Pol J Environ Stud 15(3):457–465

Rubi-Juarez H, Barrera-Diaz C, Linares-Hernandez I, Fall C, Bilyeu B (2015) A combined electrocoagulation-electrooxidation process for carwash wastewater reclamation. Int J Electrochem Sci 10(8):6754–6767

Rubio J, Zaneti R (2009) Treatment of washrack wastewater with water recycling by advanced flocculation column-flotation. Desalination 8:146–153

Tony MA, Bedri Z (2014) Experimental design of photo-Fenton reactions for the treatment of car wash wastewater effluents by response surface methodological analysis. Adv Environ Chem 1–6

WHO (2007) World Health Organization. http://www.wateronline.com/doc/world-health-organizations-10-facts-about-wat-0001

WHO (2015) World Health Organization. http://www.who.int/topics/water/en/

Wiltrout D (1973) U.S. Patent No. 3,774,625. U.S. Patent and Trademark Office, Washington, DC

Zaneti R, Etchepare R, Rubio J (2011) Car wash wastewater reclamation. Full-scale application and upcoming features. Resour Conserv Recycl 55(11):953–959

Zaneti R, Etchepare R, Rubio J (2012) More environmentally friendly vehicle washes: water reclamation. J Clean Prod 37:115–124

Efficient and Economical Application of a Spent Waste Adsorbent Cu^{2+}-Loaded Poly (AAc-AM-SH) Superabsorbent Hydrogels by Reusing It for Adsorption of Phosphate Ion

Tripti Singh and Reena Singhal

Abstract In the present study, a more potential and economical method is described to reutilize a waste adsorbent as the waste Cu^{2+}-loaded poly(AAc/AM/SH) SAHs were not undergone any regeneration process and directly applied to adsorb phosphate ion from another waste solution. The SAHs poly(AAc-AM-SH) was anionic in nature, thus show higher affinity toward Cu^{2+} ions, but it hardly adsorb anions due to its characteristics of negative charge existing on the polymeric surface. The adsorption of Cu^{2+} makes it positively charged moiety and so it is being capable of anions/anionic dye adsorption. The various factors affecting the phosphate adsorption including pH, contact time, initial concentration of the phosphate were systematically investigated. The maximum phosphate adsorption was obtained 87.62 mg/g. The adsorption data fitted the Langmuir adsorption isotherm. The desorption studies showed that the regeneration of the poly(AAc/AM/SH)–Cu SAHs adsorbent can be easily achieved. The results confirmed that poly (AAc/AM/SH) superabsorbent hydrogels loaded with Cu^{2+} ion can be applied as effective solid adsorbent for the removal of phosphate ions from waste water and aqueous effluents.

Introduction

Over the recent years, the rapid development of modern industries has increased the threat of water pollution to the environment. The chief water pollutant consist non-biodegradable matter, dyes, metal ions, hydrocarbons, anions etc. that has been rapidly increased in water. Therefore, different efficient treatment methods (such as

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chemical precipitation, cross flow filtration, chelating ion exchange, crystallization, reverse osmosis, electrochemical treatment, neutralization, and adsorption) have been developed. However, among these methods, the adsorption process is found to be a highly efficient, regenerable, economical, and promising method. Superabsorbent hydrogels (SAHs) are a special class of adsorbents which are lightly crosslinked three dimensional macromolecular polymeric networks with the ability to absorb huge amounts of water and the absorbed water is hard to remove even under pressure.

Development of SAHs adsorbents is based on the interaction of adsorbate with the active chelating functional groups such as sulfonic acid, amine group, carboxylic acid, amine hydroxyl etc. and the selectivity, effectiveness, and reusability of these SAHs can be determined by these functional groups. These active functional groups adsorb, trap and bind the adsorbate molecules, and so make these SAHs as more effective adsorbent (Karadag et al. 1995). With the development and optimization of these adsorbents, production of waste products also occurs in industrial sectors. These products mainly include the already used adsorbents, which were applied for the adsorption process. These waste adsorbents can be (i) recycled for again adsorption process by regenerating them in acidic/basic elution medium for next cycle (Kara et al. 2004), (ii) disposed or cremated. For any adsorption process as the adsorption proceeded reaches to equilibrium, the original polymeric backbone structure of adsorbent SAHs changed and they can function as a new type of the adsorbent.

In the past few decades, phosphate has been recognized as a substantial non-point-source pollutant because of over application of animal-based and manures synthetic fertilizers (Arai and Sparks 2001) the electronic industry, pigment formulation, water treatment, detergents, as well as mineral processing. The existence of trace concentration of phosphate ion in the wastewater from municipalities and industries is responsible for eutrophication problems that lead to growth of the aquatic plants, and depletion of dissolved oxygen in coastal areas, lakes, and other water bodies. Therefore, industrial and municipal wastewater having phosphate must be treated before discharging.

Acrylic acid is cheap, highly hydrophilic and acts as a good chelating agent. Polyacrylamide has high hydrophilicity, excellent resilience, and its pendant amide group acts as efficient chelating group for the ionic and polar species. Humic acid, a principal component of humic substances, is found in many places in nature. It consists of large number of functional hydrophilic groups (including carboxylates and phenolic hydroxyls, NH_2 groups and oxygen and nitrogen as bridge units) (Wang and Wang 2009). It is accepted that the removal capacity of an adsorbent is highly influenced by the adsorption conditions (such as pH, temperature and ionic strength). In our previous report, we synthesized a biodegradable multifunctional SAHs based on acrylic acid and acrylamide monomers modified with sodium humate and used this as an adsorbent for removal of Cu^{2+} (Singh and Singhal 2012). After the adsorption of Cu^{2+}, it became positively charged moiety and being capable of phosphate ion removal. Thus, this Cu^{2+}-loaded gel without any prior treatment serves as a new kind of adsorbent, i.e., metal loaded adsorbents.

The present report deals with an economical and potential method to treat a waste adsorbent. So, the novelty of the present work is to identify applicability of waste adsorbent poly(AAc/AM/SH)–Cu hydrogels for the adsorption of phosphate ions so that to provide a new potential way to use an already used adsorbent without any regeneration or purification process. The experiments were performed as a function of different pH, contact time and various initial concentrations of phosphate ion to determine the optimum conditions for the adsorption of phosphate ion from aqueous solution. Langmuir and Freundlich adsorption isotherm models were applied to the experimental isotherms and isotherms constants to validate the usefulness of this waste hydrogel in the field of wastewater treatment.

Materials and Method

Materials

Acrylic acid ((AAc), analytical grade), acrylamide ((AM), analytical grade), ammonium per sulfate ((APS), analytical grade), sodium hydroxide ((NaOH), analytical grade), N, N-methylene bisacrylamide ((NMBA), analytical grade), copper sulfate (($CuSO_4$), analytical grade), potassium dihydrogen phosphate (KH_2PO_4), hydrochloric acid (HCl) were purchased from CDH New Delhi, India. Methanol (analytical grade) was purchased from Qualikems, New Delhi. Acrylamide was recrystallized from methanol before use. Sodium humate ((SH), analytical grade), (supplied from Aldrich) was used as received. Double distilled water was used throughout the experiments.

Synthesis of Poly(AAc/AM/SH) Superabsorbent Hydrogels

AAc (7 g) and AM (7 g) were dissolved in 30 ml distilled water and after neutralizing the reaction mixture with NaOH solution, the solution was poured in a 250-ml three-neck round bottom flask which is equipped with a stirring rod, a nitrogen inlet and a reflux condenser. After that (0.20 wt% of total monomer), NMBA was added to the monomer solution, subsequently dispersed SH (0.35 g) into mixed solution. Then, reaction mixture was stirred under nitrogen atmosphere for 30 min to remove the dissolved oxygen, and after that the mixed reaction solution was heated in a thermostat oil bath for 1 h at 60 °C; then, the initiator, APS (0.40 wt% of total monomer), was introduced into the flask. The reaction solution was again stirred under nitrogen atmosphere for 2 h at 60 °C for homogeneity. The resulting reaction solution was poured into Petri-dishes and kept in a hot air oven at 60 °C for 2 h to complete polymerization and subsequent cross-linking process. After the polymerization (completion of reaction) in 2 h, the firm, SAHs, was carefully removed from the Petri-dish surface and cut into small pieces (0.1–0.5 cm in thickness).

Separation of unreacted monomers was done by washing with methanol, followed by swelling in distilled water for 4 h and then dried in an oven at 60 °C up to the constant weight. The dried hydrogels were stored in desiccators.

To prepare the Cu^{2+}-loaded SAHs poly(AAc/AM/SH), 50 mg of dry SAHs was introduced in 100 ml of Cu^{2+} ions salt solution (initial ion concentration 1 g/L) at pH 5.0 and was left in the solution for 24 h. The SAH samples were withdrawn at different time intervals (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 and 24 h) and analyzed for Cu^{2+} content left in solution. The adsorption capacity of the hydrogel for Cu^{2+} was evaluated through the following equation:

$$q_e = \frac{C_o - C_e}{m} \times V \tag{1}$$

where q_e is the amount of Cu^{2+} adsorbed at equilibrium, C_o is the initial concentration of Cu^{2+}, C_e is the equilibrium concentration of Cu^{2+} ions, V is the volume of the Cu^{2+} ions solution, and m is the mass of SAHs sample.

Desorption Study of Cu^{2+} from Poly(AAc/AM/SH)–Cu SAHs

To evaluate the stability of Cu^{2+} into poly(AAc/AM/SH)-Cu SAHs at adsorption process, 50 mg of poly(AAc/AM/SH)–Cu SAHs was added to twelve conical flasks with 100 mL of deionized water. The pH of solution of each conical flask was adjusted to 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0 and 12.0, respectively. The final Cu^{2+} concentration in the aqueous phase was determined by above given procedure. The desorption percentage was calculated by the amount of Cu^{2+} ions adsorbed on the SAHs surface and final Cu^{2+} concentration in the desorption medium. Desorption percentage was calculated using the following expression:

$$\text{Desorption percentage} = \frac{\text{Amount of Cu}^{2+}\text{ ion desorbed to the elution medium}}{\text{Amount of Cu}^{2+}\text{ ion adsorbed on the superabsorbent hydrogel}} \times 100 \tag{2}$$

Adsorption Analysis of Phosphate Ions

For the determination of phosphate adsorption experiments, 50 mg of the adsorbent poly(AAc/AM/SH)–Cu hydrogel was loaded into a conical flask with 100 ml of phosphate solution in various initial concentrations. Following the adsorption, the samples were withdrawn at different time intervals (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 and 24 h) and analyzed for phosphate content left in solution. The capacity of phosphate adsorption was also calculated using Eq. (1). To evaluate the influence of pH on phosphate ion adsorption, experiments were performed at different initial pH, ranging between 1.0 and 12.0. Initial phosphate ion concentration of 180 mg/L and 50 mg of adsorbent was used. The solutions were shaken for 24 h at 30 ± 0.5 °C. The capacity of phosphate adsorption was also calculated using Eq. (1).

Desorption and Regeneration

In order to explore the potential of reusability of adsorbent and recovery of phosphate ions, consecutive adsorption–desorption cycles were repeated five times using the adsorbent prepared following the described procedure in adsorption experiments. Desorption of phosphate ions from the SAHs poly(AAc/AM/SH)–Cu (having 87.62 mg/g) was carried out in batch mode using 50 mg adsorbent in 25 ml of 0.1 M NaOH solution (elution medium) for 48 h. The SAHs was taken out and then washed several times with distilled water followed by methanol and then dried at 60 °C for 24 h. The regenerated SAHs were used for another adsorption. Desorption ratio was calculated by applying the Eq. (2).

Results and Discussion

Effect of PH on the Desorption Behavior of Cu^{2+} from Poly (AAc/AM/SH)–Cu SAHs

The release behavior of Cu^{2+} from poly(AAc/AM/SH)-Cu SAHs was investigated at various pHs solutions under the identical conditions as the adsorption process for phosphate ion-containing water. Figure 1 shows the percent released of Cu^{2+} from poly(AAc/AM/SH)-Cu SAHs at various pH range.

It can be observed that at lower pH (pH < 3.5) the desorption of Cu^{2+} occurs extensively (>98%), due to competitive adsorption of protons for adsorption sites by substituting the Cu^{2+} from the Cu loaded hydrogel surfaces. On further increasing the pH (pH > 4.2), desorption of Cu^{2+} decreased sharply and the sample shows very little desorption (because of the chemical bonding formed due to chelation of the $–NH_2$, –COOH, and –OH groups with the Cu^{2+}).

Fig. 1 Effect of pH on percent released of Cu^{2+} from poly(AAc/AM/SH)–Cu superabsorbent hydrogel, temperature 30 ± 0.5 °C

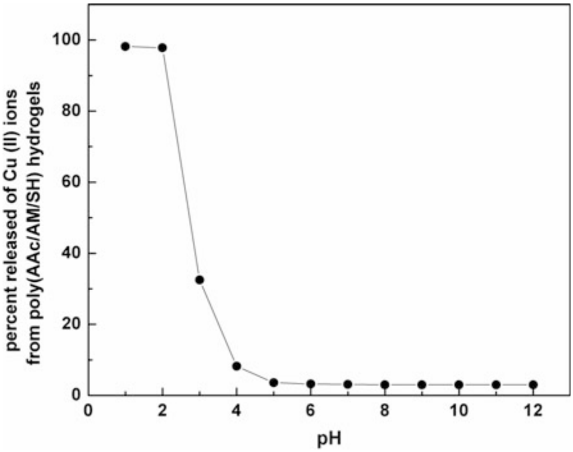
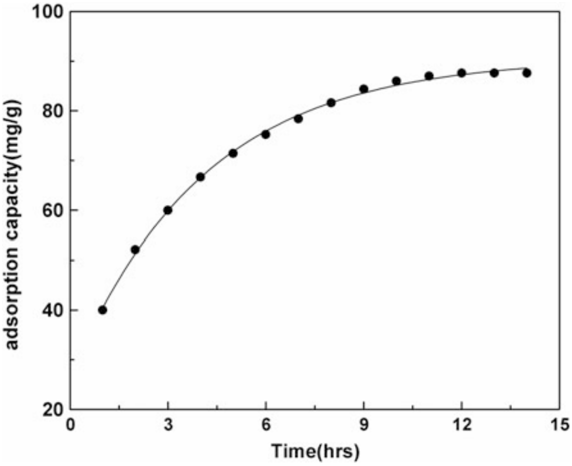


Fig. 2 Effect of contact time on the adsorption of phosphate ions onto poly (AAc/AM/SH)-Cu superabsorbent hydrogel



Effect of Contact Time on Phosphate Adsorption

Figure 2 shows the influence of contact time on the phosphate uptake. As clear from Fig. 2, the adsorption of phosphate ion increases rapidly with increase of contact time initially and then reaches at a constant value beyond which no phosphate ion was further adsorbed from the solutions

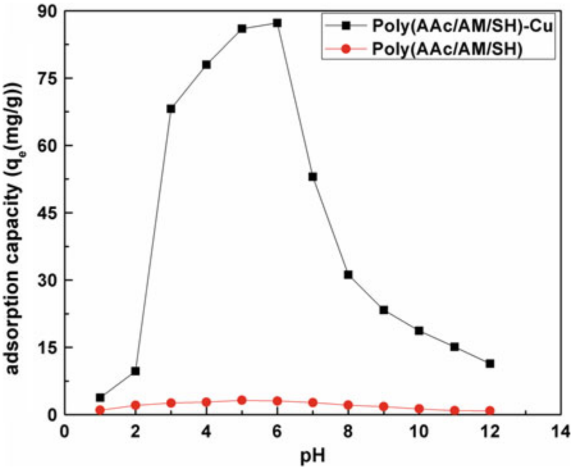
This phenomenon can be explained by the fact that, initially adsorption binding sites were void and phosphate ions may easily interact with these sites. The phosphate ion uptake almost remained constant after 12 h, and with prolonged time, the removal capacity hardly increased, so 12 h could be considered as the equilibrium contact time. The results suggest that the phosphate ion adsorption was fast at the initial part of the contact time, and thereafter it goes slower at near the equilibrium point.

Effect of PH and Ionic Strength of Solution on Adsorption of Phosphate

The pH of aqueous solution is one of the most important factors influencing the adsorption amount of cations and anions (Huang et al. 2008). In this study, influence of pHs on removal amount of phosphate ion was examined at various pHs levels namely between 2.00 and 12. At lower pHs (<2.15), the predominant species in solution is the neutral H_3PO_4, between pHs range of 2.15–7.20, the main species in solution is $H_2PO_4^-$, and at pHs values between 7.2 and 12.33 the predominant species is HPO_4^{2-} (Lee and Davis 2001). Figure 3 shows the variation in removal capacity of phosphate ion on the poly(AAc/AM/SH) SAHs and poly(AAc/AM/SH)–Cu SAHs from aqueous solution with respect to pH (Mahadavinia et al. 2004).

It was observed from the Fig. 3 that poly(AAc/AM/SH)–Cu hydrogel shows higher adsorption capacity than the poly(AAc/AM/SH) hydrogel, which shows negligible adsorption in all measured pH ranges. The phosphate ion uptake

Fig. 3 Effect of pH on the adsorption of phosphate ions onto poly(AAc/AM/SH) and poly(AAc/AM/SH)-Cu SAHs



increases sharply with an increase in initial pH (1–4) and then increased slowly until reaching a maximum 87.62 mg/g at pHs 6.1. After that on further increasing the pH, it goes down (Wang and Lin 2008). It was practically independent on pH values in the range of 5.0–6.1. When pH value was lower than 3.8 and higher than 6.1, a remarkable decrement in adsorption was observed.

What About Effect of Ionic Strength

Effect of Initial Concentration of Phosphate on Adsorption Capacity of the Poly(AAc/AM/SH)–Cu SAHs

Initial ion concentration is an important parameter so the effect of initial concentration on adsorption capacity was investigated. Figure 4 shows the adsorption capacity of the poly(AAc/AM/SH)–Cu SAHs for the phosphate ions as a function of various initial ion solution concentrations ranging from 100 to 200 mg/L (Perrin et al. 1974).

It can be observed from the Fig. 4 that adsorption amount of phosphate increased (from 72.66 to 87.62 mg/g) with increase in initial concentration of phosphate ions solution if the amount of adsorbent was constant. After reaching a maximum (87.62 mg/g) at 180 mg/L, it remained nearly constant. It can also be observed that in the initial stage the adsorption is rapid and increases gradually with progress of adsorption or with the increasing concentration of phosphate amount of removed phosphate ions increased but its adsorption percentage decreased.

Fig. 4 Variation in the adsorption capacity as a function of initial phosphate concentration using superabsorbent hydrogel poly (AAc/AM/SH)–Cu

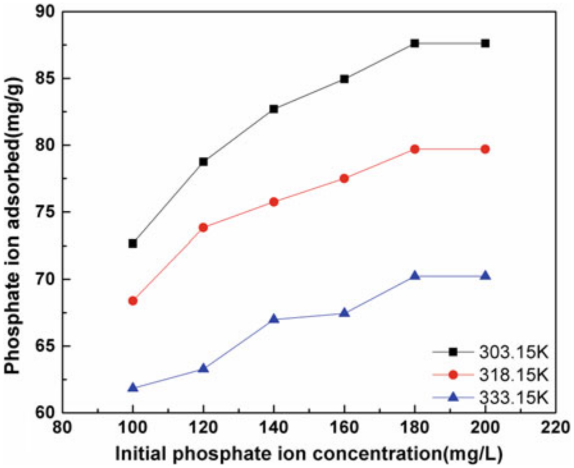


Table 1 Estimated adsorption isotherm parameters for the adsorption of phosphate ions on poly (AAc/AM/SH)–Cu SAHs in aqueous solutions

Temperature (K)	Langmuir model				Freundlich model		
	q_e (mg/g)	$q_{\max}$ (mg/g)	$K_e \times 10^3$ (L/mg)	R^2	K_f (mg/g)	n	R^2
303.15	87.62	94.33	1.245	0.99	44.66	6.80	0.98
318.15	79.70	85.47	1.180	0.99	46.77	8.88	0.94
323.15	70.23	74.62	1.116	0.98	41.11	9.06	0.96

Adsorption Isotherms

The most widely used isotherm for modeling of the adsorption data is the Langmuir adsorption isotherm. The Langmuir adsorption isotherm equation may be described as (Langmuir 1918).

$$\frac{C_e}{q_e} = \frac{1}{K_e q_{\max}} + \frac{C_e}{q_{\max}} \tag{3}$$

The Freundlich model is an empirical equation and applied to describe heterogeneous surface system by a heterogeneity factor of 1/n. The Freundlich model in linear form may be expressed as follows (Jaroniec 1983);

$$\log(q_e) = 1/\mathrm{n} \log(C_e) + \log K_f \tag{4}$$

where K_e (sorption equilibrium constant (L/mg)) and $q_{\max}$ (maximum amount of adsorption (mg/g), C_e is the equilibrium concentration of the metal ion in the solution (mg/L), q_e is the amount adsorbed at equilibrium mg/g. K_f (L/g) and 1/n (dimensionless) are the Freundlich constants related to the adsorption capacity and the degree of heterogeneity, respectively (Matti et al. 2007). The Langmuir and Freundlich constants and regression coefficients were calculated from the linear plots of C_e/q_e versus C_e and $\log(q_e)$ versus $\log(C_e)$ respectively (Ho 1999). The $q_{\max}$ values of the superabsorbent hydrogels obtained by Langmuir equation were quite consistent with the experimental one (Table 1).

Desorption/Regeneration of Adsorbent

A good solid adsorbent in addition to its high adsorption capacity should also exhibit a good regeneration capacity for potential application. The poly (AAc/AM/SH)–Cu SAHs that were applied for the adsorption of phosphate ions were placed in 0.1 M NaOH solution for 48 h and the amount of phosphate

Fig. 5 Plot of desorption ratio for phosphate ion from poly(AAc/AM/SH)-Cu hydrogels as a function of time

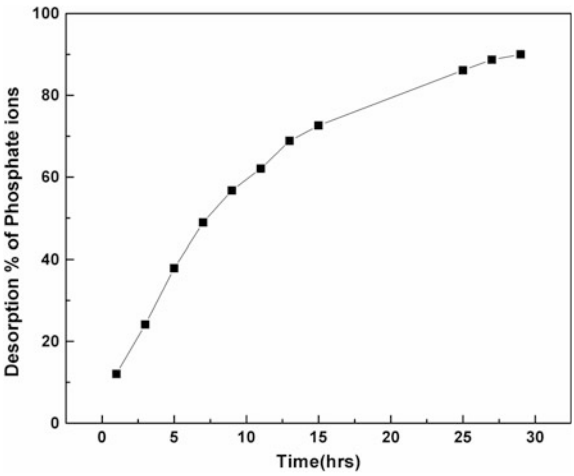


Table 2 Adsorption amount of phosphate ions after repeated adsorption–desorption cycle

Cycle No.	Adsorption capacity (mg/g)	Desorption (%)
1	87.62	94.28
2	86.45	94.10
3	85.37	93.57
4	85.01	92.91
5	83.14	92.33

desorbed to the elution medium was measured. Figure 5 displays the desorption ratio of poly(AAc/AM/SH)–Cu hydrogels (having 87.62 mg/g phosphate) as a function of time.

The desorption process reached equilibrium at about 29 h, and the desorption ratio was approximately 90%. Table 2 shows the experimental results for the adsorption capacity and times for reuse for the sample.

The adsorption capacities did not show any significant decrease after the fourth reuse cycle. After five cycles of adsorption–desorption operations, adsorption capacity of phosphate ions were around 83.14 mg/g. Therefore, it can be concluded that poly(AAc/AM/SH)–Cu hydrogel showed stable phosphate ions removal capacities after repeated regeneration and thus qualified for multiple practical application.

Conclusion

In the present study, it is attempted to provide a cost-efficient and effective method to reuse a waste adsorbent poly(AAc/AM/SH)–Cu SAHs for the phosphate ion adsorption from aqueous solution. The concentration of Cu^{2+} ions released from poly(AAc/AM/SH)–Cu SAHs decreased gradually on increasing the pH and almost stopped at pH higher than 4.5. Thus, the poly(AAc/AM/SH) SAHs after the adsorption of Cu^{2+} ions could be used directly for the removal of phosphate ion at pH > 4.5. Adsorption capacity was found to be maximum (87.62 mg/g) at pH 6.1. The adsorption isotherm agrees well with the Langmuir model as confirmed by linear fit of the plots to Langmuir equation. The results of five time consecutive adsorption–desorption cycle indicate that the poly(AAc/AM/SH)–Cu SAHs have high adsorption and desorption efficiency for the phosphate ions. The results confirmed that poly (AAc/AM/SH)–Cu SAHs can be used as effective solid adsorbent for the removal of phosphate ions from waste water and aqueous effluents, which seems the most efficient method to treat an already used adsorbent.

References

Arai Y, Sparks DL (2001) J of Colliod Interface Sci 241:317

Ho YS, Huang CIT, Huang HW (1999) Process Bio Chem 37:1421

Huang W, Wang S, Zhu Z, li L, Yao X, Rudolph V, Haghseresht F (2008). J of Hazard Mater 158: 35

Jaroniec M (1983) Physical adsorption on heterogeneous solids. Adv Colloid Interface Sci 18:149

Kara L, Uzun N, Denizli A (2004) Poly(ethylene glycol dimethacrylate-n-vinyl imidazole) beads for heavy metal removal. J Mater Hazard B106:93

Karadag E, Saraydin D, Guven O (1995) Behaviors of acrylamide itaconic acid hydrogels in uptake of uranyl ions from aqueous solutions. Sep Sci Technol 30:3287

Langmuir IJ (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc 40:1361

Lee SM, Davis AP (2001) Water Res 35:534

Mahadavinia GR, Pourjavadi A, Hosseinzadeh H, Zohuriaan MJ (2004) Modified chitosan 4 Superabsorbent hydrogels from acrylic acid -co-acrylamide) grafted chitosan with salt and pH-responsive prperties. Eur Polymer J 40:1399–1407

Mattigod SV, Fryxell GE, Parker K (2007) Inorg Chem Mun 10: 646

Perrin DD, Dempsey B (1974) Chapman and Hall, London

Singh T, Singhal R (2012) Poly (acrylic acid/acrylamide/sodium humate) superabsorbent hydrogels for metal ion/dye adsorption: effect of sodium humate concentration. J Appl Polym Sci 125:1267

Wang J, Lin W (2008) J Appl Polym Sci 109:318

Wang W, Wang A (2009) Synthesis, swelling behaviors, and slow-release characteristics of a Guar Gum-g-Poly(sodium acrylate)/Sodium humate superabsorbent. J Appl Polym Sci 112:2102

Streptomyces cavourensis Strain RD7-Mediated Decolorization of Aromatic Industrial Dye

Riddhi Naresh Dholakiya, Madhava Anil Kumar and Kalpana H. Mody

Abstract Economical and bio-friendly approaches are needed to decolorize dye-contaminated effluent causing toxic, carcinogenic and genetic effects. A novel actinomycete strain capable of decolorizing industrial effluent was isolated from Mahuva, western site of Gulf of Khambhat (GoK), Gujarat, India. The isolate was identified as *Streptomyces cavourensis* strain RD7 and was found to be potential in decolorizing methylene blue (MB) in presence of nitrogen sources like yeast and beef extracts. It was found that when 100 (mg/L) MB was supplemented with only 1.0% yeast extract, 48 and 86% decolorization was observed after 24 and 48 h of incubation, respectively. The decolorization of industrial effluent supplemented with 1.0 and 0.5% yeast extract was 49 and 22%, respectively, by *S. cavourensis* strain RD7 after 120 h. MB decolorization mechanism was revealed using analytical techniques.

Keywords *Streptomyces cavourensis* · Industrial effluents · Methylene blue
Decolorization

Introduction

The environmental pollution due to rapid urbanization and industrialization is an alarming issue showcasing an adverse impact on health and ecology (Bagewadi et al. 2011). The textile industrial effluents containing synthetic and complex aromatic molecules are environmentally detrimental (Saratale et al. 2011). Owing to their hetero-polyaromaticity, they are resistant to fading on exposure to sunlight, water and chemicals (Pandey et al. 2007). The presence of these dyes in effluents could confer to aesthetic problems (Bae and Freeman 2007). Additionally, dyes and

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their intermediates are toxic and known to have carcinogenic and mutagenic effects to the biotic components (Shah et al. 2012; Puvaneswari et al. 2006).

The extensive review on remediation of textile dye effluents suggests that physico-chemical treatment decolorizes but fails to detoxify them completely (Saratale et al. 2011; Karthikeyan et al. 2014; Vidhyadevi et al. 2014). The biologically mediated transformation can degrade/detoxify with simultaneous decolorization of dyes and effluents (Asghera et al. 2008; Daneshvar et al. 2007; Jadhav et al. 2008; Mohan et al. 2002). The biological methods are relatively inexpensive yielding metabolites of mineralized and reduced toxicity (Kumar et al. 2012). The ability of actinomycetes to decolorize several textile dyes has been demonstrated by different researchers in the recent past (Ball et al. 1989; Pasti and Crawford 1991; Paszczynski et al. 1991, 1992; Pasti-Grigsby et al. 1992; Mane et al. 2008).

The objective of the present work is to study the decolorization of MB and industrial effluent containing different dyes by an isolated actinomycete strain under aerobic condition, cheap coast and to reveal the mechanism of MB decolorization.

Materials and Methods

Chemicals, Dye and Effluent

MB (molecular formula, $C_{16}H_{18}N_3SCl$, molar mass = 319.85 g/mol; absorption maxima, λ_{max} = 666 nm) was purchased from HPC (India) in powdered form and was used as obtained without further purification. Double-distilled water was used for preparing MB solutions throughout the study. The nutrient broth and yeast extract were purchased from HiMedia (Mumbai, India). Ethyl acetate was obtained from Rankem (India). All the chemicals used were of the highest purity and of analytical grade. The textile dye effluent (λ_{max} = 586 nm) was collected in a plastic container, neutralized to pH 7.0 in order to avoid the growth of indigenous microorganisms.

Instruments

The concentrations of the dye solutions were estimated using the absorbance recorded on UV–Vis spectrophotometer Shimadzu, UV-1800, Japan. The FT-IR spectra were recorded using a GX-FT-IR system, Perkin Elmer, USA, in the frequency range of 4000–400 cm^{-1} by KBr pellet method. The ^{1}H-NMR spectra were recorded using Bruker, Avance II, 500 mx (Switzerland). The HPLC analyses of initial and products were compared using C_{18} column with HPLC grade methanol as the mobile phase in Shimadzu Corporation, RF-10 AxL. The mass spectral analyses of the degraded product were recorded on a Shimadzu, QP 2010 system.

Isolation and Screening of Actinomycetes

Marine actinomycetes were isolated from sediment samples collected from Mahuva, Bhavnagar, coastal areas of GoK (Gujarat, India). After suitable serial dilution, the samples were inoculated in modified Gause's synthetic agar medium containing (g/L): starch, 20; KNO_3, 1.0; NaCl, 0.5; K_2HPO_4, 0.5; $MgSO_4$ $7H_2O$, 0.5; $FeSO_4$, 0.01; agar, 20 and $K_2Cr_2O_7$, 0.001 was added into the medium to prevent bacterial and fungal growth.

Screening and Identification of Decolorizing Strain

100 mg/L MB in 100 mL nutrient broth and 2.0% inoculum was added and incubated under static condition at 30 °C. The reaction was incubated for 48 h until decolorization was visualized. The decrease in the absorbance values was measured using a UV–Vis spectrophotometer and compared with the abiotic controls which were always included. The decolorization experiments were performed in triplicates, and the mean value was calculated. The strains which were able to survive and decolorize 100 (mg/L) MB was employed for further experiments. The isolated colony was identified by 16SrRNA sequencing, and the sequences were submitted to National Centre for Biotechnological Information (NCBI) for obtaining the accession number. The phylogenetic evolution and relationship of the strain was revealed by constructing the phylogenetic tree.

Decolorization Experiments Using the Isolate

One hundred millilitres nutrient broth was prepared with addition of 100 (mg/L) MB, sterilized and inoculated as test and decolorization was performed under static condition at 30 °C. Aliquot (2 mL) of culture media was withdrawn at different time intervals and centrifuged at 7,000 rpm for 20 min. The decolorization was monitored by measuring the absorbance of culture supernatant at 666 nm at regular time interval of incubation (Kumar et al. 2015). The change in pH level during decolorization was observed to observe whether decolorization is due to degradation or change in pH.

Analytical Methods

The isolate was incubated with the MB, at a concentration of 100 mg/L and incubated at 30 °C under static condition. An aliquot (2 mL) of the culture media was withdrawn at different time intervals and was centrifuged at 7,000 rpm for 20 min to separate the cell mass. The supernatant was used to determine the decolorization by measuring the change in the absorbance of culture supernatants at the respective $\lambda_{\max}$. Abiotic (without microorganisms) controls were always included. The decolorization was quantitatively analysed using the UV–Vis spectrophotometer. During the UV–Vis spectral analysis, changes in the absorption spectrum of the decolorized medium were recorded and compared with the control. The percentage of MB decolorization (%D) was calculated as follows,

$$\%D = \frac{\text{Initial absorbance} - \text{Final absorbance}}{\text{Initial absorbance}} \times 100 \tag{1}$$

Decolorization of MB in Presence of Different Nitrogen Sources

In order to evaluate the effect of nitrogen sources on decolorization of MB, yeast and beef extract, either individually (0.25, 0.50 and 1.0%) or in different proportions, was incubated followed by inoculating the isolate in the medium containing MB (100 mg/L) at pH 8.0 and 30 °C under static condition.

Decolorization of Dye Effluents

To understand the applicability of a potential isolate in remediating the water contaminated with the dye and their intermediates, the effluent was incubated with 2.0% inoculum with 0.5 and 1.0 g of yeast and beef extract individually.

Extraction and Analysis of Metabolites

The decolorized media were centrifuged at 10,000 rpm for 20 min, and the degradation products in the culture supernatant were extracted, using equal volume of ethyl acetate, dried over anhydrous sodium sulphite and evaporated to dryness. MB decolorization was analysed using spectral techniques like UV–Vis spectrophotometry, and Fourier transform infrared (FT-IR) spectroscopy. The degradation of MB was confirmed by chromatographic techniques like HPLC and gas chromatography with mass spectrometry (GC-MS). HPLC analysis was carried out at room temperature by detecting the initial and final at 666 and 335 nm respectively in a UV–Vis detector and C_{18} column for 10 min run time at the flow rate 1.0 mL/min. The products of MB biotransformation were analysed using GC-MS analysis.

Results and Discussion

Isolation and Identification of MB Decolorizing Strain

Marine actinomycetes are well known for its wide applications in the production of bioactive compounds and bioremediation of contagious waste materials (Kala and Chandrika 1993). Few isolates were collected based on their different colony morphology and colour variations from different marine samples and potential isolate different isolates were screened using GSA medium from Mahuva, the study was continued with screening for potential dye degradation, one potential strain exhibiting highest decolorizing activity which was chosen for further studies, which decolorized 100 (mg/L) MB after 24 h of incubation under static condition partially. The colonies had an earthy odour, gram-positive and form fungus like branched networks and slow growing, aerobic as shown in Fig. 1.

According to the physiological and biochemical tests as BIOLOG, fatty acid profiling and 16SrRNA gene sequencing, the strain was identified as *S. cavourensis* and for 16SrRNA it was deposited to NCBI for obtaining accession number (KT 588657) and the phylogenetic relationship was revealed by constructing the tree (Fig. 2) for understanding and comparing *S. cavourensis* strain RD7 with other species of the genus *Streptomyces*.

Several reports have been established by different researchers on the decolorization of industrial dyes by actinomycetes. The decolorization of 30 and 50 mg/L of reactive blue was 95 and 87%, respectively, by *Streptomyces krainskii*

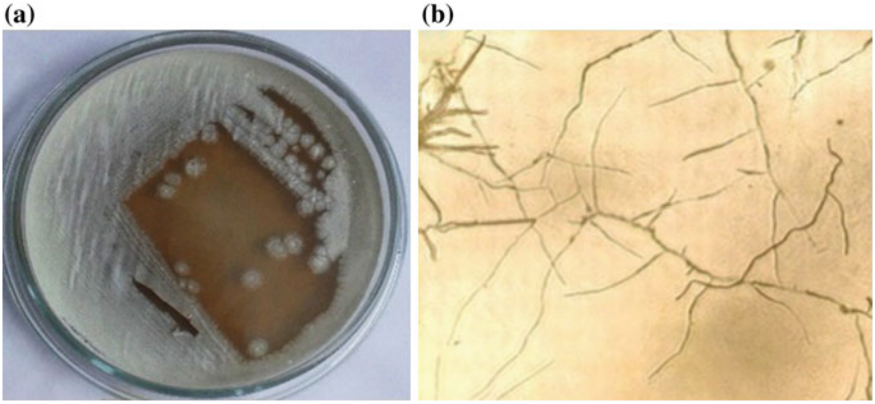

Fig. 1 Morphological and microscopic characteristics of the isolate

Fig. 2 Phylogenetic tree showing relationships among and between the genus *Streptomyces*

SUK-5 after 576 and 1152 h, respectively (Mane et al. 2008). *Streptomyces chromofuscus* A11 exhibited 89 and 83% decolorization of 50 and 100 mg/L an azo dye after 1152 h (Paszczynski et al. 1991). 50 mg/L vanillic acid was decolorized by two different strains of *S. rochei* after 336 h (Paszczynski et al. 1991). The decolorization of two synthesized azo dyes; 4-(3-methoxy-4-hydroxyphenylazo)-azobenzene-3,4′-disulfonic acid and 3-methoxy-4-hydroxy-azobenzene-4′-sulphonic acid) were tested as substrates for degradation by different *Streptomyces* sp. namely *S. rochei* A10, *S. chromofuscus* A11, *S. diastaticus* A12 and *S. diastaticu*s A13, *S. rochei* A14, *S. chromofuscus* A20, *S. viridosporus* TTA and *S. badius* 252. These strains were those that could also attack vanillic acid, which has the same ring substitution pattern (4-hydroxy-3-methoxy) as guaiacol (Paszczynski et al. 1991).

Decolorization of MB and Textile Dye Effluent by S. cavourensis *Strain RD7*

The decolorization of 100 (mg/L) MB was observed at static condition and highest visual decolorization observed after 48 h by *S. cavourensis* strain RD7. The results of MB decolorization (Figs. 3 and 4) in the presence of different proportions of nitrogen sources indicated that yeast extract supported maximum decolorization as compared to beef extract. It was also observed that presence of only 1.0% yeast

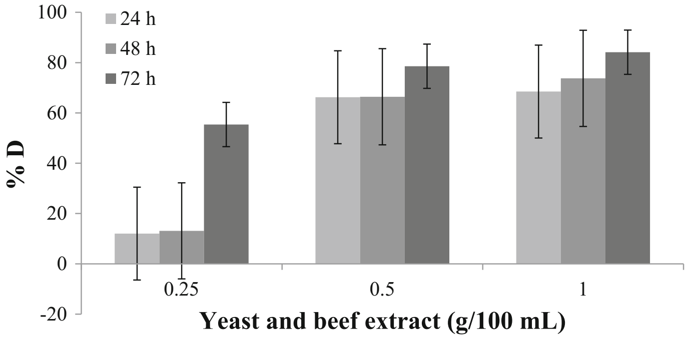

Fig. 3 MB decolorization using different mixed nitrogen source at different time interval

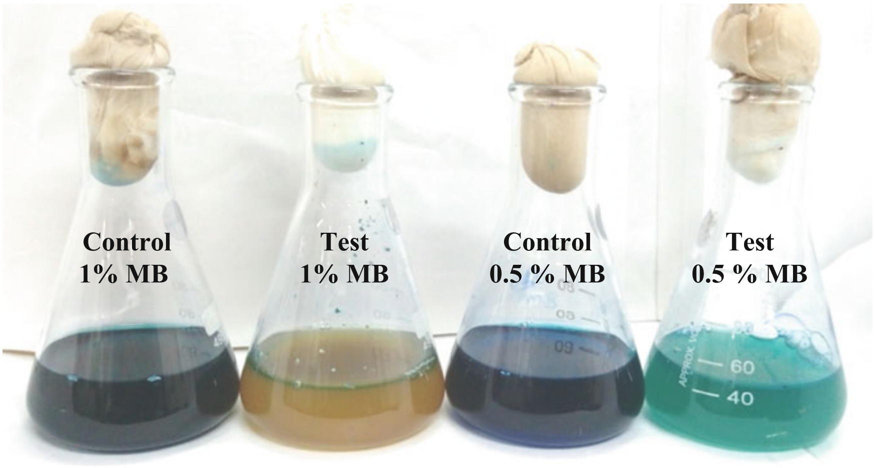

Fig. 4 MB decolorization after 48 h

extract exhibited, 48% decolorization after 24 h incubation; however, more than 88% decolorization was observed even in the presence of 0.25% yeast extract after 48 h of incubation. The applicability of *S. cavourensis* strain RD7 was further tested for its ability to decolorize the mixture of textile dye effluent as shown in Fig. 5. However, industrial effluent is not stable as it varies often vast range depending of the process did. Nowadays, India has several environmental problems due to rapid textile industrialization and its waste water is rated the most polluted effluent, which create the water pollution in the environment. To remove the polluted substances from the water body, this system is used which is based on microorganisms which capable to degrade/decolorize the compounds which is environment-friendly clean-up process and are presently gaining stature.

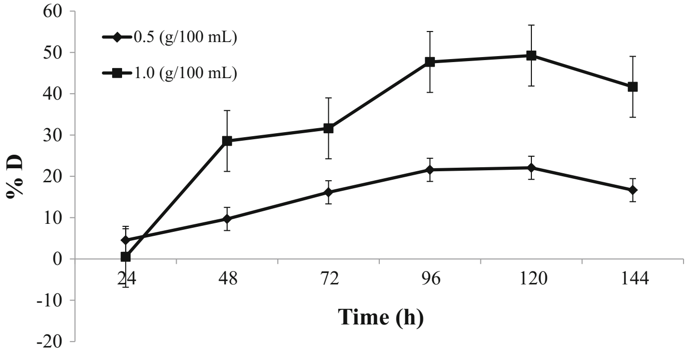

Fig. 5 Effluent decolorization using different concentration of yeast extract at different time

Analyses of MB Decolorization by *S. cavourensis* Strain RD7

UV–Vis Spectral Analysis of MB Decolorization

The mechanism of MB decolorization was analysed by UV–Vis spectrophotometry which is the preliminary technique to determine dye decolorization (Kumar et al. 2012). The UV–Vis absorbance (from 300 to 900 nm) of the initial MB and decolorized sample was scanned to examine the decolorization by *S. cavourensis* strain RD7. A visible decolorization occurred in the solution, and decolorization could be due to degradation or adsorption by the microbial cells. In this case, UV–Vis absorption peak disappeared completely (spectra not shown).

FT-IR Analysis of MB Decolorization

FT-IR spectra of the initial MB and final degraded products were compared and analysed for the variations in the fingerprint region (1500 to 500 cm^{-1}). The FT-IR spectra of control showed specific peak at 1592 cm^{-1} for the C=C stretching of the benzene ring of the mono-and para-disubstituted benzene rings. The peaks at 1322 and 616 cm^{-1} for the CH stretching vibration and sharp peaks at 1035, 1135 and 1165 cm^{-1} for the stretching vibration of CO give the perception of MB structure (Fig. 6a).

FT-IR spectra of the biodegraded product showed a peak at 938 cm^{-1} for the CH stretch, and a peak at 1641 cm^{-1} represents the formation of amides. The peak at 1126 and 1217 cm^{-1} for the CN stretch represents the formation of aliphatic amines. The peaks at 1386 and 1439 cm^{-1} stand for CH deformation. The peak at 3680 cm^{-1} for OH stretch represents high concentration of alcohols supported by

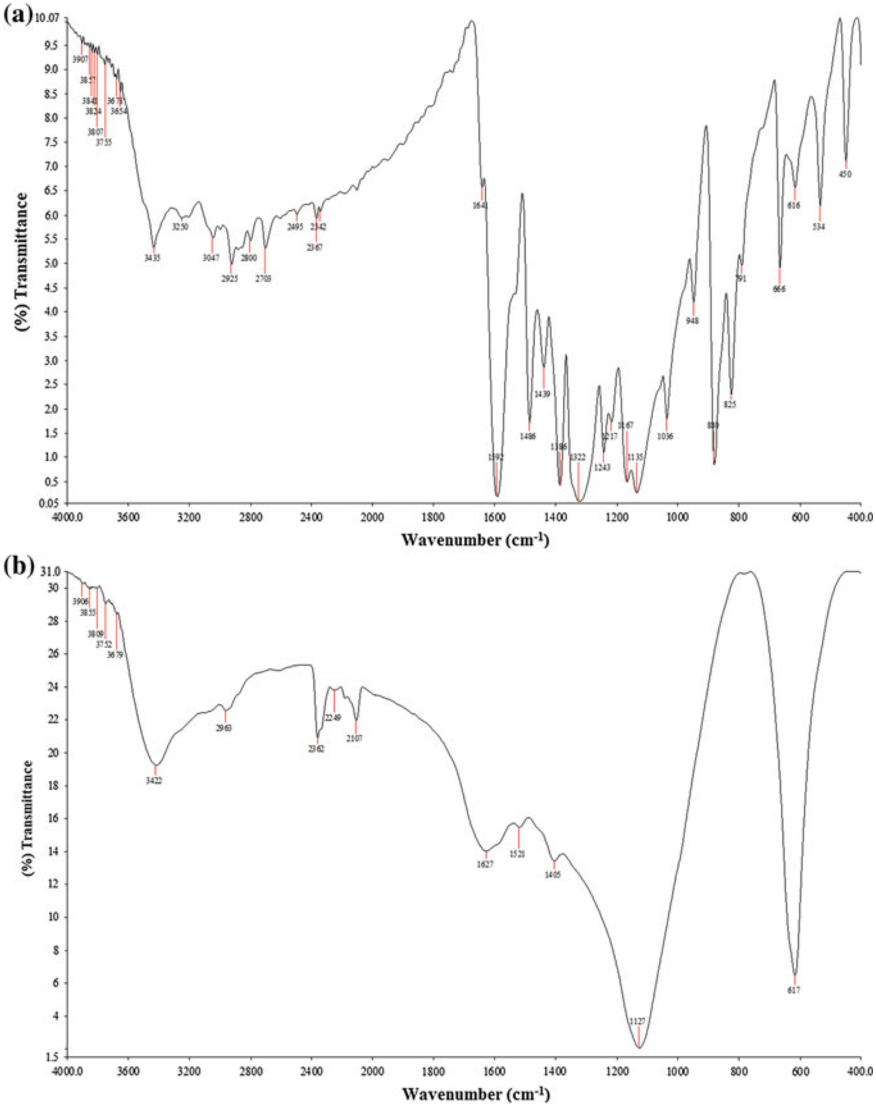

Fig. 6 FT-IR spectra of **a** MB before and **b** after degradation

the sharp peak at 616 cm^{-1}. The peaks at 3419, 2361 and 2106 cm^{-1} for the NH stretch represents the formation of primary amines produced by *S. cavourensis* strain RD7 (Fig. 6b).

HPLC Analysis of MB Degradation

The HPLC chromatogram of MB showed peak a major peak at retention time (R_t) 1.783 and shoulder peaks at 2.134, 2.362 and 2.616 min, whereas degradation product by *S. cavourensis* strain RD7 showed appearance of new peaks at R_t 1.762, 2.430, 2.656 and 4.004 min, respectively (Fig. 7).

GC-MS Analysis of MB Degradation

The mass spectral analyses of MB degradation by *S. cavourensis* strain RD7 as shown in Fig. 8 revealed that MB was biotransformed into 1,2-benzenedicarboxylic acid ($C_6H_4(COOH)_2$) with a molecular weight of 166.14 eluting out at R_t 18.310 min.

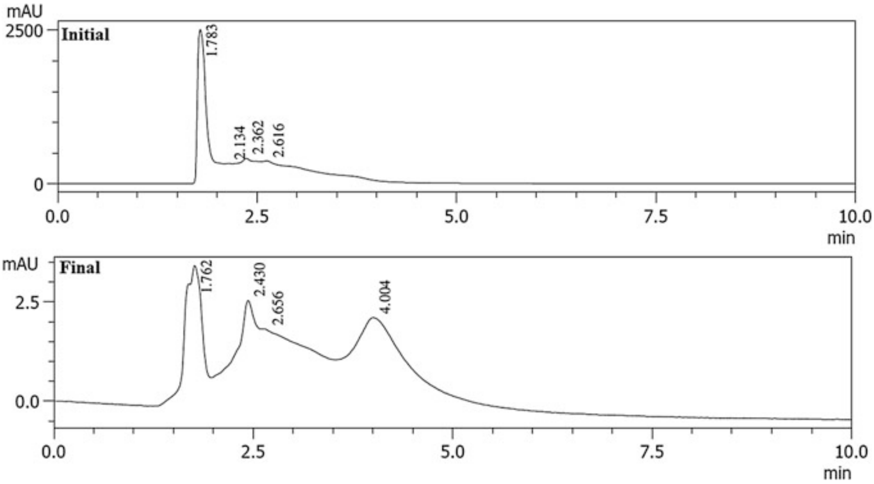

Fig. 7 HPLC profile of initial MB and degradation product

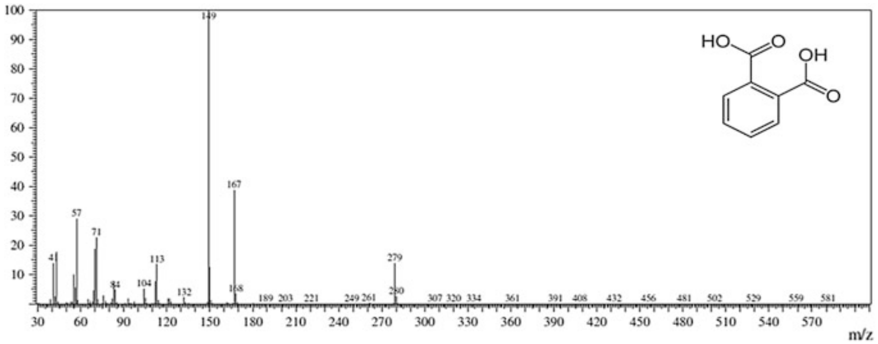

Fig. 8 Mass spectral analysis of MB degradation product by *S. cavourensis* strain RD7

Conclusions

In the present study, a marine actinobacteria *S. cavourensis* strain RD7 was isolated and capable to degrade the MB. Thus, our study suggests that marine actinobacteria possess a significant MB dye-degrading capacity with minimum coast and can be applied in bioremediation of textile and other industrial effluents containing toxic dyes.

References

Asghera M, Kausara S, Bhattia HN, Shahb SAH, Alib M (2008) Optimization of medium for decolorization of solar golden yellow R direct textile dye by *Schizophyllum commune* IBL-06. Int Biodeter Biodegr 61:189–193

Bae J, Freeman HS (2007) Aquatic toxicity evaluation of new direct dyes to the *Daphnia magna*. Dyes Pigments 73(1):81–85

Bagewadi ZK, Vernekar AG, Patil AY, Limaye AA, Jain VM (2011) Biodegradation of industrially important textile dyes by actinomycetes isolated from activated sludge. Biotechnol Bioinf Bioeng 1(3):351–360

Ball AS, Betts WB, McCarthy AJ (1989) Degradation of lignin-related compounds by actinomycetes. Appl Environ Microbiol 55:1642–1644

Daneshvar N, Khataee AR, Rasoulifard MH, Pourhassan M (2007) Biodegradation of dye solution containing malachite1 green: optimization of effective parameters using Taguchi method. J Hazard Mater 143:214–219

Jadhav SU, Kalme SD, Govindwar SP (2008) Biodegradation of methyl red by *Galactomyces geotrichum* MTCC 1360. Int Biodeter Biodegr 62:135–142

Kala RR, Chandrika V (1993) Effect of different media for isolation, growth and maintenance of actinomycetes from mangrove sediments. Indian J Mar Sci 22:297–299

Karthikeyan S, Kumar MA, Maharaja P, Rao BP, Sekaran G (2014) Process optimization for the treatment of pharmaceutical wastewater catalyzed by poly sulpha sponge. J Taiwan Inst Chem E 45:1739–1747

Kumar MA, Kumar VV, Premkumar MP, Baskaralingam P, Thiruvengadaravi KV, Dhanasekaran A, Sivanesan S (2012) Chemometric formulation of bacterial consortium-AVS for improved decolorization of resonance-stabilized and heteropolyaromatic dyes. Bioresour Technol 123:344–351

Kumar MA, Kumar VV, Ponnusamy R, Daniel FP, Seenuvasan M, Anuradha CD, Sivanesan S (2015) Concomitant mineralization and detoxification of acid red 88 by an indigenous acclimated mixed culture. Environ Prog Sustainable Energy 34:1455–1466

Mane UV, Gurav PN, Deshmukh AM, Govindwar SP (2008) Degradation of textile dye reactive navy-blue Rx (Reactive blue–59) by an isolated actinomycete *Streptomyces krainskii* SUK-5. Malays J Microbiol 2:1–5

Mohan SV, Rao NC, Karthikeyan J (2002) Adsorptive removal of direct azo dye from aqueous phase onto coal based sorbents: a kinetic and mechanistic study. J Hazard Mater 90:189–204

Pandey A, Singh P, Iyengar L (2007) Bacterial decolorization and degradation of azo dyes. Int Biodeter Biodegr 59:73–84

Pasti MB, Crawford DL (1991) Relationships between the abilities of streptomycetes to decolorize three anthron-type dyes and to degrade lignocelluloses. Can J Microbiol 37(12):902–907

Pasti-Grigsby MB, Paszczynski A, Goszczynski S, Crawford DL, Crawford RL (1992) Influence of aromatic substitution patterns on azo dye degradability by *Streptomyces* spp. and *Phanerochaete chrysosporium*. Appl Environ Microbiol 3605–3613

Paszczynski A, Pasti MB, Goszczynski S, Crawford DL, Crawford RL (1991) New approach to improve degradation of recalcitrant azo dyes by *Streptomyces* spp. and *Phanerochaete chrysosporium*. Enzyme Microb Technol 13:378–384

Paszczynski A, Pasti-Grigsby MB, Goszczynski S, Crawford RL, Crawford DL (1992) Mineralization of sulfonated azo dyes and sulfanilic acid by *Phanerochaete chrysosporium* and *Streptomyces chromofuscus*. Appl Environ Microbiol 58:3598–3604

Puvaneswari N, Muthukrishnan J, Gunasekaran P (2006) Toxicity assessment and microbial degradation of azo dyes. J Exp Biol 44:618–626

Saratale RG, Saratale GD, Kalyani DC, Chang JS, Govindwar SP (2011) Bacterial decolorization and degradation of azo dyes: a review. J Taiwan Inst Chem Eng 42:138–157

Shah PD, Dave SR, Rao MS (2012) Enzymatic degradation of textile dye reactive orange 13 by newly isolated bacterial strain Alcaliginenes faecalis PMS-1. Int Biodeter Biodegr 69:41–50

Vidhyadevi T, Murugesan A, Kalaivani SS, Kumar MA, Ravi KVT, Ravikumar L, Anuradha CD, Sivanesan S (2014) Optimization of the process parameters for the removal of reactive yellow dye by the low cost *Setaria verticillata* carbon using response surface methodology: thermodynamic, kinetic and equilibrium studies. Environ Prog Sustainable Energy 33:855–865

Rice Crop Growth and Rhizospheric Microbial Dynamics in Heavy Metals Contaminated Inceptisol

Manoj Shrivastava, Usha Mina, S. Thaplial, A. Srivastava, M. Khuant and S. D. Singh

Abstract A glasshouse pot culture study was carried out with the aim to assess the potential toxic effects of heavy metals (Cr, Ni, Cd, Hg, and Pb) on two rice varieties (Pusa 44 and PB1509). Heavy metals get accumulated in different parts of rice plant (*Oryza sativa* L.) including the grains. The highest concentration of heavy metals in this study was in the roots observed rather than shoots and grains in both the rice varieties. Soil-to-grain transfer factor for non basmati rice for Ni, Pb, Cd, Cr, and Hg was 0.070, 0.028, 0.079, 0.0058, and 0.0049, respectively, and for basmati rice for Ni, Pb, Cd, Cr, and Hg was 0.065, 0.023, 0.072, 0.0050, and 0.0038, respectively. Average microbial population was more in the rhizosphere of Pusa 44 as compared to PB1509 under control condition. The viable population of bacteria, fungi, and actinomycetes was adversely affected by increasing concentration of each heavy metal. Mycorrhizal colonization was low on roots of Pusa 44 and PB1509 under metal treatments as compared to control and was minimum (22–26%) under Hg treatment.

Introduction

Rice (*Oryza sativa* L.), an important cereal crop in global agriculture, is second (more than 150 million ha) after wheat in terms of the planting area of cereal crops. Soil contamination with heavy metals and food safety problems occur in many countries as a result of numerous human activities, particularly wastewater and solid waste disposal, mining, smelting, and processing of ores agricultural practices (e.g., the use of fertilizers, pesticides), and augmented atmospheric deposition (Adriano 2003). Heavy metal pollution is also a serious problem in India, and has become increasingly serious with the industrial development and irrigation of wastewater.

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Soil acts as a sink or filter in which heavy metals have accumulated rapidly but are depleting slowly. Some heavy metals such as chromium (Cr), lead (Pb), mercury (Hg), Nickel (Ni), and cadmium (Cd), especially in large amounts, could affect growth and productivity of plants (Cataldo et al. 1978, 1981; Najafian et al. 2012; Arun et al. 2005; Verma and Dubey 2001). These metals are mostly absorbed by plants easily and prove toxic to plants that can be observed as growth retardation as a result of alterations in biochemical process like inhibition of enzyme activity, protein penetration, and impaired nutrition (Arun et al. 2005). High heavy metal concentrations in rice grains (*Oryza sativa* L.) grown in contaminated area can present potential health and economic problems for consumers and farmers. Different physical, chemical, and biological processes acting on soil media control the fate of heavy metals in soil. Under natural conditions, concentrations of heavy metals are low in soils, except in those derived from shales (Jackson and Alloway 1992). Once metals enter the soil, they can be taken up by the standing crop, remain in soil in soluble and insoluble forms, or leach to groundwater. Flooded condition in rice-growing soil may influence metal uptake by rice plants (Reddy and Patrick 1977; Sajwan and Lindsay 1986). Strongly reducing conditions in rice soils under flooding condition favour to form stable metal sulphides that immobilize metals (Gambrell 1994).

Mercury (Hg) is a global and extremely toxic pollutant (Lindqvist 1991). Significant Hg contamination occurred due to artisanal zinc smelting, a thermometer manufacturing facility (Krishna et al. 2003), artisanal goldmining activity (Gray et al. 2002; Pestana and Formoso 2003), direct Hg mining (Nevado et al. 2003), chlor-alkali plant emissions (Biester et al. 2002), lead mining and smelting and coal-fired power plants (Novoa-Munoz et al. 2008). The primary risk of Hg exposure to terrestrial vertebrates including humans is through ingestion of contaminated food and agricultural products (Doty 2008). Nickel (Ni) toxicity is of concern for plants grown in soils receiving sewage sludge and industrial by-products. Nickel as well as cobalt (Co) toxicity may also be found in plants grown in soils formed from serpentinite or other ultrabasic rocks (McBride 1994). Lead (Pb) is another widespread toxic pollutant which has no known functions in biological systems. The major source of lead in environment is metal smelting (Caussy et al. 2003), but agriculture, industry, and urban activities are also important sources of Pb pollution (Marchiol et al. 2004). Significant increases in the Pb content of cultivated soils have been observed near urban and industrial areas where it tends to accumulate in the surface ground layer (de Abreu et al. 1998). Chromium (Cr) is a naturally occurring element found in rocks, animals, plants, soil, and in volcanic dust and gases. Chromium exists in the environment in several different forms with more common forms as chromium (III) and chromium (VI). The impact of Cr contamination in the physiology of plants depends on the metal speciation, which is responsible for its mobilization, subsequent uptake, and resultant toxicity in the plant system (Arun et al. 2005). Hexavalent Cr is considered as highly toxic and a potential human carcinogen having detrimental effects on several organs and tissues, where it promotes the formation of reactive oxygen species which cause damage to DNA. Naturally occurring cadmium (Cd) levels are extremely low. Reports indicate that Cd concentrations in non-contaminated soil vary from 0.01 to 5 mg kg^{-1} of soil (Kabata-Pendias 2004); however, fertilizers produced from phosphate ores constitute a major source of widespread cadmium pollution (Chen et al. 2007). In addition, the inappropriate disposal of Cd containing wastes has increased its emission in populated areas around the world. Although Cd is used in a number of industrial applications, the main source of Cd intake is through smoking and food (Jarup 2003). Cadmium is an element that represents serious environmental hazards because it can be absorbed via the alimentary tract, penetrates through placenta during pregnancy, and damages membranes and DNA (Kabata-Pendias 2004). Furthermore, according to (Peijnenburg et al. 2000), Cd is the metal of most concern because this poses human or animal health risks at plant tissue concentrations that are not generally phytotoxic. Apart from crop growth soil, microorganisms are greatly affected by the heavy metal contamination. Microbial biomass activity and community structure significantly influenced as a result of increased metal concentration in soil (Giller et al. 1998).

With this background, a glasshouse pot experiment was conducted to determine the effects of varying level of Cr, Ni, Cd, Hg, and Pb on rice crop growth and rhizospheric microbial dynamics in an inceptisol. Concentrations of the toxic heavy metals were assessed in soil, root, shoot, and grains of paddy crop to assess the bioaccumulation factor.

Materials and Methods

Greenhouse Experiment

Greenhouse pot culture experiments were conducted using two rice varieties, viz. Pusa 44 (non basmati) and PB1509 (basmati) in an inceptisol from Delhi. Principle chemical and physical characteristics of the experimental soils are presented in Table 1. The healthy seeds of paddy variety were surface sterilized with 0.1% mercuric chloride for 2 min and washed thoroughly with tap water and then with distilled water. Metals were added to the air-dried soils at two levels *viz*. 50 and 100 mg metal kg^{-1} soil. The heavy metals were added as sulphate. The soils were mixed in a concrete mixer with the salts of the indicated metals, filled in plastic containers with a capacity of 5 kg and incubated at field capacity for 4 weeks with repeated four wet and dry cycles to establish equilibrium with metals and soil. The pots were fertilized with the equivalent of 150 kg h^{-1} of N, 30 kg ha^{-1} P, and 60 kg ha^{-1} of K through urea, diammonium phosphate, and potassium chloride, respectively. All chemicals used were of analytical grade. Six 15-day-old rice seedlings (Pusa 44 and PB1509) raised separately in nursery were transplanted in each pot in flooded condition. The level of standing water was maintained at a height of 2.5 ± 0.5 cm above the soil surface. The investigation was 5 × 2 × 2

Table 1 Some important physiochemical properties of experimental soil

Parameter	Value
Soil order	Inceptisol
Sand (%)	45.2
Silt (%)	30.5
Clay (%)	24.3
Texture	Sandy clay loam
pH (1:2.5) (soil:water)	8.65
Organic Carbon (gkg^{-1})	12.6
Nitrogen total (gkg^{-1})	1.9
$CaCO_3$ (%)	2.7
CEC (cmol (p^+) kg^{-1})	17.1
Available P_2O_5 (mg kg^{-1})	53.9
Available K_2O (mg kg^{-1})	225
Total Cd (mg kg^{-1})	0.54
Total Cr (mg kg^{-1})	9.44
Total Ni (mg kg^{-1})	7.2
Total Pb (mg kg^{-1})	10.9
Total Hg (mg kg^{-1})	0.0086
DTPA extractable heavy metals (mg kg^{-1})	
Cd	0.06
Cr	1.87
Ni	1.12
Pb	0.78
Hg	BDL

factorial experiments, where each metal and rice variety and doses combination, replicated 4 times. The pots were arranged by following the complete randomized design (CRD).

Plant Analysis

Rice plants were harvested at the maturity. Rice plants were collected and washed thoroughly with double-distilled water and then with diluted HCl. Rice plants were cut and separated into root, shoot, and grain subsamples. All subsamples were oven-dried at 60 °C for constant weight, and the dried samples were weighed. One gram of the fine-powdered samples was weighed into a flask and digested in a mixture of concentrated HNO_3 and $HClO_4$ in a 5:1 ratio at 100 °C on a hot plate in a fume hood until finally a clear solution was obtained. The resulting solution was left overnight and made up to 50 ml with double-distilled water, and then it was filtered by filter paper and diluted to 50 ml with double-distilled water. A quality control was implemented which included analytical grade chemicals, reagent blank, one duplicate sample for every five samples, house reference materials and all required containers, glass wares, etc., which were previously soaked in 10% HCl and rinsed with double-distilled water. The concentration of heavy metal Cd, Cr, Ni, and Pb in the digested solution was measured by ICP-AES. For total mercury (THg) analysis, one gram sample of seed, shoot, and root was used for digestion at 95 °C for 24 h in a water bath with a fresh mixture acid of HNO_3/H_2SO_4 (Horvat et al. 1991). Total Hg was determined using dual-stage gold amalgamation method and cold vapour atomic fluorescence spectrometry (CVAFS) detection following method 1631 (USEPA 1999).

Soil Analysis

After harvesting the plants, the soil sample was collected, air-dried, and passed through a 2-mm sieve. Diethylene triamine pentaacetic acid (DTPA) extracted Cd, Ni, Pb, and Cr content in soil were estimated by the method developed by Lindsay and Norvell (1978) using ICP-AES and DTPA extracted Hg in soil was analysed using atomic fluorescence spectrometry. For microbial analysis, soil samples were collected from rhizosphere soil, homogenized and stored in 4 °C temperature in refrigerator, and analysed within 48 h.

Microbial Population Count

Ten gram of soil was added to 95 ml of sterile distilled water and prepared a homogenized solution from where sample was taken to make serial dilution (10^{-1} to 10^{-6}) and aliquots of the resulting solutions plated on appropriate culture media. The most frequently used readymade media such as for bacteria: nutrient agar (HIMEDIA M001), fungi: potato dextrose rose bengal (HIMEDIA M096), for actinomycetes: actinomycete isolation agar (HIMEDIA M490) and for phosphate solubilizing bacteria: Pikovskaya agar medium (Pikovskaya 1948). Standard spread plate method was followed and viable colonies were counted after 48 h of incubation.

Mycorrhizal Root Colonization

The roots were washed under running water to make it clean of soil particles followed by cutting the roots to smaller segments of 1–2 cm. Segmented roots were then hot cleaned in 10% KOH for 20 min at 90 °C and stained with trypan blue (0.05% in lacto-glycerol) for 10 min. They were then left in lacto-glycerol at 90 °C for 45 min for elimination of undesired dye particles (Phillips and Hayman 1970).

The percentage of root colonization was determined by placing the root pieces randomly on a gridded petri plate and analysed under a stereomicroscope by quantifying the intersections between lines and roots both horizontal and vertical which either appear to be colonized (coloured) or non mycorrhizal (uncoloured) (Giovannetti and Mosse 1980).

Bioaccumulation Factor (BAF)

The BAF (bioaccumulation factor, the ratio of the concentration of the element in the grain to that in the corresponding soil) was calculated for each rice sample to quantify the bioaccumulation effect of rice on the uptake of heavy metals from the soils (Liu et al. 2005). The BAF is an index of the ability of a plant to accumulate a particular metal with respect to the metal's concentration in the soil (Ghosh and Singh 2005). The BAF was computed as

$$\mathrm{BAF} = \frac{\mathrm{Cr}}{\mathrm{Cs}}, \tag{1}$$

where Cr and Cs represent the heavy metal concentrations in rice grain and soils, respectively.

Statistical Analysis

Data collected from glasshouse studies were analysed statistically by analysis of variance (ANOVA) procedure. Means were compared by the least significance difference (LSD) test ($P \leq 0.05$) (Hoshmand 1993).

Results

Dry Matter Yield

Dry matter yield (DMY) of rice root, shoot, and grain is presented in Fig. 1a, b. Results show that DMY of rice shoot that was not significantly affected by heavy metals except in Hg and Cd in Pusa 44 and Hg in PB1509 treatment at both the level as compared to control. However, grain yield in Pusa 44 is not affected by heavy metal treatments, whereas grain yield was significantly decreased in Hg treatments. Further dry matter yield of rice root is significantly reduced in both the rice varieties under metal treatments as compared to control. Sharma and Dubey (2005) reported that when rice (*Oryza sativa* L.) was grown in sand culture, root

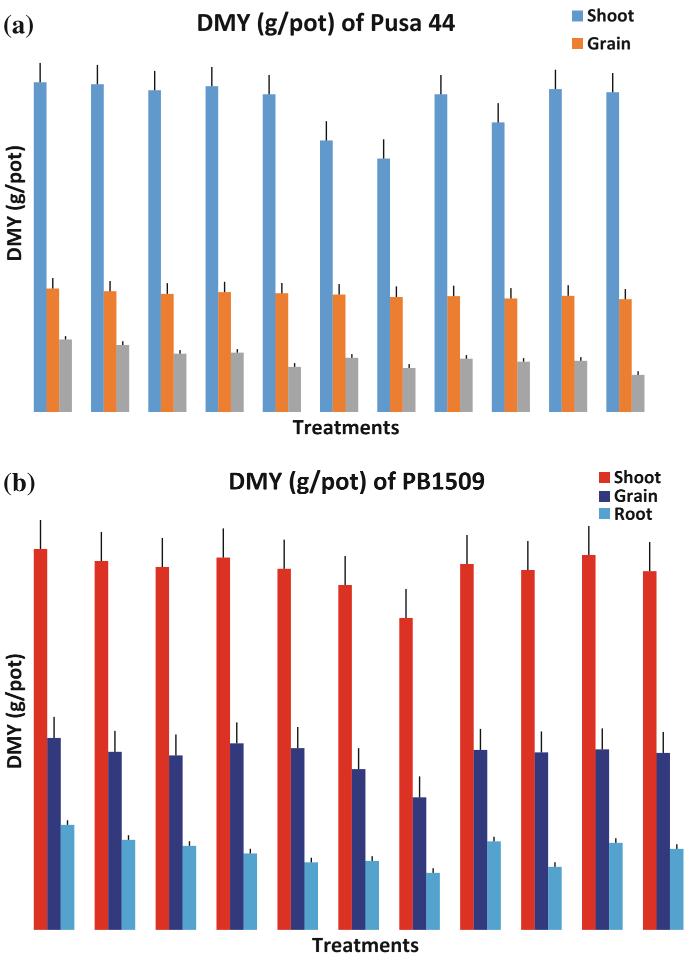


Fig. 1 **a** Dry matter yield (DMY) of rice (Pusa 44) as affected by different heavy metals. **b** Dry matter yield (DMY) of rice (PB1509) as affected by different heavy metals

growth was reduced by 22–42% and shoot growth by 25%, under lead stress. A considerable decrease in dry weights of plant parts under Pb treatment was also observed by Kosobrukhov et al. (2004). Result from this study indicates that the availability of heavy metals except Hg and Cd in this soil was not high enough to reduce plant yield. This is likely due to the soil pH above 7 limited the mobility of heavy metals. Reduced conditions increase the soil pH by consuming protons in flooded soils and hence increase retention of metal due to increased number of sites available with OH^- ion (Stahl and James 1991; Tack et al. 2006). The release of organic acids to alleviate the Al toxicity is reported (Pellet et al. 1995). Flooding created favourable environment for the growth of rice plants in the heavy metal-treated soils which restricted the translocation of heavy metal from soil to plants. The reduction of metal concentrations in rice plant parts may be due to reduced solubility of metals in flooded soils (Kashem and Singh 2001). It is reported that decreased Eh and increased pH after the submergence of soil decreased metals solubility (Zeng et al. 2011). Hydrous-oxides of Fe and Mn are considered to immobilize heavy metals by providing sites for their sorption in the soil (Brown et al. 1989). Sulphate reduction to sulphide at low Eh also favoured immobilization of heavy metals as sulphide salts (Van den Berg et al. 1998). Kashem and Singh (2001) reported immobilization of heavy metal in recalcitrant pool of soil under flooding conditions significantly reduced the bioavailability of heavy metals after submergence of rice plants resulting into reduced metal uptake by rice plants. Xiong and Lu (1993) also observed similar reduction of Cd uptake in submerged soil.

Heavy Metal Concentration in Rice

Table 2 shows the concentration of heavy metals in root, shoot, and grain of rice grown in heavy metal-treated soils. Results show that concentration of heavy metals in grain, shoot, and root were significantly increased with the increasing concentration of heavy metals in soil as compared to control in both the rice varieties. At both the levels of heavy metal application, heavy metal levels in different plant parts followed the order root > shoot > grain. In the root, highest metal content was in the order of Ni > Cd > Pb > Cr > Hg in both the rice varieties. However, in the shoot and grain metals concentration was in the order of Cd > Ni > Pb > Cr > Hg. Kibria et al. (2006) reported that Cd and Pb concentration in root, shoot, and grain of rice crop highly correlated with Cd and Pb concentration in soils, respectively. Regardless of metal and their contamination levels, the both the rice varieties absorbed almost similar quantities of heavy metals. All of these concentrations of metals except Cd and Hg are within the normal concentration range and below the critical concentration in plants based on Kabata-Pendias and Pendias (1992) in both the rice varieties.

Kumar et al. (1995) reported that the most of the Pb taken up by the plants remains in the roots which greatly restricting its translocation to above ground parts. The limited transport of Pb from roots to other organs is due to the barrier of the root endodermis (Sharma and Dubey 2005). Once inside the roots, most of the Pb is bound to ion exchangeable sites in the cell walls and extracellular precipitation as phosphate and carbonate (Sahi et al. 2002). The unbound Pb is moved through Ca channels accumulating near the endodermis (Antosiewicz 2005). Reddy and Patrick (1977) reported under reducing soil conditions, formation of Pb complexes with phosphate in/on roots, retarding Pb translocation and resulting in more Pb

Table 2 Heavy metals concentration (mg kg^{-1}) in different part of rice

Metal	Pusa 44											
	Root				Shoot				Grain			
	L1	L2	Mean	Control	L1	L2	Mean	Control	L1	L2	Mean	Control
Cr	13.1	22.0	17.5	1.36	3.6	6.1	4.85	0.24	0.278	0.592	0.435	ND
Cd	22.7	48	35	0.02	10.5	25.1	17.8	ND	3.95	7.91	5.93	ND
Hg	7.9	18.3	12.7	ND	2.25	3.12	2.69	ND	0.25	0.49	0.37	ND
Ni	18.5	54	36	0.86	8.6	19	13.8	0.054	3.4	7.1	5.25	ND
Pb	15.8	38	26.5	0.68	3.1	5.1	4.1	ND	0.92	3.28	2.1	ND
LSD ($P = 0.05$)	3.1	8.6	6.2	0.008	2.25	3.15	2.45	0.005	0.19	0.35	0.26	–
Metal	PB1509											
	Root				Shoot				Grain			
	L1	L2	Mean	Control	L1	L2	Mean	Control	L1	L2	Mean	Control
Cr	14.6	28.9	21.75	1.56	5.4	9.1	7.25	0.31	0.28	0.47	0.38	ND
Cd	23.1	51.2	37.15	0.025	9.3	23.6	16.45	ND	3.84	6.96	5.4	ND
Hg	8.1	18.9	13.5	ND	1.96	3.23	2.6	ND	0.24	0.33	0.285	ND
Ni	20.1	58.9	39.5	0.88	10.2	21.3	15.75	0.078	3.75	6.05	4.9	ND
Pb	12.5	31.9	22.2	0.76	3.15	7.2	5.18	ND	0.83	2.63	1.73	ND
LSD ($P = 0.05$)	2.8	7.5	6.8	0.007	1.98	3.15	2.35	0.0055	0.15	0.38	0.24	–

concentration in roots. Flooding condition significantly ($p < 0.05$) reduced the concentration and uptake of Cd, Ni, Cr, and Pb in rice grown in three different soils (Kibria et al. 2006). Under flooded condition, Cr remains in soil as Cr (III) which is relatively insoluble in water and tends to form hydroxide precipitates with Fe. Chromium enters plants by reduction and/or complexation with root exudates, such as organic acids, which increase the solubility and mobility of Cr through the root xylem (Bluskov et al. 2005). Both Cr (VI) and Cr (III) enter into the root cells by the symplast pathway where Cr (VI) is reduced and accumulated in the cortex (Arun et al. 2005). Even though Cr is poorly translocated to aerial parts, it is mobilized and accumulated inside tissues depending on its chemical form (James and Barlett 1983). Hexavalent Cr damages root membranes because it has a high oxidation power.

The soil carbon organic content was also quite high (Table 1), which indicated that metals were likely to be bound to organic matter to form metal-chelate complexes. Thus, the metals occurred mostly in the non available form and were very less taken up and accumulated in the paddy plants. Under submerged condition, the solubility of Hg is suppressed by HgS formation (Srivastava and Gupta 1996). Jarvis et al. (1976) reported that Cd was easily taken up by plants and transported to different parts, although it is non-essential and is of no beneficial effects on plants and animals. Moreover, Cd is toxic to animals and plants, and plants when exposed to this metal show reduction in photosynthesis and uptake of water and nutrient (Sanità Di Toppi and Gabbrielli 1999). The electrochemical potential gradient of the plasma membrane in the root cells of plants drives Cd and other cations into the root cells (Blaylock and Huang 2000). In rice, the concentration of Cd in grains is governed somewhat by its uptake and transport from roots to shoots, and to a greater extent, by the transport of Cd from shoots to grain. In a study performed in China by Liu et al. (2007), it was found that about 0.73% of the total Cd taken up by six rice cultivars was transferred to the grain. This represents an average of 1.02 mg kg^{-1}, which is 100 times higher than the concentration allowed by the European Union for Cd concentration in rice grain (Olsson et al. 2005).

Table 3 DTPA extractable heavy metals in soil (mg kg^{-1}) after the harvesting of rice

Metals	Pusa 44				PB1509			
	L1	L2	Mean	Control	L1	L2	Mean	Control
Cr	8.7	15.5	12.1	0.92	9.2	18.4	13.8	1.14
Ni	9.4	20.1	14.75	0.76	8.9	22.5	15.7	0.69
Hg	4.2	9.5	6.85	ND	5.7	9.8	7.75	ND
Cd	6	13.2	9.6	0.025	5.3	12.4	8.85	0.040
Pb	5.1	12.5	8.8	0.26	4.4	10.7	7.55	0.35
LSD (p = 0.05)	0.76	1.59	1.2	0.011	1.12	1.78	1.39	0.009

Bioaccumulation Factor (BAF)

Bioaccumulation factors (BAFs) for the heavy metal transfer from soils to rice grain are shown in Fig. 2. The ranking order of bioaccumulation factor for heavy metals was Cd > Ni > Pb > Cr > Hg for both the rice varieties. Soil-to-grain transfer factor for Pusa 44 for Ni, Pb, Cd, Cr, and Hg was 0.070, 0.028, 0.079, 0.0058 and 0.0049, respectively, and for PB1509 for Ni, Pb, Cd, C, and Hg was 0.065, 0.023, 0.072, 0.0050 and 0.0038, respectively. Among the heavy metals, BAF values were found to be higher for Cd and Ni, whereas relatively lower BAF values were found in Cr, Hg, and Pb. The food chain (soil–plant–human) is mainly known as one of the major pathways for exposure of human to soil contaminants. Soil-to-plant transfer is one of the key processes of human exposure to toxic heavy metals through the food chain (Lokeshwari and Chamdrappa 2006). When BAF $\leq$ 1, it implies that the plant only absorbs the heavy metal but does not accumulate when BAF > 1, and this indicates that plant accumulates the heavy metals (Zhuang et al. 2009). In present study, BAF values of Pb, Cd, Hg, Cr, and Ni were less than one in the rice grain which indicates that plants only absorb the heavy metals. Nickel is now considered an essential element for plant growth, but Cd is non-essential to biota, more mobile and bioavailable, toxic to humans at lower concentrations than those of plants. Crops grown on anthropogenically Cd-contaminated soils or on naturally rich in this metal (black shales) are one of the sources of Cd transport to humans (Singh and Mclaughlin 1999). However, the transfer factors (TF) of Hg were not as detrimental as some of the other heavy metals, with the trend being Cd > Zn > Cu > Pb > Hg.

Bioavailable Metals

Data on DTPA available metal which is consider plant available of bioavailable metal is presented in Table 3. Result shows that significant difference was found among the bioavailable metal contents in different metals treatment after the

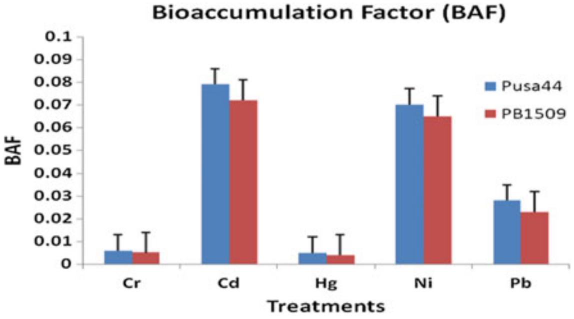


Fig. 2 Bioaccumulation factor of various heavy metals for rice crop in inceptisol

harvesting of rice crop in both the rice varieties. The content of bioavailable metal decreased as follows: Ni > Cr > Cd > Pb > Hg. The bioavailable metals pool generally associated with metal uptake by plants (Peijnenburg et al. 2007).

Microbial Population and Mycorrhizal Root Colonization

Microorganisms may be the key players in heavy metal mobilization. Soil microflora affects the solubility and speciation of heavy metal ions by secretion of various organic ligands, decomposition of organic matter, metabolite and siderophore

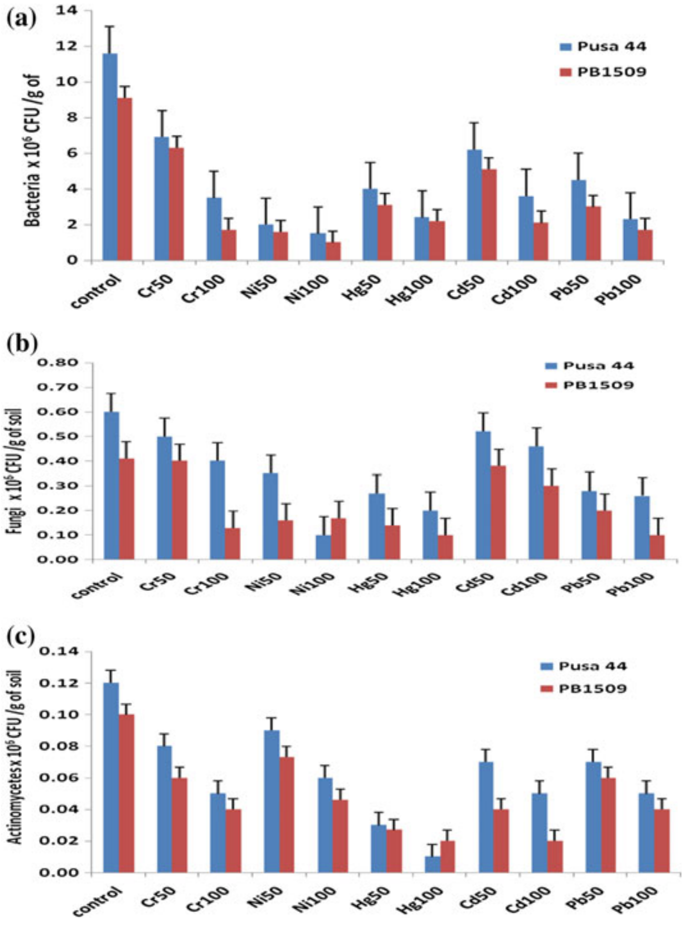


Fig. 3 **a** Bacterial population in rice rhizosphere as affected by different heavy metals. **b** Fungal population in rice rhizosphere as affected by different heavy metals. **c** Actiomycetes population in rice rhizosphere as affected by different heavy metals

release (Gadd 2004). In present study, different levels of metals (Cr, Ni, Hg, Cd, and Pb) treatment to two rice varieties (Pusa 44 and PB1509) variably affected the general and beneficial microbes' viable population in rice plants rhizosphere (Fig. 3a, b, c). Average microbial population was high in the rhizosphere of Pusa 44 as compared to PB1509 under control condition. The viable population of bacteria, fungi and actinomycetes were adversely affected by increasing concentration of each heavy metal. Minimum viable bacterial and fungal population was observed in both rice cultivars under Ni 100 ppm, whereas actinomycetes population was lowest under Hg 100 ppm treatment as compared to control treatment. Heavy metal treatments affected more adversely the population of PSB in Pusa 44 rhizosphere as compared to PB1509. In Pusa 44 rhizosphere, minimum viable PSB population was observed under Pb 100 treatment as compared to control (Fig. 4). Mycorrhizal colonization was low on roots of PB1509 than Pusa 44 under control treatment (Fig. 5). Lowest (22–26%) mycorrhizal colonization in both cultivars roots was

Fig. 4 Phosphate solubilizing bacteria (PSB) population in rice rhizosphere as affected by different heavy metals

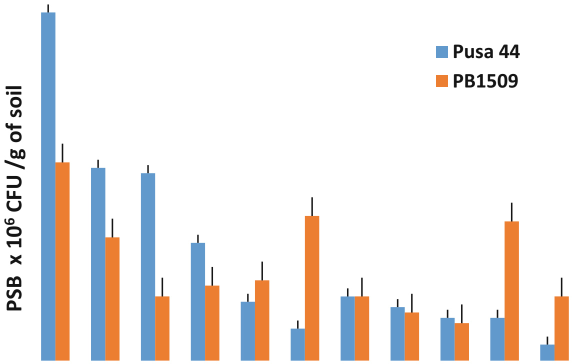
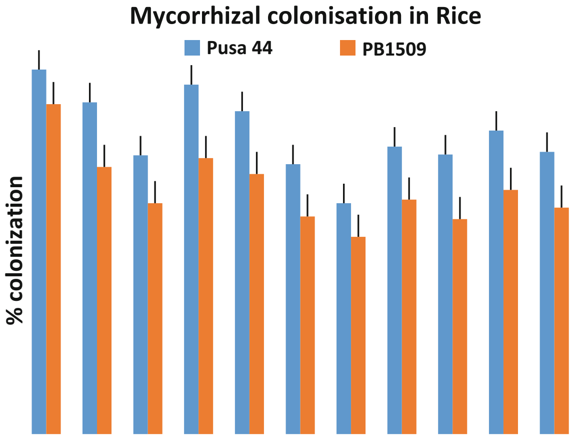


Fig. 5 Mycorrhizal colonization on rice root as affected by different heavy metals



observed under Hg 100 ppm treatments as compared to control. Our data show that heavy metals have profound effect upon the general microbial community, PSB and mychorrhizal colonization, as observed by others (Van Dijk 2008).

Conclusion

The present results showed that high concentration of heavy metals except mercury in soil do not necessarily decrease shoot and grain yield; however, root weight is significantly reduced with increasing concentration in the soil. All the heavy metals studied were found to accumulate mainly in the roots of the rice plant, while the grains contained low levels. The concentration of heavy metals in various parts of rice increased significantly with increasing metal levels in soils. The low translocation of heavy metals in the various rice parts is may be due to low bioavailability of heavy metals in the soil. The effects of heavy metals contaminated soils on rice growth and food safety are of more concern. These five heavy metals in soil are of major concern because of accumulation in rice at levels showing no phytotoxic syndromes and decrease in grain yield, but that are toxic to humans and animals through the food chain. Though, their bioavailability is reduced in the flooding condition for rice crop but there is need to assess the toxic effects of heavy metals successive crops growing in non-flooding conditions. Further heavy metals have significant effect upon the microbial community. Further studies, including sequencing of the recovered DNA fragments, are needed to identify the changes in microbial community.

References

Adriano DC (2003) Trace elements in terrestrial environments: biogeochemistry, bioavailability and risks of metals. Springer, New York (2nd edition)

Antosiewicz DM (2005) Study of calcium-dependent lead-tolerance on plants differing in their level of Ca-deficiency tolerance. Environ Pollut 134:23–34

Arun KS, Cervantes C, Loza-Tavera H, Avudainayagam S (2005) Chromium toxicity in plants. Environ Int 31:739–753

Biester H, Müller G, Schöler HF (2002) Binding and mobility of mercury in soils contaminated by emissions from chlor-alkali plants. Sci Total Environ 284:191–193

Blaylock MJ, Huang JW (2000) Phytoextraction of metals. In: Raskin I, Ensley BD (eds) Phytoremediation of toxic metals: using plants to clean up the environment. Wiley, New York, pp 53–71

Bluskov S, Arocena JM, Omotoso OO, Young JP (2005) Uptake, distribution, and speciation of chromium in *Brassica Juncea*. Int J Phytorem 7:153–155

Brown PH, Dunemann L, Schultz R, Marseher H (1989) Influence of redox potential and plant species on the uptake of nickel and cadmium from soils. Pflazcuernahr Bodenk 152:85–91

Cataldo DA, Garland TR, Wildung RE (1978) Nickel in plants. Plant Physiol 62:563–570

Cataldo DA, Garland TR, Wildung RE (1981) Cadmium distribution and chemical fate in soybean plants. Plant Physiol 68:835–839

Caussy D, Gochfeld M, Gurzau E, Neagu C, Ruedel H (2003) Lessons from case studies of metals: investigation exposure, bioavailability, and risk. Ecotoxicol Environ Safety 56:45–51

Chen W, Chang AC, Wu L (2007) Assessing long term environmental risks of trace elements in phosphate fertilizers. Ecotoxicol Environ Safety 67:48–58

de Abreu CA, de Abreu MF, de Andrade JC (1998) Distribution of lead in the soil profile evaluated by DTPA and Mehlich-3 solutions. Bragantia 57:185–192

Doty SL (2008) Enhancing phytoremediation through the use of transgenics and endophytes. New Phytol 179:318–333

Gadd GM (2004) Microbial influence on metal mobility and application for bioremediation. Geoderma 122:109–119

Gambrell RP (1994) Trace and toxic metals in wetlands. J Environ Qual 23:883–891

Ghosh M, Singh SP (2005) A comparative study of cadmium phytoextraction by accumulator and weed species. Environ Pollut 133:365–371

Giller KE, Witter E, Mcgrath SP (1998) Toxicity of heavy metals to microorganisms and microbial processes in agricultural soils: a review. Soil Biol Biochem 30:1389–1414

Giovannetti M, Mosse B (1980) An evaluation of techniques for measuring vesicular arbuscular mychorrizal infection in roots. New Phytol 84:485–500

Gray JE, Labson VF, Weaver JN, Krabbenhoft DP (2002) Mercury and methylmercury contamination related to artisanal gold mining, Suriname. Geophys Res Lett 29:201–204

Horvat M, Lupšina V, Pihlar B (1991) Determination of total mercury in coal fly ash by gold amalgamation cold vapour atomic absorption spectrometry. Anal Chim Acta 243:71–79

Hoshmand AR (1993) Experimental research design and analysis: a practical approach for agricultural and natural sciences. CRC Press, Boca Taton

Jackson AP, Alloway BJ (1992) The transfer of cadmium from agricultural soils to the human food chain. In: Adriano DC (ed) Biogeochemistry of trace metals. Lewis publishers, Boca Raton, pp 109–158

James BR, Barlett RJ (1983) Behavior of chromium in soils VII. Adsorption and reduction of hexavalent forms. J Environ Qual 12:177–181

Jarup L (2003) Hazards of heavy metal contamination. Br Med Bull 68:167–182

Jarvis SC, Jones LHP, Hopper MJ (1976) Cadmium uptake from solution by plants and its transport from roots to shoots. Plant Soil 44(1):179–191

Kabata-Pendias A (2004) Soil–plant transfer of trace elements—an environmental issue. Geoderma 122:143–149

Kabata-Pendias A, Pendias H (1992) TraceElementsin Soils and Plants. CRC Press, Boca Raton (2nd edn)

Kashem MA, Singh BR (2001) Metal availability in contaminated soils: II. Uptake of Cd, Ni and Zn in rice plants grown under flooded culture with organic matter addition. Nutr Cyc Agroecosyst 61:257–266

Kibria MG, Osman KT, Ahmed MJ (2006) Cadmium and lead uptake by rice (*Oryza sativa* L.) grown in three different textured soils. Soil Environ 25:70–77

Kosobrukhov A, Knyazeva I, Mudrik V (2004) Plantago major plants responses to increase content of lead in soil: growth and photosynthesis. Plant Growth Regul 42:145–151

Krishna MVB, Karunasagar D, Arunachalam J (2003) Study of mercury pollution near a thermometer factory using lichens and mosses. Environ Pollut 124:357–360

Kumar NPBA, Dushenkov V, Motto H, Raskin I (1995) Phytoextraction: the use of plants to remove heavy metals from soils. Environ Sci Technol 29:1232–1238

Lindqvist O (1991) Special issue of first international on mercury as aglobal pollutant. Water Air Soil Pollut 56:1

Lindsay WL, Norvell WA (1978) Development of a DTPA soil test for zinc, iron, manganese, and copper. Soil Sci Soc Am J 42:421–428

Liu H, Probst A, Liao B (2005) Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). Sci Total Environ 339:153–166

Liu J, Qian M, Cai G, Yang J, Zhu Q (2007) Uptake and translocation of Cd in different rice cultivars and the relation with Cd accumulation in rice grain. J Hazard Mater 143:443–447

Lokeshwari H, Chamdrappa GT (2006) Impact of heavy metal contamination of Bellandur Lake on soil and cultivated vegetation. Current Sci 91(5):622–627

Marchiol L, Assolari S, Sacco P, Zerbi G (2004) Phytoextraction of heavy metals by canola (*Brassica napus*) and radish (*Raphanus sativus*) grown on multicontaminated soil. Environ Pollut 132:21–27

McBride MB (1994) Environmental chemistry of soils. Oxford University Press, New York

Najafian M, Kafilzadeh F, Azad HN, Tahery Y (2012) Toxicityof chromium (Cr^{6+}) on growth, ions and some biochemicalparameters of *Brassica napus* L. World App Sci J 16:104–1109

Nevado JJB, Bermejo LFG, Martin-Dolmeadios RCR (2003) Distribution of mercury in the aquatic environment at Almaden, Spain. Environ Pollut 122:261–271

Novoa-Munoz JC, Pontevedra-Pombal X, Martinez-Cortizas A, Garcia-Rodeja GE (2008) Mercury accumulation in upland acid forest ecosystems nearby a coalfired power-plant in Southwest Europe (Galicia, NW Spain). Sci Total Environ 394:303–312

Olsson IM, Erikson J, Oborn I, Skerfving S, Oskarsson A (2005) Cadmium in food production systems: a health risk for sensitive population groups. Ambio 34:344–351

Peijnenburg W, Baerselman R, de Groot A, Leenders JD, Posthuma L, ven Veen R (2000) Quantification of metal bioavailability for lettuce (*Lactuca sativa* L.) in field soils. Arch Environ Contam Toxicol 39:420–430

Peijnenburg WJGM, Zablotskaja M, Vijver MG (2007) Monitoring metals in terrestrial environments within a bioavailability framework and a focus on soil extraction. Ecotoxicol Environ Saf 67:163–179

Pellet DM, Grunes DL, Kochian LV (1995) Organic acids exudation as an aluminium-tolerance mechanism inmaize*(Zea*mays). Planta 196:788–795

Pestana MH, Formoso ML (2003) Mercury contamination in Lavras do Sul, south Brazil: a legacy from past and recent gold mining. Sci Total Environ 307:125–140

Phillips JM, Hayman DS (1970) Improved procedures for clearing roots and staining parasitic and vesicular-arbuscular mycorrizal fungi for rapid assessment of infection. Trans British Mycol Soc 55:158–161

Pikovskaya RI (1948) Mobilization of phosphorus in soil connection with the vital activity of some microbial species. Microbiologiya 17:362–370

Reddy CN, Patrick WH (1977) Effect ofredox potential and pH on the uptake ofcadmium and lead by rice plants. J Environ Qual 6:259–262

Sahi SV, Bryant NL, Nilesh CS, Singh SR (2002) Characterization of a lead hyperaccumulator shrub, *Sesbania drummondii*. Environ Sci Technol 36:4676–4680

Sajwan KS, Lindsay WL (1986) Effects of redox on zinc deficiency in paddy rice. Soil Sci Soc Am J 50:1264–1269

Sanità Di Toppi L, Gabbrielli R (1999) Response to cadmium in higher plants. Environ Exp Bot 41:105–130

Sharma P, Dubey RS (2005) Lead toxicity in plants. Braz J Plant Physiol 17:35–52

Singh BR, Mclaughlin MJ (1999) Cadmium in soils and plants. In: McLaughlin MJ, Singh BR (eds) Cadmium in soils and plants. Kluwer Academic Publishers, pp 257–267

Srivastava PC, Gupta UC (1996) Trace elements in crop production. Oxford & IBH Publishing Co. Pvt. Ltd., New Delhi, India, p 341

Stahl RS, James BR (1991) Zinc sorption by manganese-oxide-coated sand as a function of pH. Soil Sci Soc Am J 55:1291–1294

Tack FMG, Van Ranst E, Lievens C, Vandenberghe RE (2006) Soil solution Cd, Cu and Zn concentrations as affected by short-time drying or wetting: The role of hydrous oxides of Fe and Mn. Geoderma 137:83–89

USEPA (1999) Method 1631, revision B: mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry. U.S. Environmental Protection Agency, Washington, DC, pp 1–33

Van den Berg GA, Loch JPG, Winkels HJ (1998) Effect of fluctuating hydrological conditions on the mobility of heavy metals in soils of a freshwater estuary in the Netherlands. Water Air Soil Poll 102:377–388

Van Dijk T (2008) Microbial Ecology Research Trends. Nova Science Publishers, Hauppauge, NY 11788, United States

Verma S, Dubey RS (2001) Effect of cadmium on soluble sugar and enzymes of their metabolism in rice. Biol Plant 44:117–123

Xiong LM, Lu RK (1993) Effect of liming on plant accumulation of cadmium under upland or flooding conditions. Environ Pollut 79:199–203

Zeng FR, Ali S, Zhang HT, Ouyang YB, Qiu BY, Wu FB, Zhang G (2011) The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. Environ Pollut 159:84–91

Zhuang P, McBride MB, Xia H, Li N, Li Z (2009) Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China. Science Total Environ. 407:1551–1561

Studies on the Non-symbiotic Diazotrophic Bacterial Population and Efficiency of Nitrogen Fixation in Coastal Saline Soils from Sagar Island, West Bengal

Arundhati Das, Rajkamal Srivastava, Vishal Patil and Sudipta Tripathi

Abstract Surface soils and subsurface soils were collected from three different locations, viz. Iswaripur, Mouriganga and Companichar of Sagar Island, 24 Parganas (South). Surface soils recorded higher ECe values and also recorded higher organic carbon than subsurface soils. Diazotrophic bacterial population and dinitrogen fixation were higher in surface soils. The highest population (6.87 log colony-forming unit) and nitrogen-fixing power (5.187 mg nitrogen fixed 50 mL^{-1} culture media) were observed in surface soil of Mouriganga (88° 10′ 01.6″E and 21° 49′ 03.8″N). Eight pure diazotrophic bacteria were isolated and characterized from these three locations. Most of the isolated organisms were Gram (+ve) and few were Gram (−ve). Acid production test was positive for all the organisms during different sugar utilization. All the isolates could hydrolyze starch and lactose. The organisms were catalase positive. Among the eight isolated bacteria, Sagar6 found to be the best depending on its nitrogen-fixing ability, which was isolated from subsurface soil of Mouriganga (88° 10′ 01.6″E and 21° 49′ 03.8″N). This isolate could fix up to 4.09 mg nitrogen fixed 50 mL^{-1} culture media. Sagar6 isolate promised to be a candidate for adoption in crop production in soils of Sagar Island.

Keywords Coastal saline soil · Diazotrophic bacterial population
Dinitrogen fixation

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Introduction

The biological fixation of molecular nitrogen attracts the attention of the biochemist, biologists and agricultural workers. Nitrogen fixation is widespread in the microorganisms which live in the soil, freshwater, seawater and tissues of higher plants and animals. In each of these environments, nitrogen-fixing organisms play their own specific roles. In agriculture, biological nitrogen fixation has tremendous value, since nitrogen assimilated by the microorganisms can replenish substantially the nitrogen reserves of the soil and help to improve soil fertility. Biological nitrogen makes it possible to counteract a shortage of mineral nitrogenous fertilizers and to use the fertilizers more economically.

On global basis, salt-affected soils occupy an estimated area of 952.062 million hectares of land consisting of nearly 7% of total land area (Szabolcs 1979). Salinity is a serious threat to world agriculture. In India, out of an estimated area of 187.7 million hectares of total degraded land, 8.1 million hectares are salt-affected and out of which 3.1 million hectares are in the coastal regions (Yadav et al. 1983). Among the states in India, West Bengal has the largest area (0.82 million hectares) of salt-affected soils in the coastal region, between 87° 25′E and 89°E latitude and 21° 30′N and 23° 15′N longitude, covering the districts of North and South 24 Parganas, Haora and East Midnapur. The great Sundarbans, the delta region of the river Ganges, occur in the coastal tracts of North and South 24 Parganas. Sagar Island is one of the most important islands of the Sundarbans delta. This island is located in extreme south of eastern coastal plain forming a part of the Sundarbans delta of India (Maji et al. 1998). The soil salinity shows wide spatial and seasonal variability, being minimum in the monsoon season and maximum in the summer season (Bandyopadhyay and Rao 2001). The coastal area is generally monocropped with rice during the monsoon season only. Soil salinity, imbalance of nutrients, unfavorable pH, lack of good quality irrigation water, etc., account for poor yield of crops in this region (Sen and Bandyopadhyay 2001).

Based on morphological data, it was found that the soils of the island have two distinct classes. The soils of the western side of the island facing the Hugli River having more freshwater flow are lighter in texture, and the soils from the eastern side of the island facing the Baratala/Muri Ganga Rivers having more brackish water flow are heavier in texture (Maji et al. 1998).

Changes in soil properties along with the depth are evident in the literature (Gul et al. 2011). The effect is much prominent in saline soil as the accumulation of salt during summer month occurs in the surface soil (Bandyopadhyay and Rao 2001). Based on the above discussion, this piece of work has been undertaken with the various aspects, viz. estimation of chemical properties of soils under study, estimation of nitrogen fixation of both surface and subsurface soils of three different sites under study area, total count of non-symbiotic diazotrophic bacterial population in soils both from surface and subsurface soil of three different sites of the Sagar Island and isolation, purification and characterization of free living diazotrophic bacteria from the soils under study.

Materials and Methods

A. **Study Site and Soil Sampling**:

Soils, for the present study, were collected from three different locations, viz. Iswaripur (88° 09′41.1″E and 21° 49′25.3″N), Mouriganga (88° 10′ 01.6″E and 21° 49′03.8″N) and Companichar (88° 09′18.1″E and 21° 49′28.7″N) of Sagar island, 24 Parganas (South), West Bengal, during April 2012. Four replicated soil samples from both surface (0–15 cm) and subsurface (15–30 cm) horizon were collected from each of the three locations. A brief description of lands is given in Table 1, and the location map of the observation sites is given in Fig. 1.

Altogether, 24 soil samples were collected from three sites. After collection of soil sample from each site, plant roots, visible faunas, stones, rubbles were removed and about 1 kg soil from each site was brought to the laboratory in properly labeled sterile containers. The samples were kept at 4 °C before microbial analysis of the field moist soils, and the physicochemical properties of soil were carried out with air-dried soil sample.

B. **Determination of Chemical Properties of Soil**:

Determination of Soil Reaction (pH): Soil pH was measured in a 1:2.5 soil–water suspension using a glass electrode according to the method as described by Jackson (1967).

Determination of electrical conductivity (ECe) of soil: Soil ECe was determined by measuring the electrical conductance of soil saturation extract with conductivity meter following the method described in USDA, 1954.

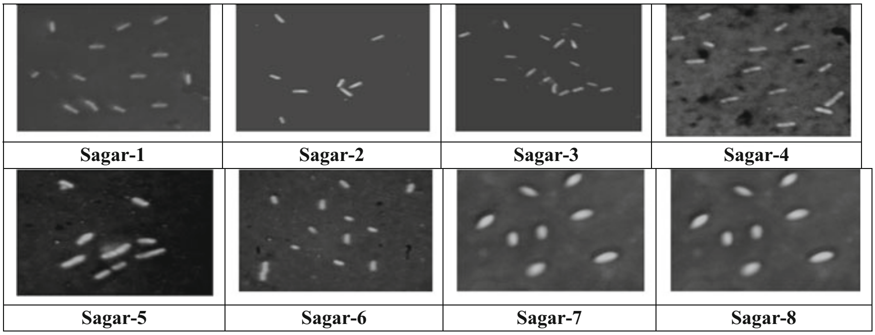
Determination of organic carbon of soil: It was determined by the method of Nelson and Sommers (1982).

Determination of total nitrogen of soil: It was determined by macro-Kjeldahl method as stated by Black (1956) with the help of Kelplus automated N analyzer.

Table 1 Chemical properties of the soils under study

Soil code	pH (1:2.5)	ECe (dSm^{-1})	Organic carbon (g kg^{-1})	Total nitrogen (g kg^{-1})
1A	8.25^{a*}	12.22^{a}	3.50^{f}	0.225^{f}
1B	8.10^{b}	9.55^{b}	3.70^{e}	0.280^{e}
2A	5.70^{f}	6.32^{c}	7.80^{b}	0.810^{a}
2B	7.01^{d}	4.65^{e}	4.90^{d}	0.612^{b}
3A	6.10^{e}	5.20^{d}	8.75^{a}	0.482^{c}
3B	7.25^{c}	3.80^{f}	5.40^{c}	0.375^{d}

*Figures denoted by same alphabets are statistically similar at 5% probability level by DMRT
$^{a–f}$ denote the decreasing value of the parameters



Sagar-1 Sagar-2 Sagar-3 Sagar-4

Sagar-5 Sagar-6 Sagar-7 Sagar-8

Fig. 1 Picture of negative staining of eight purified bacterial strains (1000X)

C. **Enumeration of Non-symbiotic Diazotrophic Microbial Population in Soil**:

A requisite quantity of soil (10 g) was transferred into 90 mL of sterile water containing sodium pyrophosphate (0.18% final concentration). Pyrophosphate was added to water after autoclaving at 121 °C. The flask was shaken for 15 min on a horizontal shaker at 200 rpm and then left to settle the soil for 15 min. The soil suspension was then serially diluted to 10–4. One mL of 10–4 dilutions was transferred to three replicated sterile petri dishes for each replicated soil sample. Fifteen mL molten LG agar media was added to each plate. After solidification of the agar, the plates were incubated at 28–30 °C for 72 h. After incubation was over, colony-forming units (CFUs) were counted in each plate. The plates, which registered CFU between 30 and 300, were only considered. The results were computed as log CFU per gram of oven dry soil.

Composition of LG medium (Döbereiner 1995): sucrose—20 g, K_2HPO_4—0.05 g, $KH2PO_4$—0.15 g, CaC_{12}—0.01 g, $MgSO_4$, $7H_2O$—0.2 g, sodium molybdate, 2 H_2O—2 mg, $FeSO_4$—0.01 g, bromothymol blue (5% solution in ethanol)—2 mL, $CaCO_3$—1 g, agar—18 g, double distilled water—1 L, pH—7.2 before autoclaving.

D. **Determination of Dinitrogen (N_2) Fixation in Soil**:

One gram of each soil sample was added to duplicate flasks containing 50 mL LG broth and then sterilized. These served as blanks. To another duplicate set of flasks containing 50 mL sterile broth, 1 g of each soil sample was added aseptically. All the flasks were incubated at 30 °C for 7 days. Total nitrogen in the broth was determined by macro-Kjeldahl method. Nitrogen fixation in soil, per 50 mL^{-1} culture media, was determined by subtracting the value of nitrogen in the blank from the nitrogen in the sample.

E. **Isolation and Purification of Non-Symbiotic Diazotrophic Bacteria**:

It was carried out by taking individual colony of the organism developed from the soil dilution in nitrogen-deficient LG agar plate followed by streaking in same agar plates to obtain single isolated colony. In this way, 8 pure cultures were obtained and were maintained in LG agar slants.

F. Phenotypic and Biochemical Characterization of the Isolates:

Colony characteristics of the isolates on nitrogen-free LG agar slants and cellular morphology by negative staining, Gram character, were determined by method of Holtz (1993). Different biochemical characteristics of the isolates were determined following the method of Holtz (1993). Composition of different media used in biochemical characteristics was given below:

(a) **Starch agar media**: peptone—10 g, yeast extract—10 g, K_2HPO_4—5 g, soluble starch—3 g, agar—15 g, dist. water—1 L, pH—7.
(b) **Glucose–Peptone broth**: glucose—5 g, peptone—5 g, K_2HPO_4—5 g, dist. water—1 L, pH—7.
(c) **Sucrose broth**: sucrose—0.5 g, peptone—0.5 g, K_2HPO_4—0.5 g, dist. water —100 mL, pH—7.
(d) **Mannitol broth**: mannitol—0.3 g, peptone—0.5 g, K_2HPO_4—0.5 g, dist. water—100 mL, pH—7.
(e) **Lactose broth**: peptone—0.5 g, beef extract—0.3 g, lactose—0.5 g, dist. water—100 mL, pH—7.
(f) **Gram's iodine**: iodine—1 g, KI—2 g, dist. water—100 mL.
(g) **Methyl red**: methyl red 0.1 g in 95% alcohol.

G. Determination of Nitrogen-Fixing Efficacy of the Isolates:

Nitrogen-fixing efficacy of the isolates was estimated by growing the isolates in nitrogen-free LG broth for seven days at 28–30 °C, followed by determination of nitrogen in the cultures as well as blanks by macro-Kjeldahl method (Allen 1957). Nitrogen-fixing efficacy was expressed as mg N fixed 50 mL^{-1} culture media.

H. Statistical Analysis:

Assigning the soil as treatment factor, analysis of variance (ANOVA) was carried out by completely randomized design (CRD) using SPSS 11.0 statistical package. The factor soil had six levels, and the replicate had four levels. The least significant difference (LSD) test was applied to evaluate the significance of differences between individual treatment factors. The treatment means were compared by Duncan's multiple range tests at 0.05 P.

Results and Discussion

Surface soils recorded higher ECe values and also recorded higher organic carbon than subsurface soils.

From Tables 1, 2, 3 and 4, it can be said that diazotrophic bacterial population and dinitrogen fixation were higher in surface soils. The highest population (6.87 log

Table 2 Nitrogen-fixing bacterial population and nitrogen-fixing power of the collected soils

Soil code	Population of n-fixing microorganisms (log colony-forming unit)	Nitrogen fixation (mg nitrogen fixed 50 mL^{-1} culture media)
1A	6.18^{b}	4.318^{c}
1B	5.28^{e}	2.500^{f}
2A	6.87^{a}	5.187^{a}
2B	5.63^{d}	2.965^{d}
3A	6.09^{c}	4.915^{b}
3B	4.99^{f}	2.565^{e}

$^{a–f}$ denote the decreasing value of the parameters

Table 3 Phenotypic characteristics of the isolates from the studied soils

Strain code	Isolated from soil	Colony characteristics on nitrogen-free LG agar slant	Morphology of cells by negative staining	Gram character
Sagar1	1A	Appear single wet colony, small, rounded, convex, opaque	Small, thin, rod shaped	Gram positive
Sagar2	1B	Appear single wet colony, small, rounded, convex, opaque	Small, thin, rod shaped	Gram negative
Sagar3	1B	Appear single wet colony, small, rounded, convex, opaque	Small, thin, rod shaped	Gram positive
Sagar4	1B	Appear single wet colony, small, rounded, convex, opaque	Small, thin, rod shaped	Gram positive
Sagar5	2A	Appear single **dry** colony, small, rounded, convex, opaque	Small, thin, rod shaped	Gram negative
Sagar6	2B	Appear single wet colony, small, rounded, convex, opaque	Small, thin, rod shaped	Gram positive
Sagar7	3A	Appear single wet colony, small, rounded, convex, opaque	Small, thin, rod shaped	Gram positive
Sagar8	3B	Appear single wet colony, small, rounded, convex, opaque	Small, thin, rod shaped	Gram negative

colony-forming unit) and nitrogen-fixing power (5.187 mg nitrogen fixed 50 mL^{-1} culture media) were observed in surface soil of Mouriganga (88° 10′ 01.6″E and 21° 49′ 03.8″N). Eight pure diazotrophic bacteria were isolated and characterized from these three locations. Most of the isolated organisms were Gram (+ve) and few were Gram (−ve). Acid production test was positive for all the organisms during different sugar utilization. All the isolates could hydrolyze starch and lactose. The organisms were catalase positive. Among the eight isolated bacteria, Sagar6 found to be the best depending on its nitrogen-fixing ability, which was isolated from subsurface soil of Mouriganga (88° 10′ 01.6″E and 21° 49′ 03.8″N). This isolate could fix up to 4.09 mg nitrogen fixed 50 mL^{-1} culture media. Sagar6 isolate promised to be a candidate for adoption in crop production in soils of Sagar Island.

Table 4 Nitrogen-fixing efficacy of the isolates

Strain code	Isolated from soil	Nitrogen fixation (mg nitrogen fixed 50 mL^{-1} culture media)
Sagar1	1A	1.90
Sagar2	1B	2.42
Sagar3	1B	1.02
Sagar4	1B	1.25
Sagar5	2A	2.54
Sagar6	2B	4.09
Sagar7	3A	2.01
Sagar8	3B	2.79

References

Allen ON (1957) Experiments in soil bacteriology. Burgees Publishing Co., Minneapolis, Minnesota, pp 83–86

Bandyopadhyay BK, Rao DLN (2001) Integrated plant nutrient management in saline soils. J Indian Soc Coast Agric Res 19:35–58

Black CA (1956) Methods of soil analysis. American Society of Agronomy, Wisconsin, USA

Döbereiner J (1995) Isolation and identification of aerobic nitrogen fixing bacteria from soil and plants. In: Alef K, Nannipieri P (eds) Methods in applied soil microbiology and biochemistry. Academic press, London, UK, pp 134–135

Gul H, Khattak RA, Muhammad D, Shah Z (2011) Physical properties of soils under sub-surface drainage system. J Agric 27(2):225–232

Holtz JD (1993) Bergey's manual of determinative bacteriology, 9th edn. Willims and Wikins, Baltimore

Jackson ML (1967) Soil chemical analysis. Prentice Hall of India Pvt. Ltd., New Delhi, India

Maji B, Bandyopadhyay BK, Sarkar D, Chatterjii S (1998) Morphological and chemical characterization of soils of Sagar Island of the Sundarban, West Bengal. J Indian Soc Soil Sci 46(1):99–103

Nelson DW, Sommers LE (1982) Total carbon, organic carbon and organic matter. In: Sparks DL, Page AL, Helmke RA, Loeppert RH, Sottanpor PN, Tabatabai MA, Johnson CT, Summer ME (eds) Methods of soil analysis, Part 2. American society of Agronomy and Soil Science, Society of American Madison, Wisconsin, pp 539–579

Sen HS, Bandyopadhyay BK (2001) Problems and prospects of managing coastal ecosystem in India with special reference to eastern ecosystem. In: Proceedings National workshop on "Development and management of problem soils for sustainable agriculture production", India, 21 December 2001

Szabolcs (1979) Review of research on salt-affected soils. Nat Resour Res 15, UNESCO, Paris

United States Department of Agriculture (1954) Diagnosis and improvement of saline and alkali soils. In: Richards LA (ed) Agriculture hand book, no. 60. Oxford & IBH Publishing, New Delhi, India. pp 1–160

Yadav JSP, Bandyopadhya AK, Bandyopadhyay BK (1983) Extent of coastal saline soils of India. J Indian Soc Coast Agric Res 1:1–6

A Critical Study on the Applicability of Forchheimer and Wilkins Equations for Nonlinear Flow Through Coarse Granular Media

Ashes Banerjee, Srinivas Pasupuleti and G. N. Pradeep Kumar

Abstract Applicability of nonlinear flow equations for flow through coarse granular media suggested by Forchheimer and Wilkins has been studied extensively. It is been observed from the literature that Forchheimer equation may represent flow in transition and turbulent regime. However, the coefficients of the equation deviate in accordance with different field, media and fluid properties. Furthermore, the complexities based on the variations render the applicability of this equation to real-life problems inefficient. On the contrary, limited studies on the Wilkins equation reflect relatively non-deviating coefficients for different size of media, henceforth validating the applicability of this equation in nonlinear flow through coarse granular media. A large dimension still remains unexplored in the area of applicability of Wilkins equation for different field and media conditions. Present study will clarify the complexities related to the application of Forchheimer equation and will provide a broader view point in the advanced research related to the flow though porous media.

Introduction

The study of flow through porous media has become an imperative subject for the researchers due to its applicability in many diversified areas resembling civil engineering, petroleum engineering, chemical engineering and environmental

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engineering. The importance of considering non-Darcy effect on confined aquifer has been discussed by Basak (1977), whereas Holditch and Morse (1976), Martins et al. (1990) studied the influence of non-Darcy flow on well performance. Henry Darcy can be credited as the pioneer of the research related to porous media. In 1856, he first experimented on a sand column apparatus and observed that the flow through a bed of filtered sand is directly proportional to the hydraulic head acting on the sand bed and inversely proportional to its depth. The relation between hydraulic gradient (i) and velocity (V) is described in Darcy's equation as

$$V = \frac{Q}{A} = -k\frac{\partial h}{\partial x} = -ki \tag{1}$$

where k is a coefficient which depends on the permeability of the layer, V is the velocity of flow, A is the area of flow, $\frac{\partial h}{\partial x} = i =$ hydraulic gradient.

Though Darcy's equation is an empirical equation based on experimental investigation but later on researchers like Whitaker (1969), Hassanizadeh and Gray (1980) provided theoretical background to the equation. It is generally expected the Darcy's law is valid for flow through laminar regime (low Reynolds number). In some flow situations like flow near a well, flow through water filters, flows through rockfill dams where the Reynolds number is high, linear relationship between V and i does not hold well anymore (Van Gent 1995; Burcharth and Andersen 1995; Hall et al. 1995). This may be because when the flow takes place through lower Reynolds number the resistance is mainly due to viscous force, as the Reynolds number increases the effect of viscous resistance decreases and the inertia force starts to dominate and as the flow becomes completely turbulent inertia force becomes the main resistive force. Taking the inertia effect into consideration, number of nonlinear relationships has been proposed by various investigators like Blake (1923), Carman (1937), Ergun (1952), Engelund (1953), Scheidegger (1960), Barr (2001) over the years to represent the flow to simulate the flow in non-Darcy regime.

Development of Nonlinear Relation

The nonlinear equations present in the literature for flow through porous media can be divided into two main categories:

1. Binomial equation
2. Power law

Binomial Equation

These types of equations are mainly in the form of

$$i = aV + bV^2 \tag{2}$$

where i is the hydraulic gradient, V is the seepage velocity, a and b are the Darcy and Non-Darcy coefficients, respectively. Equation (2) is known as 'Forchheimer equation' and was originally proposed by a German researcher named P. Forchheimer. Though the equation proposed from pipe flow analogy, the Forchheimer equation can be also be derived from Navier–Stokes equation (Ahmed and Sunada 1969; Irmay 1958; Hassanizadeh and Gray 1987; Whitaker 1996; Du Plessis and Masliyah 1988). It is obvious from Eq. (2) that aV represents the energy loss in laminar regime where bV^2 represents the energy loss in fully developed turbulent regime. Later on the equation has been modified number of times by many researchers. Forchheimer himself modified the equation adding a third term to account for transitional conditions (Scheidegger 1960)

$$i = aV + bV^2 + cV^3 \tag{3}$$

Later Eq. (2) was further modified as

$$i = aV + bV^{1.5} + cV^2 \tag{4}$$

In Eqs. (3) and (4), c is an empirical constant. Equation (3) was later generalized by Polubarinova-Kochina by adding a time-dependent term as

$$i = aV + bV^2 + c\frac{\mathrm{d}V}{\mathrm{d}t} \tag{5}$$

Most recently, the Forchheimer equation was modified for lower velocities observing that the plot between $\frac{i}{V}$ (hydraulic gradient/velocity) and V (velocity) is not a continuously rising straight line but a negative slope to a certain value of velocity (Kumar et al. 2004; Krishna and Murthy 2013).

Though Eqs. (3), (4) and (5) are modified versions of Eq. (2) and represent all three regimes namely laminar, transition and turbulent, as per McCorquodale Eqs. (2) and (3) yield same value of i for Reynolds number 600–4000. But due to its simplicity, Eq. (2) is mostly used in computation (Srinivas et al. 2014). For the same reason, Eq. (2) has been explored by number of researchers analytically and experimentally which are discussed later in this paper.

Power Law

Another type of co-relation between i and V can be found in the literature (Scheidegger 1960; Subramanya and Madav 1978) as

$$i = pV^{j} \tag{6}$$

The equation is known as Missbach equation, in which p is a coefficient determined by the properties of fluid and medium and j is an exponent varies from 1 to 2. j is 1 when the flow is laminar and tends to 2 as the flow regime approaches turbulent flow condition.

A cursory look at Eq. (6) will clarify that being the only coefficient, p accounts for the effect of number of media conditions such as porosity, size of the medium, tortuosity as well as number of fluid properties such as density and viscosity. Conclusion from such equation can be misleading or confusing.

Wilkins (1955) while investigating the permeability properties of wide range of crushed stones and glass balls derived an equation in the form of

$$V_v = C\mu^{\alpha} r^{\beta} i^{\gamma} \tag{7}$$

where V_v is the pore velocity, C, α, β, γ are the coefficients of Wilkins equation, μ is the dynamic viscosity, r is the hydraulic radius and i is the hydraulic gradient. It is obvious Eq. (7) is a modified form of Eq. (6) as it contains number of media and fluid properties such as viscosity of the fluid (μ), hydraulic radius (r). Very limited literature exists about the applicability of this equation compared to the Forchheimer equation.

Applicability of Forchheimer Equation

Forchheimer equation represents the relation between hydraulic gradient and velocity at nonlinear flow regime. Going through the literature carefully, one can observe multiple opinions regarding the flow regimes for flow though porous media (Dybbs and Edwards 1984; Fand et al. 1987; Chhabra et al. 2001; Horton and Pokrajac 2009). Generally, porous media flows can be divided into three flow regimes depending on the Reynolds number of flow (Tek 1957):

A. Laminar Regime/Darcy's Regime.
B. Transition Regime/Forchheimer Regime.
C. Turbulent Regime.

Some studies suggested that both the transition regime (Forchheimer regime) and turbulent regime can be described by Forchheimer equation (Fand et al. 1987; Burcharth and Christensen 1991; Williams et al. 1992; Skjetne and Auriault 1999),

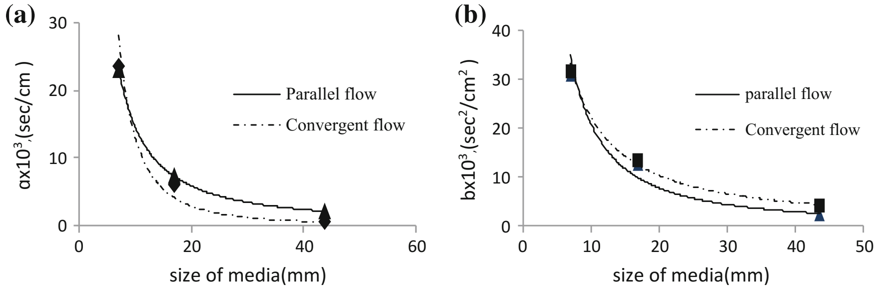

Fig. 1 **a** Variation of *a* with size of the media. **b** Variation of *b* with size of the media

but as no local measurement was done to identify the turbulent regime and to justify the statement, the regime termed as 'turbulent regime' in the earlier studies may belongs to the transition regime toward turbulent (Huang and Ayoub 2008). However, it has been seen that the values of the Darcy and Non-Darcy coefficients are different for both the regimes (Fand et al. 1987; Lage et al. 1997) and as per Lage et al. (1997) they depend on the morphology of the porous media.

Studies of number of researchers throughout the years on Forchheimer equation have clarified that the coefficients of the equation are not actual constants; they vary with number of field and media conditions. Figure 1a, b represents the effect of size of the media (media condition) on the Darcy and Non-Darcy coefficients of the Forchheimer equation for both the parallel and convergent flow. From Fig. 1a, b (Kumar and Venkataraman 1995), it is observed that the variation of Darcy and Non-Darcy coefficients is inversely proportional with the variation in media size for both parallel and convergent flow, study of Subramanya and Madav (1978), Nasser (1970), Thiruvengadam and Kumar (1997), Reddy and Rao (2006), Reddy (2005), Reddy and Reddy (2007) also support the statement, whereas Fig. 2a, b shows that the value of Darcy coefficient (*a*) and non-Darcy coefficient (*b*) increase as the convergent angle increases (Reddy et al. 2014).

Figure 3a, b (Reddy and Rao 2004) shows the variation of two coefficients for different radial lines the radial distance increases from the center of the permeameter the values of Darcy (*a*) and Non-Darcy coefficients (*b*) increases proving the effect of convergent angles. Same conclusion can be found in the studies of Kumar and Venkataraman (1995), Reddy and Rao (2006), Reddy and Reddy (2010), Venkataraman and Rao (2000). Not only size of the media and convergent angle, the Darcy and Non-Darcy coefficients vary with number of other conditions like porosity, permeability and shape of the media. The effect of porosity can be discussed with the help of Fig. 4 (Niranjan 1973). Figure 4a, b shows that Darcy and non-Darcy coefficient vary inversely with the change in porosity. This may be, as the porosity increases the velocity of the flow increases reducing the resistance toward the flow. Studies of Abbood (2009), Subramanya and Madav (1978) also support the statement.

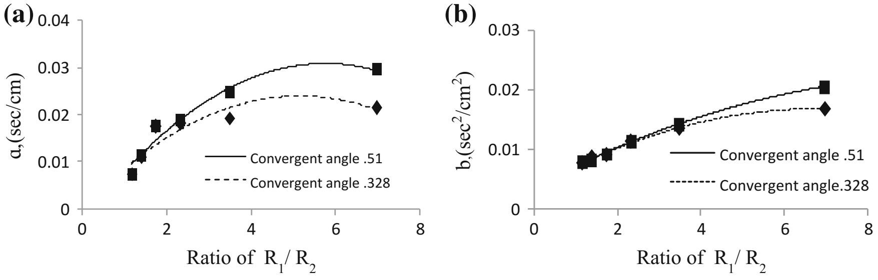

Fig. 2 **a** Variation of *a* with ratio of R_1/R_2 for different radial lines. **b** Variation of *b* with ratio of R_1/R_2 for different radial lines

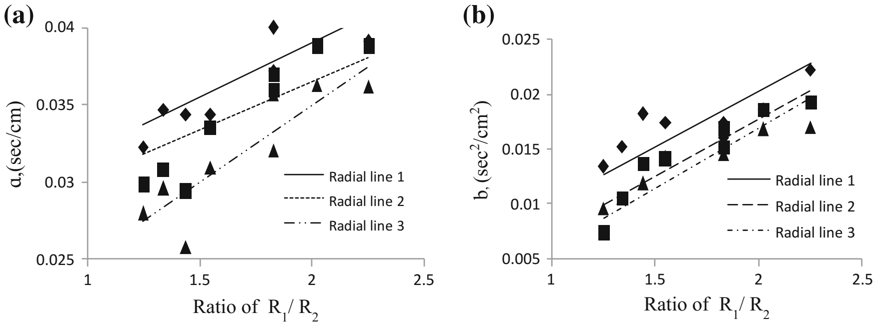

Fig. 3 **a** Variation of *a* with ratio of R_1/R_2 for different radial lines. **b** Variation of *b* with ratio of R_1/R_2 for different radial lines

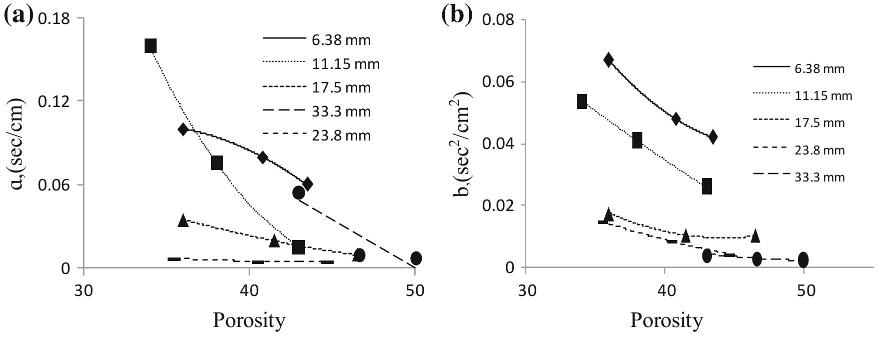

Fig. 4 **a** Variation of *a* with porosity for different media sizes. **b** Variation of *b* with porosity for different media sizes

Though the variation pattern of Darcy and non-Darcy coefficient is known for some field, media and fluid conditions, no proper relation exists between them due to complex variation pattern. As a result, it is extremely difficult to predict the value of those two coefficients in real-life situation. Some effort has been made to quantify all those effects (Engelund 1953; Ergun 1952; Blake 1923), but none of them can be stated as universal.

Applicability of Wilkins Equation

Wilkins equation is one of the many empirical equations that have appeared in the literature for non-Darcy flow through porous media. It is one of the main tools used in hydraulic design for rockfill dams. As it has already been stated, the Forchheimer equation (Eq. 2) contains two coefficients namely Darcy coefficient (a) and Non-Darcy coefficient (b). For convergent flows at larger velocities, the av term of Forchheimer equation can be neglected as the Darcian parameter a plays a relatively minor role in contributing to total friction loss (Kumar and Venkataraman 1995), so Eq. (2) reduced to a form:

$$i = bV^2 \tag{8}$$

This is similar to Eq. (6), so we can state that the Wilkins equation (Eq. 7) is a special form of Forchheimer equation with modified value of the non-Darcy coefficient (b).

The Wilkins equation contains hydraulic radius (r) and viscosity of the fluid (μ) as the media and fluid properties. For a certain fluid at a constant temperature and pressure, the viscosity will be constant so Eq. (7) becomes

$$V_v = C_1 r^{\beta} i^{\gamma} \tag{9}$$

where $C_1 = C\mu^{\alpha}$.

The values of C_1, β, γ proposed by Wilkins and other researchers are given in Table 1. The coefficient γ in the Wilkins equation can be stated as $1/j$. In Eq. (8), we have already seen the value of j varies from 1 to 2, γ varies from 1 to 0.5. The value of γ tends toward its minimum value of 0.5 when the voids are relatively large (r is large) as well as the flow velocity, and when voids are small as well as the flow velocity, the value of γ tends to its maximum value 1 (Garga et al. 1990). To be more specific, it can be stated in laminar flow the value of γ is 1, where it is 0.5 in case of fully developed turbulent flow. In between 0.5 and 1, the flow regimes go through a series of transition. The values of γ mentioned in the table represent partially developed turbulence, regardless the shape and size of the pores through which the fluid is flowing except the study of Kumar and Venkataraman (1995) for convergent flow through crushed stones of different diameter.

Table 1 Values of the coefficients of Wilkins equation as represented by various researchers

Proposed by	Type of the media	Size (mm)	Porosity (%)	Boundary condition	C_1 (m s)	β	γ
Wilkins (1955)	Crushed stone	51	40	Parallel flow	5.243	0.50	0.54
Garga et al. (1990)	Crushed stone	24.6	47	Parallel flow	5.39	0.50	0.532
Kumar and Venkataraman (1995)	Crushed stones	13.1	47.23	Convergent flow	26 (Unit not mentioned)	0.65	0.5
		20.1	48.99				
		28.9	46.16				
		47.3	47.58				
	Glass spheres	17	38.34	Convergent flow	43 (Unit not mentioned)	0.73	0.6
		20	39.36				
		30	37.59				

From Table 1, we can see the values suggested by Wilkins (1955), Garga et al. (1990) are almost similar, and the reason may be the experimental setup used by both the researchers are similar. Both the researchers used parallel column permeameter and used angular media. The table clarifies that if the field condition is same the coefficients of the Wilkins equation are not dependent on the size of the media; same conclusion can be drawn from the result obtained by Kumar and Venkataraman (1995). The experimental results on Wilkins equation also suggest that the coefficients especially the C_1 term is significantly sensitive to the variation in field condition as well as to the angularity of the media. Significant variation in the values of coefficients for the crushed rocks and glass spheres supports the statement.

Conclusion

Forchheimer and Wilkins equation are the two most used quadratic equation for the nonlinear flow through porous media. But if we closely observe at these equations we will see that the Forchheimer equation is studied and explored throughout the decades where the other one is mostly unexplored. This paper reviews applicability of Forchheimer and Wilkins equation. The study shows that though the Forchheimer equation can be applicable over all the flow regimes for nonlinear flows through porous media but the values of coefficients vary with the flow regimes and the variation pattern is not properly defined. The coefficients of this equation also vary with number of field and media condition, and the variation pattern is too complex as the field and media conditions vary simultaneously. On the other hand, the studies related to Wilkins equation are very limited but the available studies show that the coefficients of this equation are relatively constant for the size of media used and the porosity achieved may be due to the inclusion of two parameter named as hydraulic radius (r) and dynamic viscosity (μ) as the representative of media and fluid properties. Further studies can be done to find out and quantify the effect of some other field and media properties in order to consider its applicability in real-life applications for nonlinear flow.

References

Abbood W (2009) An experimental model for flow through porous media using water filter. In: Thirteenth international water technology conference, Hurghada, Egypt, 2009

Ahmed N, Sunada DK (1969) Nonlinear flow in porous media. J Hydraul Div Proc ASCE 95 (6):1847–1858

Barr DW (2001) Turbulent flow through porous media. Ground Water 39(5):646–650

Basak P (1977) Non-Darcy flow and its implications to seepage problems. J Irrig Drain Div 103 (4):459–473

Blake F (1923) The resistance of packing to fluid flow. Trans Am Soc Chem Eng 14:415–522

Burcharth HF, Andersen OK (1995) On the one-dimensional steady and unsteady porous flow equations. Coast Eng 24(3):233–257

Burcharth F, Christensen C (1991) On stationary and non-stationary porous flow in coarse granular materials. In: MAST G6-S report, Dept. of Civil Engineering. Aalborg University, Aalborg

Carman PC (1937) Fluid flow through granular beds. Trans Inst Chem Eng 15:150–166

Chhabra RP, Jacques C, Machač I (2001) Flow of non-newtonian fluids in fixed and fluidised beds. Chem Eng Sci 56(1):1–27

Du Plessis P, Masliyah J (1988) Mathematical modelling of flow through consolidated isotropic porous media. Transp Porous Media 3(2):145–161

Dybbs A, Edwards R (1984) A new look at porous media fluid mechanics—Darcy to turbulent. In: Bear J, Corapcioglu Y (eds) Fundamentals of transport phenomena in porous media. Springer, Netherlands, pp 199–256

Engelund F (1953) On the laminar and turbulent flows of ground water through homogeneous sand. Akad. for de Tekniske Videnskaber, Danmark

Ergun S (1952) Fluid flow through packed columns. Chem Eng Progress 48:89–94

Fand RM, Kim BYK, Lam ACC, Phan RT (1987) Resistance to the flow of fluids through simple and complex porous media whose matrices are composed of randomly packed spheres. J Fluid Eng ASME 109(3):268–274

Garga VK, Hansen D, Townsend RD (1990) Considerations on the design of flow through rockfill drains. In: Proceedings of the 14th Annual British Columbia Mine Reclamation Symposium, Cranbrook, 1990

Hall KR, Smith GM, Turcke DJ (1995) Comparison of oscillatory and stationary flow through porous media. Coastal Eng 24(3):217–232

Hassanizadeh M, Gray WG (1980) General conservation equations for multi-phase systems: 3. Constitutive theory for porous media flow. Adv Water Resour 3(1):25–40

Hassanizadeh SM, Gray WG (1987) High velocity flow in porous media. Transp Porous Media 2 (6):521–531

Holditch SA, Morse RA (1976) The effects of non-Darcy flow on the behavior of hydraulically fractured gas wells. J Pet Technol 28(10):1169–1179

Horton NA, Pokrajac D (2009) Onset of turbulence in a regular porous medium: an experimental study. Phys Fluids 21(4):045104(1)–045104(13)

Huang H, Ayoub A (2008) Applicability of the Forchheimer equation for non-Darcy flow in porous media. SPE J 13(01):112–122

Irmay S (1958) On the theoretical derivation of Darcy and Forchheimer formulas. Trans Am Geophys Union 39(4):702–707

Krishna R, Murthy S (2013) An experimental study on flow of water through porous media in laminar, transition and turbulent regime. Int J Emerg Technol Adv Eng 3(4):559–569

Kumar GNP, Venkataraman P (1995) Non-Darcy converging flow through coarse granular media. J Inst Eng (India): Civ Eng Div 76(5):6–11

Kumar GNP, Thiruvengadam T, Murali M (2004) A further study on Forchheimer coefficients as applied seepage flow. ISH J Hydraul Eng 10(2):1–13

Lage J, Antohe BV, Nield DA (1997) Two types of nonlinear pressure-drop versus flow-rate relation observed for saturated porous media. J Fluids Eng ASME 119(3):700–706

Martins JP, Milton-Tayler D, Leung HK (1990) The effects of non-Darcy flow in propped hydraulic fractures. In: Proceedings of the SPE annual technical conference, New Orleans, Louisiana, USA, 1990. Society of Petroleum Engineers

Nasser MSS (1970) Radial non-linear flow through porous media. Master of Applied Science thesis. University of Windsor, Windsor, Canada

Niranjan HS (1973) Non-Darcy flow through porous media. Master of technology thesis

Reddy BNP (2005) An experimental study on the effect of converging boundary on flow through porous media. ISH J Hydraul Eng 11(2):73–89

Reddy BNP, Rao RM (2004) Convergence effect on the flow resistance in porous media. IE (I) J 85:36–43

Reddy BNP, Rao RM (2006) Effect of convergence on nonlinear flow in porous media. J Hydraul Eng 132(4):420–427

Reddy BNP, Reddy MR (2007) Efficiency of steady non-uniform flow through homogeneous porous media. ISH J Hydraul Eng 13(2):53–65

Reddy BNP, Reddy MRK (2010) Energy loss in the flowing fluid through porous media with convergent boundaries. J Indian Water Resour Soc 30(3):30–36

Reddy BNP, Krishnaiah S, Reddy MR (2014) Convergent angle effect on non-uniform flow through porous media. J Inf Knowl Res Civ Eng 3(1):152–159

Scheidegger AE (1960) The physics of flow through porous media. University of Toronto Press, Toronto

Skjetne E, Auriault J-L (1999) High-velocity laminar and turbulent flow in porous media. Transp Porous Media 36(2):131–147

Srinivas P, Kumar GNP, Jayachndra K (2014) Quantification of effect of convergence in porous media flow. In: 5th international conference on porous media and their applications in science, engineering and industry, Hawaii, 2014

Subramanya K, Madav M (1978) Linear and non-linear flow through porous media. Technical Report 22, submitted to central board of irrigation and power

Tek MR (1957) Development of a generalized Darcy equation. J Pet Technol 9(06):45–47

Thiruvengadam M, Kumar G (1997) Validity of Forchheimer equation in radial flow through coarse granular media. J Eng Mech 123(7):696–705

Van Gent MRA (1995) Porous flow through rubble-mound material. J Waterw Port Coast Ocean Eng 121(3):176–181

Venkataraman P, Rao PRM (2000) Validation of Forchheimer's law for flow through porous media with converging boundaries. J Hydraul Eng 126(1):63–71

Whitaker S (1969) Advances in theory of fluid motion in porous media. Ind Eng Chem 61(12): 14–28

Whitaker S (1996) The Forchheimer equation: a theoretical development. Transp Porous Media 25 (1):27–61

Wilkins JK (1955) Flow of water through rockfill and its application to the design of dams. New Zealand Eng 10(11):382–387

Williams A, Burcharth H, Den Adel H (1992) The permeability of rubble mound breakwaters. New measurements and new ideas. Coast Eng Proc 23(1):1720–1733

Numerical Modeling and Design of a Fishery Port Near Ezhimala Promontory

T. P. Dhanya and Kiran G. Shirlal

Abstract MIKE 21 BW is the state-of-the-art numerical modeling tool for studies and analysis of wave disturbance in ports, harbors, and coastal areas. MIKE 21 BW has been used successfully for the analysis of operational and design conditions within the port. For development of a port, it is of vital importance to consider the environmental conditions prevailing at the site of development. Proposed fishing harbor is at Puthiyangadi in Madayi Panchayath of Kannur District in Kerala. The current study addresses the modeling of two port layout through the use of Boussinesq wave model and selection of best layout and hence the breakwater design.

Introduction

Proposed fishing harbor at Puthiyangadi in Madayi Panchayath of Kannur District in Kerala is to the immediate south of Ezhimala Promontory. The new fishing harbor is proposed toward the west of existing fish landing center at Puthiyangadi. Considerable fishery activities are already present at this region. About 100 mechanized boats, 50 inboard vessels, and 150 OBM vessels (Harbor Engineering Department-August 2015) are currently utilizing the limited facilities available in the port. The layout of the breakwater to form the basin can only be arrived via proper model studies. Different methods are used to study shoreline changes in the coastal area. Among them, mathematical modeling is considered as an effective technique. (Santosh et al. 2015). MIKE 21 BW is the state-of-the-art numerical modeling tool for studies and analysis of wave disturbance in ports, harbors, and coastal areas. MIKE 21 BW has been used successfully for the analysis of operational and design conditions within the port and harbor. By the inclusion of surf and

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swash zone dynamics, the application range is extended further into coastal engineering. MIKE 21 BW is capable of reproducing the combined effects of all important wave phenomena of interest in port, harbor, and coastal engineering.

Objectives

The objective of the present study is to carry out numerical modeling using MIKE 21 BW model for the development of port near Ezhimala Promontory along with the design of breakwater.

Project Location

Proposed fishing harbor at Puthiyangadi in Madayi Panchayath District is to the immediate south of Ezhimala Promontory is shown in Fig. 1.

This promontory juts out into the sea for a distance of about 3.6 km from the shoreline and consists of rock cliffs of about 10–20 m height along the coastline. The new fishing harbor is proposed toward the west of the existing fish landing center at Puthiyangadi. This is an open beach, and beach landing is resorted to land

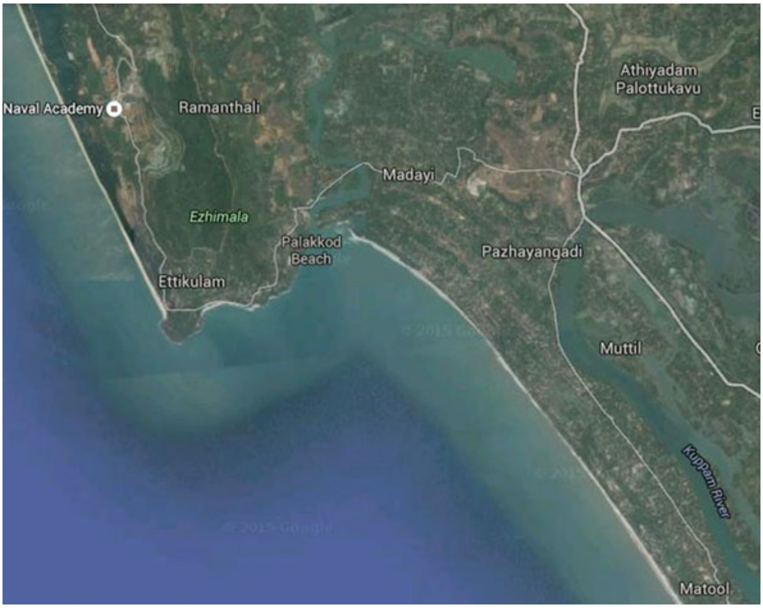

Fig. 1 Project location

the fish catch here. This area is about 1.5 km from the river mouth along the coastline toward the south. The least width of river just upstream of the river mouth is 74 m. The width of the river is less than 100 m for a length of about 300 m upstream of the river mouth. Since there is a bottle neck of less than 100 m width for a long stretch of 300 m near the river mouth, it will be dangerous and difficult to have mechanized fishing crafts navigate through this area, if a full-fledged harbor is made inside the river. This is another reason why the location of the harbor is chosen on the open sea coast near the existing FLC at Puthiyangadi (Harbor Engineering Department-August 2015).

Design of Fishery Port

The methodology adopted for the modeling of fishery port using Boussinesq model is given below.

MIKE 21 BW—Boussinesq Model

MIKE 21 BW is the state-of-the-art numerical modeling tool for studies and analysis of wave disturbance in ports, harbors, and coastal areas. MIKE 21 BW has been used successfully for the analysis of operational and design conditions within the port and harbor. By the inclusion of surf and swash zone dynamics, the application range is extended further into coastal engineering.

MIKE 21 BW is capable of reproducing the combined effects of all important wave phenomena of interest in port.

Bathymetry

Providing MIKE21 BW with suitable model bathymetry is essential for obtaining reliable result. Setting up the bathymetry requires more than specifying a 2D array of accurate water depth covering the area of interest. It also includes the appropriate selection of area to be modeled, the grid spacing, location and type of boundaries, etc. We are interested in determining the wave disturbance conditions in Puthiyangadi for the following offshore conditions (at 8 m depth CD):

Significant wave height, $H_{m0} = 3$ m
Spectral peak wave period $T_p = 8$ s

The data have been collected from the port and are shown in Fig. 2, and using this data the bathymetry has been prepared and is shown in Fig. 3.

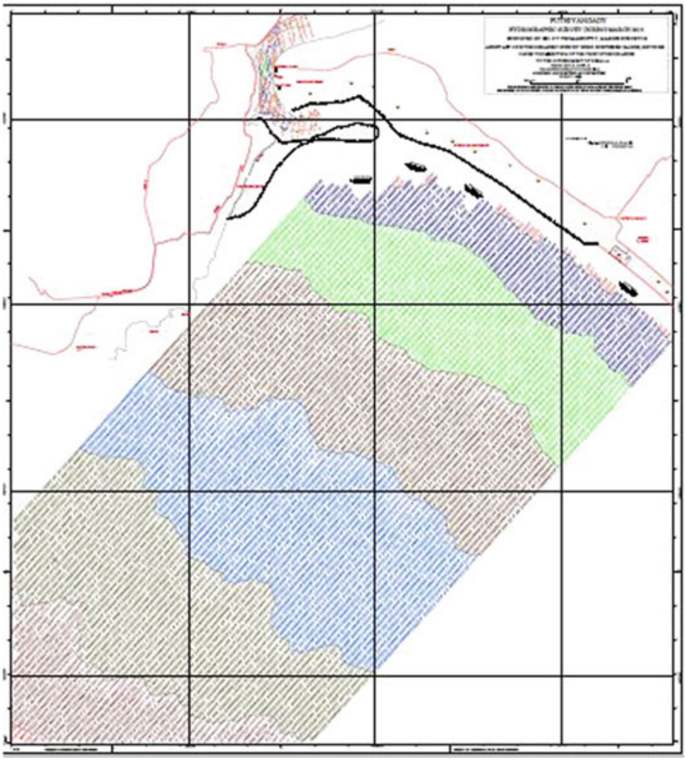

Fig. 2 Data obtained from the port

Sponge Layer

Sponge layer is providing for absorbing wave which is reflecting back to the offshore. In the present case, we will apply sponge layer along 3 offshore part of the model domain. Therefore, the land value at the shoreline has been changed from 10 to 5 along a section where sponge layer is needed, as shown in Fig. 4.

Porosity Layer Map

A porosity layer map is used to model either partial reflection or transmission through various types of structures. If porosity values are backed up by land, partial reflection will take place. The typical procedures to change the bathymetry value from the initial land value to another value that is 8 along all structures having partial reflective properties are shown in Fig. 5.

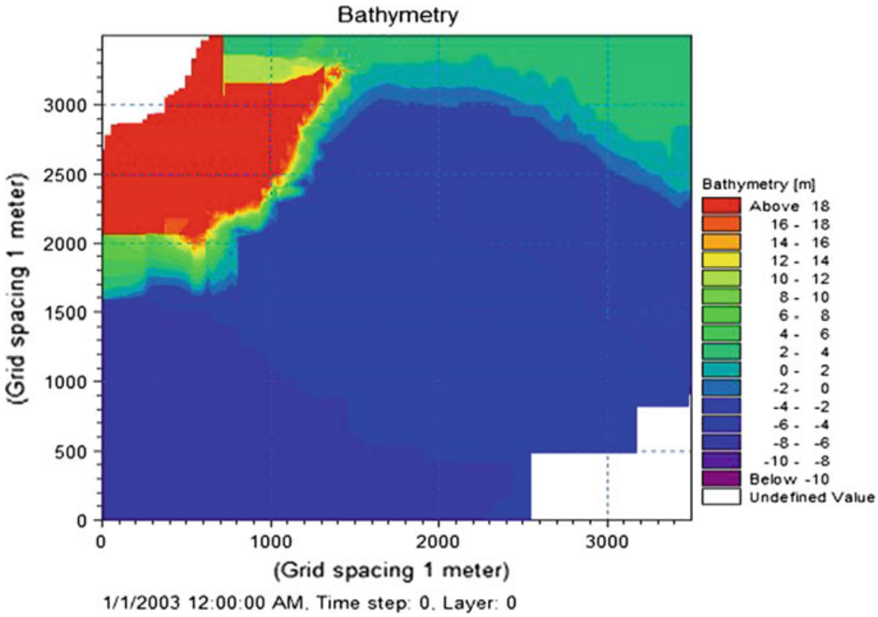

Fig. 3 Bathymetry

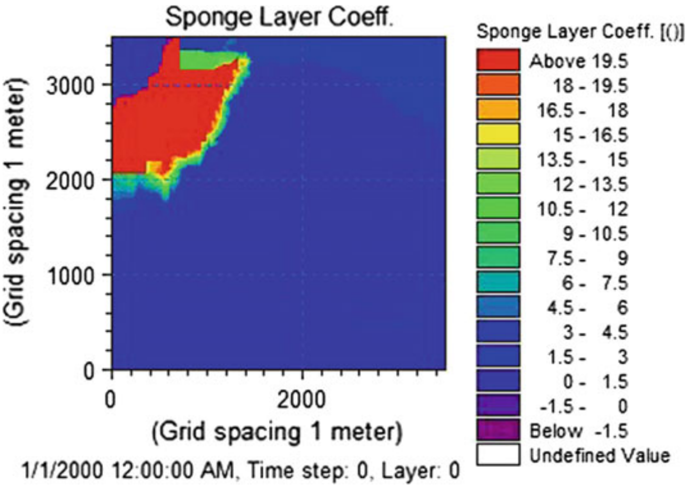

Fig. 4 Sponge layer

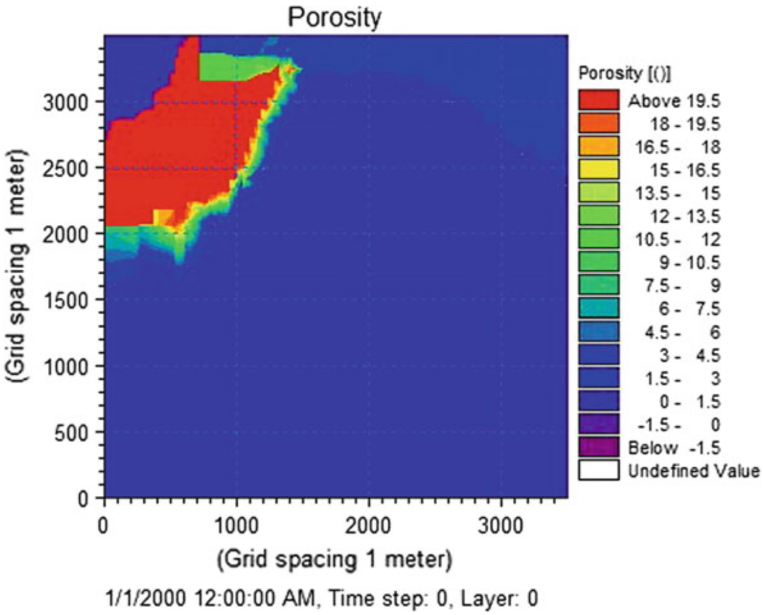

Fig. 5 Porosity layer map

Internal Wave Generation Data

The offshore waves are specified as internal wave generations of the incident wave field along a specified generation line. The advantage of using internal generation is that sponge layers can be placed behind the generation line to absorb waves leaving the generation domain as shown in Fig. 6.

Alternative Port Layout

Considering all the requirements and preliminary technical details of the site, two suggestions have been proposed.

Suggestion-1

The main breakwater PQRST starts from the beach at 500 m north of the existing fish landing center and follows the streamlined path in such a way that deposition of sediments inside the basin near the curved portion is minimized since the direction of the sediment movement is from the river and along the coastline. So the main

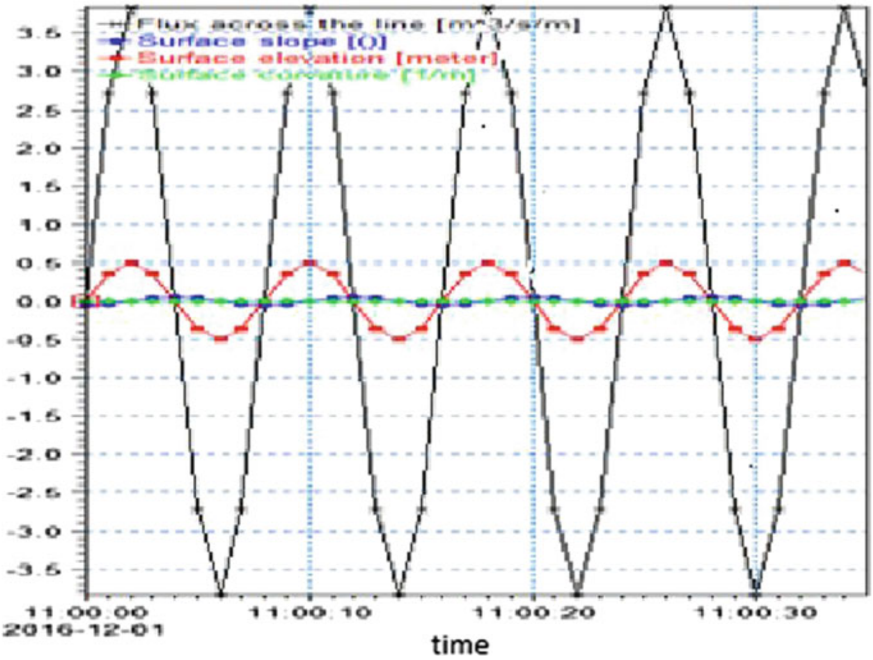

Fig. 6 Internal wave generation data

breakwater PQRST prevents the accumulation of sediment inside the breakwater. It has a total length of 870 m, and the head reaches up to 4 m depth from CD. The harbor entrance is 100 m wide. The leeward breakwater is 375 m long. The harbor basin is 500 m wide at the land side and has a total area of 14 ha. It is shown in Fig. 7.

Suggestion-2

The second breakwater is also proposed by considering the movement of sediment so that it prevents the accumulation of sediment inside the breakwater. The main breakwater AB and CD starts from the beach at 500 m north of the existing fish landing center. It has a total length of 600 m, and the head reaches up to 4 m depth from CD. The harbor entrance is 100 m wide. The harbor basin is 500 m wide at the land side. It is shown in Fig. 8.

Considering all the analysis undertaken by inputting bathymetry, sponge layer, porosity layer map, internal wave generation data in MIKE 21 BW, it is concluded that suggestion 1 layout is the best layout.

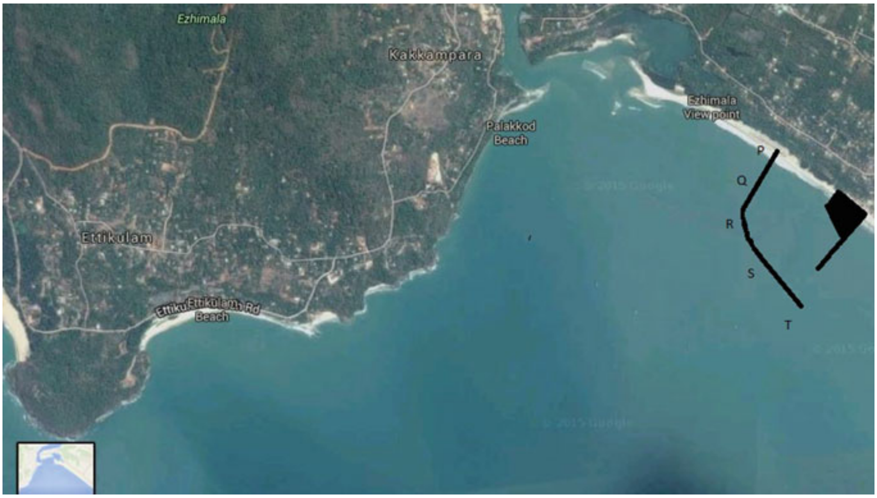

Fig. 7 Breakwater layout—suggestion 1

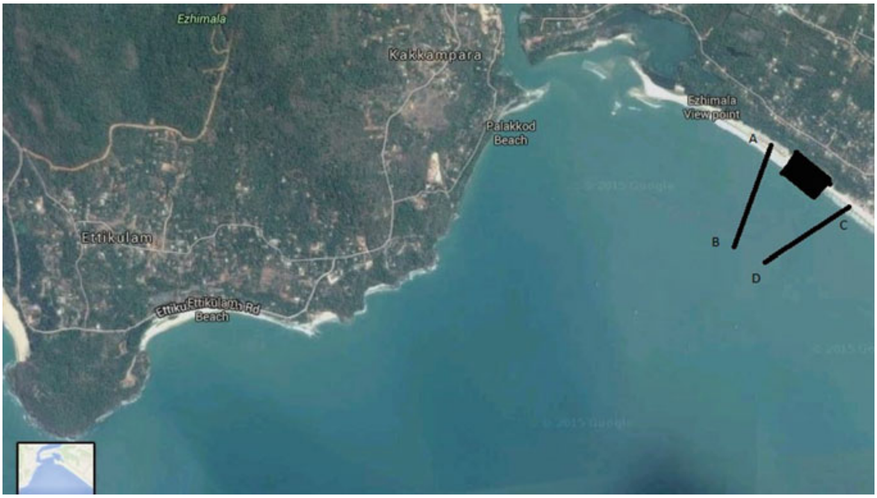

Fig. 8 Breakwater layout—suggestion 2

Recommendation

Preliminary studies undertaken and based on that two port layouts have been suggested. In order to select the best layout, numerical modeling/physical modeling is required. Numerical modeling has been undertaken, and it is obtained that layout 2 is the best layout. It has been determined that equivalent cube size of the armor unit of the breakwater is 1.002 m and the mass is 2.66 T.

References

Harbor Engineering Department Suggestion for breakwater alignment-August (2015)
MIKE 21 Software Boussinesq wave module step-by-step training guide
MIKE 21Software BW Boussinesq Wave Module user guide
MIKE 21Software Boussinesq wave module scientific documentation
Santosh et al (2015) Design of fishing harbour layout in high littoral drift zone. Procedia Eng 116 (2015):320

Part II
Solid Waste Management

Management of Urban Solid Waste in Shimla—A Case Study

Zuneid Brar

Abstract Urban India is facing huge challenges for coping with the infrastructural requirements of the ever-increasing population. As per the Census 2011, the population of India was 1.21 billion, of which 31% live in cities. The management of municipal solid waste remains a major infrastructure requirement that needs to be improved although in recent years the management of municipal solid waste has been a major environmental issue in all urban areas of our country. Improper and inadequate management of municipal waste causes adverse effects on environment, such as air, water and land pollution along with global warming. Estimation on the quantity and the characteristics of municipal solid waste and its forecasting over the planning period is the key to a successful solid waste management plan. The increase in urbanization and growth in population have revealed the need for sustainable development, and developing innovative solutions to these existing problems and effective management of municipal solid waste is one of them. In this paper, a case study of Shimla in Himachal Pradesh is carried out to know about its existing solid waste management system. The study reveals that the amount of municipal solid waste generated by Shimla is approximately 9.30 MT. This depicts that waste generation per capita per day is 350 gm/capita/day in the city. The waste generated is disposed of unscientifically in open dumps, and also open incineration is carried out, which causes problem to public health and environment. The study includes the parameters of waste management beginning from the sources, collection, transportation and final disposal.

Introduction

The term solid waste comprises the waste material that is neither in liquid nor in gaseous state. Major categories of wastes included in the term solid waste are municipal solid waste, agricultural wastes, industrial wastes, ash from thermal

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power plants and hazardous waste. Waste of any kind is the outcome of human activities. Management of solid wastes is a major challenge these days for the administrators, engineers and planners. Huge volumes of wastes are generated and need to be collected, transported and finally disposed of. These operations have to be carried out speedily and efficiently without incurring excessive cost or damage to the environment.

Solid waste dumping poses a great threat because it leads to problems of land pollution if openly dumped, water pollution if dumped in low lands, and air pollution if burnt. An integrated management of solid waste approach must be followed. In many developing countries, the system for managing waste is primitive and cannot cope with huge volumes of wastes being generated. It is a common site to find large heaps of garbage festering all over cities these days. The problem gets further complicated due to large population and obsolete techniques employed for waste management. Insanitary methods adopted for disposal of solid wastes is a serious health concern. Techniques and technologies, however, are available, and indigenous methods can be developed for managing these wastes properly. In view of this government of India has launched various initiatives through Ministry of Urban Development for ensuring effective solid waste management at Urban Local Body (ULB) level. In order to streamline the municipal solid waste management system, the MoEF formulated the Municipal Solid Waste (Management and Handling) Rules (2000). Also, an elaborate tool for implementation of these rules was prepared by the MoUD in the form of Municipal Solid Waste Manual in 2000. Despite huge investments and the encouragement of the Central Government to invest in and adapt to the MSW (M&H) Rules, 2000, improvement in this sector is slow.

The integrated municipal solid waste management includes basic activities like generation, collection, transfer and transport, separation and recycling, and disposal that are essential components of any efficient system (Fig. 1).

The purpose of the work is to investigate the current status and forthcoming challenges of solid waste management in Shimla city. Shimla was examined for its solid waste management system. Shimla is often addressed as the “queen of hills”.

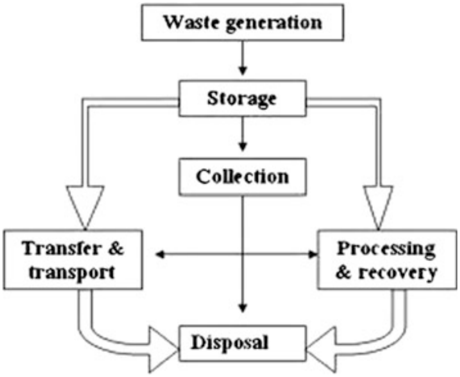

Fig. 1 Integrated solid waste management

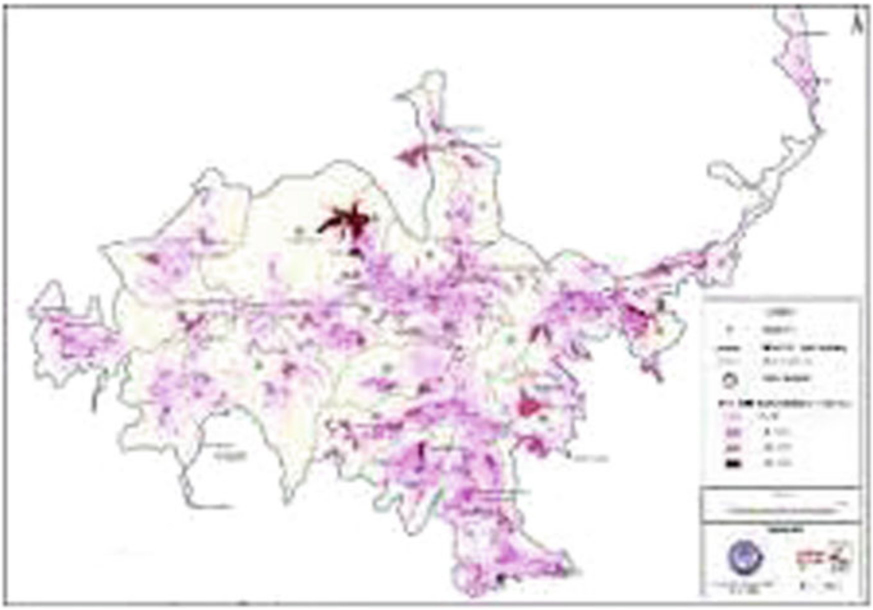

Fig. 2 City plan of Shimla

Shimla has a population of 171,817. Shimla is situated in the Central Himalayas at 31° 4′–31° 10′N latitude and 77° 5′–77° 15′E longitude. Discovered in 1819 by the British, Shimla has evolved from a small hill settlement to one of the popular tourist destinations in India. Part of Himachal Pradesh was carved out of the erstwhile Punjab state in 1966, and Shimla became the capital of newly formed state of Himachal Pradesh in 1971. The topography of Shimla is characterized by rugged mountains, steep slopes and deep valleys. Shimla is located at an altitude of 2130 m above mean sea level. It experiences cold winters during December–February, with temperatures ranging from 0 to 13 °C.

The total area under the jurisdiction of MC Shimla also has increased after merger of New Shimla, Totu (including some parts of Jutogh) and Dhalli areas to 35.00 km^2. At present, Municipal Corporation of Shimla (MCS) is divided into 25 wards covering urban core and urban peripheries. Figure 2 shows the plan of the city Shimla.

Municipal Solid Waste

The term municipal solid waste defines most of the non-hazardous solid waste from the city, town or village that requires routine or periodic collection and transportation to disposal site. Municipal solid waste comprises of main two terms: trash and refuse. Refuse includes garbage and rubbish. The former includes the decomposable materials and latter non-putrescible matter such as paper, glass, metal, cans. Trash includes bulky waste materials which require special handling. There are many categories of municipal solid waste, such as food waste, rubbish, commercial waste, institutional waste, street sweeping waste, industrial waste, construction and demolition waste. Municipal solid waste management refers to the public service of handling municipal solid waste via collection and subsequent transfer, treatment, disposal and recycling. Waste generation rate in Indian cities ranges between 200 and 870 grams/day (Rana et al. 2014). The per capita waste generation in urban India is about 0.5 kg/day (Das 2005). Integrated solid waste management is the mantra for the good practice in solid waste management. The environmental degradation as well as health impact of people caused by inadequate disposal of the waste can be expressed in terms of the contamination of surface and ground water through direct waste contacts or leachate.

Waste Generation

The physical composition of waste of Shimla is obtained as a percentage of different constituents and is given in Table 1 (Personal communication with the employee of the dumping site, management of urban solid waste of Shimla, a second high-level seminar). It was found that a major fraction of urban municipal solid waste in Shimla consists of organic matter in a higher content, recyclables and inert waste. The daily waste generation in Shimla city is approximately 93.0 MT. This depicts that waste generation per capita per day is 350 gm/capita/day in the city. The moisture content ranges from 40 to 70% (Sharholy et al. 2007). The actual percentage of recyclables discarded as waste is unknown due to informal picking of waste which is generally not accounted. Some of the future challenges for the management of solid waste are increasing quantities and changing composition, increasing severity of adverse impacts increasing the cost of waste management,

Table 1 Composition of municipal solid waste in Shimla

S. No.	Components	Percentage (%)
1	Metal	1.02
2	Glass/ceramics	3.70
3	Food and carbon waste	29.0
4	Paper and cardboard	18.10
5	Textile	6.80
6	Plastic	14.50
7	Rubber/leather	5.80
8	Inert	11.40
9	Misc. combustible	4.80
10	Misc. non-combustible	12.0

limited policy framework and lack of political priority. The quantity of municipal solid waste generated depends upon a number of factors such as food habits, standard of living, degree of commercial activities and seasons. With increasing urbanization and changing lifestyles, Indian cities generate eight times more waste than they did in 1947 (Kumar and Goel 2009). Presently, about 90 million tons of solid waste is generated annually as by-products of industrial, mining, municipal, agricultural and other processes. The composition and quantity of solid waste generated form the basis on which the management system needs to be planned, designed and operated.

Waste Collection and Storage

Waste collection and storage are the main functional elements of solid waste system. Shimla lacks a proper storage system for waste. The collection of waste is done in haphazard manner although various attempts were made by MC Shimla to effectively implement door-to-door garbage collection since the formulation of Door to Door Garbage Collection Bye-laws in 2006. Shimla Environment, Heritage Conservation and Beautification (SEHB) Society was registered in 2009 under the Himachal Pradesh Societies Registration Act 2006. This society is responsible for the door-to-door collection from households under the supervision of Commissioner (President) and Corporation Health Officer (Member Secretary). The society has provided two colored bins—yellow and green to households/commercial establishments/institutions, etc., for primary storage and segregation of garbage. The yellow bin is for non-biodegradable waste, and green bin is for biodegradable waste storage within the establishments.

The waste-collecting bins or containers are placed at places nearby to the residential and commercial areas. People dispose of their waste into these containers. The residents are found to throw waste outside these bins, which creates havoc and unsanitary conditions around the area. The Municipal Corporation of the Shimla should make provision for more suitable door-to-door waste collection services, and bins should be placed at more places so as to avoid any unsanitary and unhealthy conditions. Waste is littered on the roads as well as streets, which is not only spoiling the aesthetic beauty of the place, but also degrading the environment. Due to the less availability of the bins people are throwing waste outside the overflowing bins. The Municipal Corporation of Shimla has collaborated with the many private companies for increasing the efficiency of collection of waste and majorly paying attention toward door-to-door collection of municipal solid waste. With the augmentation of doorstep collection services, the Municipal Corporation of Shimla could achieve making of container-free areas by reducing more containers and compact buckets. Similarly, storage of municipal solid waste at the source is substantially lacking in Shimla. The bins provided for the collection of the waste are common bins, and there is no segregation of the waste. A fraction of the municipal solid waste generated remains uncollected on streets. Many studies on urban environment have revealed that the municipal solid waste collection efficiency is a function of two major factors, i.e., manpower availability and transport capacity (Kumar and Goel 2009; Sharholy et al. 2007). Both of these major factors are found lacking in the municipal solid waste system of the Shimla.

Waste Transportation

Removal of garbage is a very important aspect of solid waste management, and method of transportation is vital. Transportation implies conveyance from point of collection to the point of final disposal either directly or through the transfer system. The municipal solid waste collected from the dustbins is transported to the disposal site. In Shimla, waste is collected from the bins placed at the nearby places and then transported to the disposal site. Transportation of waste from the collection points to the treatment plant and landfill is the operated and managed by Municipal Corporation of Shimla. The entire city's waste is collected and transported through 40 different vehicles with varying capacities. For transportation purposes the Municipal Corporation of Shimla has collaborated with a few private agencies for providing the vehicles. These vehicles are called tippers, Pick-Ups (hydraulic), Pick-Ups (non-hydraulic inspection vehicle), Compactors, which vary in sizes. The trucks used for transportation of municipal solid waste are generally of open body type and usually kept uncovered; thus, during transportation the waste tends to spill on the road, resulting in unhygienic conditions.

Transfer stations are not used yet, and the same vehicle which collects the refuse from the dustbins takes it to the disposal site. Due to the lack of land availability the Shimla Municipal Corporation is unable to set up a separate transfer station system for segregating the waste. With the upcoming concern on proper and integrated solid waste management, the ward-level routing and loading plan has been developed by Municipal Corporation of Shimla with the help of The Deutsche Gesellschaft fur Internationale Zusammenarbeit (GIZ). The ward-level route and waste collection points are plotted at the ward-level map. Municipal Corporation of Shimla also plans to set up a waste transfer station at Darni ka Bagicha where a discharge treatment facility was in operation earlier (Bharti et al. 2014). This transfer station will also support the optimization of the routing and loading activities of the city. The waste from northeastern and centrally located wards collected by smaller Pick-Ups can be transferred in the Compactors, transfer containers and transported to the new commissioned treatment plant. Municipal Corporation of Shimla also proposes to install the chute systems for directly putting up the waste in collection vehicle in inaccessible areas.

One more factor that adds up to the worst conditions is the unawareness among the common people as well as the authorities. Collection and transportation activities constitute approximately 80–95% of the total budget of the municipal solid waste management; hence, it forms a key component in determining the economics of the entire municipal solid waste management system (Rana et al. 2014; Singh et al. 2014).

Waste Processing

Processing of waste helps in achieving the best possible benefit from the every functional element of the solid waste management. Processing involves a system for recycling and waste recovery processes. No such efforts are being made in the Shimla by the municipal corporation. The waste coming is of mixed form, and no segregation or recycling facility is being provided. The segregation of waste at source and promotion of recycling or reuse of segregated materials reduce the quantity of waste and burden on landfills and also provide raw materials for manufacturers (Bharti et al. 2014). The Municipal Corporation of Shimla also plans to set up a recycling unit and a waste segregation center in the coming future so as to lessen the burden of waste going to the landfill. Treatability for the processing of solid waste depends on the physico-chemical characteristics of the waste. Due to nutrient value of organic matter, percentage of biodegradable component in municipal solid waste is the most important influencing factor in treatability.

Waste Disposal

Disposal is the final element in the solid waste management, i.e., it is the ultimate fate of all solid waste. Disposal is the most important element as it includes planning, administrative setup, finance, technology support and their interdisciplinary relationships. Disposal is referred to as the different treatments which are given to the waste for avoiding environmental and health hazards. Success of solid waste management system is directly related to disposal efficiency. It is decided upon how much of the total dumped waste is finally disposed properly. To dispose waste in an efficient way, technical knowledge, trained manpower, appropriate infrastructure and availability of land are required.

In Shimla, the major disposal site is at Darni ka Bagicha. It is an open dump, but funds have been available for the implementation of secured landfill adjoining the treatment plant from the Ministry of Urban Development in 2012. The stipulated time for the construction and operation of the sanitary landfill is estimated as two years. The engineered disposal facility is proposed to be developed on Public–Private Partnership (PPP) model. The scientific disposal of the municipal waste will mitigate the environmental hazards associated with open dumping. Figure 3 shows the dumping site. The site receives waste from the Municipal Corporation of Shimla's waste haulers, which receive waste from the private haulers. The municipal solid waste coming to the dump is disposed of without giving any prior treatment which causes severe environmental and health risks. The progress in

Fig. 3 Dumping site at Shimla

moving toward sanitary landfills and/or disposing through well-designed and well-operated incinerators is rather slow mixed comes to the site which is then dumped in the site as it is without giving any treatment. Compost formation was done for only a year, but with no proper sale and loss to the corporation it was stopped. It is a non-engineered site where no prior efforts have been made to ensure environmental protection.

Current Practices

The Municipal Corporation of Shimla is taking steps to convert the open dumping site into the sanitary landfill with specifications given in Schedule 3 of Municipal Solid Waste Management and Handling Rules, 2000. Efforts have been made to cap the area of the landfill. Apart from this the leachate treatment and gas extraction plants and monitoring wells are also planned.

Conclusions and Recommendations

Waste management should not merely revolve around collection, transportation and disposal of waste once it is generated and even segregated. In fact, the need of the hour is sustainable waste management reducing the waste and controlling the products that create undesirable waste. In India, the product goes to the user and the user generates waste is the basic model. The municipality collects and landfills it, recycles or burns it, thus destroying the precious natural resources. The segregation of waste at source and promotion of recycling or reuse of segregated materials reduce the quantity of waste and burden on landfills and provide raw materials for manufacturers. The composition of waste shows mainly organic matter, so composting can be a good method for treatment and production of soil amendment. The rapid increase in the quantities of municipal solid waste and inability to provide daily collection services may cause a nuisance and health hazards. In Shimla Municipal Corporation such situations arise frequently due to inefficient and non-scientific municipal solid waste practices implemented. There should be proper liner systems installed at the site with the facility of leachate and gas collection. The decentralized biogas plants based on solid waste will be the ideal solution. It will also help to generate electricity which will be an additional advantage. Public awareness should be created among masses to inculcate the health hazards of the wastes. Littering of municipal solid waste should be prohibited. Moreover, house-to-house collection of municipal solid waste should be organized through methods like collection on regular pre-informed timing and scheduling.

Presently, in Shimla, at the level of waste generation and collection, there is no segregation at the source of the compostable matter from the other non-biodegradable and recyclable wastes. Proper segregation would lead to better options and opportunities for scientific disposal of waste. Recyclable units must be set up so that the recyclable waste could be transported directly to them which would in turn pay a certain amount to the corporation's adding to their income. As an academic awareness is our responsibility to make people aware about society's problem. Thus, to make this a success, it is essential that the waste producers should cooperate and effectively participate in the waste management efforts of the Shimla Municipal Corporation.

Finally, the study concludes that the lack of resources such as financing, infrastructure, suitable planning and data, and leadership are the main barriers in municipal solid waste management of Shimla. The increases of service demand combined with the lack of resources for municipality are putting a huge pressure on the existing municipal solid waste management system in Shimla.

References

Bharti O, Singh A, Singh DP, Sood V (2014) Effective solid waste management practises: a case study in Shimla. Waste management and resources utilization

Census (2011) Available at: http://www.census2011.co.in/facts/topstaterural.html

Das RR (2005) Concepts of environmental science. Paragon International Publishers, New Delhi

Kumar KN, Goel S (2009) Characterisation of municipal solid waste and a proposed management plan for Kharagpur, West Bengal, India. Resour Conserv Recycl 53:166–174

Rana R, Ganguly Rajiv AKG (2014) Solid waste management in Chandigarh—a case study. J Civ Eng Environ Technol 1(4):67–70

Sharholy M, Ahmad K, Mahmood G, Trivedi RC (2007) Municipal solid waste management in Indian cities—a review. Waste Manag 28:459–467

Singh RP, Yadav D, Sohail A, Siddiqui AA (2014) Status and challenges in solid waste management: a case study of Aligarh city. 1(4):19–24

The Municipal Solid Waste (Management and Handling) Rules (2000) Available at: www.envfor.nic.in/legis/hsm/mswmhr.html

New Trends for Wastewater Treatment and Their Reuse Using Ceramic Membrane Technology: A Case Study

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Abstract Membrane bioreactor (MBR) process employs conventional activated sludge process and membrane filtration providing greater treatment efficiency in terms of reduction of organic matter, suspended solids and pathogens. MBR process is widely being used for the treatment of municipal wastewater, water recycling in buildings, treatment of wastewater in small communities, treatment of wastewater, etc. An attempt has been made for the treatment of kitchen-sink wastewater (KSW) using indigenously developed ceramic membrane-based pilot

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scale membrane bioreactor from a low-cost composition of α-alumina and clay. Tubular single-channel and multichannel ceramic microfiltration membranes have been used in the cross-flow mode for the treatment of the wastewater. The porous ceramic membranes have an excellent chemical, mechanical and thermal resistance property. These membranes have been successfully used in our laboratory for separation of iron and arsenic from contaminated ground water. In the present study, separation efficiency of the ceramic membranes has been evaluated alone and in combination with biological pretreatment. Performance of the separation process has been studied in terms of the permeate quality and permeate flux. Considerable reduction in COD, BOD and suspended solids has been observed by suitable process design and controlling the process parameters. The efficiency can be further enhanced to a great extent so that CSIR-CGCRI-developed low-cost ceramic membrane could be an affordable technology.

Introduction

Membrane bioreactor technology has become a promising technique for wastewater treatment employing the use of activated sludge and membrane separation. Membrane bioreactor process is advantageous over conventional activated sludge process, resulting in stable and high effluent quality (Tolkou et al. 2014). Some of the conventional treatment technologies include biological oxidation (Lina and Ahmad 2006), chemical coagulation (Kim et al. 2009; Mo et al. 2007; Kumar et al. 2009) and adsorption (Laasri et al. 2007; Wang and Zhu 2005). Visvanathan et al. (2000) have studied the membrane bioreactor in aerobic and anaerobic modes for wastewater treatment. Treatment of municipal wastewater using membrane bioreactor resulted in 95% reduction in organic loading and 90% removal of ammonia (Gupta et al. 2008). But membrane fouling, lower sustainability in high pH, high pressure, short durability, etc., of polymeric membranes limit the use of membrane bioreactors.

In this regard, ceramic membranes having a greater chemical and thermal stability and a greater shelf life seem to be a more significant and breakthrough innovation in the field of wastewater treatment and reuse (Pizzichini et al. 2005). Pressure-driven membrane processes like microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) have mostly been used for the treatment of various types of wastewater depending on the nature of pollutants present in specific wastewater. Ceramic membrane-based bioreactors were employed for treatment of sewage water in submerged more having different pore sizes. The process resulted in 95% reduction in carbonaceous material and 98% ammoniacal nitrogen with a significant reduction in protein and carbohydrate (Jin et al. 2009). Submerged ceramic membrane bioreactor of tubular configuration was studied for the treatment of high-strength wastewater, resulting in 99% removal of suspended solids and 98% removal of COD (Sun et al. 2003). Ceramic membranes are also employed in the tertiary treatment of wastewater for the removal of suspended solids, pathogens, phosphorus, organic compounds, nitrogen, etc. (Pagana et al. 2006).

CSIR-Central Glass and Ceramic Research Institute has indigenously developed clay–alumina-based ceramic membranes for the treatment of wastewater and drinking water (Bandyopadhyay et al. 2006; Roy et al. 2007; Bhattacharya et al. 2011). In the present study, a case study on the application of ceramic microfiltration-based membrane bioreactor for the treatment and reuse of domestic wastewater is illustrated.

Materials and Methods

Wastewater

Wastewater was collected from CSIR-CGCRI office canteen during lunch time (Table 1). The wastewater was characterized in terms of turbidity, pH, TDS, conductivity, COD, BOD, TSS, etc. Turbidity of the samples was measured in a turbidimeter (2100AN IS Turbidimeter, Hach, USA). Conductivity, pH and TDS of samples were measured using YSI Multiparameter (Professional Plus, Ohio, USA). BOD was measured using BOD Track Apparatus of Hach, USA, and COD was measured in COD Digester (Spectralab, India) using dichromate reflux method followed by titration with standard ferrous ammonium sulfate solution. Oil and grease were measured by standard laboratory method using hexane. Total suspended solid (TSS) was analyzed using Millipore filter apparatus (Tarson make). All measurements were performed following standard methods for analysis of water and wastewater as per American Public Health Association (APHA). The chemicals used in the experiment were of GR grade (M/s. Merck, India).

Activated Sludge

Activated sludge used for the study was collected from a sewage treatment plant.

Table 1 Characteristics of untreated canteen wastewater

Parameter	Raw wastewater
Turbidity (NTU)	130
pH	8.9
Conductivity (μS/cm)	1792
TDS (mg/L)	1235
Salinity (ppt)	0.97
TSS (mg/L)	72.5
Oil and grease (g/L)	3.8
COD (mg/L)	1600

Experimental Setup

Membrane Bioreactor Study

Membrane bioreactor consists of two steps. One is bioreactor study in continuous batch mode, and other one is membrane filtration.

Batch Study

Batch-scale study was performed with kitchen wastewater using activated sludge process. Nutrients like dextrose (C source), ammonium nitrate (N source), magnesium chloride (trace element), ferric chloride (Fe source), potassium dihydrogen phosphate (P and K source) and dipotassium hydrogen phosphate (P and K source) were used for the rapid growth of microorganisms. The sample was well aerated for proper mixing to bring the organisms, oxygen and nutrients together, and to remove metabolic waste products along with the formation of flocculent sludge containing different types of microbial community. Schematic representation of batch study is shown in Fig. 1.

Dose Optimization

Three sets of batch study were conducted for the optimization of activated sludge dose with constant dose of nutrient and aeration time as described in Table 2.

Further experiments were conducted with optimized sludge dose (0.5 g/L) to establish organic load removal efficiency.

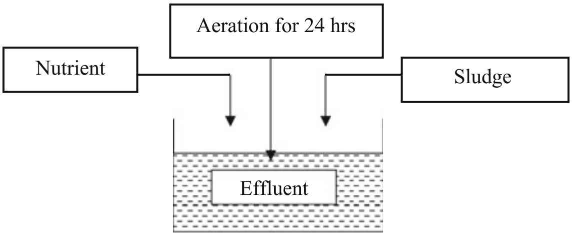

Fig. 1 Schematic representation of batch study

Table 2 Experimental condition

Exp no.	Feed volume (L)	Sludge dose (g/L)	Nutrient dose (mL/L)	Aeration time (h)
BR 1	1.0	0.25	5	24
BR 2	1.0	0.50	5	24
BR 3	1.0	1.0	5	24

Table 3 Experimental condition

Exp. No.	Reactor volume (L)	Feeding rate (mL/min)	Overflow rate (mL/min)	Sludge dose (g/L)	Aeration
BR 4–7	50	100	100	0.5	Continuous
BR 8–10	50	25	25	0.5	Continuous

Continuous Bioreactor Study

In the continuous study, the wastewater was subjected to biological treatment using only activated sludge. In one set, the experiment was carried out for 7 h/day, and in another set, the study continued for 80 h (Table 3).

Ceramic Microfiltration

The microfiltration study of bio-treated wastewater was carried out in a cross-flow microfiltration (CMF) unit fitted with porous ceramic membrane prepared from a low-cost composition of α-alumina (80%) and clay (20%). In this study, multi-channel ceramic membrane was used. The experimental setup consisted of a tubular membrane module (SS) horizontally fitted feed tank (SS, capacity 10 L), liquid recirculating pump, inlet and outlet pressure gauge and valves. Experiments were conducted taking 8 L of feed solution. Different transmembrane pressures (TMP) were maintained in the range of 0.4–1.2 kg/cm^2 to observe the effect of operating pressure on the permeate flux. Filtration was continued for 2 h at a constant pressure of 1.0 kg/cm^2 TMP. The permeate flux was measured at specific time intervals, and permeate samples were subjected to the characterization for different parameters. After each run, the system was thoroughly cleaned with deionized water. The ceramic membrane was cleaned with dilute nitric acid solution and then deionized water. A schematic of the entire process is shown in Fig. 2.

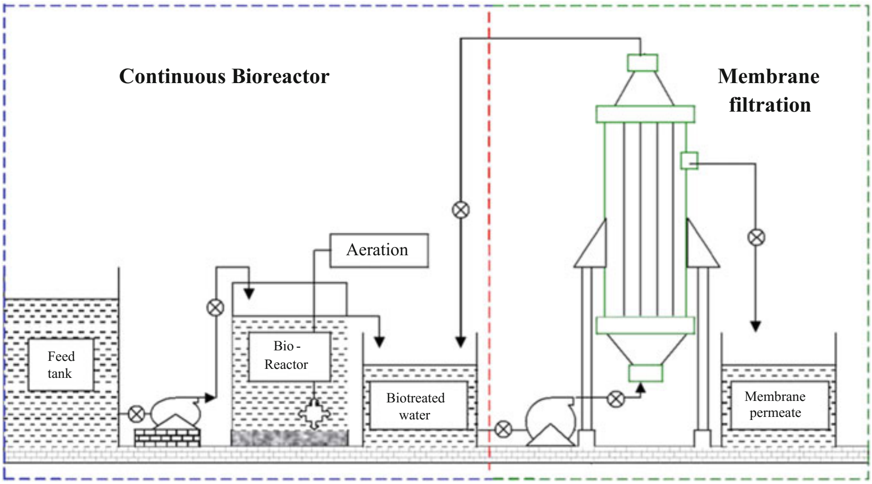

Fig. 2 Schematic representation of continuous membrane bioreactor

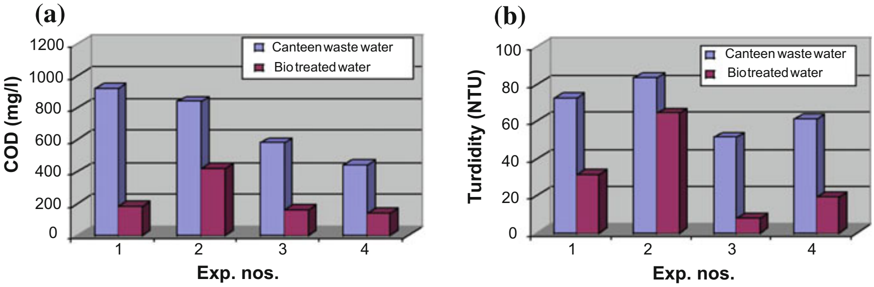

Fig. 3 **a** COD reduction and **b** turbidity reduction during batch-scale bio-treatment

Results and Discussion

Batch-Scale Biological Treatment: COD and Turbidity Removal

Considerable reduction in COD and turbidity was observed during batch bioreactor study. Turbidity was reduced from an initial 60–80 NTU to 10–60 NTU with COD being reduced to 180 mg/L from 900 mg/L (Fig. 3). This trend was observed for continuous MBR study for 7 h (Fig. 4) and 80 h (Fig. 5).

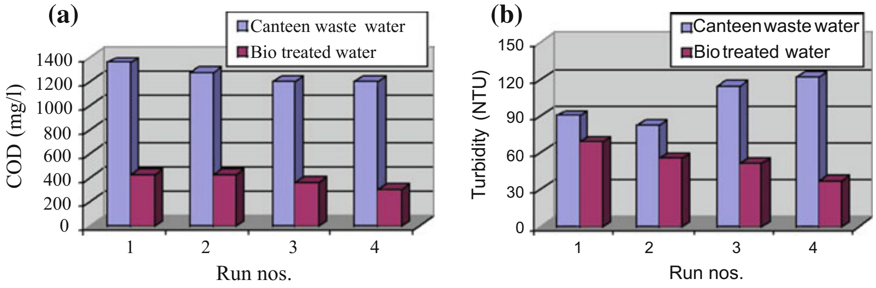

Fig. 4 **a** COD reduction and **b** turbidity reduction during continuous bio-treatment (for 7 h)

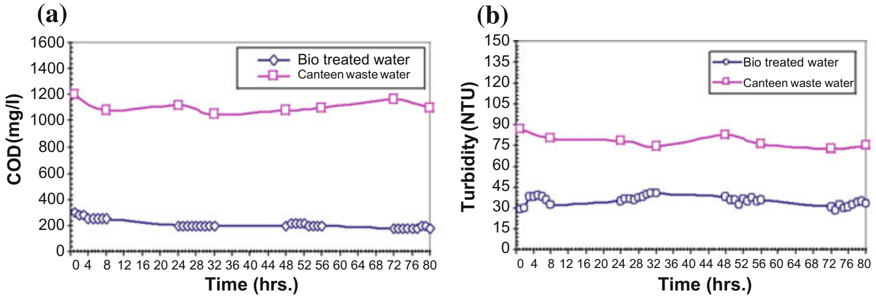

Fig. 5 **a** COD reduction and **b** turbidity reduction during continuous bio-treatment (80 h)

Continuous Biological Treatment for 7 h (Exp No. BR 4–7): COD and Turbidity Removal

See Fig. 4.

Continuous Biological Treatment for 80 h (Exp. No. BR 8–10): COD and Turbidity Removal

See Fig. 5.

Microfiltration Study: Characteristics of Permeates, COD Removal

MF of bio-treated canteen wastewater resulted in turbidity below 1 NTU (Table 4) with considerable reduction in COD, i.e. 90%. Flux rate of about 65 LMH was obtained that attained a steady state within 60 min of operation (Fig. 6).

Table 4 Characteristics of the raw and treated samples of canteen wastewater

Parameter	Membrane filtration	Bioreactor		Discharge standard
		Continuous	Batch study	
Turbidity (NTU)	0.424	35	56	<1
pH	8.69	8.85	8.53	6.0–8.5
Conductivity (μS/cm)	1690	1520	1700	–
TDS (mg/L)	968	1065	1212	–
Salinity (ppt)	0.64	0.69	0.7	–
TSS (mg/L)	22	41	–	100
Oil and grease (g/L)	0.02	0.07	–	–
COD (mg/L)	160	200	500	250

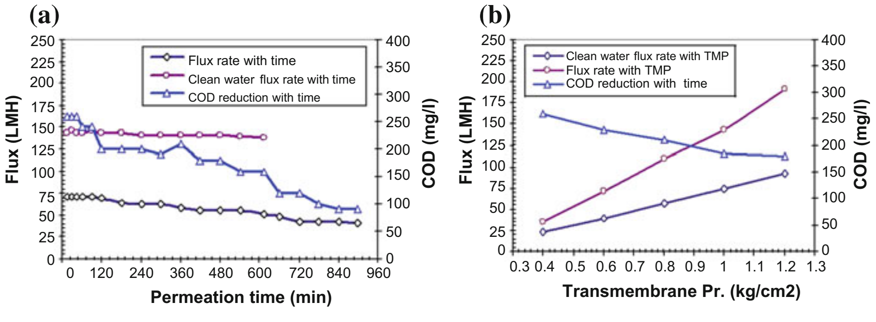

Fig. 6 **a** Flux rate and COD reduction with time at constant TMP of 1 kg/cm^2 and **b** flux rate and COD reduction with varying transmembrane pressure during cross-flow microfiltration study of bio-treated water

Conclusion

Wastewater originated from various sources, viz. domestic and municipal units, industrial sectors, contains a significant amount of toxic inorganic and organic pollutants which requires a suitable treatment before discharging to the environment. Recycling of wastewater could effectively minimize the pollutant loads on environment, as well as prevent the depletion of fresh water resources. Wastewater can be recycled in large quantity for industrial processes and also for agricultural and irrigation activities. An effective treatment of wastewater is essential for its further reuse. In the ceramic membrane-based bioreactor study of kitchen wastewater, considerable reduction in COD, BOD and suspended solids could be observed. With the suitable process design and the process parameters control, the efficiency can be enhanced further to a great extent so that low-cost ceramic membrane could be an affordable and attractive technology for such applications. Ceramic membrane-based filtration is proposed as a cleaner and greener technology for wastewater treatment. The feasibility of recycling the treated wastewater for agriculture, aquaculture and industrial processes depends on the nature of effluent. The overall study reflects that CSIR-CGCRI, Kolkata,-developed indigenously low-cost tubular clay–alumina-based ceramic microfiltration membrane process could be a viable and eco-friendly option for the effective treatment of domestic wastewater.

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References

Bandyopadhyay S, Kundu D, Roy SN, Ghosh BP, Maiti HS (2006) Process for preparing water having an arsenic level of less than 10 PPB. US Patent 7014771

Bhattacharya P, Ghosh S, Sarkar S, Majumdar S, Bandyopadhyaya S (2011) Effectiveness of biosorption assisted microfiltration process for treatment of domestic wastewater. Bioremediat J 15:206–217

Gupta N, Jana N, Majumder CB (2008) Submerged membrane bioreactor for municipal wastewater treatment process: an overview. India J Chem Technol 15:604–612

Jin L, Ng HY, Ong SL (2009) Performance and fouling characteristics of different pore-sized submerged ceramic membrane bioreactors (SCMBR). Water Sci Technol 59:2213–2218

Kim J, Song I, Oh H, Jong J, Park J, Choung Y (2009) A laboratory scale graywater treatment system based on a membrane filtration and oxidation process—characteristics of graywater from a residential complex. Desalination 238:347–357

Kumar P, Prasad B, Chand S (2009) Treatment of desizing wastewater by catalytic thermal treatment and coagulation. J Hazard Mater 163:433–440

Lina AG, Ahmad J (2006) Biological treatment of textile waste water using sequencing batch reactor technology. Environ Model Assess 11:333–343

Laasri L, Elamrani MK, Cherkaoui O (2007) Removal of two cationic dyes from a textile effluent by filtration-adsorption on wood sawdust. Environ Sci Pollut Res 14:237–240

Mo J, Hwang JE, Jegal J, Kim J (2007) Pretreatment of a dyeing wastewater using chemical coagulants. Dyes Pigm 72:240–245

Pagana A, Stoitsas K, Zaspalis VT (2006) Applied pilot-scale studies on ceramic membrane processes for the treatment of wastewater streams. Global NEST J 8:3–30

Pizzichini M, Ruso C, Di Meo C (2005) Purification of pulp and paper wastewater, with membrane technology, for water reuse in a closed loop. Desalination 178:351–359

Roy SN, Bandyopadhyay S, Kundu D, Ghosh BP, Maiti HS (2007) Apparatus for the preparation of arsenic free water. US Patent 7309425

Sun DD, Zeng JL, Tay JH (2003) A submerged tubular ceramic membrane bioreactor for high strength wastewater treatment. Water Sci Technol 47:105–111

Tolkou A, Zouboulis A, Samaras P (2014) The incorporation of ceramic membranes in mbr systems for wastewater treatment: advantages and patented new developments. Recent Pat Eng 8:1–9

Visvanathan C, Aim RB, Parameshwaran K (2000) Membrane separation bioreactors for wastewater treatment. Crit Rev Environ Sci Technol 30:1–48

Wang S, Zhu ZH (2005) Sonochemical treatment of fly ash for dye removal from wastewater. J Hazard Mater 126:91–95

Using Conversations to Enhance Pro-environmental Practices in High-Rise Public Housing: A Comparative Study Between Mexico and Australia

A. O. Aldape-Garcia

Abstract Environmental degradation around the world has been strongly echoed by the media and governments in Western societies. Therefore, environmental education has become such a popular topic that the majority of people these days recognize the environment as something that should be preserved. This trend is pushing us to integrate messages about environmental protection into our daily conversations and practices. In this work, a cross-context ethnographic study was undertaken in the Collingwood high-rise public housing site in Melbourne, Australia, and Tlatelolco high-rise public housing site in Mexico City, Mexico. Positioning theory was utilized as the theoretical framework of analysis in order to understand how conversations were constructed through moral positions (positioning acts) within the participants' socio-physical context. The data analysed revealed that some residents used their social networks to enhance the fostering of pro-environmental practices and increase awareness of the wise consumption of natural resources and the care for surrounding gardens and parklands. The results showed that some residents were predisposed to semi-actively care for the built and natural environments, that is, usually always under their own terms, resources and capabilities, and by using their social networks to influence others.

Keywords Conversations · Environment · Education · High-rise
Public · Housing

Introduction

This study took place in two high-rise public housing sites but in two different geographical locations: the Collingwood high-rise public housing site is located in the City of Melbourne, Australia, and the Tlatelolco high-rise public housing site

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situated in Mexico City, Mexico. Three key factors influenced my decision for selecting these two sites: (a) the geographical convenience and accessibility to these sites, (b) the existence of community venues located inside each of the high-rise sites where I could invite residents to take part in this study and (c) language shared with the participants (English and Spanish).

The Tlatelolco high-rise public housing (officially known within the Mexican Literature as '*El ConjuntoUrbano Presidente Adolfo LópezMateos de Nonoalco Tlatelolco*') is popularly identified just as 'Tlatelolco' by residents in Mexico City (Marez 2010). During the late 1950s, the construction of Tlatelolco began as a plan to relocate slum settlements in the northern part of the city as a response of the high demand for affordable housing (De Garay 2004). After the Second World War, many Mexican researchers and architects focused on the European functionalist movement, in which the architectural structure was determined by the causal trends of human behaviour within enclosed spaces (De Garay 2002, 2004). Tlatelolco high-rise public housing was inaugurated on the 21st of November 1964, and it was advertised in all the nation's newspapers as "the monumental high-rise complex in Mexico which symbolized a new and unique architectural age aiming to regenerate the impoverished and degraded inner zones in the Mexico City" (Marez 2010). Tlatelolco originally numbered 102 buildings, accommodating 11,908 apartments and housing around 50,000 residents at that time; however, 32 buildings were destroyed and others declared non-inhabitable after the 1985 earthquake which claimed hundreds of lives within the site (Alfaro et al. 1987). This tragic event marked Tlatelolco forever, changing the social fabric and the infrastructural arrangements in many areas of the site (Marez 2010). With economic support from the government, thousands of residents decided to leave their apartments for a new home, and one quarter of the population moved out of Tlatelolco due to the fear of facing another deadly earthquake (Cisneros 1986). According to the Census of Population and Households' report carried out by the National Institute of Statistic and Geography (INEGI), Tlatelolco's population by the year 2010 was counted in 27,843 residents (Vivir en Tlatelolco 2015).

The Collingwood high-rise public housing site was built in 1958 by originally containing three-storey housing blocks, but later, between 1967 and 1971, to make way for 20-storey tower blocks (Costello 2005). Pressured by church groups to regulate and control the growing ghettos and slums of many suburbs, premier Henry Bolte declared in 1955 that "bad houses made bad people" (Tippet and Niall 1995, p. 21) and set about on a large-scale confiscation and demolition of over 7000 homes across Melbourne's inner suburbs, with residents distributed to commission flats half a city away (Vaarwerk 2016). Hence, the Collingwood site was also developed from an imperative need to house a growing number of people who were living in poor conditions, and many migrants who had moved into the area from the 1960s to the 1970s (Costello 2005). Collingwood experienced a relatively stable population between 1996 and 2001, but over the last decade, the population increased by 7.7% (City of Yarra 2015). The current residents are culturally diverse, including newly arrived migrants from Africa and the Middle East, as well as some Europeans and Indigenous Australians (Myconos 2010). Nowadays, the Collingwood site encompasses three 20-storey buildings containing 600 households with just over 1500 residents (City of Yarra 2015, Butler 2013).

Getting into the Field

I spent 3 months of fieldwork within the Collingwood site and 4 months within the Tlatelolco site looking for unique narratives from residents, and traces of evidence, such as field notes and pictures, that could lead me to answer the research question posed for this study which is explained in the theoretical framework section. In Mexico, the cultural centre 'Ernesto Gomez Cruz' and the sport centre '5 de Mayo' situated within the Tlatelolco site in *Delegacion Cuauhtémoc*, offer cultural and educational activities for residents such as drama, painting, computer courses and sport activities. These venues offered an excellent space to undertake the intended fieldwork and to make contact with potential participants living in Tlatelolco. In Australia, the Collingwood high-rise site was chosen for a number of reasons. Foremost was access to the 'Collingwood Neighbourhood House' which "offers a range of social, recreational and educational activities and programs that meet the needs of the diverse-multicultural community" (City of Yarra 2012). The Collingwood Neighbourhood House provides a friendly environment for the high-rise public housing community to meet and create connections among the culturally diverse residents (City of Yarra 2012). This venue offered a space to have contact with residents living in different buildings within the site and could be seen as a strategic location for the fieldwork pursued in this research.

Opportunities for Research in Environmental Practices

Pro-environmental behaviours and practices are most likely to be determined by physical factors which can occur in diverse social situations allowing actions for conservation, each associated with different causal factors and experiences (Gough 1999, 2002). Results of empirical work (Walton and Austin 2011) and non-empirical work (Wener and Carmalt 2006; Yau 2010a, b, 2011, 2012a, b) in high-rise public housing contexts have shown that people's pro-environmental practices can be shaped through interactions with external physical elements inherent to urban structures and locations. However, there has been very little research examining the extent to which external factors significantly impact on residents' practices for conservation. In addition, studies in human behaviour have demonstrated that living in sterile urban environments can impact on residents' behaviours as a result of the isolation from natural environments and the local community (Coley et al. 1997; Gifford 2007, 2014). For example, conventional high-rise buildings tend to separate residents physically from nearby neighbourhoods and green areas (Wener and Carmalt 2006; Gifford 2007; Yuen et al. 2006).

But, what exactly is a practice? The meaning of practice has developed with time and has become highly debatable in recent years, especially when compared with the concept of behaviour. Despite extensive research and debate about the distinction between practice and behaviour, there is still no unified understanding of what a practice is (Schatzki et al. 2001), and the best way to analyse it still remains controversial (Shove and Spurling 2013). Some theorists, for instance, focus on the elements that compose a practice (Shove and Spurling 2013; Hargreaves 2011; Reckwitz 2002; Shove 2010; Shove et al. 2012). Others, like Schatzki (1996, 2003) and Warde (2013), concentrate on the linkages or nexus among those elements. Reckwitz (2002) explains that "a practice exists as a block or a pattern which can be filled out by a multitude of single and often unique actions". Morris et al. (2012) use Reckwitz's work to describe a more extensive definition of practices. These authors claim that practices can be understood as arrangements of numerous interconnected physical and socio-psychological elements, such as social norms, knowledge and values, which shape people's actions as part of their everyday life.

Theoretical Framework

It can be assumed that the socio-physical and environmental factors that residents experience whilst living in high-rise public housing are psychosocial constructions derived from the world they live in. In other words, residents' thoughts and learnings are the product of close interactions within this specific context. This ontological assumption enabled me to crystalize the main research question for this study: What external entities affect pro-environmental practices of residents living in high-rise public housing? Based on this premise, I will propose a constructionist-based theoretical framework in order to understand how people differentiate, construct and understand the contextual elements encompassed in high-rise public housing sites and how these influence practices for conservation. Hence, I will argue that there are three main existing entities: people, the high-rise sites and the natural environment that dynamically influence residents' practices.

Why these three main entities and not something else? Well, the main ontological assumption that I am proposing here is based on the undeniable fact that people, the high-rise sites and the natural environment physically exist and have a fundamental role in constructing the meaning of the socio-physical context for residents. These types of contexts enclose human practices which are inherently tied to these high-rise sites. The Tlatelolco and Collingwood sites, therefore, encompass these three main ontological entities or in Schatzki's words "the sites' inherent parts" (Schatzki 2003). It is within the 'sites' where social phenomena take place and Schatzki puts an emphasis on the spatial connotation where human practices have location in time and space. The location in practice-place is 'where' it occurs in the space of the high-rise sites, that is, particular practices and their actions are tied to a specific physical space within the site (Schatzki 2003). Schatzki also argues that sites have a teleological purpose by assigning a specific location for certain practices. Based on his argument, I can justify that the material arrangements that compose the Tlatelolco and Collingwood sites can actively influence residents' agency when constructing meanings and use them to undertake pro-environmental practices.

A site is a material arrangement of people, things, artefacts and organisms that produce a specific configuration, that is, a meaning or an identity (Schatzki 2003). In this regard, Spinosa et al. (1997) adds that site comprises a specific range of activities, a specific type of human identities, a specific physical context and a unique way or style that coordinates those arrangements. These material arrangements allow physical connections among all the entities that compose the site and allow the social constructions of actions and practices. Therefore, for this paper, I decided to use Schatzki's constructionist approach on social practices which was aligned with his concept of site-based ontology and the three main ontological assumptions proposed at the beginning of this section as well as with the theoretical framework that I intented to use for this work: Positioning Theory. I adopted Schatzki's approach through positioning theory as a way to deconstruct and analyse the connections among these three ontological entities/meanings in order to know how these influenced residents' agency when performing pro-environmental practices. Finally, the main aim of this study was to explore stories and descriptions from residents about how the natural environment, the site infrastructure and the social context influenced the execution of pro-environmental practices.

Positioning Theory

The constructionist approach taken for this study led me to choose positioning theory as the most suitable theoretical framework of analysis where residents could socially construct common meanings of reality through discursive practices. The amalgamation between practice and discourse brought originality to this work as it tried to explore the connections between residents' agency and the objective ontological realities of the sites which could be reflected in social discourse (Harré and Van Lagenhove 1999). Also, positioning theory was aligned with the selected methodology that complies with the ontological precepts of site ontology and its epistemological implications proposed by Schatzki (2003). But, what is positioning theory? Davies and Harré (1990, p. 62) defined positioning theory as "a possibility in known forms of talk, position is what is created in and through talk and the speakers and hearers take themselves up as persons". Harré and Van Langenhove (1999, p. 2) add that the concept of "position is general enough to capture diversity, but precise enough to help to articulate the 'ephemeral conditions' that matter so much in social life".

Positioning theory here functioned as a guiding framework to understand how these residents approached their socio-physical context to undertake practices that benefit the environment. I refered to positioning theory to defragment and reconstruct residents narratives about other residents (talk about talks), in order to refer to the assignment of moral positions of the speakers within the discursive construction of their personal stories. Hence, these stories make their practices comprehensible and definite as social acts (Harré and Van Lagenhove 1999). The central ideas of position theory are to explain how the psychological phenomena are produced in social relations and how the multisource torrent of everyday life can be reconstructed into distinct episodes (Harré and Van Lagenhove 1999; Ofreneo and Montiel 2010).

Social episodes of everyday life can be defined as a sequence of events (or happenings) in which two or more people engage according to some principles of unity or cultural value (Marez 2010). To understand the dynamics of social episodes, positioning theory looks at a mutually determinant triad composed of: (a) positions, (b) storylines and (c) speech acts (Harré and Van Lagenhove 1999). Positions are the moral locations that people take in a conversations based on the local system of rights, duties and obligations within a social episode (the local moral order). "The positions that people take in conversations are linked to storylines" (Ofreneo and Montiel 2010). Storylines are patters of sequences of events that are often linked with sociocultural narratives; however, storylines and positions are not freely constructed as they are directly derived from the individuals' contexts (Harré and Van Lagenhove 1999). Finally, speech acts are those actions that are socially significant to a given situation and context which provide meaning to the unfolding conversations (Harré and Moghaddam 2003; Zelle 2009).

Methods

Based on the social characteristics of the participants, such as poor literacy and low socio-economic conditions, it was decided that observations, field notes and semi-structured interviews would be the best methods to obtain quality data during the fieldwork period. These non-numerical data were actively analysed and organized using the *Nvivo 10 application* which helped me to classify, sort and arrange the material obtained and examine relationships across all the information obtained. I also used this software to find patterns and themes and to locate valuable evidence to support my arguments for this study. Ethical considerations were also taken into account in order to protect the dignity and privacy of the participants as well as my safety as a researcher.

From the 32 semi-structured interviews carried out in both sites with residents and ex-residents, I will only focus on four fragments of individual interviews in this work. For space limitations, only one fragment of each testimony will be displayed as evidence. Two fragments are from the Collingwood high-rise public housing site in Melbourne, Australia, and the other two are from Tlatelolco high-rise public housing site in Mexico City, Mexico.

Practices for conservation narrated in a retrospective account by the participants fulfil the requirements to be treated as separate case studies. In this regard, Ranging and Baker (1992) point out that a case study needs to satisfy some requirements: Firstly, these four narratives were identified as established cases during development of the research process because they were physically bounded to a specific reality in space and time. Secondly, these four cases were gradually constructed with empirical evidence obtained with semi-structured interviews, field notes and pictures as observations. They eventually took shape during the course of the research. Finally, Raging and Becker (1992) claim that cases are conventions because they are seen as "general theoretical constructs that structure ways of seeing social life".

Procedure

First, I looked at first-order positioning where residents located themselves and others within a moral space by using several storylines (Harré and Lagenhove 1999). Second, as a consequence of first-order positioning, I linked it with performative and accountive positioning, where people positioned themselves and others within a descriptive storyline (Harré and Lagenhove 1999). The residents' speech acts, contained within storylines, can have psychosocial influences on persuading others to perform certain practices, or, in the words of Harré and Lagenhove (Harré and Lagenhove 1999), "have immediate perlocutionary effect". Then, the residents accounted for their previous positions at the time of performing a particular practice. Thirdly, I discussed how residents' positioning was tied to their given local moral orders at the time of performing social practices (Harré and Lagenhove 1999). Finally, deliberate self-positioning allowed me to explain residents' agencies, points of view or biographical details as strategies to influence others to foster pro-environmental practices (Harré and Lagenhove 1999).

In the following section, I will describe experiences that I had with these special residents and ex-residents, who, regardless of their cultural background and multiple social constraints, have sustained close bonds and connections with the high-rise communities. At the end of the stories, I will link my interpretations and insights from residents to positioning theory in order to start acknowledging the potential of these particular residents of creating awareness about the care of natural surroundings up to the point of influencing others to undertake pro-environmental practices. These particular stories were enriched with ethnographic methods such as field notes, and pictures in order to construct a more tangible notion of the multiple realities that exist in these communities.

After the analysis of the data, I concluded that four of the individual interviews presented in this study played a crucial role in revealing deep insights and themes about the influences of the social relations among residents, and their interactions with physical and natural contexts. As a result of this, the analysis of the data focused on the narratives of those residents, who were 'talking and doing things', could identify events, facts and people that contributed to the recognition of the external elements or sources that constructed pro-environmental practices on site.

Participants

Lalo: Lalo is Latino man in his early 40s who has lived in Tlatelolco for 20 years. He does not get involved in community activities very often, although he is totally aware of conservation of natural resources at home, and the care of the environment around his building. I came to know him when he was picking up his son from a Taekwondo class in one of the cultural–sport centres in Tlatelolco.

Chio: Chio is a married Latino woman in her 30s who has developed an attachment to her community and the local natural environment in Tlatelolco. She has lived in the Tlatelolco high-rise public housing for 15 years, and she is proud of being a resident of Tlatelolco and of the history, culture and identity that it brings to many Mexicans.

Joseph: An Anglo-Australian man in his late 40s, Joseph, was the first interviewee in my research in Australia. Joseph lived in the urban Collingwood high-rise public housing estate for three years, but moved to another public housing estate because of personal issues of mental illness, disability and violence that he faced with other residents at that time. Despite his problems, he developed an attachment and retained a feeling of membership to Collingwood high-rise public housing, which allowed him to share his knowledge and experiences with other residents who currently live there.

Ha: Ha is a Vietnamese lady who does casual volunteer work at the Collingwood Neighbourhood House. Ha used to live in Collingwood high-rise public housing in the early 80s as a refugee, but she moved out from the flats many years ago. Today, she is not only a loved member of the entire high-rise community, but also an important conduit for the Vietnamese community and other groups living in the flats.

In the following table (Table 1), it is explained how the fragments of each participant's social episodes were analysed. The storylines allowed identifying how participants positioned themselves and others within their given local moral order as well as the category of the practice and the role taken when addressing their moral position. The main parts of each storyline were highlighted in bold letters to show the main message. Moreover, the main pronouns were also highlighted in order to see how participants took their own moral positions. Finally, these storylines were complemented with ethnographic methods such as field notes and pictures derived from direct observations.

Table 1 Storyline analysis using positioning theory

User of storyline	Storyline	Position of self ('I')	Position of others ('you/they')	Role in practices for conservation	Storyline category	Field note or picture
Lalo (Mexico)	"…it depends how you approach them [scavengers/pepenadores], and many times **I** have been successful in this regard because **some of them listened to my suggestions about avoiding the messiness of the work with the rubbish...**"	First-order position as resident. **'I'** have the right to talk about this topic because **I** live here.	**He** challenged the scavengers as **they** have revised their second and third order positioning. **'They'** listened his suggestion by modifying their practices.	Mediator	Negotiation	 Rubbish scattered by scavengers. Source: compiled for this study, 10/12/2013.
Chio (Mexico)	"In my building, **we** organized a strategy that was putting plastic bags attached to trunk trees around our building, so in that way people could use them to pick their dogs' droppings**. I was encouraging people saying "please use them"** but **I** realized that we need much more education in that regard..."	She deliberately positioned herself and others (**I** and **them**) as the ones with the rights as residents and duties towards environmental protection to create a strategy to stop a harmful practice within the site.	She deliberately positioned other people living outside her building as not very enthusiastic or apprehensive about her attempt to minimize pollution caused by dogs' droppings.	Promoter	Planner-strategist and executioner	Field note: I could not see many wild dogs around the complex but certainly lots of pet dogs taken for a walk by their owners. Field note on 11/10/2013.

(continued)

Table 1 (continued)

User of storyline	Storyline	Position of self ('I')	Position of others ('you/they')	Role in practices for conservation	Storyline category	Field note or picture
Joseph (Australia)	"**I said to the gentleman [Kevin, another resident] look I am going to get it ready for you, so you can plant your plants**. **He** is not a young fellow anymore, so the garden needed to be pulled up, dug up and cultivated… and **I said to him I will do that for you Kevin!** He said "That will be great Joseph…no rush" **he** said. Next week **we** are getting some fertilizer..."	Knowing his position within the local moral order in Collingwood he personally position himself as someone who can assist another resident to perform apro-environmental practice in the community garden when saying "**I** will do that for **you**"	Using first-order positioning he position Kevin (**he**) as an old man who is lacking of strength to work in the garden. He deliberately positioned this resident as the one who needed assistance to perform a specific practice.	Facilitator	Performer of pro-environmental practices	 Garden bed inside the Collingwood neighborhood house. Source: compiled for this study, 06/07/2013.
Ha (Australia)	"**I** think they don't care and understand what is going on there **you** know [with the environment]. **I** think **they** [just] don't care. Yeah, **when I tell them they don't do anything for improving or doing more things [for the environment] you know. I** just have seen very little improvement..."	By using the pronoun **'I'**, she positioned herself in first-order position as a resident who has the right and duty to spread the word and inform other residents about pro-environmental practices.	She deliberately positioned others as unconcerned with the care of the local environment.	Informant/ Educator	The effects of communicating about pro-environmental practices.	 Community kitchen where residents gather and talk. Source: compiled for this study, 21/06/2013.

Discussion

The four fragments presented above showed that these residents could promote, inform or negotiate practices for conservation through conversations in their respective high-rise site. By talking with other residents, and doing activities with them at the same time (speech-acts), I found that particular ways of environmental care were created in high-rise public housing as purposeful messages were embedded within the discourses of the speakers. In some way, these specific messages appeared to promote practices for conservation. The analysis revealed common points found in each of the cases: (a) knowing who integrates their local social network within their buildings and (b) knowing and foreseeing the dynamics of the diverse local moral orders related those networks. These two points will be explained more thoroughly as follows:

(A) Knowing Who Integrates Their Local Social Network with Their Buildings

Despite the difficulties that social contexts might pose, these residents have found ways of integrating their intentional discourses into their local moral orders. By doing this, they were able to open specific communication channels with members of their own networks, or, even other networks, to talk, teach or just gossip about issues related to pro-environmental practices such as waste disposal and gardening. In this regard, I can associate their role with Dunbar's (1996, p. 1) work where he points out that there are members in the community "who know who is friends with whom, who dominates and who is subordinate, who owes a favour in return for a favour granted in the week before, who has remembered a past slight". In other words, residents had to deal with the unavoidable ambiguities that form part of the complex social whirl that they were immersed in.

(B) Knowing and Foreseeing the Dynamics of the Diverse Local Moral Orders

The years of experience that these residents had in their communities allowed them to know the constant changes in social episodes linked to the situations that emerged in particular scenarios. Also, they knew what types of practices were related to those episodes, and the symbols needed to start conversational connections with other residents. Furthermore, some residents even foresaw how a social episode might unfold and what the effects would have. With this, I am not saying that their hints or predictions were accurate, but acknowledging the diversity of social episodes that occured in their communities enabled them to confidently move throughout the networks making the social cohesion process much easier for other residents.

Social discourse was utilized by residents to morally position their role within their social networks, which, in turn, anabled other members in the network to locate their position into the existing local moral order. For example, cooking for others as ‘a volunteer’, and then speaking about the environment, or attaching plastic bags to trunk trees for the dogs’ droppings as ‘member of the community’, and then, speaking about the benefits of it for the local environment, and so on. These were examples of how the discursive practices emerged from defined tacit roles in which words and actions were combined with materialities (food or plastic bags) in which purposeful messages were embedded along the lines. For example, putting plastic bags on trees was an individual practice that symbolized the goodwill to improve the local natural environment in the community. These actions helped to the listener (other residents) to be more attentive to the conversation as the speaker was morally positioned as someone who deserves to be heard.

Conclusion

Practices for conservation were slowly integrated into conversations among residents in both high-rise public housing sites. The form and dynamism that these conversations developed depended on the agency of the speakers which allowed them to take specific moral positions directly linked to the existing local moral orders. The segments presented in this study were clear examples of how residents utilized their moral positions within their respective socio-physical context to promote the fostering of pro-environmental practices.

The data obtained from the interviews and the different ethnographic methods suggest that some residents used elements of their socio-physical context to influence other residents to foster pro-environmental practices, and in this way, promoting awareness about local environmental degradation. Inferences based on residents’ declarations suggest that their ultimate goal was not to change other residents’ behaviours or practices but acknowledging as ‘something good’ if their actions had that effect on others. It also appeared that they were doing something ‘morally right’ when communicating and passing information on to other residents, although, the ultimate decision of appreciating that information was left to the listener. Their speech-acts seemed to focus to the main ontological realities posed at the beginning of this work: (a) the welfare of ‘people’, (b) the maintenance of high-rise ‘sites’ and (c) the care of surrounding ‘gardens and park lands’.

The intention of these speech-acts was to enhance a greater awareness of pro-environmental practices in the community. Participants highlighted the importance of developing social connections with other people, which, in turn, were used to communicate purposeful messages not only about environmental improvement, but also about a diversified range of topics. Further research is needed about how information about conservation of natural environments can be actively transmitted and delivered by using social networks in high-rise public housing contexts in order to deliver the right information to residents within the right time and space. Finally, the comparison participants’ story-lines in both sites showed that their own attachment to place was originated from diverse reasons which help them to construct and acquire specific moral positions in order to place intentional speech-acts at the heart of enhancing pro-environmental practices.

References

Alfaro MS, Garcia AA, Lucas M, Villar CM (1987) Problematica Urbana y reconstruccion de la unidad habitacional Nonoalco Tlatelolco (Tesis no publicada). En Sociologia, Universidad Utonoma Metropolitana, Mexico

Butler G (2013) Heritage evidence: amendment C207. Arden Macaulay Heritage Review, Melbourne, Australia. Available from: http://www.melbourne.vic.gov.au/SiteCollectionDocuments/statement-graeme-butler.pdf

Cisneros SA (1986) Organizaciones Sociales en la reconstruccion habitacional de la Ciudad de Mexico. Estudios Demograficos y Urbanos 3(1)

City of Yarra (2012) Neighbourhood houses and learning centres in the city of Yarra. Available from: https://www.yarracity.vic.gov.au/the-area/things-to-do/neighbourhood-houses-and-learning-centres

City of Yarra. Population density: Profile dwelling (2015) Available from: http://profile.id.com.au/yarra/dwellings?EndYear=2006&WebID=130

Coley RL, Sullivan WC, Kuo FE (1997) Where does community grow?: The social context created by nature in urban public housing. Environ Behav 29(4):468–494

Costello L (2005) From prisons to penthouses: the changing images of high-rise living in Melbourne. Hous Stud 20(1):49–62

Davies B, Harré R (1990) Positioning: the discursive production of selves. Social Behav 20 (1):43–63

De Garay G (2002) Rumores y retratos de un lugar de la modernidad: historia oral del Multifamiliar Miguel Alemán, 1949–1999. Universidad Nacional Autónoma de México, Facultad de Arquitectura

De Garay G (2004) Modernidad Habitada: Multifamiliar Miguel Aleman Ciudad de Mexico, 1949–1999. Instituto Mora, Mexico

Dunbar RIM (1996) Grooming, gossip, and the evolution of language. Harvard University Press, Cambridge, Mass

Gifford R (2007) The consequences of living in high-rise buildings. Archit Sci Rev 50(1):2

Gifford R (2014) Environmental psychology matters. Annu Rev Psychol 65:541–579

Gough S (1999) Significant life experiences (SLE) research: a view from somewhere. Environ Educ Res 5(4):353–363

Gough S (2002) Whose gap? Whose mind? Plural rationalities and disappearing academics. Environ Educ Res 8(3):273–282

Hargreaves T (2011) Practice-ing behaviour change: applying social practice theory to pro-environmental behaviour change. J Consum Cult 11(1):79–99

Harré R, Van Langenhove L (1992) Varieties of positioning. Social Behav 20:393–407

Harré R, Moghaddam FM (2003) The self and others: positioning individuals and groups in personal, political, and cultural contexts. Praeger, Westport

Harré R, Van Lagenhove L (1999) Positioning theory: moral contexts of intentional action. Blackwell, Oxford Malden

Marez TMA (2010) La Unidad Habitacional Nonoalco Tlatelolco: Memoria y apropiacion del espacio urbano (Tesis no publicada). Escuela Nacional de Antropologia e Historia (INAH)

Morris J, Marzano M, Dandy N, O'brien L (2012) Theories and models of behaviour and behaviour change. In: Forestry, sustainable behaviours and behaviour change: theories. Forest Research, United Kingdom

Myconos G (2010) Recycling rising high: an evaluation of the high rise public housing recycling project. Melbourne, Australia, p 30

Ofreneo MAP, Montiel CJ (2010) Positioning theory as a discursive approach to understanding same-sex intimate violence. Asian J Soc Psychol 13(4):247–259

Ragin CC, Becker HS (1992) What is a case?: exploring the foundations of social inquiry. Cambridge University Press, London

Reckwitz A (2002) Toward a theory of social practices: a development in culturalist theorizing. Eur J Soc Theory 5(2):243

Schatzki TR (1996) Social practices: a Wittgensteinian approach to human activity and the social. Cambridge University Press, New York

Schatzki TR (2003) A new societist social ontology. Phil Soc Sci 33(2):174–202

Schatzki TR, Knorr-Cetina K, Savigny EV (2001) The practice turn in contemporary theory. Routledge, New York

Shove E (2010) Beyond the ABC: climate change policy and theories of social change. J Environ Plann 42(6):1273–1285

Shove E, Spurling N (2013) Sustainable practices: social theory and climate change. Advances in sociology. Routledge, Hoboken

Shove E, Pantzar M, Watson M (2012) The dynamics of social practice: everyday life and how it changes. SAGE, London

Spinosa C, Dreyfus HL, Flores F (1997) Disclosing new worlds: entrepreneurship, democratic action, and the cultivation of solidarity. MIT Press, Cambridge

Tippet G, Niall J (1995) High-rise hell, The Sunday Age, p. 21

Vaarwerk A (2016) Suburbs in the sky: high rise commission flats and the Melbourne imagination. Available from: https://www.killyourdarlings.com.au/2016/05/suburbs-in-the-sky-high-rise-commission-flats-and-the-melbourne-imagination/

Vivir en Tlatelolco (2015) Tlatelolco y la ciudad al momento: Censo de Población y Vivienda 2010. 2015; Available from: http://vivirtlatelolco.blogspot.com.au/2011/11/poblacion-de-tlatelolco.html

Walton T, Austin DM (2011) Pro-environmental behavior in an urban social structural context. Sociol Spectr 31(3):260–287

Warde AA (2013) What sort of a practice is eating? Routledge, London, pp 17–30

Wener R, Carmalt H (2006) Environmental psychology and sustainability in high-rise structures. Technol Soc 28(1–2):157–167

Yau Y (2010a) Domestic waste recycling, collective action and economic incentive: the case in Hong Kong. Waste Manag 30(12):2440–2447

Yau Y (2010b) Engaging homeowners in building care in Hong Kong: drivers and barriers. J Build Appraisal 6(1):35–48

Yau Y (2011) Collectivism and activism in housing management in Hong Kong. Habitat International 35(2):327–334

Yau Y (2012a) Multicriteria Decision Making for Homeowners' Participation in Building Maintenance. Journal of Urban Planning & Development 138(2):110–120

Yau Y (2012b) Stakeholder engagement in waste recycling in a high-rise setting. Sustain Dev 20 (2):115–127

Yuen B, Yeh A, Appold SJ, Earl J, Ting J, Kwee LK (2006) High-rise living in Singapore public housing. Urban Stud 43(3):583–600

Zelle G (2009) Exploring the application of positioning theory to the analysis of organisational change. Australian and New Zealand Academy of Management Conference

Environmental and Infrastructural Features of High-Rise Public Housing Buildings and Their Impact on Resident's Pro-environmental Practices

A. O. Aldape-Garcia

Abstract Pro-environmental practices in urbanized areas have been explored extensively during the last decades. However, very little research has been undertaken to explore residents' pro-environmental practices when living in high-rise buildings, and much less in the high-rise public housing contexts. In addition, extensive research has been limited to the buildings' architectural-environmental performances relating to design and distribution, and their effects on residents. Furthermore, it is generally assumed that residents living in high-rise public housing do not consume considerable amounts of natural resources because of their 'well-designed' living spaces. However, interactions with external factors that compose the socio-physical context such as the high-rise sites' infrastructure and social context can influence and shape residents' pro-environmental practices. This cross-context ethnographic study between two high-rise sites, Collingwood in Melbourne, Australia and Tlatelolco in Mexico City, Mexico, explored whether some immediate external synergies played a decisive role when residents did or did not undertake pro-environmental practices. The results showed that synergies with the infrastructure and social context in both sites influenced to some extent residents' pro-environmental practices and enhance environmental awareness. However, these external factors were not decisive in determining the execution of such practices.

Introduction

During the last century, the design and construction of high-rise public housing buildings have drawn little attention to the performances of effective pro-environmental practices, such as the saving of water and electricity in and out of the apartments as well as proper waste disposal. In post-colonial countries such as

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Australia and Mexico, the designs of buildings during the nineteen hundreds tended to be imported from Europe (Arthurson 2004; De Garay 2004; Hayward 1996), and therefore not able to cope with the weather and geological conditions of the land. Moreover, the designs of these buildings seem to increase the sense of isolation (Gifford 2007) and decrease connectedness from local green areas and wildlife (Westphal 2003). With time, these physical elements seem to be factors of consideration for residents when fostering and executing pro-environmental practices. Hence, the question I have formulated for this study is: what factors derived from infrastructure and environmental elements in high-rise public housing in Australia and Mexico impact on the execution and fostering of pro-environmental practices?

The design of old high-rise sites appears to leave the care of the environment exclusively in residents' hands. Therefore, the buildings' physical features can be seen as externalities influencing behaviours and practices. In other words, the design of flats, building and communal service facilities (such as laundrettes and waste disposal areas) can impact positively or negatively when deciding to undertake an action that could help to preserve natural resources or local green areas. Also, the physical infrastructure of the site can influence the social interactions among residents and the contact with the natural environment. On this view, Barker (2008) points out that physical structures can influence behaviour structures (behavioural patterned arrangements) which in turn can influence the capacity of people to make free choices within their socio-physical contexts.

The Natural Environment and Its Impact on High-Rise Structures

Although there is a vast body of the literature about eco-architectural designs and construction development techniques about high-rise buildings for residential purposes, there is still very little research about environmental elements affecting high-rise structures such as the geographical location and the climate (e.g. Iwata and Oguchi 2009; Xu et al. 2011). Even much less research has been undertaken about the impacts that these two environmental factors have on their residents (e.g. Al-Kodmany and Ali 2013). With this review, it seems that the tendency of constructing more sustainable residential buildings is growing stronger in this century (e.g. Bojić and Yik 2007; Vaziri and Kellier 2009; Zhang et al. 2009). However, a thorough scrutiny on this topic failed to find research about the tripartite relationship among landscape features, climate and high-rise structures, particularly in Australia and Mexico where this research took place. Overtime, researchers seem to have become more interested in studying the buildings' infrastructure as well as the impacts on residents' behaviours and practices soon after residential high-rise buildings have been affected by natural phenomena inherent to each geographical location. The literature on this topic has pointed out that there are two main environmental phenomena pertaining to the geographical location: heatwaves (White-Newsome et al. 2011) and earthquakes (e.g. Bangash 2011; Cogurcu 2015; Peng-Xuan et al. 2014; Saatcioglu et al. 2013; Tempesta et al. 2013; Yuxin et al. 2009). Based on sources cited for this topic, it is clearly evident that earthquakes are the most studied natural phenomena that have affected residential high-rise buildings around the world.

The effects of earthquakes on high-rise public housing can range from the unfortunate loss of infrastructure and residents' lives to the slow deterioration of communal facilities caused by cyclical aftershocks or minor earthquakes during the buildings' lifetime (Chiu and Chi 2013). These effects can impact indirectly on the execution of practices for conservation; for example, the recycling facilities can be damaged or destroyed, and waste collection systems disrupted temporally, implying more time and effort from residents to dispose of their wastes (UNEP 1995). Also, water, electricity and natural gas systems damaged by earthquakes in and out of urban infrastructures (Adachi and Ellingwood 2008) might take weeks to be restored, meaning that valuable natural resources could be lost as the pipes can be broken underground or inside walls. Heatwaves, on the other hand, have been scarcely researched, and only two recent empirical studies (e.g. Kim and Ryu 2015; White-Newsome et al. 2011) have reported some effects on residents living in high-rise structures. Although heatwaves do not have the same catastrophic and long term impacts as earthquakes, they certainly have the potential to dangerously affect residents in vulnerable situations, such as the elderly and people with disabilities (White-Newsome et al. 2011). The empirical study undertaken by Kim and Ryu (2015) reports that during summer time there are a considerable number of emergency calls from residents living in high-rise and low-rise structures which were built in particular geographical locations within or next to densely urbanized areas. According to both authors, these phenomena usually occur when the temperature of the buildings tend to rise dramatically during summer time because the orientation of the buildings' surface tend to be exposed to direct solar radiation for long periods of time. Previous empirical studies undertaken by Persson et al. (2006) and Cheung et al. (2005) showed that the orientation factor can severely impact the temperature of the apartments and the energy consumption from residents in order to be either cool in summer, or warm in winter. Persson et al. (2006) work focus on the designs and materials of the windows of the apartments and describes them as fundamental elements for temperature management indoors. Also, Cheung et al. (2005) study focuses more on the elements that contribute to the insulation of the building (the envelope design) as a passive way to save energy.

The work of White-Newsome et al. (2011) revealed that heatwaves can force residents to modify their practices by using more resources, such as water and electricity, and other actions to cool down their homes. For example, some residents can make physical adaptations to their apartments, using fans and/or air conditioners, taking one or more showers a day, going to the ground floor, and as a last option, leaving their apartments (White-Newsome et al. 2011). What this tells us is that the effect of heatwaves might be a strong impediment for residents to undertake actions for conservation of water and energy, as well as those who have acquired a practice for conservation already. In this regard, Eliasson (2000, in Kim and Ryu 2015, p. 192) points out that “climatic knowledge has very low impact in urban design and planning” because of institutional barriers, conflict of interest of developers or stakeholders and other multiple factors.

Climate and Geology of Mexico City

Mexico City is situated 2,250 m (7,380 feet) above the sea level with climates ranging from the subtropical highland to the alpine tundra with moderate winter temperatures fluctuating from 0° to 15°, and mild summer temperatures ranging in average from 15° to 34° (Jáuregui 2000; Park and Allaby 2013). After the Second World War, Mexico City’s natural environments were severely degraded and polluted due to rapid economic development, and the growth of the population mainly in poor neighbourhoods on the outskirts of the City (Conde and Ospina 2012; Jáuregui 2005). In general terms, Mexico City has mild weather, but climate change and regional environmental depletion are believed to be the main reasons of short periods of extreme weather such as electrical storms, flash flooding, and heatwaves (Conde and Ospina 2012). An exhaustive scrutiny of the literature was unsuccessful in finding reports of extreme climate events affecting Tlatelolco’s infrastructure or residents’ practices for conservation. Only some online media reports revealed that flash flooding events can disrupt traffic within and outside the site (e.g. Hernandez 2015; Zalazar 2015) but with no serious impact on the site’s infrastructure or risks to the well-being of residents.

Mexico City is located in the southern part of the North American tectonic plate, very close to the joining point (subduction zone) with the Cocos plate on the Pacific Ocean and the Caribbean plate in which convergent boundaries cause irregular distribution of the seismic activity, slow slip movements, and non-volcanic earthquakes and tremors (Kostoglodov et al. 2003; Manea et al. 2013; Payero 2008). Therefore, the city is considered to be in an earthquake prone location which increases the vulnerability of older high-rise structures of being seriously damaged, and therefore, putting residents at risk (Brouwer 2003). Although, Mexico City has historically been stricken by earthquakes (Garcia and Suarez 2001; Pereyra 2015) the 8.1 magnitude earthquake in 1985 seriously hit the Tlatelolco high-rise public housing, knocking down some its high-rise towers and killing hundreds of residents, and injuring thousands more on site (Gunn 2012; The Red Cross 1986; Walker 2013). Because of the magnitude this natural phenomenon, there is already a vast body of the literature (e.g. Cassaro and Martínez 1987; Esteva 2014; Monsiváis 2005; Santos-Reyes et al. 2014) about its impact on Tlatelolco high-rise public housing. After the catastrophic earthquake hit Mexico City in 1985, some researchers commenced exploring more deeply its geographical location and the geology of the land (e.g. Chavez et al. 1994; Murillo 1995) as well as the psychological effects of this natural phenomenon on residents (e.g. Galindo 2010). However, very little research has been undertaken about the long term effects of earthquakes on the buildings' infrastructure or communal facilities in Tlatelolco and how these might impact on residents.

Climate and Geology of the City of Melbourne

Melbourne's moderate oceanic climate is well known for the variable weather conditions throughout the entire year due to its location on the borderline with hot inland areas and the cold southern ocean (Sturman and Tapper 2006). However, the encounter between these two climates is responsible for all sorts of severe weather conditions such as thunderstorms, hail, powerful gales, and heavy rain (Linacre and Geerts 1997; Sturman and Tapper 2006). Moreover, the merging of these climates can produce several cold fronts even during the hot summer days in the State of Victoria (Sturman and Tapper 2006). The lowest temperatures in Melbourne can range on average between 1.1° and 6.7° in winter time, and reach as high as 45.6° in summer time (Australian Bureau of Meteorology 2015). Contrary to Mexico City's location, the City of Melbourne is located towards the centre of the Indo-Australian tectonic plate, away from volatile seismic subduction zones, which gives more stability to the region (Keep and Schellart 2012; Young 2011). However, the state of Victoria has been hit by significant earthquakes in the past, ranging from 5.0 to 5.7 in magnitude, but usually, the epicentres are located away from the City of Melbourne (Geoscience Australia 2015). Although this city has historically been hit by minor tremors, usually derived from earthquakes inland, there has been no severe damage to urban infrastructure or human casualties reported (e.g. Gregory 2009; Hingston and Chisholm 2014; Pountney 2000). With a thorough review of the literature, and scrutinized reports from Geoscience Australia (2015); it appears that earthquakes in the City of Melbourne do not represent a threat to Collingwood's infrastructure or residents' lives. Therefore, it can be assumed that earthquakes do not have a significant influence on residents' pro-environmental practices.

Heatwaves in Australia

During the Australian summer, extreme weather conditions, such as heatwaves, are not unusual, although, expert Australian meteorologists (e.g. Plummer et al. 2013) have pointed out that heatwaves are becoming longer or atypical due to delay of the Australian monsoon and the slowing down of the weather system over the continent. Although there is not a unified definition of a heatwave within the literature, it can be defined as periods of at least 'three days and two nights' of hot weather that might be accompanied by high humidity especially in countries with oceanic climates like Australia (Meehl and Tebaldi 2004; Parker et al. 2014). Moreover, heatwaves are a distressing issue for a wide range of the population because of "the impacts that these events have on human health, activities, and on the natural environments" (Smith et al. 2013, p. 811). In Australia, only one empirical study undertaken by Farbotko and Waitt (2011) and some media reports (e.g. Adler 2009; Cook 2014; Dow 2015) have highlighted the effects of heatwaves on residents living in public housing around the City of Melbourne. Heatwaves in Australia can be lethal for those people living in very vulnerable conditions in high-rise public housing contexts as in 2014 one fatality was reported due to the extreme heat generated in the apartment of the victim (Cook 2014). Farbotko and Waitt's (2011) study confirms that vulnerable residents, such as the elderly and people with disabilities living alone, are the most at risk of suffering heat distress. Their study also showed that during the heatwave period the likelihood of electrical blackouts due to the over-use of air conditioners, and residents had no option but to leave their apartments in order to cope with the high temperatures. This phenomenon is occurring more often in Melbourne, and people are forced more frequently to spend some nights in open spaces. For example, it has been reported that residents living in public housing face even a much tougher situation as they have to spend some nights in nearby gardens and parks to escape the suffocating heat in their flats (Adler 2009). Additionally, Melbourne City Council have announced plans for evacuating workers and residents in cases of extreme heat and air-conditioner failure, allocating them in shadowed and cooler venues such as the Melbourne Cricket Ground, the Melbourne Town Hall and the Melbourne Exhibition and Convention Centre (Dow 2015).

The Social Context in High-Rise Public Housing

Traditionally high-rise public housing buildings have been commonly associated with difficult social contexts due to the social stigma that has been historically affixed to these urban contexts in western societies (Darcy 2013; Gifford 2007; Tinkler 2003). Moreover, social stigma not only has demonized these urban sites but also has had a deep psychological impact on residents' lives (Arthurson 2004; Yuen et al. 2006). Some studies have suggested that these social housing contexts are not suitable for families with young children (e.g. Costello 2005; Dubrow and Garbarino 1989) and other vulnerable people such as the elderly and single mothers with teenage children (Fuerst and Petty 1991; Ireland et al. 2003). Extensive literature (e.g. Fagan et al. 2006; Fuerst and Petty 1991; Ireland et al. 2003; Pacione 1984; Spence 1993; Yuen et al. 2006) have highlighted that high-rise public housing sites around the world still deal with three main deviant behaviours or practices: drug dealing, vandalism and violence.

Poverty and diverse social problems have been the common themes which have been characterized affecting the inhabitants of high-rise public housing. Therefore, there has been considerable interest in exploring these difficult contexts; and extensive empirical research (e.g. Ireland et al. 2003; Pacione 1984; Townsley et al. 2014; Weatherburn et al. 1999) and non-empirical research (e.g. Arthurson 2008; Costello 2005; Dalton and Rowe 2004; Fagan et al. 2006; Fuerst and Petty 1991;

Gifford 2007; Spence 1993) have focused on the causes that contribute to the exacerbation of deviant behaviours in high-rise public housing. The literature revealed that drug trading (Dalton and Rowe 2004; Fagan et al. 2006), vandalism (Pacione 1984; Weatherburn et al. 1999), and crime involving violence (Costello 2005; Darcy 2013; Ireland et al. 2003; Spence 1993; Townsley et al. 2014) appeared to be the most prevalent deviant behaviours in these urban settings affecting socialization outdoors and also polluting and damaging local greeneries around the sites. However, little attention has been paid to how these types of behaviours have impacted on resident's engagement with pro-environmental practices indoors and outdoors.

Main Psychosocial Factors to Consider for This Study

This work will focus on the main three ontological assumptions of reality; however, it is important to acknowledge the role that some psychosocial factors play on people's practices for conservation. Acknowledging the role of psychosocial factors in this work is necessary in order to holistically understand why pro-environmental practices can or cannot be undertaken. For many years, researchers within the psychological (e.g. Duerden and Witt 2010; Gifford 2014; Howell 2013; Whitmarsh and O'Neill 2010), behavioural (e.g. Barr 2007; Clark et al. 2003; Csutora 2012; Hargreaves 2011; Lucas et al. 2008) and educational areas (e.g. Hager 2011; Hassan et al. 2009; Kopnina 2014; Rodriguez-Barreiro et al. 2013) have tried to explain the rationale of how people do or do not engage in pro-environmental practices. Due to their different areas of knowledge and backgrounds, most researchers have tried to explain these factors from their own perspectives. For instance, marketing and management scientists (e.g. Hargreaves 2011; Kip Viscusi et al. 2011; Swami et al. 2011) have investigated the external factors role that influences on people's choices, such as the price of a product, policy implementation, level of income, and other socioeconomic characteristics directly related to people's practices.

Psychologists, on the other hand, tend to explore psychosocial factors related to this type of behaviour such as values, beliefs, attitudes, motivations (e.g. Bamber and Moser 2007; De Groot and Steg 2008, 2009; Kaiser et al. 1999; Nordlund and Garvill 2002). A thorough literature review of several behavioural models (e.g. Ajzen 1991; Grob 1995; Hines et al. 1987; Kollmuss and Agyeman 2002; Stern 2000) and more recent derived studies related to pro-environmental behaviours (e.g. Blok et al. 2014; Nisbet and Gick 2008; Shove 2010) led me to identify three main groups of factors that may influence practices for conservation: (a) external factors, (b) internal factors and (c) demographic factors. Within the literature, several examples can be found which show specific demographic factors (e.g. Garcia et al. 2013; Larson et al. 2011; López-Mosquera et al. 2015), and internal-psychological factors (e.g. Edgerton et al. 2007; Gifford 2014; Wener and Carmalt 2006) influencing pro-environmental behaviours. However, in this work, these factors will not be the main focus as they cannot be ontologically assumed to exist or emerge from immediate realities. Nevertheless, it is important to acknowledge them in order to have an integral understanding of how these factors influence pro-environmental practices. For example, in the area of psychology, there are many factors that influence human behaviours; but within the pro-environmental behaviour literature (e.g. Biel and Thøgersen 2007; Blok et al. 2014; De Groot and Steg 2008, 2009; Geller 1995; Glicken 1998; Hager 2011; Howell 2013; Karp 1996; Koger and Scott 2007; Olli et al. 2001; Ross 2002; Stern 2000; Stern et al. 1999; Thøgersen 2006, 2009), the following common internal factors were identified: (a) social norms, (b) cognitive factors and (c) affective factors. Also, there are several demographic factors that can influence pro-environmental practices, but the most common found within the literature were: age, income, gender and education.

Theoretical Framework: Site Ontology and Positioning Theory

In this study, positioning theory will be the main theoretical framework of analysis as it explores how the social phenomena are developed within specific socio-material contexts and how meanings are constructed from them. This theory is strongly related with the domain social constructionism as it deals with external socio-physical elements and the wide range of multiple connections and relationships among them (Harel and Papert 1991). Social constructionism, in this regard, points out that social phenomena are produced within and through conversations and conversation-like events and activities (Harré and van Lagenhove 1999; Lock and Strong 2010). In other words, the constructive base of positioning theory focuses on the socio-physical contexts rather than individual cognitive processes. This research aims to contribute to the understanding of the social phenomena of high-rise sites' architectural design and features influencing the residents' engagements with pro-environmental practices. In order to start exploring this phenomenon, I will pose a basic ontological question: What entities exist or can be said to exist influencing practices for conservation? This question, however, might generate tensions with cognitivist views, because in a strict sense, constructionist approaches should not deal with ontological assumptions (Korobov 2010). Nevertheless, this study does not look at cognitive processes of how thought is generated by the participants but rather how discourse and context jointly construct meaning.

What motivated me to undertake this research was my own ontology derived from the previous experiences of being a resident of high-rise public housing in Mexico City from 1991 to 1993. Multiple lived experiences on site allowed me to have a clear understanding of what it meant to live in a high-rise public housing context and what possible realities were derived from it. Therefore, my ontological assumption was based on three main existing elements that compose residents' general reality: people, infrastructure and the natural environment. Hence, there was an imperative need of finding suitable ontological term that aligned with the selected theoretical framework for this study. After thorough scrutiny and understanding of the relationship between being and reality, the term ‘site ontology’ proposed by Theodore Schatzky suggests that the social phenomena can be explored and deconstructed by also examining the sites where humans exist and thrive. Schatzki strongly supports the idea that “the contexts involved, called ‘sites’, are context of which some of what exists or occurs within them, are inherently parts” (Schatzki 2003, p. 176). As I aligned my ontological assumptions with Schatzky’s site-ontology, there are epistemological implications that should be taken into consideration in order to give coherence and logic to how meaning is produced or co-constructed. Firstly, it proposes to deconstruct the phenomenon under study by social events delimiting the activities that compose them. Secondly, it uncovers the possible arrangements and links that exist among the social events that compose such phenomenon. Thirdly, it reveals further connections with a broader context or networks. And finally, it traces the links of human and non-human action to reveal as many ways of associations as possible that give harmonious and logical accounts to the phenomena and point out the existence of tensions, gaps or contradictions that might need further exploration (Schatzki 2003). As a whole, this whole process will allow me to reveal how knowledge is constructed from the existing realities (the ontological truths).

Positioning Theory

The constructionist approach taken for this study led me to choose positioning theory as the most suitable theoretical framework of analysis where residents socially constructed common meanings of reality through discursive practices. The amalgamation between practice and discourse brings originality to this work as it tries to explore the connections between residents’ agency and the objective ontological realities of the sites which can be reflected in social discourse (Harré and van Lagenhove 1999). Also, Positioning Theory is aligned with the selected methodology that complies with the ontological precepts of site ontology and its epistemological implications proposed by Schatzki (2003). But, what is Positioning Theory? Davies and Harre (1990, p. 62) defined Positioning Theory as “a possibility in known forms of talk; position is what is created in and through talk and the speakers and hearers take themselves up as persons”. Harré and van Langenhove (1992, p. 2) add that the concept of “position is general enough to capture diversity, but precise enough to help to articulate the ‘ephemeral conditions’ that matter so much in social life”.

Positioning theory here will function as a guiding framework to understand how these residents approach their socio-physical context to undertake practices that benefit the environment. Also, I will refer to positioning theory to defragment and reconstruct residents narratives about other residents (talk about talks), in order to refer to the assignment of positions of the speakers within the discursive construction of their personal stories. Hence, these stories will make their practices comprehensible and definable as social acts (Harré and van Lagenhove 1999). The central ideas of position theory are to explain how the psychological phenomena are produced in social relations and how the multisource torrent of everyday life can be reconstructed into distinct episodes (Harré and van Lagenhove 1999; Ofreneo and Montiel 2010).

Social episodes of everyday life can be defined as a sequence of events (or happenings) in which two or more people engage according to some principles of unity or cultural value (Marez 2010). To understand the dynamics of social episodes, positioning theory looks at a mutually determinant triad composed of: (a) positions, (b) storylines, and (c) speech acts (Harré and van Lagenhove 1999). Positions are the moral locations that people take in a conversations based on the local system of rights, duties and obligations within a social episode (the local moral order). "The positions that people take in conversations are linked to story lines" (Ofreneo and Montiel 2010, p. 248). Storylines are patters of sequences of events that are often linked with socio-cultural narratives, however, storylines and positions are not freely constructed as they are directly derived from the individuals' contexts (Harré and van Lagenhove 1999). Finally, speech acts are those actions that are socially significant to a given situation and context which provide meaning to the unfolding conversations (Harré and Moghaddam 2003; Zelle 2009).

Methods

Based on the social characteristics of the participants, such as poor literacy and low socio economic conditions, it was decided that observations, field notes, and semi-structured interviews would be the best methods to obtain quality data during the fieldwork period. These non-numerical data were actively analysed and organized using the *Nvivo 10 application* which helped me to classify, sort and arrange the material obtained, and examine relationships across all the information obtained. I also used this software to find patterns and themes and to locate valuable evidence to support my arguments for this study. Ethical considerations were also taken into account in order to protect the dignity and privacy of the participants as well as the safety of the researcher. From the 32 semi-structured interviews carried out in both sites with residents and ex-residents, I will only focus on four fragments of individual interviews in this study. For space limitations, only one fragment of each testimony will be displayed as evidence. Two fragments are from the Collingwood high-rise public housing site in Melbourne, Australia, and the other two fragments are from the Tlatelolco high-rise public housing site in Mexico City, Mexico.

Practices for conservation were narrated in a retrospective account by the participants, which fulfils the requirements to be treated as separate case studies. In this regard, Ragin and Becker (1992) point out that a case study needs to satisfy some requirements: Firstly, these four cases were identified as established cases during development of the research process because they were physically bounded to a specific reality in space and time. Secondly, these four cases were gradually constructed with empirical evidence obtained with semi structured interviews, field notes and pictures as observations. They eventually took shape during the course of the research. Finally, Raging and Becker (1992) claim that cases are conventions because they are seen as "general theoretical constructs that structure ways of seeing social life".

Procedure

Firstly, I will be looking at order positioning where residents locate themselves and others within a moral and physical space by using several story-lines (Harré and van Lagenhove 1999). Secondly, as a consequence of first order positioning, I will link it with performative and accountive positioning, where people position themselves and others within a descriptive story-line (Harré and van Lagenhove 1999). The residents' speech acts, contained within story-lines, can have psychosocial influences on persuading or convincing others to perform certain practices. Or, in the words of Harré and van Lagenhove (1999, p. 397), "have immediate perlocutionary effect". Then, the residents will account for their previous positions at the time of performing a particular practice. Thirdly, I will discuss how residents' positioning is tied to their given local moral orders and the physical space at the time of performing pro-environmental practices (Harré and van Lagenhove 1999). Finally, deliberate self-positioning will allow me to explain residents' agencies, points of view, or biographical details of how the buildings' infrastructural design has influenced their practices for conservation (Harré and van Lagenhove 1999).

In the following section, I will deal with experiences that I had with residents and ex-residents, who, regardless of their cultural background and multiple social constraints, have sustained close emotional bonds and social connections with the high-rise communities. At the end of the stories, I will link my interpretations and insights from residents to positioning theory in order to start acknowledging the awareness that residents have developed about the care of natural surroundings up to the point of influencing others to pro-environmental practices. These particular stories were enriched with ethnographic methods such as field notes, and pictures in order to construct a more tangible notion of the multiple realities that exist in these communities. After the analysis of the data, I concluded that four of the individual fragments presented in this study played a crucial role in revealing deep insights and themes about the influences of the social relations among residents, and their interactions with the physical and natural contexts. As a result of this, the analysis of the data focused on the narratives of those residents who were 'talking and doing things' and could identify events, facts and people that contributed to recognizing the external elements or sources for practices for conservation. In the following table (Table 1) the main pronouns were highlighted in order to see how participants took their own moral positions.

Table 1 Storyline analysis using positioning theory

User of storyline	Storyline	Position of self ('I')	Position of others ('you/them')	Impact on pro-environmental practices	Storyline category	Field note or picture
Neil (Australia)	"**I** will give a perfect example of isolation on my floor. **I** have been on my floor for about eight years, and just recently **I** met a person for the first time…what **we** ended up really is with people just living in their own little box, and [almost] no one ventures out of their box..."	By using the pronoun **I** he first positioned himself as a resident who has the right to express an opinion about the isolating effect that the buildings and apartments' infrastructure have on residents.	He indirectly positioned the community (**we**) and himself (**I**) as being influenced by the infrastructure of buildings and apartments as they promote isolation among residents.	Lack of contact with surrounding green areas.	The isolating effect that the buildings' infrastructure and design have on residents.	 Building in Collingwood high-rise public housing. Source: compiled for this study: 6-11-2013.
Victorino (Australia)	"Nah! **They** are too hot! … [I live on the floor] nine, in the middle. **I** get sun in the mornings but in the afternoons **it** gets terribly hot… [I use] a little fan, everybody should have an air conditioner..."	By using the pronoun **I**, he positions himself into the physical context of the interior of his apartment. This experiential account gave him the right to express an opinion about the temperature due the orientation of the building.	He directly positioned his appartment as not comfortable by using the pronouns **they** and **it.**	Increase the unnecessary use of electricity using fans and air conditioners.	Buildings' design and orientation effects on the apartments' temperature and energy consumption due to the local weather.	 Orientation of the buildings impacts directly on the increase of the temperature inside apartments. Source: compiled for this study: 27-06-2013

(continued)

Table 1 (continued)

User of storyline	Storyline	Position of self (‘I’)	Position of others (‘you/them’)	Impact on pro-environmental practices	Storyline category	Field note or picture
Ceci (Mexico)	“Yes, it is true. The security and cleanliness as well as the maintenance of the complex have decayed…lots of **people** moved in after the 1985 earthquake and the people seem to be careless about this issue. **I** think that **the local government** has not given us support in this regard...”	By using the pronoun **I**, she acquired the right to directly position the local government and residents who moved in after the 1985 earthquake as responsible of the insecurity and the lack of cleanliness on the site.	In this case, she only used the nouns of ‘local government and people’ to assign a specific moral attribute: irresponsible.	Local greeneries can be affected by the lack of maintenance from the government and residents’ care. Therefore, these may have a direct affect on the engagement of outdoor practices for residents.	Social and infrastructural impacts on residents.	Field note: There are many parts/zones of the site that need maintenance such as gardens and buildings. I felt somewhat saddened by those images. I wondered how these factors influence the mental well-being of residents in the long term. Field note on 12-12-2013.
Licha (Mexico)	“**I** used to live on the ground floor, and **I** used to have the lights of the kitchen on all day because it was very dark. [Now] **I** do not need to turn on the lights until very late in the afternoon because **I** live in a top floor...”	By using the pronoun **I**, in first order positioning, she gives an experiential account about how the location of the building’s floors can make a big difference on using and saving energy in the apartments.	She indirectly positioned the physical position of the apartment as the cause of overusing or saving electricity by using the pronoun **it**.	Effects on energy consumption practices.	Buildings’ design and orientation and their impact on energy consumption.	 Facade’s orientation in a building in the Tlatelolco site. Source: compiled for this study, 21-11-2013.

Discussion

This study showed the factors derived from architectural features (or physical elements) in high-rise public housing in Australia and Mexico that impacted on the execution of pro-environmental practices. I actively used first and second order positioning to help and encourage participants to produce deep accounts of which accounts emerged from diverse forms of positioning. Firstly, it was clearly noticed that the discursive production related to the execution of practice for conservation in both countries was concentrated more on the explicit and deliberate positions towards the buildings infrastructure or the local district to assign a moral attribute of inhibiting pro-environmental practices. However, the architectural designs or physical features of the buildings and apartments in both sites did not appear to be a total impediment on residents' pro-environmental practices. Nevertheless, other residents, the local governments and non-residents, did impact on the execution of some pro-environmental practices such as gardening or outdoor activities in green spaces. Secondly, some residents use moral traits to indirectly position the buildings' design or the local governments as responsible for the lack of maintenance of the entire site and overuse of natural resources such as electricity.

Explicit and deliberate positioning. These two forms of positioning were the most consistent across the two sites. Generally, many residents explicitly positioned themselves with the right to directly position the buildings' design and infrastructure as well as the local authorities as responsable for discouraging the execution of pro-environmental practices. Additionally, an explicit position came along with a deliberate position; although, sometimes either explicit or deliberate positioning was the only form contained in an episode. Deliberate positioning showed a constant pattern when participants positioned the buildings' design or infrastructure or the local governments in terms of agency or when referring to specific actions that were or were not performed. These two forms of positioning employed the subject pronoun 'it' when talking about the buildings, apartments and the local government or environmental events, such as heatwaves and earthquakes.

Indirect positioning of the physical entities (the buildings) and local governments. Descriptive storylines were evidenced as pattern of indirect positioning. Several episodes with a specific pronoun or reference, such as the pronoun 'it', were widely used; and therefore, mental, physical, or moral traits were used to place the apartments, buildings and sites with a specific position. Often, moral traits where the common pattern for using indirect positioning, and as it happened with deliberate and explicit positioning, the final intention of using indirect position was to assign or labelling the physical features of the sites as responsible for not make it easier for resident to perform pro-environmental practices.

The self-positioning and mutual positioning of residents. Although in the four examples showed in this paper did no show this type of positioning, self-positioning was the third consistent form of position that residents showed during several episodes in both sites in several interviews for this study. With this form of positioning, residents were acquiring or sharing moral responsibility of the infrastructural and environmental depletion. Usually, these episodes were highly evocative within time and place in order to give a clear picture of the situation. Further, this form of positioning allowed them to express feelings and emotions which, in turn, allowed me to identify the perlocutionary force of some utterances contained within the participants' storylines.

Conclusion

This study explored how both high-rise public housing site's infrastructure and design influenced residents' practices for conservation in two different geographical locations. Although both sites shared some communalities, such as the poor social conditions and difficult social contexts, these were not detrimental for undertaking practices for conservation. Also, the geographical location per se did not play a major role on fostering or inhibiting residents' pro-environmental practices. Positioning theory allowed to analyse and understand residents social episodes based on their own experiential perspectives. Residents produced descriptive storylines which showed how the buildings, local weather, and local geology can directly or indirectly have an effect on certain practices.

The infrastructural design of the buildings contributed to resident's isolation within their apartments impacting negatively on social and environmental connectedness. For example, simple features of the buildings' designs in both sites, such as orientation towards the sunlight, can severely impact on the increase of the apartment's temperature and electricity consumption. Additionally, the deficiency of services provided and maintenance of the sites seems to also contribute to residents' lack of engagement with surrounding greeneries as these could produce negative feelings in residents. Another issue that was noted is that the buildings' designs were not suitable for the local weather and geology of Melbourne and Mexico City. For example, it was inferred from residents' fragments that the harsh weather of Melbourne, and the unstable geology of Mexico City, made the buildings not entirely suitable for residental ocupancy. High temperatures in Collingwood seemed to be the most significant environmental concern as residents may consume more electricity in order to cope with the hot days during the Australian summer.

The effects of earthquakes in Tlatelolco seemed to have long term effects in changing the social fabric of the site as well as the quality of the services provided such as maintenance and cleaning services. Finally, this study has also demonstrated that these factors, or external realities, should be taken into consideration for future building planning and design in order to complement and improve environmental performance of modern high-risepublic housing to be built in the future. However, further research is recommended for very specific pro-environmental practices such as water conservation, waste recycling and disposal as well as other practices that contribute to the local environmental improvement.

References

Adachi T, Ellingwood BR (2008) Serviceability of earthquake-damaged water systems: effects of electrical power availability and power backup systems on system vulnerability. Reliab Eng Syst Saf 93:78–88. doi:10.1016/j.ress.2006.10.014

Adler J (2009) High-rise hothouses; state quibbles on units aircon plea, p 001. Retrieved from https://ezp.lib.unimelb.edu.au/login?url=https://search.ebscohost.com/login.aspx?direct=true&db=edsnbk&AN=12C27A6554231338&site=eds-live&scope=site

Ajzen I (1991) The theory of planned behavior. Organ Behav Hum Decis Process 50(2):179–211. doi:10.1016/0749-5978(91)90020-T

Al-Kodmany K, Ali MM (2013) The future of the city: tall buildings and urban design. WIT Press, Southampton, Boston

Arthurson K (2004) From stigma to demolition: Australian debates about housing and social exclusion. J Housing Built Environ 19(3):255–270

Arthurson K (2008) Australian public housing and the diverse histories of social mix. J Urban Hist 3:484

Australian Bureau of Meteorology (2015) Climate statistics for Australian locations. Retrieved 06 July 2015

Barker C (2008) Cultural studies: theory and practice. Sage, Los Angeles

Bamber S, Moser G (2007) Twenty years after Hines, Hungerford, and Tomera: a new meta-analysis of psycho-social determinants of pro-environmental behaviour. J Environ Psychol 27:14–25

Bangash MYH (2011) Earthquake resistant buildings [electronic resource]: dynamic analyses, numerical computations, codified methods, case studies and examples. Springer, Berlin, New York

Barr S (2007) Factors influencing environmental attitudes and behaviors: a U.K. case study of household waste management. Environ Behav 39(4):435–473. doi:10.1177/0013916505283421

Biel A, Thøgersen J (2007) Activation of social norms in social dilemmas: a review of the evidence and reflections on the implications for environmental behaviour. J Econ Psychol 28 (1):93–112. doi:10.1016/j.joep.2006.03.003

Blok V, Wesselink R, Studynka O, Kemp R (2014) Encouraging sustainability in the workplace: a survey on the pro-environmental behaviour of university employees. J Cleaner Prod 106 (1):55–67. doi:10.1016/j.jclepro.2014.07.063

Bojić M, Yik F (2007) Application of advanced glazing to high-rise residential buildings in Hong Kong. Build Environ 42(2):820–828. doi:10.1016/j.buildenv.2005.09.021

Brouwer G (2003) Quake-prone Mexico City tops off record skyscraper. Civ Eng 73(2):16

Cassaro MA, Martínez RE (1987) The Mexico earthquakes, 1985: factors involved and lessons learned: proceedings of the international conference, Camino Real Hotel, Mexico City, Mexico, 19–21 Sept 1986. American Society of Civil Engineers, New York

Chavez GF, Sanchez SF, Campillo M, Yves P (1994) El terremoto de Michoacán de septiembre de 1985: efectos de fuente, trayecto y sitio. Fisica de la Tierra 6:157–200

Cheung CK, Fuller RJ, Luther MB (2005) Energy-efficient envelope design for high-rise apartments. Energy Build 37(1):37–48. doi:10.1016/j.enbuild.2004.05.002

Chiu C-K, Chi K-N (2013) Analysis of lifetime losses of low-rise reinforced concrete buildings attacked by corrosion and earthquakes using a novel method. Struct Infrastruct Eng Maint Manag Life-Cycle Des Perform 9(12):1225–1239. doi:10.1080/15732479.2012.681790

Clark CF, Kotchen MJ, Moore MR (2003) Internal and external influences on pro-environmental behavior: Participation in a green electricity program. J Environ Psychol 23(3):237–246. doi:10.1016/s0272-4944(02)00105-6

Cogurcu MT (2015) Construction and design defects in the residential buildings and observed earthquake damage types in Turkey. Nat Hazards Earth Syst Sci 15(4):931–945. doi:10.5194/nhess-15-931-2015

Conde C, Ospina N (2012) Historias del Clima de la Ciudad de Mexico: Efectos observadosy perspectivas. Retrieved from http://www.cvcccm.unam.mx/documents/libros_cvcccm/Inf_Final_Final%20Final%20HC_Conde.pdf

Cook H (2014) Airconditioning plea for public housing tenants. Home Affairs. The Age. http://www.theage.com.au/victoria/airconditioning-plea-for-public-housing-tenants-20140208-328ul.html

Costello L (2005) From prisons to penthouses: the changing images of high-rise living in melbourne. Hous Stud 20(1):49–62. doi:10.1080/0267303042000308723

Csutora M (2012) One more awareness gap? The behaviour-impact gap problem. J Consum Policy 35(1):145–163

Dalton T, Rowe J (2004) A wasting resource: public housing and drug use in inner-city Melbourne. Hous Stud 19(2):229–244. doi:http://www.tandfonline.com/loi/chos20

Darcy M (2013) From high-rise projects to suburban estates: public tenants and the globalised discourse of deconcentration. Cities 35:365–372. doi:10.1016/j.cities.2012.10.010

Davies B, Harre R (1990) Positioning: the discursive production of selves. Social Behav 20(1): 43–63

De Garay G (2004) Modernidad habitada: Multifamiliar Miguel Aleman, Ciudad de Mexico, 1949–1999. Instituto Mora, Mexico

De Groot JIM, Steg L (2008) Value orientations to explain beliefs related to environmental significant behavior. J Environ Behav 40(3):330–354

De Groot JIM, Steg L (2009) Mean or green: which values can promote stable proenvironmental behavior? Conserv Lett 2(2):61–66

Dow A (2015) If Melbourne’s heat bowls you over, take refuge at the MCG, p 9. Retrieved from https://ezp.lib.unimelb.edu.au/login?url=https://search.ebscohost.com/login.aspx?direct=true&db=n5h&AN=SYD-6J8HNRFCWZOAJT338BB&site=eds-live&scope=site

Dubrow NF, Garbarino J (1989) Living in the war zone: mothers and young children in a public housing development. Child Welfare 68(1):3–20

Duerden MD, Witt PA (2010) The impact of direct and indirect experiences on the development of environmental knowledge, attitudes, and behavior. Environ Psychol 30(4):379–392

Edgerton E, Romice O, Spencer C (2007) Environmental psychology: putting research into practice. Newcastle, U.K. (ed.), p 350

Esteva G (2014) The new ‘what to do?’ How civil society is re-encountering itself in Mexico, from the 1985 earthquake reconstruction to the Zapatistas. NACLA Rep Am 3:58

Fagan J, Davies G, Holland J (2006) Paradox of the drug elimination program in New York City public housing. J Poverty Law Policy 13:415

Farbotko C, Waitt G (2011) Residential air-conditioning and climate change: voices of the vulnerable. Health Promot J Austral 22(4):S13–S16

Fuerst JS, Petty R (1991) High-rise housing for low income families. Publ Int 103:118–130

Galindo E (2010) Intervención de psicólogos de la UNAM Iztacala después de los sismos de 1985 en México. Retrieved from http://dspace.uevora.pt/rdpc/bitstream/10174/13116/1/Galindo%20(2010)%20Intervencion-de-psicologos-de-la-UNAM-sismos1985.pdf

Garcia V, Suarez G (2001) Los sismos en la historia de Mexico. CIESAS (ed), pp 281

Garcia X, Muro M, Ribas A, Llausàs A, Jeffrey P, Saurí D (2013) Attitudes and behaviours towards water conservation on the Mediterranean coast: the role of socio-demographic and place-attachment factors. Water Int 38(3):283–296. doi:10.1080/02508060.2013.794641

Geller ES (1995) Actively caring for the environment: an integration of behaviorism and humanism. Environ Behav 27(2):184–195. doi:10.1177/0013916595272004

Geoscience Australia (2015) Australian Government. Retrieved 06 July 2015, from http://www.ga.gov.au/earthquakes/list.do?isRegionSelected=true&region=Vic

Gifford R (2007) The consequences of living in high-rise buildings. Archit Sci Rev 50(1):2–16

Gifford (2014) Environmental psychology matters. Annu Rev Psychol 65:541–579. doi:10.1146/annurev-psych-010213-115048

Glicken J (1998) Environment and social values. Hum Ecol Risk Assess 4(4):779

Gregory P (2009) Tremors shake Melbourne's south-east. Sydney Morning Herald. Retrieved from http://www.smh.com.au/national/small-earthquakes-shake-melbournes-southeast-20090922-g0du.html

Grob A (1995) A structural model of environmental attitudes and behaviour. J Environ Psychol 15 (3):209–220

Gunn AM (1985) In: Rinard Hinga B (ed) Ring of fire: an encyclopedia of the Pafic Rim's earthquakes, Tsunamis, and Volcanoes, ABC-CLIO, LLC, Santa Barbara, California

Hager LD (2011) Tools for teaching cognitive psychology: using public service announcements for education on environmental sustainability. Teach Psychol 38(3):162–165. doi:10.1177/0098628311411784

Harel I, Papert S (1991) In: Harel I, Papert S (eds) Constructionism: research reports and essays, 1985–1990/by the Epistemology & Learning Research Group, the Media Laboratory, Massachusetts Institute of Technology. Ablex Publishing Corporation, Norwood

Hargreaves T (2011) Practice-ing behaviour change: applying social practice theory to pro-environmental behaviour change. J Consum Cult 11(1):79–99

Harré R, van Langenhove L (1992) Varieties of positioning. J Theory Soc Behav 20:393–407. doi:10.1111/j.1468-5914.1991.tb00203.x

Harré R, van Lagenhove L (1999) Positioning theory: moral contexts of intentional action. Malden/Blackwell, Oxford/Mass

Harré R, Moghaddam FM (2003) In: Harré R, Moghaddam FM (eds) The self and others: positioning individuals and groups in personal, political, and cultural contexts. Praeger, Westport

Hassan A, Osman K, Pudin S (2009) The adults non-formal environmental education (EE): a scenario in Sabah, Malaysia. Soc Behav Sci 1(1):2306–2311. doi:10.1016/j.sbspro.2009.01.405

Hayward D (1996) The reluctant landlords? A history of public housing in Australia. Urban Policy Res 14(1):5

Hernandez M (2015) Lluvia, granizo y viento afectan once delegaciones del D.F. Terra Noticias. Retrieved 08 July, 2015, from http://noticias.terra.com.mx/mexico/df/lluvia-granizo-y-viento-afecta-11-delegaciones-del-df,33984ac7447919fb028a9e5400ceee41mko8RCRD.html

Hines JM, Hungerford HR, Tomera AN (1987) Analysis and synthesis of research on responsible environmental behavior: a meta-analysis. J Environ Educ 18(2):1–8. doi:10.1080/00958964.1987.9943482

Hingston C, Chisholm C (2014) Magnitude 2.7 earthquake shakes up residents in Melbourne's outer east. The Age, Melbourne

Howell RA (2013) It's not (just) "the environment, stupid!" values, motivations, and routes to engagement of people adopting lower-carbon lifestyles. Environ Change 23(1):281–290

Ireland TO, Thornberry T, Loebe R (2003) Violence among adolescents living in public housing: a two-site analysis. Criminology and Public Policy 3(1):1–38. doi:10.1111/j.1745-9133.2003.tb00019.x

Iwata OH, Oguchi T (2009) Factors affecting late twentieth century land use patterns in Kamakura City, Japan. Geogr Res 47(2):175–191. doi:10.1111/j.1745-5871.2008.00559.x

Jáuregui E (2005) Possible impact of urbanization on the thermal climate of some large cities in México. Atmósfera 18(4):247–248

Jáuregui O (2000) El clima de la Ciudad de México. Universidad Nacional Autónoma de México, Instituto de Geografía

Kaiser FG, Wolfing S, Fuhrer U (1999) Environmental attitude and ecological behaviour. J Environ Psychol 19(1):1–19

Karp DG (1996) Values and their effect on pro-environmental behavior. Environ Behav 28 (1):111–133. doi:10.1177/0013916596281006

Keep M, Schellart WP (2012) Introduction to the thematic issue on the evolution and dynamics of the Indo-Australian plate. Aust J Earth Sci 59(6):807–808. doi:10.1080/08120099.2012.708360

Kim S, Ryu Y (2015) Describing the spatial patterns of heat vulnerability from urban design perspectives. Int J Sustain Dev World Ecol 22(3):189–200. doi:10.1080/13504509.2014.1003202

Kip Viscusi W, Huber J, Bell J (2011) Promoting recycling: private values, social norms, and economic incentives. Am Econ Rev 101(3):65–70

Koger SM, Scott BA (2007) Psychology and environmental sustainability: a call for integration. Teach Psychol 34(1):10–18. doi:10.1207/s15328023top3401_3

Kollmuss A, Agyeman J (2002) Mind the gap: why do people act environmentally and what are the barriers to pro-environmental behavior? Environ Educ Res 8(3):239–260. doi:10.1080/13504620220145401

Kopnina H (2014) Revisiting education for sustainable development (ESD): examining anthropocentric bias through the transition of environmental education to ESD. Sustain Dev 22(2):73–83. doi:10.1002/sd.529

Korobov N (2010) A discursive psychological approach to positioning. Qual Res Psychol 7 (3):263–277. doi:10.1080/14780880902822321

Kostoglodov V, Singh SK, Santiago, JA, Franco SI, Larson KM, Lowry AR, Bilham R (2003). A large silent earthquake in the Guerrero seismic gap, Mexico. Geophys Res Lett 30(15):1807. doi:10.1029/2003GL017219

Larson LR, Whiting JW, Green GT (2011) Exploring the influence of outdoor recreation participation on pro-environmental behaviour in a demographically diverse population. Local Environ 16(1):67–86. doi:10.1080/13549839.2010.548373

Linacre E, Geerts B (1997) Climates and weather explained: an introduction from a southern perspective. Retrieved from https://ezp.lib.unimelb.edu.au/login?url=https://search.ebscohost.com/login.aspx?direct=true&db=cat00006a&AN=melb.b5492887&site=eds-live&scope=site, http://site.ebrary.com.ezp.lib.unimelb.edu.au/lib/unimelb/Doc?id=10057321

Lock A, Strong T (2010) Social constructionism: sources and stirrings in theory and practice. Cambridge University Press, New York

López-Mosquera N, Lera-López F, Sánchez M (2015) Key factors to explain recycling, car use and environmentally responsible purchase behaviors: a comparative perspective. Resour Conserv Recycl 99:29–39. doi:10.1016/j.resconrec.2015.03.007

Lucas K, Brooks M, Darnton A, Jones JE (2008) Promoting pro-environmental behaviour: existing evidence and policy implications. Environ Sci Policy 11(5):456–466

Manea VC, Manea M, Ferrari L (2013) Review article: a geodynamical perspective on the subduction of Cocos and Rivera plates beneath Mexico and Central America. Tectonophysics 609:56–81. doi:10.1016/j.tecto.2012.12.039

Marez TMA (2010) La Unidad Habitacional Nonoalco Tlatelolco: Memoria y apropiacion del espacio urbano (Unpublish bachelor degree thesis). Social Anthropology Bacherlor Degree Thesis, Escuela Nacional de Antropologia e Historia (INAH)

Meehl GA, Tebaldi C (2004) More intense, more frequent, and longer lasting heat waves in the 21st Century. Science 305(5686):994–997. doi:10.1126/science.1098704

Monsiváis C (2005) No sin nosotros: los días del terremoto, 1985–2005/Carlos Monsiváis. Ediciones Era, México

Murillo JMM (1995) The 1985 Mexico earthquake. Revista Geofisica Colombiana 3:5–19

Nisbet EKL, Gick ML (2008) Can health psychology help the planet? Applying theory and models of health behaviour to environmental actions. J Can Psychol 49(4):296–303

Nordlund AM, Garvill J (2002) Value structures behind proenvironmental behavior. J Environ Behav 34(6):740–756

Ofreneo MAP, Montiel CJ (2010) Positioning theory as a discursive approach to understanding same-sex intimate violence. Asian J Soc Psychol 13(4):247–259

Olli E, Grendstade G, Wollebaek D (2001) Correlates of environmental behaviours: bringing back social context. Environ Behav 33(3):181–208

Pacione M (1984) Evaluating the quality of the residential environment in a high-rise public housing development. Appl Geogr 4:59–70. doi:10.1016/0143-6228(84)90005-5

Park C, Allaby M (2013) Köppen classification system. Oxford University Press

Parker TJ, Berry GJ, Reeder MJ (2014) The structure and evolution of heat waves in southeastern Australia. J Clim 27(15):5768–5785. doi:10.1175/JCLI-D-13-00740.1

Payero JS, Kostoglodov V, Mikumo T, Iglesias A, Perez-Campos X, Clayton RW (2008) Nonvolcanic tremor observed in the Mexican subduction zone. Geophys Res Lett 35(7):1–6. doi:10.1029/2007GL032877

Peng-Xuan D, Xiao-Qun Z, Ying L, Qing L (2014) Analysis of demand for the structure of earthquake-resistant and energy-saving buildings of the rural areas in Beijing. Study Civil Eng Archit 3:125–129

Pereyra LE (2015) Dos siglos de temblores. Retrieved 10 July 2015, from http://www2.ssn.unam.mx:8080/website/jsp/ICyT/8612/dos.htm

Persson M-L, Roos A, Wall M (2006) Influence of window size on the energy balance of low energy houses. Energy Build 38:181–188. doi:10.1016/j.enbuild.2005.05.006

Plummer N, Trewin B, Jones D (2013) What's causing Australia's heat wave? Retrieved 06 July 2015 from http://theconversation.com/whats-causing-australias-heat-wave-11628

Pountney M (2000) Tremor raises quake spectre. Herald Sun 027. Retrieved from https://ezp.lib.unimelb.edu.au/login?url=https://search.ebscohost.com/login.aspx?direct=true&db=edsnba&AN=0FCE88C3D1420C1A&site=eds-live&scope=site

Ragin CC, Becker HS (1992) What is a case?: exploring the foundations of social inquiry. Cambridge University Press, Cambridge

Rodriguez-Barreiro LM, Fernandez-Manzanal R, Serra LM, Carrasquer J, Murillo MB, Morales MJ, Del Valle J (2013) Approach to a causal model between attitudes and environmental behaviour: a graduate case study. J Clean Prod 48:116–125

Ross N (2002) Cognitive aspects of intergenerational change: mental models, cultural change, and environmental behavior among the Lacandon Maya of Southern Mexico. Hum Organ 2:125

Saatcioglu M, Palermo D, Ghobarah A, Mitchell D, Simpson R, Adebar P, Hong H (2013) Performance of reinforced concrete buildings during the 27 February 2010 Maule (Chile) earthquake. Can J Civ Eng 40(8):693–710. doi:10.1139/cjce-2012-0243

Santos-reyes J, Gouzeva T, Santos-reyes G (2014) Earthquake risk perception and Mexico City's public safety. Procedia Eng 84:662–671. doi:10.1016/j.proeng.2014.10.484

Schatzki TR (2003) A new societist social ontology. Philoso Soc Sci 33(2):174–202

Shove E (2010) Beyond the ABC: climate change policy and theories of social change. J Environ Plann 42(6):1273–1285. doi:10.1068/a42282

Smith TT, Zaitchik BF, Gohlke JM (2013) Heat waves in the United States: definitions, patterns and trends. Clim Change (3–4):811

Spence LH (1993) Rethinking the social role of public housing. Hous Policy Debate 4(3):355–368. doi:http://www.tandfonline.com/loi/rhpd20

Stern PC (2000) Toward a coherent theory of environmentally significant behavior. J Soc Issues 56 (3):407–424. doi:10.1111/0022-4537.00175

Stern PC, Dietz T, Abel T, Guagnano GA, Kalof L (1999) A Value-Belief-Norm theory of support for social movements: the case of environmentalism. Hum Ecol Rev 6(2):81–95

Sturman A, Tapper N (2006) The weather and climate of Australia and New Zealand, 2nd edn. Oxford University Press, Melbourne

Swami V, Chamorro-Premuzic T, Snelgar R, Furnham A (2011) Personality, individual differences, and demographic antecedents of self-reported household waste management behaviours. J Environ Psychol 31:21–36

Tempesta D, Curcio G, De Gennaro L, Ferrara M (2013) Long-term impact of earthquakes on sleep quality. PLoS ONE 8(2):1–9. doi:10.1371/journal.pone.0055936

The Red Cross (1986) Mexico one year after the earthquake. Int Rev Red Cross (0020-8604) 26 (254):294

Thøgersen J (2006) Norms for environmentally responsible behaviour: an extended taxonomy. J Environ Psychol 26:247–261. doi:10.1016/j.jenvp.2006.09.004

Thøgersen J (2009) The motivational roots of norms for environmentally responsible behavior. Basic Appl Soc Psychol 31(4):348–362. doi:10.1080/01973530903317144

Tinkler C (2003) Ghetto blast at high-rise flats. Sunday Herald Sun 6

Townsley M, Reid S, Reynald D, Rynne J, Hutchins B (2014) Risky facilities: analysis of crime concentration in high-rise buildings. Trends Issues Crime Crim Justice (476):461–480

UNEP (1995) Earthquake waste symposium Osaka, 12–13 June 1995: proceedings. Technical publication series: issue 2. Retrieved from http://www.unep.or.jp/ietc/Publications/TechPublications/TechPub-2/Earthquake_waste_symposium(TP2).pdf

Vaziri L, Kellier L (2009) Sustainability is possible for an urban high-rise: Florida Atlantic University solar roof case study. J Green Build 4(4):33–38

Walker L (2013) Earthquake: Civil Society in the Rubble of Tlatelolco, 1985–1988. Stanford University Press

Weatherburn D, Lind B, Ku S (1999) 'Hotbeds of Crime?' Crime and public housing in urban Sydney. Crime Delinq 45(2):256

Wener R, Carmalt H (2006) Environmental psychology and sustainability in high-rise structures. Technol Soc 28(1–2):157–167. doi:10.1016/j.techsoc.2005.10.016

Westphal (2003) Urban greening and social benefits: a study of empowerment outcomes. J Arboric 29(3):137–147

White-Newsome JL, Sánchez BN, Parker EA, Dvonch JT, Zhang Z, O'Neill MS (2011) Assessing heat-adaptive behaviors among older, urban-dwelling adults. Maturitas 70:85–91. doi:10.1016/j.maturitas.2011.06.015

Whitmarsh L, O'Neill S (2010) Green identity, green living? The role of pro-environmental self-identity in determining consistency across diverse pro-environmental behaviours. J Environ Psychol 30(3):305–314. doi:10.1016/j.jenvp.2010.01.003

Xu K, Kong C, Li J, Zhang L, Wu C (2011) Suitability evaluation of urban construction land based on geo-environmental factors of Hangzhou, China. Comput Geosci 37(8):992–1002. doi:10.1016/j.cageo.2011.03.006

Young E (2011) Earthquakes don't only occur near our neighbours Japan and New Zealand—they're common in Australia too. Retrieved from http://www.australiangeographic.com.au/topics/science-environment/2011/10/earthquakes-in-australia/

Yuen B, Yeh A, Appold SJ, Earl G, Ting J, Kwee LK (2006) High-rise living in singapore public housing. Urban Stud 43(3):583–600. doi:10.1080/00420980500533133

Yuxin P, Heqing Z, Ku BHB (2009) Guangzhou social workers in Yingxiu: a case study of social work intervention in the aftermath of the Sichuan 5.12 earthquake in China. China J Soc Work 2(3):151–163. doi:10.1080/17525090903211705

Zalazar L (2015) Inundacion en domicilio y vehiculos varados, consecuencia de fuerte lluvia. Retrieved 08 July 2015, from http://www.gbmradio.com/movil/ver.php?id=29918

Zelle G (2009) Exploring the application of positioning theory to the analysis of organisational change. Retrieved from http://ro.uow.edu.au/cgi/viewcontent.cgi?article=1614&context=commpapers

Zhang Y, Chen D, Chen L, Ashbolt S (2009) Potential for rainwater use in high-rise buildings in Australian cities. J Environ Manage 91(1):222–226. doi:10.1016/j.jenvman.2009.08.008

Municipal Solid Waste Management with Uncertainty Analysis for Urban Cities

Vinai Singh, R. M. Singh and N. R. Rawal

Abstract The problem of municipal solid waste management (MSWM) is a complex, multidisciplinary problem involving economic and technical aspects, regulatory normative constraints. The waste amount and management practices in different regions, nations and cities of the world also affect selection of management options. The prime aim of any solid wastes management plan is to ensure safe, efficient and economic collection, transportation, treatment and disposal of wastes, and to ensure that the system operates satisfactorily for the current as well as for the foreseeable future scenarios considering the pressures on resources such as land, finance and in addition intensifying environmental regulations. The selection of an optimum configuration of transportation routes, treatment technologies and disposal sites is prime importance in MSWM. In this paper, a mixed integer linear (MIL) optimization model has been developed considering uncertainty in waste quantity as well uncertainty in the unrecovered waste. The relationship between increase in waste quantity and increase in the total cost involved in waste management is investigated and found to be nonlinear.

Keywords Municipal solid waste management (MSWM) · Optimization formulation · Landfills · Fuzzy logic · Incinerator · Truck depot and uncertainty characterization

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Introduction

MSW is the major problem being faced by municipalities because it involves a huge expenditure and receives scant attention (Sharholy et al. 2007). Solid wastes are the result of urbanization and development and have emerged a serious threat to environment (Rawal and Singh 2013). It is not only a technical problem but it also is strongly influenced by political, legal, socio-cultural, environmental and economic factors, as well as available resources. Landfill has been widely used for municipal solid waste (MSW) disposal all over the world. In developing countries, it is considered as a reliable and a cost-effective method if adequate land is available (Gupta et al. 2007). MSW is normally disposed of in an open dump in many Indian cities and towns, which is not the proper way of disposal because such crude dumps pose environmental hazards causing ecological imbalances with respect to land, water and air pollution. Solid waste essentially managed by municipal authorities in India to keep neat and clean city (MoEF 2000). The consideration of complex interactions among collection and transportation systems and the facilities for waste management (waste reduction and disposal) is required for solid waste management. Municipal solid waste management (MSWM) is one of the major environmental problems of Indian cities (Sharholy et al. 2008).

The order of preference in terms of solid waste management strategies may be source reduction (selection of optimized waste source centres), reuse, or recycling, incineration with energy recovery or without energy recovery and landfill disposal (Peavey et al. 1985). The basic input for municipal solid waste (MSW) management is the solid waste quantities, which changes with respect to time at an increasing rate. Also the land available for the waste disposal facilities is increasingly becoming a scarce resource due to growing awareness about the associated environmental risk in the proximity to these facilities. In order to cope with the uncertainties involved in the solid waste quantities of waste-management facilities, an efficient and sustainable SWM plan is required (Srivastava and Nema 2011). Uncertainity plays an important role in most solid waste problems (Srivastava and Nema 2011; Rawal and Singh 2013).

In this paper, a mixed integer linear (MIL) optimization model has been developed considering uncertainty in waste quantity as well as uncertainty in the unrecovered waste with different values of possibility level of waste quantity. The mathematical formulation of the optimization model was solved using commercially available optimization software Lingo 10.0 (Lingo 10.0, User's Guide 2006).

Mixed Integer Linear Optimization Model for Municipal Solid Waste Management

The methodologies first address the issue of collection of municipal solid waste by minimization of the vehicle routes. The optimized collection points are further utilized in the development optimization model of MSW. Thus, the present work proposed methodology to address the issues of MSW in a comprehensive manner. In addition, the model proposed in this paper has been formulated taking conditions of typical city in Asian countries.

The physical components of the MSW optimization model are shown in Fig. 1 (Rawal and Singh 2013). The optimization model consists of investment and management costs, transportation costs and operational costs from the use of repairing of trucks. The benefits from energy generation, RDF production, compost and recycling is to be subtracted from the overall cost.

The constraints include waste flow constraints; facility availability; capacity of available facilities; site selection; environmental; landfill saturation constraints etc. It is being assumed that waste source is located at one point of an individual areas; MSW separation is done at the waste source locations (collection points). MSW operations proposed in the model are on daily basis. The optimization model is

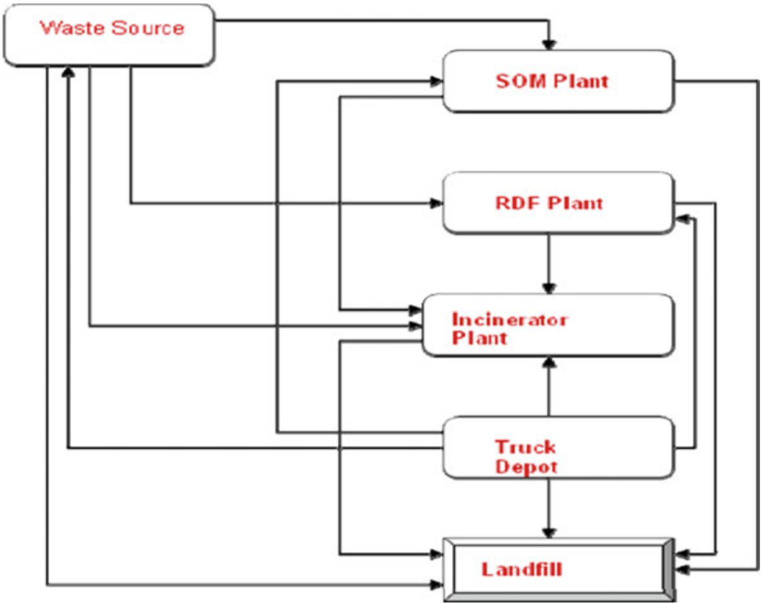


Fig. 1 The physical component of MSW model

presented as a mixed integer linear program. The description of new variables and the models are presented below:

Following are the indices used in this paper:

$i = 1, 2, \ldots,$: location of waste sources (collection points); $j = 1, 2, \ldots,$: location of incinerators; $k = 1, 2 \ldots,$: location of sanitary landfills; $r = 1, 2, \ldots,$: location of replacement trucks depots; $l = 1, 2, \ldots,$: truck type and $g = 1, 2, \ldots,$: waste type. Here are variables of the problems:
$\beta lijg$, $\beta likg$: amount of waste (in tons) of type g collected everyday by trucks of type l from a waste source i to an incinerator at j and a landfill at k, respectively.
$\lambda ljkg$, $\lambda lhkg$: amount of waste (in tons) of type g collected everyday by trucks of type l from an incinerator at j, to a landfill at k, respectively.
$Xlgij$, $xlgij$: the total number of trips and total no of truck of type l used every day to carry waste of type g from waste source i to an incinerator at j.
$Ylgij$, $ylgij$: total number of trips and total no of truck of type l used every day to carry waste of type g from an incinerator at j to a landfill at k.
zj, zk, zr: Boolean variables indicating, respectively, the presence of an incinerator at j, a landfill at k and a trucks depot at r.
wj, wk: amount of waste transported everyday, respectively, to an incinerator at j and a sanitary landfill at k.
Tl: The number of trucks of type l used everyday.
T: The total number of trucks (excluding replacement trucks) used everyday.
Zl: The number of replacement trucks of type l required everyday.

Input Data

Following are input variables used in optimization model:

$alij$, $alik$: The expected number of trips a truck of type l can make, respectively, per day between waste source at i and an incinerator at j and a landfill at k.
$blik$: The expected number of trips a truck of type l can make, respectively, per day between an incinerator at j and a landfill at k.
αl: capacity (in tons) of a truck of type l.
ρl: probability that a truck of type l breaks down in a day.
$vlij$, $vlik$: the transportation cost per unit of waste carried by a truck of type l from a waste source at i to an incinerator at j and a landfill at k.
$elrk$, $elrj$, $elri$: the cost of moving a truck of type l from a replacement trucks depot at r to a landfill at k, an incinerator at j and a waste source at i, respectively.
G_i: waste quantity generated at source.
vj: revenue generated per unit of waste at an incinerator at j.
fc_l: the cost of repairing of truck of type l, $l = 1 \ldots, L$.
Wi: amount of waste at source i.

γ: fraction (%) of unrecovered waste, at an incinerator at *j* that requires disposal to a landfill.
Qj, Qk, Qr: capacity per day, respectively, for an incinerator at *j*, a landfill at *k*, and a replacement trucks depot at *r*.
Cj, Ck, Cr: fixed cost incurred in opening an incinerator at *j*, a landfill at *k* and a replacement trucks depot at *r*, respectively.
cj, ck,: variable cost incurred in handling a unit of waste at an incinerator at *j* and a landfill at *k*, respectively.

Objective Function

Minimize

$$I_{\mathrm{MI}} = (I_1 + I_2 + I_3)_{\mathrm{MI}} - A_{\mathrm{MI}}. \tag{1}$$

$$I_1(z, w, X, Y) = \{\text{Part I (Investment and management expenses)} \\ + \text{par}t\text{ II (Transportation cost)}$$

$$\text{Part-I} = \left[\sum\nolimits_j \left(C_j z_j + c_j w_j\right) + \sum\nolimits_k \left(C_k z_k + c_k w_k\right)\right]. \tag{2}$$

$$\text{Part-II} = \left[\sum\nolimits_{jgli} v_{lij}\beta_{lijg} + \sum\nolimits_{kgli} v_{lik}\beta_{likg} + \sum\nolimits_{jglik} W_{ljk}\lambda_{ljkg}\right]. \tag{3}$$

The component I_2 gives expenses owing to the use of replacement trucks,

$$I_2(n, z) = \sum\nolimits_{rkl} e_{lrk}n_{lrk} + \sum\nolimits_{rjl} e_{lrj}n_{lrj} + \sum\nolimits_{ril} e_{lri}n_{lri} + \sum\nolimits_r C_r z_r. \tag{4}$$

Component I_3 gives the total cost for repairing of all trucks required in the daily management of waste,

$$I_3(x, y, n) = \sum\nolimits_l fc_l(T_l + Z_l). \tag{5}$$

Component *A* gives the benefits at the plants owing to the production of electric energy, compost and refuse derived fuel.

$$A(w) = \sum\nolimits_j v_j(1 - \gamma)w_j. \tag{6}$$

Constraints

(a) The mass balance constraint at waste generation source ensures that all the waste quantities generated at various sources must be transported to the treatment and disposal stations. In constraint, we make sure that the total waste moved from each waste collection point *i* is at least be equal to the amount of waste found at that point.

$$\sum\nolimits_{glj} \beta_{lijg} + \sum\nolimits_{kgl} \beta_{likg} \geq G_i, \tag{7}$$

or

$$\sum\nolimits_{glkj} W_{glkj} \geq G_i, \tag{8}$$

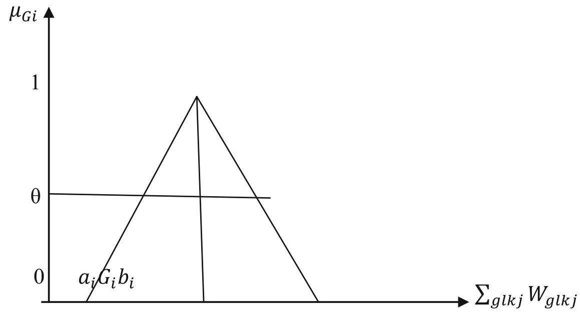
where $\sum_{glkj} W_{glkj} = \left(\sum_{glj} \beta_{lijg} + \sum_{kgl} \beta_{likg}\right)$ is the total waste of g type, collected from the source by l type, of truck and transported to the incinerator j and landfill k. G_i is the waste quantity generated at source.

Solid waste quantity (G_i) computed in Eq. (8) is assumed as fuzzy and denoted by $\widetilde{G}_i = (G_i, a_i, b_i)$, where G_i, $G_i - a_i$ and $G_i + b_i$ are the most possible most pessimistic and most optimistic value of solid waste quantities generated at source i. a_i and b_i define the extreme deviations of waste quantity at source i on left- and right-hand sides, respectively. Equation (8) can be written as Eq. (9) incorporating fuzzy number and inequalities.

$$\sum\nolimits_{glkj} W_{glkj} \geq \widetilde{G}_i. \tag{9}$$

The aspiration level of DM is expressed using the fuzzy number following the membership function. The fuzzy waste quantities shown in Fig. 2 can be expressed

Fig. 2 Membership functions for solid waste quantities



as Eq. (10), incorporating the aspiration level with respect to uncertain waste quantities.

$$\left\{\begin{array}{ll} 1, & \sum_{glkj} W_{glkj} \leq G_i - a_i \\ \mu_{\tilde{G}_i} = 1 - \frac{G_i - \sum_{glkj} W_{glkj}}{a_i}, & G_i - a_i \leq \sum_{glkj} W_{glkj} \leq G_i \\ 1 - \frac{\sum_{glkj} W_{glkj} - G_i}{b_i}, & G_i \leq \sum_{glkj} W_{glkj} \leq G_i + b_i \\ 0, & \text{else} \end{array}\right\}. \tag{10}$$

The aspiration of the DM is completely fulfilled if $\sum_{glkj} W_{glkj} = \widetilde{G}_i$. It also means that the membership function $\mu_{\tilde{G}_i}$ will be equal to 1. If the minimum aspiration level is violated the condition $\sum_{glkj} W_{glkj} \leq G_i - a_i$ holds. This indicates that even the minimum target of waste management will not be achieved resulting in complete dissatisfaction of the DM. In case of $\sum_{glkj} W_{glkj}$ varying between $G_i - a_i$ and $G_i + b_i$ the satisfaction level will vary between 0 and 1. For interpretation of the membership function in decision, the DM will be required to define possibility level θ of waste quantity deviation. With the incorporation of possibility level θ in Eq. (10), it can be expressed as Eq. (11).

$$\mu_{\tilde{G}_i} \geq \theta. \tag{11}$$

Equation (9) can be written as Eqs. (12) and (13) in order to include the possibility level of deviation in waste quantities.

$$\sum_{glkj} W_{glkj} \geq G_i - a_i(1 - \theta). \tag{12}$$

$$\sum_{glkj} W_{glkj} \leq G_i + b_i(1 - \theta). \tag{13}$$

(b) In this constraints, we guarantee that the amount of waste carried away from every plant to a landfill is at least be equal to the amount of waste found at that plant.

$$\gamma w_j \leq \sum_{jglik} \lambda_{ljkg}. \tag{14}$$

The maximum capacities for the processing plants are accounted for. These constraints mean that the amount of waste taken to these plants should not exceed the plant capacities.

$$w_j \leq Q_j z_j. \tag{15}$$

In constraint, the same thing is done for sanitary landfills.

$$t_k \leq Q_k z_k \tag{16}$$

(d) The total number of replacement trucks of type l cannot be less than the expected number of daily truck breakdowns of the type l. With constraint, we ensure that there is at least one depot for the replacement trucks.

$$\sum\nolimits_{rk} n_{lrk} + \sum\nolimits_{rj} n_{lrj} + \sum\nolimits_{ri} n_{lri} \geq T_l. \tag{17}$$

$$\sum\nolimits_{r} z_r \geq 1. \tag{18}$$

(e) The number of trucks in a depot cannot exceed its capacity and other constraint means that the total number of replacement trucks is not too big compared to the total number of trucks used per day.

$$\sum\nolimits_{lk} n_{lrk} + \sum\nolimits_{lj} n_{lrj} + \sum\nolimits_{li} n_{lri} \leq Q_r z_r. \tag{19}$$

$$\sum\nolimits_{r} Q_r z_r \leq T. \tag{20}$$

(f) Once the flow to either plant or sanitary landfill is positive, that plant or landfill must actually exist.

$$\beta_{lijg} \leq Q_j z_j, \quad \beta_{likg} \leq Q_k z_k, \quad \lambda_{ljkg} \leq Q_k z_k. \tag{21}$$

(g) Constraints can be referred to as waste flow fixing constraints. The reason is that when there are benefits at some node there is a tendency to move as much waste as possible to that node as long as there is space on the truck. In such a case, what is "carried" on the truck that includes false waste may go beyond the amount at a waste source; this is undesirable because the interest is in the precise amount of waste picked from the source.

$$\beta_{lijg} \leq W_i, \; \beta_{likg} \leq W_i, \; \lambda_{ljkg} \leq \gamma w_j. \tag{22}$$

(h) The variables in constraints are defined as non-negative; these give the amount of waste that flows between various nodes.

$$\beta_{lijg} \geq 0, \; \beta_{likg} \geq 0, \; \lambda_{ljkg} \geq 0. \tag{23}$$

(i) The variables in constraints are defined as non-negative integers. These give the number of trucks used between two nodes in the model per day, excluding replacement trucks.

$$x_{lijg},\ \text{integer} \geq 0,\ x_{likg},\ \text{integer} \geq 0,\ y_{ljkg},\ \text{integer} \geq 0. \tag{24}$$

(j) The variables in constraints are defined as non-negative integers. These give the number of replacement trucks required everyday in the waste management program. We note that the breakdown of a truck can occur anywhere in the road network followed by the trucks. For purposes of locating the truck depots, it is assumed that these breakdowns occur at either a waste collection point or at a plant or at a landfill.

$$n_{lrk},\ \text{integer} \geq 0,\ n_{lrj},\ \text{integer} \geq 0,\ n_{lri},\ \text{integer} \geq 0. \tag{25}$$

(k) The variables are defined as Boolean. These are used to determine the existence of either a plant or a landfill.

$$z_j \in [0, 1],\ \ z_k \in [0, 1],\ \ z_r \in [0, 1]. \tag{26}$$

In this constraints, we guarantee that the amount of waste carried away from every plant to a landfill is at least be equal to the amount of waste found at that plant.

It can be seen that the presented fuzzy model is a nonlinear model in case of unknown waste quantity and values of θ and γ. The model is solved as fuzzy parametric programming model using the approach discussed by (Rawal and Singh 2013).

Study Area

Allahabad is one of the representative urban Indian cities and situated at 25° 25′ north latitude and 81° 58′ east longitude. It is about 627 km from Delhi and about 815 km from Calcutta (Sharholy et al. 2007). Allahabad is an ancient city of India, considered holy, because it is built on the confluence (Sangam) of the rivers Ganga, Yamuna and Saraswati (T.D. 1989). The city has a population of about 1,506,119 inhabitants (AMC 2003). Allahabad Municipal Corporation (AMC) is responsible for the management of the MSW generated in the city.

As per information provided by Allahabad Nagar Nigam (ANN 2007), the entire city is divided into 80 municipal wards within 20 sanitary wards and generated

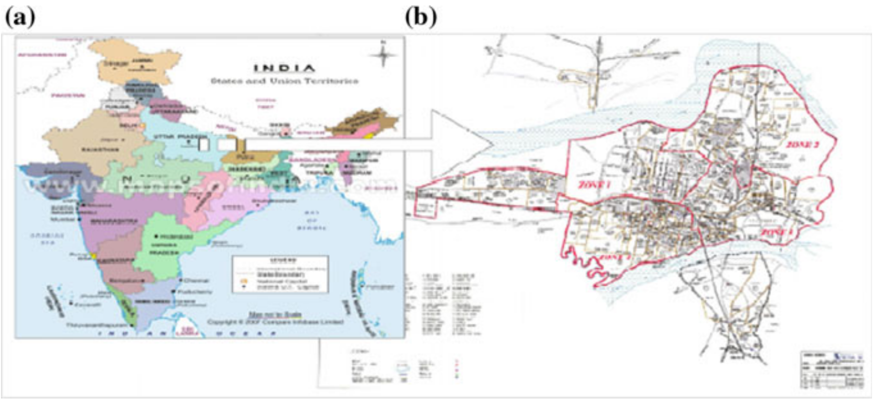


Fig. 3 Study area. **a** Map of India. **b** Allahabad city in Uttar Pradesh

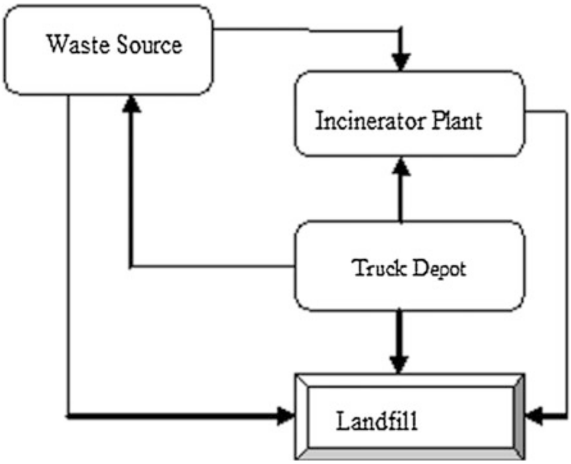


Fig. 4 Schematic representation of scenario

430 g per capita per day. For the purpose of solid waste management, the Allahabad city is divided into five zones as shown in Fig. 3. In this study, Zone 3 is considered. The schematic representation of study area is shown in Fig. 4. Zone 3 comprises of 1 Source, 1 Incinerator, 1 Landfill and 1 Depot and covers 16 wards out of 80 wards. At the moment city does not have existing waste management component, so some of the parameters value is subjective.

It is assumed that there is number of waste sources (wards) in a zone. The waste specified generated in a particular ward is as termed as waste source. The capacity of vehicle starts at a first waste source as a common collection point and visits to nearest waste source and picks up the waste, when a vehicle is not full, it needs to go to the closest available waste source. When a vehicle is full, it needs to return to the first waste source.

Results and Discussion

The vehicle routing model is able to solve modest-sized zone 3. We have utilized total distance of 66302.07 meters for collection of all waste from wards to common collection point ward 24 (Rawal et al. 2010).

Schematic representation of scenario is presented in Fig. 4. Here, we considered one waste source (collection point) at ward 24, one incinerator at ward 53, one truck depot at ward 10 and one landfill site at ward 21. It is assuming that all the truck used to carry waste is of same capacity, i.e. 4.5 tons.

Variables

$u12$, $u14$, respectively, represent the amount of waste (in tons) collected everyday by trucks of capacity 4.5 tons from a waste source at 1 to an incinerator at 2 and a landfill at 4; $v24$: represents the amount of waste (in tons) collected everyday by trucks of capacity 4.5 tons from an incinerator at 2 to a landfill at 4; $x12$, $x14$,: respectively, represent the number of trucks of capacity 4.5 tons used everyday to carry waste from a waste source at 1 to an incinerator at 2 and to a landfill at 4; $y24$: number of trucks of capacity 4.5 tons used everyday to carry waste from an incinerator at 2 to a landfill at 4; $n31$, $n32$, $n34$,: respectively, represent the number of trucks of capacity 4.5 tons used everyday from a replacement trucks bank at 3 to a waste source at 1, an incinerator at 2 and a landfill at 4; $w2$ ($= u12$), $t4$,: respectively, represent the amount of waste transported everyday to an incinerator at 2 and a landfill at 4. Uncertainty in waste amount has been taken 5% in the total amount of waste quantity.

Input Data/Parameters Used

The 10, 6, respectively, are expected number of trips (single trips) a truck of capacity 4.5 tons can make everyday from a waste source at 1 to an incinerator at 2 and a landfill at 4; 6 is the expected number of trips a truck of capacity 4.5 tons can make everyday between and incinerator at 2 and a landfill at 4; 0.28, 5.39, respectively, are the transportation costs per ton of waste transported from a waste source at 1 to an incinerator at 2 and a landfill at 4; 5.36 is the transportation per ton of waste moved from an incinerator at 2 to a landfill at 4; 2.53, 2.83 and 5.56 respectively, are the costs of moving a replacement truck of capacity 4.5 tons from a replacement trucks depot at 3 to a waste source at 1, an incinerator at 2 and a

Table 1 Different values of cost (INR) with different values of (θ) at each different values of (γ)

$\gamma\rightarrow$	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
$\theta\downarrow$									
0	5979.8	29522.4	51,028	55144.9	55144.9	55144.9	55144.9	55144.9	55144.9
0.1	6379.52	29572.3	51077.8	55194.8	55194.8	55194.8	55194.8	55194.8	55194.8
0.2	6379.52	29572.3	51077.8	55194.8	55194.8	55194.8	55194.8	55194.8	55194.8
0.3	6779.24	29622.3	51177.5	55244.8	55244.8	55244.8	55244.8	55244.8	55244.8
0.4	6779.24	29622.3	51177.5	55244.8	55244.8	55244.8	55244.8	55244.8	55244.8
0.5	7129.04	29672.2	51227.3	55294.7	55294.7	55294.7	55294.7	55294.7	55294.7
0.6	7129.04	29672.2	51227.3	55294.7	55294.7	55294.7	55294.7	55294.7	55294.7
0.7	7528.76	29722.2	51,327	55344.7	55344.7	55344.7	55344.7	55344.7	55344.7
0.8	7528.76	29722.2	51,327	55344.7	55344.7	55344.7	55344.7	55344.7	55344.7
0.9	7928.48	29772.1	51426.7	55394.6	55394.6	55394.6	55394.6	55394.6	55394.6
1	7129.04	29822.1	51227.3	65444.6	65444.6	65444.6	65444.6	65444.6	65444.6

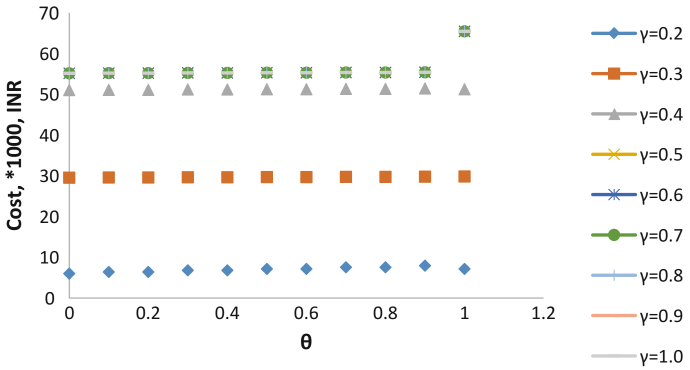


Fig. 5 Different values of cost (INR) with different values of (θ) at each different values of (γ)

landfill at 4; 1500 is the revenue per unit of waste from an incinerator at 2; 108.04 is the amount of waste (in tons) at a waste source at 1; 0.30 is the fraction (%) of unrecovered waste at an incinerator at 2; 75, 3, and 200 are the respective capacities for an incinerator at 2, a repairing of trucks depot at 3 and a landfill at 4; 800 and 44.56 are the respective costs of handling a ton of waste at an incinerator at 2 and a landfill at 4; 10,000 is cost of repairing truck; 0.13: probability that a truck breaks down in a day. The possibility level of waste quantity deviation (θ) varies between 0 and 1 for each value of fraction (%) of unrecovered waste (γ) which varies between 0.2 and 1. Different values of cost (INR) with different values of (θ) at each different values of (γ) are shown in Table 1, and the graphical presentation is shown in Fig. 5.

Sensitivity Analysis

In order to demonstrate sensitivity of total cost with respect to fraction (%) of unrecovered waste (γ) at an incinerator at 2 and possibility level of waste quantity deviation (θ) at a source at 1. Detail sensitivity analysis is performed by varying unrecovered waste γ varies over the different intervals from (0.2, 1.0) and also varying possibility level of waste quantity deviation (θ) with different intervals from (0.0, 1.0) at each value of unrecovered waste γ as shown in Fig. 5. It is observed that the total cost falls with lower values of γ and θ; this is because the lower the value of γ, the more efficient the plant is, and consequently the more benefits will be obtained. In other words, increase in cost as fraction of unrecovered waste was found to increase in the model. After the value of $\gamma = 0.4$, a constant cost of Rs. 55144.85–55394.6 are obtained by mixed integer linear model. As the % of unrecovered waste increases, benefits from incinerator decreases and transportation cost from incinerator to landfill also increases. This cause overall increase in the cost. The relationship between increase in waste quantity and increase in the total cost involved in waste management is found to be nonlinear.

Conclusions

The mixed integer linear programming model presented in this work is suitable for MSW management for Indian cities like Allahabad in India. The route optimization is embedded in MSW management. In this way, the methodology presented here demonstrates a comprehensive framework of MSW management. The sensitivity analysis indicated that the total cost lowered with high quality of incinerators (with lesser unrecovered wastes) in given case. The work certainly has advantages over previous approaches which uses a deterministic value of waste amount. Uncertainty in the optimal waste management (in terms of total optimal cost) is more than uncertainty in waste amount. A fuzzy parametric model has been presented in the present study for the long-term planning with uncertain parameters. Unlike the existing models, the uncertainties in waste quantities and capacities of waste management facilities have been addressed as inbuilt feature in the model in terms of the shape of membership function. The output of model gives a set of alternative solutions for the range of membership function, which reflects the specified aspiration level. The application of the methodology to urban city like Allahabad shows the potential applicability of the methodology to other urban cities.

References

Allahabad Municipal Corporation (AMC) (2003) Allahabad Nagar Nigam, Uttar Pradesh, India (unpublished data)

Allahabad Nagar Nigam (ANN) (2007) A DPR report on integrated plan of MSW management for the city of Allahabad by M/s Tetra Tech India Ltd. Delhi

Gupta S, Choudhary N, Alappat J (2007) Bioreactor landfill for MSW disposal in Delhi. In: Proceedings of the international conference on sustainable solid waste management, Chennai, India, pp 474–481

Lingo 10.0 (2006) User's Guide, Lindo Systems Inc., 1415 North Dayton Street, Chicago, Illinois, 60622

Ministry of Environment and Forests (MoEF) (2000) The Gazette of India. Municipal solid waste (management and handling) rules. New Delhi, India

Peavey HS, Donald RR, Gorge G (1985) Environmental engineering. McGraw-Hill Book Co., Singapore

Rawal N, Singh RM, Vaishya RC (2010) Mathematical models for optimal management of solid wastes in urban areas. In: 3rd international perspective on current and future state of water resources and the environment international conference (ASCE) will be held on the Indian Institute of Technology (IIT) Madras, Jan 5–7

Rawal N, Singh RM (2013) Optimal municipal solid wastes management with uncertainty characterization using Fuzzy Theory. In: Proceedings of seventh international conference on bio-inspired computing: theories and applications (BIC-TA 2012), Advances in Intelligent Systems and Computing 202, Springer, India. doi:10.1007/978-81-322-1041-2_10

Sharholy M, Ahmad K, Vaishya RC, Gupta RD (2007) Municipal solid waste characteristics and management in Allahabad, India. Sci Dir Waste Manag 27:490–496

Sharholy M, Ahmad K, Gauhar M, Trivedi RC (2008) Municipal solid waste management in Indian cities—a review. Waste Manag 28(2):459–467

Srivastava AK, Nema AK (2011) Fuzzy parametric programming model for integrated solid waste management under uncertainty. J Environ Eng 137:69–83

Tourism Department (T.D.) (1989) Introduction of Allahabad. U.P. Government, Lucknow, India

Solid Waste Management Through Vermi- and Phosphate-Enriched Composting Techniques for Sustainable Agriculture

A. B. Singh and M. C. Manna

Abstract Metropolitan cities of India generated about 64.8 million tonnes (Mt) of city refuse during 2010. This waste material had a potential to prepare 9.1 Mt of compost. The production of municipal solid waste (MSW) is expected to increase to 107 Mt by 2030. Big cities like Delhi, Mumbai and Kolkata with population greater than 10 million are generating 4000–6000 tonnes of MSW daily. Other cities such as Bhopal, Nagpur, Chennai and Bangalore are producing about 1500–3000 tonnes of MSW per day. Although about 41% of these wastes contain biodegradable organic matter, only 8.9 Mt of MSW are composted which accounts for 8.6% of the total MSW. For the efficient recycling of biodegradable organic wastes, composting technologies viz; vermi-composting, phospho-compost, microbial-enriched compost and phospho-sulpho-nitro-compost preparation have been developed, using agro-industrial wastes, MSW and distillery effluents, amended with certain mineral/mining waste materials (rock phosphate, micas and pyrites) for increasing the nutrient supply potential of the composts. Methods have been standardized to decompose city wastes by earthworm alone or P-enriched earthworm compost using rock phosphate. It was observed that the vermi-composting process is faster than conventional composting because the material passes through earthworm gut, whereby the resulting earthworm castings are rich in microbial activity. The present study suggests that the vermi-compost and P-enriched vermi-compost are becoming important alternative to conventional compost and farmyard manure (FYM) sources for organic farming due to shortage in the supply of dung and use of vermi-compost to improve soil physical, chemical and biological conditions, thereby enhancing productivity and sustainability of agriculture.

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Introduction

The per capita waste generation rate in India has increased from 0.44 kg/day in 2001 to 0.5 kg/day in 2011. There are 53 cities in India with a million plus population, which together generate 31.5 million tonnes per year of MSW at a per capita waste generation rate of 500 g/day. Management of solid wastes has become one of the biggest problems being faced today. To avoid the wastage of resources and to minimize the environmental damage, there is a need for better recycling techniques. Biodegradable MSW is the second largest organic source available in the country. These wastes contain mostly non-biodegradable material, heavy metals, pathogens, etc. Recycling of such a heterogeneous mixture of waste has become a problem and challenge for the municipalities from collection, safe disposal and recycling point of view. Thus, recycling of MSW through enrichment techniques has not only greater amounts of valuable plant nutrients compared to ordinary compost but has a high degree of humification and so may contain less phytotoxic materials and pathogens. Their efficient management is indispensable for the sustainability of different cropping systems on arable lands and reclamation of salt-affected and degraded lands. Thus, the city wastes are generally a good source of nutrients and organic carbon. Their conversion into compost is desired to serve the twin objectives of cleaning the environment and augmenting the well-needed organic carbon in soil as our soils are showing the signs of fatigue and forcing decline in the productivity (Manna et al. 2006). There is a growing realization that the adoption of ecologically sustainable farming practices can not only reverse the declining trend in the crop productivity but also protect the environment. Therefore, there is a growing interest in the development of cost-effective and eco-friendly technological option for waste management.

MSW Availability

As per report (May, 2000) of Ministry of Urban Development (MoUD), Government of India, 100,000 Mt MSW was generated daily in the country. During the year 2004–2005, Central pollution Control Board (CPCB) through National Environmental Engineering Research Institute (NEERI), Nagpur, conducted a survey in 59 cities/towns and estimated 39,031 tonnes per day MSW generation in the 59 cities/towns. The survey conducted by the Central Institute of Plastics Engineering and Technology (CIPET) at the instance of CPCB has reported the generation of 50,592 tonnes of MSW per day in the year 2010–11 in same 59 cities/towns.

Manual composting of MSW is commonly practiced in small towns. The produced compost can be sold, and the system is normally operated on no profit, no loss basis. The production of MSW is expected to increase 107 Mt by 2030 (Table 1). The MSW generated in India in 2015 can produce about 10.3 Mt compost. Table 2 provides information on all types of organic sources available in India and their nutrient potential.

Table 1 Municipal solid waste generation from urban areas in India and estimated quantity of compost production from it

Year	MSW (Mt/annum)	Compost (Mt/annum)
2005	57.5	8.1
2010	64.8	9.1
2015	73.4	10.3
2020	82.2	11.7
2025	94.4	13.2
2030	107.0	15.0

Source www.esa.un.org/unup (2003)

Table 2 Organic resources and their nutrient supply potential

Agricultural/animal/city wastes	Quantity (Mt)	N (Mt)	P_2O_5 (Mt)	K_2O (Mt)
Rice	110.5	0.61	0.18	1.38
Wheat	82.6	0.48	0.16	1.18
Sorghum	21.0	0.52	0.23	1.34
Sugarcane	40.9	0.40	0.18	1.28
Pulses	13.7	1.60	0.51	1.75
Cattle dung	1227.8	1.84	1.23	0.61
Animal urine	800	1.60	0.08	1.60
Sheep and goat	45	0.27	0.06	0.45
Poultry wastes	1.00	2.17	2.00	2.20
Horses	0.48	1.51	0.35	1.80
City refuse	150	0.75	0.34	0.63
Sewage sludge water	1460 Mt m^2 $year^{-1}$	0.04	0.01	0.18
Total	3952.98	11.79	5.33	14.4

Manna and Ganguly (1998)

MSW Recycling by Composting

Although about 40% of matter in MSW is considered to be biodegradable, only 14% (9.1 Mt) of the MSW were recycled in compost. MSW may consist of paper, plastics, metals, rubber, glass, medical disposables, plastic tubes, ceramic/earthen pots, waste from construction activities, etc. Management of such a heterogeneous mixture of biodegradable and non-biodegradable fractions becomes a problem for the municipalities from collection, safe disposal and recycling point of view. It contains 35.2–47.1% compostable materials, 2.1–5.4% plastics, 0.4–0.5% rubber and leather, and the rest is non-degradable fractions. Analysis of MSWs showed that the total amount of N, P and K in them is about 132,000 tonnes currently and that could increase to 218,000 tonnes by 2030.

Vermi-Composting

Vermi-composting is a method of composting with worms and differs from conventional composting in several ways. In vermi-composting, there is a saving of nearly two months in composting time compared to conventional compost. In general, there are different methods of vermi-composting under field conditions.

For the production of vermi-compost, open permanent pits of 10 ft length × 3 ft width × 2 ft deep were constructed under the tree shade, which was about 2 ft above ground to avoid entry of rainwater into the pits. Brick walls were constructed above the pit floor, and 10-cm-diameter 5–6 holes were perforated in the pit wall for aeration. The holes in the wall were blocked with nylon screen (100 mesh) so that earthworms might not escape from the pits. Partially decomposed dung (dung about 2 months old) was spread on the bottom of the pits to a thickness of about 3–4 cm. This was followed by addition of layer of litter/residue and dung in the ratio of 1:1 (w/w). A second layer of dung was then applied followed by another layer of litter/crop residue in the same ratio up to a height of 2 ft. Two species of epigeic earth worms, viz. *Eisenia foetida* and *Perionyx excavatus*, were inoculated in the pit. Moisture content was maintained at 60–70% throughout the decomposition period. Jute bags (gunny bags) were spread uniformly on the surface of the materials to facilitate the maintenance of suitable moisture regime and temperature conditions. Watering by sprinkler was often done. The materials were allowed to decompose for 15–20 days to stabilize the temperature because to reach the mesophilic stage, the process has to pass the thermophilic stage, which may come in about 3 weeks. Earthworms were inoculated in the pit or heap with 10 adult earthworms per kg of waste material, and a total of 500 worms were added to each pit or heap. The materials were allowed to decompose for 110 days. The forest litter decomposed much earlier (75–85 days) to farm residue (110 ± 5 days).

P-Enriched Vermi-Compost

In India, about 260 Mt of rock phosphate deposit has been estimated at present. The low-grade rock phosphate is used as a direct source of *P* for crop production, especially in acid soil and long-duration plantation crops. However, there is very little experimental work available on the effect of mixing rock phosphate with different qualities of organic sources and their application in neutral or alkaline soils. For the production of P-enriched vermi-compost, earthworm species, viz. *E. foetida* and *P. excavatus*, were inoculated in the pit. Moisture content was maintained at 60–70% throughout the decomposition period. Jhabua rock phosphate (30–32% P_2O_5) was used @ 2.5% P_2O_5 of waste material with the same dimension of pit or heap as mentioned earlier. The total *P* content was improved by about 3–4% on materials dry weight basis (Table 3).

Table 3 Chemical composition of vermi-compost and P-enriched vermi-compost prepared from soybean straw

Parameters	Vermi-compost	P-enriched vermi-compost
Ash (%)	51.0	52.5
TOC (%)	27.2	26.5
C/N ratio	14.3	13.6
N (%)	1.90	1.95
P_2O_5 (%)	2.05	4.0
K_2O (%)	0.80	0.86
WSC (%)	0.94	0.88
Mn (ppm)	500	540
Zn (ppm)	100	100
Cu (ppm)	44	46

Singh et al. (2005)

Silpaulin Portable Vermi-Bed

For the production of vermi-compost, Silpaulin portable vemi-bed of 12 ft length × 4 ft width × 2 ft deep was kept under the tree shade, which was about ½ ft above ground to avoid entry of rainwater into the beds. In portable vermi-bed, partially decomposed organic wastes and dung were added in the ratio of 1:1 (w/w). Two species of earthworms, viz. *E. foetida* and *P. excavatus*, were inoculated in the bed. Moisture content was maintained at 60–70% throughout the decomposition period. Jute bags (gunny bags) were spread uniformly on the surface of the materials to facilitate the maintenance of suitable moisture regime and temperature conditions.

Vermi-Wash

Advances in vermiculture technology have recently led to novel products like vermi-wash. This product has now caught the attention of not only commercial vermiculturists but also the farmers. Farmers in their own way have started collecting vermi-wash for foliar application. For the preparation of vermi-wash, one-kilogram adult earthworms devoid of casts (approximately numbering 1000–1200 worms) are released into a trough containing 500 mL of lukewarm distilled water (37–40 °C) and agitated for two minutes. Earthworms are then taken out and again washed in another 500 mL at room temperature (± 30 °C) and released back into the tanks. The agitation in lukewarm water makes the earthworms to release sufficient quantities of mucus and body fluids. Transferring into ordinary water is to wash the mucus sticking still on to their body surface, and also this helps the earthworms to revive from the shock.

Enriched MSW compost can be prepared in 75 days. Enriched MSW contains relatively higher amounts of available plant nutrients as compared to ordinary (un-inoculated) MSW compost. The heavy metals can be reduced by segregating

Table 4 Quality of microbial-enriched compost and without bio-inoculum compost

Chemical parameters	Microbial-enriched compost	Without bio-inoculum compost
PH	6.96	6.21
EC (dsm^{-1})	1.052	1.529
CEC [c mol (p+)/kg]	95	56
Total organic carbon (%)	11.3	12.3
Total *N* (%)	0.73	0.65
C:N ratio	15.4	18.9
K (%)	0.79	0.704
HWS carbon (ppm)	252	168
Dehydrogenase activity (ppm)	37.5	56.5
HWS carbohydrates	725	675

Manna and Sahu (2012)
HWS Hot water soluble

the garbage before spraying of inoculums. Composting helps to produce higher-quality manure, and the usual period of composting is shortened from 6 to 2.5 months. The prospect exists to enrich compost in urban peripherals and use it in crop production and the compost is safe to the environment (Table 4).

Heavy metals generally found in mixed waste composts are zinc, copper, cadmium, lead, nickel and chromium. Majority of the samples do not comply with Indian quality control standards for total potassium, total organic carbon, total phosphorus and moisture content and exceeded the quality control limits for heavy metals contamination by Pb and Cr. The study also found that incidence of heavy metals in MSW compost from small cities is less than half of that from bigger cities, but the compost still does not clear the quality control standards in all instances. If all MSW generated in India in the next decade is composted as mixed waste and used for agriculture, it has potential to introduce 73,000 tonnes of heavy metals into agricultural soils Annepu (2012).

Various studies have been carried out at Indian Institute Soil Science to evolve efficient ways to ensure improvement in available nutrient status of microbial-enriched compost and reduce heavy metals content. MSW compost after 6–8 weeks of decomposition contains approximately 12.0% TOC and 0.73% N. MSW compost application increased soil organic carbon, available N, P, K, soil respiration, dehydrogenase activity and alkaline phosphatase activity (Manna et al. 2001, 2003). In fact, soil microbial biomass carbon increased by the application of compost about twofold more than with inorganic source owing to the presence of easily water-soluble carbon which acts as a source of energy for soil organisms. Therefore, from different studies it is clear that MSW compost if utilized effectively in the form of compost may improve their quality in the shortest possible time, which, in turn, provides a balanced nutrition to crop plants, improves soil biological health and sustains crop production (Table 5). In other words, to raise better crop, an integrated nutrient supply through organic and inorganic is a must.

Table 5 Comparative effectiveness of MSW composts and recommended dose of fertilizers on crop productivity in different soils of India

Soils and crops	Treatment input	Rate (tonnes/ha) applied	Crop yield (tonnes/ha)	Reference
Black soil	100% NPK	–	2.75	Manna et al. (2003)
(Soybean, 3 years)	PSNC prepared from city garbage	5.0	2.43	
Black soil	100% NPK	–	5.12	Manna et al. (2003)
(Wheat 3 years)	50% NPK + residual effect of 5 tonnes/ha/year PSNC prepared from city garbage after soybean	–	4.16	
Alluvial soil	100% NPK	–	1.04	Hijra et al. (1994)
(Green gram, 1 year)	PSNC prepared from city garbage	10	1.03	
Black soil	100% NPK	–	2.80	Manna et al. (2001)
(Wheat, 3 years)	PSNC prepared from city garbage	5	2.65	
Black soil	100% NPK	–	5.2	Manna et al. (2001)
(Wheat, 3 years)	50% NPK + residual effect of 5t/ha/year PSNC prepared from city garbage after soybean	–	4.37	

NPK Recommended dose of fertilizer; *PSNC* phospho-sulpho-nitro-compost

Conclusion

The recycling of organic wastes through composting methods is the key technology for the safe disposal and production of organic manures and minimization of environmental pollution. Vermi-composting, one of the waste recycling techniques, is faster than conventional composting because the material passes through earthworm gut, whereby the resulting earthworm castings become rich in microbial activity. Municipal solid waste is suitable for composting because of the presence of good amount of biodegradable organic matter. Enriched MSW compost can be prepared in 75 days, and the compost contains relatively higher amounts of available plant nutrients as compared to ordinary (un-inoculated) MSW compost. The heavy metals in MSW compost can be reduced by segregating the garbage before spraying of inoculums. Composting helps to produce higher-quality manure, and the usual period of composting is shortened from 6 to 2.5 months. There is a need for periodic monitoring of heavy metals in MSW compost so that quality could be insured and contamination could be prevented. The utilization of MSW compost would not only help in recycling of MSW but also increase the fertility of soil. Composting can be adapted country wide to recycle/reuse the organic residues as solid waste management option.

References

Annepu RK (2012) Sustainable solid waste management in India. M.Sc. thesis, Columbia University, New York

Hajra JN, Sinha NB, Manna MC, Islam N, Banerjee NC (1994) Comparative quality of phosphocompost and single super phosphate and response of green gram (*Vigan radiata Lwileczek*). Trop Agric (Trinidad) 71:147–149

Manna MC, Ganguly TK (1998) Recycling of organic wastes: its potential turnover and maintenance in soil-a review. Agric Rev 19(2):86–104

Manna MC, Ghosh PK, Ghosh BN, Singh KN (2001) Comparative effectiveness of phosphate enriched compost and single super phosphate on Yield, uptake of nutrients and soil quality under soybean-wheat rotation. J Agric Sci (Cambridge) 137:45–54

Manna MC, Ghosh PK, Ganguly TK (2003) Comparative performance of four sources of enriched phospho-compost and inorganic fertilizer application on yield, uptake of nutrients and biological activity of soil under soybean-wheat rotation. J Food Agric Environ (Finland) 1 (2):203–208

Manna MC, Ghosh PK, Ganguly TK, Singh AB, Tripathi AK (2006) Phosph-sulpho-nitro-compost: production and evaluation. Bull No 2. IISS, Bhopal, pp 1–11

Manna MC, Sahu A (2012) Accelerated composting technique for municipal solid wastes recycling in India. Asian J Soil Sci 7(2):245–248

Singh AB, Manna MC, Ganguly TK, Tripathi AK (2005) Vermicomposting: a technology for recycling of organic wastes, Bulletin No 1/2005. IISS, Bhopal, pp 1–13

Production of Asphaltene Binders from Solid Waste Generated in Leather Industry

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Abstract In the present work, an attempt has been made to make leather waste into modified bitumen a pavement material through pyrolysis followed by solidification/ stabilization process. The pyrolysed tannery buffing dust was characterized by SEM, FTIR, TGA and CHNS analyser. The pyrolysed TBD was effectively solidified/stabilized using aged bitumen. Pyrolysed solid tannery waste is made into modified bitumen and analysed for its Physical characteristics. The leachability of the stabilization of Cr (III) in the solidified matrix was confirmed through TCLP method. Thus, this study illustrates the recycling of buffing dust, a problematic waste in leather making to a societally useful material for road construction.

Keywords Buffing dust · Pyrolysis · Chromium (III) · Solidified blocks
Modified bitumen

Introduction

India is one of the major leather producers, and nearly 0.75 million tons of raw hides/skins is processed annually. Conversion of 1 ton of raw hide/skin into leather generates nearly 200–300 (25%) kg of solid waste, i.e. chromium-containing leather waste (CCLW), and rest only 70% of the material is converted into leather, and the remnant becomes non-tanned waste, or it lost in wastewater as fat-soluble

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protein and solid-suspended pollutants. Some of the solid wastes such as raw hide/skin trimmings, fleshings, chrome shavings, leather trimmings find uses in other industries; however, waste like buffing dust does not find any use. As they are fine particles and also contain chromium, current practice of dumping in vacant site causes severe health and environmental problems. The production of chromium-containing solid waste in tanneries has been recognized as a problem for many years, and increasing pressure from environmental authorities has demanded a solution of such a problem (Gammoun et al. 2007). The obnoxious gases such as oxides of sulphur, ammonia and other volatile organic compounds are emitted from tannery buffing dust during the thermal decomposition. Shavings, trimmings, buffing dust and splits from the chromium tanning of hides and skins have been disposed in landfills. Increasing local legislations on waste disposal, unavailability of land, high operation cost incurred in conventional treatment systems like land filling and incineration have stimulated the search for better, cost-effective and eco-friendly treatment. Among the pollution abatement strategies, source reduction is good; however, process modifications could not be adapted. Next best available option observed is recycling and reusing of waste materials (Brown et al. 1996; Cabeza et al. 1999; Silveria et al 2002; Mu et al. 2003; Kamaludeen et al. 2003; Rivela et al. 2004 Saravanabhavan et al. 2004).

Pyrolysis of wastes is one of the best methods that could render reusing of waste as it can convert wastes into gas, liquid and solid fractions with different applications. Also, the energetic efficiency in pyrolysis is lower than that in combustion, making the process cost-effective too. The gas that produced during pyrolysis can be reused as fuel, and the oil can be used as a raw material for chemicals. The carbonaceous residue can be burnt as fuel or safely disposed fixed on the carbonaceous matrix (Cassano et al. 1997; Imai and Okamura 1991; Petruzelli et al. 1995; Sivaparvathi et al. 1986a, b; Yilmaz et al. 2007).

Solidification/stabilization is another technique for disposal of solid waste containing heavy metals as they can protect the environment from contamination. Stabilization involves mixing of wastes with binding agents like cement, asphalt, fly ash and clay. Many research works have been performed using this technique for recycle of leather wastes such as tannery sludge with clay (Basegio et al. 2002; Abdul Kadir and Mohajerani 2011; Koki and Jimoh 2015), tannery waste with ceramics (Abreu and Toffoli 2009), incinerated chrome shavings with alumina (Abreu and Toffoli 2009; Basegio et al. 2006), stabilizing tannery waste with building materials (Xu et al. 2009), solidification with cement and aggregates (Abtahi et al. 2010).

In this paper, the carbonaceous matrix of the tannery solid waste containing the chromium metal was pyrolysed to produce microfibre carbon (MFC) followed by the utilization of MFC for making modified bitumen. The purview of the current research is to study the behaviour of chromium after a pyrolytic process and the stabilization process. Chromium is bounded in the pyrolytic residual ash compared to the tannery solid waste on both oxidation states chromium (III) and chromium (VI).

Materials and Methods

Collection and Characterization of TSW, MFC and Modified Bitumen

TSW used in the study was collected from Blue Diamond leather manufacture industry in Chennai, Tamil Nadu. The TSW and MFC were characterized for moisture content, ash content and chromium (III) and chromium (VI) according to the DIN protocol. Thermogravimetric analysis (TGA) and elemental analysis were carried out to find its thermal stability and elemental composition such as carbon, hydrogen, nitrogen, sulphur respectively. SEM analysis was carried out to determine the morphology of MFC and modified bitumen, and Fourier transform infrared (FTIR) studies were carried out to determine the functional groups in the MFC.

Instrumental Analysis

TGA was carried out to determine the weight loss with respect to temperature in order to fix the heating segment pattern of incineration. The dried samples were analysed under nitrogen atmosphere using Q50 TA instruments. The samples were heated in a platinum pan from 0 to 800 °C at the rate of 5 °C/min. The elemental CHNS content of the TSW and MFC was determined using CHNS Vario micro-CHNSO15091002 analysers. SEM analysis of MFC and modified bituminous mixture was determined using Hitachi S-3500 N scanning electron microscope. FTIR of MFC was determined by PerkinElmer Spectrum2 instruments.

Estimation of Chromium (III) and Chromium (VI)

About two grams of the TSW sample was gently stirred for 3 h with 100 ml of 0.13 mol of dipotassium hydrogen orthophosphate at pH 8.0 and filtered. Out of it, 10 ml of the solution was added with 2 ml of 2 N sulphuric acid and made up to 25 ml. Two millilitre of 0.5% diphenylcarbazide was added followed by the addition of 0.5 ml of orthophosphoric acid. The solution was kept for colour development for 15 min, and the absorbance was measured at 540 nm. The calculated concentration was chromium (VI). Total chromium was estimated using the above method after digesting the samples using acid mixtures (10 ml HNO_3: 10 ml H_2SO_4: 10 ml $HClO_4$) followed by the oxidation using potassium permanganate and sodium azide. Chromium (VI) is subtracted from total chromium to get chromium (III).

Moisture Content

The moisture content was calculated by Eq. (1). Initially, 2 g of sample was taken in the silica crucible and placed in the air oven at 110 °C; after 1 h, the sample was cooled and the final weight was taken.

$$\text{Moisture content } (\%) = (\text{Initial weight} - \text{final weight})/(\text{initial weight}) \times 100 \tag{1}$$

Ash Content

The ash content was calculated by Eq. (2). Initially, 2 g of sample was taken in the silica crucible and placed in the furnace at 550 °C; after 1 h the sample was cooled and the final weight was taken.

$$\text{Ash content } (\%) = (\text{Initial weight} - \text{final weight})/(\text{initial weight}) \times 100 \tag{2}$$

Preparation of Microfibrous Carbon (MFC)

The pyrolysis of a TSW in the O_2 atmosphere has been carried out in a stainless steel (316 grades) vertical retort of weight 13 kg, which was placed inside an electrical furnace. The outer jacket of the lid of the pyrolysis vessel was fitted with pipe; it has 7 cm thickness in order to prevent condensation of volatile organic compounds back into pyrolysed vessel, which increases energy recovery efficiency and prevents the heat dissipation from the reactor. The condensed organic compounds are collected in the condenser. The flue gas from the incinerator was scrubbed in a scrubber. The scrubber is a PVC column of height 1.5 and 0.175 m diameter to remove acidic vapours using alkaline water. Water required for scrubbing the flue gas was provided through a pump of capacity 0.5 HP. Provisions were made for characterizing the scrubbing solution used in the scrubber. The MFC was collected from the stainless steel vessel.

Solidification and Stabilization of MFC

Preparation of Bituminous Mixture

The residual ash (MFC) was collected from the furnace after pyrolysis of TSW was powdered and quantified. Aged bitumen (HRRC, Tamil Nadu) was used as a binder.

Asphalt mixer horizontal AIM 575 was used to prepare the asphalt mixture blocks. This machine is used for laboratory mixing of bituminous materials to prepare the specimens to be used for various asphalt tests. The machine mainly consists of a main frame, variable speed mixer, elevating system, heating pot, electrical control box. About 100 g of aged bitumen and various amount of residual ash (1–15 g) was mixed for making modified bitumen. It was prepared to mix in the heating pot with the variable speed mixer. The mixing portion was taken from the heating pot and transferred to aluminium sample container, and AIM 512-1 Universal Penetrometer was used to determine the penetration value of modified bitumen.

Physical Character of Modified Bitumen

Penetration test of modified bituminous mixture was determined by using AIM 512-1 model instrument. The bituminous mixture was taken in the aluminium container, and the test is carried out in the room temperature. Softening point test of the modified bituminous mixture was carried out by AIM 561-1 model instrument, and this ring ball method gives characteristic nature of the modified bitumen. AIM 532 model instrument is used to determine the viscosity of the modified bitumen.

Leachability Test

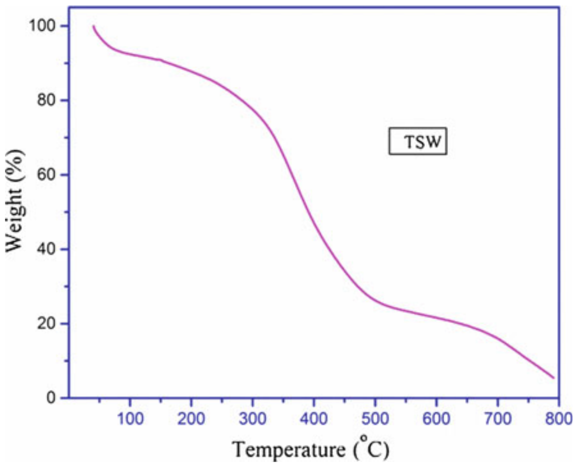
The leachability of the metals from the solidified samples of pyrolysed TSW blocks was determined by Toxicity Characterization of Leachate Procedure test (TCLP). TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphase wastes. It is usually used to determine EP toxicity of a hazardous waste. The bituminous mixture of weight 20 g was placed in a TCLP cylinder with 100 ml of extraction fluid (5.7 ml of glacial acetic acid in 500 ml of water and then adjust to pH 4.95). The contents were agitated in a TCLP rotator agitator at 30 rpm for 18 h, and the liquid phase was separated from the solid phase by filtration through a 0.6–0.8 μm borosilicate glass fibre under pressure of 50 psi (340 kPa). The liquid phase was analysed for chromium (III) and chromium (VI) ion to determine metal fixation efficiency.

Results and Discussion

Characteristics of Buffing Dust

The moisture content, ash content, chromium (III) and chromium (VI) of the TSW were 4.51%, 87.51%, 0.73 mg/g and 65.48 μg/g, respectively.

Fig. 1 TGA of TSW



Elemental Analysis

The elemental composition of the TSW was carbon 52.73%, hydrogen 2.80%, nitrogen 8.92% and sulphur 2.89% (67.33%). The elemental analysis suggests that 67.33% of the organic matter in the TSW and remaining 32.67% were inorganic components like metal salts.

TGA

TGA of TSW (Fig. 1) shows that the weight loss at 94.1 °C is due to elimination of moisture as well as organic volatile compounds. TGA records depict a weight loss in the temperature ranges from 240.3 to 576.5 °C, which can be attributed to the decomposition of organic compounds in the TSW into intermediate compounds. The intermediate compounds were volatilized off that left behind the ash content in the temperature range from 679.4 to 790.6 °C. The ash contains only 5% of inorganic compounds like metals and metal salts. The remaining things are decomposed.

Characterization of Microfibrous Carbon (MFC)

Characteristics of MFC

The moisture, ash, chromium (III) and chromium (VI) contents of the MFC were 2.69%, 74.42%, 0.81 mg/g and 5.50 μg/g, respectively.

Elemental Analysis

The elemental composition of the MFC was carbon 49.43%, hydrogen 1.20%, nitrogen 3.18% and sulphur 1.76% (55.57%). The elemental analysis suggests that the MFC contains inorganic components because after pyrolysis most of the organic matters are decomposed and converted to carbon. The carbon contains mainly oxygen and metal, so elemental analysis gives the idea about the composition of element in the carbon which was further conformed by EDX spectrum.

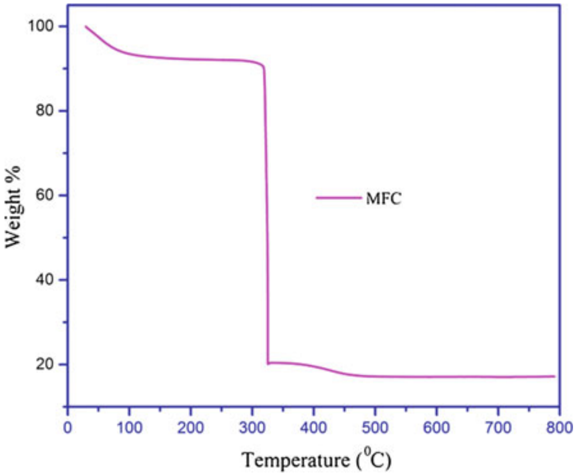
TGA of MFC

Figure 2 shows the TGA of MFC. The weight loss at 65–100 °C was due to the loss in the moisture content. And almost 72% loss observed from 291–347°C may be due to the carbonization of organic molecules. The remaining percentage observed at 800 °C was due to the residual inorganics.

FTIR of MFC

Figure 3 shows the FTIR spectrum of MFC. It has a strong and broad envelope at 3500–3000 cm^{-1} which may be due to the bounded water molecule. The C–O symmetric and asymmetric stretching exhibited as 1580 and 1185 cm^{-1} respectively. The peak at 547 and 472 cm^{-1} is due to the presence of metal oxide band (chromium oxide).

Fig. 2 TGA of MFC



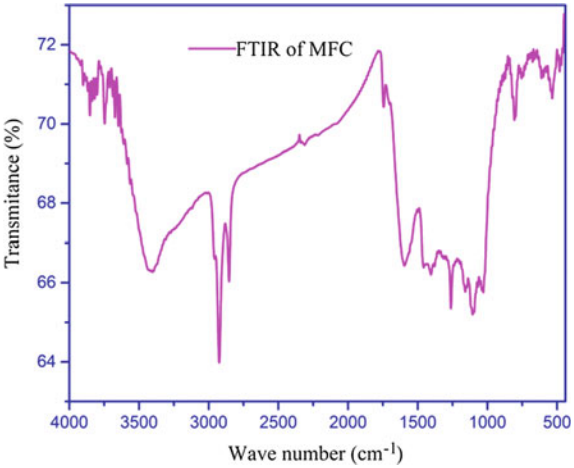


Fig. 3 FTIR analysis of MFC

SEM with EDX Analysis of MFC

Figure 4 shows SEM photomicrographs of MFC. The temperature is the most important factor which determines the size and shape of the MFC growth after pyrolysis; one more factor is that the presence of metal or metal salts determines the fibrous structure of the residual ash (MFC). The MFC rope (Fig. 4b) can be easily distinguished, and the metal particles are dispersed in the product; it is clearly in Fig. 4a. The average diameter of the MFC is 129 nm. EDX spectral analysis (Table 1 and Fig. 5 intensity of metal peaks) reveals that the MFC contains approximately 78.04 wt% carbon, 0.59 wt% chromium, 19.91 wt% oxygen and 0.68 wt% chlorine, 0.78 wt% silicon. The organic compounds in the tannery solid waste are decomposed after pyrolysis, and remaining part contains mostly inorganic compound like carbon, metal and metal salts.

Characterization of Modified Bitumen

SEM Analysis of Modified Bitumen

Figure 6 shows the SEM image of Modified Bitumen Sample. Both the Fig. 6a and b debits that the fibrous structure of the material is responsible for the proper binding of MFC with the bituminous material. Some of the cubical shaped particle in the picture may be due to the chromium in MFC which binds well with the heteroatom present in the bitumen.

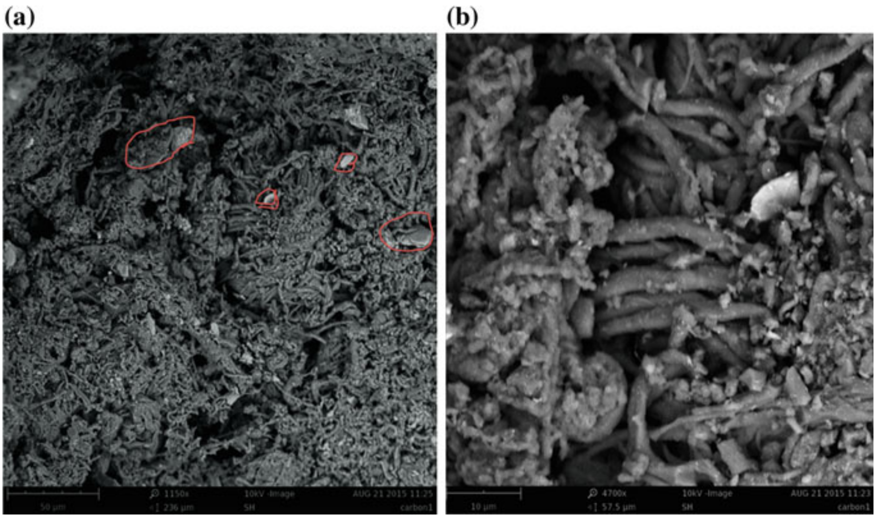


Fig. 4 SEM analysis of MFC **a** metal particle in MFC, **b** nanofibrous structure of MFC

Table 1 EDX spectral data of MFC

Elements	Approximate concentration	Intensity concentration	Weight %	Weight% sigma	Atomic %
C K	16.86	0.9661	70.33	3.96	78.04
O K	2.11	0.3542	23.90	4.00	19.91
Si K	0.38	0.9304	1.65	0.34	0.78
Cl K	0.37	0.8285	1.81	0.36	0.68
Cr K	0.45	0.7911	2.30	0.60	0.59

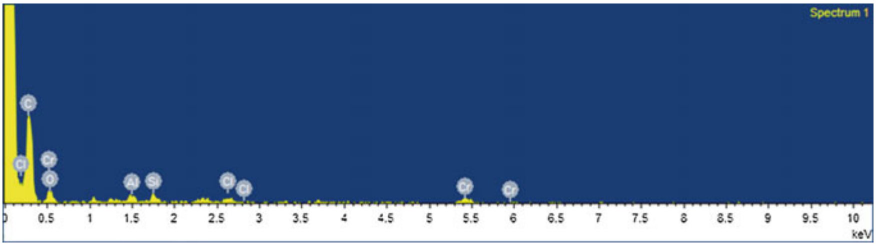


Fig. 5 EDX spectrum of MFC

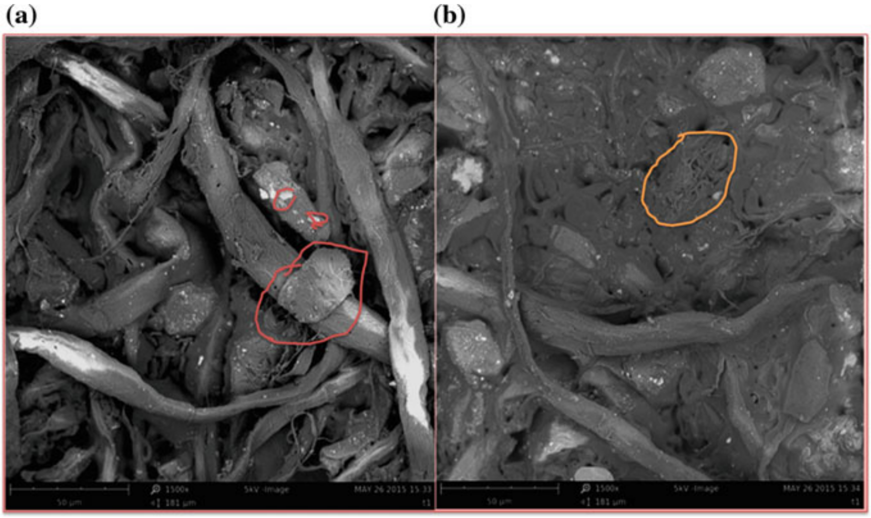


Fig. 6 SEM analysis of modified bitumen **a** MFC and chromium in bitumen, **b** bitumen contains MFC

Physical Characterization for Modified Bitumen

See Table 2.

Penetration Test for Modified Bitumen

Figure 7a and Table 2 show the penetration test for the modified bitumen. The aged bitumen shows the penetration around 31 dmm, but with the addition of MFC (1–15 g) the penetration value was decreased because the addition of MFC can bind with the aged bitumen and brittleness of the aged bitumen is changed.

Table 2 Rheological tests for modified bitumen

Modified bitumen samples	Penetration values (dmm)	Softening point (temperature when ball touches the bottom, °C)	Viscosity (220 °C, time taken to flow 50 cc of the binder)
Control	31	58	36
5% MFC	27	67	57
10% MFC	23	86	62
15% MFC	21	100	67

Softening Point for Modified Bitumen

The softening point of the modified bitumen is increased, compared with control; the addition of inorganic matrix can change heating resistance of the bitumen. So, the compound is thermally stable compared with control. Figure 7b and Table 2 display that the modified bitumen can change the character of the aged bitumen.

Viscosity of Modified Bitumen

Viscosity of modified bitumen is decreasing with time. The modification of the aged bitumen strongly binds with the MFC; it decreases the viscosity of the control; at the same time, the brittleness nature of the control was also changed. Figure 7c and Table 2 clearly give this modification which decreases the viscosity of the modified bitumen with gradual addition of MFC.

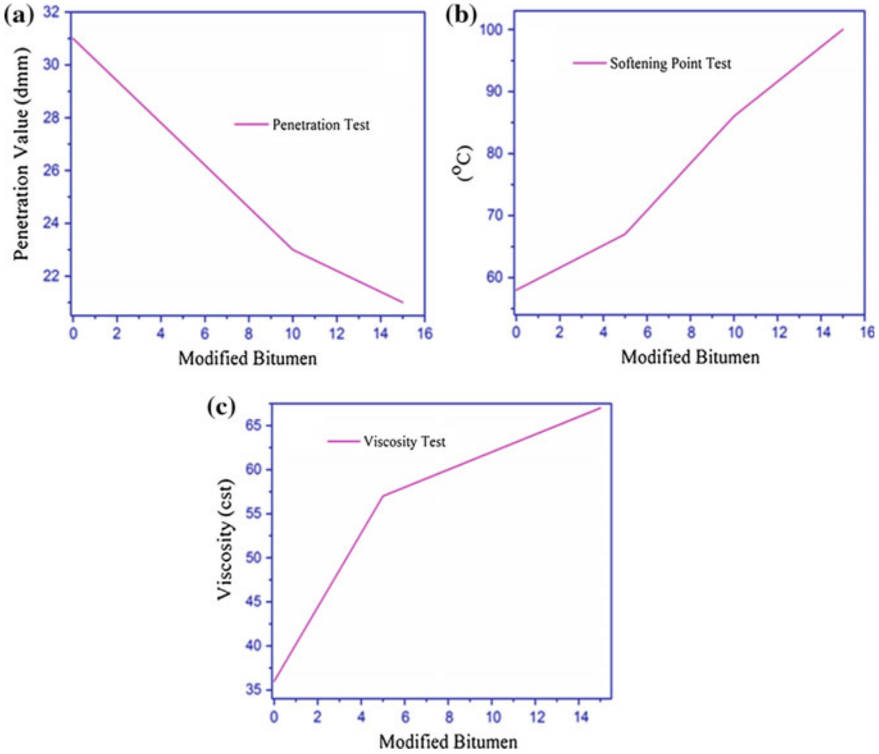


Fig. 7 Physical character of modified bitumen

Conclusion

Successful pyrolysis of tannery buffing dust was done, and microfibrous carbon of particle size in the range 50–70 nm was prepared. The behaviour of chromium under pyrolytic process was studied. Solidification and stabilization of chromium as modified bitumen were carried out. The rheological test results showed that the penetration decreases, softening point increases and the viscosity also decreases. The TCLP analysis shows that there is no leaching of chromium (III) and chromium (VI) after solidification and stabilization.

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References

Abdul Kadir A, Mohajerani A (2011) Bricks: an excellent building material for recycling wastes–a review

Abreu MA, Toffoli SM (2009) Characterization of a chromium-rich tannery waste and its potential use in ceramics. Ceram Int 35:2225–2234

Abtahi SM, Sheikhzadeh M, Hejaz SM (2010) Fiber—reinforced asphalt concrete. Constr Build Mater 24:871–877

Basegio T, Berutti F, Bernardes A, Bergmann C (2002) Environmental and technical aspects of the utilization of tannery sludge as a raw material for clay products. J Eur Ceram Soc 22:2251–2259

Basegio T, Haas C, Pokorny A, Bernardes AM (2006) Production of materials with alumina and ashes from incineration of chromium tanned leather shavings: environmental and technical aspects. J Hazard Mater 21:1156–1164

Brown EM, Taylor MM, Marmer WN (1996) Production and potential uses of co-products from solid tannery waste. J Am Leather Chem Assoc 91(10):270–276

Cabeza LF, Taylor MM, Brown EM (1999) Treatment of sheepskin chrome shavings. Isolation of high value protein products and reuse of chromium in the tanning process. J Am Leather Chem Assoc 94(7):268–287

Cassano A, Drioli A, Molinari R, Bertolutti C (1997) Quality improvement of recycled chromium in the tanning operation by membrane processes. Desalination 108:193–203

Gammoun A, Tahiri S, Albizane A (2007) Separation of motor oils, oily wastes and hydrocarbons from contaminated water by sorption on chrome shavings. J Hazard Mater 145(1–2):148–153

Imai T, Okamura H (1991) Studies on incineration of chrome leather waste. J Am Leather Chem Assoc 86:281–294

Kamaludeen SPB, Arunkumar KR, Avudainayagam S, Ramasamy K (2003) Bioremediation of chromium contaminated environments. Indian J Exp Biol 41(9):972–985

Koki IB, Jimoh WLO (2015) Assessment of heavy metals in tannery solid waste from Challawa Industrial Estate, Kano State, Nigeria. Int J Res Environ Stud 2:33–40

Mu C, Lin W, Zhang M, Zhu Q (2003) Towards zero discharge of chromium-containing leather waste through improved alkali hydrolysis. Waste Manag 23(9):835–843

Petruzelli D, Passino R, Tiravant G (1995) Ion exchange process for chromium removal and Recovery from tannery wastes. Ind Eng Chem Res 34:2612–2617

Rivela B, Moreira MT, Bornhardt C, Méndez R, Feijoo G (2004) Life cycle assessment as a tool for the environmental improvement of the tannery industry in developing countries. Environ Sci Technol 38(6):1901–1909

Saravanabhavan S, Thanikaivelan P, Rao JR, Nair BU, Ramasami T (2004) Natural leathers from natural materials: progressing toward a new arena in leather processing. Environ Sci Technol 38(3):871–879

Silveira ICT, Rosa D, Monteggia LO, Romeiro GA, Bayer E, Kutubuddin M (2002) Low temperature conversion of sludge and shavings from leather industry. Water Sci Technol 46 (10):277–283

Sivaparvathi M, Suseela K, Nanda SC (1986a) Hydrolytic action of Pseudomonas Aeruginosaon chrome shavings. Leather Sci 33:8–11

Sivaparvathi M, Suseela K, Nanda SC (1986b) Purification and properties of Pseudomona Aeruginosa protease causing hydrolysis of chrome shavings. Leather Sci 33:303–307

Xu N, Zhang C, Qiang X, Zhang B (2009) Building Materials from Stabilization/Solidification of TannerySludge. China Leather 13:13

Yılmaz O, CemKantarli I, Yuksel M, Saglam M, Yanik J (2007) Conversion of leather wastes to useful products. Resour. Conserv. Recy 49:436–448

Performance and Morphological Changes in Aerobic Sludge Biomass Under Stressed Condition Imposed with Copper(II) in Feed

Abhisek Mondal, Rajneesh Kumar and Mohammad Jawed

Abstract The published literature indicates inadequate assessment of imposed stresses on activated sludge morphology. This work aims to study the aerobic sludge biomass morphology under imposed stress and its impact on overall performance. The aerobic sludge biomass was grown up to MLSS concentration of 3800 mg/L on lactogen feed in a batch reactor of 7 L capacity. 400 mL of the aerobic sludge biomass was transferred into two 1-L capacity batch reactors CO1 and R1. These reactors were operated with fill, react, settle and withdraw modes with time period of 5, 1390, 30 and 15 min, respectively, for one complete cycle time of 24 h. The control reactor CO1 was fed with lactogen giving an initial COD level of 1100 mg/L while other stressed reactor R1 was also fed with lactogen along with 5 mg/L of Cu(II). The presence of Cu(II) in feed started to show adverse impact on stressed reactor R1 performance after 10th d of operation as effluent COD started to show increasing trends compared to control reactor CO1. On 15th d of operation, high effluent COD for reactor R1 (1050 mg/L) was observed compared to that of control reactor (85 mg/L). The settling velocity and SVI of aerobic sludge biomass from stressed reactor R1 improved due to adverse impact of Cu(II) but at the cost of high effluent COD. The microscopic and FESEM observations indicated the absence of filamentous micro-organisms in stressed reactor R1 compared to the controlled reactor on 15th d of operation, thereby showing drastic changes in morphology of aerobic sludge biomass due to the presence of Cu(II) in its feed.

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Introduction

Several studies have shown that aerobic biological treatment units get affected with change in substrate, operational and environmental conditions, leading to poor reactor performance. Substrates containing a fraction of toxic substances adversely affect biomass growth which in turn affects biotransformation processes. On the other hand, the effluent quality of an aerobic treatment system depends on bio-separation process. Settling and thickening of aerobic sludge biomass are directly related to floc structures, which depends on chemical, physical and biological factors that influence the balance between filamentous and floc-forming bacteria (Pujols and Canler 1992; Námer and Ganczarczyk 1993; Li and Ganczarczyk 1992). Massé et al. (2006) studied the response of activated sludge process to high sludge retention time (SRT) using domestic wastewater. The increase in organic concentrations in the effluent in terms of protein, polysaccharide and total COD was attributed to increase in SRT. The change in sludge morphology was studied by laser diffraction analysis, microscopic observations, turbidity and sludge volume index (SVI) measurement which suggested growth of filamentous bacteria at higher SRT values. Liao et al. (2006) studied the effect of SRT (in the range of 4–20 days) on sludge floc structure, size distribution and morphology in laboratory-scale sequencing batch reactors (SBRs) fed with glucose-based synthetic wastewater for a year. The morphology of sludge flocs at lower SRTs (4–9 days) was usually more irregular than that at higher SRTs (16–20 days). Wilèn and Balmèr (1998) attempted to correlate structure, size and size distribution of activated sludge biomass with the dissolved oxygen (DO) concentration using pilot-scale completely mixed reactors. The lower DO concentrations (0.5–2.0 mg/L) produced sludge with poorer settling properties and higher turbidity of the effluent than higher DO concentrations (2.0–5.0 mg/L). The deteriorated settling properties were attributed to excessive growth of filamentous bacteria and the formation of porous flocs. Li (2005) investigated effect of Fe(III) on floc characteristics of activated sludge in nine parallel SBRs. Concentrations of Fe(III) up to 23.8 mg/L decreased suspended solids and turbidity in effluent but overdosage resulted in deterioration. Scanning electronic microscopic observation suggested significant changes in floc morphology and reduction in filamentous micro-organisms available for the formation of large aggregates at high Fe(III) concentrations. Gikas (2007) studied effects of Ni(II) on the maximum specific growth rate of activated sludge in a modified batch system. Concentrations of Ni(II) up to 27 mg/L stimulated growth of activated sludge. Further increase in Ni(II) concentration resulted in growth inhibition. Ong et al. (2004) investigated effect of Cu(II) and Cd(II) containing synthetic wastewater on activated sludge micro-organisms using SBR. The COD removal efficiency decreased from 90 to 75% after addition of 5 mg/L Cu(II) and 15 mg/L Cd(II) in the base solution. The addition of Cu(II) and Cd(II) affected significantly the activities of activated sludge micro-organisms in the bio-oxidation process.

The use of activated sludge process for domestic as well as for industrial effluent treatment has captured a great deal of attention. Several past studies have revealed the impact of operational, feed and environmental conditions on the performance of activated sludge process; however, there is a lack of study to correlate the performance with the sludge morphology. Also, the past researchers have not paid enough attention to see what happened to the aerobic biomass when subjected to stress conditions. Hence, the present study investigates performance and morphological changes in aerobic sludge biomass under stressed condition imposed by adding Cu(II) in the feed.

Materials and Methods

Growth of Suspended Aerobic Sludge Biomass

The aerobic biomass was grown in a 7-L capacity batch reactor made of opaque PVC pipe of internal diameter 200 mm and height 310 mm. The reactor was filled with mixed aerobic biomass (grown previously in small reactors using domestic sewage as seed and lactogen as feed substrate), and the volume was made up to 7 L with tap water and fed with 1 g of lactogen/L (giving a feed COD value of 1100 mg/L). The contents of the reactors were aerated with air continuously. After 24 h, the aeration was stopped and settleable contents of the reactor were allowed to settle for 30 min. The supernatant was withdrawn from the reactor. The reactor was fed with lactogen feed and volume made up to 7 L and aeration restarted. This operation was continued to maintain aerobic sludge biomass for carrying out the planned studies. The details are available elsewhere (Mondal 2015).

Performance and Morphological Changes in Aerobic Sludge Biomass

Two 1-L capacity plastic breakers were used as batch reactors for this study. The reactors were filled with 400 mL of mixed liquor from the suspended aerobic biomass reactor, and the final volume was made up to 1 L. The reactors were operated in batch mode with a filling time of 5 min, reaction time of 1390 min, settling time of 30 min, decanting time of 15 min, altogether 24 h for a complete cycle. The experimental set-up used is shown in Fig. 1. The control reactor (designated as CO1) was fed with 1 g of lactogen (Nestle 2014), while the other reactor (designated as R1) was fed with 1 g of lactogen along with 5 mg/L of Cu(II). Thereafter both the reactors were aerated for 5 min, and then, the aeration was stopped to collect liquid samples for analysing initial parameters such as pH, dissolved COD, alkalinity, Cu(II) concentration and reactor temperature. Thereafter aeration in all reactors was restarted and was continued for the rest of the reaction

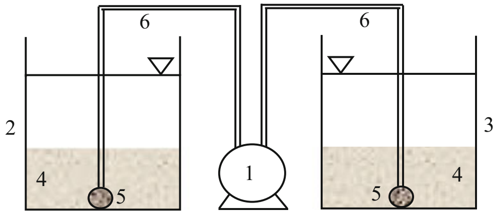


Fig. 1 Schematic of experimental set-up used

1. Aquarium air pump
2. Control reactor CO1
3. Reactor R1
4. Aerobic sludge biomass
5. Aeration stone
6. Flexible silicon tube

time period. The liquid withdrawn during the decanting period was used for analysing effluent parameters such as pH, dissolved COD, alkalinity and Cu(II) concentration. The initial and effluent parameters were estimated every alternate day.

Analytical Techniques Used

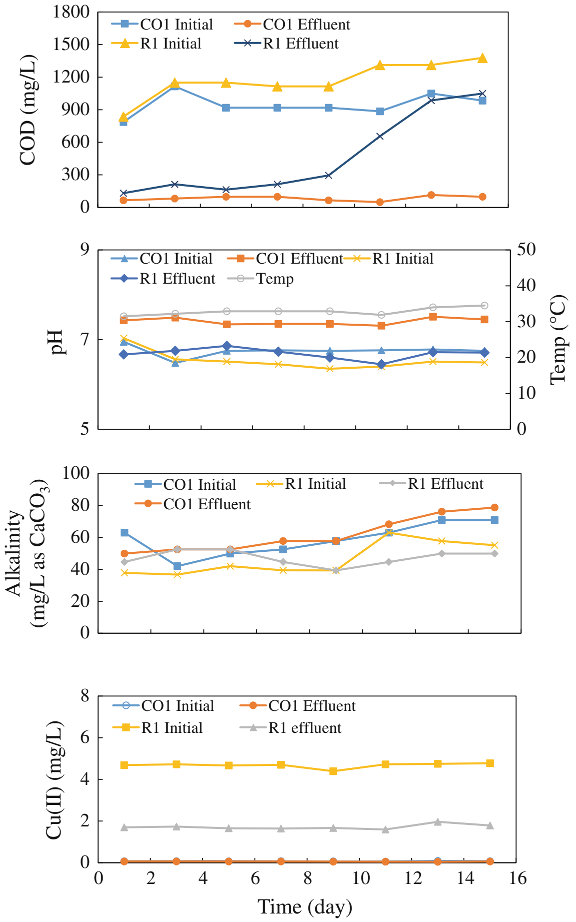
Chemical oxygen demand (COD), pH, alkalinity, Cu(II) concentration and solid analysis of biomass were carried out as per standard methods (APHA 2005). The sludge interface settling measurement was carried out as per method suggested by Peavy et al. (1985). The sludge volume index (SVI) for aerobic biomass of both the reactors was estimated as per method suggested by Metcalf and Eddy (2003). The microscopic observations were made using a compound microscope (×100) with a digital camera attachment.

Results and Discussion

Performance of Aerobic Sludge Biomass

The performance of aerobic sludge biomass was assessed over a period of 15-d operation. The gross variations in initial and effluent parameters are shown in Fig. 2. It clearly indicated adverse impact of Cu(II) in reactor R1 in terms of higher effluent COD compared with control reactor CO1 after 10th d of operation. The effluent COD in reactor R1 was observed to be less than 200 mg/L up to 10th d of operation and thereafter it increased steadily. The effluent COD on 15th d of operation was observed to be around 1050 mg/L in reactor R1 compared to around 85 mg/L in control reactor CO1. However, no variations were observed in reactor pH and alkalinity levels throughout. Also no variations in effluent Cu(II) concentration in reactor R1 was observed. The control reactor CO1 had shown a small initial concentration of Cu(II) which is due to the presence of Cu(II) in lactogen, i.e. 0.28 mg per 100 g lactogen (Nestle 2014).

Fig. 2 Variation in initial and effluent parameters of reactors CO1 and R1



Aerobic Sludge Biomass Characteristics

The impact of Cu(II) on changes in aerobic biomass characteristics was assessed through biomass solid analysis, estimating sludge interface settling and sludge volume index (SVI) once in every 3 d in both the reactors. Mixed liquor suspended solid (MLSS) and mixed liquor volatile suspended solid (MLVSS) concentrations for reactors CO1 and R1 are presented in Table 1. The MLSS and MLVSS concentrations for reactor R1 were relatively lower compared to control reactor CO1. It indicated inhibition of aerobic biomass growth in reactor R1 in the presence of Cu (II). The lower MLVSS levels in reactor R1 might be responsible for deterioration in biotransformation process, thereby deteriorating the effluent quality in terms of COD.

The sludge interface settling test results for biomass of reactors CO1 and R1 are shown in Fig. 3 while estimated interface settling velocities are tabulated in

Table 1 Solid analysis results

Biomass withdrawn on	Solid concentration			
	MLSS (mg/L)		MLVSS (mg/L)	
	Reactor CO1	Reactor R1	Reactor CO1	Reactor R1
1st d	1533.33	1533.33	1266.67	1266.67
4th d	4000.00	2866.67	3466.67	2533.33
7th d	4066.67	3333.33	3933.33	3200.00
10th d	3300.00	3200.00	3100.00	2800.00
13th d	2700.00	1900.00	2300.00	1500.00

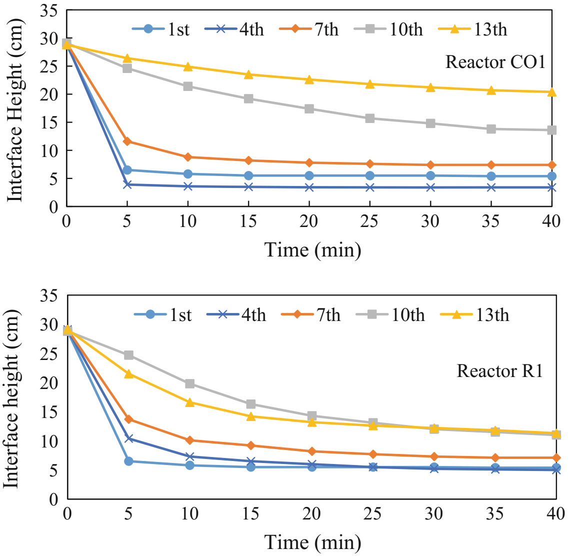


Fig. 3 Sludge interface settling tests for biomass withdrawn on 1st, 4th, 7th, 10th and 13th d of operation from reactors CO1 and R1

Table 2 Interface settling test results

Biomass withdrawn on	Interface settling velocity (m/h)	
	Reactor CO1	Reactor R1
1st d	2.68	2.68
4th d	3.02	2.24
7th d	2.10	1.85
10th d	0.54	0.49
13th d	0.47	0.91

Table 2. The settling velocity of aerobic biomass in reactor CO1 is observed to decrease significantly towards the end of the study indicating filamentous growth. However, comparatively higher interface settling velocity was observed for reactor R1 biomass towards the end of the study. The presence of Cu(II) in reactor R1 feed might have inhibited growth of filamentous biomass.

Table 3 Sludge volume index results

Biomass withdrawn on	Sludge volume index (mL/g)	
	Reactor CO1	Reactor R1
1st d	47.37	47.37
4th d	27.50	59.30
7th d	63.93	72.00
10th d	151.51	131.25
13th d	203.70	152.63

The estimated sludge volume index (SVI) for biomass of both the reactors CO1 and R1 is tabulated in Table 3. The SVI values for control reactor CO1 increased significantly indicating growth of filamentous bacteria towards the end of the operation. In case of reactor R1, similar trends (increasing SVI values) were observed but with relatively lower values of SVI compared to control reactor. Possibly, the presence of Cu(II) inhibited growth of filamentous bacteria in reactor R1.

Microscopic Observations of Aerobic Sludge Biomass Morphology

The biomass samples were withdrawn from reactors CO1 and R1 on 1st, 5th, 10th and 15th d of operation and microscopic observations were carried out. The images of biomasses are shown in Fig. 4. The growth of gram-negative filamentous bacteria was observed for control reactor CO1, whereas the same was not observed for reactor R1 biomasses. A careful look suggests significant change in biomass morphology of reactor R1 biomass compared to that of reactor CO1. The microscopic observations presented gradual growth of filamentous bacteria in reactor CO1, whereas irregular morphology of aerobic biomass was observed in reactor R1. The change in microbial morphology could be attributed to the presence of Cu(II) in reactor R1 feed.

Field Emission Scanning Electron Microscopy Observation of Aerobic Sludge Biomass Morphology

The biomass samples from reactors CO1 and R1 withdrawn on 15th d of operation were analysed in field emission scanning electron microscope (FESEM). The images are shown in Fig. 5. The biomass of control reactor CO1 appeared to be full of filamentous bacteria. On the other hand, no filamentous bacteria were visible in the biomass of R1. It indicated drastic change in morphology of reactor R1 biomass due to the presence of Cu(II) in its feed.

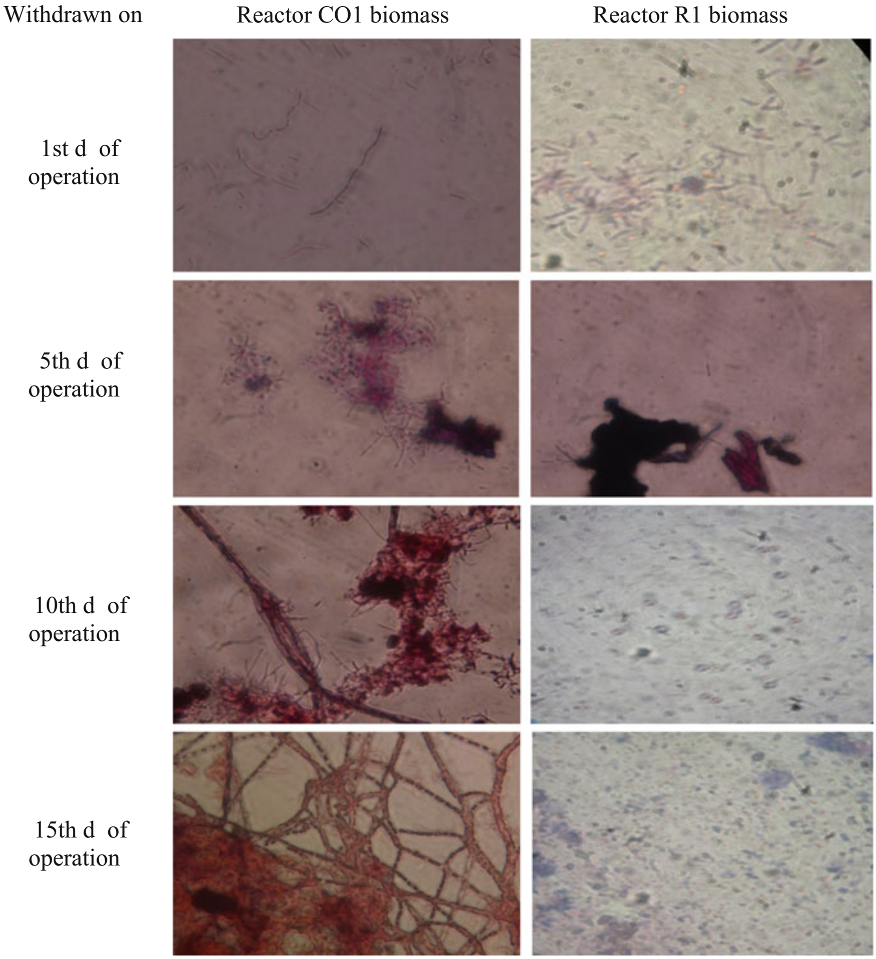
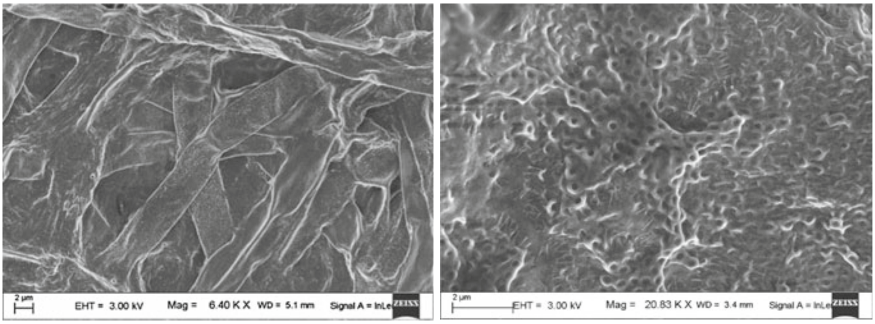


Fig. 4 Microscopic images (×100) of aerobic biomass withdrawn from reactor CO1 and R1

Summary

The results of this study, in general, indicate significant negative impact on aerobic sludge morphology due to the presence of Cu(II) in the feed. The reactor performance in terms of effluent COD deteriorated due to the presence of Cu(II) as it inhibited growth of filamentous micro-organisms. However, the presence of Cu(II) in reactor R1 feed led to improved sludge interface settling velocity and SVI but at the cost of higher COD in effluent. The microscopic and FESEM observation clearly indicated drastic changes in morphology of aerobic sludge biomass of reactor R1 due to the presence of Cu(II) in its feed.



Reactor CO1 biomass

Reactor R1 biomass

Fig. 5 FESEM images of aerobic biomass withdrawn on 15th d of operation from reactors CO1 and R1

References

APHA (2005) Standard methods for the examination of water and wastewater, 20th edn. American Public Health Association, American Water Works Association and Water Environment Federation, Washington, DC, USA

Gikas P (2007) Kinetic responses of activated sludge to individual and joint nickel (Ni(II)) and cobalt (Co(II)): an isobolographic approach. J Hazard Mater 143:246–256

Li J (2005) Effects of Fe(III) on floc characteristics of activated sludge. J Chem Tech Biotech 80:313–319

Li DH, Ganczarczyk JJ (1992) Advective transport in activated sludge flocs. Water Environ Res 64:236–240

Liao BQ, Droppo IG, Leppard GG, Liss SN (2006) Effect of solids retention time on structure and characteristics of sludge flocs in sequencing batch reactors. Water Res 40:2583–2591

Massé A, Spérandio M, Cabassud C (2006) Comparison of sludge characteristics and performance of submerged membrane bioreactor and an activated sludge process at high solids retention time. Water Res 40:2405–2415

Metcalf and Eddy Inc (2003) Wastewater engineering—treatment and reuse, 4th edn. Tata Mc-Graw-Hill, New Delhi, India

Mondal A (2015) Performance and morphological changes in activated sludge under stressed condition, Phase–I M Tech thesis progress report. Department of Civil Engineering, IIT Guwahati, India

Námer J, Ganczarczyk JJ (1993) Settling properties of digested sludge particle aggregates. Water Res 27:1285–1294

Nestle (2014) Nutrition facts. Nestle Consumer Services, PO Bag 2, New Delhi–110001 (ConsumerServices@in.nestle.com)

Ong S, Limb P, Seng C, Hirata M, Hano T (2004) Effects of Cu(II) and Cd(II) on the performance of sequencing batch reactor treatment system. Proc Biochem 40:453–460

Peavy HS, Rowe DR, Tchobanoglous G (1985) Environmental engineering. McGraw-Hill, New Delhi, India

Pujols R, Canler JP (1992) Biosorption and dynamics of bacterial populations in activated sludge. Water Res 26:209–212

Wilèn B, Balmèr P (1998) The effect of dissolved oxygen concentration on the structure, size and size distribution of activated sludge flocs. Water Res 33:340–391

Four-Pronged Preprocessing Approaches for Maximum Utilization of Raw Tannery Sludge by Earthworms

Ankita Swati and Subrata Hait

Abstract The tanning industry is one of the most pollution-intensive and export-oriented industries. Transformation of raw hides into finished leather requires large volume of freshwater and consequently generates wastes in the form of tannery effluents and tannery sludge. The major challenges for safe disposal of tannery sludge being generated from the biological treatment of tannery effluent are linked to its large volume and its characteristics such as high water content, organic matter, chloride and heavy metals content. Vermicomposting employing earthworms has emerged as suitable technique for processing various organic wastes to produce valuable end product, i.e., vermicompost for agronomic applications. Preprocessing is warranted before utilization of raw tannery sludge by earthworms during vermicomposting due to toxicity owing to its characteristics. In this context, four-pronged aerobic preprocessing approaches based on (i) dry weight, (ii) wet weight and (iii) earthworm stress factor such as salinity of raw tannery sludge as well as (iv) water holding capacity of partially dried cow dung as bulking material have been attempted in this study to achieve its maximum utilization by *Eisenia fetida*. Results showed that a 13-day aerobic preprocessing period is the minimum requirement for the maximum utilization of raw tannery sludge by earthworms without mortality at 3:1 ratio (i.e., 75% tannery sludge and 25% partially dried cow dung) on wet weight basis. The maximum amount of raw tannery sludge that can be utilized by *E. fetida* was about 292.2 L with 9.22% solids content per 100 kg of partially dried cow dung with 42.13% moisture content.

Keywords Tannery sludge · Maximum utilization · Toxicity · Earthworms Preprocessing · Vermicomposting

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Introduction

The tanning industry is pollution-intensive and export-oriented industry. In India, there are about 42,000 units with 88% of the major tanneries clustered in Tamil Nadu (TN), Uttar Pradesh (UP) and West Bengal (WB), comprising of about 75% small-scale units, 20% medium-sized and 5% as large-scale units (Gupta et al. 2014). The tanning units both small and large scale are mostly clustered along the major river banks such as River Palar (in TN) and River Ganga (in UP and WB) as they require huge amount of freshwater about 40 m^3 for all unit operations involved in tanning processes for transformation of one tonne of raw hides into tanned leather (Sundar et al. 2001). Further, the tanning units generate huge amount of tannery effluent of about 1200–1300 m^3/day and 150 kg of tannery sludge from their treatment per tonne of raw hide processed (Vig et al. 2011). Further, it has been reported that only about 20% of the large number of chemicals used in the tanning process is absorbed by raw hides/skins and the rest is released as waste (UNIDO 2005). Earlier, the tanning industries are used to discharge their toxic effluents into the flowing surface water and dispose the hazardous sludge in open lands, thereby causing pollution of soil, surface water as well as groundwater due to high ground water table or leaching into the surface water and subsurface aquifers. However, the general approach adopted in India for treatment of tannery effluent has been the commissioning of common effluent treatment plants (CETPs) for tannery clusters with 50% of the capital cost of such CETPs as subsidy to the tanning industry (Tare et al. 2003). Most CETPs treating tannery effluent prescribe preliminary treatment for removal of grits and chromium (Cr) in the tannery itself before centralized biological treatment (Tare et al. 2003). Depending on the activated sludge process (ASP) or upflow anaerobic sludge blanket (UASB) process-based CETP, it has been reported that the sludge derived from the treatment of tannery effluent varies in composition but usually contains very high moisture content, lime, Cr, residual sulfides, chlorides and organic matter (i.e., proteins, hair) (Contreras-Ramos et al. 2004; Kiliç et al. 2011). Apart from the common mineral elements such as Al, Fe, Ca, Mg, Na, K and Si and major nutrients, i.e., N and P in both organic and inorganic forms present insignificant quantities, the presence of heavy metals such as Cr, Cd, Pb, Hg, As, Cu, Ni and Zn and pathogens mostly of fecal origin makes tannery sludge hazardous in nature (Contreras-Ramos et al. 2004; Haroun et al. 2009; Kilic et al. 2011; Vig et al. 2011). In general, the tannery sludge is disposed off onto the land without any treatment, thereby posing serious threat to biota and environment. Vermistabilization has emerged as eco-friendly technique for stabilization of various organic wastes including tannery sludge with the potential for significant immobilization of heavy metals using earthworms. Application of vermicomposting process for stabilization of various toxic industrial wastes includes tannery wastes (Ravindran et al. 2008; Vig et al. 2011), paper mill wastewater sludges (Negi and Suthar 2013), textile mill sludges (Kaushik et al. 2008) and sugar industry sludges (Khwairakpam and Bhargava 2009; Prakash and Karmegam 2010). Further, being a "zero discharge" process, the vermistabilization will augment well with the tanneries in lieu with various river basin environmental management plans. Nevertheless, preprocessing of the tannery sludge is to be warranted before utilization by earthworms during vermicomposting due to the toxicity owing to its characteristics.

However, the raw tannery sludge in its crude form is toxic to earthworms due to higher concentration of organic matter, heavy metals, chromium salts, limes, pathogens and others. The basic premise of the present study is to maximize the utilization of raw tannery sludge by earthworms without any mortality or harmful effects on the worms. Various studies have suggested different approaches such as dilution of wastes, removal of calcium salts, lime amendments and acclimatization of worms in order to reduce the toxicity making it palatable for the earthworms. However, it requires either the use of chemicals that may pose an additional challenge to biological degradation or may have adverse effects on the worms. Several researchers have suggested 15–20 days of "pre-composting" which is an integrated approach of composting followed by vermicomposting although for "pre-composting" to function effectively a large compost heap is needed that may trap the heat generated by the metabolic processes. Therefore, a simple alternative to the labor-intensive and time-consuming pre-composting process is aerobic "preprocessing" where the reaction systems are kept at room temperature with frequent turning, thereby eliminating toxic noxious gases and making the substrate suitable for earthworms to act on. The respective worms are then introduced into the systems but only for the limited period of time. This preprocessing step is same as pre-composting but performed on a smaller scale utilizing lesser amount of reaction substrate. This process is continued till earthworms show positive response toward the substrate. Preprocessing experiments are conducted in order to determine the sustainability of earthworms with the goal of maximum utilization of raw tannery sludge by earthworms on laboratory scale. Critical review of scantly available scientific studies on vermistabilization of tannery sludge reveals that the maximum utilization of raw tannery sludge in its crude form by earthworms has not been considered in any study by taking into account the various stress factors for earthworms such as chlorides, sulfates and Cr present in it. In this context, four-pronged aerobic preprocessing approaches based on (i) dry weight, (ii) wet weight, (iii) earthworm stress factor such as salinity of raw tannery sludge and (iv) water holding capacity of partially dried cow dung as bulking material have been attempted in this study to achieve its maximum utilization by *Eisenia fetida* without any mortality or harmful effects on the worms.

Materials and Methods

Tannery Sludge

Primary clarified raw tannery sludge (RTS) was collected on periodical basis from two different common effluent treatment plant (CETP) units: upflow anaerobic sludge blanket (UASB)-based CETP at Unnao, Kanpur, and activated sludge process (ASP)-based CETP at Banthar, Kanpur. Complete physicochemical characterization of the collected raw tannery sludge was performed prior to experimentation for preliminary determination of the various stress contributing factors active during preprocessing of RTS by earthworms.

Bulking Material

Cow dung (CD) is used as the bulking material for the experiment. It was partially air-dried in the sun for one week in order to remove unwanted gases (methane, ammonia, carbon dioxide) and heat that may cause harm to earthworms. The physicochemical characteristics of CD were also determined prior to experimentation.

Earthworm

Exotic earthworm species *E. fetida* of different age groups were procured from a vermiculture unit “Subhasree” at Deoghar, Jharkhand. The earthworms were cultured in small circular laboratory-scale plastic containers using partially dried cow dung as bedding and feeding material. The earthworms (both juvenile and adult) were randomly picked from the stock culture and were then used for the investigation.

Experimental Methods

Physicochemical Analysis of Raw Tannery Sludge and Bulking Material

All the parameters of RTS and CD were analyzed in accordance with the procedures outlined in the Standard Methods (APHA et al. 2012). Moisture content (MC) and total solids (TS) were determined by drying the samples to constant weight at 70 ± 2 °C and 105 °C, respectively for 24–72 h using hot air oven. For determination of pH, oxidation reduction potential (ORP), electrical conductivity (EC), total dissolved solids (TDS), 1:10 (w/v) suspension of samples in distilled water was prepared with continuous stirring at 230 rpm for 30 min, and thereafter, the solution parameters were measured using pH meter and conductivity/TDS meter. Volatile solids content (loss on ignition) was obtained by combusting the dried samples (at 105 °C) in muffle furnace at 550 ± 5 °C for 2 h. Elemental analysis was done using atomic absorption spectrophotometer (Thermofischer Scientific, USA) by digesting dried samples (USEPA 3052 method) in microwave digester (Anton Paar GMBH, Austria). The ionic concentrations both anionic and cationic were determined using Ion Chromatography (882 Compact IC plus, Metrohm), and the sample was prepared by dissolving 1 g of the dried sample in 100 mL of distilled water.

Four-Pronged Preprocessing Approaches for Maximum Utilization of Raw Tannery Sludge by E. fetida

The study was conducted in order to determine the maximum utilization of raw tannery sludge by earthworm *E. fetida* without any form of stress and/or physical deformities by following four-pronged preprocessing approaches. The approaches that have been attempted in this study to achieve the maximum utilization were based on (i) dry weight (DW), (ii) wet weight (WW), (iii) earthworm stress factor such as salinity of raw tannery sludge (SL) as well as (iv) water holding capacity of partially dried CD as bulking material (WH). The main purpose of this experimentation is to observe and to assess whether earthworms when introduced into the different reaction system were stable or not and up to what percentage of RTS is acceptable and/or palatable for earthworms. For experimentation, owing to high water content and low solid content, the RTS was used in crude form (slurry) without any physical and/or chemical pre-treatment as most of the components were present in soluble form and was mixed in different proportions depending on the approaches.

On dry weight basis, the RTS was mixed with the bulking material in different proportions of 100:0, 90:10, 75:25, 50:50, 25:75, 10:90 (CD:RTS) owing to the solid content of RTS (i.e., 93.64 ± 0.84 and 53.16 ± 3.79 g/L for Banthar and Unnao RTS, respectively) in DW reactors. Similarly, for WW reactors the bulking material was mixed with the RTS in the ratio of 100:0, 90:10, 75:25, 50:50, 25:75, 10:90 on wet weight basis. As CD has the ability to absorb the water content of the RTS, thereby making it suitable for earthworms to act on. Therefore, in WH reactors, the RTS was mixed with the CD in the different percentages of its maximum water holding capacity (WHC) on wet weight basis such as 20, 40, 60 and 80%. However, salinity refers to the sodium or chlorides content and can be correlated with the EC of the solution (Contreras-Ramos et al. 2004; Haroun et al. 2004) and it has been reported that high salinity or EC can adversely affect the microbial community involved in the process and thus the biotransformation of the organic matter during vermistabilization. Therefore, the EC of all the reactors was determined during the preprocessing of RTS amended with cow dung as bulking material. The total reaction mixture weight was kept 1 kg consisting of CD and RTS in all the reactors. The different reactors were then kept at room temperature with frequent turning in order to ensure proper supply of oxygen for aerobic degradation as well as elimination of volatile toxic gases that were being produced. The moisture content of the mixture in the reactors was always maintained between

60 and 70% by sprinkling tap water during the entire period to preserve the microbial activity. The mixtures from different reactors were collected initially (first day) as well as after every three days to analyze for various physicochemical parameters like pH, ORP, EC, TDS, TS, volatile solids (VS) and MC during the process.

Results and Discussion

Physicochemical Analysis of Raw Tannery Sludge and Bulking Material

Raw tannery sludge shows wide variations in its properties based on the nature of the raw material used (i.e., hides/skins obtained from cows, sheep, goats, buffaloes or others) and nature of the finished product to be processed (i.e., whether processing for shoes, jackets, bags and others). Apart from the two primary factors, there are other contributing factors such as seasons, tanning agent, water consumption, scale of the tanning unit and availability of the treatment facility. Based on the two primary factors, viz. nature of raw material and finished product, every tanning unit uses different range of chemicals, salts and tanning agent that determines the characteristics and/or composition of the tannery sludge. The RTS collected from both the CETPs, i.e., ASP-based and UASB-based plants, was dark gray in color, pungent odor, with moisture content more than 90%, alkaline and toxic as indicated by their high salt concentration. The physicochemical characteristics of RTS along with their ionic concentrations from the different CETPs and CD are reported in Tables 1, 2 and 3, respectively. It has been observed that certain ions were in high concentration irrespective of the CETPs such as chromate, sulfates and chlorides. Further, the elemental composition obtained upon microwave-assisted digestion following USEPA 3052 of RTS has shown the presence of some heavy metals such as Fe, Cu, Zn, Pb, Cd, Co, Mn, Ni and others as mentioned in Table 4.

Table 1 Physicochemical parameters of RTS from different CETPs ($n = 6$)

Parameters	RTS, Banthar	RTS, Unnao
pH	8.75 ± 0.03	8.8 ± 0.01
EC (mS/cm)	22.1 ± 0.04	16.1 ± 0.02
ORP (mV)	−61 ± 2.08	−64 ± 2.81
TDS (g/L)	14.5 ± 0.02	10.5 ± 0.05
TS (g/L)	93.64 ± 0.84	53.16 ± 3.79
VS (g/L)	34.97 ± 1.10	17.65 ± 1.35
MC (%)	90.7 ± 1.56	94.8 ± 0.72

Table 2 Ionic concentrations of RTS from different CETPs ($n = 1$)

Parameters (mg/g)	RTS, Banthar	RTS, Unnao
Fluoride	0.0887	0.0968
Chloride	267.579	236.9115
Nitrite	N.D.	N.D.
Bromide	0.0354	0.0426
Nitrate	0.0219	0.0406
Phosphate	0.0264	0.0444
Sulfate	106.1089	67.9573
Arsenate	0.0535	N.D.
Chromate	24.9465	17.6978
Lithium	0.0007	0.0017
Ammonium	0.0899	0.0118
Potassium	22.9153	13.6723

N.D.: Not detected

Table 3 Physicochemical characterization of partially dried CD ($n = 1$)

pH	9.08 ± 0.72	Lithium (mg/kg)	N.D.	Chloride (mg/kg)	1314.5
EC (mS/cm)	6.06 ± 0.03	Sodium (mg/kg)	846.4	Nitrite (mg/kg)	N.D.
ORP (mV)	−74 ± 2.94	Ammonium (mg/kg)	73.3	Bromide (mg/kg)	N.D.
TDS (g/L)	3.92 ± 0.36	Potassium (mg/kg)	3535.8	Nitrate (mg/kg)	66.1
VS/TS (%)	65 ± 0.59	Calcium (mg/kg)	959.6	Phosphate (mg/kg)	1550.4
WHC (%)	79.27 ± 0.87	Magnesium (mg/kg)	491.9	Sulfate (mg/kg)	345.0
MC (%)	42.13 ± 0.61	Fluoride (mg/kg)	12.1	Arsenate (mg/kg)	N.D.
				Chromate (mg/kg)	N.D.

N.D.: Not detected

Table 4 Elemental composition of RTS from different CETPs ($n = 4$)

Parameters	RTS, Unnao	RTS, Banthar
Method	*EPA 3052*	*EPA 3052*
Sodium (mg/g)	1.4038 ± 0.002	1.4465 ± 0.002
Calcium (mg/g)	0.4392 ± 0.114	0.1610 ± 0.045
Magnesium (mg/g)	0.5519 ± 0.021	0.6967 ± 0.003
Aluminum (mg/g)	1.5424 ± 0.055	2.0020 ± 0.760
Cobalt (mg/g)	0.0113 ± 0.003	N.D.
Nickel (mg/g)	0.1465 ± 0.040	N.D.
Manganese (mg/g)	0.2832 ± 0.011	0.0846 ± 0.016
Zinc (mg/g)	0.1921 ± 0.003	0.2055 ± 0.048
Copper (mg/g)	0.2779 ± 0.001	0.0417 ± 0.003
Iron (mg/g)	8.1652 ± 0.095	1.6187 ± 0.211
Chromium (mg/g)	19.6466 ± 0.027	19.0295 ± 0.021
Lead (mg/g)	0.0795 ± 0.002	N.D.

N.D.: Not detected

Four-Pronged Preprocessing Approaches for Maximum Utilization of Raw Tannery Sludge by E. fetida

In DW approach, due to low solid and high water content, the reaction mixture became watery with the decrease in bulking material and increase in RTS concentration. It was observed that only 10% of the RTS can be used for the study, while in R25 reactor the mixture became unfit for introduction of earthworms with addition of only half of the required volume. Similar results were obtained for UASB-CETP RTS. Therefore, this approach was not further extended. Similarly, in WW approach, following 13 days aerobic preprocessing it was observed that the earthworm *E. fetida* was unstable and showed physical deformities when exposed to reactor containing 75% of RTS from Banthar, while the worms were stable in 75% of RTS from Unnao, CETP further supporting the finding that Unnao RTS is less toxic than Banthar. The high concentration of salts and chromate may be one of the factors. Exhibits 1 and 2 show the stability, i.e., survival of earthworms (*E. fetida*), when introduced in the respective reactors systems for a definite period of time. The various physicochemical parameters analyzed during the preprocessing of the reaction mixture containing different proportions of RTS from both the CETPs are reported in Figs. 1a–c, 2a–c and Table 5. Furthermore, in WH approach, it was observed that the earthworms were stable and showed no physical deformations within 4 days of preprocessing suggesting that the reaction mixture containing RTS of up to 80% of the WHC of the CD was acceptable for earthworms. The following observation is shown in Exhibit 3. Salinity is defined as the high salt content mostly due to sodium or calcium salts. As these salts contribute to the dissolved component of the solution, their presence can be correlated with the obtained EC. The present study posits that earthworms were unstable in those reactors that had EC above 15 mS/cm and showed physical deformations such as splitting of the bodies into fragments, secretion of yellowish fluid or formation of blisters. Therefore, in UASB-CETP-based RTS the earthworms showed stability even at 75% of RTS although it was not applicable with ASP-CETP-based RTS. This finding was valid for reactors containing RTS on the WH basis of CD also as in all those reactors the EC was well below 15 mS/cm (Table 5).

Exhibit 1 Response of *E. fetida* in ASP-CETP RTS-based systems

Reactors	Day 1 (1 h)	Day 2- Day 3 (3 h)	Day 4-Day 7 (6 h)	Day 8 -Day 10 (12 h)	Day 11-Day 13 (24 h)
R10	░	░	░	░	░
R25	░	░	░	░	░
R50	▒	░	░	░	░
R75	▓	▓	▓	▓	▓
R90	█	█	█	█	█

Exhibit 2 Response of *E. fetida* in UASB-CETP RTS-based systems

Reactors	Day 1 (1 h)	Day 2- Day 3 (3 h)	Day 4-Day 7 (6 h)	Day 8 -Day 10 (12 h)	Day 11-Day 13 (24 h)
U10					
U25					
U50					
U75	░				
U90	▓	▓	▓	▓	▓

STABLE	░ **STABLE** Remained on Surface	▒ **UNSTABLE** Tried to Escape	▓ **EARTHWORMS NOT ADDED**

R stands for reactors containing ASP-CETPs RTS and CD; *U* stands for reactors containing UASB-CETPs RTS and CD; 10, 25, 50, 75, 90 = % of RTS in the reaction mixture

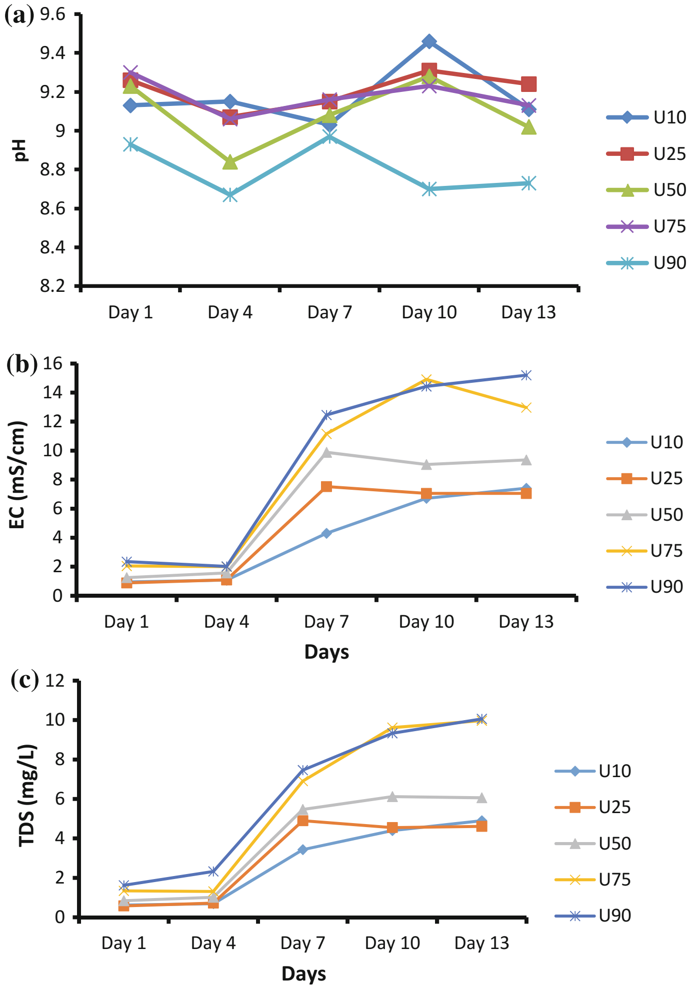

Fig. 1 **a** Variation in pH during preprocessing of Unnao RTS. **b** Variation in EC during preprocessing of Unnao RTS preprocessing of Unnao RTS. **c** Variation in TDS during preprocessing of Unnao RTS

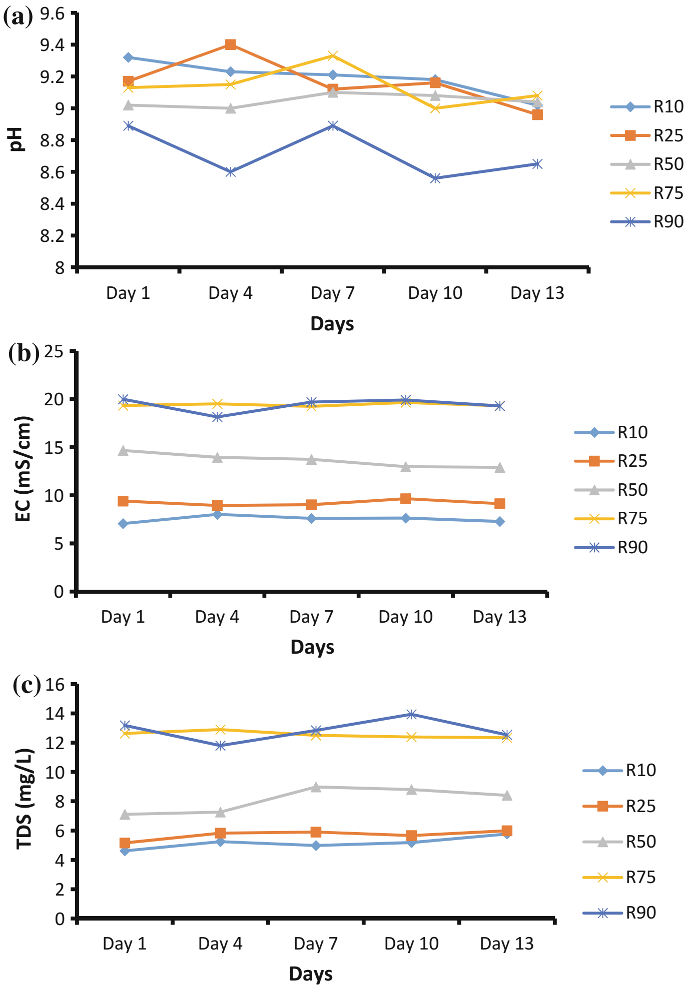

Fig. 2 **a** Variation in pH during preprocessing of Banthar RTS. **b** Variation in EC during preprocessing of Banthar RTS. **c** Variation in TDS during preprocessing of Banthar RTS

Based on the different approaches followed, it was observed that after thirteen days of preprocessing of RTS up to 75% of Unnao RTS and 50% of Banthar RTS were acceptable by earthworms on wet weight basis. It has been observed that the EC shows an increasing trend with days in case of RTS from Unnao, while very little variation was observed in case of Banthar RTS and the EC values were much greater than those of Unnao. Since TDS is directly correlated with the EC, therefore similar trend with respect to EC was obtained for both the sludges collected from two different CETPs (i.e., ASP based and UASB based). The VS showed a gradual decrease suggesting decomposition and degradation of organic material during the

Table 5 Changes in physicochemical parameters during preprocessing of reaction mixture on wet weight basis

Reactors	ORP (mV)	VS/TS (%)	MC (%)	Day	ORP (mV)	VS/TS (%)	MC (%)	Reactors
R10	−87	64.49	68.07	Day 1	−76	62.73	68.33	U10
R25	−77	63.21	67.76		−85	61.98	71.47	U25
R50	−71	62.56	66.22		−82	59.68	74.34	U50
R75	−75	60.83	74.41		−84	55.97	81.67	U75
R90	−63	54.98	83.89		−65	57.24	86.28	U90
R10	−72	60.27	64.28	Day 13	−77	57.98	67.21	U10
R25	−68	58.29	62.01		−81	53.83	64.95	U25
R50	−74	63.47	60.15		−74	56.66	70.64	U50
R75	−73	56.79	64.11		−78	51.9	66.49	U75
R90	−51	49.84	76.96		−57	53.73	82.48	U90

R stands for reactors containing ASP-based RTS and CD; *U* stands for reactors containing UASB-based RTS and CD; 10, 25, 50, 75, 90 = % of RTS in the reaction mixture

Exhibit 3 Response of *E. fetida* in WH reactors

Reactors	Day 1 (6 h)	Day 2 (12 h)	Day 3 (18 h)	Day 4 (24 h)
W20				
W40				
W60				
W80				

STABLE

W stands for both the reactors containing ASP- and UASB-based RTS and CD in different reactors, respectively; 20, 40, 60, 80 = % WHC of CD in the reaction mixture

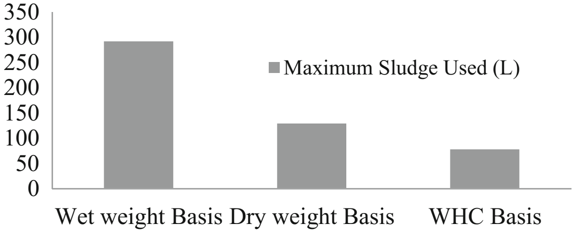

Fig. 3 Maximum utilization of RTS per 100 kg of CD following different approaches

preprocessing duration resulting in stabilization of the reaction substrate, and subsequently, a gradual increase in the TDS and EC of the reactor systems was observed. The moisture content of the entire reactor systems was maintained to about 60–70%. Following the four different approaches, it was observed from experimentation that maximum sludge utilization was obtained when the raw tannery sludge was mixed with bulking material on wet weight basis (Fig. 3). The maximum sludge acceptable by earthworms was on wet weight basis and about 292.2 L of raw tannery sludge (9.22 ± 1.88% solid content) can be utilized per 100 kg of bulking material (42.13 ± 0.61% moisture content) used on wet weight basis. The present study posits that earthworms were unstable in those reactors that had EC above 15 mS/cm and showed physical deformations such as splitting of the bodies into fragments, secretion of yellowish fluid or formation of blisters. Therefore, in UASB-CETP-based RTS the earthworms showed stability even at 75% of RTS although it was not applicable with ASP-CETP-based RTS. This finding was valid for reactors containing RTS on the WHC basis of bulking material also as in all those reactors the EC was well below 15 mS/cm.

Conclusions

Based on the content of the heavy metals, chromium and different ions present in the raw tannery sludge, it can be said that the Banthar's (ASP-based CETPs) raw tannery sludge is more hazardous than the Unnao's (UASB-based CETPs). From the present analysis, it could be stated that a minimum of 13 days are required for the initial aerobic preprocessing is warranted for stabilization of the raw tannery sludge for *E. fetida* to act on them. Also, maximum utilization of raw tannery sludge by *E. fetida* was obtained when the sludge was mixed with the bulking material (cow dung) on wet weight basis, i.e., based on the water content of the tannery sludge. Further, it can be stated that a 13-day aerobic preprocessing period is the minimum requirement for the maximum utilization of raw tannery sludge by *E. fetida* without mortality at 3:1 ratio (i.e., 75% tannery sludge and 25% partially dried cow dung) on wet weight basis. The maximum raw tannery sludge acceptable by earthworms was on wet weight basis and about 292.2 L of raw tannery sludge (9.22 ± 1.88% solid content) can be utilized per 100 kg of bulking material (42.13 ± 0.61% moisture content) on wet weight basis. Moreover, apart from the other stress contributing factors such as heavy metals and Cr, salinity is one of the major stress factors active during the aerobic preprocessing of the raw tannery sludge.

References

APHA, AWWA, WEF (2012) Standard methods for the examination of water and wastewater. 22nd edn. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC

Contreras-Ramos SM, Alvarez-Bernal D, Trujillo-Tapia N, Dendooven L (2004) Composting of tannery effluent with cow manure and wheat straw. Biores Technol 94(2):223–228

Gupta S, Sharma M, Singh UN (2014) Tannery clusters in India and waste management practices in tannery intensive states–inventory and status. J Environ Sci Toxicol Food Technol 8:2319–2399

Haroun M, Idris A, Omer S (2004) Composting of tannery sludge with chicken manure and rice bran Suranaree. J Sci Technol 11:300–307

Haroun M, Idris A, Omar S (2009) Analysis of heavy metals during composting of the tannery sludge using physicochemical and spectroscopic techniques. J Hazard Mater 165(1–3):111–119

Kaushik P, Yadav YK, Dilbaghi N, Garg VK (2008) Enrichment of vermicomposts prepared from cow dung spiked solid textile mill sludge using nitrogen fixing and phosphate solubilizing bacteria. The Environmentalist 28(3):283–287

Khwairakpam M, Bhargava R (2009) Bioconversion of filter mud using vermicomposting employing two exotic and one local earthworm species. Biores Technol 100(23):5846–5852

Kiliç E, Puig R, Baquero G, Font J, Colak S, Gürler D (2011) Environmental optimization of chromium recovery from tannery sludge using a life cycle assessment approach. J Hazard Mater 192(1):393–401

Negi R, Suthar S (2013) Vermistabilization of paper mill wastewater sludge using *Eisenia fetida*. Biores Technol 128:193–198

Prakash M, Karmegam N (2010) Vermistabilization of pressmud using *Perionyx ceylanensis*. Mich Biores Technol 101(21):8464–8468

Ravindran B, Dinesh SL, Kennedy LJ, Sekaran G (2008) Vermicomposting of solid waste generated from leather industries using epigeic earthworm Eisenia foetida. Appl Biochem Biotechnol 151(2–3):480–488

Sundar VJ, Ramesh R, Rao PS, Saravanan P, Sridharnath B, Muralidharan C (2001) Water management in leather industry. J Sci Ind Res 60:443–450

Tare V, Gupta S, Bose P (2003) Case studies on biological treatment of tannery effluents in India. Air Waste Manage Asso 53:976–982

UNIDO (United Nations Industrial Development Organization) (2005) Cost of tanned waste treatment. In: 15th session of the leather and leather products industry panel. Leon, Mexico

Vig AP, Singh J, Wani SH, Dhaliwal S (2011) Vermicomposting of tannery sludge mixed with cattle dung into valuable manure using earthworm *E. fetida* (Savigny). Biores Technol 102 (17):7941–7945

Impacts of Pit Latrine Additives on Volatile Solids and *E. coli* in Faecal Sludge

Ednah Kemboi, Jack van de Vossenberg, Christine Hooijmans and Grover Mamani

Abstract Indiscriminate disposal of faecal matter is a health risk. Although sanitation facilities provide the first barrier to the spread of diseases, full pits may pose more risks. Therefore, it is a necessity to treat faecal sludge (FS) to reap the benefits of sanitation. This paper describes a laboratory and field pilot study of the effects of 10 additives on the volatile solids (VS) and *E. coli* concentrations in black water and FS, respectively, over a period of two weeks. The additives were dosed at 1.7% with one run for FS dosed at 3.4%. Generally, the additives showed no significant difference with the controls, except two of chemical origin (Ikati and Soda) which had VS reduction >38% and *E. coli* below detection limit at low total solids (TS) concentrations. However, performance of these additives reduced at higher TS concentrations. Further research on the optimal dosages of these two additives that yield sanitised and stabilised sludge is warranted.

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Introduction

Sanitation in the world has been improving albeit slowly for the last two decades. It is reported that since 1990, an extra 2.1 billion people have access to improved sanitation bringing the sanitation coverage to an estimated 68% (JMP 2015). The number of people served by onsite systems is estimated to be about 2.7 billion people (Strande 2014). Regardless of the improvements made, 15% of the world population, which are about 2.4 billion people, still are not served by improved sanitation systems, with about 40% practicing open defecation (JMP 2015). Moreover, owners of pit systems which are full are regarded as lacking access to improved sanitation (Bhagwan et al. 2008a, b).

Indiscriminate disposal of untreated faecal matter is a health hazard. Untreated faecal matter is laden with pathogens which cause illnesses such as diarrhoea, cholera and dysentery (Wisner and Adams 2002). According to WHO (2013), diarrhoea is the second highest cause of death in children under five with an estimated 760,000 children dying annually. When faecal matter comes into contact with water sources, it pollutes the water, leading to water borne diseases when contaminated water is consumed. In addition, flies which breed on faecal matter may transfer pathogens to the food, and if the flies are present in large densities, then it may lead to break out of trachoma in children (Harvey 2007).

The large concentration of the population in emergency situations coupled with factors such as inadequate supply of clean water, and lack of sanitation facilities led to explosion of diarrhoeal diseases. Further, pollution of available water sources by faecal matter will exacerbate the situation resulting in death especially of children, if not controlled on time (Connolly et al. 2004).

To avoid disposal of untreated faecal matter into the environment, treatment options that can sanitise (kill pathogens) and stabilise faecal matter (reduce vector attraction) need to be employed in the immediate phase of emergencies. Several chemical and biological processes have been tested in the field for their efficacy in an emergency set-up. Studies carried out to establish efficacy of treatments in the context of an emergency concluded that treatment of faecal sludge using urea, lime and lactic acid fermentation can sanitise faecal sludge safely in between 3 and 15 days, if certain conditions are provided (de Pooter 2014; González Pérez 2014; Malambo 2014; Nobela 2014).

However, the studies did not investigate the stability of the end product. Further research is required to determine other treatment methods that can be employed to sanitise and stabilise faecal sludge. Manufacturers of additives claim that their products increase the rate of decomposition. Earlier research on the use of additives to stabilise faecal matter gave mixed results; some state that biological additives work (Jere et al. 1998; Taljaard et al. 2003) while others claim that they do not work (Buckley et al. 2008; Foxon et al. 2008; Bakare 2011). The observed differences may be attributed to the difference in stabilisers, method of application and management issues (number of users, almost full pits, ownership of facility and whether the pit was or was not in use during the experimental period).

Earlier Studies on Use of Pit Latrine/Septic Tank Additives

Manufacturers and suppliers of septic tank and pit latrine additives claim that the additives reduce the rate of latrine fill-up by increasing the rate of degradation of organics. A limited number of scientific studies have been carried out to determine the efficacy of bio-additives to increase the decomposition of pit latrine contents. Five studies were indentified when searching the scientific literature. Four of these studies were carried out within projects of Water Research Commission (WRC) South Africa while the remainder was carried out in Zimbabwe by Blair laboratories. Some of the studies were carried out in situ, whereas others were carried out both at a lab-scale and in situ.

Jere et al. (1998) carried out a study to determine the efficacy of a bio-additive named bio-organic breakdown compound to degrade solids in a pit latrine eventually leading to volume reduction. The bio-organic breakdown compound is described as "non-pathogenic spore forming bacteria". This study carried out in a rural area of Zimbabwe made use of four lined walls pit latrines which were almost full, with number of users ranging from 5 to 13. The bio-additive was applied weekly for four weeks through injection using a perforated tube that allowed adequate mixing of the pit contents and the additive. The height of the pit contents, COD, BOD, total solids, suspended solids, organic and inorganic solids was determined. The results indicated that the additives led to significant reduction in height of the contents of the pit. In addition, it showed that the BOD and COD reduced continuously during the treatment but increased after the treatment stopped. The reduction in COD and BOD in the study is attributed to the additive which increased the rate of degradation. Although the results presented showed some changes, Foxon et al. (2008) noted some shortfalls of the study. The study did not have a pit treated as a control; thus, how significant the reported changes are cannot be quantified statistically. Moreover, the effect of the application method (injection under pressure) and water cannot be singled out so that the actual effect of additives only could be determined. Notwithstanding the identified shortfalls, the authors point out that the additives have the potential of breaking down latrine organics thereby slowing down the fill-up rates.

Another study carried out by Taljaard et al. (2003) sought to establish whether additives would improve the degradation of organics in pit latrines. The study entailed laboratory tests to determine the ability of 12 additives to aid the decomposition of organics and field tests (2 additives) to determine volume reduction. The contents of the additives were described in terms of the type and/number of micro-organism and/or enzymes present and the conditions under which the product was useful. The lab test was carried out under aerobic conditions in a fully automated Micro-Oxymax respirometer where measurements of oxygen consumption and/or carbon dioxide production were used to determine the biodegradability. This led to choosing two additives which were later tested in the field: product B which is consortia of aerobes and anaerobes ($\approx 10^8$ cfu/g) mixed with enzymes, and product M which contained 5 strains of bacteria ($\approx 10^6$ cfu/g), yeast and enzymes. The field test involved tests on blocks of latrines each with 3 latrines, whereby each pit was dosed with a recommended dose of 100 g per pit, and 25 L of water poured everyday. The control had an equal amount of water poured. The change in height measured using a marked pole ranged between 13 and 22 cm and 3 and 5 cm for product B and M, respectively. In addition, the fly problem was eliminated and the odour reduced in pits treated with B, whereas those treated with M still had odour and reduced fly population. The control showed no change with regard to height, odour and fly problems. The large variance in height measurements recorded for the replicates of pits treated with each product could not allow the difference in efficiency of treatments to be statistically evaluated. Notwithstanding the stated reason, the author concluded that the additives have a potential to increase degradation of organics, thus reducing pit volumes.

Buckley et al. (2008) carried out a field study of one brand of additive and measured the change in height of the latrine contents to calculate the reduction in volume. The results obtained gave no observable trend between the height lost and bio-additive. In addition, the method of simple height loss determination was subjective and less accurate due to changes in shape of latrine contents. The change could be attributed to water ingress which led to flattening of heaps. Moreover, the observations linked the volume reduction to other factors such as the ownership and management of pit.

The inadequate evidence linking additives and biodegradation (Buckley et al. 2008), and the shortfalls of evaluated studies carried out by other researchers led to development of protocols which guide tests for efficacy of additives (Foxon et al. 2008). The protocol allowed an experimental set-up where the effect of additive on the degradation process could be singled out. The set-up was run for between 27 and 46 days, whereby the mass loss was measured every three days, whereas the COD and moisture content were determined at the start and end of experiment. The experiment results showed that mass loss under anaerobic set-up was negligible while that under aerobic condition was 22 times higher and was significant at 0.8 kg/m^2/day. However, the comparison of replicates within treatments and between treatments and the controls in the aerobic set-up showed negligible differences in COD removal and moisture. Consequently, mass loss was attributed to dehydration and biological activity mediated by micro-organisms naturally present in faeces. This lead to the conclusion that additives do not improve the rate of degradation.

Bakare (2011) applied the protocol developed by Foxon et al. (2008) to test the efficacy of additives to increase degradation as well as reducing pit contents using improved distance measurements. He evaluated the effect of two products on the mass loss of VIP sludge exposed to the air at the lab. Product A was described as a free flowing powder containing 5 billion cfu/g of bacteria, with a wide pH and temperature application range, applicable in various sanitation systems and reduces odour. Product B was described in terms of functions it renders: it completely removes fly and odour problems enhance reduction of solids and yield a stable product similar to compost. The results showed insignificant mass loss during 30 days treatment with product A 0.69 g/day/jar, B 0.62 g/day/jar, control

0.69 g/day/jar and water reference 0.63 g/day/jar. Further, the products were tested in the field each on 8 pit latrines and the controls on 7 pit latrines each. The reduction in height of pit contents was evaluated over six months using infrared and stereographic imaging techniques. The infrared distance measurements showed the pits treated with water only had significant reduction compared to the rest. However, this was refuted by the result of the stereographic imaging—which gives better accuracy—which showed no significant difference between the treatments and the controls. The author attributed this to the effect of water causing flattening of the topmost part of the pit. In conclusion, VIP sludge treated with the said additives showed neither improved degradation nor volume reduction.

Notwithstanding the findings on the efficacy of biological additives, there seems to be a promise with using biological additives to treat faecal sludge as indicated by isolated studies treating different types of wastes. These studies have shown the ability of isolated microbes and/or enzymes to aid in increasing the rate of degradation in different substrates and conditions (Gaikwad et al. 2014; Lakshmi et al. 2014; Merrylin et al. 2014). For example, Lakshmi et al. (2014) observed that preliminary treatment of waste activated sludge (WAS) with NaOH and treatment with two *Bacillus* bacterial strains extracted from WAS led to better performance in destruction of organics in an aerobic digester. Also, using of cation binding substances such as zeolite, citric acid and EDTA for preliminary treatment followed by a mixture of 3 enzymes—endo- and exo-cellulase and alpha-amylase improved the rate of hydrolysis. The amount of soluble COD was increased, whereas the suspended solids were greatly reduced in the enzyme treated sludge (Wawrzynczyk et al. 2007).

From the foregoing examples, biological additives (bacteria and/or enzymes) likely have the potential to degrade faecal sludge if the optimal conditions and the right "consortia" are established. Therefore, as part of the Emergency Sanitation Project (ESP), WASTE and her sanitation partners through funding from the Humanitarian Innovation Fund (HIF) initiated this research which was carried out to determine whether commercially available additives can stabilise and sanitise faecal sludge.

Materials and Methods

Experimental Set-Up

The experimental set-up was done in two phases. The first phase was a laboratory scale experiment treating black water, carried out at UNESCO-IHE, Delft, the Netherlands, while the second phase was the field study treating faecal sludge (FS) in Blantyre, Malawi, at the Sochi wastewater treatment plant.

Lab-Scale Experimental Set-Up

The lab-scale set-up entailed use of 500 mL bottles which were filled with 300 mL of sample. The black water used for the tests was obtained from Landustrie Sneek BV. Landustrie is treating black water from the toilets in its office block and factory in Sneek, Friesland province in the north of Holland. Thirty litres of the black water was collected in three 10-L-jerrycans and stored at UNESCO-IHE in the cold room at 4–6 °C. Two trials were performed. The first trial was run for 2 weeks, whereas the second trial was run for a week only.

The set-up was composed of bottles with black water and 5 different additives, control and water reference, each designed as a triplicate (see Fig. 1). For both trials, about 10 L of sample was drawn from all the three jerrycans in approximately equal volumes. It should be noted that the contents in the jerrycans were swirled before being poured out. Afterwards, the drawn sample was stirred using a glass rod every time before dispensing to the bottles. The first set of bottles was filled for each additive then the second and the third, respectively to ensure minimal differences of sample properties. *E. coli w*as added to the sample used in trial 2 (1% which is approximately 10^7/mL of *E. coli* ATCC 25922 obtained from the laboratory at UNESCO-IHE) because the *E. coli* concentrations in the raw black water were low.

In the first trial, one replicate was taken out of the experiment after 7 days because less black water remained after collection of sample for determination of total solids/volatile solids. COD, *E. coli*, total coliforms enumeration was done on samples from the triplicate set-up per additive treatment. On the other hand, all tests in trial 2 were done on samples from the triplicate set per additive treatment, when

Fig. 1 Lab-scale experimental set-up

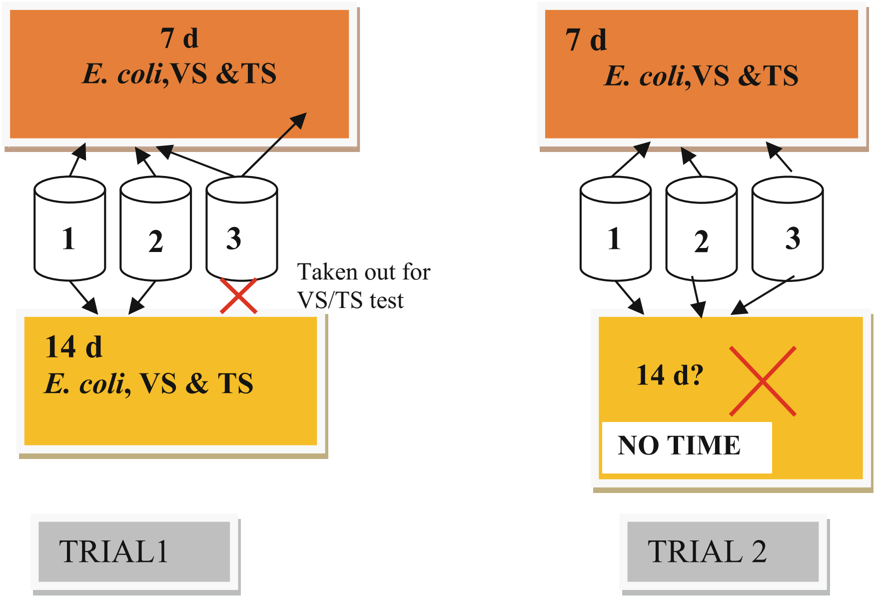

Fig. 2 Lab-scale testing scheme

the experimentation was concluded after 7 days due to time constraints (Fig. 2). The black water in the bottles was stirred using a magnetic stirrer before the sample for analysis was drawn.

The control set-up was made up of a unit in which neither water nor additives were added, whereas the water reference set-up contained addition of water only to the black water. The additives tested in the lab-scale are numbered 1–5 (Table 1). There were no dose instructions for the additives except Aquaclean. Aquaclean dosage entails mixing 1.9 L of the additive with 8 L of water for septic tanks up to capacities of 9463 L (2500 US gallons). The additive dosage was scaled down to the volume of the tested black water. The total volume of the additive and dilution water was expressed as a % of the black water volume. This yielded 1.7% v/v which was adopted for all additives. For the powdered additives, the 1.7% w/w was adopted.

Field Experiment in Blantyre, Malawi

The field study was carried out in Blantyre, Malawi. The set-up consisted of the additives used in the lab-scale experimentation and an extra 3 additives. Two types of set-up were carried out. The first set-up made in 2 L buckets was carried out for 8 additives S. No. 1–8 (Table 1) with control and water reference (Fig. 3). For

Table 1 Additives used for this study

S. No.	Additive	Active ingredients	Source
1	Biomax (BM1 enzyme)	A natural blend of thermophilic aerobic bacteria with optimal temperature of 70–80° and enzymes that break down the waste. The enzymes are keratinase, lipase and cellulase. In thermophilic processes dosed at 0.1% to FS	http://www.publics.bg/en/news/6768/Rapid_Thermophilic_Digestion_Technology.html
2	Ikati	By-product of soda ash mining. Crystalline product. Used in village schools in Kenya to achieve volume reduction in pit latrines	Hardwares in Kenya. May be sold by the name "Magadi"
3	EM (effective micro-organisms)	A brown liquid readily flowing	No info regarding the product supplied from Sanergy
4	Aquaclean	This is a proprietary formula of bacteria produced in USA. It contains vegetative bacteria representing aerobic, anaerobic, facultative, chemo-synthetic and photo-synthetic bacteria which make it versatile across many working conditions	http://nova-q.ie/products/aquaclean.html (accessed March, 2015)
5	Soda	Lab grade sodium carbonate	
6	Saniloo (Micromune)	A microbial consortium of beneficial bacteria. 1 mL of Saniloo contains more than 13 million bacterial cells (heterotrophic plate count)	Sanitation World, South Africa
7	Rid-X	A formulation of bacteria and enzymes. The ingredients which are in percentages between 10 and 20% include "A-amylase, bacteria, complex with amylase and proteinase, cellulose, subtilisin carlsburg and triacylglycerol lipase"	http://www.rid-x.com/faq.shtml; http://www.rbnainfo.com/MSDS/US/Rid-X-Septic-Treatment-US-English.pdf (accessed March, 2015)
8	Terraktiv	Contains effective micro-organisms (EM), molasses, water, sea salt, EM-ceramic powder, green gold, apple cider vinegar. It is used for domestic use as cleaner for the sewage treatment plant as an accelerator and stabilizer for the pond, for stable manure or control of odour	http://www.triaterra.de/triaterra-aktiv (accessed March, 2015)

(continued)

Table 1 (continued)

S. No.	Additive	Active ingredients	Source
9	Men xu ly be phot	Contains useful micro-organisms that destroy viruses and worms. Ensures environmentally clean products	Supplied by: C. TY CP CONG NGHE SINH HOA HA NOI, HA NOI TECHNOLOGY BIOCHEMISTRY JSC, So7, day B15, TT Bao Tang HCM, Lieu Gial, Ba Dinh-Ha Noi
10	Magic pit	Marketed for the treatment of septic tanks and pit latrines. Its contents are harmless bacteria which accelerate the degradation of human wastes, kill pathogens as well as eliminate odours (product package)	
11	Safety gel	White in appearance and is used to assist control infections by absorbing liquids in spillages, urinals, bedpans, vomit bowls etc.	http://www.safetygel.co.uk/

Fig. 3 Field experimental set-up (L-R 2 L buckets and 50-L buckets)

comparative purposes, the additive dosage adopted in the lab-scale was used to test the effect of additives on faecal sludge. The additive dosage implemented was 1.7% v/v or w/w like the one in the lab scale. The second set-up was carried out in 50 L containers for three treatments (viz. 7–9), control and water reference due to limited quantities of additives 1–8 (Fig. 3). The additive dose recommended by the suppliers was adopted (Fig. 3; Table 2). The additives were weighed and added to the containers containing faecal sludge and mixed using a stick.

Table 2 Recommended additive dose

S. No.	Additive	Recommended dose	Dilution	Remark
6	Saniloo	2 L, day 1, 2 L day 30 and 1 L day 60 for pit latrines (2 m^3). As % 0.1% v/v day 1, 0.1% v/v day 30 and 0.05 v/v day 60	None	A standard pit latrine volume taken as 2 m^3. The first dose only was implemented
7	Rid-X	8 oz (240 mL) for septic tanks up to 5680 L (1500 gallons) dose 0.004% of tank volume	None	
8	Terraktiv	10% v/w	1:10	Density of sludge taken as 1000 kg/m^3
9	Men be phot	200 g for 1 m^3 septic tank. Dose 0.02% w/w	None	Density of sludge taken as 1000 kg/m^3
10	Magic pit	1 sachet for 1 pit latrine. Adopted 1 sachet for 35 kg of FS. Adopted dose 0.17% v/w	1%	Density of sludge taken as 1000 kg/m^3
11	Gel	10 g for up to 1 L of fluid (1% w/w)	None	The full product name is safety gel

The testing scheme followed in the field experiment is shown in Fig. 4.

The performance of the additives in trial 1 to reduce VS and remove *E. coli* was low; thus, a second trial in which the additive dose was doubled was carried out. 3 Extra additives (SN 9–11, Table 1) were obtained from WASTE and her partners. Trial 2 entailed the testing of additives numbered 2–11 (additive 1 ran out) at a dose of 3.4% w/w or v/w to faecal sludge. Treatments containing additives 2–6 and 9–11 (10 at recommended dose and 3.4%) together with the control and water reference were set-up in 2-L containers, whereas additives 6–8, 10 and water reference were set-up in 50 L.

The contents of the containers were stirred for about 2 min before the samples were drawn for analysis. The samples were then drawn using a long handled sampling container or the tap. In trial one, half the sample was drawn through the tap at the lower part and the remainder scooped from within the 50-L containers. The sample from the 2-L buckets was scooped after mixing using a table spoon. For trial 2, the sample was scooped because the thick sludge blocked the tap in the 50 L.

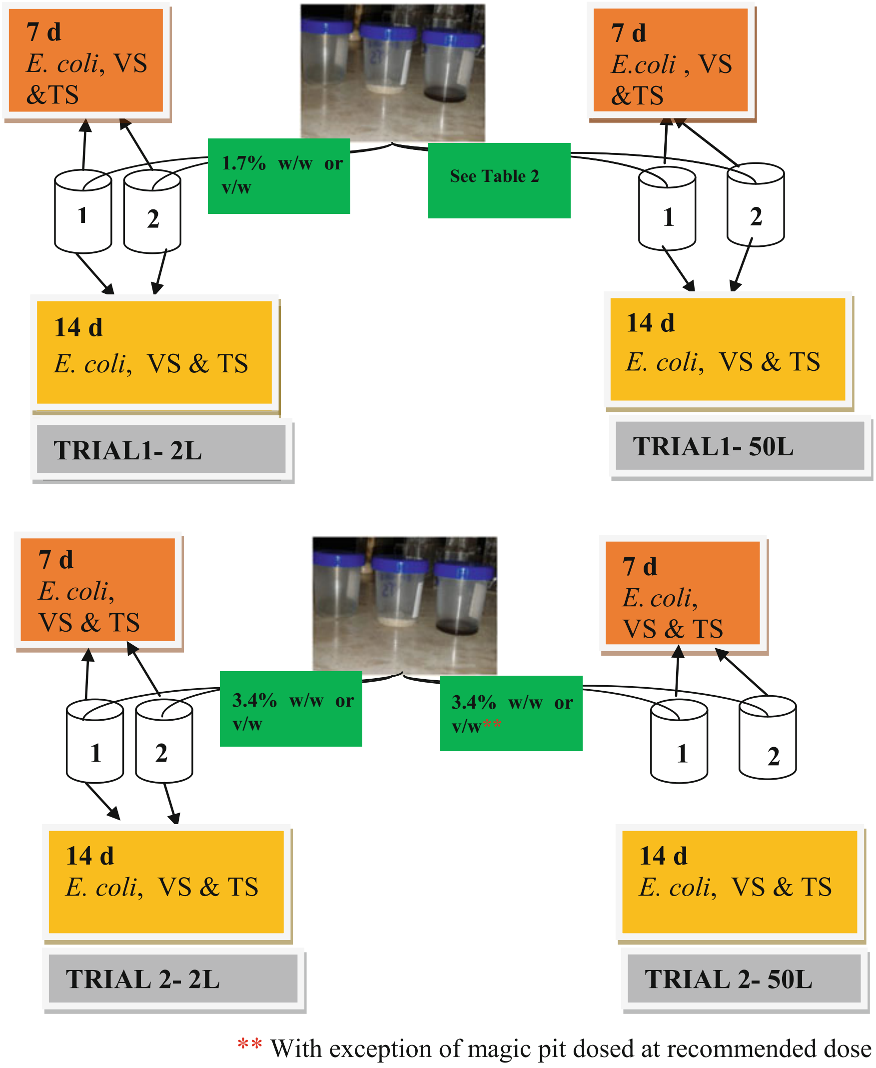

Fig. 4 Field study testing scheme

Analytical Methods

The analytical methods adopted were from standard methods (APHA 2012). The measurement of VS/TS was the gravimetric method SM 5540G (APHA 2012). This entails measurement of a sample 25–50 g which was placed in a pre-weighed evaporating dish (W_1). The evaporating dish should have been prepared for the test by igniting it at 550 °C for 1 h and cooled in a desiccator. The weight of the sample and the evaporating dish was taken as W_2. The samples were then evaporated to dryness using a steam bath. Afterwards, the samples were dried in an oven at 103 °C for 12 h, cooled in a desiccator and weighed, W_3. The dried sample was then ignited in a muffle furnace at 600 °C for 2 h. Weight of the evaporating dish and the ash was measured after cooling, W_4. The enumeration of *E. coli* was made using the plate count method. Chromocult coliform agar (Merck Millipore) was used to facilitate the enumeration. The inoculated Petri dishes were placed in an incubator for 24 h at 37 ± 2 °C.

Results and Discussion

The characterisation of the black water and the faecal sludge used in this study is shown in Table 3.

Table 3 Characterisation of the samples used in the study

Parameter	Units	Black water	FS1	FS2
Total COD	g O_2/L	17–27	18 ± 1	140 ± 15
	mg O_2/g dry weight	1460–2390	1300 ± 70	840 ± 80
Soluble COD	g O_2/L	7.58[a]	n.d.	n.d.
Total solids	g/L	10–19	14 ± 1	n.d.
	g/kg wet sample	7–19	14 ± 1	170 ± 2
	%	0.71–1.85	1.35	16.97
Volatile solids	%	57–77	65.91	71.36
NH_4–N	g N/L	1.0[a]	1.37 ± 0.5	4.7 ± 0.2
	mg/g dry weight	n.d.	100 ± 40	28 ± 1.1
TN	g N/L	2.16[a]	18.0	15.3
	(%)	(≈0.22%)	1.8%	1.53%[1]
pH	(–)	6.96–7.05	6.95–7.52	6.81–7.25
Temperature	°C	17–21	21	21
Ambient air temperature	°C	n.d.	18–27	18–27
E. coli	cfu/100 mL	2.44E06–2.77E09	5.80E+07	4.03E+07
Total coliforms	cfu/100 mL	1.22E+05	3.10E+07	4.60E+09
Salmonella	cfu/100 mL	–	6.00E+06	4.33E+06

[a] Done on 1 sample only in duplicate; all the remaining samples, *n* = 3

[1] Expressed as a %. Test procedure ISO17025—determination of TN by back titration

n.d. Not determined

FS1 Faecal sludge in trial 1; *FS2* faecal sludge in trial 2

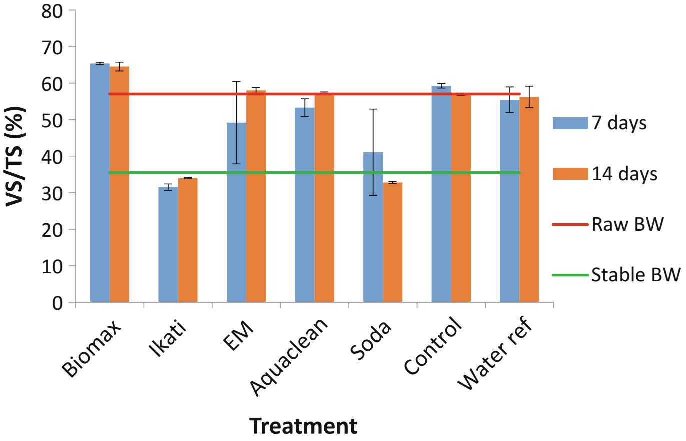

Fig. 5 VS/TS (%) of treated black water (95% confidence of the mean)—trial 1 (additive dosage 1.7% w/w or v/w to black water)

Effect of Additives on VS/TS in Black Water/Faecal Sludge

A stable sludge has VS/TS less than 60% and has achieved a volatile solids reduction $\geq$38% (EPA 1993; EEA 1997). The findings from trial 1 treating black water are shown in Fig. 5.

Ikati and Soda which are additives of chemical origin achieved volatile solids reduction greater than 38% after two weeks of treatment. The remaining additives which are of biological nature, and the controls barely achieved any reduction in the VS/TS. This might be attributed to a short treatment period which may have not been adequate for the adaptation of the micro-organisms to the conditions as well for growth. The same trend was observed in the second trial.

In the field trials, at low concentrations of total solids (1.35%), Ikati and Soda achieved a stable sludge, whereas the rest of the additives and the controls under performed (see Fig. 6). At higher total solids concentrations ($\approx$17%) none of the additives achieved significant volatile solids reduction, notwithstanding the doubling of the additive dose (Fig. 7).

The findings from the treatment of faecal sludge indicate that the performance of the additives in stabilising the sludge (read VS/TS reduction) is dependent on the concentration of the total solids in the sludge to be treated. The performance reduced drastically when the concentration of the solids increased.

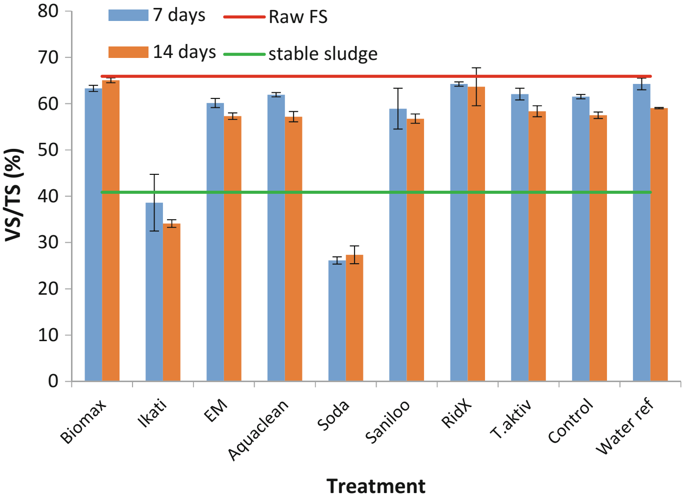

Fig. 6 VS/TS (%) of treated FS (95% confidence of the mean)—2 L containers, trial 1 (additive dosage of 1.7% w/w or v/w to FS)

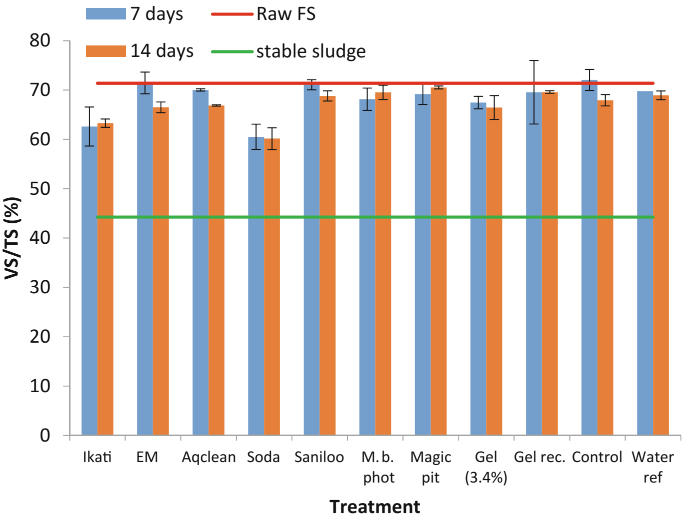

Fig. 7 VS/TS (%) of treated FS (95% confidence interval)—2 L containers, trial 2 (additive dosage of 3.4% w/w or v/w to FS)

Effect of Additives on *E. coli* Concentrations

The concentrations of *E. coli* in treated black water and faecal sludge were enumerated and compared to the WHO guideline value for restricted agriculture which is <1000 cfu faecal coliform/100 mL (100 g) of sample. Sanitised sludge is one which meets WHO guideline for restricted agriculture. In general, the products Ikati, Soda and safety Gel show a significant reduction in pathogen levels. This may be attributed to the higher pH which is maintained throughout the treatment period. This is in agreement with results of earlier published results that investigated faecal coliform die-off in waste stabilization ponds that besides other factors, pH > 8.5 lead to decline in faecal coliforms (Ouali et al. 2014). Moreover, the pH range was/almost over the range of survival for most bacteria (Mara and Horan 2003).

The reduction of *E. coli* in faecal sludge treated with Ikati and Soda may be further attributed to the disinfecting effect of carbonate. Carbonate was found to be the cause of die-off of *E. coli* K12 in manure from dairy farms (Diez-Gonzalez et al. 2000; Arthurs et al. 2001). However, the log reduction achieved was lower due to the lower additive dosages used in this experiment. Moreover, the total solids concentration in the field study was higher than the 3% in the manure treated.

In the treatment of black water, generally, all additives achieved reductions similar to those of the controls but for Ikati and Soda (Figs. 8 and 9) which are additives of chemical origin. It should be noted that Biomax had an explosion of colonies in the first trial. Therefore, for presentation purposes, the concentrations were equated to that in the raw sample. The better performance of Ikati and Soda was attributed to the synergistic performance of higher pH and the concentration of carbonate. Carbonate ion has a disinfecting effect (Diez-Gonzalez et al. 2000; Park and Diez-Gonzalez 2003). The plates counted were from undiluted sample. For this test, the limit of detection is 3 logs assuming a single colony grew on the plate containing undiluted sample.

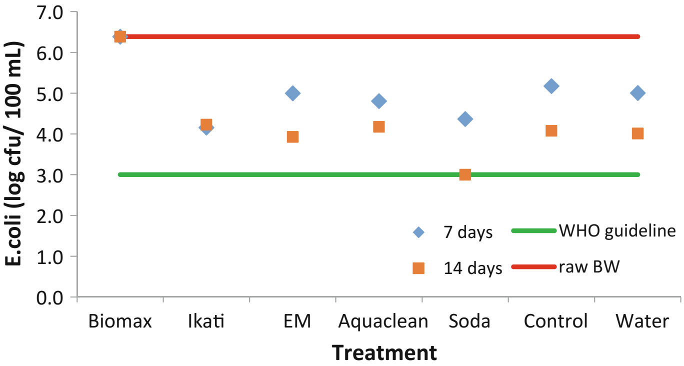

Fig. 8 *E. coli* concentrations in treated black water—trial 1 (additive dose 1.7% w/w or v/w). Soda just met the WHO guideline

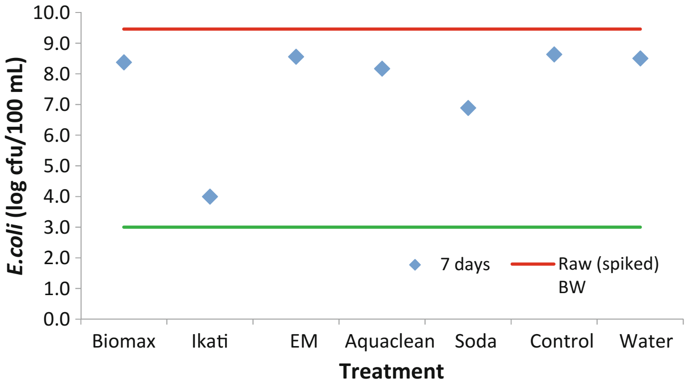

Fig. 9 *E. coli* concentration in treated black water—trial 2 (additive dose 1.7% w/w or v/w)

E. coli ATCC 25922 (added to sample in trial 2) seemed more sensitive to Ikati than Soda when compared to *E. coli* naturally present in faeces. Also, there is some treatment achieved with Biomax unlike in trial 1 where growth explosion was observed.

The *E. coli* concentrations in treated faecal sludge were enumerated after 1 week and 2 weeks since the beginning of the treatment. It can be generally observed that all additives achieved reduction in *E. coli* concentrations between the two weeks of treatment for additives applied at 1.7% v/w or w/w (Fig. 10). Due to few colonies observed after 1 week of treatment, the enumeration of colonies for Ikati and Soda in the second week is on an undiluted sample. Ikati recorded values under the detection limit as well as below the WHO standard for restricted irrigation after 2 weeks. On the other hand, Soda which had lower concentrations after one week had an increased number of colonies in week 2 indicating a likely re-growth of the bacteria.

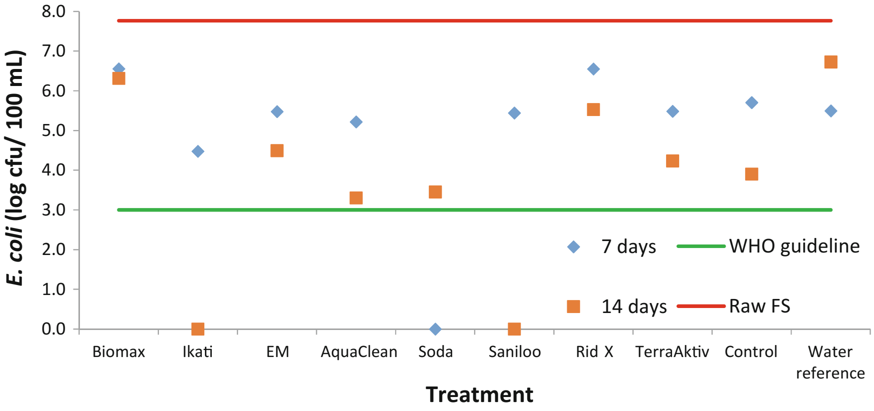

Fig. 10 *E. coli* concentrations treated FS-2 L containers, trial 1 (additive dosage of 1.7% w/w or v/w to FS)—Ikati, Soda and Saniloo show significant reduction

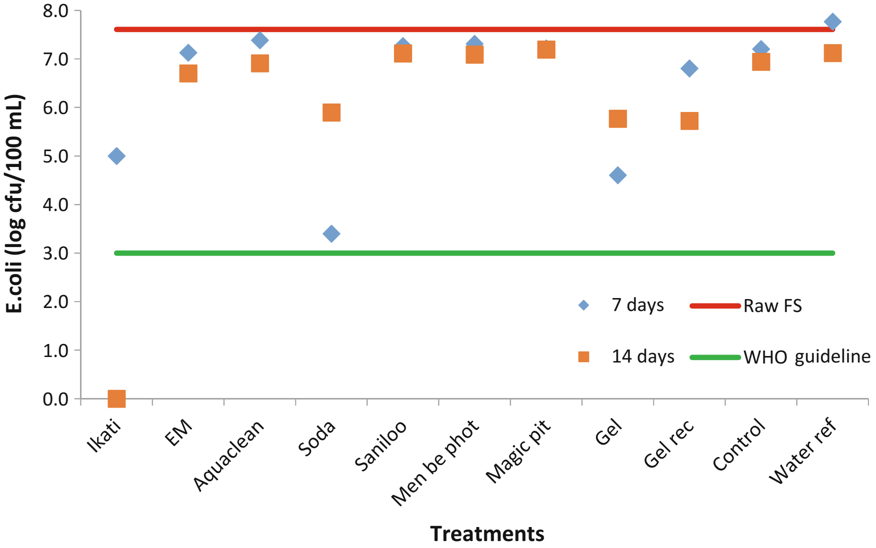

Fig. 11 *E. coli* concentration in treated FS-2 L containers, trial 2 (additive dose of 3.4% w/w or v/w to FS). Ikati had colonies below detection limit after 14 days

Although log reductions were lower than in other trials, the additives displayed a similar trend in the second trial. Soda displayed the same trend between the first and second weeks of treatment where there might be re-growth of *E. coli*. Unlike the first trial, none of the additives met the WHO guideline in the first week. Ikati registered colonies below detection limit after the second week. For Gel, dosage at 3.4% achieved a higher log reduction than at 1% (recommended dose). Saniloo barely achieved any reduction in the second trial (Fig. 11).

Statistical Analysis

To establish whether usage of the additives had any impact on the VS/TS and *E. coli* concentrations, a statistical analysis using ANOVA was undertaken. One way ANOVA was used to quantify the effect of the additives after which post hoc Tukey–Kramer HSD test was used to establish which pairs were significantly different. With respect to the VS/TS, it was found that in all trials, there is at least one additive which is significantly different regardless of the treatment duration. On the other hand, the treatment duration has no effect on the VS/TS at the end of the treatment period. However, the substrate properties, specifically the total solids, have an effect on the residual VS/TS for the faecal sludge and none for black water. This could be attributed to the fact that the concentrations in black water in the second trial are twice that in the first trial; whereas for the faecal sludge, it is 12 times that in trial 1 (Table 3). Further, higher concentrations of total solids might have reduced the efficacy of the additive as seen in trial 2 of faecal sludge treatment where despite the higher additive dosage, the residual VS/TS was still high.

Treatment of faecal sludge with Ikati and Soda consistently showed significant differences with the control and other treatments at 7 days and 14 days, respectively. However, the two additives show no difference between themselves. Therefore, depending on other factors, i.e. sanitisation and costs, any of the two additives can be adopted if treatment time is 14 days or longer, then Ikati should be chosen.

Statistical analysis of the *E. coli* concentrations was carried out to establish the effect of the additive treatment on *E. coli* removal after 7 and 14 days of treatment. The various additives but for Biomax had no effect on the die-off of *E. coli* naturally present in black water. Biomax favoured growth of *E. coli* which was too many to be enumerated. The concentrations in the controls and the rest of additive treated sludge were of the same magnitude. On the other hand, Ikati and Soda have significant effect on *E. coli* die-off in the black water spiked with lab *E. coli*. This indicates that lab *E. coli* are less resistant to Biomax because die-off occurs unlike in trial 1 whereby growth occurred.

For the treatment of faecal sludge with lower solids concentration, Soda achieved the greatest removal, residual *E. coli* concentrations being significantly lower than the controls and other treatments both at 7 days and 14 days after treatment commenced. After 14 days treatment, both Soda and Ikati have significantly lower *E. coli* concentrations compared to the rest. The additives that consistently had lower removal was Biomax and Rid-X.

When the solids concentration in the faecal sludge increased, the case in sludge used in trial 2, the additives Ikati, Soda and Gel (dose 3.4% w/w) achieved significant reduction in *E. coli* concentrations after 7 days treatment. However, Soda had a re-growth of bacteria and had concentrations that were of similar magnitude to the controls when treatment was stopped at the end of two weeks.

Conclusions

In general, the additives studied did not attain a stable sludge at the end of two weeks treatment. Two of additives tested showed promise to stabilise faecal sludge. Ikati and Soda consistently showed better stability of the end product under conditions of low total solids concentrations, where the two products meet the stability index of VS/TS <0.6 and VSR of $\geq 38\%$. Moreover, the post hoc Kramer HSD evaluation of ANOVA results indicates that there is significant difference between the VS/TS ratios of Ikati and Soda and the other additives and the controls at the various TS levels. However, no difference exists between Ikati and Soda whether measured at 7 days or at 14 days. Consequently, the choice whether to use Ikati or Soda will depend on other factors such as cost and the ease of availability.

At high total solids concentration, none of the treatments attained significant reduction of VS/TS. This implies that the performance of the additives is dependent on the TS concentrations. Consequently, it may be desirable to dose the additives as a function of this concentration.

With regard to sanitisation, three products which are of chemical origin, Ikati, Soda and Safety Gel show a significant reduction in pathogen levels. This may be attributed to the higher pH which is maintained throughout the treatment period.

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References

APHA (2012) Standard methods for the examination of water and wastewater. Washington, D.C., American Public Health Association (APHA), American Water Works Association (AWWA), Water Pollution Control Federation

Arthurs CE, Jarvis GN, Russell JB (2001) The effect of various carbonate sources on the survival of *Escherichia coli* in dairy cattle manure. Curr Microbiol 43(3):220–224

Bakare BF (2011) Scientific and management support for ventilated improved pit latrines (vip) sludge content. PhD thesis. University of Kwa-Zulu Natal Durban, South Africa

Bhagwan J, Still D, Buckley C, Foxon K (2008a) Challenges with up-scaling dry sanitation technologies. Water Sci Technol 58(1):21

Bhagwan J, Still D, Buckley C, Foxon K (2008b) When last did we look down the pits. WISA Paper

Buckley CA, Foxon KM, Brouckaert CJ, Rodda N, Nwaneri C, Balboni E, Couderc A, Magagna D (2008) Scientific support for the design and operation of ventilated improved pit latrines (VIPs) and the efficacy of pit latrine additives. Pretoria, South Africa, Water Research Commission

Connolly MA, Gayer M, Ryan MJ, Salama P, Spiegel P, Heymann DL (2004) Communicable diseases in complex emergencies: impact and challenges. Lancet 364(9449):1974–1983

de Pooter L (2014) Ammonia treatment based on urea addition sludge and wastewater treatment in emergency situations. MSc thesis. Delft University of Technology Delft, The Netherlands

Diez-Gonzalez F, Jarvis GN, Adamovich DA, Russell JB (2000) Use of carbonate and alkali to eliminate *Escherichia coli* from dairy cattle manure. Environ Sci Technol 34(7):1275–1279

EEA (1997) Sludge treatment and disposal. Management approaches and experiences. ISWA's working group on sewage and waterworks sludge. Copenhagen, Denmark, European Environment Agency

EPA (1993) Federal register rules and regulations. Standards for use or disposal of sewage sludge. Washington DC, Environmental Protection Agency

Foxon KM, Mkhize S, Reddy M, Buckley CA (2008) Laboratory protocols for testing the efficacy of commercial pit latrine additives. Water SA 35(2):228–235

Gaikwad GL, Wate SR, Ramteke DS, Roychoudhury K (2014) Development of microbial consortia for the effective treatment of complex wastewater. J Bioremed Biodegradation 5(4)

González Pérez ME (2014) Sanitising faecal sludge with ammonia (from urea) in the context of emergency situations. MSc thesis. UNESCO-IHE Delft, The Netherlands

Harvey PA (2007) Excreta disposal in emergencies: a field manual, Loughborough University

Jere M, Chidavaenzi M, Nhandara C, Bradley M (1998) The effect of non-pathogenic bacteria on latrine sludge. In: 24th WEDC conference, Islamabad, Pakistan

JMP (2015) 25 years progress on sanitation and drinking water. 2015 Update and MDG Assessment. U.S.A., World Health Organization (WHO)/United Nations Children's Fund (UNICEF)

Lakshmi MV, Merrylin J, Kavitha S, Kumar SA, Banu JR, Yeom I-T (2014) Solubilization of municipal sewage waste activated sludge by novel lytic bacterial strains. Environ Sci Pollut Res 21(4):2733–2743

Malambo DH (2014) Sanitizing faecal sludge using lactic acid bacteria in the context of emergency situations. MSc thesis. UNESCO-IHE Delft, The Netherlands

Mara D, Horan N (2003) Handbook of water and waste water microbiology. Academic Press, London

Merrylin J, Kaliappan S, Kumar SA, Yeom I-T, Banu JR (2014) Enhancing aerobic digestion potential of municipal waste-activated sludge through removal of extracellular polymeric substance. Environ Sci Pollut Res 21(2):1112–1123

Nobela HN (2014) Sanitizing faecal sludge with lime in a context of emergency situations. MSc thesis. UNESCO-IHE Delft, The Netherlands

Ouali A, Jupsin H, Ghrabi A, Vasel JL (2014) Removal kinetic of *Escherichia coli* and enterococci in a laboratory pilot scale wastewater maturation pond. Water Sci Technol 69(4):755–759

Park GW, Diez-Gonzalez F (2003) Utilization of carbonate and ammonia-based treatments to eliminate *Escherichia coli* O157:H7 and Salmonella Typhimurium DT104 from cattle manure. J Appl Microbiol 94(4):675–685

Strande L (2014) Chapter 1: global situation. In: Strande et al (eds) Faecal sludge management: systems approach for implementation and operation. London, United Kingdom, IWA publishing

Taljaard L, Venter A, Gorton D (2003) Evaluation of different commercial microbial or microbial-derived products for the treatment of organic waste in pit latrines. Pretoria, South Africa, Water Research Commission

Wawrzynczyk J, Recktenwald M, Norrlöw O, Dey ES (2007) Solubilisation of sludge by combined chemical and enzymatic treatment. Afr J Biotech 6(17):1994–1999

WHO (2013) Diarrhoeal disease: fact sheet. World Health Organization, Geneva, Switzerland

Wisner B, Adams J (2002) Environmental health in emergencies and disasters: a practical guide. WHO, Geneva

Enriched Compost Production Technique from Water Hyacinth

Arti Mathur, Sanjeev Kumar Mathur, A. B. Singh and A. Subba Rao

Abstract Water hyacinth is an aquatic weed known for causing a series of problems for aquatic life. If utilized properly, it can act as an extremely important alternative source of organic material for the production of nutrient-enriched organic manure by a composting technique. Water hyacinth has remarkable nutritive properties which can not only result in healthy aquatic system but help generation of enriched manure for application to the soil for sustainable productivity. In the present study, different enriched composts were produced from water hyacinth, viz. *phospho-compost, phospho-compost with lime, phospho-nitro compost, phospho-sulpho-nitro compost, vermicompost and microbial-enriched compost*. Among these composts, the highest percentage of N was found in phospho-nitro compost and phospho-compost. The highest percentage of P and K were noted in phospho-sulpho-nitro compost (P 0.89 and K 1.04%) and the lowest percentage of P and K recorded in control (P 0.56 and K 1.02%). The other compost characteristics were also determined and discussed.

Keywords Water hyacinth · Compost · Phospho-compost
Phospho-nitro compost · Vermicompost · Microbial-enriched compost

Introduction

The water hyacinth (*Eichhorina crassipes*) is a floating obligate plant that belongs to family Pontederiaceae. Water hyacinth plant differs in size from a few inches to over three feet tall. It has showy lavender flowers, and its leaves are rounded and

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Plate 1 Water hyacinth

leathery, attached to spongy and sometimes inflated stalks. It is one of the most productive plants on earth and considered as one of the world's worst invasive aquatic weed (Gopal 1984; Malik 2007) which grows in all types of fresh water (Plate 1).

The water hyacinth occurs in 23.15% of the wetland area of north-east region of India, where it is kept under control by natural predators (Abbasi et al. 1998). Due to its fast growth and the robustness of its seeds, the water hyacinth has since then caused major problems in the whole area. It has an average annual productivity of 50 dry (ash-free) tonnes per hectare per year.

Compost is typically not a fertilizer, although when used at normal rates it can reduce the fertilizer nutrient requirement. Compost can increase the water holding capacity of sandy soils and can improve structure and water movement through heavier textured soils that are high in silt and clay contents. By increasing the organic matter content of the soil, biological activity can be enhanced. Water and nutrient holding capacity of soils can be improved by compost application. Compost has the ability to suppress fungal diseases; research in this area is ongoing. Composts prepared from different organic wastes differ in their quality and stability. This mainly depends upon the composition of the raw material used for the composting and conditions of composting process (Gaur and Singh 1995; Ranalli et al. 2001).

Composting is a bio-oxidative process in which the microorganisms transform the more easily biodegradable organic matter into carbon dioxide, water vapour, and other minerals (mineralization process) or, with time, into more stable organic matter (humification process) called humic substances which are physically very similar to the humus present in soil (Kalamdhad et al. 2011). Composting refers to the conversion of green waste into organic fertilizer, the compost as the end product. Composting is the biological decomposition and stabilization of organic substances under condition that allows development of the thermophilic temperature as a result of biologically produced heat, with a final product sufficiently stable for storage and application to land without any adverse environmental effect (Haug 1993).

Much work has been carried out in different parts of the world to develop environmentally sound and appropriate methods for the management and control of water hyacinth (Kafle et al. 2009). It recapitulated that the utilization of water hyacinth for composting has proved economically viable across the world (Gajalakshmi et al. 2001). Researchers have recently substituted bean straw with water hyacinth as animal feed (raw material) (Tag El-Din et al. 1992), for solid-phase fermentation for making pulp, paper and paper board and for vermicomposting of water hyacinth (Gupta et al. 2007). However, a novel technology with ecologically sound and economically viable approach is needed to solve the problem of aquatic weed disposal and management. With an aim to solve the problems associated with water hyacinth, the investigation has been made to prepare compost by using water hyacinth to improve nutritional contents by incorporation of different amendments. The project will be beneficial for those cities where the problems of aquatic weeds are much that can be overcome through removal of such weeds. The compost preparation by exploitation of water hyacinth will help to treat this aquatic weed in a way which will further enhance the productivity of soil, thereby keeping various ponds and lakes of the city in healthy state. This compost will provide an alternate method in contrary to conventional composts with an added advantage over chemical fertilizers. Therefore, water hyacinth biomass (harvested from water hyacinth in fasted natural water bodies) has been tested as an effective source for bio-compost production through different types of composting techniques.

Materials and Methods

This experiment was conducted at the research farm of ICAR-Indian Institute of Soil Science, Bhopal (geographical location 23° 18″N latitude, 77° 24″E longitude, altitude 485 m amsl). Water hyacinth as a source of organic waste material collected from Kaliasot river, Bhopal, and cow dung from a nearby dairy farm. Rock phosphate, lime, urea, microbial-enriched compost and epigeic earth worms were arranged from Soil Biology Division, ICAR-IISS, Bhopal.

The details of experimental set-up are given below:

(a) **Experimental set-up**: There were seven pits for composting, and dimensions of each compost pits were length 6′ × 3′ × 2.5′ (L × B × D). Approximately 500 kg freshwater hyacinth was chopped into small pieces and filled in each of those pits along with cow dung in the ratio of 2:1 as shown in Fig. 1.

- The bottom most layer of farm yard manure was about 1 in. thickness containing about 10 kg.
- The second layer above the manure compost's layer was of chopped freshwater hyacinth which was about 5 in. thickness needed containing about 15.7% of total water hyacinth.
- The third layer above second layer was of fresh cow dung which was about 2 in. thickness containing approximately 13.33% of cow dung.

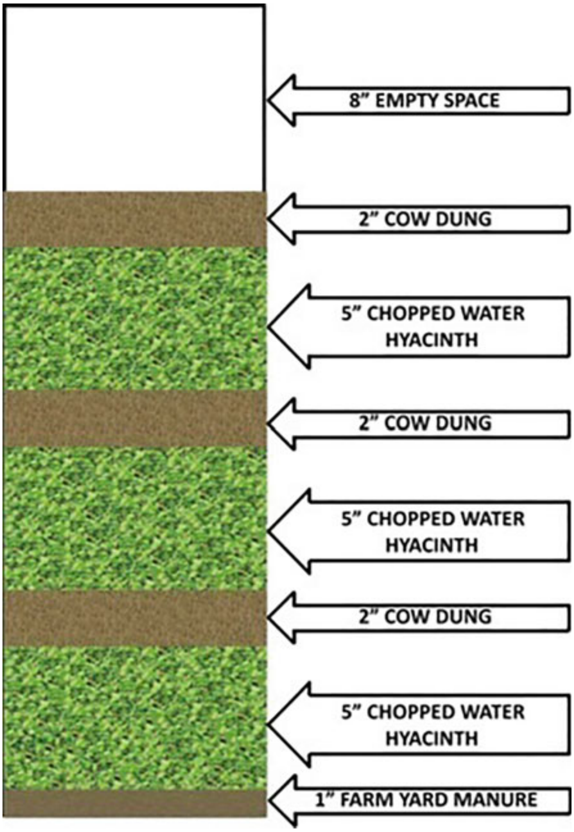


Fig. 1 Order of different layers of materials constituted for carrying out composting in pit

- The fourth layer above the cow dung layer was of chopped freshwater hyacinth (~15.7% of total water hyacinth) of 5 in. thickness.
- The fifth layer above fourth layer was of fresh cow dung (~13.33%) of 2 in. thickness.
- The sixth layer above the fifth layer was of chopped fresh water hyacinth (~15.7%) of 5 in. thickness.
- The seventh layer above sixth layer was of fresh cow dung (~13.33%) of 2 in. thickness. Each pit remained empty by about 8 in. for turning and watering operation.

In each pit, different materials were used for composting freshwater hyacinth with cow dung. It was observed that after 21 days, material in each pit was partially decomposed, and then in each pit various treatments were imposed as mentioned in Table 1 Earthworms and microbial culture were inoculated after 32 days. Following treatments were applied in each of those prepared pits (Plate 2).

As per the shown table, above-mentioned materials were applied in each pit. Fungal inoculums (*Aspergillus awamori*, *Aspergillus heteromorphous and Rizomucor pusillus*) were mass multiplied on potato dextrose broth for enhancing the decomposition

Table 1 Composition of different materials used for composting from water hyacinth

S. No.	Material	Quantity (kg)	Total material (%)
1	Water hyacinth + Cow dung	77 + 40	15.7 + 13.3
2	Rock phosphate	2.925	2.5
3	Lime	2.34	2
4	Urea	0.06	0.5
5	Gypsum	11.7	10
6	Earthworm	2	–
7	Microbial culture	0.0585	–

Plate 2 **a**, **b** Filling of pits, **c** covered pits to facilitate composting, **d** turning

Table 2 Different types of compost

S. No.	Constituents/treatments	Compost type	Pit
1	Water hyacinth and cow dung (T1)	Control	1
2	Water hyacinth, cow dung and rock phosphate (T2)	Phospho-compost	2
3	Water hyacinth, cow dung and rock phosphate, lime (T3)	Phospho-sulpho-compost	3
4	Water hyacinth, cow dung and rock phosphate, lime, urea (T4)	Phospho-nitro compost	4
5	Water hyacinth, cow dung and rock phosphate, gypsum, urea (T5)	Phospho-sulpho-nitro-compost	5
6	Water hyacinth and cow dung, epigic earthworm (T6)	Vermicompost	6
7	Water hyacinth and cow dung, microbial culture (T7)	Microbial-enriched compost	7

Table 3 Ratio of quantities of materials in different composting treatments

S. No.	Compost type	Quantities of materials							
		WH[a] (in kg)	CD[a] (in kg)	RP[a] (in kg)	L[a] (in kg)	U[a] (in gm)	Gyp[a] (in kg)	MC[a] (in gm)	EW[a] (in No.)
1.	Control (T1)	77	40	–	–	–	–	–	–
2.	Phospho-compost (T2)	77	40	2.925	–	–	–	–	–
3.	Phospho-sulpho-compost (T3)	77	40	2.925	2.34	–	–	–	–
4.	Phospho-nitro-compost (T4)	77	40	2.925	2.34	600	–	–	–
5.	Phospho-sulpho-nitro-compost (T5)	77	40	2.925	2.34	600	11.7	–	–
6.	Vermicompost (T6)	77	40	–	–	–	–	–	2500 adult worm
7.	Microbial-enriched compost (T7)	77	40	–	–	–	–	58.5	–

[a] Water hyacinth (*WH*), Cow dung (*CD*), Rock phosphate (*RP*), Lime (*L*), Urea (*U*), Gypsum (*Gyp*), Microbial culture (*MC*), Earthworms (*EW*)

process. Seven different types of composts were prepared by incorporating the materials in varied ratios as shown in Tables 2 and 3.

Analytical Techniques: Different parameters were analysed for the characterization of both substrates (water hyacinth and cow dung) and products (water hyacinth compost) by dry ashing and wet oxidation method (Issac and Johson 1975). Moisture contents were measured by gravimetric method (AOAC 1990). pH of raw material and final composts (Jackson 1973) was determined by hydrogen ion activity of the soil–water system. EC (Jackson 1973) was measured in substrates and composts. TOC (Kjeldahl 1883) was determined by titration method, ash % (Issac and Johson 1975) by using dry ashing method. Total Nitrogen (N) in substrates and composts was determined by (Kjeldahl 1883). A suitable sample is digested with a strong acid so that it releases nitrogen which can be determined by a suitable titration technique. Substrates and composts samples for N determination were digested in sulphuric acid at a temperature between 360 and 410 °C. Total phosphorus (P) in substrates and composts was determined by diacid digestion method (Jackson 1973). Total Potassium (K) in raw material and final composts was determined after digestion by using flame photometer by the method of Jackson (1973). The substrates and composts sample for K estimation were digested in diacid. In addition digest obtained from dry ash is also taken for K determination. C:N ratios (Sánchez-Monedero 2001) TOC and TN of compost ratio is C:N ratio. Cation exchange capacities in different substrates and composts (Knudsen et al. 1982) were determined.

Statistical Analysis: All the results reported are the means of three replicates. Repeated measures treated with analysis of variance (ANOVA) were made using statistical analysis to determine any significant difference among the parameter analyzed for different treatments.

Results and Discussion

Composting of water hyacinth biomass was completed in 7–8 weeks. The mature composts were black in colour, granular and fibrous with pleasant earthy smell compared with control mixture which was light brown in colour, coarse in appearance with a foul smell. The appearance of black colour is indicative of its maturity (Plate 3). Pandharipande et al. (2004) reported that the mature compost must be dark brown or black granular spongy in feel and smell normally.

Water hyacinth and cow dung constituted the main ingredients in this study for the preparation of composts. Varied compositions of chemicals, earthworms and microbes have important role in the decomposition of substrates. The macronutrients in raw material and final composts (T1, T2, T3, T4, T5, T6 and T7) were determined. Initial studies performed with S1 and S2 showed significantly higher levels of nitrogen and potassium in S1 in comparison with S2.

The evaluated values of water hyacinth mentioned in Table 4 show that the moisture content is 78% which is found to be similar with the work reported by Ojeifo et al. (2002), Praveen and Padmaja (2010). The contents of other properties and macronutrients shown in Table 4 such as pH, EC, ash, TOC, TN, TP, TK and Na% were 8.1, 0.48, 28, 40, 2.06, 0.48, 1.86 and 0.52%, respectively. The findings of the study were further compared and found to be nearly similar to the studies conducted by Parra et al. (1974), Ojeifo et al. (2002), Khan and Sarwar (2002), Malik (2007), Praveen and Padmaja (2010), Basu et al. (2011). The Na contents present in the water hyacinth and manure may not pose any problem as most crops may not be affected. Most of the K and Na present in water hyacinth plant were water-soluble. The water hyacinth is rich in N and K among macronutrients and iron and manganese among the micronutrients. The results obtained for physico-chemical of substrates and amended water hyacinth composts are further discussed in detail.

Table 6 provides the data on analysis of water hyacinth composts made with incorporation of different organic, mineral and microbial cultures. The general properties of composts and the nutrient compositions of composts varied depending on the amendments applied to the organic manure. With the addition of P through rock phosphate, the phosphorous concentration increased in the compost. The carbon-to-nitrogen ratio in all the compost is near to 20:1, indicating good maturity of the compost. The N contents and K contents have also exceeded 1.00%.

Moisture (**%**): Moisture loss during the composting process can be viewed as an index of decomposition rate since the heat generated during decomposition leads to vaporization. Optimum moisture is required for organisms to survive. The preliminary moisture contents with water hyacinth and cow dung were 78 and 53%, respectively (Table 6 and Fig. 2). The moisture content in prepared composts (T1–T7) was found in the range of 52–77% while the control showed moisture content of 64%, which is much lower than the individual substrate moisture content.

Plate 3 **a** Matured composts (control, phospho-compost, phospho-compost with lime), **b** matured composts (phospho-nitro compost, phospho-sulpho-nitro compost, vermicompost, microbial-enriched compost)

Umsakul et al. (2010) have reported 70% moisture content at the final week of composting of water hyacinth.

pH: pH of composts varied from slightly alkaline to neutral in range from 7.07 to 7.77 (Table 6 and Fig. 2). The difference in pH of different mixtures can be attributed to differences in physico-chemical characteristics of contents used in the

Table 4 Evaluation of physiochemical parameters of water hyacinth and cow dung

S. No.	Parameter	Water hyacinth (S1)	Cow dung (S2)
1	Moisture (%)	**78**	53
2	Dry matter (%)	12	47
3	pH	8.1	6.2
4	EC	0.48	0.40
5	Ash (%)	28	25
6	TOC (%)	**40**	25
7	TN (%)	**2.06**	1.08
8	TP_2O_5 (%)	0.48	0.41
9	TK (%)	**1.85**	0.41
10	C: N	19:1	23:1
SED		**26.07**	**20.96**

process. Pramanik (2010) have postulated that decomposition of organic matter leads to the formation of ammonium (NH_4^+) and humic acids. The combined effect of these two oppositely charged groups actually regulates the pH of compost leading to a shift of pH towards neutrality or acidity. The variation in pH values may be due to N and P mineralization and decomposition of organic matter into intermediates of organic acids, ammonium and humic acids (Ndegwa and Thompson 2000). These two groups actually regulate the pH of compost leading to a shift of pH towards neutrality. pH of composts produced from different treatments was neutral to slight alkaline, which is within the optimal range for plant growth (Goh and Haynes 1977).

Electrical conductivity: Electrical conductivity (EC) of vermicompost was higher than initial wastes. The EC reflects the salinity of any material, and it is a good indicator of the applicability and utility of a compost or vermicompost for agricultural purpose. The EC was in the range of 0.892–2.352 dSm^{-1} for different composts (Table 6 and Fig. 2). This increase in EC might have been due to release of different mineral ions, such as ammonium, potassium etc. (Kaviraj and Sharma 2003).

Ash %: High ash content indicates possible: (i) excess mineralization (old compost) (ii) contamination with dirt base material during turning (iii) poor quality feedstock or (iv) soil or mineral products added. Finding the source and reducing ash are often the fastest means of increasing nutrient quality of compost. Ash values may be disturbed by lixiviation, inopportune blending of soil during turnover operations and even deliberate incorporation of insoluble minerals (Godden et al. 2004). An increase in ash % was seen after compost preparation in comparison with the substrates. Lime is generally recommended to correct soil acidity as evidenced with pH values 7.91 and 7.77 for T3 and T4, respectively (Table 6 and Fig. 2).

Increased ash % in composts may be due to addition of mineral products to the substrates (T2).

Total Organic Carbon: Reduction in organic matter and total C-content has direct correlation with rate of decomposition (Ros et al. 2006) so, the total organic content of composts is measured. Total organic C-content was observed to be 40% for water hyacinth which was decreased with composting. The highest per cent reduction was observed 21% with T2 followed by T1 and T7 (23.3 and 24.4%) composts (Table 6 and Fig. 2). Reduction in total organic C-content may be due to greater availability of easily biodegradable substances which were mineralized by microbes during respiration and thereby releasing CO_2 (Benito et al. 2003). These results are in agreement with the previous studies on vermicomposting of agricultural and industrial wastes (Gupta et al. 2007; Suthar 2010; Yadav and Garg 2011).

Total Nitrogen: Total N content of compost depends on the initial N content present in the feed material and the degree of decomposition (Crawford 1983). Presence of N rich weeds having lesser toxicity proved to be favourable for microbial mineralization of raw material. Decrease in pH, mineralization of protein in organic material and conversion of ammonium nitrogen into nitrate may be responsible for addition of N in compost (Yadav and Garg 2011). Total nitrogen (TN) content in the prepared composts was approximately equal to initial substrate (S2). The initial TN content of the substrates was 2.06 and 1.08 g kg^{-1} for S1 and S2, respectively, whereas TN content of treated composts was in the range of 1.16–1.23 g kg^{-1} after composting (Table 6 and Fig. 2). Plaza et al. (2007) have reported that the nitrogen content of vermicompost increased due to mineralization of C-rich materials and, possibly, due to the action of N-fixing bacteria. Decreases in pH may be another important factor in nitrogen retention by compost which otherwise may be lost as ammonia at higher pH values. The difference in TN content of composts was different from each other.

Total Phosphorous: Phosphorus is also an essential element for plant growth which is also increased on composting. This may be due to transformation of unavailable forms of phosphorus to easily available forms by microbial enzymes like alkaline and acid phosphatases, etc. On composting, phosphorous content was enhanced in all composts. Maximal increase was found in compost (T5) approx 58.90% followed by T4 (57.1%) and T3 (55.4%) composts. Acid phosphatases and alkaline phosphatases may be responsible for this transformation (Ghosh et al. 1999). After vermicomposting, phosphorus content was the highest in T4 and T5, and minimum in T1, CD + WH mixture (Table 6 and Fig. 2). Bayon Le and Binet (2006) have reported that some amount of phosphorus is converted to more available forms partly by earthworm gut enzymes, i.e., acid phosphatases and alkaline phosphatases. Action of phosphorus-solubilizing microorganisms present in earthworm's casts may also be responsible for the release of phosphorus in vermicomposting (Prakash and Karmegam 2010).

Total Potassium: The potassium (K) content was greater in all the composts than initial waste (S2) (Table 5). The increase in potassium content was 1–2% in the composts as compared with K content in control (Table 6 and Fig. 2). The differences in the results can be attributed to the differences in the chemical nature

Table 5 Analysis of parameters of water hyacinth prior to composting

S. No.	Parameters (water hyacinth)	Results obtained	References					
			1[a]	2[b]	3[c]	4[d]	5[e]	6[f]
1	Moisture (%)	78	–	80.4	–	–	92.8	–
2	Dry matter (%)	12	–	10.2	–	–	–	–
3	pH	8.1	–	–	–	7	8.1	5.35
4	EC	0.48	–	–	–	–	0.46	–
5	Ash (%)	28	19.2	27.2	–	–	41.7	–
6	TOC (%)	40	34.9	–	33	33	33.8	21.5
7	TN (%)	2.06	1.61	–	1.94	1.94	1.95	1.23
8	TP (%)	0.48	0.31	0.79	–	–	0.54	0.39
9	TK (%)	1.86	3.81	4.6	–	–	0.97	2.09
10	Na (%)	0.52	0.56	0.37	–	–	–	–
11	C: N	19.4:1	21:1	–	17:1	17:1	36:1	17:1

1[a]: Parra et al. (1974); 2[b]: Ojeifo et al. (2002); 3[c]: Khan and Sarwar (2002); 4[d]: Malik (2007); 5[e]: Praveen and Padmaja (2010); 6[f]: Basu et al. (2011)

of the initial raw materials. Suthar et al. (2008) has reported 104–160% increase in potassium content during vermicomposting. Sangwan et al. (2010) have also reported an increase in K in vermicomposts after bioconversion of sugar industry waste. Kaviraj and Sharma (2003) have reported that enhanced number of microflora present in the gut of earthworms which might have played an important role in the process and increased potassium content during vermicomposting.

Sodium: There was slight difference in sodium content (Na) in all the composts as compared to initial substrates combination (Table 5). Final Na content was in the range of 0.018–0.036. The increase in Na content was 0.72–1.40 fold in the final composts as compared to Na content in control substrates combination. Variation in the Na content may be due to the difference in initial feed substrate characteristics in different composts Yadav and Garg (2011). The Na content was different in all the composts except in T4. An increase in Na % was observed with T2 (21.2%), T3 (31.4%) and T6 (5.8%) while with T5 (−31.5%) and T7 (−5.1%) Na % was reduced (Table 6 and Fig. 2).

C:N ratio: Initial C:N ratio was in the range of 19.42–23.15 (at 0 day), but after 45 days there was a significant change in the C:N ratio in all the composts. The C:N ratio decreased in compost T2 and T7 while an increase in C:N ratio was observed in compost T3, T4, T5 and T6 (Table 6 and Fig. 2). The increase in C:N ratio may be due to the *N* loss mainly through ammonia volatilization, whereas the enhanced C:N ratio resulted due to losses of carbon mainly as carbon dioxide, the carbon content of the compostable material decreased with time and N content per unit material increased. Final C:N ratio was in the range of 17.5–26.89. The lowest C:N

Table 6 Analysis of physico-chemical parameters of seven different types of water hyacinth composts

S. No.	Water hyacinth composts	Parameters									
		Moisture (%)	pH	EC	Ash (%)	TOC (%)	TN (%)	TP (%)	TK (%)	Na (%)	C: N
1	Control (T1)	64	7.53	1.927	58	23.3	1.14	0.56	1.02	0.0274	220.4
2	Phospho-compost (T2)	57	7.47	2.073	63	21	1.20	0.86	1.03	0.0332	117.5
3	Phospho-compost (Lime) (T3)	68	7.91	1.119	43	31.6	1.27	0.87	1.03	0.0360	224.8
4	Phospho-nitro compost (T4)	52	7.77	2.352	36	35.5	1.32	0.88	1.04	0.0272	226.8
5	Phospho-sulpho-nitrocompost (T5)	69	7.07	1.302	57	23.8	1.17	0.89	1.04	0.0187	220.5
6	Vermicompost (T6)	77	7.76	0.892	51	27.2	1.16	0.59	1.03	0.0291	223.4
7	Microbial-enriched compost (T7)	78	7.72	1.254	56	24.4	1.23	0.58	1.03	0.026	119.8
CD ($P = 0.05$)		5.116	0.056	0.485	3.399	3.329	0.068	0.114	NS	0.005	1.556

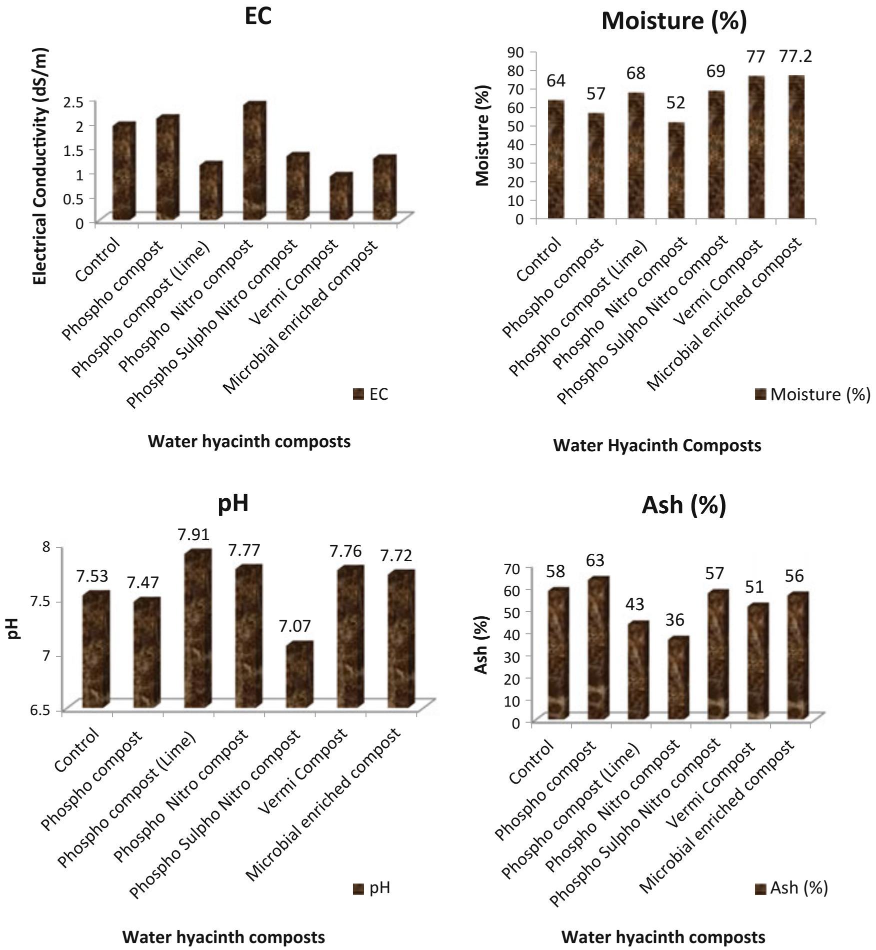


Fig. 2 Graphical comparisons of physico-chemical parameters of seven different types of water hyacinth composts

ratio was in T2 containing water hyacinth, cow dung and rock phosphate (17.5) while the highest in compost T4 containing water hyacinth, cow dung, rock phosphate, lime and urea had the highest C:N ratio (26.89). The C/N ratio decreased and was <20 at the end of the process, suggesting the compost had reached an acceptable degree of maturation. [Electron transfer capacity as a rapid and simple maturity index for compost (Wang et al. 2012).] However, Hirari et al. (1983) have stated that the C:N ratio cannot be used as an absolute indicator of compost maturity since the values for well-composted materials present a great maturity variability, due to characteristics of the waste used.

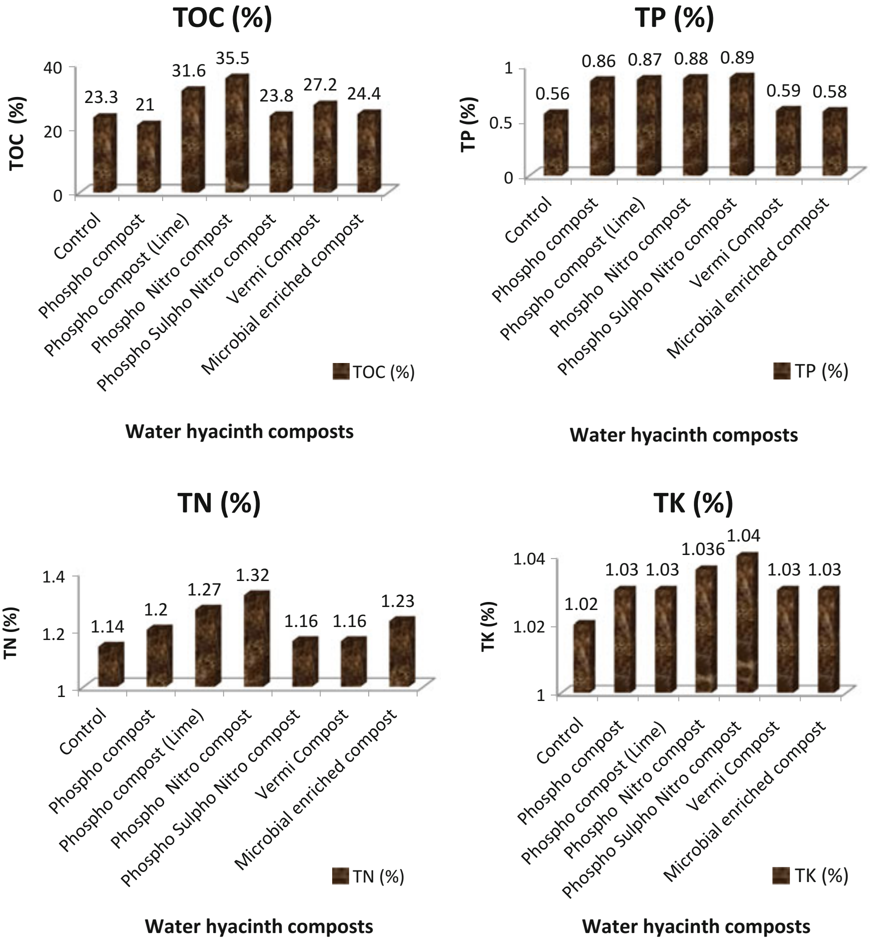
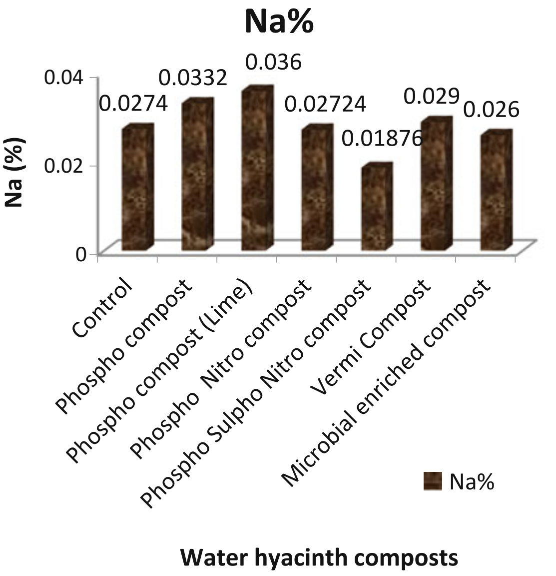


Fig. 2 (continued)



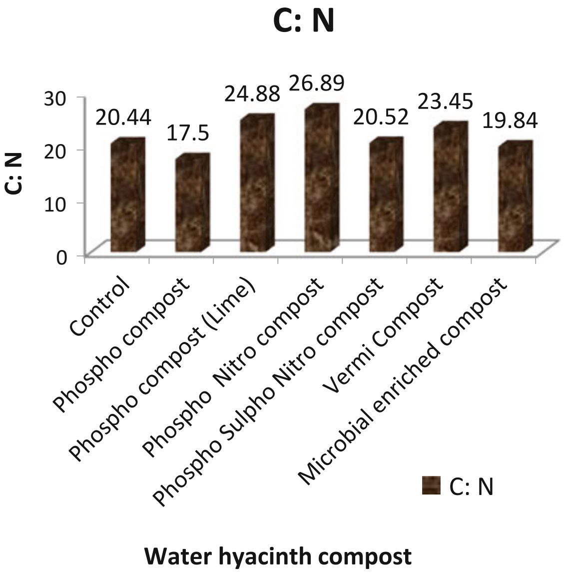


Fig. 2 (continued)

Conclusion

The water hyacinth has high nutritive properties that can be used for the production of nutrient-enriched compost which not only result in healthy aquatic system but also add as an advantage on agricultural land when hyacinth compost is applied. The results of the current study have shown that the water hyacinth composts prepared by combining different amendments, such as rock phosphate, lime, urea, gypsum microbial cultures and earthworm, have the highest percentage of N in phospho-nitro compost and in phospho-compost with lime and their values are 1.32 and 1.27, respectively, whereas the control compost gave the lowest percentage value of N that is 1.14. The highest percentages of P and K were found in phospho-sulpho-nitro compost that are P 0.89, K 1.04 and the lowest percentage of P and K in control compost (P 0.56 and K 1.02). The phospho-compost with lime gave the highest value of sodium percent that is 0.36 where the phospho-sulpho-nitro compost gave the lowest percent of sodium. The C:N ratio in all the composts is near to 20:1, indicating good maturity of the compost.

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References

Abbasi SA (1998) Weeds of despair, and hope. In: Wetlands of India, Discovery Publishing House, New Delhi, pp 12–21

AOAC (1990) Official methods of analysis: association of analytical chemists, 14th edn. Washington, USA, 22209

Basu M, Bhadoria BS, Mahapatra SA (2011) Influence of soil ameliorants, manures and fertilizers on bacterial populations, enzyme activities, Nfixation and P solubilization in peanut rhizosphere under lateritic soil. Brit Microbiol Res 1:11–25

Bayon Le, Binet RC (2006) Earthworm changes the distribution and availability of phosphorous in organic substrates. Soil Biol Biochem 38:235–246

Benito M, Masaguer A, Moliner A, Arrigo N, Palma RS (2003) Chemical and microbiological parameters for the characterization of the stabilizing and maturing of pruning waste compost. Biol Fert Soils 37:184–189

Crawford JH (1983) Review of composting. Process Biochem 18:14–15

Gajalakshmi S, Ramasamy EV, Abbasi SA (2001) Potential of two epigeic and two anecic earthworm species in vermicomposting of water hyacinth. Bioresource Technol 76(3):177–181

Gaur AC, Singh G (1995) Recycling rural and urban wastes through conventional and vermicomposting. In: Tandon HLS (ed) Recycling of Crop Animal, Human and Industrial Wastes in Agriculture. Fertilizer Dev and Consultation Orgn, New Delhi, pp 31–49

Ghosh M, Chattopadhyay GN, Baral K (1999) Transformation of phosphorus during vermicomposting. Bioresource Technol 69(2):149–154

Goh KM, Haynes RJ (1977) Evaluation of potting media for commercial nursery production of container grown plants. New Zeal J Agric 20:363–370

Gopal B (1984) Influence of water hyacinth cover on the physiochemical characteristic of water and phytoplankton composition in a reservoir near Jaipur India. Hydrobiology 6:859–865

Gupta R, Mutiyar PK, Rawat NK, Saini MS, Garg VK (2007) Development of a water hyacinth based vermireactor using an epigeic earthworm Eisenia foetida. Bioresource Technol 98:2605–2610

Haug RT (1993) The practical handbook of composting engineering. Lewis publishers, Boca Raton

Hirari M, Chanyasak V, Kubota H (1983) A standard measurement for compost maturity. Biocycle 24:54–56

Issac RA, Johnson WC (1975) Collaborative study of wet and dry techniques for the elemental analysis of plant tissue by atomic absorption spectrophotometer. J AOAC 58:436

Jackson ML (1973) Soil Chemical Analysis. Second edition Printice Hall of India Pvt. Ltd, New Delhi, India

Kafle MR, Kafle G, Balla MK, Dhakal L (2009) Results of an experiment of preparing compost from invasive water hyacinth (Eichhornia crassipes) in Rupa lake area, Nepal. J Wetlands Ecol 2:17–19

Kalamdhad AS, Singh WR, Dhal GC (2011) Agitated pile composting of water hyacinth. In: 2nd international conference on environmental science and development vol 4, pp 79–84

Kaviraj, Sharma S (2003) Municipal solid waste management through vermicomposting employing exotic and local species of earthworms. Bioresource Technol 90(2):169–173

Khan S, Sarwar KS (2002) Effect of water-hyacinth compost on physical, physicochemical properties of soil and rice yield. Pak J Agron 1(2–3):64–65

Kjeldahl J (1883) A new method for the determination of nitrogen in organic matter. Z Anal Chem 22:366

Knudsen D, Peterson GA, Pratt PF (1982) Lithium, Sodium and Potassium In: AL Page et al (eds) Methods of Soil Analysis part 2 Agronomy Monograph No 9, Am Soc Agron, Madison WI, USA, pp 225–246

Malik A (2007) Environmental challenge vis a vis opportunity: the case of water hyacinth. Environ Inter 33(1):122–138

Ndegwa PM, Thompson SA (2000) Effects of C-to-N ratio on vermicomposting of biosolids. Bioresource Technol 75(1):7–12

Ojeifo M, Ekokotu PA, Olele NF, Ekelemu JK (2002) A review of the utilisation of water hyacinth: alternative and sustainable control measures for anoxious weed, pp 71–78

Pandharipande SL, Gadekar S, Agrawal R (2004) Bioconservation of press mud (a waste from sugar industry). Asian J Microbiol Biotechnol Environ Sci 6:87–88

Parra JV, Hortenstine CC (1974) Plant nutritional content of some Florida water hyacinths and response by Pearl Millet to incorporation of water hyacinths in three soil types. J aquat plant manag 12:85–90

Plaza C, Nogales R, Senesi N, Benitez E, Polo A (2007) Organic matter humification by vermicomposting of cattle manures alone and mixed with two-phase olive pomace. Bioresour Technol 9:5085–5089

Prakash M, Karmegam N (2010) Vermistabilization of press mud using Perionyx ceylanensis Mich. Bioresour Technol 101:8464–8468

Pramanik P (2010) Changes in enzymatic activities and microbial properties in vermin compost of water hyacinth as affected by pre-composting and fungal inoculation: a comparative study of ergosterol and chitin for estimating fungal biomass. Waste Manage 30:1472–1476

Praveen AA, Padmaja CK (2010) Bioconversion of municipal solid waste (MSW) and water hyacinth into organic manure by fungal consortium. J Sustainable Dev 3:91–97

Ranalli G, Bottura G, Taddei P, Garavani M, Marchetti R, Sorlini C (2001) Composting of solid and sludge residues from agricultural and food industries bioindicators of monitoring and compost maturing. J Environ Sci Health 36:415–436

Ros M, García C, Hernández T (2006) A full-scale study of treatment of pig slurry by composting: Kinetic changes in chemical and microbial properties. Waste Manag 26(10):1108–1118

Sánchez-Monedero MA, Roig A, Paredes C, Bernal MP (2001) Nitrogen transformation during organic waste composting by the Rutgers system and its effects on pH, EC and maturity of the composting mixtures. Bioresource Technol 78(3):301–308

Sangwan P, Kaushik CP, Garg VK (2010) Vermicomposting of sugar industry waste (press mud) mixed with cow dung employing an epigeic earthworm Eisenia fetida. Waste Manag Res 28 (1):71–75

Suthar S (2010) Recycling of agro-industrial sludge through vermitechnology. Ecol Eng 36:1028–1036

Suthar S, Singh S, Dhawan S (2008) Earthworms as bio indicator of metals (Zn, Fe, Mn, Cu, Pb and Cd) in soils: is metal bioaccumulation affected by their ecological category. Ecol Eng 32:99–107

Tag El-Din AR (1992) Utilization of water-hyacinth hay in feeding of growing sheep. Indian J Anim Sci 62(10):989–992

Umsakul K, Dissara Y, Srimuang N (2010) Chemical, physical and microbiological changes during Composting of the water hyacinth. Pakistani J Biol Sci 13(20):985–992

Yadav A, Garg VK (2011) Recycling of organic wastes by employing Eisenia fetida. Bioresource Technol 102(3):2874–2880

Wang W, Yuan T, Wang K, Cui B, Dai Y (2012) Combination of biological pretreatment with liquid hot water pretreatment to enhance enzymatic hydrolysis of Populus tomentosa. Bioresource Technol 107:282–286

Smart Dustbins: An Approach for Sustainable Solid Waste Management in Smart Cities

A. C. Sati and K. Sudhakar

Abstract Solid waste management is a challenging problem in today's world because of increasing population and changing lifestyle. The solid waste does not only create cleanness issue but also environmental issues. In this paper, we discuss the characteristics and existing status of municipal solid waste, generation and collection in Indian cities and with the help of the collected data we propose a model for sustainable solid waste management for the smart cities, which includes door-to-door, smart collection of waste and smart dustbin approach. Finally, the advantages and the challenges in implementation of the model are also discussed.

Keywords Solid waste management · Smart dustbins
Smart waste collection system

Introduction

India is the second largest country in the world, with a population of 1.21 billion. India is facing a sharp contrast between its increasing urban population and available services and resources. Solid waste management (SWM) is one such service where India has an enormous gap to fill. Proper municipal solid waste (MSW) disposal systems to address the burgeoning amount of wastes are absent. The current SWM services are inefficient, incur heavy expenditure and are so low as to be a potential threat to the public health and environmental quality (Annepu 2012). Improper solid waste management deteriorates public health, causes environmental pollution (Sharholy et al. 2008), accelerates natural resources degradation, causes climate change and greatly impacts the quality of life of citizens

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(Jha et al. 2007). This paper is an attempt to propose a model for sustainable solid waste management for the smart cities, which includes door-to-door, smart collection of waste and smart dustbin approach.

Characterization of Municipal Solid Waste

Municipal solid waste (MSW) is defined as the waste which comes from residential areas, government and private offices, shops and public places (i.e., airports, railway stations, bus stands and public parks), but solid waste does not include construction waste, industrial waste or sewage waste (Keisham and Paul 2015). Table 1 shows the variety of waste generated from different sources of municipal solid waste.

Characterization of waste is necessary to know changing trends in composition of waste. Based on composition/characterization of waste, appropriate waste collection system, transportation, processing and disposal technologies could be selected. According to the studies done by CPCB and NEERI (Waste Generation and Composition 2014), the waste characterization in 20 cities is indicated in Table 2.

Solid Waste Management: Present Status in India

Collection, transportation and disposal are three essential steps in the solid waste management. The first key step in this process is collection of waste, which also designates the collection efficiency of any city. In India, inefficient collection and

Table 1 Sources and types of municipal solid waste (Division of Technology, Industry and Economics 2015)

Sources	Typical waste generators	Types of solid waste
Residential	Single and multifamily dwellings	Food wastes, paper, cardboard, plastics, textiles, glass, metals, ashes, special wastes (bulky items, consumer electronics, batteries, oil and tires) and household hazardous wastes
Commercial	Stores, hotels, restaurants, markets and office buildings	Paper, cardboard, plastics, wood, food wastes, glass, metals, special wastes and hazardous wastes
Institutional	Schools, government center, hospitals and prisons	Paper, cardboard, plastics, wood, food wastes, glass, metals, special wastes and hazardous wastes
Municipal services	Street cleaning, landscaping, parks, beaches and recreational areas	Street sweepings, landscape and tree trimmings, general wastes from parks, beaches and other recreational areas

Table 2 Solid waste composition of 20 major cities in India (Waste Generation and Composition 2014)

S. No.	Name of City	Compostable (%)	Recyclables (%)	C/N Ratio	HCV (Kcal/Kg)	Moisture (%)
1	Agra	46.38	15.79	21.56	520	28
2	Ahmedabad	40.81	11.65	29.64	1180	32
3	Allahabad	35.49	19.22	19	1180	18
4	Bangalore	51.84	22.43	35.12	2386	55
5	Bhopal	52.44	22.33	21.58	1421	43
6	Chandigarh	57.18	10.91	20.52	1408	64
7	Chennai	41.34	16.34	29.25	2594	47
8	Delhi	54.42	15.52	34.87	1802	49
9	Guwahati	53.69	23.28	17.71	1519	61
10	Hyderabad	54.2	21.6	25.9	1969	46
11	Jaipur	45.5	12.1	43.29	834	21
12	Jammu	51.51	21.08	26.79	1782	40
13	Kanpur	47.52	11.93	27.64	1571	46
14	Nagpur	47.41	15.53	26.37	2632	41
15	Patna	51.96	12.57	18.62	819	36
16	Pune	62.44	16.66	35.54	2531	63
17	Thiruvananthapuram	72.96	14.36	35.19	2378	60
18	Varanasi	45.18	17.23	19.4	804	44
19	Vijayawada	59.43	17.4	33.9	1910	46
20	Visakhapatnam	45.96	24.2	41.7	1602	53

inappropriate final disposal of MSW are two of the major problems faced in municipal solid waste management system (Keisham and Paul 2015). Various collection system deployed by the municipalities collects less than 50% of the total waste generated, which results in scattering of waste in open dumps or waste disposal in unplanned manner or open burning of the waste, leading to the environmental and health issues (Sharholy et al. 2008).

In India, about 0.1 million tons of municipal solid waste generated every day, which is approximately 36.5 million tons per year. The per capita waste generation in Indian cities lies from 200 to 600 g/day, which is increasing at a rate of about 1.3% per year in India (Department of Economic Affairs 2009). Table 3 depicts the total and per capita solid waste generation in 20 major cities in India.

In Indian context, the municipal solid waste is generally stored in rectangular-shaped bins made up of metal or plastics, which are neither in closed condition nor emptied regularly, leading to wicked smell and other environmental and health-related concerns. On the other hand, for municipalities it is very difficult to estimate the real-time data of the waste container (Intelligent Waste Management BURBA 2015). At most of the places, the number of bins is inadequate in size and quantity, resulting in scattering of waste, which causes choking of drains (Sunil Kumar and Bhattacharyya 2009). All cities, regardless their size, their

Table 3 Municipal solid waste generation of 20 major cities in India (Waste Generation and Composition 2014)

S. No.	Name of city	Population	Area (km^2)	Waste quantity (TPD)	Waste generation rate (kg/c/day)
1	Agra	1,275,135	140	654	0.51
2	Ahmedabad	3,520,085	191	1302	0.37
3	Allahabad	975,393	71	509	0.52
4	Bangalore	4,301,326	226	1669	0.39
5	Bhopal	1,437,354	286	574	0.4
6	Chandigarh	808,515	114	326	0.4
7	Chennai	4,343,645	174	3036	0.62
8	Delhi	10,306,452	1483	5922	0.57
9	Guwahati	809,895	218	166	0.2
10	Hyderabad	3,843,585	169	2187	0.57
11	Jaipur	2,322,575	518	904	0.39
12	Jammu	369,959	102	215	0.58
13	Kanpur	2,551,337	267	1100	0.43
14	Nagpur	2,052,066	218	504	0.25
15	Patna	1,366,444	107	511	0.37
16	Pune	2,538,473	244	1175	0.46
17	Thiruvananthapuram	744,983	142	171	0.23
18	Varanasi	1,091,918	80	425	0.39
19	Vijayawada	851,282	58	374	0.44
20	Vishakhapatnam	982,904	110	584	0.59

Source CPCB, Government of India (2004–2009)

geographical location or their economic level, spend huge amount of money every year for waste collection rather than its management (Bandyopadhyay 2015). The urban local bodies spend approximately Rs. 500–1500 per ton on collection, transportation, treatment and disposal of solid waste. About 60–70% of the total amount is spent on collection, 20–30% on transportation and less than 5% on final disposal. Out of the total municipal waste collected, on an average 94% is dumped on land and only 5% is composted (Keisham and Paul 2015).

Smart Cities in India

In India, cities accommodate nearly 31% of India's current population and contribute 63% of GDP. Urban areas are expected to house 40% of India's population and contribute 75% of India's GDP by 2030. This requires comprehensive development of physical, institutional, social and economic infrastructure. All are important in improving the quality of life and attracting people and investment, setting in motion a virtuous cycle of growth and development. Development of smart cities is a step in that direction. Recently Indian Government has announced the proposal for 100 smart cities. The Smart Cities Mission is an innovative and new initiative by the Government of India to drive economic growth and improve the quality of life of people by enabling local development and harnessing technology as a means to create smart outcomes for citizens (Smart Cities Mission 2015). Cities which are not clean do not exhibit a smart character. Cities which are clean are perceived to be smart, providing a healthier environment and a better quality of life (Bandyopadhyay 2015). Therefore, municipal solid waste management plays a key role in the development of the smart cities by deploying technology in waste collection and transportation process.

Smart Waste Collection and Smart Dustbin Technique

All activities in the human civilization are accomplished by taking raw materials and energy, as resources, from the nature. The unwanted by-product of all the activities is the waste, as illustrated in Fig. 1. The problem of municipal solid waste

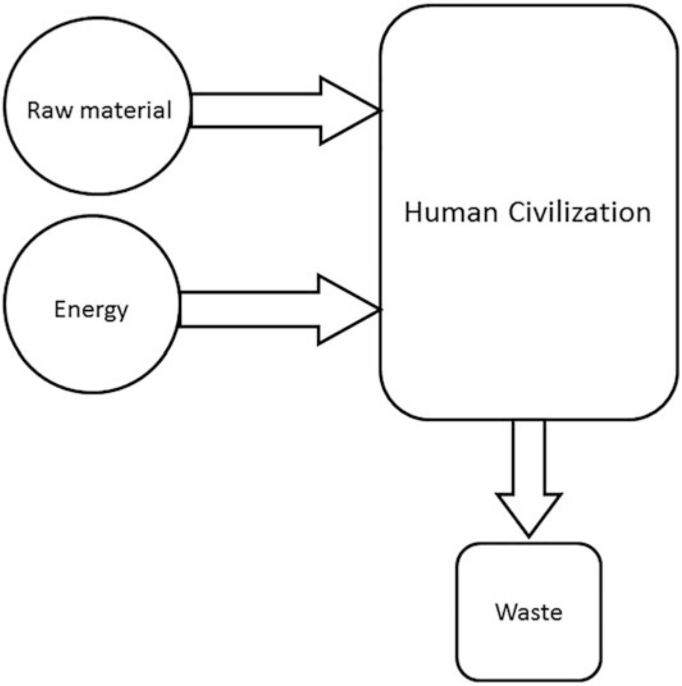

Fig. 1 Block diagram representation of waste generation cycle by human civilization

could be avoided by incorporating sustainable solid waste management model, which converts the whole generated waste back into the resources (i.e., raw materials and energy), as shown in Fig. 2.

In India, the waste collection is done by ULBs (urban local bodies) and the recyclable materials are collected by waste pickers. In the process of waste collection, hardly any technology is used. So this model also includes a proper technological network for waste collection, transportation and their monitoring (Catania and Ventura 2014) using GPS, RFID (Abdoli 2009; Glouche and Couderc 2013) and GSM technology (Bamodu 2013). The smart waste collection unit comprises of a vehicle for the waste transportation and smart dustbin for waste collection. The smart bin contains dedicated chambers for different categories of wastes (i.e., organic, inorganic, inerts etc.). In Fig. 3 H1, H2, H3, stands for House No. 1, House No. 2, etc., are those houses, from where waste has to be collected. For the representation of the model, only seven houses are taken into the consideration. The waste is collected using smart waste collection system from each house. The organic (biodegradable) part of the collected waste is sent to the bio-digester. The recyclable materials are sent to recycling plants, and inerts are sent to WTE (waste-to-energy) plants. The RFID, GSM and GPS technology is incorporated in the waste collection in order to make it easier and more efficient.

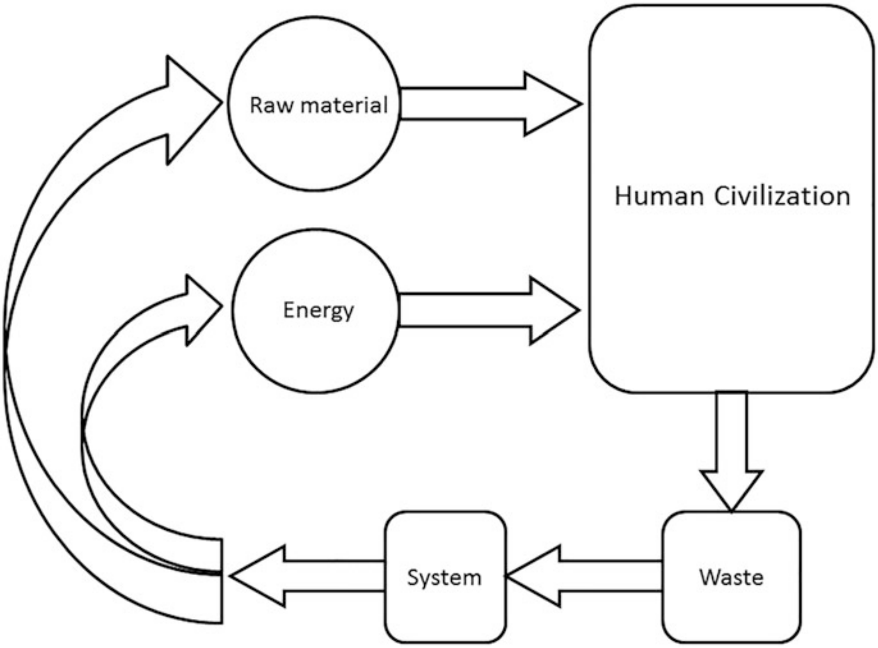

Fig. 2 Solid waste management system with human civilization's waste generation cycle

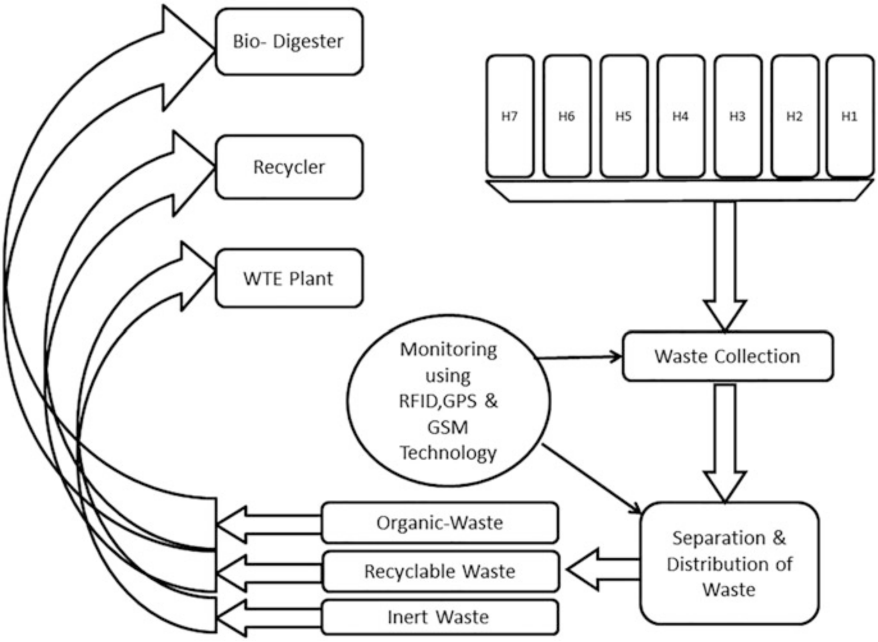

Fig. 3 Block diagram of proposed model for sustainable solid waste management

The model takes the source separation into account, and the organic part of the MSW goes for anaerobic digestion (bio-methanation). The process of anaerobic digestion not only produces biogas (a source of renewable energy) but also the digested slurry, which is a virtuous fertilizer for agricultural use. The other methods for treating organic portion of the MSW (i.e., composting and vermicomposting) are not advised in this model because these methods do not produce any kind of renewable energy, and the composting, practiced in India, is mechanical–biological treatment (MBT) but has been unsuccessful in long run as the quality of the compost produced by the MBT plants was of low grade with high heavy metal concentration and low nutrient value (Annepu 2012). The recyclable portion of the MSW would be sent to recycling plants. The process of recycling would not only conserve our natural resources but it also saves the extra amount of energy, which otherwise would have been wasted in extracting the material from its natural form. This model does consider the modern WTE (waste-to-energy) plants (having pollution control technology, which can dramatically reduce the emission of dioxins and furans (Annepu 2012)) but only for the inert materials or substances which, otherwise, cannot be recycled or used in any other way except for land filling.

Future Perspective

Advantages

With increase in the population and changing lifestyle, the per capita waste generated in India is increasing every year. Table 4 shows the future perspective of population growth and its impact on the generation of municipal solid waste, till 2041.

The studies show that in coming years the amount of waste generated is going to increase tremendously. In order to handle the future scenarios, a systematic technological model for the municipal solid waste management is needed. This model is perceived to have following advantages in relation to the current solid waste management system:

I. A useful and scientific way to handle the big amount of waste.
II. Creation of new employment opportunities in solid waste management sector.
III. The model plays a key role in the development of the smart cities.
IV. The model also reduces the problem of area requirement for the landfill sites by increasing recycling and collection efficiency of solid waste.
V. Reduction in the GHG (green house gases) emission from open dumping and landfill sites.

Challenges:
Challenges in the realization of this model are listed as follows:

I. The segregation of collected waste into biodegradable, non-degradable and inertcategory is the main challenge.
II. Realization of smart door-to-door collection systems.
III. Realization of various types of standalone smart dustbins for different applications, e.g., a small smart dustbin for the public transport buses and railways, so that people would be having an option to keep the waste into the dustbin rather than throwing it outside the buses or trains.

Table 4 Population growth and impact on overall urban waste generation and future predictions until 2041 (Annepu 2012)

Year	Population (millions)	Per capita	Total waste generation (thousand tons/year)
2001	197.3	0.439	31.63
2011	260.1	0.498	47.30
2021	342.8	0.569	71.15
2031	451.8	0.649	107.01
2036	518.6	0.693	131.24
2041	595.4	0.741	160.96

IV. Realization of dustbins of appropriate size and shape to put it in the public place (e.g., at bus stands, railways stations etc.), where people usually through the garbage.
V. Selection of appropriate technological tools for designing the prototype of the smart door-to-door collection system and smart dustbin.
VI. Technological and economic feasibility analysis of the designed prototype in real-time conditions.

Concluding Remarks

The problem with present solid waste management system is that the bins are common for both compostable and non-compostable waste collection, through which it becomes extremely difficult to segregate the variety of collected waste. The solution to this problem is to have smart dustbin and smart door-to-door waste collection systems approach. The study also concludes that the technological interventions in municipal solid waste collection have huge potential, in substantially enhancing the waste collection efficiency, which results in better quality of life, improved cleanliness and reduction in the harmful effect of solid waste on the environment.

References

Abdoli S (2009) RFID application in municipal solid waste management system. Int J Environ Res 3(3):447–454

Annepu RK (2012) Sustainable solid waste management in India. M.S. thesis, Department of Earth and Environmental Engineering, Fu Foundation School of Engineering and Applied Science, Columbia University, New York

Bamodu O (2013) Application of mobile technology in waste collection. Int J Appl Sci 4

Bandyopadhyay S (2015) Smart meters for accounting smart solid waste mangement for smart cities in India. In: Proceedings REAL CORP 2015, May 2015. ISBN: 978-3-9503110-8-2

Catania V, Ventura D (2014) An approach for monitoring and smart planning of urban solid waste management using smart-M3 platform. In: Proceeding of the 15th conference of FRUCT association

Department of Economic Affairs, Ministry of Finance, Government of India, Position paper on the solid waste management sector in India, public private partnerships in India (Online). Nov 2009

Division of Technology, Industry and Economics. State of Waste Management in South East Asia, Types of Wastes-Sources and Composition, United Nations Environment Programme (Online). Accessed on 04 Oct 2015

Glouche Y, Couderc P (2013) A smart waste management with self-describing objects. SMART 2013, The second international conference on smart systems, devices and technologies

Intelligent Waste Management BURBA: Bottom up selection, collection and management of URBAN waste with intelligent waste containers (IWAC), a success story in intelligent waste management (Online). Accessed on 26 July 2015

Jha AK, Sharma C et al (2007) Greenhouse gas emissions from municipal solid waste management in Indian mega-cities: a case study of Chennai landfill sites. Chemosphere

Keisham S, Paul B (2005) A review on the recent scenario of municipal solid waste management in India. Int J Eng Res General Sci 3(3)

Sharholy M, Ahmad K, Mahmood G, Trivedi RC (2008) Municipal solid waste management in Indian cities—a review. Waste Manage 28:459–467

Smart Cities Mission: A step towards Smart India (Online). Accessed on 04 Oct 2015

Sunil Kumar JK, Bhattacharyya et al (2009) Assessment of the status of municipal solid waste management in metro cities, state capitals, class I cities, and class II towns in India: an insight. Waste Manage 29:883–895

Waste Generation and Composition, Studies of Central Pollution Control Board (Online). Accessed on 14 Sep 2014