Water Treatment Technologies for the Removal of High-Toxicity Pollutants

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Published in cooperation with NATO Public Diplomacy Division

Proceedings of the NATO Advanced Research Workshop on
Water Treatment Technologies for the Removal of High-Toxicity Pollutants
Kosice, Slovak Republic
13–17 September 2008

Library of Congress Control Number: 2009936957

ISBN 978-90-481-3496-0 (PB)
ISBN 978-90-481-3495-3 (HB)
ISBN 978-90-481-3497-7 (e-book)

Published by Springer,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

www.springer.com

Printed on acid-free paper

CONTENTS

PREFACE

Water is essential for life, a strategic resource for every country and population. Its availability and sanitary safety is highly connected with the health and economy status of population. Burden of disease due to polluted water is a major public health problem throughout the world. Many pollutants in water streams have been identified as toxic and harmful to the environment and human health, and among them arsenic, mercury and cadmium are considered as high priority ones.

Providing population with safe drinking water became the priority and at the same time a big challenge for the modern society. Many funding agencies in various countries have assigned a high priority to the environmental security and pollution prevention. UN, being one of them, launched the "International Decade for Action: Water for life 2005–2015." Therefore, today's political and social climate presents an important opportunity to implement principles of sustainable development and to preserve resources essential for future life. This process requires interdisciplinary approach; it is critically important to stimulate interactions between medical doctors, chemists, physicist, materials scientists, engineers and policy makers, which are already experienced in their specific areas. It is also our ethical obligation to preserve existing water resources and existing eco systems enhancing their biodiversity.

The NATO Advanced Research Workshop *"Water Treatment Technologies for the Removal of High-Toxicity Pollutants"* took place on September 13–17, 2008 in Košice, Slovak Republic. Slovak Republic is a country located in Central Europe, surrounded by Czech Republic, Poland, Ukraine, Hungary and Austria. Košice is the country's second largest city; is a hub of industry, commerce, science and culture of East Slovakia. Institute of Geotechnics, Slovak Academy of Sciences and School of Public Health "A. Stampar", Medical School, University of Zagreb were co-organizing institutions.

Forty-two participants from 14 countries including Croatia, Belgium, Bulgaria, Belarus, Greece, Italy, Moldova, Portugal, Russia, Serbia, Slovakia, Turkey, Ukraine and the USA attended the meeting. Sixteen invited speakers and 26 specialists including young scientists and postgraduate students, discussed the problems related to high toxicity pollutants (i.e. As. Hg, Cd, etc.) in environment, especially in drinking waters. They also referred to the latest technological innovations in the treatment of water streams, including speciation and modeling, needed to secure the city's water supply. Policy making, as a mean to increase environmental security was also discussed.

The Advanced Research Workshop was divided in sessions covering latest views of the underlying nature of toxic species in waters, fundamental principles of treatment technologies, modelling and policy making. Four sessions were defined as (a) arsenic and other high priority pollutants in waters, chemistry and toxicity, (b) health effect and environmental security, (c) treatment, modelling, and (d) policy making in the areas of health protection, treatment selection, protection of resources and crisis response.

The above-described topics are covered in the book. Formal presentations are included in the book along with the most interesting and valuable young scientist's and postgraduate student's works presented as posters at the workshop. It is unfortunate that a book can not reflect the passionate exchange of ideas that happened during discussions and informal meetings. It is our believe that this book will be a valuable source of information to the scientific community that deals with water aspects and a helpful guide for policy makers and public health specialists.

We would like to point out that this meeting was a continuation of a series of meetings of CCMS Pilot Study on *"Clean Products and Processes"* group and resulted in the strengthening of an existing network of scientists and specialists from NATO, Partner and Mediterranean Dialogue Countries. We are proud that new scientists joined this network and created new collaborative links and personal friendships. This added value is always beyond scientific borders.

Such a constructive ARW is the outcome of efforts by participants, lecturers and co-directors. This meeting would not be possible and successful without volunteers from the Institute of Geotechnics of SAS, Kosice, who handled everyday logistics with utmost consideration and efficiency. We would also like to express our sincere gratitude to the NATO Science for Peace and Security (SPS) Programme, its Programme Director of Environmental Security Dr. F. Pedrazzini and his Assistant Ms. L. Campbell-Nolan for encouragement, expertise, and financial support. Special thanks should be addressed to Mr. Wil Bruins from NATO Publishing Unit of the Springer Academic Publisher, who has provided us with much appreciated assistance, valuable guidance and patience. The co-directors together with international organizing committee hopefully anticipate that this ARW provides continued success for all participants as they extend collaboration in their field of interest.

The Editors

NANOMATERIALS FOR CHEMICAL–BIOLOGICAL – PHYSICAL INTEGRITY OF POTABLE WATER

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Abstract Water in general is ubiquitous facilitator for sustaining life. With ever increasing population worldwide and consumption of enormous energy, the water supplies continue to deteriorate in quality. Major contributing factors include outdated water treatment systems; unbalanced supply-chain management; non-uniform waste discharge regulations; and increased industrialization and urbanization worldwide. Hence, it is extremely important to monitor, control, and maintain 'water quality' – typically defined as physical, chemical and biological characteristics of potable water in relationship to a set of standards. In an attempt to develop a uniform standard for water quality and to provide safe drinking water worldwide, advances in nanoscale materials devices and systems are utilized to evaluate chemical, biological, and physical characteristics of water and remediate sediments, contaminants, and disease vectors. Furthermore, interaction of nanomaterials with its environment is crucial to understand for developing remediation strategies. A matrix of parameters that governs interaction of nanomaterials with their environments is discussed in context of evaluating chemical, biological, and physical integrity of drinking water.

Keywords: Nanomaterials; pollution; water; sustainability

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

1. Introduction

Water is an ubiquitous facilitator for sustaining life and covers more than 70% of the Earth, yet ~1% is be used for drinking purposes without processing, filtering or melting polar ice caps and appears to be dwindling as the global population grows and industry and agriculture require increased quantities of water. It is well known that an increase in population and consumption of fossil fuels have led to increased pollution worldwide. Although a correlation between environmental pollution and global warming is debatable, the effects of pollution and its impact on human health are irrefutable. Pollution in large cities has reached an alarming level and is widely perceived to be a leading contributor to chronic and deadly health disorders and diseases affecting millions of people each year. A recent study indicated that 1.3 billion people do not have access to safe drinking water and 35% of people in developing countries die from water related problems. According to the World Health Organization (WHO), diarrhea alone accounts for mortality of an estimated 1.8 million people every year, of which an estimated 88% are children in developing countries. Past trends indicate that global consumption of water will likely double in the next 20 years, yet issue of water is singularly undervalued. Furthermore and interestingly, a large sector of the world's population have no access to fossil fuels, yet suffer from the adverse impact of pollution due to transport through air, water, and soil. Certain developing countries have implemented studies and measures, such as cap-and-trade, carbon credit, purchasing pollution credit, efforts to sequester CO_2, use of alternate energy sources, etc., to limit emission of green-house gases (GHG). Figure 1 illustrates pollutions footprint of various sources of energy and a proposed "future distributed-source energy solution",[1] while the right panel shows water pollution pathways and a prototype of a water pollution monitoring system.

Hence, it is extremely important to monitor, control, and maintain water quality – typically defined as physical, chemical and biological characteristics of potable water in relationship to a set of standards. Water quality is a rather complex subject and is intrinsically tied to the regional ecology; hence standards vary from region to region. In an attempt to develop a uniform standard for water quality and to provide safe drinking water, advances in nanoscale materials devices and systems are utilized to evaluate chemical, biological, and physical characteristics and decontaminate water.

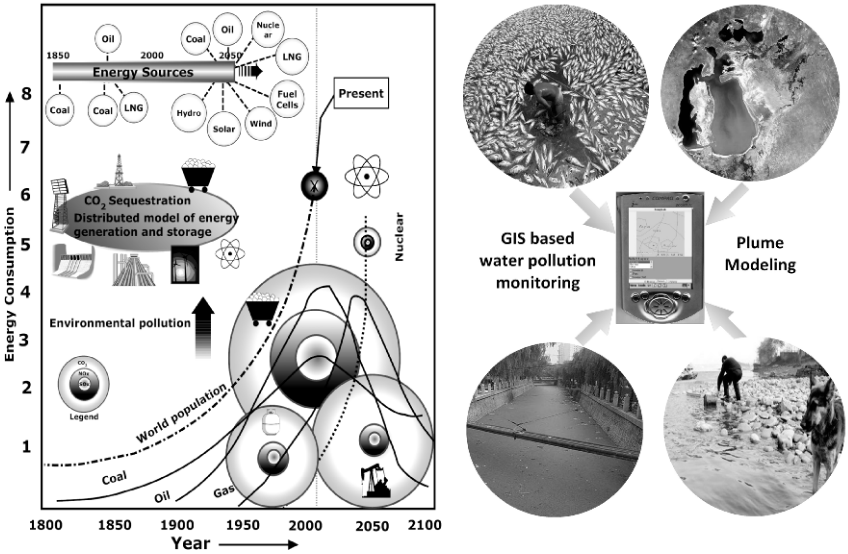

Figure 1. An overview of sources of energy, pollution level, and distributed model of energy in the future.[1] Right panel shows water pollution pathways and monitoring system

Materials approaching nanoscale dimensions exhibit atypical characteristics with numerous unique applications. Advances in synthesis and characterization methods have provided the means to study, understand, control, or even manipulate the transitional characteristics between isolated atoms and molecules, and bulk materials. Nanotechnology solutions are essential because the abiotic and biotic impurities are most difficult to separate in water are in the nanoscale range. Notwithstanding the advances and benefits of nanotechnology, there is perceived possible erosion of individual confidence and tipping of the playing field on the beneficial use of nanomaterials – encompassing risk, ethical, and legal considerations. To address such concerns, interaction of a nanomaterial with its environment and its dependence on physicochemical properties, toxicity, and its environmental impact is relevant to understand. To offset the possible risks associated with nanotechnology, recently, "voluntary codes of conduct" were introduced. It is argued that a well defined risk assessment modality is needed, as the "voluntary code of conduct" for using nanomaterials is somewhat trepidation based and not entirely on scientific methodology. An overview of general risk assessment practices and current research efforts for assessing nanotechnology risks is suggested by the authors and is discussed elsewhere.[2] Furthermore, to develop a water quality intervention mechanism that employs simple, inexpensive and robust technologies appropriate for the developing world, it is critical to understand the fate and transport of various contaminants and pollutants – natural, intentional or inadvertent industrial release, runoff from agricultural areas, urban storm water runoff, abandoned or uncontained mines, and discharge of untreated sewage. The objective of this investigation is to make water safe through purification and filtration/storage at the point-of-use (POU).

2. Water Purification – Impact and Opportunity Nexus

Providing for abundant fresh water for human use is among one of the most pressing priorities facing international community for the reasons stated in Section 1. Unfortunately, the problem set of water purification is rather diverse due to different geographic locations and also complex issues requiring individual, local, regional, national, and even international solution platforms. Despite advances in large scale, conventional purification and disinfectant systems for both ground and surface water sources employing chlorine dioxide, ozone, and ultraviolet irradiation, there are reports of disease outbreaks from waterborne infections. In addition to microbial contamination from bacteria, protozoans, and viruses, the water supply contains previously undiscovered pathogens and pharmaceuticals – viz. antibiotics, steroids, and common over-the-counter (OTC) painkillers causing adverse affects in younger generations. Hence, a number of disinfection technologies, including both POU and point-of-entry (POE) have been deployed to address the contamination issues.

The opportunity nexus for water purification consists of (a): Environment – decontamination technologies to minimize environmental impact, globalization, urbanization, and other emerging issues to ensure adequate clean supply of potable water. (b): Energy generation – as the energy demand continues to increase, water consumption for such plants is expected to increase between 30–50% (depending upon efforts to reduce consumption of fossil fuels). (c): Agriculture – increase in population will require greater water supplies for irrigation and livestock and new mechanisms for enhanced agricultural water conservation and increased recovery and reuse of irrigation runoffs; (d): Health – as the water supply continues to be excessively strained, production and access to clean potable water is closely related to human health. As mentioned above that ~1.3 billion people lack access to clean water and over 2.4 billion people lack improved sanitation resulting in diarrhea, cholera and food-poisoning. In addition, several regions worldwide have increased amount of arsenic in water supplies leading to toxicity. Pathophysiology of arsenic includes disruption of ATP production; inhibits pyruvate dehydrogenase and energy-linked reduction of NAD+, mitochondrial respiration, increased hydrogen peroxide production leading to oxidative stress; and metabolic interferences leading to death from multi-system organ failure. Several studies have linked long-term exposure to small concentrations of As with cancer and cardiovascular, pulmonary, immunological, neurological and endocrine effects; thus necessitating studies for developing efficient methods for removing As from drinking water. (e): Security – maintaining water supply chain integrity has been a major challenge for military. Water supply chain has emerged as one of the main targets for terrorism. Mechanisms are intentionally omitted here for security reasons; needless to mention that maintaining water security is one of the primary areas of the author. Furthermore, U.S. EPA has initiated a WaterSentinel program for the design, development, and deployment of a robust, integrated water surveillance system to provide real-time system wide water quality monitoring, critical contaminants sampling and analysis, and public health surveillance. The complexity of the WaterSentinel program is expected to be modified using nanomaterials based sensors, improvised signal distribution and transmission, and decision support technology. (f): Economy – the congressional budget office in the U.S. estimated in late 1990s that the average cost of water and wastewater services represented ~0.5% of household income and it is anticipated that by 2020 the cost are projected to be ~0.6–0.9% of national household income. With increasing population, pollution, energy consumption, and associated health impact, dependence of economy of water becomes a rather complex issue impacting country's potential for prosperity. To enhance economic prosperity, the issue of abundant clean water has emerged to quintessential for international community for economic prosperity and maintaining quality of life index for its citizens.

3. Materials in Reduced Dimensions

Solids in reduced dimensions are tantamount to reduction of the coordination number; hence the electrons have less opportunity to hop from site to site; thus reducing kinetic energy of electrons. A higher Coulomb interaction/bandwidth ratio at a site enhances electron correlation and Mott-transition leading to the appearance of magnetism. Furthermore, the symmetries of the system are lowered and the appearance of new boundary conditions leads to surface and interface states. A change of the quantization conditions alters the Eigen value spectrum and transport properties of the solid. A high surface area/volume ratio in nanoscale materials changes physical properties. Thus, systems in reduced dimensional tend to display novel characteristics arising due to dimensionality thus leading to tremendous potential.

3.1. INTERACTIONS WITH MEDIUM

Size and surface collectively control characteristics of nanoscale materials due to the existence of large boundaries adjoining its surrounding medium in conjunction with interplay of physicochemical interactions. The surface free-energy is size-dependent and hence increases almost inversely with the decreasing feature sizes of the material. Nanomaterial-medium system response that is attributable to reduced dimensions is fundamental to developing a scientific model that predicts its pathways for toxicity. Such modality is an exceedingly complex task due to a large matrix of parameters consisting of nanomaterials, the surrounding environment, and influencing mechanisms of interactions. Hence, as the production and diversity of nanoparticles increases, it is important to understand how engineered nanoparticles and biological systems interact in terms of bio-physico-chemical properties of engineered nanoparticles. An extensive investigation is in progress in the context of specific functions ranging from bio-nanomaterials interface to toxic potential of industrial pollution. The characteristics that provide beneficial aspects are also believed to be responsible for toxicity of nanomaterials. Consequently, nanoparticle toxicity is studied in context of its ability to induce tissue damage through the generation of oxygen radicals, electron–hole pairs, and oxidant stress by abiotic and cellular responses.[3] Nanoparticles, which are cationic, are also believed to induce toxicity via acidifying endosomes that lead to cellular toxicity and apoptosis in epithelial lung through endosomal split through proton sponge mechanism (PSM), mitochondrial targeting, and cytosolic deposition. Nanomaterials composed of redox-active elements are particularly reactive and can possibly provoke potentially damaging chemical transformations. Even chemically benign nanoparticles may become active by light absorption. Hence, fundamental understanding of a nanomaterial-surrounding medium is vital to sustaining technological advances of nanoscale materials (Figure 2).

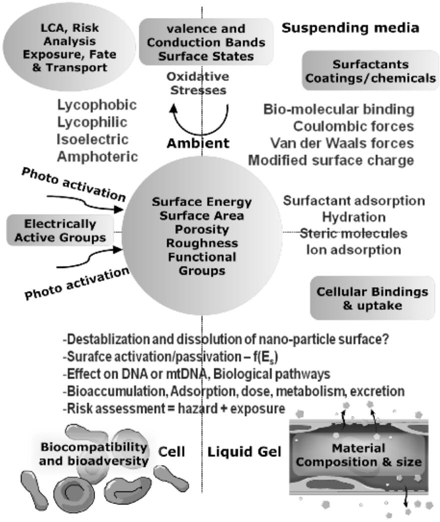

Figure 2. Nanoparticles/medium/cell Interaction – physico-chemical characteristics

4. Water Contamination Sensors and Detectors and Decontamination

Due to urgent need of water purification systems worldwide, the challenge facing scientific community is a long-term vision for sustainable, abundant, clean potable water using economically viable, disruptive and emerging technologies, and advanced sciences convergence paradigm. This new approach necessitates in-line sensing and detection of contaminants from metallic impurities, bacteria, viruses, protozoans, unused pharmaceuticals, and inadvertent or deliberate introduction of chemicals harmful to human consumption. In conceivable weapons of mass destruction and terrorism (WMDT) scenario, rapid identification of events (viz. water contamination) will allow first responders and emergency personnel to implement critical decisions in real-time. Conventional detection methods require time-consuming steps to arrive at meaningful data. As an example, methods such as enzyme linked immunosorbent assay (ELISA) and polymerase chain reactions (PCR) have been employed for pathogen detection. In clinical medicine, decentralized laboratory facilities allow mobile facilities for clinical analysis through direct-reading, portable, lab-on-chip (LOC) systems with wireless communications capabilities to centralized servers and command and control units. Nanostructured materials based sensor platforms will significantly impact data collection, processing, and recognition to enable the direct detection of biological and chemical agents in a label-free, parallel, multiplexed format and over broadly dynamic range. This platform utilizes functionalized nanotubes, nanowires, and nanoparticles to detect a broad range of molecules and molecular binding with high sensitivity and selectivity.

4.1. NANOMATERIALS BASED CHEMICAL–BIOLOGICAL SENSORS

Biosensors are intrinsically simple and inexpensive systems that use molecules – usually enzymes, antibodies, or nucleic acids – to recognize simple molecules of interest via hydrogen bonding, charge–charge interactions and other biochemical interactions to provide pertinent molecular information (Figure 3a). Progress in nanomaterials and advances in fabrication processes provide opportunity to modify, embed in host matrix, or even customize the nanoparticles for use as highly sensitive and selective sensing materials. Nanomaterials based sensors are used in several configurations such as SPR (Figure 3b), electrochemical, optical, electrical transduction, and as shock-wave generators for applications ranging from homeland security to studying the environment pollution.

Carbon nanotubes (CNTs) are conducting, act as electrodes, generate electro-chemiluminescence (ECL) in aqueous solutions, and can be derivatized with a functional group that allows immobilization of biomolecules. CNTs have high surface/volume ratios for adsorption, and have surface/weight ratios $\sim$300 m^2/g. The uniform chemical functionalization of CNTs is essential to fabrication of biosensors. Oxidation of nanotubes with HNO_3–H_2SO_4 leads to high concentrations of carboxylic, carbonyl, and hydroxyl groups on its surface and removal of the tip to expose the tube interior. Carboxyl groups can readily be derivatized by a variety of reactions allowing linking of biomolecules. The covalent modification of CNTs

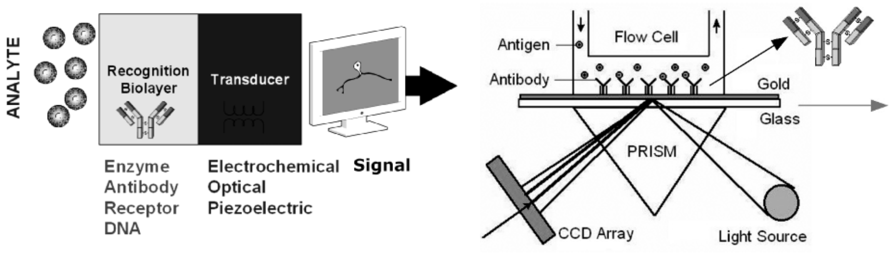

Figure 3. (a) Electrochemical sensor basics. (b) SPR based sensor[4]

facilitates creation of well-defined probes, which are sensitive to specific intermolecular interactions. Integration of the transducer and probe enables quick, accurate, and reversible measurement of target analytes without the use of reagents. Using sequence-specific attachment, NT-based electronic devices with specific molecular-recognition features of DNA are reported in literature.[5] Covalent modification of single wall CNTs (SWNTs) offers mapping of functional groups at a molecular resolution. During interaction with the polymer coatings, the electrical properties of the nanotubes are altered, enabling detection of the molecules leading to a very sensitive sensing mechanism. The mesoporous carbon matrix is used for stable immobilization of the biological molecule, and C_{60} serves as an electron mediator. Both C_{60} and NTs are good electron mediators when used with a mesoporous carbon matrix. Efforts to sort batches of CNTs by length using high-speed centrifuges and functionalization to develop sensors, genetic analysis, proteomics, drug screening, clinical diagnostics and bio-warfare agent detection are underway.

The SPR detection technique is a rapid, real-time, and requires no labeling, and involves immobilizing antibodies by a coupling matrix on the surface of a thin film of precious metal, such as nanoparticles of gold deposited on reflecting surface of an optically transparent wave-guide. The precise angle at which SPR occurs depends on several factors (Figure 3b). A main response is the refractive index of the metal film, to which target molecules are immobilized using specific capture molecules or receptors along the surface, that cause a change in SPR angle, which is monitored in real-time by detecting changes in the intensity of the reflected light. The rates of change of the SPR signal can be analyzed to yield apparent rate constants for the association and dissociation phases of the reaction.

Various other sensor platforms, viz.: (a): chemo-mechanical micro-cantilever array to provide a quantitative and label-free platform for high-throughput multiplexed biomolecular analysis for detection of various biomolecules based on binding, (b): microarrays chips fabricated using technique matrix assisted pulsed laser evaporation (MAPLE) and laser induced forward transfer (LIFT) for deposition of biopolymers and a variety of biomolecules to detect micro-organisms, and (c): aligned-CNT probes for biomolecular recognition based on charge transport at the CNT transducer with the accuracy down to molecular level are under investigation.

Recent advances in molecular biology are used to study the effects of proteins and drugs on gene expression, viz. gel mobility shift, filter binding, DNA foot-printing and fluorescence-based assays. Most of these methods; however, are indirect and require various labeling strategies. In recent years, there has been a growing interest towards design of electrochemical DNA biosensors that exploit interactions between surface-confined DNA and target drugs/biological molecules for rapid screening.[6,7] Binding of small molecules to DNA primarily occurs in three modes: electrostatic interactions with the negative-charged nucleic sugar-phosphate structure, binding interactions with two grooves of DNA double helix, and intercalation between the stacked base pairs of native DNA. Most electrochemical sensors use different chemistries; and employ interactions between the target, the recognition layer and an electrode. We have followed numerous approaches to electrochemical detection including direct electrochemistry of DNA and devices based on DNA-mediated charge transport chemistry. In direct electrochemical DNA sensors, the analysis is based on a guanine signal where a base-pairing interaction recruits a target molecule to the sensor, allowing monitoring of drug/biological molecule-DNA interactions, which are related to the differences in the electrochemical signals of DNA binding molecules for DNA bar-coding. It is vital to develop sensing strategies to maintain critical dynamics of target capture to generate a sufficient recognition signal. Standard electrochemical techniques, such as differential pulse voltammetry (DPV), potentiometric stripping analysis (PSA), square-wave voltammetry (SWV), etc. are used as genosensors. Since genosensors are compatible with existing micro and nanofabrication technologies, they enable design of low-cost, devices that offer potential for detection and diagnosis via credit card-sized sensor arrays.

4.2. WATER POLLUTION REMEDIATION, STRATEGIES, AND SYSTEMS

One of the objectives of our ongoing research is to develop an economical and portable water pollution remediation and monitoring system to be distributed as stand-alone unit to population who otherwise do not have access to clean water. Eventual goal is to study its feasibility for large scale water purification/decontamination for commercial applications. Our earlier efforts[8] to monitor atmospheric pollution in metropolitan cities is intended to serve as a model for monitoring water pollution/contaminants as well.

Earlier efforts[9] were focused to investigate and mitigate water contaminants such as Arsenic (As), which is found in the natural environment and also from anthropogenic activities. As (III) is four to ten times more soluble in water than As (V), and ten times more toxic than As (V). We have employed a method based sorption on iron (III) oxides, such as amorphous hydrous ferric oxide (FeOOH), poorly crystalline hydrous ferric oxide (ferrihydride) and goethite (α-FeOOH) which have been found to be effective in removing both As (V) and As (III) from aqueous solutions. Preliminary results with synthetic akaganeite (β-FeOOH) have shown that the maximum capacity of the sorbents is around 75 mg of As per gm of akaganeite. Also, quite good results were obtained with synthetic magnetite/maghemite, with a maximum capacity of ~40 mg of As per gm of sorbent. Incorporating iron oxides/oxyhydroxides based nanostructures in zeolites and nanoscale zero-valent iron (nZVI) technology provides a method for high capacity As removal. Unfortunately, nanomaterials with small particle size (around 20–50 nm) are not suited well for sorption columns. However, with magnetite/maghemite, separation can be easily accomplished in a high gradient magnetic field. One of the methods under investigation is to incorporate selected nanomaterials into a well organized host. Nanoporous and microporous crystals, such as molecular sieves (zeolites) are ideal hosts for accommodation of organic and inorganic molecules and polymer chains due to their uniform pore size and ability to sorb molecular species. Incorporating iron oxides/oxyhydroxides based nanostructures in zeolites and nanoscale zero-valent iron (nZVI) technology would provide a necessary means for high capacity As removal. This method in conjunction with membrane and filtration technologies will eventually produce clean water.

Titanium oxide (TiO_2) modified by nanoparticles of transition metal oxides is widely used for photocatalysis due to its chemical stability, photoactivity, and non-toxicity. We have also investigated various ways in which nanomaterials can successfully be used to reduce/isolate water contamination and odor. The nanostructured photocatalysis produces fast photocatalytic degradation in organics, bacteria, spores, and viruses, and thus have great potential for water decontamination. As an example, employing immobilized Ti films, produced by sol-gel process, 10 ppmv weak UV light of 1 $\mu W/cm^2$ was sufficient to decompose compounds. In an experiment, 150 μL of an *E. coli* suspension was placed under weak UV (1 mW/cm^2) illuminated TiO_2-coated glass plate. Under these conditions, there were no surviving cells after only 1 h of illumination, showing antibacterial effect.[10] Bacteria removal from water requires a complete understanding of communication between cells and bacteria and is essential to the advancement of the new field of synthetic biology, where populations of genetically altered bacteria are "programmed" for specific functions. Such re-programmed bacterial gene circuits offer a wide variety of applications in water purification. A process known as "quorum sensing" – is a cell-to-cell communication mechanism that enables bacteria to sense and respond to variation in the density of the bacteria in a given environment, irrespective of microbe. Hence sensing potential, viz. linking of an action to the number of cells and the size of their environment, provides insight into the fundamental design of quorum sensing systems, framework for studying dynamics, and synthetic gene circuits.

With advances in functionalization of nanomaterials, a variety of nanomaterials have been studied for their abilities to detect and mitigate pollutants in air, water, and soil. Of special interest are functional nanoparticles that can be used to develop membranes. Of special interest are ceramic membranes with "self-cleaning" catalytic surface and porous polymer-metal nanocomposite membrane with biocidal characteristics. Employing electro-spinning process several polymers/ceramers with loading[11] were studied for membrane material developments. Further advances in membrane materials technology such as increased structural and functional complexity, structure–function coupling, and process intensification need further investigation. For nanocomposite membranes, role of nanoparticle dispersion and distribution within host matrix, nanoparticle–matrix adhesion, change in structure and characteristics are critical.

CNTs based membranes offer ultra efficient transport of water through these ultra-narrow molecular structures. These smooth, hydrophobic surfaces of the CNTs tend to allow frictionless flow of water, enabling transport rates an order of magnitude greater than the transport in conventional pores. CNT based membranes provide a rare combination of transport efficiency and selectivity rendering CNT based membranes a highly promising technological platform for the next generation. Several configurations ranging from arrays encapsulated with Si_3N_4, polymeric/ CNTs membranes, and chemically functionalized NT membranes to alter the channel permeability. Yet another approach is based on dendrimers, termed as dendrimer enhanced filtration (DEF), which is capable of removing dissolved substances. Dendrimers are highly branched 3D globular nanopolymers with controlled composition and architecture. Many functional reactive sites, binding pockets/molecule, and their globular shapes provide for easier filtration in contrast to the long chain polymers. Functionalized dendrimers bind with the target contaminants in aqueous solution and change in pH value (acidity) causes dendrimers to bind/release its target solutes. In addition to dendrimers, hydroxylated C_{60} or fullerol are non-toxic and exhibit photochemical activity, thus offering potential for water disinfection capability. A yet new approach termed as nanomaterials enhanced electrically switched ion exchange (ESIX) technology which is based on conducting polymers/CNT Nanocomposites, offers a cost effective method for removal of radiative Cs, chromate, and perchlorate from ground water.

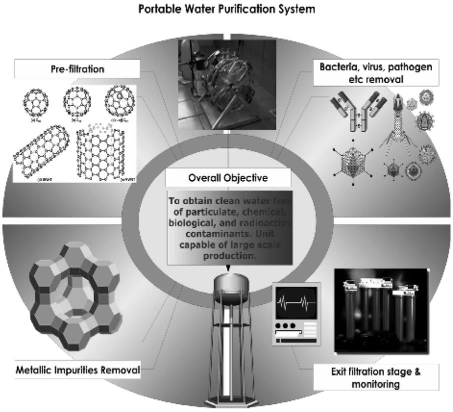

Figure 4. Different stages of a proposed portable water purification system

The method employs principles of ion exchange and electrochemistry for the removal of toxic ions from waste effluents. Hence, based on effluent contaminants, a multi-stage, customized water nanofiltration system in suggested for removal of contaminants ranging from sediments, metal ions, chemical impurities and biological molecules, as shown in Figure 4.

5. Sustainability – Environment, Economy, and Society

According to the U.S. Environmental Protection Agency (EPA), sustainable development has been expressed as meeting the needs of the present without compromising the ability of future generations to meet their own needs. The modern definition of sustainability refers to the capability of an ecosystem to maintain ecological processes, functions, biodiversity and productivity into the future. To support a collective effort to keep natural resources within the sustainable development aspect of the Earth's finite resource limits, nanotechnology offers the means to support the sustainable development by employing principles of green nanotechnology.[10] An extension of the above study is to study the fate and transport of nanomaterials and to conduct a general risk-assessment to keep the public at-large informed.

5.1. LIFE CYCLE ANALYSIS AND RISK ASSESSMENT

Life cycle analysis in conjunction with proactive risk assessment will ensure appropriate measures as reasonable scientific evidence is established. It also provides for technology to gain social acceptance based on its unambiguous assessment that the technology can be applied to a large scale production without harming the environment and the health of workers and general population. The general framework includes nomenclature and characterization; environmental fate and transport; and hazard identification – exposure and identification. Several methods and opinions have been evolved over a period of time, as an example, the Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) has adopted an opinion on "the appropriateness of existing methods to assess the potential risks associated with engineered and adventitious products of nanotechnologies". As a result, several recommendations were made addressing various uncertainties with regard to potential health hazards and exposure, addressing gaps in knowledge; and further developing guidelines and methods.

One important aspect is risk assessment which is analysis based on a three prong approach viz. assess, manage, and communicate. Nanotechnology risk assessment occurs in a climate of uncertainty and change; therefore, effective decision making by participating experts is critical for a successful outcome. The Delphi Technique is a structured interactive group communications technique effective for reaching consensus about judgments, forecasts, or decisions from expert panels.[2] The Delphi Technique benefits decision making and forecasting processes involving expert panelists in many ways and has proven effective in the exploration and forecasting of novel, complex, or uncertain problems or events; and the technique overcomes social barriers related to diversity, hierarchy, personality, or hardened conflicts.

5.2. FATE AND TRANSPORT OF NANOMATERIALS

The mode of transport, interaction and chemical affects on the human body of atmospheric pollutants is not well understood. A comprehensive and fundamental investigation into the dynamic transport of nanomaterials in the environment and its impact on human health and ecology is needed to guard public welfare. The complex nature of naturally occurring and engineered nanomaterials and transport, either in the environment or via different exposure routes with human body necessitates an ontological modality. A matrix of parameters which govern fate and transport modeling of nanomaterials such as exposure routes, chemical composition, surface structure, solubility, size and shape effects, toxicity, absorption, distribution, metabolism, agglomeration, and excretion rate and mechanisms is under investigation. Biodegradation and bioaccumulation of nanomaterials should be sufficiently addressed due to impacts on human health. Studies relating to the thermodynamic properties, interfaces, and free energy of nanoparticles as a function of particle size, composition, phase and crystallinity influence particle dissolution in a biological environment. The accumulation, dispersion, and functional surface groups play an important role in cytotoxicity and in evaluating pathways of cellular uptake, sub cellular localization, and targeting of sub cellular organelles.

6. Conclusions and Way Forward

The chapter addresses potential opportunities of nanotechnology based water purification technologies arising from potential environmental, health, safety, socio-economic, and other issues related lack of clean water reserves worldwide. A balanced perspective based on a shared understanding of these challenges, opportunities for using nanotechnology for water supply and sanitation challenges, and risks and other issues are addressed.

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RAINWATER COLLECTING AS A PART OF IMPLEMENTATION OF THE SUSTAINABLE DEVELOPMENT PRINCIPLES ON CROATIAN ISLANDS – OLD HABITS FOR NEW ERA

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Abstract The article investigates availability and quality of drinking water along with possibilities of rainwater harvesting, as an element of sustainable development on four Croatian islands. Investigated islands, represent two main regions: northern and southern Adriatic coast. This division corresponds with gravity to two main macro regional centers on the coast and it is common in demographic, economic and sociological research. Data on local water resources, conditions and type of water supply, quality of water, prices, consumption of water, number and condition of cisterns and demographic records are collected and analyzed. Also, meteorological data on annual rainfall in past 26 years are collected and analyzed. Drinking water quality corresponds with Croatian law regarding physical and chemical parameters, while most of microbiological parameters are unacceptable. The results point out modest possibility of developing public water supply on islands. Average annual rainfall indicates that harvesting of rainwater should be integrated as additional water source on investigated islands which

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

would save great quantities of the drinking water that are used as technical water and for the other purposes such as agriculture or forest fires. Also that would lower the household expenses for the water and diminish water crisis during the tourist season months. Natural water resources on Croatian islands are scarce and it is our ethical obligation to preserve them in favor of existing eco systems and long term exploitation.

Keywords: Rainwater harvesting; Croatia; islands; sustainable development; drinking water

1. Introduction

Croatian coast is a specific by its great number of islands, islets, cliffs and crags, all together 1246 which make it second biggest archipelago on Mediterranean, with surface little less than 3,300 km^2. Out of them 47 are permanently inhabited and 28 only trough the summers. They take account of almost 3,100 km^2 of surface, although only 20 of those exceed surface of 20 km^2. Thus some very small islands are inhabited.[1] They are permanent or temporary home for 117,655 people, who live in 260 small towns or villages or just lighthouses. Only 10 islands have more than 1,000 inhabitants. Out of the inhabited, the closest island to the coast is island of Krk, while the most outlying is Palagruža.[2] Geographically and environmentally Croatian islands are favorable for living since ancient times. Also, in past 100 years their beauty made them tourist attraction of first category. That trend produces phenomenon of doubling up to quintupling the island population during the summer months as well as unplanned building without adequate infrastructure, main problem being lack of constant and quality sources of drinking water.[3]

Croatian mainland is rich in water resources coming from Panonic basin, while coast is supplied from Karst basin. Islands are geographical part of the coast but tectonically removed during the history, so the water sources are either; deep and scarce, either surface accumulations that are shallow and inconstant.[4] As a whole, Croatia is covered 77% with controlled water supply system, mostly in seven coastal counties, where it reaches even 97% of coverage. Although all of the islands are part of coastal counties, the coverage is significantly lesser and it ranges from rare 95% to only 13%.[5] The overall annual infrastructure construction growth in Croatia is around 1%, with expected growth up to 90% of coverage due to the geographical specificity such as high mountains and distant or small islands where communal water supply system is not economically sustainable.[4] There are several ways how island population is supplied with drinking water. Traditionally cisterns for rainwater harvesting were part of most of the homes and there was one or two public cistern in the center of the town or village. Today most of them are abandoned and those still in use, are filled with rainwater and water from tankers because of the poorly maintained collection systems and their surroundings. They are mostly in use on smaller and distant islands or as additional water sources. The islands with their own water resources and developed enough settlements have controlled local water supply systems, and those that are close enough to the mainland are connected with water pipelines.[6]

Sustainable development is concept launched over 20 years ago saying that development is sustainable "when it meets the needs of present generations without compromising the ability of future generations to meet their own needs", and it is still our central paradigm. However constant redefinition of the processes in human society is implying that development should mean more than just raising income or goods. Communities and individuals now understand that sustainability encompasses much more such as quality of life issues, predominantly health, educational standards and general social wellbeing.[7] In context of islands this implies sustaining contemporary quality of living without threatening the character and potential of each locality. There are three main criteria for sustainable development that have to be addressed in detail environmental sustainability, social stability and economical growth that would advance general quality of life. Most of Croatian islands are geographically isolated so they became small cultural micro cosmoses with specific ecosystems. Some of the islands are last genetic isolates that can be found in Europe.[8]

In this article we will try to demonstrate that harvesting of rainwater should be integrated as additional water source on the Croatian islands. That would contribute to the implementation of principles of sustainable development and save great quantities of the drinking water that is used as technical water and for the other purposes such as agriculture or forest fires. Also that would lower the household expenses for the water and diminish water crisis during the summer months.

2. Materials and Methods

We examined four Croatian islands Krk, Mljet, Vis, and Lastovo that represent two main regions: northern Adriatic coast and southern Adriatic coast. This division corresponds with gravity to two main macro regional centers Rijeka and Split and it is common in demographic, economic and sociological research.[9]

Krk is the biggest and the island closest to the coast, with one town and six counties both on the coast and inland. There is petrochemical industry on the island, and strongly developed high capacity tourist industry. Krk has area of 405.78 km^2, and 17,860 inhabitants.[2] **Mljet** is in category of bigger islands, has only rural settlements and part of the island is protected National park. Tourist capacity is low, but number of daily visiting tourists is high. Mljet has area of 100.41 km^2, and 1,111 inhabitants.[2] **Lastovo** is small, least inhabited island with only rural settlements. The whole island is in the category of Park of Nature. Tourist capacity is low. Lastovo has area of 46.87 km^2, and 853 inhabitants.[2] **Vis** is the most distant island from the coast, administratively two settlements have status of the town and three islets belong to the island, one being Palagruža, the most outlying Croatian border, inhabited with only lighthouse keeper. Tourist capacity is medium with fast and strong increasing trend. It is former military base, which left specific waist when abandoned. There is possibility that some of the water resources might be polluted. Vis has area of 90.3 km^2 and 3,617 inhabitants.[2]

All above mentioned characteristics fulfill criteria that describe overall spatial and temporal island distribution within Croatian coast such as north and south, big island vs. small, distant vs. close to the coast, densely vs. scarcely populated, local water sources vs. without, urban vs. only rural dwellings, existence of water supply system vs. cisterns, water tankers or desalination plants. Samples of water along with data on water use were collected during the summer and winter periods, along with data on local water sources, conditions of all types of water supply systems, and prices of water. Water sample analyses were performed using standard analytical methods approved by State office for metrology,[10] at the Primorsko–goranska County Institute for Public Health, that are available for the public, and at the School of Public Health "A. Stampar". For the projection analysis of the rainwater collection the official data on rainfall during past 26 years are obtained from Meteorological and hydrological institute of Croatia. Rainfall is measured by pluviometer and expressed in millimeter value.[11]

3. Results

Collected data on rainfall on four examined islands are given in Tables 1. and 2. Significant variations on the monthly level are visible, while they are lost at the yearly level. These variations are consequence of high air streams that are bringing the rain, and they vary from year to year. However these variations are canceled when means of rainfall values for long periods of time are calculated. Some other differences between islands are visible; island that is north, closer to the coast and bigger have more rainfall than those on the south and further from the coast. Vegetation and elevation also play the role in the quantity of the rainfall. Rainfall on the coastal side and peaks of the coastal mountains is heavier which influences the rainfall on the islands closer to the coast. Similar

TABLE 1. Total yearly rainfall, in the 26 years period on four examined islands

Year	Krk	Mljet	Lastovo	Vis
1981	1,265.4	755.7	639.1	746.1
1982	1,015.7	1,016.8	909.5	329.6[a]
1983	761.7	461.6	368.0	225.6[a]
1984	1,580.4	658.8[a]	643.7	729.0
1985	995.6	800.6	757.1	784.2[a]
1986	851.6[a]	816.9	678.0	703.9
1987	[b]	927.3	705.0	673.2
1988	[b]	734.1	595.3	506.8
1989	[b]	651.3	478.0	426.0
1990	[b]	681.5	479.1	620.4
1991	[b]	579.3	368.4	478.5
1992	[b]	637.5	636.4	551.4
1993	[b]	816.6	708.8	533.0
1994	[b]	688.4	665.8	649.2
1995	[b]	1,146.0[a]	845.6	978.6
1996	[b]	1,099.1	774.8	987.4
1997	[b]	693.7	594.2	671.8
1998	962.7[a]	660.9	490.8	660.7
1999	1,200.4	733.9	563.1	620.1
2000	1,346.1	613.0	391.6	555.5
2001	1,109.3	576.7	411.8	632.6
2002	1,634.9	758.2	907.0	949.7
2003	842.2	472.1	376.9	599.5
2004	1,376.2	995.8	858.3	926.6
2005	1,175.1	954.3	746.8	924.1
2006	1,043.0	850.6	588.2	747.3

[a] In those years data were not available for every month
[b] No data available for the whole year

results are reported in some other studies.[12] As expected highest rainfall is in winter months November, December and January, while lowest in the summer. Also, in the summer the biggest variations are noticed. On the south islands it has been recorded up to 2 months without or very little rain Figure 1. Although it has been a lot of debate on global warming, and on some islands rise of mean summer temperatures up to 2°C are noticed,[6] our data do not indicate visible diminish of the rainfall. Some years could be called dryer in comparison to the other, but there is no visible trend of dry years.

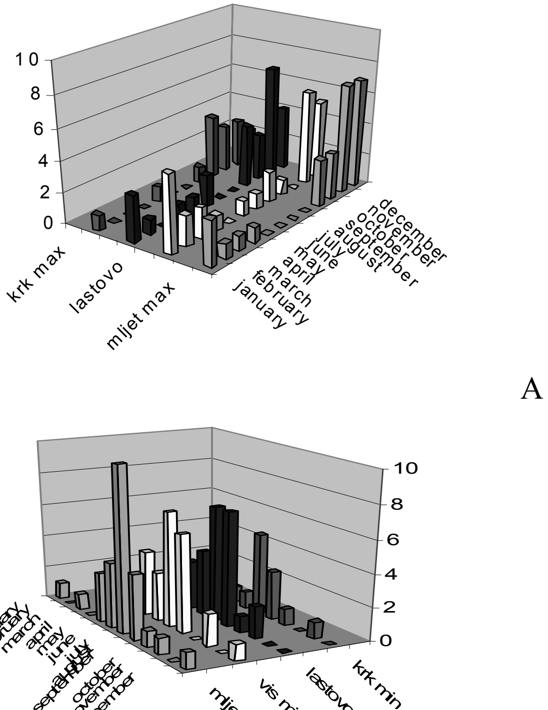

Figure 1. Frequency of extreme rainfall values in individual months in 26 years period. (A) – maximums, (B) – minimums

TABLE 2. Monthly mean rainfall in the 26 years period on four examined islands

Month	Krk	Mljet	Lastovo	Vis
January	99.5	70.0	62.1	75.3
February	91.2	71.3	55.0	65.0
March	91.4	6.4	56.1	58.2
April	80.3	65.7	45.5	56.0
May	83.5	43.2	34.3	27.5
June	58.7	35.8	30.8	38.4
July	35.8	18,0	13.7	22.8
August	72.7	43.2	31.8	46.2
September	158.8	68.3	59.6	55.1
October	156.8	85.7	70,0	49.9
November	138.3	102.6	82.3	90.4
December	114.7	103.5	86.3	103.6

TABLE 3. Description of water systems on four examined islands

Island	Type of water supply	Population covered (%)	Quality problems	Type of treatment	Official water supply company
Krk	Local water supply system using surface accumulations	70	Temperature disinfection by products, microbiology	Filtration, flocculation, chlorination	More than 1, regular sanitary control
	Cisterns	30			
Mljet	Desalinization Water tankers, Rainfall	45 (13%) households on pipeline	Temperature color, hardness, Fe, micro-biology	Chlorination NaOCl	1, irregular sanitary control
	Cisterns	87			
Lastovo	Desalinization of local borehole springs, water from tankers	77	Temperature, color, conductivity, hardness, Fe, microbiology	Chlorination 16-17% NaOCl and $Na_2S_2O_5$	1, irregular sanitary control
	Cisterns	23			
Vis	Shallow springs Cisterns	95 5	Hardness, Pb, microbiology	Chlorination 15% NaOCl	More than 1, irregular sanitary control

TABLE 4. Permanent difficulties in water production on four examined islands

Parameter	Krk	Mljet	Lastovo	Vis
Temperature	↑	↑	↑	–
Color	–	↑	↑	–
Conductivity	–		↑	–
Hardness	–	↑	↑	↑
Cd	–	–	–	–
Pb	–	–	–	↑
Fe	↑	↑	↑	–
Mn	↑			–
Aerobic mezofilic bacteria 22°C and 37°C	↑	↑	↑	↑
Total coliforms	–	↑	↑	↑
Fecal coliforms	–	↑	↑	↑
Sulforeducing clostridia	–	↑	↑	–

↑ Increased values

– Values within maximal allowed values

Data on water supply system and what are the most common reasons for not meeting sanitary regulations are given in Tables 3 and 4. Results show high coverage with water supply systems but those systems are in poor conditions and not operating under sanitary requirements. Water recourses are scarce which is visible by low capacity from 2.5 to 37 L/s. Only on island Krk capacity is somewhat higher 130 L/s. Capacity of desalinization processes, also, is very low 3–5 L/s depending on the salt concentration. Although water is treated in all supply systems quality problem remains present, predominantly as microbiology standards due to the poor technical maintenance, unprotected water springs and irregular disinfection. Overload during the summer months is damaging the system and population that remains during the winter has not enough means to restore it. Out of chemical pollution most dangerous are Pb and chlorination by products.

4. Discussion

Rainwater harvesting is not a novelty, it has been in practice in many island communities through out the world since ancient times. Today it is encouraged equally in arid areas and communities both rural and urban that have developed awareness for the environment and resources preservation.[13] In addition significant economic, social and environmental benefits can be achieved by using it for some of our requirements. In the modern world it is hard to expect that it would completely substitute municipal water supplies, but it could reduce dependence on mains water. Some governments have introduced legislation mandating new standards of energy and water efficiency ratings that must be incorporated into new dwellings that includes rainwater harvesting.[14]

Croatian islands are ideal candidate communities for incorporating mandatory rainwater harvesting. There are several reasons for that. Most of the Croatian islands have problems with quality and quantity of drinking water. The sources on the islands are scarce and shallow. In summer months, that is period of minimal or low renewal of water sources, great number of tourists use twice more water than local population, and to the personal use we have to add great quantity of the water for recreational use in hotel complexes. For example island Krk visit around 500,000 tourists who spend around 2 millions of nights during the year. In comparison with 17,860 inhabitants this is more than 25-fold increase.[15] Mljet and Lastovo are small communities with status of National Park and Park of Nature where even smaller number of tourists can cause disturbance in their fragile water supply system equilibrium.

The prices of water vary through out the Croatia from 0.6 to 10 euros for m^3, with average between 0.5 to 2.1 euros, depending on the calculation of the local authority and not the actual cost of the delivery. The situation on the islands is even more complicated, because water is transported by the water tankers owned by county water supply system and price is higher than on the coast. Also the price is different for the local population and other property owners what create space for various illegal manipulations. Also, on some islands private providers of water appeared, sometimes without license and with water without health inspection, priced according to their own estimation. In 2001 in Croatia the average yearly expenditure for water per household was 1.8% GDP.[16] The projections are, that the water prices in Croatia which are at the present social category and not reflecting real costs, will increase until 2015. They will be around 3 euros for m^3 and should be equal for all users. However, European directive is that price of the water should not exceed 4% of average salary and that is the target price that Croatian waterworks company recommends.[17] Now the question is how that directive will be applied and how will that affect poorer communities on the islands. Usually economical instruments like mechanism of the prices are not effective in the terms of water preservation and in the most cases the poorest social groups are the most adversely affected. Beside tourism, island communities live on the agriculture production which consumes water as well. For the irrigation of the gardens or smaller lots of the land water from the water supply system is used. Also, during the summer months, bushfires and wildfires are common on the both coast and islands, and even for that, drinking water is used. One working hour of firefighter airplane that can catch sea water costs around 5,000 euros, there are only three of them and in most of the cases firefighters are forced to use whatever sources of water they have at hand. It is absurd that streets are washed with sanitary approved water and it has been only a year that in Zagreb (capital) street washing with technical water is implemented.

Our results show that despite big meteorological variations there is enough rainfall throughout the year that rainwater harvesting would be viable. Main requirement of over 50 mm/month for at least half of the year of rainfall is fulfilled.[18] This is in concordance with some other authors who did similar projections for some other Croatian islands. Their main conclusion is that proper roof construction (or catchment's area) and cistern volume, are essential for sustainable filling of the cisterns even during the summer months.[12] In principle the collection of rainwater is more efficient way of water production in island conditions than transportation or desalinization. Rainwater harvesting may catch up to 90% of precipitation. Of course if it is used for drinking it requires large storage facilities and elaborated protocol of conservation and disinfection, but if it is used for technical water such as toilet cleaning, washing of goods or agriculture process of conservation is much simpler. Consequently rainwater collection should be regarded as supplementary rather than a main source of water supply in private and municipal cisterns. Municipality of Vodice small tourist town in central Croatian coast was the first to implement rainwater harvesting for the hotels and apartment houses. After the expansion of the water pipeline network due to the new tourist developments, water supply system collapsed. This is the only example of official rainwater harvesting on the coast. According to Matic[12] in order to be of satisfactory use the volume of cisterns should be 25–35% of total requirements for the water for the family of four, which is between 36 and 48 m^3. It is hard to estimate what is the average volume of the cisterns on the Croatian islands, and what is the number of those still in use or the number of those that need some level of reconstruction. Such a type of information could be of enormous importance in the situation of the crisis, both natural or man made. First response in the process of the mitigation is crucial for the survival and number of the casualties. Southern part of Croatian coast is tectonically unstable and due to its geomorphologic formation, inconvenient road network and state borders, in case of earthquake, parts of the Croatian coast could easily remain cut off for some period of time. Creation of the various resources networks that could be quickly mobilized should be one of the goals of local governments. In such scenarios, islands could serve as temporary refugee areas or even water resource areas. Network creation for water resources even on the neighborhood level could be of great help in cases of forest and bush fires when they occur close to the inhabited areas.

4.1. SUSTAINABLE CONSUMPTION-CHANGE OF PARADIGM

During past decades we can identify attention shift from the production to the consumption and effect when technological improvements and eco-efficiency are counterbalance by volume of the consumption.[19] For ages people used to live in the pace with nature and seasonality which is ruptured by modernization and non-stop availability. However the responsibility for sustainable development can not be on whole on the consumers. Modernization is changing the paradigm of traditional consumer behavior, and in the case of water consumption it is much easier to use than to save water. In the traditional Mediterranean culture water was asset that was captured and economized. Tourism has brought new requirements that support water use in the setting that has no unlimited resources. So, even new questions that are entering the ethical sphere could be raised. Is tourist consumption ethical? It seems that sustainability does not come naturally and that human dimension has to be taken into account, particularly social environment that is enhancing the system of “want” and “like”. When the environmental impact of consumption is negative the entire process of planning, buying, using and disposal should be analyzed.[19] As the efforts for the framing positive environmental consumer behavior European Union launched framework program of sustainable production and production. In the case of the Croatian islands some old methods such as rainwater harvesting could be reintroduced for new living conditions. Local authorities should be main forces in the proceses of development of local environment and health and social determinants. Experiance has shown that progress is possible only if all stakeholders are motivated and mobilized.

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FISH CONSUMPTION AND MERCURY BODY BURDEN IN WOMEN OF REPRODUCTIVE AGE FROM URBAN AREA IN CROATIA

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Abstract Mercury entering aquatic environment can be transformed by microorganisms into toxic methyl-mercury that biomagnifies in aquatic organisms. Seafood consumption is primary exposure route to mercury for humans. The most vulnerable groups are unborn and young children. The aim of this article is to investigate if there possible connection of fish consumption and mercury body burden in women of reproductive age in Croatia.

Keywords: Mercury; fish consumption; hair; women; Croatia

1. Introduction

Environmental mercury pollution, as a public health problem, is well recognized by scientific community. Mercury (Hg) is highly toxic heavy metal which causes adverse health effects in humans. It occurs in three forms: elemental, inorganic and organic, and its reactivity, biological effects and toxicity varies among them.[1] In nature it occurs as the mineral cinnabar, but anthropogenic sources from commercial exploitation, particularly by the chlor-alkali industry, laboratory chemicals and medical measuring devices such as thermometers, sphygmomanometers are more significant.[1,2] Once released into environment mercury becomes global problem by creating a "pool" which is continuously mobilized, deposited and remobilized.[3,4] Elemental and inorganic Hg in aquatic environment could be transformed

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

by methanogenic bacteria into a most toxic organic compound for humans, methyl-mercury (MeHg).[5] Ingested mercury shows high affinity for bounding with sulfhydryl groups in animal proteins, and in that way it bioaccumulates in aquatic organisms and biomagnifies through the food chain.[5] Depending on habitat, species, size and age fish could contain different concentrations of MeHg, but in general predators at the top of the food chain have higher concentrations.[4,5] Previous studies show that fish consumption is primary route of human exposure to MeHg for population that is not occupationally exposed. Estimations are that fish consumption contributes for 80%–90% of total human exposure to mercury of which 75%–100% is MeHg. Increased values of MeHg in humans are directly associated with fish consumption frequency.[3,6]

Several mercury poisoning incidents in the period from 1950s to 1970s throughout of the world demonstrated the severity of mercury toxicity. MeHg accumulates in the human body tissues including the central nervous system, hart muscle and kidneys, but the main affected organ is the brain, especially vulnerable over neurodevelopmental period.[2] MeHg also passes through placenta and it is excreted in breast milk.[8] Exposure to high doses of MeHg during pregnancy can cause fetal death, mental retardations and long term disabilities.[2,9] Nowadays, chronic exposure in children and adults can cause serious damage of the nervous system, impairments of hearing and speech, ataxia and visual constriction.[10]

In spite of these known facts mercury continues to be used for various industrial processes and medical facilities.

To minimize exposure to MeHg, many industrialized countries established maximal allowed concentrations of mercury for fish and seafood for human use.[11] United States have set up consumption advisories for locally caught fish with recommendations for commercial fish consumption, especially for pregnant or lactating women, women of reproductive age and young children.[12,13] The European Food Safety Authority also has put out guidelines on fish consumption for certain vulnerable groups but they are weak and not widely implemented.[14]

In Croatia as possible source of aquatic mercury pollution, chlor-alkali plant located in Kaštela bay on the southern part of the coast was listed. Plant was closed in 1990, after 41 years of activity, but during that period between 22 and 56t of Hg was deposited in the bay.[15] As a possible consequence, total and organic mercury concentrations were measured in certain type of fish, sea food and even sediments samples in Adriatic Sea.[11,15–17] But still, there is a lack of data about mercury transfer in food chain and negative health effects of exposure.[15] In Croatia recommendations about fish consumption and prevention measures to non-occupational mercury exposure are not established. Although the Croatian Regulatory Act defines maximum allowed levels of toxic trace elements in nutritional product including sea food there are not advisory limits for fish intake for groups of population that might be at risk.[18]

The aim of this preliminary research was to give the snapshot of the mercury exposure level among women of reproductive age from urban area in Croatia and to investigate possible connection of mercury concentrations in women hair with their fish consumption habits as well as origin of fish.

2. Materials and Methods

2.1. SAMPLE

Sample consisted of 75 women aged 22 to 40, living in the urban area of Zagreb for at least 5 years, non-smokers, not exposed to x-ray treatment or therapy in last year and did not use any kind of medicaments, including contraception. Included participants reported that are healthy and confirmed absence of occupationally or incidentally exposure to mercury. The study was approved by the Ethics Committee of the Medical School University of Zagreb in Croatia and all participants signed written consent. The research was conducted in a period from April to July 2008 in Zagreb, a capital of Croatia.

Participants were interviewed about dietary habits along with health-environment-life style questions that would indicate potential personal sources of mercury exposure. The questionnaire included questions regarding health status, medication therapy, age, body weight and height, body mass index, number of dental amalgam fillings, pregnancy status, lactation and number of children. Fish consumption frequency, which included number of fish meals, species, type and origin of fish and way of its preparation was investigated. Following options for the number of fish meals were offered: never, two to three times per year, one time per month, two times per month, one time per week and two to three times per week.

2.2. BIOMARKER

MeHg is incorporated into hair follicles proportionally to its concentrations in blood, and it makes hair a good indicator of exposure in people who consume contaminated fish and are not occupationally or incidentally exposed to inorganic or elemental Hg.[2,19,20] Total mercury and methyl-mercury levels in hair are linearly related.[21] The relationship between exposure to Hg and its concentration in hair has been particularly well studied. Hair grows at approximately 1 cm per month and is an applicable tool to assess tHg and MeHg exposure level for defined period, depending on the length of the hair.[22]

Due to mercury deposition and non-invasiveness of sample collection, hair has been chosen as a biomarker of exposure. The hair samples have been collected according to a standardized method.[23,24] The hair sample was cut with stainless-steel scissors on their full length on 1 cm^2 from the occipital region closest to the scalp. A minimum of 0.50 g was gathered with aim to get the length of 12 cm where possible. The adhesive paper was marked indicating the end of hair closest to the scalp. The samples were placed in a releasable plastic bag and stored until analysis. Hair was cut in 5 mm long pieces, washed with acetone once, then three times with demineralised water and finally again with acetone and then dried at room temperature. The whole procedure is described by the International Atomic Energy Agency (IAEA).[25]

2.3. DETERMINATION OF HG

Total mercury in hair was measured using the atomic absorption spectrometry (AAS) method, on a single purpose instrument AMA 254 (Advanced Mercury Analyser), ALTEC Ltd, Praha, Czech Republic. Hair samples weighted 2 to 5 mg were placed in nickel boat and dried, than combusted at 750°C and decomposed in an oxygen atmosphere on a catalytic column. Produced Hg vapour was trapped quantitatively on the surface of a gold amalgamator and then completely evaporated at 900°C and analysed by atomic absorption spectrometry using a silicon UV diode detector at 253.65 nm. The total analysis time is approximately 5 min.

The advantage of the AMA 254 instrument is that no sample chemical pre-treatment is acquired, in comparison with the cold vapour atomic absorption spectrometry method (CVAAS), the most commonly used technique for tHg determination. The results of mercury determination in some samples by AMA-254 suggested results consistent with the conventional CVAAS.[26] This technique is designed for fast and accurate determination in various environmental and biological liquid or solid samples. Complete technical parameters and functioning of instrument are described in previous articles.[27,28] Each hair sample was analysed in triplicate.

Questionnaire construction and sample analysis was performed at the Andrija Stampar School of Public Health, Medical School, University of Zagreb at the Department of the Environmental and Occupational Health.

2.4. STATISTICAL ANALYSIS

Statistical analysis included descriptive statistics and Kolmogorov–Smirnov test for distribution determination. All confidential intervals (CI) were estimated with 95% probability levels. Differences between groups were analyzed using the $\chi 2$ test. P value < 0.05 was considered statistically significant. Software SAS (SAS Institute Inc., Cary, NC, USA) Property Software Release 8.2 (TS2M0) Licensed to SRCE, Site 0082452004, was used for analysis.

2.5. FISH AVAILABILITY IN THE SUPERMARKETS

Also local supermarkets chains in Zagreb were searched for the availability of fresh, frozen or canned fish and sea food. We specifically looked for the origin of the products.

3. Results

All women who were included in the sample answered all the questions and were divided into two groups: vegetarian 17 (23%) and non-vegetarian 57 (77%).

All 75 women had detectable levels of mercury in hair. The results show range of total mercury values from highest level of 3.90 μg/g in hair to lowest level of 0.02 μg/g (mean 0.67 μg/g). The lower values of tHg in hair from 0.02 to 0.19 μg/g were detected in 17 (23%) women – vegetarian who did not consume fish at all.

The concentration of 1 μg/g Hg in hair is a level corresponding to the intake dose calculated by US EPA based on the most protective reference dose of 0.71 μg/kg body weight per week set by United States National Research Council (USNRC). It is also the limit we are referring to in this study. Above the most protective reference dose of 1 μg/g were 11 (14.8%) women. On the other hand, all 75 women had values below the benchmark dose of 10 μg/g Hg in the hair, set by World Health Organization in 1990.[29] Level of 10 μg/g Hg is level at which is accepted that there are clear neurological effects. Concentrations of tHg in hair of participants are given in Table 1.

TABLE 1. Concentrations of tHg μg/g in participant's hair

	Participants total (n = 75)	
	Non-vegetarians	Vegetarians
Sample size	58	17
Lowest value	0.2169	0.0207
Highest value	3.9304	0.1988
Median	0.6414	0.0721
95% CI for the median	0.4366 to 0.7456	0.04415 to 0.1002
Interquartile range	0.3357 to 0.8762	0.04892 to 0.09325

Applied Kolmogorov–Smirnov test shows that data distribution of measured tHg concentration in entire sample did not follow a normal distribution. When group of non-vegetarians and vegetarians were compared statistically significant difference was obtained in tHg in hair samples, ($P < 0.0001$), indicating that women who consume fish have significantly higher mercury concentrations in hair than women that do not eat fish all. Number of fish meals eaten in defined periods of time is presented in Table 2.

TABLE 2. Fish consumption frequency

	Non-vegetarians sample size n = 58
Fish consumption:	
2–3 times/year	10
1 times/month	6
2 times/month	11
1 times/week	27
2–3 times/week	4

The average fish consumption among non-vegetarian participants in sample was one meal per week.

Consumed fish is predominantly of local origin, canned tuna from unknown origin, but in most cases packed in Thailand. Freshwater fish, mostly trout, is consumed approximately nine to ten per year and is always from local ponds. Carp is consumed once or twice per year, while catfish, pike or perch even more rarely. Canned sardines and mackerel from Adriatic Sea along with frozen imported fish and sea food also are rarely consumed. Most of the examinees eat fresh fish prepared at home or occasionally at the restaurants. In Zagreb, fish is sold on the several open air fresh produce markets located in the various parts of the town. Availability depends on the day in the week and it lasts from the early morning until midday. The large domestic and international supermarkets chains in Croatia contributed to availability of fresh, canned and frozen fish on the market. Eight chains are dominant on the market out of which four of them had fresh freshwater fish exclusively from Croatian ponds, and only two had fresh sea fish from Croatia or imported. All supermarkets had canned fish and frozen fish and sea food imported from different foreign countries. It is interesting that product declaration sometimes indicate different country of fishing, packaging and exporting of the same product.

4. Discussion

The results of this preliminary research gave the snapshot of the mercury exposure level in women of reproductive age from Croatia. Measured values of tHg, that represents the MeHg in participant's hair, have shown that mercury in tested women could be linked to the fish consumption. As recommended, concentration of 1 μg/g Hg in hair is a level that should not be exceeded in women of reproductive age and represents a dose below which is not likely to expect neurological negative impact on foetus or breastfed children.[24] The US EPA recommended level is more precautionary or protective of public health and this level is the one which the European Commission refers to in its Extended Impact Assessment.[3]

In Croatia the common opinion is that locally caught fish from Adriatic Sea is not contaminated with mercury. These beliefs became questionable, since the latest study by Srebočan[30] in 2007 show that 41% of the captive Atlantic bluefin tuna farmed in Adriatic Sea contain mercury above the maximum level of 1 μg/g wet weight defined by the European Commission Decision and Croatian legislation. The explanation for that could lie in fact that farmed tuna was feed with defrosted sardines and herrings which origin is not known. Opposite to that, other study of both shellfish and fish showed lower than maximum allowed values of Hg in the samples caught in Croatia.[11] This could be explained with the fact that fish biomass index in Croatian territorial waters shows descending trend in period between 1996 and 2000. Displayed negative situation is most probably result of high intensity of fishing and reduced capabilities of fish resources to revitalize and grow up to the size where accumulated Hg is of higher concentrations. In general disappearance of larger fish specimens is observed in Adriatic Sea on the Croatian territorial waters.[31]

Fish provides number of healthful proteins, vitamins, minerals and it is essential source of omega-3 fatty acids that are important for foetal neurodevelopment and should make part of balance diet for adult and children throughout the whole life.[32] In Croatia majority of women are still creators of the lifestyle of the whole family and they are the guardians of the children's and in many cases overall family health. Nutrition is one of the most important factors in attaining those goals. However, when both parents are working and urban, hustle life pace imposes the need for the easiest purchase and fastest food preparation possible. Lifestyle has changed trends in food purchasing "once a week or 2 weeks" and preparation shifting towards "ready to use". Therefore, women are often forced to buy everything in one supermarket that is opened whole day and use canned or frozen fish and seafood instead of fresh one from fresh produce market. One would expect that in the country with more than 5,835 km of the coast line, out of which 4,058 km comprise a coastline of islands, more locally caught fish would be on the market but it is not so. For example, in one big domestic Croatian supermarket on August 2008, frozen fish from Poland, Pakistan, Turkey, Argentina, Tanzania, Spain, Italy and Island was found, along with imported frozen fish but packed in local factories that are often mistaken for a locally caught fish. Market is full of imported canned tuna from unknown origin (on declaration is stated only who is packaging it) with the acceptable price which makes it attractive ingredient.

On the other hand data on average fish consumption in Croatia of 9 kg per person in 2006,[33] indicate that overall consumption is very low and that as the consequence we can expect that general population in Croatia is exposed at level below the tolerable intake.[11,16] However, population living in the coastal areas and islands consume considerably larger amounts of fish (authors' unpublished data) which indicates that pregnant and lactating women, along with the small children should balance the quantity of fish in their diet.[11]

Most of the research has been focused on sea fish while the portion of the population consumes freshwater fish mostly carp, that is farmed in artificial ponds that may be contaminated with anthropogenic mercury as well. Also carp meat is widely used as one of the ingredients for various fish products like fish fingers or fish burgers. So, even this rout of investigation should be followed. As a conclusion we can state that further research through detailed biomonitoring of hair, blood, urine and fish samples is needed at a larger population, with specific focus on Croatian coastal region and islands where higher exposure has been identified.

Education should be integrated part of the policy making towards protection of the vulnerable groups.

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ORIGIN OF ARSENIC IN DRINKING WATERS IN THE WEST BACKA DISTRICT OF SERBIA

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Abstract Danger to the public health through exposure to toxic arsenic compounds in drinking water remains a continuing problem. Because people may be inadvertently exposed to arsenic through contaminated drinking water, it is extremely important to monitor arsenic level and to remove it from sites where arsenic could contaminate groundwater. We measured total (both inorganic and organic) arsenic content in groundwater and drinking water at various sites in the West Backa district of Serbia. In 42 of 69 samples of water drawn from tube wells in the west Backa district of Serbia, we found the total arsenic concentration to be well above the current maximum contaminant level of 10 parts per billion (ppb or μg/L) for drinking water. Thirteen of these wells had water with arsenic concentrations above 50 μg/L. The highest arsenic content (148 μg/L) was found at one location. Consequently, nearly half of population in this district is potentially at risk of arsenic poisoning. Water from tube wells from 45–60 m deep had arsenic concentrations of less than 25 μg/L. Water from deeper wells had greater variation (0–148 μg/mL) in arsenic concentrations. These variations in

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

natural underground waters relate to the hydro-geologic properties in this part of the Pannonian plain. We concluded that the depth of a tube well in this district offers a rough prediction of arsenic contamination, but only for wells no deeper than 60 m. Association of increased arsenic concentration in drinking water and epidemiology of certain diseases should be studied in this area.

Keywords: Arsenic; groundwater; drinking water; chronic arsenic exposure; Pannonian plain

1. Introduction

Arsenic is an extremely toxic metalloid that is hazardous to human health. People and other living organisms are exposed to toxic arsenic compounds primarily through water. Acute or chronic exposure to arsenic causes a variety of toxic effects.[1,2] Chronic exposure to arsenic characteristically affects skin (melanosis and keratosis), and frequently disrupts normal functions of most body systems, e.g. reproductive, respiratory, cardiovascular, gastrointestinal, hematological, immunological, and neurological systems.[3] Ingestion of inorganic arsenic may cause lung, bladder, skin and liver cancers as well.[4,5] Arsenic is absorbed from the gastrointestinal tract following ingestion of arsenic containing water or food, and it can be inhaled as particulates from arsenic-containing air. Although up to 75% of inorganic arsenic and its metabolites are eliminated by the kidney and other routes, arsenic accumulates in keratin-containing tissues, such as nails and hair. There is no apparent age or gender related difference for arsenic retention or toxicity,[6] except in case of colon cancer; incidence is likely to be causal for males but not females.[7]

The underlying mechanism of arsenic toxicity involves formation of various organic-arsenical compounds, several of which have been identified in living organisms. The inorganic arsenicals, arsenites As (III) and arsenates As (V), are also toxic, because these compounds interfere with biochemical processes that are important for cell function and growth. The chemical similarity of arsenic to phosphorous likely accounts for the many biologic effects of arsenic.[8] Inorganic arsenic inhibits various enzymes by reacting with their sulfhydryl (−SH) groups,[9] and it replaces phosphorous in phosphates of DNA.[10] Soluble inorganic arsenicals are more toxic than the organic ones, and trivalent forms are more toxic than pentavalent ones.[11]

Earth's crust is the primary source of arsenic in environmental systems, including water, air, soils/sediments, and biota. Arsenic levels in groundwater average around 1 to 2 μg/L.[12,13] Elevated arsenic concentrations in groundwater are generally the result of natural geochemical activity; arsenates are usually the predominant species, but some groundwaters contain up to 50% arsenites. Severe contamination of groundwater with arsenic was reported in certain areas in several different countries. For example, water arsenic levels in Bangladesh were 3,200 μg/L, in Mexico, 624 μg/L, in Taiwan 671 μg/L, in Hungary 174 μg/L, in Serbia (351 μg/L), and in the USA (490 μg/L), as reported by refs.[14–21], respectively. The World Health Organization (WHO) set the maximum permissible level of arsenic in drinking water at 10 ug/L in 2001. It is apparent that a significant percentage of the population in these affected regions is exposed to arsenic concentrations in drinking water that exceed the maximum permissible level. For that reason, monitoring of arsenic concentrations in drinking water, especially in areas that may have dangerously high levels, should be not only encouraged, but also mandated. It may be necessary in such areas to apply existing technologies for arsenic removal to reduce contamination of drinking water to the permissible level.

The purpose of our study was to document arsenic concentration in drinking water at various sites in the West Backa district of Serbia, and to measure arsenic in the groundwater from various hydro-geological layers. Our hypothesis is that the depth of a tube well could be related to the amount of arsenic and thus might predict the extent of contamination that would affect drinking water.

2. Materials and Methods

Water samples were collected from 69 individual tube wells and from 11 piped systems supplied by two or more of these wells. The majority of inhabitants of the West Backa district of Serbia use wells (ground water) as a source of drinking water. Less than 5% of the inhabitants who live at farms in this district acquire their drinking water directly from hand tube or dug wells. The greater part of the population uses water from municipal systems that are located in four towns (Sombor, Apatin, Kula, and Odzaci), and in thirty smaller villages. The entire district occupies 2,420 km^2, and according to the 2002 census, there are 213,242 inhabitants in the district. The region is characterized by plains around the Danube to the west and a slightly sloping area in the central part; the Telecka Plateau to the east has an average altitude of 90 m. The depth of the tube wells in the district ranged from 45 to 175 m.

The arsenic content in water was expressed as the concentration of arsenic (III) after converting all arsenic species to the trivalent form. Thus, both inorganic arsenic that constitutes the highest toxicological risk and organic arsenic species are reported together as total arsenic.

Potassium iodide and tin (II) chloride were used to convert As (V) to As (III), and then sodium tetrahydroborate in the presence of HCl converted As (III) to arsine. The hydride generation reaction for arsine production follows:

$$\mathrm{As\,(OH)_3 + 3BH_4 + 3H^+ \rightarrow AsH_3 + 3BH_3 + 3H_2O} \qquad (1)$$

$$\mathrm{BH_3 + 3H_2O \rightarrow H_3BO_3 + 3H} \qquad (2)$$

Arsine was removed from the solution by aeration with nitrogen and directed to a hydrogen flame where its content was read by atomic absorption spectrometry at 193.7 nm. The limit of detection by this method is 0.6 μg/L. This method is both accurate and convenient for determination of total arsenic where the content in water samples ranged from 1 to 20 μg/L. When the arsenic concentration was higher than 20 μg/L, the sample was diluted appropriately to ensure accurate readings.

Standard solutions for identification and quantification of the arsenic compounds were prepared according to the instructions of the supplier (Mallinckrodt Baker, Phillipsburg, NJ, USA). All other substances were purchased from the same supplier. The stock solutions were diluted to the desired concentration with double-distilled water just before use. We analyzed the data by regression analysis using statistical software (GraphPad Instat).

3. Results

Table 1 summarizes the arsenic concentrations in groundwater sampled from the various sites. The majority of samples (42) taken from the wells in the region had an arsenic content greater than 10 μg/L, and 13 of these samples had concentration higher than 50 μg/L. The highest arsenic content (148 μg/L) was found in water from the Bogojevo location.

If the drinking water samples came from two or more wells with variable arsenic contents, the measured concentration of this metalloid would reflect the mixture from multiple sources. Obviously, this could result in lower concentrations than that from a single well with high arsenic content. Seven

TABLE 1. Depth of the wells and arsenic content in water

Name of places	Depth of each tube well (m)	Arsenic concentration in each well (μg/L)	Arsenic concentration in the pipe systems (μg/L)
Aleksa Šantić	100	38	38
Apatin	60, 55, 60, 60, 60, 55, 60	8, 5, 8, 2, 21, 12, 0	7
Bački Brestovac	150	21	21
Bački Gračac	80	53	53
Bački Monoštor	120, 120	81, 82	81
Bački Breg	80	9	9
Bezdan	60, 60, 60	6, 24, 3	8
Bogojevo	114	148	148
Čonoplja	150, 150	41, 37	40
Crvenka	130,130	9,10	10
Deronje	160	9	9
Doroslovo	110, 120, 120	68, 44, 41	53
Karavukovo	80, 80, 80, 80, 80	14, 5, 84, 40, 31	37
Kljajićevo	150, 150, 150, 150	40, 34, 35, 34	38
Kolut	60	18	18
Kula	45, 45, 45, 45, 150, 50	0, 7, 2, 1, 88, 10	20
Kupusina	60	6	6
Lalić	100	68	68
Lugovo	140	57	57
Nova Crvenka	130	3	3
Odžaci	60, 60	20, 8	15
Prigrevica	60	2	2
Ruski Krstur	120	130	130
Ratkovo	100	73	73
Riđica	80, 80	59, 46	54
Sivac	60	14	14
Sombor	150, 130, 60, 170, 60, 60, 60, 130, 60	55, 25, 10, 39, 9, 7, 20, 40, 13	26
Sonta	80	4	4
Srpski Miletić	123	108	108
Stanišić	80	24	24
Stapar	150	30	30
Svetozar Miletić	58	7	7
Telečka	60	12	12
Žarkovac	80	7	7

piped systems (Backi Gracac, Bogojevo, Lalic, Lugovo, Ratkovo, Ruski Krstur, and Srpski Miletic) supplied single wells with arsenic concentrations higher than 50 μg/L. In nine of the piped systems, the arsenic level exceeded the current maximum contaminant level of 10 μg/L, and two others exceeded 50 μg/L.

Figure 1 shows the relationship between the arsenic content of underground waters and the well depth. Water from shallower wells (depth from 45 to 60 m) contained less than 25 μg/L of arsenic, while the majority of deeper wells (between 100 to 150 m deep) had higher arsenic contamination. However, deeper underground water that came from tube wells located in Deronje and Sombor where wells were 160 and 170 m deep had 9 and 39 μg/L of total arsenic, respectively. From statistical analysis of samples (n = 69) used to determine the relationship between the depth of underground water and its arsenic content, we determined a correlation coefficient (r) of 0.4647.

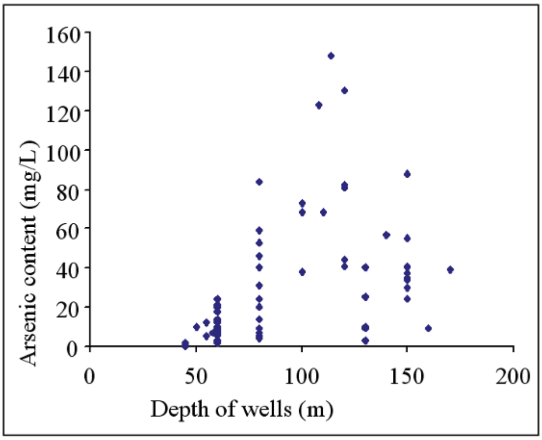

Figure 1. Correlation scatter diagram: relationship of arsenic concentration and depth of well (r = 0.4647)

4. Discussion

The results of our study revealed arsenic contamination greater than 10 μg/L in tube well waters from the West Backa district of Serbia. The elevated arsenic concentrations presumably result from natural geochemical activity in this region that was once the Pannonian Sea. Before the end of the tertiary period, the Danube River flowed into the Pannonian sea, but then river had broken through the Djerdap gorge to flow into the Black sea.[22] Thus, a common process determined the geological structure of the Pannonian plain and affected the hydro-geological properties for whole region.[18] Sediments from the Tertiary Period are found at specific depths over the entire region. One band is localized between 100 and 240 m, and the other between 940 and 1970 m. Sediments from the Holocene Epoch, consisting primarily of sand and pebbles, appear at a level generally no deeper than 60 m. A layer of grey-yellow sand-marl clay from the Pleistocene Epoch and Pliocene Epoch lies between the two water horizons at a depth of about 75 m. This boundary forms a non-permeable interlayer that extends over a very wide area and prevents the mixing of the two water horizons.[23] Our finding of the highest arsenic content in underground waters from a depth of 60 to 150 m indicates that the source of this mineral is most likely geologic strata formed in the Miocene Epoch. Table 2 presents the geologic timeline.

Data relating the depth of tube wells to groundwater arsenic concentrations in West Backa district show that water sampled from shallower wells (depth from 45 to 60 m) has arsenic concentrations of no more than 24 μg/L. Water from deeper wells was generally higher in arsenic, but groundwater from very deep wells showed only a moderate increase in arsenic content. Thus, one can roughly predict the arsenic concentration in underground waters at well depths not exceeding 60 m.

TABLE 2. Geologic timeline. Three periods of mesozoic era, six periods of paleozoic era, and three eons of precambrian time are not presented in this table

Era, period, or time	Epoch	Time
Cenozoic Era (recent life)		
Quaternary period	Holocene	10,000 years ago to the present
	Pleistocene	1.8 million–10,000 years ago
Tertiary period	Pliocene	5–1.8 million years ago
	Miocene	24–5 million years ago
	Oligocene	34–24 million years ago
	Eocene	55–34 million years ago
	Paleocene	65–55 million years ago
Mesozoic Era (middle life)		248–65 million years ago
Paleozoic (ancient life)		540–248 million years ago
Precambrian time		4.5 billion–540 million years ago

Because arsenic in natural underground waters is mostly in the form of inorganic arsenic compounds, much of the community drinking water in this area constitutes a public health threat. Various measures applicable to piped systems could be implemented to prevent exposure to arsenic in drinking water,[24] and it is technically possible for individual households to remove arsenic.[25] This method could be used by inhabitants of farms located beyond the piped system water supply, although this technology is not yet completely reliable. Although regular monitoring of water supply systems in the West Backa district since 1998 showed increased arsenic concentrations,[26] only the Ruski Krstur pipe system, which supplies 5,000 people, has technology in place for the removal of arsenic from drinking water. The wells on individual farms are not yet prepared to address this problem.

It is clear that a significant part of population, nearly 50%, in the West Backa district of Serbia is exposed to arsenic in drinking water in concentrations above 10 μg/L. The population served by nine different pipe systems receives drinking water with arsenic concentrations higher than 50 μg/L. This district is mainly an agricultural region with some wine producers on the Telecka plain. Intensive agriculture requiring the heavy use of agrochemicals, especially arsenic-containing pesticides, could further enlarge arsenic exposure. Whatever the source, chronic exposure to arsenic via water in the West Backa district could present a serious health threat. Further studies should document not only accumulation of arsenic in hair and nails of inhabitants that are exposed to arsenic in drinking water, as was done in a neighboring part of Croatia,[27] but such studies could also confirm chronic arsenic intoxication as the cause of certain specific tissue lesions, for example, skin affection (e.g., melanosis, hyperkeratosis, and cancer), and malignancies of various body systems (e.g., respiratory, gastrointestinal, and urogenital tract).

In our pilot study, we have found that in the West Backa district there is gradual increase in the incidence of gastric carcinoma, melanoma, and leukemia (from 2001 to 2007). Thus, we plan to explore various noxious factors, including exposure to arsenic that might be associated to these diseases.

At the very least, communities should minimize further risk of arsenic toxicity by removal of arsenic from ground water and drinking water.[28] Application of available technology can achieve concentrations below the maximum permissible concentration of 10 μg/L.

5. Conclusions

1. Majority of tube well-waters in the west Backa district of Serbia have total arsenic concentrations higher than 10 μg/L. Nearly half the people in this area have chronic arsenic intoxication. Regular arsenic monitoring and removal to achieve concentrations less than 10 μg/L should be implemented, and arsenic in hand-tube wells or dug wells on individual farms should be similarly reduced.
2. Level of arsenic in underground waters is related to hydro-geologic properties at certain depths in this part of the Pannonian plain.
3. The depth of a tube well provides a rough prediction of water arsenic concentration in this district, but only for wells that are from 45 to 60 m deep. Water from deeper wells showed a wider variation (0 to148 μg/L) of arsenic concentration.

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MAGNETIC ZEOLITE AS ARSENIC SORBENT

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Abstract A natural zeolite (clinoptinolite type) was modified by iron oxides and a novel magnetic zeolite was produced. The novel sorbent was prepared by a co-precipitation of Fe(III) and Fe(II) in the presence of NaOH and natural zeolite. The zeolite structure was used as a host for the precipitated magnetic iron oxides. The new material had properties that combined the good sorption affinity for oxyanions of iron oxides with the high affinity of zeolite for cations. The particles produced could be easily used in sorption columns for dynamic studies. They had also good magnetic properties and could be separated from dispersions with the application of a magnetic field. The magnetic zeolite was tested under batch conditions for the removal of As from model water solutions. The effect of pH, arsenic concentration, temperature and solid to liquid ratio were studied. The magnetic zeolite was found effective for the removal of arsenic from water streams and its capacity was above the average capacity of sorbents studied in literature. The conditions for best arsenic removal were established.

Keywords: Arsenic; magnetic zeolite; iron oxides; sorption

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

1. Introduction

Arsenic is a natural element, which behaves like a metal. It is present in the environment both naturally and due to certain human activities. It is found in water streams, soils and rocks, atmosphere and organisms. About one third of the arsenic in the atmosphere comes from natural sources, such as volcanic emissions, and the rest comes from man-made sources. Other natural sources of arsenic comprise weathering reactions and biological activity. Arsenical pesticides and fertilizers, fossil fuel combustion, mining, smelting and other industrial activities represent man-made sources of arsenic.

The presence of arsenic in water streams poses serious threat to human health. Exposure to arsenic through drinking water can cause acute and chronic poisoning. Acute arsenic poisoning involves vomiting, dryness of mouth and throat, muscle cramps, abdominal pain, tingling of the hands and feet, circulatory disorders, nervous weakness and other health problems. Long-term exposure can cause, e.g. chronic weakness, loss of reflexes, weariness, gastritis, colitis, hyperkeratosis, hyperpigmentation, cardio-vascular diseases and disturbance in the peripheral vascular and nervous systems.[1]

Arsenic occurs in several oxidation states (−3, 0, +3, +5) but in water environment the most predominant forms are oxyanions of trivalent arsenite As(III) and pentavalent arsenate As(V). Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Generally, As(V) is more prevalent in surface water (oxidising environment) while As(III) is more likely to occur in anaerobic ground waters (reducing environment). It is also well known that is more difficult to remove As(III) from water than As(V).[2,3]

Arsenic may occur in organic forms as well. The dominant organic forms of As found in water are methyl ad dimethylarsenic compounds. Organic forms may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important. Generally, inorganic forms are more toxic and mobile than the organic ones, while As(III) is considered to be 5–20 times more toxic and four to ten times more soluble in water than As(V).

Various treatment methods have been proposed and used for arsenic removal from water streams, such as sorption and ion exchange, precipitation, coagulation and flocculation, reverse osmosis, membrane technologies, electrodialysis, biological processes, lime softening, etc. Among them, sorption processes are considered to be more promising due to their cost/

efficiency factor. The most common used sorbents are based on iron compounds (goethite, akaganeite, etc.) and aluminium compounds (activated alumina, γ-Al_2O_3 or gibbsite $Al(OH)_3$). Sorbents based on iron compound are the most frequently used. For arsenic removal, several iron (III) oxides/ oxyhydroxides but also others materials based on iron oxides/hydroxides, e.g. iron oxide-coated sand, granular ferric hydroxide, iron-coated cement, iron-coated alumina, magnetically modified zeolite are used.[2,4–7]

2. Experimental

2.1. REAGENTS

Analytical grade chemicals were used in all experiments. Model solutions were prepared by dissolving $AsHNa_2O_4.7H_2O$ in deionized water; $NaNO_3$ was used as electrolyte (0.01 M and 0.1 M). The pH of the solutions was adjusted with suitable concentrations of analytical grade NaOH and HNO_3.

2.2. PREPARATION AND CHARACTERIZATION OF SORBENT

Natural zeolite (clinoptinolite type) from Nizny Hrabovec (Slovakia) was used for the preparation of the modified magnetic zeolite. Natural zeolite (<5 μm fraction, air classified by Alpine 100 MZR, Alpine AG, Germany) was added in a reaction vessel together with salts of Fe(III) and Fe(II) and a suitable quantity of NaOH was added. The dispersion was stirred and magnetic zeolite was produced. The new sorbent was washed and dried. Its surface area and pore volume was measured (Gemini 2360) and its point of zero charge was calculated from zeta potential measurements (ZetaPlus, Brookhaven Instruments). Its magnetic properties were measured as well (KappaBridge KLY-2, Geofyzika Brno). The characteristics of natural zeolite, pure iron oxides (prepared without the presence of zeolite) and magnetic zeolite are given in Table 1.

TABLE 1. The characteristics of natural zeolite, pure iron oxides and modified zeolite

Properties	Natural zeolite	Iron oxides	Modified zeolite
Surface area (m^2/g)	36.360	125.717	113.489
Total pore volume (cm^3/g)	0.062	0.212	0.151
pH_{PZC}	Not defined	6.49	4.86
Magnetic susceptibility (10^{-6} SI units)	577	702,778	310,361

2.3. SORPTION EXPERIMENTS

The sorption properties of modified zeolite were tested under batch conditions. The effect of pH, ionic strength, initial arsenic concentration, sorbent concentration, temperature, contact time of sorbent and arsenic solution were studied. The experiments were performed in a rotary shaker set at 30 rpm and equilibrium time 24 h. The arsenic quantity in solutions was determined by AAS and UV-Vis spectrophotometry before and after the sorption experiments.

3. Results and Discussion

3.1. EFFECT OF SOLUTION pH AND IONIC STRENGHT

It is well known that the pH of solution plays an important role in sorption experiments in aqueous systems. It determines the aquatic chemistry of the system and also the charge density of the solid surface. It is related to the sorption mechanisms and reflects the nature of the physicochemical interactions of the species in solution and the active sites on the sorbent.[8] For this reason, the pH is one of the first parameters that are examined in sorption studies.

Zeolites (natural or synthetic) are very well known for their effectiveness in metal cation removal from water streams. They have been studied also for the removal of radioactive materials (i.e. thorium and uranium) and found to be quite effective.[9] Iron oxides have been used effectively in arsenic removal from water streams. Their effectiveness increases with a decrease of the particle size. Nanosize materials are found to be very effective on the removal of As from water.[10] However, the subsequent solid/liquid (S/L) separation is more difficult as the particle size decreases. Magnetic iron oxides have the advantage of easy S/L separation but due to their small particle size are not suitable as fillers in sorption columns. The magnetic zeolite produced here has shown good magnetic properties and also size suitable for sorption columns.

The effect of solution pH on the sorption capacity of natural zeolite, pure iron oxides and magnetic zeolite at ambient temperature is given in Figure 1. The initial As concentration was 100 mg/L and the sorbent concentration was 2 g/L. It is obvious that natural zeolite itself is not able to remove As(V) from water streams. Magnetic iron oxides are effective with a capacity of 33 mg As(V)/g sorbent. The magnetic zeolite produced within this study had also a good capacity of around 28 mg As(V)/g sorbent. This shows that the iron oxides on the zeolitic matrice make the material an effective sorbent for As. The magnetic zeolite combines the good efficiency of natural zeolite for cations removal with the efficiency of iron oxides for As removal and also has good magnetic properties. It seems to be a promising material.

The solution pH plays an important role. The best removal was observed at pH 2.0 for both iron oxides and magnetic zeolite. The efficiency was reduced almost linearly with increase of the pH. This coincides well with the surface charge of the particles. The PZC of iron oxides is at 6.5 and of magnetic zeolite at pH 4.9 (see Table 1). So, both sorbents are positively charged at pH 2.0. The main species of As(V) at pH 2.0 to 6.5 is $H_2AsO_4^-$ as published by Vaclavikova.[2] The electrostatic forces are attractive and contribute to sorption. As the pH increases the charge of the sorbents decreases and becomes negative at pH values over their respective PZC. So, the electrostatic forces decrease and even become repulsive at alkaline pH values. Even though, the best sorption is observed at pH 2.0, the solubility of iron oxides in this pH makes its use undesirable. Analysis of the filtrates after sorption has shown significant amounts of soluble iron at pH 2.0. However, no iron was detected at pH 3.5. For this reason further sorption studies were made at pH 3.5.

The ionic strength of the solution usually affects sorption, as it determines the extent of the electric double layer around the sorbent particles and affects the electrostatic forces between the sorbent and the charged species. So, the effect of various electrolyte concentrations (0, 0.01 and 0.1 M $NaNO_3$) on the sorption of As(V) on magnetic zeolite as a function of solution pH was studied. The results are shown in Figure 2. It is obvious that the presence of electrolyte does not affect the sorption capacity of the magnetic zeolite at the whole pH range studied (pH values 2.0 to 9.0). This

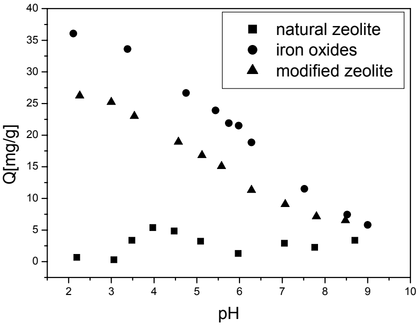

Figure 1. Comparison of sorption properties of natural zeolite, iron oxides and magnetic zeolite

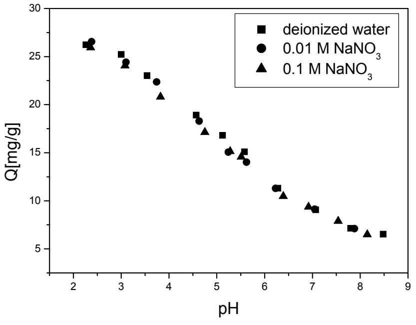

Figure 2. Effect of pH of solution and ionic strength on As(V) sorption onto modified zeolite

seems contradictory to the usual effect of ionic strength; it could be explained if a strong chemical interaction between As(V) species and sorbent is present. Then, the electrostatic forces are affected by the presence of electrolyte but their contribution to the overall sorption driving force is not significant and so sorption is not affected significantly.

3.2. EFFECT OF INITIAL ARSENIC CONCENTRATION

The effect of initial arsenic concentration (20–200 mg/L) was studied with 2 g/L sorbent concentration, ambient temperature and pH values 3.5 and 7.0. The results are given in Figure 3. Sorption isotherms were fitted using the Freundlich model. The maximum sorption capacity was around 33 and 19 mg As(V)/g for pH values 3.5 and 7.0 respectively. The coefficient of determination (R^2) was over 0.95 and shows a good agreement of the model to the experimental data. As expected the sorption capacity was much higher at acidic pH (3.5) than at neutral (pH 7.0). However, the results at pH 7.0 are considered promising, as it is the usual pH of drinking water treatment.

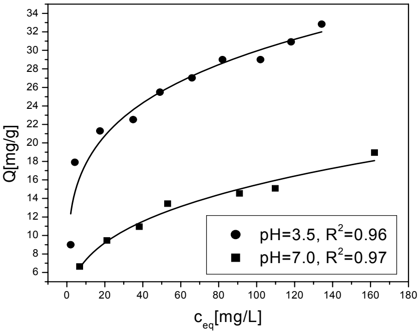

Figure 3. Effect of initial arsenic concentration

3.3. EFFECT OF CONTACT TIME OF SORBENT AND ARSENIC

In the practice of contaminants removal by sorption from water streams, the kinetics of the reaction plays an important role. Quick kinetics means that only a small residence time is necessary on the sorption column and the total cost of equipment per unit of contaminant removal is small. So, the knowledge of the reaction kinetics is very important. In practical terms is more important to have a sorbent with fast kinetics and smaller final capacity than a sorbent with high capacity but slow kinetics. Maximum removal of the contaminant in a short time is desired.

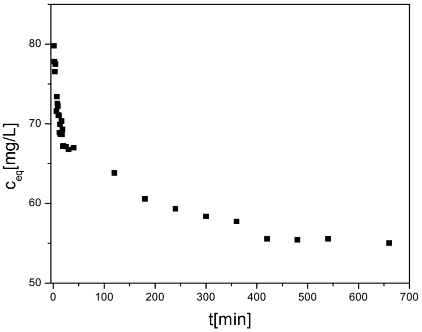

Figure 4. Effect of contact time of magnetic zeolite and arsenic

The kinetics of the arsenic removal from the aqueous solution with an initial arsenic concentration 100 mg/L, sorbent concentration 2 g/L, pH 3.5 and ambient temperature is presented in Figure 4. The curve is composed of two terms: a fast initial removal (in the first 60 min of treatment) and a slower subsequent removal up to equilibrium, which was obtained after 420 min of treatment. The process is considered relatively fast and this means that the sorbent could be used in sorption columns (dynamic conditions).

3.4. EFFECT OF TEMPERATURE

The effect of temperature on arsenic sorption was investigated at four different temperatures (ambient, 30°C, 40°C and 50°C) with an initial arsenic concentration 100 mg/L, sorbent concentration 2 g/L and pH 3.5. The experimental results are presented in Table 2. The maximum sorption capacity increased slightly with increasing temperature, which indicates a chemical sorption of arsenic onto magnetic zeolite.[2] The maximum sorption capacity (at 50°C) was around 27 mg/g.

TABLE 2. The effect of temperature on arsenic sorption

T[°C]	Q[mg/g]
Ambient temperature	19
30	21
40	25
50	27

3.5. EFFECT OF SORBENT DOSE

The effect of sorbent dose was studied at ambient temperature, initial arsenic concentration 100 mg/L and sorbent concentration 0.5–10 g/L. The results are presented in Table 3. Increase of the sorbent dose in solution caused a decrease of the observed sorption capacity of magnetic zeolite and an increase of the removal efficiency (E%). The decrease in capacity is due to the availability of more sorption sites with the increase of the S/L ratio and not enough arsenic to fill all the available sites. This is not so important in practical use. The important fact is that with more sorbent the removal efficiency increases significantly. So, this sorbent seems to be a good candidate for use under dynamic conditions (sorption columns).

TABLE 3. Effect of sorbent dose on arsenic sorption

Sorbent dose [mg/L]	Q[mg/g]	E[%]
0.5	21	11
1.0	20	20
2.0	19	40
5.0	15	75
10.0	9	96

4. Conclusions

A novel magnetic zeolite was produced by co-precipitation of Fe(II) and Fe(III) in the presence of natural zeolite and NaOH. The novel sorbent had good sorption properties for As(V) removal from water streams as it has been proven by sorption experiments at pH 3.5 and 7.0. The kinetics of As(V) removal was fast enough and the sorbent was considered as a good candidate for use in sorption columns. It also had good magnetic properties and could be easily separated from dispersions by application of magnetic field. The maximum observed capacity was 28 mg As(V)/g sorbent at pH 3.5. The best removal efficiency (96%) was observed with a sorbent concentration of 10 g/L.

Acknowledgements This work has been supported by Science and Technology Assistance Agency, project No. APVT-51-017104 and Scientific Grant Agency VEGA, project No. 2/0087/08.

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MODELING AND SIMULATION OF HEAVY METALS REMOVAL FROM DRINKING WATER BY MAGNETIC ZEOLITE

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Abstract Recent decades have witnessed a growing awareness and concern about the availability and quality of drinking water. The impact on human health of high toxicity compounds, including heavy metal, such as lead, cadmium, arsenic, among others, has lead to ever lower limits for a wide variety of chemicals. To respond to these challenges there is a need to develop new and even better methods to purify drinking water. Besides experimental work, process modeling and simulation plays a key role in the development of new treatment processes for drinking water. This paper focuses on the separation of heavy metals from drinking water by adsorption, in particular for arsenic removal. Common modeling and simulation strategies for this process are presented, being their relative merits discussed and

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

assessed. The process is illustrated with real experimental data obtained from an adsorption system based on a modified magnetic zeolite. This article also examines how modeling and simulation can be used in practice, to support the development of new and better processes for the removal of heavy metals from drinking water, to improve the purification process, and meet the current and future requirements.

Keywords: Toxic metals; arsenic; removal; adsorption; iron oxides; magnetic zeolite

1. Introduction

Contamination by heavy metals is found in many parts of the world, and occurs in both organic and inorganic forms in natural water, which is their major way of transport in the environment. It is originated either from natural activities due to erosion of rocks and sediments in the earth's crust and leaching from the mineral sources, or from anthropogenic activities such as mining and extraction of metals, followed by their utilization in many industrial sectors, agriculture, veterinary and human medicines, and common day life activities. Although they are essential to life of some organisms that require them in small quantities, especially for co-enzymes or hormones such as the copper and iodine growth hormone, metals are toxic if present in excessive amounts. For humans, the primary source of ingestion is through drinking water due to their relatively high solubility, although in some specific cases eating contaminated food can be relevant depending on the circumstances.

Some of the most common heavy metal pollutants are mercury, cadmium, arsenic, copper, plumb, zinc, chromium, nickel, iron, and selenium. Arsenic (As) is one of the most serious due to its prevalence and occurrence in the environment mainly due to natural causes.[1] Arsenic is a semi-metal major constituent of at least 245 different minerals, and it is mainly associated with sulfide minerals along with copper, nickel, lead, gold, cobalt, or other metals. Despite being widely used (e.g. in metallurgy, catalysts, electronics, glassware manufacture, pesticides, wood preservatives, cattle and sheep dips, as growth promoter in pigs, sleeping sickness and syphilis treatment), it is its reputation as a poison that has attracted the most attention over the ages, and in a way provides the backdrop to the current worldwide concern about the adverse health effects of long-term low level exposure.[2]

Arsenic occurs in the environment in different oxidation states: As^{5+}, As^{3+}, As^0 and As^{3-}. The pentavalent arsenic (+5) or arsenate, and the trivalent arsenic (+3) or arsenite are the two most common oxidation states in drinking water. The valence states of −3 and 0 rarely occur in aquatic environments. The most important factors controlling the stability and dominance of the various arsenic species are the redox potential (Eh) and pH. Other factors include the climate, the soil type under the same pH conditions, presence of other organic and inorganic compounds, such as ferrous and/or manganese ions, ammonium ions, sulfide, methane and natural organic matter, can influence and determine the arsenic ultimate toxicity and mobility.[3]

Continuous exposure to arsenic leads to accumulation in tissues (e.g. skin, hair and nails) resulting in various clinical symptoms such as hyperpigmentation and keratosis. A large number of epidemiological studies confirmed that arsenic inhalation and ingestion may cause several adverse health effects such as peripheral vascular diseases, cardiovascular disease, neuropathy, polyneuropathy, hepatopathy, diabetes mellitus, hypertension, skin lesions, decreased birth weights of infants, and a high risk of various internal and skin cancers in humans. Fetal loss and premature delivery may occur even at low exposure levels (<10 μg/L), and verbal IQ and long term memory can also be affected.[4]

Regulations defining permissible levels in the environmental media and controlling exposure to arsenic in workplace have raised public awareness of possible hazards and led to reductions or even banning of certain applications. In order to achieve a high quality of water intended for human consumption and to protect public health in countries, the World Health Organization (WHO), the European Commission (EC) and United States Environmental Protection Agency (U.S. EPA) recently revised the arsenic standard and recommended a lower maximum contaminant level (MCL) from 50 to 10 μg/L, in drinking water. A more recent proposal of U.S. EPA put forward an even lower drinking water standard of 5 μg/L, based on a re-evaluation of chronic arsenic toxicity to humans, as found in relatively large populations receiving potable water with high arsenic levels over several decades.[5]

Conventional methods for arsenic removal include among others, coagulation, flocculation and precipitation,[6] adsorption and ion exchange,[7] membrane filtration,[8,9] reverse osmosis,[10] biological processes,[11] chemical and photocalatytic oxidation[12] and electrochemical removal.[13] Adsorption processes are the most applied today to meet the current drinking water standards, showing a good efficiency to cost ratio for higher arsenic concentrations. Granular adsorbents (e.g. ferric or aluminium oxides) are commonly used with high performance.[14] Among them, iron compounds (e.g. hematite, magnetite, or goethite) are still considered promising for a sustainable solution and have been reported to be effective and promising adsorbents for arsenic removal from aqueous solutions.[15–17]

Although the large variety of treatment methods, the present state of knowledge and technology is still insufficient to solve the arsenic problem in different settings and for the different types of groundwater and arsenic levels found, and there is a need to optimize the process of water purification.[18] Moreover, existing technologies are costly, or their reliability, safety, and treatment of residues and sub-products are not satisfactory especially for small treatment plants. Also, existing methods are not very effective at lower initial arsenic concentrations or fail to reach the regulatory limit of 10 μg/L, especially for As(III) that is more difficult to be removed.[19] Therefore, there is a clear need to develop inexpensive, environmentally friendly, reliable, and efficient technologies for arsenic removal from drinking water, with the aim of complying with the new target limit, and to be prepared for new and more stringent limits of arsenic in water.

An excellent way to improve our knowledge and to develop better processes for heavy metals removal from drinking water is to perform experimental work together with theoretical studies. Thus, this article describes the modeling and simulation of adsorption processes that are the most widely used in practice to purify water. A preliminary study was done, as part of an experimental research project aiming to develop an adsorption process for arsenic removal from water.[20] The novel adsorbent incorporates iron oxide based magnetic nanoparticles into a zeolite, which seems to be a promising and economical method for application in small units.

Section 2 of this paper describes how adsorption systems can be modeled and simulated leading to better and improved processes. Also, special care is given on how to estimate the parameters needed for the model, either from correlations available in literature or from especially designed experiments.

Section 3 presents the case study of an adsorption process for arsenic removal, explaining and critically assessing its modeling and simulation.

Section 4 presents the main conclusions and some suggestions for the model improvement, such as using new experimental data or other theoretical approaches.

2. Modeling and Simulation of Adsorption Systems

2.1. MODELING AND SIMULATION FRAMEWORK

Mathematical modeling is helpful in process analysis, to design new adsorption processes or to improve the understanding of existing ones. Depending on how they are derived, process models can be of three types: (a) theoretical, developed from fundamental chemistry and physics principles; (b) empirical, obtained from mathematical or statistical analysis of process operating data; or (c) semi-empirical, a compromise between the previous two types.[21]

A process model allows at best an approximation of the real process described mathematically. It facilitates the design and analysis of the full-scale system, reducing the number of pilot-scale tests required. This way one can evaluate and optimize the various operating conditions and design parameters, decide what processes have to be placed upstream and downstream, select controlling settings, design the control law and strategy for the new process, and train the plant operating personnel in a more effective way.

The construction of a mathematical model, for a physico-chemical process or unit operation, can be seen as a sequential and iterative procedure. It tries as much as possible to mimic the physical reality within limits dictated by the mathematical complexity that needs to be addressed in practice. The main steps in process modeling and simulation are described in Figure 1.

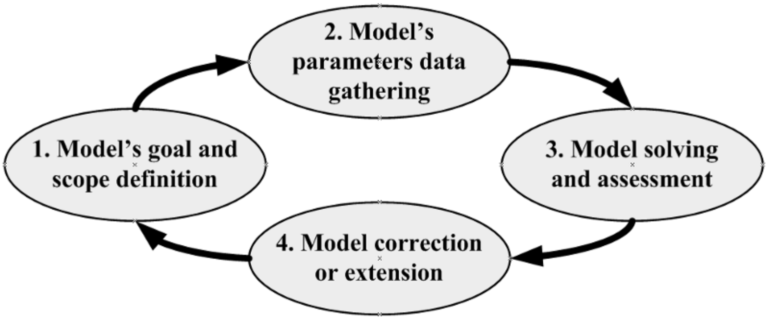

Figure 1. Framework for process modeling and simulation

1. As a first step it is crucial to clearly define the goals and the system boundaries for the model. The main parts of the system to be modeled should be identified, as well as the interactions among them, and the

required level of detail. Note that the more complex a model is the more difficult or even impossible it is to solve. Based on a detailed observation of the system behavior a process drawing is built and rules of thumb applied to decide which aspects should be relevant and thus have to be considered. This step has a qualitative nature and involves the identification of relevant experimental or empirical data, such as knowledge about similar systems, legislation and pertinent regulations. For better definition of the model, the practitioner may consider the 4W's, i.e. to question what, when, where, and why. Examples include: What are the purposes and real benefits of the model? Will it be used to explain experimental trends or for predictive and design purposes? Should it consider steady-state or transient operation? How to balance trade-offs between the model's level of detail and the time and effort needed to obtain and verify its solution? The answer to these and many other questions may help determine the assumptions to be made, the final complexity of the model, and how numerical values can be obtained from the model equations.

2. The next step involves the gathering of all the physical and chemical data needed, such as thermodynamic properties and conservation and rate laws. Sometimes experiments have to be performed to determine some of the model parameters, particularly in complex systems where many different physical phenomena may occur. Based on the information gathered, the law's equations of mass conservation, momentum, energy and others are written to describe the system behavior. Depending on the assumptions, algebraic or differential equations may be obtained. Here it is convenient to write the conservation and auxiliary equations in dimensionless form to identify what key parameters are controlling the system behavior, and to allow the extension of the model results to other systems with different sizes but the same dimensionless parameters values. Finally, a qualitative analysis of the model equations should be performed to ensure that all the relevant aspects are included.
3. When the system is completely defined in mathematical terms, the model equations can be solved to determine the system response to one or more independent variables. An extensive variety of analytical and numerical methods are available to solve a wide range of models. Many of them are available in ready to use computer packages for the entire process modeling, like the Computational Fluid Dynamics (CFD) software. After obtaining the model numerical or analytical solution, one needs to assess if it is valid and describes well the real behavior and performance of the system/process under study. As most of the

models equations are highly nonlinear and may have more than one solution, their validity should be qualitatively analyzed. Only after that the solution can be compared with the experimental or operating data to determine its adequacy to describe the system under study.

4. Depending on the previous analysis, one may need to correct or extend the model, based on its capability to describe the system under study and to meet the intended goals. Naturally, extensions of the model may be sought if the results obtained are not adequate, and this process may be repeated iteratively till the adequate level of rigor is achieved. Eventual changes may involve increasing the model complexity, or fine-tuning it to better account for the phenomena controlling the system behavior.

The model complexity heavily depends on the practitioner capacity, available data, computational power, and the study purposes. Some authors start with a simple model of the process, using the minimum number of parameters, and then increase its complexity, as the knowledge about its gradual increase.[22] Also, experiments to determine the influence of operating conditions (e.g. temperature and mixture composition) are usually lengthy and costly to perform. Thus process modeling and simulation are valuable substitutes and can be a cost effective solution for process design, allowing one to quickly assess the influence of many design variables.

The framework described above is applied in this work to design an adsorption system. The final goal when modeling an adsorption system is to describe and predict the behavior and performance of the adsorption unit. Also important is to predict the breakthrough curves for the compounds of interest. This information is essential to design the units and to define the production and regeneration cycles.

In brief, first, one needs to define the components to be separated, the feed conditions, and restrictions to the system operation. Then, the adsorbent(s) can be selected, normally based on experiments performed as much as possible for the final operating conditions. Information about costs and physical properties from other adsorption systems can be useful to limit the possibilities when choosing the materials to be used. After selecting the adsorption material and qualitatively defining the operating conditions, follows the process modeling and simulation. Here, one needs information about the physical and chemical properties of the fluids and of the adsorbent to be used. For example, about how the different materials interact with each other that can be obtained from literature or experiments. The application of the mass and energy conservation principles lead to an equations system, which after solving allows one to describe the system and to design it together with the auxiliary equipment. Finally, if the model is not adequate for the process description, new experiments or model changes are needed, in particular, the consideration of transport phenomena deemed irrelevant initially yet significant to the system behavior.

2.2. MODELING OF ADSORPTION SYSTEMS

When modeling any complex process such as adsorption in a fixed bed, it is convenient to identify any possible analogies with other processes. Thus, two different approaches are normally considered when modeling adsorption in packed beds: continuum and staged models. Continuum models assume that the fluid and solid phases can be seen as a continuum media, where the mass and energy balance equations for an infinitesimal slice of the packed bed are written. Staged models consider that the local structure is represented by simple elements interconnected with each other. Although mathematically different, they give similar predictions when the adequate parameters are used. Since the system to be modeled in this work is based on a fixed bed, the focus will be on the continuum models, although discrete models are briefly presented. Empirical models can also be found in the literature, but they are not considered in this work.

2.2.1. *Fixed Bed Adsorption – Continuum Models*

The application of the conservation laws to an infinitesimal slice of packed bed (Figure 2) lead to partial differential equations. The flow field is normally assumed to be plug flow or described by dispersion model.

For the former, Eq. 1 of the general mass balance equation can be written[23–25]

$$D_L \frac{\partial^2 C}{\partial x^2} = v \frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} + \frac{\rho_{ap}(1-\varepsilon)}{\varepsilon} \frac{\partial q}{\partial t} \tag{1}$$

where C is the solute concentration in the fluid, q is the solute concentration in the solid, v is the fluid average velocity, ε is the bed porosity, D_L is the axial dispersion coefficient, and ρ_{ap} is the apparent density of the adsorbent. Both ε and D_L are assumed to be constant. The previous equation is the mathematical statement of the mass conservation principle, which means that for a differential bed element the difference between the entrance and exit mass fluxes is equal to the accumulation in the fluid and solid phases.

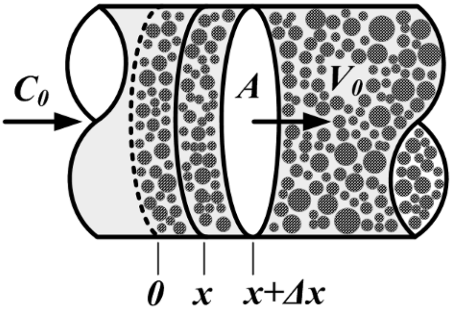

Figure 2. Infinitesimal slice of a fixed bed adsorbent

Eq. 1 should be solved using the following set of boundary and initial conditions

$$t = 0 \Rightarrow C = q = 0 \tag{2}$$

$$z = 0 \Rightarrow vC\,|_{x=0^-} = vC\,|_{x=0^+} - D_L \frac{\partial C}{\partial x}\,|_{x=0^+} \tag{3}$$

$$z = \ell \Rightarrow \frac{\partial C}{\partial x} = 0 \tag{4}$$

where ℓ is the length of the fixed bed. The last two conditions correspond to the Danckwerts set of boundary conditions, valid for closed systems.

As in staged models, the Eq. 1 has two independent concentration variables, C and q. An additional equation is needed to close the equations' system, in particular to describe the time variation of the adsorbed concentration. It is through this term that the adsorption equilibrium and the mass transfer resistance are incorporated into the model. When the resistance to mass transfer is negligible, it can be assumed that $q = C_i$, being C_i the concentration at the fluid solid interface, which value is determined from C and using the adsorption equilibrium relationship.

Two types of mass transfer resistance can be considered: internal to the particle due to diffusion of the adsorbate inside the solid and external to the particle due to the existence of a stagnant film surrounding the particle. When external mass transfer is controlling the process, the condition of equal fluxes at the interface imposes that

$$\frac{\partial q}{\partial t} = K_F a\left(C - C_i\right) \tag{5}$$

where K_F is the external mass transfer coefficient, and a is the interfacial specific area of the particle that corresponds to the ratio between area and volume of an adsorbent particle.

When the internal diffusion resistance is dominant, it is more convenient to replace q in Eq. 1 by the average concentration inside the particles, $\overline{q}$, resulting in the following expression

$$D_L \frac{\partial^2 C}{\partial x^2} = v\frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} + \frac{\rho_{ap}(1-\varepsilon)}{\varepsilon}\frac{\partial \overline{q}}{\partial t} \tag{6}$$

The term involving $\overline{q}$ can be determined from the mass balance written for an adsorbent particle and in the fluid-solid interface. Assuming that they have a spherical shape, the following equations can be written

$$\frac{\partial^2 q}{\partial t} = \frac{D_{eff}}{r^2}\left(r^2 \frac{\partial q}{\partial r}\right) \tag{7}$$

$$\frac{\partial \overline{q}}{\partial t} = \frac{3D_{eff}}{R_P}\frac{\partial q}{\partial r}\Big|_{r=R_P} ; \overline{q} = \frac{3}{R_P}\int_{V_P} qr^2 dr \tag{8}$$

where D_{eff} is the solid effective diffusivity, r is the radial coordinate in the particle, and R_P is the particle radius. Note that the last equation imposes that the mass fluxes at the interface are equal. The mass balance equation for the particle should be solved taking into account the initial condition imposed for Eq. 1 and the following boundary conditions in the particle

$$r = 0 \Rightarrow \frac{\partial q}{\partial r} = 0\text{, symmetry condition} \tag{9}$$

$$r = R_P \Rightarrow q = C_i\text{, equilibrium at the interface} \tag{10}$$

In some cases both terms of mass transfer resistances are relevant and must be combined together, leading to the following expression for the equality of fluxes at the interface

$$\frac{3D_{eff}}{R_P}\frac{\partial q}{\partial r}\Big|_{r=Rp} = K_F a(C - C_i) \tag{11}$$

Other forms of expressing the mass transfer resistance may be found in literature.[24,25] One of the most interesting is the LDF (Linear Driving Force) approximation, which states that the term $\partial\overline{q}/\partial t$ may be expressed as proportional to the concentration in the fluid and adsorbed phase

$$\frac{\partial \overline{q}}{\partial t} = f(q, C) \tag{12}$$

where f is a function that depends on the main mass transport mechanisms. For the situation where diffusion in the adsorbent is dominant $f = k(q^* - \overline{q})$, where q^* is the adsorbate concentration in the solid surface, defined by the equilibrium relationship.

Results showed that in most situations this model is adequate to describe adsorption processes, both for gases and liquids. The expressions for k can be obtained by solving the mass balance equations for the adsorbent particles, and identifying the main terms controlling its behavior. Depending on the controlling mass transfer mechanisms and characteristics of the adsorption equilibrium, many expressions for k can be found in literature.[23–25]

2.2.2. *Fixed Bed Adsorption – Staged Models*

Staged models of adsorption systems normally consist of a sequence of stirred vessels, where a fluid and solid coexist (Figure 3). This type of models is normally used to describe chemical reactors, transport phenomena in porous media, among others.[26–28]

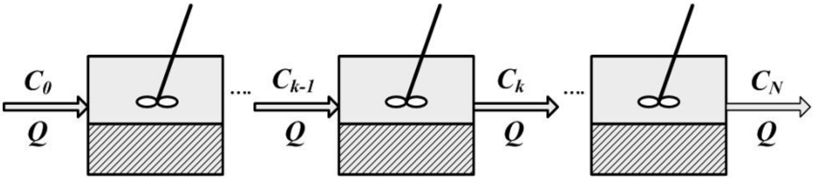

Figure 3. Example of a staged model

It assumes well-mixed reactors with equal volumes and that the interconnecting elements have no volume and no influence in the system behavior. Taking into account these conditions, the mass balance equation for stage k can be written in the form

$$\varepsilon Q C_{k-1} = \varepsilon Q C_k + \varepsilon V_k \frac{dC_k}{dt} + (1-\varepsilon) V_k \frac{dq_k}{dt} \tag{13}$$

where C_k and C_{k-1} respectively represent the fluid concentrations in stage k and $k-1$ (immediately before), q_k is the concentration in solid phase, Q is the flow rate through the bed, and V_k is the stage volume, related to the total volume and the number of stages, N, by the relation $V_k = V/N$.

For each stage a similar equation can be written, leading to a system of N coupled ordinary equations. The initial conditions are:

$$t = 0 \Rightarrow C_k = q_k = 0, k = 1,...,n \tag{14}$$

$$t = 0 \Rightarrow C_0 = f(t) \tag{15}$$

The last initial condition represents the variation of adsorbate at the entrance of the fixed bed, usually assumed to be a step. The term dq_k/dt represents the dynamical behavior of the solid phase, and its definition includes the adsorption equilibrium and the possible internal and external mass transfer resistances. Different strategies were proposed in literature to determine this term and a different mass transfer resistance, such as the LDF model.[24] Despite its simplicity, adsorption systems are normally modeled using continuum models, where a lot of experience and published work already exists.[23–25,29] They will be used in this work to model arsenic removal by adsorption.

2.2.3. *Solution of the Conservation Equations*

As stated before, these two types of models have very different mathematical behaviors, and require rather different strategies to be solved. Although analytical solutions are possible in some cases, they are restricted to situations controlled by specific processes. Many analytical solutions are found in literature,[23–25] and in some situations they are very helpful to describe and design adsorption processes.

Generally, staged models where linear driving forces are used to represent the particle mass transfer, lead to ordinary differential equations systems. For continuous models the application of the conservation laws' equations leads to partial equations, coupled with ordinary differential equations depending on the models. Therefore, staged models are somewhat easier to solve using numerical methods, requiring less memory space and computational power when compared with continuum models. However, even for these situations numerical difficulties may arise from the physical nature of the problem. Fixed bed adsorption is a dynamic process, in which concentration waves travel throughout the bed, and sometimes inside the adsorbent particles, where they become very sharp and the numerical error can be very large. Thus, care must be taken when integrating the balance equations, in particular in the zone where strong concentration variations may occur.

Finite difference and diverse forms of weighted residual methods can be used, in particular orthogonal collocation[2,9] Both types of methods involve the discretization of the mass and heat balances resulting in a system of algebraic or coupled ordinary equations. The availability of excellent solver capabilities for stiff systems makes it possible to efficiently obtain a solution. Although weighted residual methods are more accurate, they are more difficult to program when compared to finite difference methods. Also as no weighted residual method is superior to the others, the choice is ultimately done by the practitioner.

2.2.4. *Selection of Adsorbent and Operating Parameters*

The selection of the adsorbent material and the most adequate operating parameters are done independently from the modeling and simulation.

Adsorption is a physical phenomenon in which the fluid molecules form bonds and become attached to the solid surface.[24] Different affinities between molecules and specific surfaces are used to separate compounds in gaseous or liquid mixtures. Adsorption is an interesting alternative to separate similar compounds (e.g. isomer separation), at very low concentrations, or if extreme conditions of temperature and pressure are required to perform the separation using an alternative method. The following characteristics are desirable for an adsorbent material:

- High adsorption capacity
- High surface area
- Selectivity to the components of interest
- Equilibrium easily reversed to facilitate the reutilization of the adsorbent

The adsorbent material considered in this study consists of iron oxide magnetic nanoparticles (magnetite) incorporated into a natural zeolite, which manufacture is described in detail by Vaclavikova.[30] Besides having a large internal specific surface, from 60 to 80 m^2/g, the adsorbent material can be easily separated from a mixture of particles using a simple magnet, as shown in Figure 4, allowing its utilization with other adsorbents and contaminants.

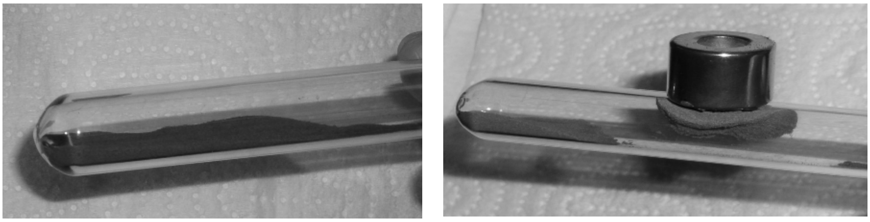
(a) (b)

Figure 4. Mixture of (a) magnetic zeolite and other particles; (b) separation using a simple magnet

The adsorbent material is tested in batch experiments, considering two situations: the use of magnetite nanoparticles and magnetite incorporated into a zeolite. The main parameters analyzed are the pH and the ionic strength of the solution, the adsorption capacity, and the possible presence of iron ions in the solution. The main results are listed below.

- The optimal pH to perform the separation is around 3.5 to which, a good adsorption capacity is obtained (around 30 mg(As(V))/g(adsorbent) and the dissolving of iron oxide due to reaction with arsenic ions is minimal and may be neglected.
- The zeolite combined with magnetite nanoparticles reduces the overall adsorption capacity, as expected, but the qualitative influence is maintained. Thus, it can be concluded that the zeolite particles do not have a significant influence in the adsorption equilibrium. The adsorption capacity for those conditions is around 20 mg (As(V))/g(adsorbent).

Different transport phenomena may control the system behavior and only through modeling and specific experiments it is possible to gauge their relative importance. Extensive reviews are found in literature describing and characterizing modeling and simulation of adsorption systems.[23–25,31]

The previous general models include parameters that need to be accounted for the various transport phenomena occurring simultaneously on an adsorption system, in particular:

- Number of stages in series, N, or axial dispersion coefficient D_L, that are related with the flow field and the mass transfer in the fluid
- D_{eff} and K_F that are linked with the resistance to mass transport
- Parameters of the adsorption equilibrium relationship

Although these parameters can be determined by fitting experimental data to the general model, this approach can be very time consuming and computational intensive. A good strategy to determine some of the main parameters involves performing specific experiments under controlled conditions.

As arsenic removal takes place in liquid phase, the pH and ionic composition of the feed may influence the separation efficiency. These parameters are determined experimentally, varying the total quantities of adsorbent and adsorbate in stirred vessels. Literature is also a valuable source of information from similar systems. Other operating parameters of interest are the adsorbent capacity and its selectivity to the compound(s) to be separated, which depend on the temperature and components concentration. Since this is a slightly exothermic process, heat transfer could be accounted for, yet as the arsenic concentration is low, these effects are negligible.

To know how the component concentration in the solution and adsorbent vary with each other, it is essential to determine the adsorption isotherm, i.e. equilibrium relationship between the concentrations of arsenic adsorbed and in solution, which can be done at the same time to the best adsorbent and optimal operating conditions. Also, one needs to know if the adsorbent can be regenerated and how.

Adsorption always takes place in dynamic conditions, in batch or fixed bed units. Thus, to model an adsorption unit one needs to know how the concentration profiles travel in time through the bed. They are the result of the interplay between adsorption equilibrium and rate processes involving the mass transfer between different phases.

The hydrodynamic parameters can be determined from the Residence Time Distribution, RTD, for the flow through the packed bed. The relative importance of the mass transport in the fluid or into the particles and the parameters that control both phenomena can be determined using a tracer that is not adsorbed. Also, a tracer that does not enter into the particles can be used to confirm and check the results obtained for the parameters related with the flow around the particles in particular for D_L.

The determination of D_{eff} and K_F can be done carrying out adsorption experiments in stirred vessels, normally operated in batch mode.

D_{eff} can be obtained under controlled conditions, especially for negligible mass transfer resistance. The comparison with RTD experiments, when performed, can be used to see if the results are valid, and if the external mass transfer or other aspects should be considered. Thus, batch experiments are relevant.

3. Arsenic Removal by Adsorption in Fixed Bed

The previous section makes an overall presentation of adsorption in fixed bed, with a focus on different mass transport mechanisms, and characterizes adsorption processes. In this section, the framework introduced before is used to analyze and describe arsenic removal by adsorption, to purify drinking water for human consumption.

3.1. KINETICS OF ARSENIC ADSORPTION IN BATCH SYSTEMS

Some of the key parameters needed to model and simulate adsorption in a fixed bed can be determined by experiments performed in stirred vessels. It involves the mixing of known quantities of adsorbent and a solution of adsorbate and then the following of its solution concentration history.

Considering the adsorber model, including relevant kinetic and mass transfer phenomena, the relevant parameters can be estimated.

Several models such as homogeneous surface diffusion, dual resistance mass transfer, and pore diffusion, have been extensively used to describe batch experiments.[32–38] Most of these experiments are performed for isothermal conditions and the mixing conditions are such that the particle mass transfer resistance may be neglected. Depending on the models, one can also estimate the external mass transfer coefficient.

For the adsorption kinetics, it is possible to assume a simple kinetic model based on the analogy between adsorption and catalytic chemical reactions. Some authors proposed models of this type for a wide variety of sorption systems, usually considering first and second order kinetics.[39] Assuming that the adsorbed quantities are proportional to the number of active sites, the adsorption kinetics can be expressed as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{16}$$

where q_t and q_e, for adsorption in batch, in a well agitated and constant volume vessel, are expressed as:

$$q_e = \frac{C_0 - C_e}{\rho}, \quad q_t = \frac{C_0 - C_t}{\rho} \tag{17}$$

where C_0 and C_e are the initial and equilibrium adsorbate concentrations, respectively, C_t is the concentration at any time, and ρ is the ratio between the adsorbent mass and the particle free liquid volume.

Integrating Eq. 16 for the initial condition $t = 0 \Rightarrow q_t = 0$, a linearized pseudo-second order rate equation is obtained:

$$\frac{1}{qt} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \tag{18}$$

The constants are obtained by linear fitting t/q_t as function of t. In this work, experiments were performed, in isothermal conditions and pH = 3.1, in a vessel of 1,000 mL of a 50 mg/L solution of arsenic with 2 g of magnetic zeolite, for a 500 rpm impeller velocity. Samples of 1 mL were taken at several times to determine the adsorbate solution concentration history, until a limit behavior is reached. The experimental data obtained for arsenic adsorption in the magnetic zeolite is well described by the second order irreversible model, obtaining k = 34.60 mg(ads)/mg(As)min with a correlation factor $R^2 = 0.998$.

Although pseudo-kinetics models describe the adsorption process, they are useless to determine the relevant mass transport mechanisms. Adsorption kinetics depend on a variety of processes, including the transport of the adsorbate from the solution to the particle, characterized by K_F, its diffusion inside the particle, characterized by D_{eff}, and finally adsorption in the active sites. Batch adsorption can be used to assess all those parameters. D_{eff} is determined assuming no external mass transfer limitations and dominant pore diffusion. For spherical particles, the following expression is used

$$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_{eff} t}{r_p{}^2} \right) \tag{19}$$

where r_p is the average particle radius. For large times, in particular when $q_t/q_e > 70\%$, the series first term is enough and D_{eff} may be estimated by fitting linearly $\ln(1 - q_t/q_e)$ versus t. The predicted value of $D_{eff} = 9.46 \times 10^{-14}\ \mathrm{m^2/s}$, which is in agreement with the reported values of the effective diffusivity in zeolites for liquid phase.[23]

As referred above, the LDF approximation is a common and in many cases good strategy to model adsorption systems. For the batch adsorber, assuming the uptake proportional to the difference between the amount adsorbed in the surface, q_s, and the average amount in the adsorbent, $\bar{q}$, is obtained from Eq. 20.

$$\frac{\partial \bar{q}}{\partial t} = K_{LDF}\left(q_S - \bar{q}\right);\ K_{LDF} = \frac{15 D_h}{R_P{}^2} \tag{20}$$

where K_{LDF} is the proportionality constant of the model, and D_h is the homogeneous diffusion coefficient, similar to D_{eff}, but considering the possible external mass resistance effects. For the batch adsorber the following overall mass balance holds

$$\bar{q} = \left(C_0 - C\right)\frac{V}{M} \tag{21}$$

where C_0 and C are the concentration of adsorbate in solution, and V/M is the adsorbent quantity per unit volume of solution. For the system under study, the Langmuir isotherm describes well the adsorption equilibrium,[30] in the form

$$q_S = \frac{Q_{Max}.K_L C}{1 + K_L C};\ Q_{Max} = 74.7\ \mathrm{mg/g};\ K_L = 0.0021\ \mathrm{g/L} \tag{22}$$

For a Langmuir isotherm the following dimensionless mass balance can be written for the concentration in solution[40]

$$\frac{dy}{dt}+K_{LDF}\left(\frac{\xi K_L C_0}{1+K_L C_0 y}+1\right)y=K_{LDF}a \tag{23}$$

$$y=\frac{C}{C_0}\,;\ \xi=\frac{Q_{Max}}{C_0}\frac{M}{V}\,;\ q_s=\frac{Q_{Max}K_L C}{1+K_L C} \tag{24}$$

Equation 23 can be analytically solved for the initial condition $t=0\Rightarrow y=1$, resulting in the expression

$$t=\frac{-1}{K_{LDF}}\left\{\frac{1}{2b}\ln\left[\frac{y^2+ay-b}{a-b+1}\right]+\left[\frac{2b-a}{2b(\alpha-\beta)}\right]\right\}\ln\left[\frac{(1-\beta)(y-\alpha)}{(1-\alpha)(y-\beta)}\right] \tag{25}$$

$$a=\xi-1+\frac{1}{K_L C_0}\,;\ b=\frac{1}{K_L C_0}\,;\ \alpha,\beta=\frac{-a\pm\sqrt{a^2+4b}}{2} \tag{26}$$

K_{LDF} can be estimated fitting the experimental data either to the analytical solution or directly by integrating the general mass balance equation. In this work the second option was followed and the results (presented in Figure 5) show that the LDF model fits well the experimental results for the initial times. However, for long times the experimental data deviates more and more from the model predictions.

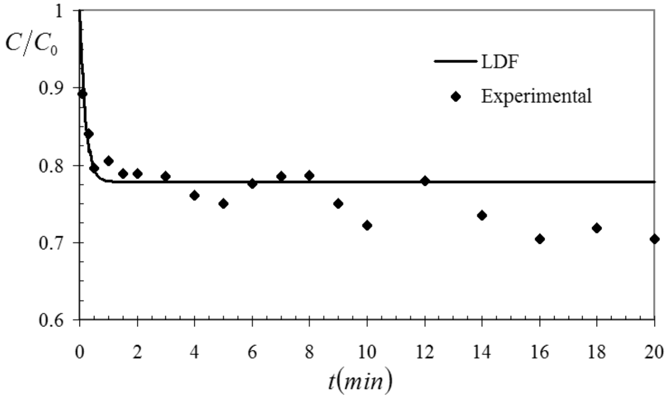

Figure 5. Comparison between experimental data and predictions of the LDF model for the adsorber

Considering the experimental data until $t = 10$ min, a K_{LDF} = $4.094\ \text{min}^{-1}$ is obtained, and using Eq. 20, a $D_h = 2.84 \times 10^{-10}\ \text{m}^2/\text{s}$ is obtained. When compared with D_{eff} obtained from the experimental data and long times, a significant difference is observed. Because D_h and D_{eff} are obtained for short and long times, respectively, this result may mean that inside the particles there are two different mechanisms of mass transport, each one characterized by its own effective diffusivity coefficient. According to Rutven[23] and Yang,[24] when considering adsorption in zeolite particles the diffusion in macro and micropores (associated with the zeolite crystals) is relevant and should be considered simultaneously. Also, Dong[29] considers that diffusion in the particle void space and the solid may be characterized by different effective diffusion coefficients. At present it is not possible to define whether D_{eff} represents diffusion in solid phase (micropores) or D_h represents diffusion in the pore space (macropores). Future experiments and modeling efforts will allow one to properly define the correct mass transfer mechanisms and determine their parameters.

3.2. COLUMN ADSORPTION EXPERIMENTS

To determine the behavior of the adsorbent in conditions close to those used in practice, and to gauge if a continuum model can reproduce the experimental results, several column experiments were performed. A fixed bed with a 1 cm diameter and 12.3 cm height was used in the experiments. The packed bed is composed of magnetic zeolite with different diameters, and its height can be varied. Before the breakthrough experiments, the column was rinsed with water for 24 h, to stabilize the packing and to remove any contaminant. At a given time, a solution of a fixed amount of arsenic with a pH around 3.5 and a flowrate of 3 mL/min was introduced to the system, and the exit concentration of arsenic was followed in time. Note that as arsenic is determined using atomic absorbance, no information is available about the different arsenic ion species present. Also, the pH and iron concentration were controlled to gauge any possible adsorbent changes.

No significant temperature variations were observed in the experiments. Also, the iron concentration in the stream exiting the packed bed is not significant, showing that the adsorbent does not change appreciably during the experiments. Concerning the pH, depending on the rinsing solutions characteristics, two situations were observed. First, the adsorption capacity strongly depends on the pH value; in particular it lowers as pH increases. Second, if the solution has a pH of around 8.0, as the arsenic solution has a different value, the pH will also change. Thus, the breakthrough curve should be steeper if pH varies when compared with the situation where pH remains approximately constant, as shown by experimental data (not included in this article).

Presently no information is available on how the Langmuir isotherm constants vary as a function of pH. Also, the model including those effects will be rather complex and may need much more information. Thus, a constant pH of 3.5 is considered in this work for the experiments.

Because of different flow conditions in fixed bed and in adsorber, different mass transfer mechanisms may control the process. The significant parameters can be obtained from correlations available in literature, or from adsorber batch or Residence Time Distribution, RTD, experiments. The last type is relevant because it can be performed for the same flow conditions and adsorption experiments, and it will be considered in future studies. For this work correlations will be used instead.

The main parameters of interest depending on the flow field are the external mass coefficient, K_F, and the axial dispersion coefficient, D_L. Both parameters are estimated using the following correlations[25]

$$Sh = \frac{1.09}{\varepsilon} \mathrm{Re}^{0.33}\, Sc^{0.33}\,; \quad Sh = \frac{K_F D_P}{D}\,; \quad Sc = \frac{\mu}{\rho D} \tag{27}$$

$$\frac{1}{Pe} = \frac{\gamma_1 \varepsilon}{\mathrm{Re}\, Sc} + \gamma_2\,; \ \mathrm{Re} = \frac{\rho v D_P}{\mu}\,; \ Pe = \frac{v D_P}{D_L} \tag{28}$$

where Sh, Sc, Re, and Pe are dimensionless numbers named Sherwood (also known as Biot number), Schmidt, Reynolds and Peclet respectively, D is the molecular diffusion coefficient for arsenic in water, γ_1 and γ_2 are two constants that can be obtained from literature. Considering[41] $D = 2.89 \times 10^{-10}\ \mathrm{m}^2/\mathrm{s}$ and taking into account the experimental geometrical and flow conditions, $Sh = 27.48$ and $Pe = 24.07$ are obtained leading to $K_F = 1.59 \times 10^{-5}\ \mathrm{m/s}$ and $D_L = 3.97 \times 10^{-7}\ \mathrm{m}^2/\mathrm{s}$, respectively. Sh is lower than 50, implying that under the experimental conditions the external mass transfer can be significant and thus, should be taken into account.[29]

Results of the RTD experiments (not presented in this work) showed that under experimental conditions the mass dispersion needs to be taken into account, confirming that the mass transfer inside the particles is significant. Thus, a model able to describe the behaviour of the adsorption system should be based on dispersed plug flow model, including the external mass transfer resistance characterized by K_F. The internal mass transfer resistance is described by the LDF model and results of batch experiments. The system is described by the following three equations in dimensionless form

$$\frac{\partial y_b}{\partial \theta} = \frac{1}{Pe}\frac{\partial^2 y_b}{\partial x^2} - \frac{\partial y_b}{\partial x} - \xi_p \frac{d\overline{y}}{d\theta} \tag{29}$$

$$\frac{d\overline{y}}{d\theta} = N_p\left(y_b - y_f\right) \tag{30}$$

$$y_f = \frac{-A\sqrt{B^2 + 4AD}}{2A} \tag{31}$$

where the dimensionless variables and parameters are given by the following expressions

$$Pe = \frac{u.\ell}{D_L}\ ;\ \xi_p = \frac{1-\varepsilon}{\varepsilon}\rho.a_p\frac{q_E}{C_0} \tag{36}$$

$$N_p = \frac{K_F.a_p.\tau.C_0}{\rho.a_p.q_E}\ ;\ \beta = \frac{K_{LDF}.\tau.Q_{\max}.K_L.C_0}{q_E}\ ;\ \alpha = K_{LDF}\tau \tag{37}$$

$$A = C_0 N_p\ ;\ B = N_p - C_0 y_b + \beta\ ;\ D = \alpha\overline{y} + N_p y_b \tag{35}$$

The equations system should be solved for the following initial (Eq. 32) and boundary conditions (Eq. 33).

$$t = 0 \Rightarrow y_b = \overline{y} = 0 \tag{32}$$

$$x = 0 \Rightarrow 1 = y_b\,|_{x=0+} - \frac{1}{Pe}\frac{\partial y_b}{\partial x}\,|_{x=0+}\ ;\ x = \ell \Rightarrow \frac{\partial y_b}{\partial x}\,|_{x=\ell} = 0 \tag{33}$$

The numerical integration of this system will be presented in future work, aiming to assess the adequacy of the proposed model, or if it should modified.

4. Conclusions and Future Work

In this work some of the key aspects concerning modeling and simulation of adsorption systems are described and reviewed. It was focused on the removal of heavy metals from water intended for human consumption and particularly arsenic. Different types of models were compared, describing how they take into account the diverse equilibrium and kinetic phenomena and methods to determine the significant parameters.

A case study regarding the adsorption of arsenic from water using a novel magnetic adsorbent was studied. Although the results were preliminary and experimental studies were still required, it was possible to conclude from the batch experiments that the adsorption was well described using a pseudo second order model, and two different mechanisms for mass transport were relevant to describe adsorption in the particles.

The main aspects that should be accounted for when modeling adsorption columns were identified in this work, and a model was proposed that took into account all of them. Future studies may include, among others, the detailed modeling of the batch adsorber experiments using the explicit mass balance in the particles, the study of the influence of contaminants such as phosphate that may impact the adsorption of arsenic, and the investigation on how the magnetic zeolite may be regenerated for future use.

Acknowledgements This work has been supported by Science and Technology Assistance Agency, project No. APVT-51-017104.

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SORPTION OF METAL IONS FROM AQUEOUS SOLUTION ON FIXED-BEDS OF IRON-BASED ADSORBENTS

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Abstract The possibility of using a packed-bed in column configuration of akaganéite or goethite to remove metal ions (like zinc, cadmium, arsenates and chromates) from aqueous solutions was the aim of the present review paper. Synthesized material was used in two forms, i.e. in fine powder of nanocrystals and in the form of grains (as granular). The main examined parameters were the quantity of sorbent in the column, the presence of ionic strength, the solution pH value and the metals speciation, including the presence of complexing agents. The removal efficiency of the column was examined and compared. Typical adsorption models were discussed and the bed depth – service time equation has been applied to the sorption results in order to model the column operation.

Keywords: Akaganéite; goethite; packed-bed; column operation

1. Introduction

Although filtration is one of the principal unit operations in the treatment of potable water, the filtration of effluents is rather less practiced; usual examples are the achievement of supplemental removals of suspended solids from wastewaters of biological and chemical treatment processes, and also the removal of chemically precipitated phosphorus. Sorptive filtration was found[1] to present a promising technique, as today there is a tendency for combined and compact processes, offering both the need for effluent treatment due to environmental reasons, plus may be the recovery of metal values that otherwise perhaps will be lost, and perhaps more

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

importantly water reuse. Adsorption by activated carbon has a long history of use in treating municipal, industrial and hazardous wastes.

When discharged directly into rivers, polluted wastewater poses a great risk to the aquatic ecosystem, whilst discharge into the sewage system negatively affects bio-sludge activity and leads to contamination of the excess sludge to be disposed of. As a result of the standards specified in the Water Resources Act, industry takes precautions against these risks by treating dangerous components in a partial stream, i.e. before being mixed with other types of wastewater. So, research was focused, among other, to the development of highly selective bonding agents with fast reaction kinetics for the removal of heavy metal ions.[2]

Ferric oxides and hydroxides are another good example extensively studied in the literature; fixed-bed operation constitutes the appropriate configuration mode for large-scale applications as those of water and wastewater treatment. Fixed-bed sorption filters filled with an iron based sorbent were used to remove a range of heavy metals.[3] The homogeneous surface diffusion model and two of its derivatives were used to model anion breakthrough curves with granular ferric hydroxide adsorption filters.[4]

Hydrous oxides and oxyhydroxides has been known recently to control trace elements removal, although their use has been limited, mostly due to competition from the commercially available in several phases, particle sizes and surface areas, oxides of aluminum or active carbon.[5] These oxyhydroxides are available only as fine powders or are generated in aqueous suspensions as a hydroxide floc or gel. In these forms they retain their desirable sorptive properties for trace elements, but are limited to reactor configurations that incorporate large sedimentation basins or filtration units for subsequent separation. Under such conditions, the separation and regeneration of these materials can be difficult. These disadvantages can be overcome if the oxide is available in granulated form, thereby permitting its use in fixed-bed design. In addition, the comparative insolubility of iron oxides permits their use under greater extremes of pH than most other oxide materials. Such a characteristic is important for regeneration, and for the removal of anionic and cationic contaminants, for which simple pH adjustment is often sufficient.

Batch tests were examined during the sorption of arsenate oxyanions from dilute aqueous solution onto synthetic akaganéite, β-FeO(OH)[6].The effect of the sorbent and pollutant concentration, the contact time, temperature, solution pH value, and ionic strength variation on the treatment process was mainly investigated during this study. Typical adsorption isotherms were determined, which were found to fit sufficiently the typical

Langmuir equation. Arsenate could specifically adsorb on akaganéite surface. Electrostatic effects on oxide surfaces could, in certain instances, account for the enhancement of adsorption in multi-adsorbate systems. As(V) oxyanions were also removed by goethite.[7]

The same material, akaganéite nanocrystals, was also investigated for cadmium cations removal.[8] The effects of adsorbent amount, initial cadmium concentration, pH value of solution, concentration of background electrolyte ions and temperature variation on the treatment process of cadmium removal by akaganéite were investigated. Cadmium removal was shown to decrease with the increase of the electrolyte ions in solution. The adsorption isotherm of cadmium on akaganéite (for a solution without electrolyte ions in solution) was expressed by the Langmuir as well as the Freundlich model. All the obtained evidences lead to a mechanism of weak chemisorption possibly describing the removal process. Similar results were obtained for Zn removal.[9] Akaganéite was also surface modified with surfactants and for instance, applied to arsenite ions removal.[10]

2. Materials and Methods

The preparation of akaganéite by precipitation from an aqueous solution of the chloride salt and the investigation of relative surface properties of the iron oxyhydroxide gel were the aims of the initial paper in this area.[11] A new advantageous method using ammonium carbonate as precipitating agent was presented by which the synthesis of akaganéite was accomplished. Akaganéite was transformed to iron oxide hydroxide (FeOOH) and finally to hematite (α-Fe_2O_3) after thermal treatment at 473 and 673 K, respectively. The use of a volatile agent for the hydrolysis process, the special method of chloride ion removal, as well as the freeze-drying technique, led to the production of a material consisting of nanocrystals with high surface area and defined pore size distribution.

The method used in this work favoured the synthesis of β-FeO(OH) without the use of an additive (i.e. urotropin). Contrary to what has been reported about the competitive activity of OH^- versus Cl^- ions, as the pH of the hydrolysis process was increased up to 8, the obtained material was well confirmed to be nanocrystalline akaganéite with considerable features and morphology. This finding may be of significance for magnetic material applications, where the quest for higher magnetic recording densities and better magnetic colloids demand very small particles.

Very finely divided particles might well exhibit properties not predictable from those of the bulk. The prepared material consisted of nanocrystals 2–6 nm in size, with a high specific surface area (330 $m^2 g^{-1}$) and narrow pore size distribution (1–6 nm) with a maximum at 3.6 nm. The surface area was slightly decreased for the sample calcined at 373 K, while the total pore volume of 0.35 $cm^3 g^{-1}$ was preserved.

The synthesis of iron oxyhydroxides and hydroxides was then reported, by the use of a novel, simple and low-cost method.[12] The preparation involves the hydrolysis of aqueous solutions of ferric salts followed by membrane purification and freeze drying of the products. Three different iron precursors have been tested and combined to three different volatile precipitating agents. The obtained products were akaganéite, goethite and iron(III) hydroxide. Irrespective of the starting materials used, all three products, although different in chemical nature, presented some very interesting and unique features; they consisted of nanoparticles with mean sizes ranging from 1 to 10 nm and they had very high surface areas and pore sizes in the meso- and micropore regions. The produced materials were examined by powder x-ray diffraction for crystalline phase identification, TEM and XRD for particle size estimation and nitrogen sorption for surface area, pore volume and pore size distribution measurement.

The particle size of the nine produced samples ranged from 1 to 10 nm. Since the same compounds were previously produced in many other published works, starting from the same materials, with much bigger particle size and considerably lower surface areas, it can be concluded that the particular method used in this work, namely membrane purification followed by freeze-drying, makes the critical difference and drives the preparation towards the synthesis of valuable nanocrystalline products.

3. Modelling Packed-Bed Sorption

Sorption is, by definition, a general term describing the attachment of charged species (like the toxic metal ions) from a solution to a coexisting solid surface. Sorption kinetics may be controlled by several independent processes that can act in series or in parallel. These processes fall in one of the following general categories: (1) bulk diffusion, (2) external mass transfer (film diffusion), (3) chemical reaction (chemisorption) and (4) intraparticle diffusion. Kinetic analyses not only allow estimation of sorption rates but also lead to suitable rate expressions characteristic of possible reaction mechanisms.[13]

During operation of a fixed-bed adsorption column the service time of the system can be related to the bed depth for a given set of experimental conditions. The initial solute (pollutant) concentration fed to the column, is desired to be reduced in the final effluent to a pre-determined value, usually imposed by the respective environmental regulation laws. At the beginning of sorbing operation, when the sorbent material is still unused, the exit concentration is actually lower, than the permitted one. As sorption proceeds and the sorbent material is being gradually saturated, the effluent concentration increases and reaches the so-called "breakthrough" point. Various methods for the designing of fixed-bed columns have been suggested, such as the length of unused bed (LUB) theory, the empty bed residence time procedure, etc., as reviewed in reference.[14] The respective theory for the model as applied to gas adsorption was also presented.[15]

The modelling of metals sorption on goethite fixed-beds was earlier reported[16]; hexavalent chromium oxyanions and zinc cations in presence also of complexing agents were tried. The Bed Depth-Service Time (BDST) model has been applied to the experimental results. Goethite was initially synthesized according to a standard method, from ferric nitrate nonahydrate dissolved in ammonia solution and aged in potassium hydroxide. The resulted powdered material was subsequently granulated/crystallized (following a method developed at the Technical University of Berlin by Driehaus).[16] During previously performed batch equilibrium experiments the maximum adsorption capacity for granulized goethite was found for Cr(VI) and for Zn(II).[17]

A solid diffusion controlled process was used to describe the fixed bed operation in another case.[18] Also, apart from the BDST, a mass transfer model, the Thomas model and the Yoon-Nelson one have been tried elsewhere.[19] In fact, the original work on the BDST model is from a long way back in 1920, carried out by Bohart and Adams.[20]

The major aim when sizing adsorptive columns is the ability to predict the service time until the column effluent exceeds a pre-defined solute (pollutant) concentration. The Bed Depth-Service Time model relates the service time of a fixed-bed with the height of adsorbent in the bed, hence with its quantity, because quantity is directly proportional to the bed height. The measurement of sorbent quantity is more precise than the determination of the respective volume, especially for the case of granules. Therefore, sorbent quantity is being preferable used, instead of the bed height. An appropriate equation was proposed by Chang and Ku.[21]

Despite the apparent simplicity of fixed beds they are difficult to design accurately because the progress of the mass transfer zone (MTZ) introduces time into the equations.[22] To solve the problem rigorously it is necessary, in most practical applications, to solve sets of partial differential equations that describe the mass and heat transfer phenomena. Several short-cut design techniques exist but they can vary considerably in their accuracy. The uncertainties, which arise and the simplifications that are often required inevitably introduce conservatism into the bed sizing calculations. In turn, this leads to equipment sizes and adsorbent inventories being larger than the minimum requirements.

It is fortunate that in most fixed bed adsorption processes of commercial interest the shape of the mass transfer zone remains unaltered as it progresses through the majority of the bed, because this leads to substantial simplifications in design. For a favourable isotherm, particularly one of Type I, the mass transfer wave spreads from shock front as it progresses through the initial region of the bed. The shape of the isotherm causes the MTZ to take an asymptotic pattern form and become stable at some distance from the inlet. For the BDST method the assumption is that the adsorption rate is proportional to both the residual adsorbent capacity and the remaining adsorbate concentration. This equation, which describes in general how the MTZ progresses through a single fixed bed of adsorbent, can be adapted to include series of fixed beds and moving bed systems.[22]

The application of different flowrates of wastewater through the column can be calculated by multiplying the original slope by the ratio between the original and new flowrate, because changing the flowrate linearly is not expected to have any effect on the ordinate intercept.[23] A variation in feed concentration of metals can be determined by performing some correcting calculations according to Hutchins[24]; so, various modifications of the BDST model exist. Correlation of the model incorporating a time-dependent term has been developed by McKay and his coworkers.[25] The typical (from gas absorption, distillation, extraction etc.) transfer unit approach, with NTU and HTU, was also applied for the case.[14,22]

4. Discussion of Results

In recent years, contamination of ground and surface waters with heavy metals has become a major concern. The knowledge of the oxidation state of pollutant ions is often a prerequisite for the application of efficient treatment methods, as in the case of arsenic. The inhibition of conventional metal precipitation, due to the presence of chelating or complexing compounds, as acetate, citrate and tartrate ions, ammonia, EDTA etc., which may be present in most real wastewater streams, is another problem for examination. Thermodynamic equilibrium diagrams and software packages (such as Mineql+) have been employed to construct aqueous speciation diagrams for the metals under investigation and then, interpret the removal mechanism involved.

The chemical speciation was presented for an aqueous solution containing simultaneously hexavalent chromium and EDTA species. Although an interaction between Cr(VI) and EDTA species is not feasible, it can be suggested, based on their distribution, that a strong competition for the same sorption sites is possible to take place between CrO_4^{2-} and $EDTAH_2^{2-}$ anions. This competition results to lower efficiency regarding the adsorption of chromate in the case of the Cr(VI)/EDTA mixed solution, comparing to single Cr(VI) solution. Inversely, in the case of Zn(II) aqueous solution the addition of EDTA caused an increase of adsorption efficiency.[16] Same conclusion was found for chelated copper.[21]

The contact time, a major design parameter, is usually expressed as the empty bed residence time, EBRT or EBCT.[25] From the iso-removal lines, being inplots in the figure, regarding column operation under constant experimental conditions (except of sorbent dosage), the main parameters of BDST equation can be calculated. From the slope of the lines the adsorption capacity can be calculated, while from the intercept the rate constant of adsorption. From the respective linear equation, the necessary quantity of sorbent for a pre-selected service time period can be directly calculated until a defined breakthrough concentration. The results of performed experiments are usually summarized in the form of a table.[16]

In order to obtain the full bed capacity, the value at 50% breakthrough is often used, based on the approximate assumption that the S-shaped breakthrough is symmetrical about the 50% breakpoint. However, this is frequently not the case and can be due to a number of causes, such as irreversibility of the sorption process at high sorbent solid-phase loadings, uneven flow patterns through the bed and the system may take a long time to reach equilibrium. Special care should be exercised when determining the applicability of short-cut methods for a particular design problem.[22]

Column experimental data in terms of COD for a textile industry effluent have been correlated using the BDST model.[26] The results from the model were then used to design a pilot adsorption rig at the plant. The performance of the pilot plant column was accurately predicted by scale-up from the bench scale columns. Elsewhere,[27] the service time of adsorbent beds (of calcined bauxite) under different flow rate and influent concentration of arsenates were predicted also using the BDST model and were compared with experimental observations; the observed data on service time and breakthrough curve correlated well with the theoretical values.

The possibility of using a packed-bed (in column configuration) of akaganéite to remove oxyanions like As(V) and cations like Cd from aqueous solutions was the aim of an aforementioned study.[5] Synthesized akaganéite was used in two forms, i.e. in fine powder (of nanocrystals) and in the form of grains (as granular). A comparison was also made for goethite, a material with surface area of 130 m^2 g^{-1}. Akaganéite presented a greater adsorption capacity than that of goethite, although the pH of the treated solution in the case of goethite was adjusted to 3.5 or 5.

The BDST model, finally, was found to be a simple but effective methodology for designing and controlling the removal of toxic ions for waters. Empirical (short-cut) methods are still used extensively for the design of fixed beds.

Acknowledgements Many thanks are due to Martin Lehmann for his collaboration and help, mainly during the early part of the work in this scientific field.

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REMOVAL OF ARSENIC FROM DRINKING WATER - CROATIAN EXPERIENCE

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Abstract The groundwater of northern Croatia usually contains high concentrations of iron, manganese, ammonia and arsenic, and is therefore unsuitable for use as drinking water without the appropriate treatment. The existing water treatment plants in this area, applying conventional biofiltration methods, remove iron, manganese and ammonia efficiently, but arsenic, appearing at concentration levels as high as 300 μg/L, is not removed. Thus, a simple and widely applicable water treatment procedure for the simultaneous removal of arsenic is needed. To find the most suitable water treatment procedure, several technologies employing adsorption, ion-exchange, and membrane processes were tested. A number of laboratory-scale and pilot-plant field experiments were performed on typical groundwater from numerous locations of northern Croatia. The results of the experiments undoubtedly indicate that the simplest and most efficient arsenic removal process from ground water is the adsorption of arsenic on iron(III) hydroxide. Moreover, this process is simply implemented on the existing water treatment facilities, ensuring that the arsenic concentrations in the effluent are as low as $\gamma(As) < 10$ μg/L.

Keywords: Groundwater; arsenic removal; water treatment

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

1. Introduction

The groundwater of northern Croatia usually contains high concentrations of iron, manganese, ammonia, and arsenic, and is therefore unsuitable for use as drinking water without appropriate treatment. Several water treatment plants are presently in operation, mainly constructed 20–30 years ago. These plants generally, applying conventional aeration and bio-filtration processes, eliminate iron, manganese, and ammonia efficiently. However, arsenic, appearing at concentration levels as high as 300 μg/L, is not removed sufficiently. Thus, a simple and widely applicable water treatment procedure for the simultaneous removal of arsenic on the existing treatment plant is needed. Moreover, the capacity of existing water treatment facilities is inadequate and plans for construction of additional plants are necessary. The question is which technologies should be used at the new water treatment plants?

To define the most suitable and widely applicable water treatment procedure for the typical groundwaters of northern Croatia, numbers of laboratory experiments and extensive field studies, on the existing treatment plants and/or pilot plants, were performed.[1–3] The intention of this paper was to present part of the experience collected during the last two decades working on the problems of simultaneous iron, manganese, ammonia, and arsenic removal from groundwaters in Croatia. Consequently, this paper will give an overview of new concepts used in water treatment processes, based on conventional, as well as advanced, procedures.

2. Experimental

Standard laboratory glassware, equipment, and separation columns volume of 15 mL were used for the laboratory scale experiments.

The pilot-plant used in field experiments, enabling open or closed aeration and filtration at flow rates 0.05 L/s, is presented schematically on Figure 1. The pilot plant was equipped with microprocessor-based control systems providing autonomous operation, chemical dosing, and data acquisition functions.

The general chemical parameters of the water, such as alkalinity, total hardness, calcium, magnesium, etc., were determined using standard analytical methods.[4] The concentrations of iron, manganese, and arsenic were determined spectrophotometricaly with 1,10 phenantroline[4], PAN[5] and silver diethyldithiocarbamate,[4] respectively, or by using ICP-MS

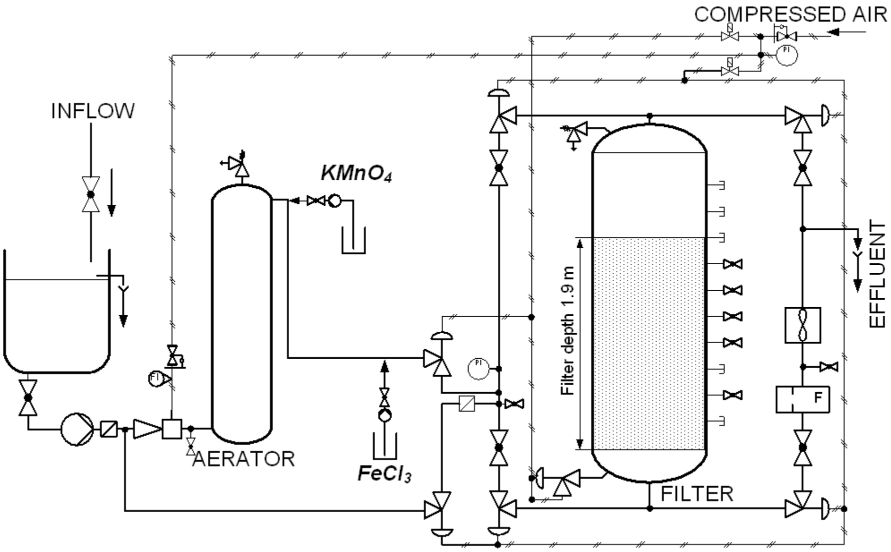

Figure 1. Schematic of pilot plant used in field experiments

(Perkin Elmer, ELAN DRC-e) according to US EPA method 200.8.[6] Ammonium was determined spectrophotometricaly by the method according to Wagner.[7] A field spectrophotometer (HACH, Model DR2000) was used for the spectrophotometric measurement.

3. Results and Discussion

The characteristic composition of groundwaters of northern Croatia is summarized in Table 1. Evidently, the groundwaters of the whole area contain elevated concentration of iron, manganese, and ammonium. However,

TABLE 1. Characteristic composition of groundwaters of northern Croatia

	Location				
Parameter	Ravnik	Požega	Vinkovci	Osijek	MCL
Temperature, t/°C	13.4	11.2	13.1	16	<25
pH	7.34	7.29	7.24	7.72	6.5–8.5
COD, γ(O2)/mg/L	2.21	0.91	0.88	4.01	3
Iron, γ(Fe)/mg /L	1.48	0.01	0.53	1.2	0.2
Manganese, γ(Mn)/mg/L	0.23	1.02	0.15	0.09	0.05
Ammonia, γ(NH3)/mg/L	0.87	0.03	0.38	2.01	0.5
Arsenic, γ(As)/µg/L	n.d.	n.d.	0.08	277	0.01

occasional arsenic is present, too. Thus, the best available technology for the removal of iron, manganese, and ammonia has to be defined in a way that is capable of removing arsenic as well.

3.1. REMOVAL OF IRON, MANGANESE, AND AMMONIUM FROM GROUNDWATER

The existing water treatment plants of northern Croatia, applying conventional aeration and bio-filtration processes, efficiently eliminate iron, manganese and ammonia. Moreover, for the water containing ammonia, the applied biological process seems to be the only reliable solution. Thus, there is no need to look for some other process solutions.

The process of nitrification, the microbial process of ammonium oxidation, is especially important in groundwater treatment. The process has two stages. In the first stage, ammonium is converted into nitrites, with the aid of a group of bacteria known as *Nitrosomonas*. Subsequently, the nitrites are converted into nitrates with a different group of bacteria, the *Nitrobacter*. These processes can be represented by the chemical equations[8,9]:

$$NH_4^+ + 1.5\ O_2 = NO_2^- + 2\ H^+ + H_2O$$

$$NO_2^- + 0.5\ O_2 = NO_3^-$$

The nitrification is followed by the reduction of the alkalinity of water. For each mole of NH_4^+ that oxidizes to NO_2^-, approximately 2 mol of HCO_3^- are used.[8,10–12] This means that the alkalinity of water is reduced by that corresponding value and that pH is changed. This is important for nitrification. Change in pH can be so significant as to limit the process of nitrification, or even to stop the process completely in relatively "soft" waters. However, due to relatively high alkalinity of the groundwaters of northern Croatia, pH is not significantly changed.

It is important to note that in practice, ammonium oxidation represents a limiting stage of the entire process.[9,10] This means that nitrites will not appear in larger quantities when the whole process is well established.

The growth and metabolism of autotrophic nitrifying bacteria is optimal in neutral to slightly alkaline region (pH = 7–8), the natural pH range of the groundwaters of northern Croatia (Table 1). However, pH region for complete nitrification is strictly limited to *Nitrobacter*, due to the toxicity of both, free ammonium (in the alkaline pH region) and nitrous acid (in the acidic pH region).[13]

During the biological nitrification processes relatively large quantities of oxygen is consumed. Theoretically, for 1 mol of ammonium ion (NH_4^+) to oxidize into a nitrate ion (NO_3^-), two oxygen molecules (O_2) are used. This means that by removal of 1 mg/L NH_4-N, 4.6 mg/L of oxygen is consumed.[14]

Obviously, microorganisms also participate in the oxidation processes of iron(II) and manganese(II) removal. The microorganisms of the genus S*iderocapsa* seem to have the most significant role.[1,2,15] This is especially important for manganese oxidation because chemical, as well as chemical-catalytic oxidation of manganese with oxygen is an extremely slow process at the natural pH < 8 of the groundwater.[16]

The overall processes of iron and manganese removal is represented by the equations:

$$4\ Fe^{2+} + O_2 + 10\ H_2O\ =\ 4\ Fe(OH)_3 + 8\ H^+$$

$$2\ Mn^{2+} + O_2 + 2H_2O\ =\ 2\ MnO_2 + 4H^+$$

Based on the stoichiometric relations in the above equations, one can conclude that the removal of 1 mg/L of iron and manganese use up 0.14 and 0.29 mg/L of oxygen, respectively.[17] Thus, the amount of oxygen used in iron and manganese removal is relatively small when compared to 8–9 mg/L O_2 in water aerated by air. Namely, the concentration of iron and manganese in groundwater rarely exceeds 5 and 0.2 mg/L, respectively.

Concerning oxygen consumption, the presence of ammonium in groundwater is obviously the most critical. As noted above, 1 mg/L NH_4-N uses 4.6 mg/L O_2. If groundwater concentration of ammonium exceeds 1 mg/L NH_4–N, which is often the case in northern Croatia, insufficiency of oxygen in bio-filers may occur. Thus, the treatment plants differ depending on the concentration of ammonium in groundwater. At ammonium concentrations <1 mg/L NH_4–N, the simple open system of aeration and gravitational filtration can be used. At ammonium concentrations >1 mg/L NH_4–N, the closed system of pressurized aeration and filtration, ensuring sufficiently high oxygen concentration, is necessary.

In both cases, the process is performed in relatively simple facilities consisting of an aerator and a biological filter (Figure 2). Filtration rates usually range from 5 to 12 m/h. However, in special cases, filtration rates as high as 20 m/h may be used.

Extensive studies using pilot plants[2] shows that the majority of the iron, manganese and ammonium removal processes takes place in the upper filter layers. Typical concentration profiles across the bio-filter for some of the constituents are presented on Figure 3. The shape of the curves obtained could be described by Eq. 1:

$$\frac{C_A}{C_{Ao}} = \exp\left(- \frac{k}{U^n} * L \right) , \qquad (1)$$

where C_{Ao} is the initial concentration of substance A; C_A, is the concentration of substance A at depth L/m of the biological filter; and U/m*h^{-1}, is the filtration rate. Thus, based on the experimental data, the rate constants k and n, could be determined as shown in Table 2.

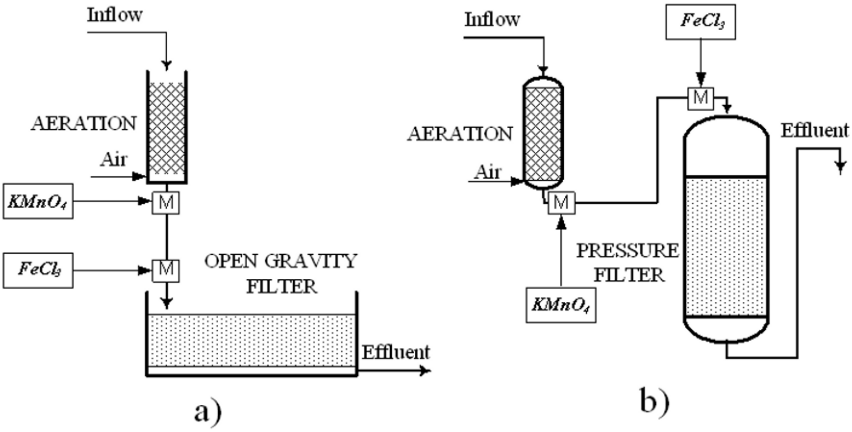

Figure 2. Single stage iron, manganese, and ammonium removal facility (without $KMnO_4$ and $FeCl_3$ dosing), with simultaneous removal of arsenic (with $KMnO_4$ and $FeCl_3$ dosing): (a) open aeration system; (b) closed, pressurized aeration and filtration system

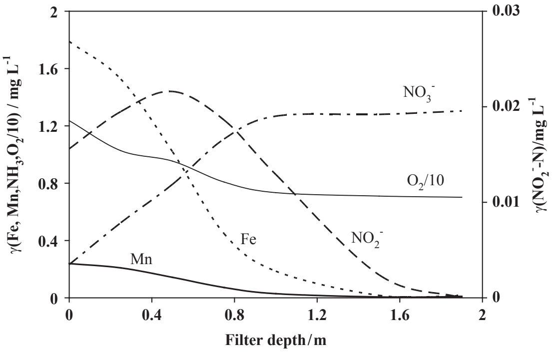

Figure 3. Concentration profiles of iron, manganese, ammonium, nitrite, nitrate and oxygen in the bio-filter

TABLE 2. The values of rate constants k and n of Fe, Mn, and NH_3 concentration profiles (Eq. 1) in a biological filter.[2] Water temperature 11–15°C

Substrate	Fe	Mn	NH_3
k h	294	30.2	27.9
N	1.53	0.74	0.65

Equation 1 and data from Table 2 can by used for optimal filter bed design, depending on the initial substrate concentration, filtration rate and desired removal efficiency.

3.2. REMOVAL OF ARSENIC FROM GROUNDWATER

Arsenic can efficiently be removed from groundwater through adsorption to iron(III) hydroxide. The effect of adsorption is greater for arsenic(V) than for arsenic(III). Since arsenic is present in groundwater in the arsenic(III) form, the first stage of the process is to oxidize arsenic(III) to arsenic(V), usually with solution of $KMnO_4$. In the second stage of the process, iron(III) chloride is added to form iron(III) hydroxide for adsorption of arsenic. Then, the iron(III) hydroxide formed, together with the adsorbed arsenic, is removed in a filtration step.[18–21] Consequently, arsenic can be efficiently removed, simultaneously with iron, manganese and ammonia using single stage bio-filtration. However, the plants have to be equipped with dosing systems for solutions of $KMnO_4$ and $FeCl_3$ as schematically presented on Figure 2.

The advantage of the process is in its simple installation to existing and/or new plants for iron, manganese and ammonium removal.[22] Several groundwater treatment plants in Croatia were put in operation during the last decade (Vinkovci, Osijek, Gradište) and successfully uses the described process. Typical arsenic concentrations of the effluent in dependence on the iron(III) chloride doses at the water treatment plant Osijek, are shown on Figure 4. Evidently, arsenic concentrations $\gamma(As) < 50$ µg/L of the effluent are easily obtained by addition 4–5 mg/L Fe (in form of iron(III) chloride) into raw groundwater, containing as high as 200–300 µg/L arsenic. However, the concentration of the arsenic in the effluent should be as low as $\gamma(As) < 10$ µg/L. Obviously, the iron(III) chloride doses have to be increased. Alternatively, possible further measures should be examined to increase the efficiency of arsenic removal to concentrations $\gamma(As) < 10$ µg/L, while avoiding significant increase in iron(III) chloride use.

Several other technological solutions, as finishing treatment steps, were examined, including: application of membrane technologies, ion exchangers, as well as some commercially available arsenic absorbers.

The application of hollow fiber ultra filtration membranes (Zenon ZeeWeed 500) was found to be very promising. However, presiding the ultrafiltration, additional adsorption step, by addition 2–3 mg/L Fe (in form of iron(III) chloride) have to be applied.

The use of ion exchangers (Lewatit S6328A, Bayer) ensures excellent quality of the effluent, especially short after the regeneration step, as shown on Figure 5. Unfortunately, the breakthrough of 10 µg/L arsenic appears at relatively low bead volumes (BV), and is extremely influenced by the composition of groundwater.

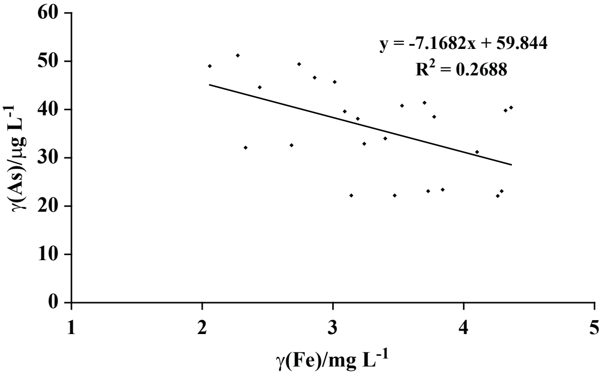

Figure 4. Arsenic concentrations of the effluent in dependence on the iron(III) chloride doses at the water treatment plant Osijek

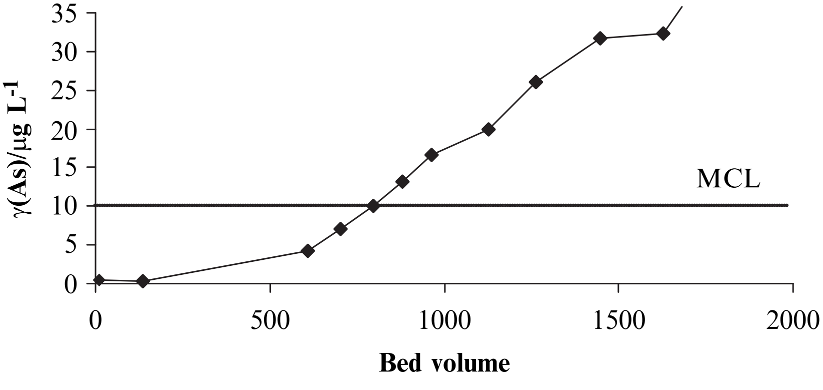

Figure 5. Typical arsenic breakthrough curve of ion exchanger Lewatit S6328A, Bayer

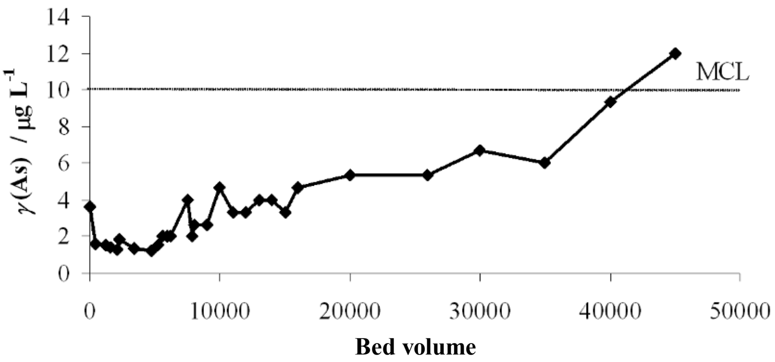

Figure 6. Typical breakthrough curve for arsenic removal on Bayoxide E33, Bayer

Similarly to ion exchangers, the capacity of the commercially available arsenic removal mass, Bayoxide E33 from Bayer, is largely influenced by the composition of groundwater treated. In natural conditions, the breakthrough of 10 μg/L As may appear already at BV as low as 40,000, as shown on Figure 6. This material becomes quickly saturated, thus requires replacement in relative short time intervals.

Obviously, the mentioned alternative procedures of arsenic removal require additional cost-intensive capital investments. Besides this, they are followed with significant operational costs as well. Thus, the mentioned alternative technological solutions seem to not be the best choice.

Returning back to the problem of arsenic removal by adsorption on iron(III) hydroxide, a few questions are still waiting for answers. First, what is the efficiency limit of the process and how is it reached? Or, in a more practical point of view, how are arsenic concentrations $\gamma(\mathrm{As}) < 10$ μg/L obtained in the effluent using as low as possible quantities of iron(III) hydroxide for adsorption?

The Freundlich equation for describing arsenic adsorption is:

$$\frac{X_{As}}{m_{Fe}} = K * [As]^{1/n} \qquad (2)$$

where: X_{As} represents the amount of arsenic removed; m_{Fe} is the amount of iron used for adsorption; [As] is the concentration of arsenic in the effluent; and K and n have constant values. Using this equation with value of $n = 1$, and value of $K = 0.00186$ L/μg, determined experimentally, the adsorption process was simulated at different conditions. The results of the calculations confirmed the applicability of a multi-step adsorption process with iron(III) hydroxide for arsenic removal – far below the concentration limit of γ(As) = 10 μg/L. This was experimentally also confirmed using pilot-plants. Arsenic concentrations γ(As) < 5 μg/L were obtained treating groundwater, containing γ(As) = 300 μg/L, in a three-step adsorption process, consuming only 4–5 mg/L Fe.

4. Conclusion

The results of the experiments undoubtedly indicate that the simplest and most efficient arsenic removal process from ground water is the adsorption of arsenic on iron(III) hydroxide. This process has been successfully implemented on some of the existing water treatment facilities in Croatia, ensuring that the arsenic concentrations in the effluent are γ(As) < 50 μg/L. Moreover, arsenic concentrations in the effluent, as low as γ(As) < 10 μg/L, can be most simply obtained by applying a multi-step adsorption process using iron(III) hydroxide.

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ARSENIC OXIDATION BY MEMBRANE CONTACTORS

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Abstract This chapter deals with the potential of membrane contactors for the oxidation of As(III) with air. In particular, experiments carried out on a flat membrane module of 40 cm^2 of membrane area, equipped with a polypropylene membrane of 0.2 μm pore size, are presented and discussed. Oxidation experiments have been also performed without using membranes by: (1) stirring the water stream; (2) introducing air/oxygen into the water stream through a tube; (3) introducing air/oxygen into the water stream through a porous unit. With respect to the different systems analysed, membrane contactors lead to lower mass transport resistances in the liquid phase, significantly reducing the times for oxidation.

Keywords: Arsenic; membrane contactors; water treatment

1. Introduction

Arsenic is a well-known toxic species and its content into water has to be carefully controlled. The WHO has, in fact, fixed a maximum arsenic content in drinking water of 10 ppb in order to reduce health risks. Worldwide, different are the countries affected by the problem of arsenic

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

contaminated waters, such as Bangladesh, India, Chile, China, Argentina, Mexico, Taiwan, etc.

In water arsenic can be present both as As(III) and As(V). The trivalent form of arsenic is the most toxic and also the most difficult to remove. Many of the employed techniques are, in fact, more effective for the removal of arsenic in its pentavalent form, while giving a lower efficiency of removal for arsenite. Therefore, a pre-oxidation step to convert As(III) into As(V) is often needed before the arsenic removal step. Different are the oxidation agents that can be used for this purpose. Based on the fact that often surface waters have a higher content of As(V), whereas in groundwaters As(III) prevails, air could be considered as a good oxidation agent. However, only air is not preferred because the oxidation rate achievable is generally slow, whereas it can be enhanced by the presence of dissolved iron and irradiation with ultraviolet light.[1–4] For example, Lowry and Lowry[4] compared three different systems of aeration of water containing arsenic: spray aeration, staged bubble aeration and packed tower aeration. In each case, they performed the aeration over 6 h period and, after, they stored the aerated water for 5 days. For all the systems analyzed, they did not obtain a significant oxidation of the arsenite.

Based on the above considerations, often the oxidation is achieved by using agents such as ozone, hydrogen peroxide, chlorine, which, however, have the main disadvantage of being a health hazard as well, if not properly monitored and managed. Oxidation can be also carried out with manganese oxides with the issue that solid manganese compounds can be formed.

The aim of this contribution is to investigate the potential of membrane contactors for the oxidation of As(III) with air. It is expected, in fact, that by membrane contactors it should be possible to operate with lower mass transfer resistances at the aqueous side with respect to traditional aeration systems, with a consequent improvement of the oxygen transport in the liquid and a reduction of the oxidation time. Membrane contactors are membranes-based systems where microporous, and often hydrophobic membranes are used to promote the mass transfer between phases. They find successful applications in different fields of industrial productions, especially in the electronic, food and beverage sectors.[5] In this work, experiments have been carried out on a flat membrane module of 40 cm^2 of membrane area, equipped with a polypropylene membrane of 0.2 μm pore size. Oxidation experiments have been also carried out without membranes by: (1) simply stirring the water stream; (2) introducing air/oxygen into the water stream through a tube; (3) introducing air/oxygen into the water stream through a porous unit.

The effect of different operating conditions on the efficiency of the process has been analyzed and the degree of oxidation achieved, as well as the operating time needed, have been compared for all the tested systems.

2. Materials and Methods

In this section information on the materials and oxidation systems used for carrying out the experiments, as well as on the analytical methods employed for monitoring the As(V), formation are reported.

2.1. PREPARATION OF THE FEED SOLUTIONS

The feed solutions consisted of distilled water and As(III) and have been prepared starting from 1 L of "mother solution" containing 100 ppm of As(III). The distilled water was previously deareated, in order to avoid any possible oxidation before the tests.

2.2. OXIDATION SYSTEMS

Four different systems for aerating the feed solution have been studied, as reported below.

2.2.1. *Injection Through a Tube*

Air is added in the liquid through a tube directly connected to the gas bottle (see Figure 1a). The system has been used also for performing some tests with pure oxygen.

2.2.2. *Injection Through a Porous Unit*

A porous unit, connected at the end of the tube coming from the gas bottle, is immersed in the feed solution (see Figure 1b). Tests with both air and oxygen have been made with this set-up.

2.2.3. *Stirring*

The feed solution is continuously stirred by a magnetic stirrer (see Figure 1c).

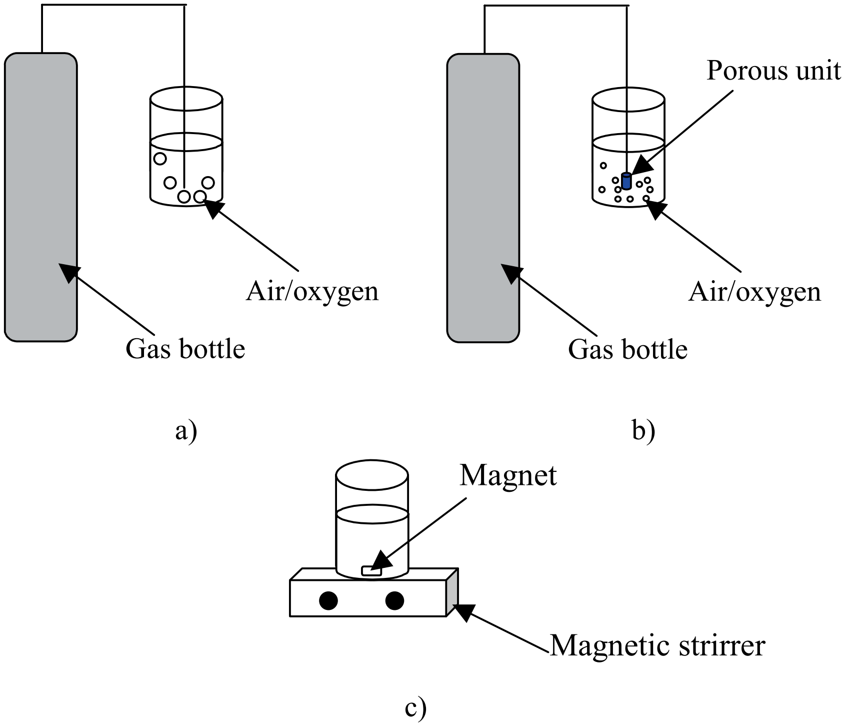

Figure 1. Oxidation systems used: (**a**) injection through a tube; (**b**) injection through a porous unit; (**c**) stirring

2.2.4. *Aeration by Membrane Contactors*

The lab set-up used for carrying out the tests with membrane contactors is shown in Figure 2. It consists mainly of a flat membrane module, a peristaltic pump for re-circulating the feed stream, a tank containing the feed, jacket for controlling the temperature, a thermometer for measuring the temperature of the feed solution, manometers for measuring the feed and gas pressures, a flow meter for measuring the air flow rate.

In the membrane module it is sandwiched a flat sheet of a microporous hydrophobic membrane purchased by Membrana, Germany (material: polypropylene, pore size: 0.2 μm, thickness: 91 μm). The effective membrane area inside the module is of 40 cm^2. The feed solution is re-circulated to the module at the desired flow rate and, when the desired operating temperature is reached, the air stream is sent in counter-current flow mode, so that the experiment starts.

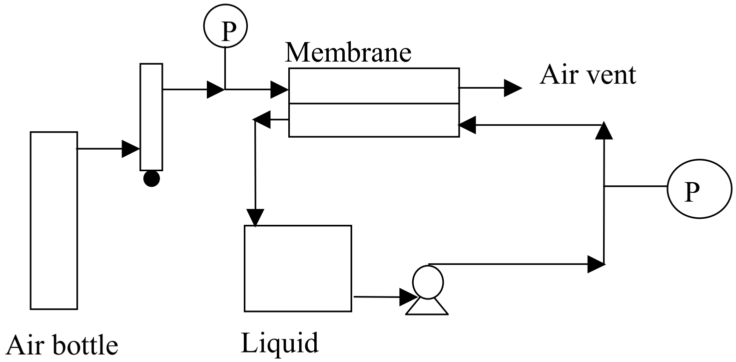

Figure 2. Membrane contactors lab set-up

Due to the hydrophobicity of the membrane, the aqueous phase can not penetrate through the micropores and the interface between air and water is established at each pore mouth. Therefore, the air, after diffusing through the micropores, reaches the liquid stream at the pore mouth and the contact between the two phases is established (see Figure 3).

From the interface, the oxygen contained into the air has to dissolve into the aqueous feed and to diffuse towards the liquid bulk, so that it can be able "to meet" the As(III) present and to react with it.

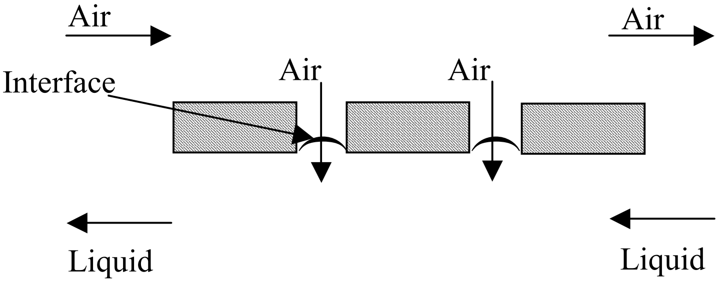

Figure 3. Liquid aeration through the membrane micropores

2.3. ANALYTICAL METHODS

The total arsenic content into the feed solution has been determined by ICP-OES (Perkin Elmer), whereas the content of the As(V) produced has been obtained by a spectrophotometer (UV-160, Shimadzu). In particular, a colorimetric method has been used for preparing both samples and standards[6] and the absorbance has been measured at 840 nm.

3. Results and Discussion

The main results of the oxidation tests carried out on the four oxidation systems are presented and discussed in the following part. During the experiments the performance of the systems at different operating conditions has been analyzed. Figure 4 shows the oxidation degree achieved in time with the injection of air through a tube for two feed concentrations of As(III). For a content of As(III) of 0.5 ppm, no oxidation is obtained, while a 2% of oxidation is registered after 16 h for a content of 0.25 ppm.

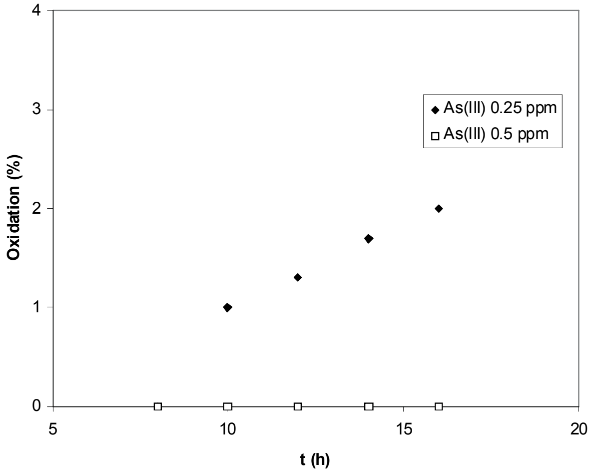

Figure 4. As(III) oxidation with time as function of the feed concentration. Injection of air through a tube. Q_{air}, 37 L/h; P_{air}, 1 bar; V_{feed}, 40 ml; pH, 3; T, 15°C

The effect of the feed volume on the oxidation degree is reported in Figure 5. The lower are feed volumes the higher is the oxidation, reaching values of 22% at 16 h and 54% at 40 h.

The performance of the injection through a tube is compared to that of the injection through a porous unit in Figure 6. At the same operating conditions, by aerating the feed through the porous unit it is possible to increase the oxidation degree (a value of 4% is obtained after 8 h against the 2% achieved in 16 h by the aeration through a tube). This result could be attributed to the better dispersion of air bubbles, which are smaller and in a higher number, leading to a better transfer of air inside the feed solution, with a reduction of the oxidation time.

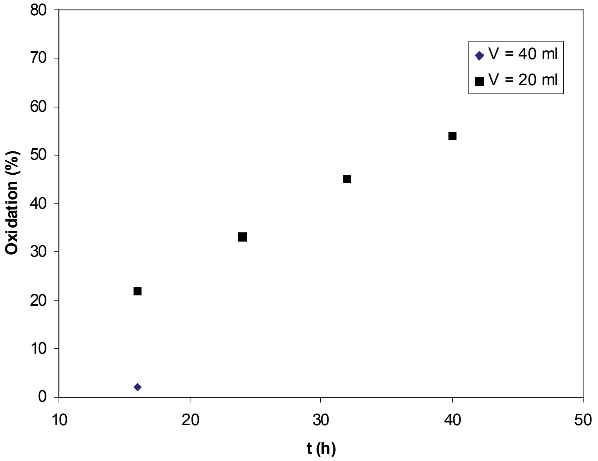

Figure 5. As(III) oxidation with time as function of the volume of feed. Injection of air through a tube. Q_{air}, 37 L/h; P_{air}, 1 bar; $C_{As(III)}$, 0.25 ppm; pH, 3; T, 15°C

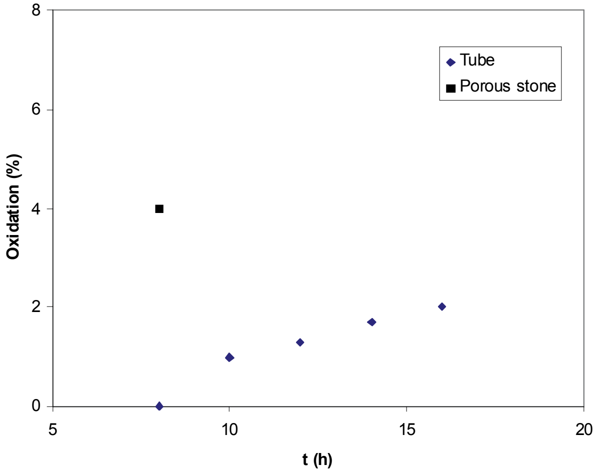

Figure 6. As(III) oxidation with time for the two injection systems analyzed. Q_{air}, 37 L/h; P_{air}, 1 bar; $C_{As(III)}$, 0.25 ppm; V_{feed}, 40 mL; pH, 3; T, 15°C

By using pure oxygen instead of air, a higher oxidation degree is obtained with both systems (see Figure 7). In particular, with the injection through a tube, 5% of oxidation is reached after 16 h, whereas by using the porous unit an oxidation of 25% is obtained already after 8 h. The increase in the oxidation degree is more significant for the porous system, indicating that the injection through a tube is not an efficient way for promoting the mass transport inside the feed solution.

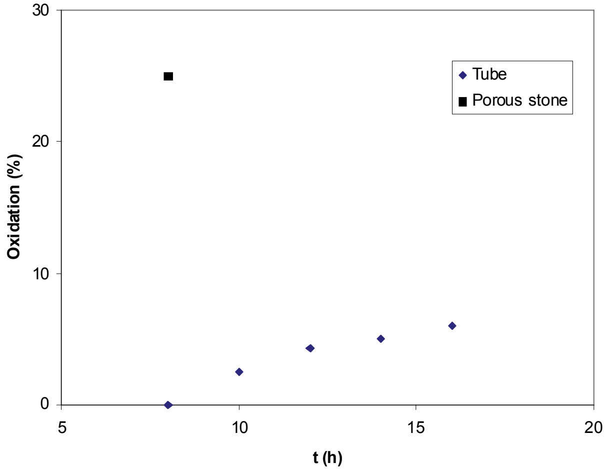

Figure 7. As(III) oxidation with time for the two injection systems analyzed. Q_{oxygen}, 37 L/h; P_{oxygen}, 1 bar; $C_{As(III)}$, 0.25 ppm; V_{feed}, 40 mL; pH, 3; T, 15°C

Tests at two different values of pH have been carried out by injecting oxygen through the porous unit and are reported in Figure 8. Lower pHs seem to favor the oxidation process.

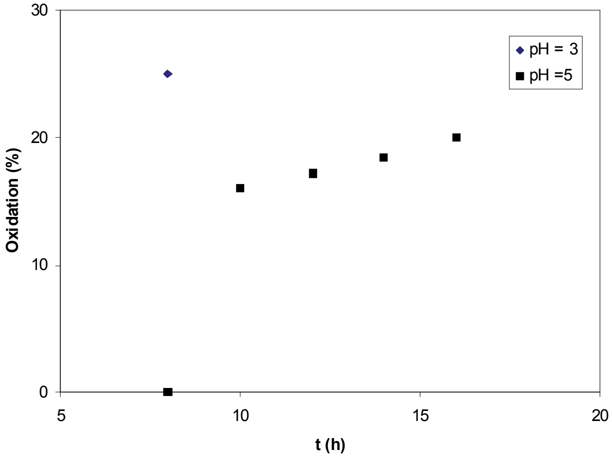

Figure 8. As(III) oxidation with time as function of the feed pH. Injection of oxygen through a porous unit. Q_{oxygen}, 37 L/h; P_{oxygen}, 1 bar; $C_{As(III)}$, 0.25 ppm; V_{feed}, 40 mL; T, 15°C

The effect of the operating temperature is shown in Figure 9 for the stirring tests. Lower temperatures increase the solubility of the air into the feed and, therefore, the quantity of oxygen available for the reaction.

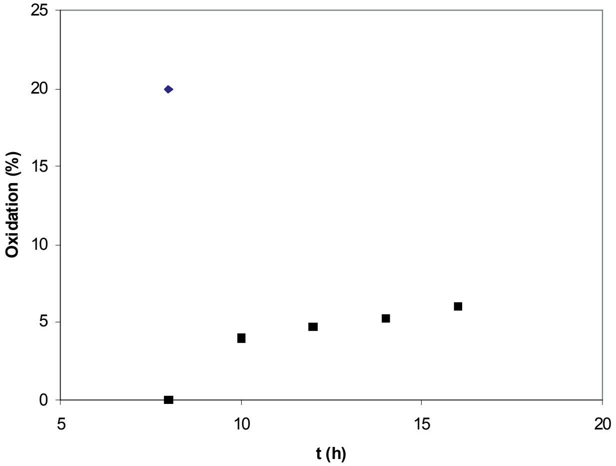

Figure 9. As(III) oxidation with time as function of the temperature. Stirring test. $C_{As(III)}$, 0.25 ppm; V_{feed}, 40 ml; pH, 3

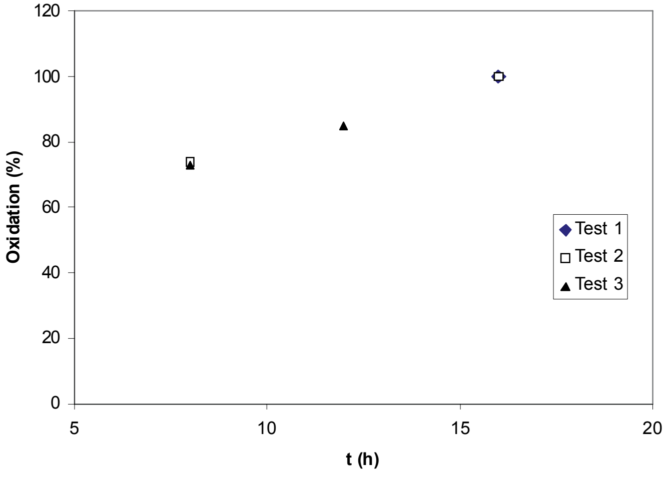

Figure 10. As(III) oxidation with time by membrane contactors. Q_{air}, 37 L/h; P_{air}, 1 bar; Q_{liq}=Q_{max}, 40 L/h, $C_{As(III)}$, 0.25 ppm; V_{feed}, 40 mL; pH, 3; T, 15°C

With membrane contactors tests have been made using only air as oxidant agent. The liquid flow rate was always set to the maximum value possible for the lab set-up used (40 L/h). In Figure 10 are reported the results of three set of experiments, carried out at the same operating conditions to verify their reproducibility. In particular, the data refer to the analysis of samples taken after 16 h (test 1), after 8 and 16 h (test 2) and after 8 and 12 h (test 3). The oxidation values are practically coincident for the three tests and, already after 8 h a 73% of oxidation is achieved, becoming complete after 16 h.

By increasing the feed volume there is a decrease of the oxidation degree, as previously observed (see Figure 11).

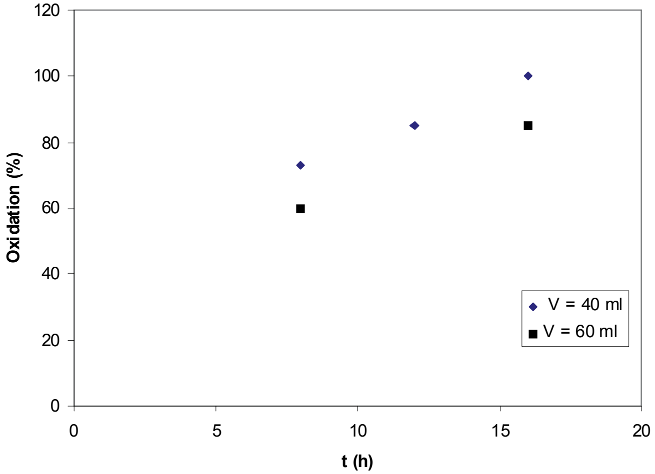

Figure 11. As(III) oxidation as function of the feed volume. Membrane contactors. Q_{air}, 37 L/h; P_{air}, 1 bar; Q_{liq}=Q_{max}, 40 L/h, $C_{As(III)}$, 0.25 ppm; pH, 3; T, 15°C

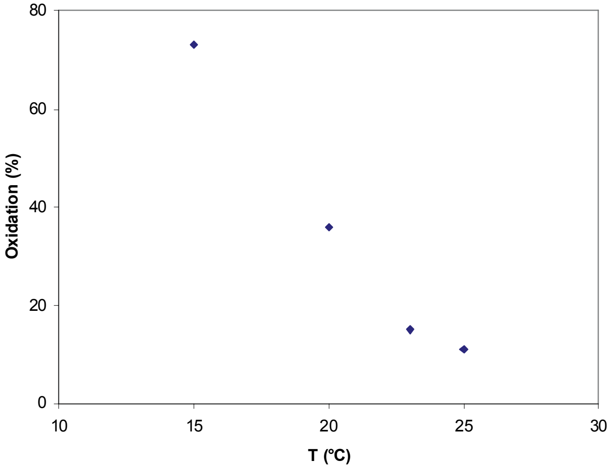

Figure 12. As(III) oxidation as function of the temperature. Membrane contactors. Q_{air}, 37 L/h; P_{air}, 1 bar; Q_{liq} = Q_{max}, 40 L/h, $C_{As(III)}$, 0.25 ppm; V_{feed}, 40 mL; pH, 3

The oxidation degree as function of the temperature for 8 h of test, is shown in Figure 12. As already stated, lower temperatures led to higher oxidation degrees (73% at 15°C against 11% at 25°C).

Figure 13 compares the four systems used for the As(III) oxidation. Best results are achieved with membrane contactors, while the worst are those of the injection of air through a tube. The oxidation degree increases when oxygen is used, and this increase is more significant when the injection is made through the porous unit. Finally, the stirring gives similar values of the oxygen injection through the porous unit.

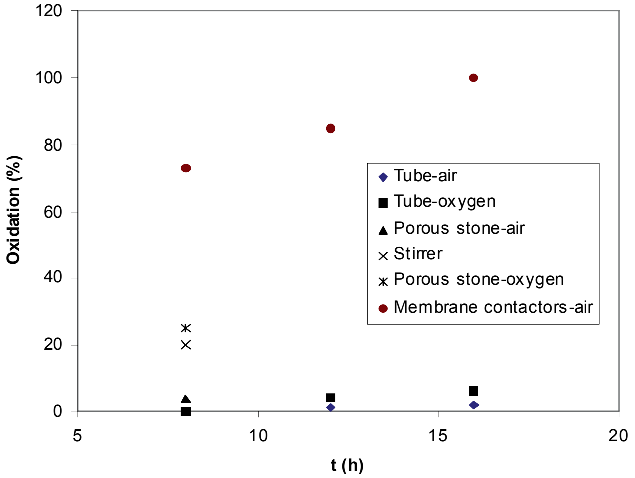

Figure 13. Comparison among the four oxidation systems analyzed. Q_{air}= Q_{oxygen}, 37 L/h; P_{air}= $P_{oxygenr}$, 1 bar; Q_{liq}=Q_{max}, 40 L/h, $C_{As(III)}$, 0.25 ppm; V_{feed}, 40 mL; pH, 3; T, 15°C

As already noticed, the observed difference in results has to be related to the different mass transfer resistances which are established in the feed solution for the various systems analyzed.

4. Concluding Remarks

The oxidation of As(III) to As(V) has been carried out in different systems and the effect of various operating conditions has been analyzed.

In particular, stirring, injection through a tube, injection through a porous unit and membrane contactors have been employed. The time required for the oxidation is reduced operating at low values of temperature, pH, volume of feed and As(III) content into the feed. By comparing the two injection units, higher oxidation degrees are achieved by injecting the air/oxygen through a porous device, probably due to the better dispersion of gas bubbles, which are smaller and in a higher number, leading to a better transfer of the oxidant agent inside the feed solution, with a consequent reduction of the oxidation time. The mass transfer at the aqueous side is further enhanced by using membrane contactors for introducing air into the feed. For example, after 8 h an oxidation degree of 73% is reached by membrane contactors and air, followed by the 25% obtained by the injection of oxygen through the porous unit, the 20% of the stirring, the 4% of the porous unit with air, the 0% of the injection through a tube with both air and oxygen. Moreover, after 16 h, membrane contactors led to a complete oxidation.

From the achieved preliminary results, membrane contactors appear to be an interesting option for avoiding the use of dangerous and expensive oxidant agents, allowing to efficiently carry out the process with air.

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ARSENIC SPECIES ISOFORMATION – A KEY PROBLEM FOR WATER PURIFICATION

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Abstract Current research suggests that drinking water is the most common pathway for arsenic long-term low dose exposure. It would be advantageous to identify treatment processes that economically remove arsenic from potable water. Therefore, the first objective of this study was to identify the factors, including raw water quality and treatment process parameters, which cause effective (and ineffective) arsenic removal at water treatment plants. Arsenic in groundwater occurs in two oxidation states, As(III) (arsenite) and As(V) (arsenate). Since the removal of arsenic depends on its speciation, determining which species are present in the water is crucial. It is of paramount importance to convert all arsenic species in the ground water to As(V) before any treatment for arsenic removal. In the most treated waters As(V) accounted for almost 100% of the dissolved arsenic. Oxidation is clearly inadequate, if resultant water contains any As(III), and higher degree of oxidation should lead to improved arsenic removal overall. Many authors have shown that conversion between the inorganic forms of arsenic As(III) and As(V) is likely. There is no universally accepted method for preserving As species in water samples. Field separation was investigated as a mean of eliminating the need for preservation. Using small ion exchange cartridges in the field has proven to be a reliable method of separating arsenic species. Once separated, the fractions with the different species are analyzed in a good equipped analytical laboratory.

Keywords: Arsenic speciation; arsenite; arsenate; species conversion; isoformation; water treatment; field separation

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

1. Introduction

Arsenic can be in high concentrations found in water that has flowed through arsenic-rich rocks. Severe health effects have been observed in populations drinking arsenic-rich water over long periods in countries worldwide.

Arsenic sources:

- Arsenic is widely distributed throughout the earth's crust.
- Arsenic is introduced into water through the dissolution of minerals and ores, and concentrations in groundwater in some areas are elevated as a result of erosion from local rocks.
- Industrial effluents also contribute with arsenic to water in some areas.
- Arsenic is also used commercially e.g. in alloying agents and wood preservatives.
- Combustion of fossil fuels is a source of arsenic in the environment through dispersed atmospheric deposition.
- Inorganic arsenic can occur in the environment in several forms, but in natural waters, and thus in drinking water, it is mostly found as trivalent arsenite As(III) or pentavalent arsenate As(V). Organic arsenic species, abundant in seafood, are very much less harmful to the health, and are readily eliminated by the body.

1.1. EFFECTS

Chronic arsenic poisoning that occurs after long-term exposure through drinking water is very different from acute poisoning. Immediate symptoms on an acute poisoning typically include vomiting, esophageal and abdominal pain, and bloody "rice water" diarrhea. Chelation therapy may be effective in acute poisoning but should not be used against long-term poisoning.

The symptoms and signs that arsenic causes appear to differences between individuals, population groups and geographic areas. Thus, there is no universal definition of the disease caused by arsenic. This complicates the assessment of the burden on health of arsenic. Similarly, there is no method to identify those cases of internal cancer that were caused by arsenic from cancers induced by other factors.

Long-term exposure to arsenic via drinking water causes cancer of the skin, lungs, urinary bladder, and kidney, as well as other skin changes such as pigmentation changes and thickening (hyperkeratosis).

Increased risks of lung and bladder cancer and of arsenic-associated skin lesions have been observed at drinking water arsenic concentrations of less than 0.05 mg/L.

Absorption of arsenic through the skin is minimal and thus hand-washing, bathing, laundry, etc. with water containing arsenic do not pose human health risk.

Following long-term exposure, the first changes are usually observed in the skin: pigmentation changes, and then hyperkeratosis. Cancer is a late phenomenon, and usually takes more than 10 years to develop.

The relationship between arsenic exposure and other health effects is not clear-cut. For example, some studies have reported hypertensive and cardiovascular disease, diabetes and reproductive effects.

Exposure to arsenic via drinking water has been shown to cause a severe disease of blood vessels leading to gangrene in China (Province of Taiwan), known as ‘black foot disease’. This disease has not been observed in other parts of the world, and it is possible that malnutrition contributes to its development. However, studies in several countries have demonstrated that arsenic causes other, less severe forms of peripheral vascular disease.

According to some estimates, arsenic in drinking water will cause 200,000–270,000 deaths from cancer in Bangladesh alone.

Arsenic is a known carcinogen, causing cancers of the skin, lungs, bladder and kidney. Current research suggests that drinking water is the most common pathway for long-term low dose exposure. Arsenic contaminated drinking water has caused serious health problems in many countries including: India, Bangladesh, Argentina, Chile, Taiwan, the United States and Canada.

1.2. WHO’S REGULATIONS

WHO’s norms for drinking water quality go back to 1958. The International Standards for drinking water established 0.20 mg/L as an allowable concentration for arsenic in that year. In 1963 the standard was re-evaluated and reduced to 0.05 mg/L. In 1984, this was maintained as WHO’s “Guideline Value”; and many countries have kept this as the national standard or as an interim target. According to the last edition of the WHO Guidelines for Drinking water Quality[1]:

- Inorganic arsenic is a documented human carcinogen.
- 0.01 mg/L was established as a provisional guideline value for arsenic.
- Based on health criteria, the guideline value for arsenic in drinking water would be less than 0.01mg/L.

- Because the guideline value is restricted by measurement limitations, and 0.01 mg/L is the realistic limit to measurement, this is termed a provisional guideline value.

The WHO Guidelines for drinking water Quality is intended for use as a basis for the development of national standards in the context of local or national environmental, social, economic, and cultural conditions.

Ground water is the main source of drinking water for most small communities. Drinking water poses the greatest threat to public health from arsenic. Exposure at work and mining and industrial emissions may also be significant locally.

1.3. GLOBAL SITUATION

The delayed health effects of exposure to arsenic, the lack of common definitions and of local awareness as well as poor reporting in affected areas are major problems in determining the extent of the arsenic in drinking water problem.

Reliable data on exposure and health effects are rarely available, but it is clear that there are many countries in the world where arsenic in drinking water has been detected at concentration greater than the guideline value, 0.01 mg/L or the prevailing national standard. These include Argentina, Australia, Bangladesh, Chile, China, Hungary, India, Mexico, Peru, Thailand, and the United States of America. Countries where adverse health effects have been documented include Bangladesh, China, India (West Bengal), and the United States of America. Examples are:

Seven of 16 districts of West Bengal have been reported to have ground water arsenic concentrations above 0.05 mg/L; the total population in these seven districts is over 34 million and it has been estimated that the population actually using arsenic-rich water is more than 1 million (above 0.05 mg/L) and is 1.3 million (above 0.01 mg/L).

According to a British Geological Survey study in 1998 on shallow tube-wells in 61 of the 64 districts in Bangladesh, 46% of the samples were above 0.010 mg/L and 27% were above 0.050 mg/L. When combined with the estimated 1999 population, it was estimated that the number of people exposed to arsenic concentrations above 0.05 mg/L is 28–35 million and the number of those exposed to more than 0.01 mg/l is 46–57 million.

Environmental Protection Agency of The United States of America has estimated that some 13 million of the population of USA, mostly in the western states, are exposed to arsenic in drinking water at 0.01 mg/L, although concentrations appear to be typically much lower than those encountered in areas such as Bangladesh and West Bengal.

2. Water Treatment Procedures for Arsenic Removal

Water treatment plants remove some arsenic in conventional processes, such as iron (Fe) removal and softening, but these processes are not optimized for arsenic removal. Substantial data exist regarding arsenic levels in community water supplies, especially treated samples. However, data on both raw and treated samples for a given system are not as readily available. Clearly, understanding the removal efficiency of existing systems will be an important component for the proper application of treatment methods. Therefore, the initial objective was to determine the current arsenic removal efficiency of community water treatment plants that have significant amounts of arsenic in their raw water. It would be advantageous to identify treatment processes that economically remove arsenic from potable water. Therefore, the first objective of this study was to identify the factors, including raw water quality and treatment process parameters, which cause effective (and ineffective) arsenic removal at water treatment plants.

Many factors affect sorption of arsenic to metal oxides and, therefore, the efficiency of arsenic removal, including the metal to arsenic ratio, the pH, the arsenic oxidation stage, and the concentrations of other substances that sorb to hydrous ferric oxide (HFO).[2]

During coagulation and filtration, arsenic is removed through three main mechanisms[3]:

- Precipitation: the formation of the insoluble compounds $Al(AsO_4)$ or $Fe(AsO_4)$.
- Coprecipitation: the incorporation of soluble arsenic species into a growing metal hydroxide phase.
- Adsorption: the electrostatic binding of soluble arsenic to the external surfaces of the insoluble metal hydroxide.

2.1. ARSENIC CHEMISTRY

Arsenic in groundwater occurs in two oxidation states, As(III) (arsenite) and As(V) (arsenate). Arsenous acid (H_3AsO_3) has a pK_a value of 9.2, so in the pH range of most groundwater's there is relatively little of its conjugate base H_2AsO_3 (Figures 1 and 2). The sum of concentrations of H_3AsO_3 and H_2AsO_3 is denoted As(III). Arsenic acid (H_3AsO_4) has pK_a values of 2.7, 6.8, and 11.5, which are similar to those of phosphoric acid. In the pH range of groundwater the concentrations of H_2AsO_4 and $HAsO_4^{2-}$ are much greater than those of H_3AsO_4 and AsO_4^{3-} (Figure 2). The sum of concentrations of H_3AsO_4, H_2AsO_4 , $HAsO_4^{2-}$, and AsO_4^{3-} is denoted As(V). Although methylated forms of arsenic are sometimes found in surface waters, they have only rarely been found in groundwater, except in cases of gross contamination by herbicides.[4] Shraim[5] did find low concentrations (<2 mg/L) of methylated species in groundwater from West Bengal, although the inorganic arsenic concentration in those samples was extremely high (>300 mg/L). In most published studies of arsenic speciation, both As(III) and As(V) were found and the less abundant species was at least 2% of the total arsenic.[6] In these studies, As(III) was generally predominant under reducing conditions while As(V) was predominant under oxidizing conditions. As(III) oxidation by air is likely to be incomplete. Korte and Fernando[7] found only As(III) in shallow wells in an alluvial aquifer in Missouri.

While there are several important arsenic minerals (e.g. arsenopyrite (FeAsS) and orpiment (As_2S_3)), most arsenic in the solid phase is associated with common iron minerals, including iron oxyhydroxides (e.g. FeOOH) and pyrite (FeS_2). Arsenic may be released from these minerals by desorption or reductive dissolution of the arsenic-bearing mineral. The most common cause of widespread arsenic contamination is thought to be release from iron oxyhydroxides, probably due to the reaction of iron oxyhydroxides with organic carbon. Oxidation of sulfide minerals such as pyrite is also an important source of arsenic, and has been identified as the primary arsenic source in some aquifers in Wisconsin and Michigan.

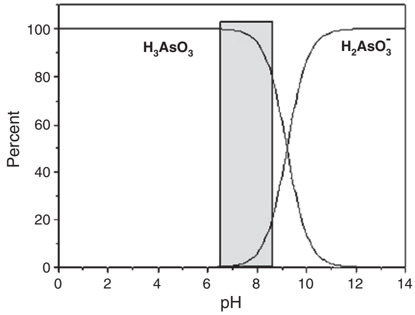

Figure 1. Concentrations of the As(III) species H_3AsO_3 and H_2AsO_3 at different pH values. The shaded area is the pH range of most groundwaters

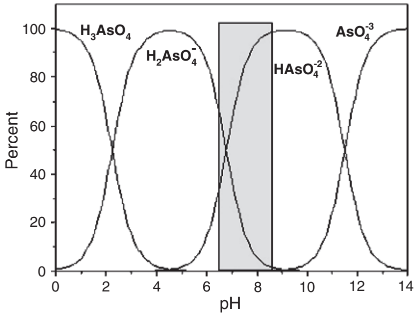

Figure 2. Concentrations of the As(V) species H_3AsO_4, H_2AsO_4 , $HAsO_4^{2-}$, and AsO_4^{3-}at different pH values. The shaded area is the pH range of most groundwaters

Both As(III) and As(V) adsorb to particles of the hydrous oxides of iron[2] and aluminum. That is, under certain conditions addition of iron or aluminum oxide to an As(III) or As(V) solution will reduce the dissolved arsenic concentration even though the solution is under saturated with respect to known arsenic containing minerals. Sorption of As(V) depends on the pH. In simple systems with only iron and arsenic, sorption is nearly complete at low pH values and low at high values. The transition region shifts to higher pH values for higher iron to arsenic ratios.

Arsenic sorbs too many common aquifers materials, such as metal oxides and clays, and this is what is thought to limit the mobility of arsenic in most aquifer systems. Hydrous ferric oxide (HFO) sorbs both As(V) and As(III)[2,8,9] but the sorption of As(V) is stronger[10]. If HFO is subsequently reduced, the sorbed arsenic may be re-released into solution. At neutral pH values As(III) is more mobile than As(V) because it is less strongly adsorbed on most mineral surfaces.

Aqueous carbonate, ferrous iron and organic matter (OM) in groundwater can influence the sorption of arsenic. Sorption of carbonate at common ground water concentrations significantly reduces the tendency of arsenic to sorb on HFO, and high concentrations of carbonate could cause the displacement of arsenic.[8] Silica and phosphate may also interfere with arsenic sorption or promote arsenic desorption.[11,12] Organic matter may influence arsenic sorption to HFO and, as a result, increase arsenic mobility in aquifer systems. High concentrations of free sulfide due to sulfate reduction reactions may cause precipitation of sulfide minerals, such as As_2S_3 or FeAsS, removing arsenic from solution.

Nanofiltration (NF) is a promising technology for arsenic removal since it requires less energy than traditional reverse osmosis membranes. Several studies have shown that nanofiltration is capable of removing the oxidized form of arsenic [As(V)] while the reduced form of arsenic [As(III)] is poorly removed. To exploit this difference it has been suggested that a pretreatment step which oxidizes the As(III) to As(V) would improve the performance of membrane filtration, but this has never been demonstrated. The second experiment investigated the arsenic oxidation capabilities of manganese dioxide (MnO_2) and the rate at which the oxidation occurs.[13] The feed water contained primarily As(III), however, when filtered by MnO_2 at an Empty Bed Contact Time (EBCT) of only 1 min, the dominant form of arsenic was the oxidized form [As(V)]. At an EBCT of 2 min the oxidation was nearly complete with the majority of the arsenic in the As(V) form. The MnO_2 filter removed little arsenic. The third and final experiment investigated the benefit, if any, to combining the membrane filtration and MnO_2 treatment investigated in the first and second experiments. The effect of MnO_2 pretreatment was dramatic.[14] Once pretreated with MnO_2 the passage of arsenic through all of the membranes dropped to 4 µg/L, corresponding to approximately 91–98% removal. Nanofiltration alone is not a suitable technology to remove arsenic contaminated waters where As(III) is the dominant species. When combined with MnO_2 pre-oxidation, the arsenic rejection performance of nanofiltration is dramatically improved.

Most arsenic removal technologies are most effective at removing the pentavalent form of arsenic (arsenate), since the trivalent form (arsenite) is predominantly non-charged below pH 9.2. Therefore, many treatment systems include an oxidation step to convert arsenite to arsenate. Oxidation alone does not remove arsenic from solution, and must be coupled with a removal process such as coagulation, adsorption or ion exchange.

Arsenite can be directly oxidized by a number of other chemicals, including gaseous chlorine, hypochlorite, ozone, permanganate, hydrogen peroxide, and Fenton's reagent (H_2O_2/Fe^{2+}). Some solids such as manganese oxides can also oxidize arsenic. Ultraviolet radiation can catalyze the oxidization of arsenite in the presence of other oxidants, such as oxygen.[15] Direct UV oxidation of arsenite is slow, but may be catalyzed by the presence of sulfite,[16] ferric iron[17] or citrate.[18] Chlorine is a rapid and effective oxidant, but may lead to reactions with organic matter, producing toxic trihalomethanes as a by-product. Chlorine is widely available globally, though if improperly stored it can lose its potency rapidly.

In Europe, and increasingly in the USA, ozone is being used as an oxidant. In developing countries, ozone has not been widely used. An ozone dose of 2 mg/L, contacted with the water for 1 min prior to filtration, has been shown to be effective in oxidizing iron and manganese, at the same time removing arsenic and other metals to below detection limits.[15] At a similar ozone dose, arsenite was shown to have a half-life of approximately 4 min.[19] Ozone is also a potent disinfectant, but unlike chlorine, does not impart a lasting residual to treated water.

Permanganate effectively oxidizes arsenite, along with Fe(II) and Mn(II). It is a poor disinfectant, though it can produce a bacteriostatic effect. Potassium permanganate (KMnO4) is widely available in developing countries, where it is used as a topical antibiotic for minor cuts. It is relatively stable with a long shelf life. Residual manganese in treated water should not exceed the WHO guideline of 0.5 mg/L.[1] Hydrogen peroxide may be an effective oxidant if the raw water contains high levels of dissolved iron, which often occur in conjunction with arsenic contamination. So it is of paramount importance to convert all arsenic species in the raw water to As(V) before any treatment for arsenic removal. In the most treated waters As(V) accounted for almost 100% of the dissolved arsenic. Oxidation is clearly inadequate if finished water has any As(III), and higher degree of oxidation of those waters that have As(III) should lead to improved arsenic removal overall.

2.2. ARSENIC STABILITY IN WATER SAMPLES

The distribution of arsenic varies depending on the water source. Since the treatment of arsenic depends on its speciation, determation of species, which are present in the water, is crucial (Table 1).

TABLE 1. Arsenic species in lake water from Montana region (μg/L)

Sample	As(V)	As(III)	MMA	DMA	As (total)
1	25	12	1	5	42
2	24	15	3	3	44
3	26	18	2	3	49
4	26	12	1	4	42
5	35	13	4	3	56
6	35	18	3	2	60
7	8	5	1	1	13
8	11	8	1	2	21
9	32	11	3	1	48
10	4	4	0.1	0.1	8
11	3	3	0.1	0.1	6
12	5	3	0.1	0.2	8
13	5	3	0.1	0.1	8
14	4	3	0.0	0.0	7

If there is conversion between the species during shipment to the laboratory, the results may misrepresent the forms of arsenic present.

Data available in the literature concerning the stability of arsenic in water samples have shown that conversion between the inorganic forms of arsenic As(III) and As(V) is likely.[20–24] The rate and nature of the conversion depends on the characteristics of the water sample and the sample storage conditions.

Working with reagent grade water, studies have reported a reduction of As(V) to As(III) over time.[20,23,25] In both cases, microbiological activity is suggested as the cause for the change. In other studies researchers have observed oxidation from As(III) to As(V) as well as reduction from As(V) to As(III).[24] In natural waters, arsenic has been found to undergo similar oxidation or reduction reactions.[23] A comprehensive study showed that the change in arsenic distribution was unique for each water source. Random shifts in distribution were observed: oxidation of arsenic in some cases and reduction in others.[22]

The storage temperature has been shown to have a significant influence on the stability of arsenic species. To varying degrees colder storage temperatures have been shown to lessen the conversion of species.[22–24]

Some studies have reported that lower arsenic concentrations result in more rapid conversion kinetics[23,24]; however, others report no relation between concentration and conversion kinetics.[22]

The formation of iron precipitates or complexes containing arsenic has been shown to affect the concentration of water samples containing arsenic.[22] Several studies have noted decreasing arsenic concentrations in solutions containing arsenic and iron.[20–23]

Due to the formation of iron precipitates and the unpredictable shifts in arsenic speciation, chemical preservation of arsenic samples is recommended.[20–23]

2.3. STABILIZING ARSENIC SPECIES FOR ANALYSIS

There is no universally accepted method for preserving.[26] Various acids have been investigated for their ability to maintain a stable distribution of inorganic arsenic species[27]: ascorbic, acetic,[22] hydrochloric,[20,21] sulphuric[20] and nitric.[20,23] The acids tested preserved the total arsenic concentration; however, they can influence the speciation. Sulphuric and nitric acid were successful at preserving the arsenic speciation provided iron was not present.

To prevent the interference of iron in the preservation of arsenic species ethylenediaminetetraacetic acid (EDTA) has been used to sequester the iron that can co-precipitate with arsenic. This has been demonstrated in three separate studies.[20–22] In the later study, Gallagher et al. show that while EDTA is effective at preventing the formation of iron-arsenic co-precipitates, a change in speciation is still possible. Using acetic acid in conjunction with EDTA prevents the formation of iron-arsenic co-precipitates and the interconversion of arsenic species.[22]

There is no consensus in the literature about preserving arsenic speciation in water sample.

2.4. FIELD SEPARATION TECHNIQUES

In light of the uncertainty surrounding the preservation of arsenic samples and the likelihood that speciation change or arsenic co-precipitation will occur, field separation was investigated as a means of eliminating the need for preservation.[28] Using small ion exchange cartridges in the field has proven to be a reliable method of separating different forms of arsenic.[29,30] At pHs of natural waters, 6.5 to 8.5, As(V) is negatively charged while As(III) is neutral. This allows anion exchange media to retain the As(V), while allowing the neutral As(III) to pass through the column.

Several different trials have shown that field speciation methods match more sophisticated laboratory methods without the need for preservation[6,26,31,32] and at a relatively low cost. Using a 0.45 μm filter to prefilter the sample is recommended. This ensures that the capacity of the exchange media is not prematurely exhausted by arsenic co-precipitates, which can form in the presence of iron, manganese and aluminum cations.[20,26,32] Rather then filter out solid arsenic co-precipitates, Bednar et al. suggested using EDTA to sequester the cations in order to prevent co-precipitation at the head of the exchange media.[20]

Once the species have been separated on the anion exchange column, the arsenic samples can be preserved with acid and the total arsenic concentrations measured. The uncharged species, such as As(III), can be determined by analyzing the treated samples. The charged species can be determined directly by eluting them from exchange media using an acid such as hydrochloric acid[32,33] or nitric acid[20] or indirectly by calculating the difference between the total arsenic concentration and the concentration of uncharged arsenic species.[26]

Miller et al. have shown that a field separation technique based on anion exchange over estimates the concentration of As(III) since some forms of arsenic (dimethylarsinate (DMA) and monomethylarsinate (MMA)) are not retained by the column and thus included in the As(III) measurement.[33] Other errors can be introduced if the capacity of the column is exceeded.[20,30]

2.5. DETECTION METHODS

Once separated the samples must be analyzed. In the literature, the hydride generation (HG) and inductively coupled plasma–mass spectrometry (ICP-MS) are commonly used to detect and measure arsenic concentrations.

Hydride generation involves the production of volatile hydrides upon a chemical treatment with a strong reducing agent, typically sodium borohydride[32] (NaBH4). Hydride generation can be coupled with various types of spectrometry: atomic absorption (HG-AAS), atomic fluorescence (HG-AFS), atomic emission (HG-AES) or mass spectrometry (HG-MS). The primary advantage of HG techniques is that only gaseous hydrides are introduced to the detector and the remaining sample matrix is discarded. As a result, chemical interference is eliminated. Unfortunately, the complexity of this technique can be time consuming and thus costly. The detection limit of HG generation techniques has been reported[32] as low as 0.05 μg/L.

Inductively coupled mass spectroscopy (ICP-MS) is a very sensitive detection method, which is generally combined with sophisticated separation methods, such as high performance liquid chromatography (HPLC), to achieve very low detection limits.[26] This is now the most effective tool in many arsenic research laboratories.[5] Although ICP-MS provides rapid and sensitive arsenic measurements, interferences from chloride can present a problem.[26]

3. What Should Be Done?

3.1. MEASUREMENT

Accurate measurement of arsenic in drinking water at levels relevant to health requires laboratory analysis, using sophisticated and expensive techniques and facilities as well as trained staff not easily available or affordable in many parts of the world.

Analytical quality control and external validation remain problematic.

Field test kits can detect high levels of arsenic but are typically unreliable at lower concentrations of concern for human health. Reliability of field methods is yet to be fully evaluated.

3.2. PREVENTION AND CONTROL

The most important remedial action is prevention of further exposure by providing safe drinking water. The cost and difficulty of reducing arsenic in drinking water increases as the targeted concentration lowers. It varies with the arsenic concentration in the source water, the chemical matrix of the water including interfering solutes, availability of alternative sources of low arsenic water, mitigation technologies, amount of water to be treated, etc.

Control of arsenic is more complex where drinking water is obtained from many individual sources (such as hand-pumps and wells) as is common in rural areas. Low arsenic water is only needed for drinking and cooking. Arsenic-rich water can be used safely for laundry and bathing. Discrimination between high-arsenic and low-arsenic sources by painting the hand-pumps (e.g. red and green) can be an effective and low cost means to rapidly reduce exposure to arsenic when accompanied by effective health education.

Alternative low-arsenic sources such as rain water and treated surface water may be available and appropriate in some circumstances. In the places, where low arsenic water is not available, it is necessary to remove arsenic from drinking water:

- The technology for arsenic removal for piped water supply is moderately costly and requires technical expertise. It is inapplicable in some urban areas of developing countries and in most rural areas worldwide.
- New types of treatment technologies, including co-precipitation, ion exchange and activated alumina filtration are being field-tested.
- There are no proven technologies for the removal of arsenic at water collection points such as wells, hand-pumps and springs.
- Simple technologies for household “point-of-use” removal of arsenic from water are few, which includes reverse osmosis and have proven to be sustainable in each different setting.
- Some studies have reported preliminary successes in using packets of chemicals for household treatment. Some mixtures combine arsenic removal with disinfecting. One example, developed by the WHO/PAHO Pan American Center of Sanitary Engineering and Environmental Sciences in Lima, Peru (CEPIS), has proven success in Latin America.

3.3. URGENT REQUIREMENTS

- Large-scale support to the management in developing countries, with substantial severely affected populations.
- Simple, reliable, low-cost equipment for field measurement.
- Increased availability and dissemination of relevant information.
- Robust affordable technologies for arsenic removal at wells and in households.

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DISTRIBUTION AND SPECIATION OF ARSENIC IN GROUNDWATERS AND TAP WATERS OF EASTERN CROATIA

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Abstract The presence of arsenic in the groundwater of Eastern Croatia was found almost 20 years ago; however, the extent of this anomaly is still unknown. There is a growing need to improve the knowledge of arsenic distribution in the region as well as of As speciation since As(III) is more toxic and less strongly retained in water treatment processes. Different methods for the determination of As speciation and species preservation have been proposed in the literature, but preservation of As species is still

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

subject of scientific debate. In the present study, two analytical approaches (HPLC-ICP-MS and field speciation) have been used to study arsenic speciation in raw groundwater (at 31 different locations) and tap water (at 11 locations). Samples for laboratory speciation were preserved with EDTA, a commonly used preservative when using HPLC-ICP-MS technique. It was shown that EDTA conservation alone is not sufficient for species preservation, at least not for long (≥30 days) periods of storage. It was shown that shallow aquifers were not contaminated by arsenic, while deeper aquifers were generally more affected. Arsenic in the tested groundwater was present predominantly in dissolved form as As(III). As(V) was the predominant species in the residents' tap water. These results contribute to a greater understanding of hydrogeochemical settings in the area. They also have important implications on the protection of public health and will be helpful for the choice of a cost-effective arsenic removal technology.

Keywords: Groundwater; arsenic; speciation; eastern Croatia

1. Introduction

During the last decade, the presence of arsenic in the groundwater was reported from many countries all over the world.[1] Arsenic is a human carcinogen. Thus, drinking water contaminated by arsenic has been considered as a global problem. Arsenic exists under different chemical species in groundwater; inorganic arsenite (As(III)) and arsenate (As(V)) are predominant, but low amounts of organic species (monomethyl- and dimethylarsenic) may also be found.[2] Regarding their toxicity, inorganic arsenic species arsenite As(III) and arsenate As(V) are more toxic than organic species. Moreover, As(III) is more toxic than As(V) species.[3] The efficiency of arsenic removal from drinking water depends on its speciation, As(V) being more easily removed than As(III).[4,5] Thus, the knowledge of individual concentrations of As(V) and As(III) is essential.

The presence of arsenic in the groundwater in Eastern Croatia (Osijek-Baranya and Vukovar-Srijem Counties) was found many years ago, and a great deal of work has been done for arsenic removal, especially in the water supply company Vodovod-Osijek plc.[6] However, little was known about the extent of the arsenic contamination in the area. Santo et al.[7] gave the first data regarding the state of the arsenic contamination in Osijek-Baranya County, while for the Vukovar-Srijem County data are scarce.

Current Croatian regulation[8] allows up to 50 µg/L of As in drinking water. However, Croatia needs to adopt the new maximum admissible level of 10 µg/L in the year 2015. Therefore, Croatia is facing big challenges in finding alternative water resources and/or remediating As-contaminated groundwater in a cost-effective way. Thus, there is a need to improve our knowledge on arsenic distribution throughout Eastern Croatia, the origin of this anomaly, and the processes that control the release of As into the groundwater. Furthermore, the knowledge of arsenic speciation is necessary for risk assessment as well for appropriate choice of arsenic removal technology.

Arsenic species are very unstable in natural waters; their distribution depends on the redox conditions, pH, and the presence of precipitating metals such as iron, organic matter, as well as on microbial activity.[9] Thus, the preservation of the arsenic species before laboratory analyses is very important. Filtering the samples removes microorganisms that can affect As speciation[10] and it is used together with the addition of preservatives to prevent any changes in arsenic species distribution. Ethylenediaminetetraacetic acid (EDTA) at various concentrations[11–14] has been used to preserve arsenic species distribution due to possibility to chelate metal cations, buffer the sample pH and reduce microbial activity.[11,15] Moreover, sample preservation with EDTA is preferred for determination of As(III), As(V), MMA and DMA by HPLC-ICP-MS.[16–18] However, Gault et al.[14] and Polya et al.[12] showed that EDTA was ineffective in preservation of the inorganic As species in groundwater, and Samanta and Cliford[9] used a mixture of EDTA and acetic acid to preserve the distribution of inorganic species in the groundwater. Thus, species preservation prior to analysis is still the subject of scientific debate.[14]

Field separation procedures using solid phase extraction (SPE) cartridges are applied to avoid changes in arsenic speciation due to sample storage and inadequate preservation.[9,19,20]

The objective of the present study is to gain knowledge on arsenic distribution and speciation in groundwaters of Estern Croatia as well to compare data of arsenic speciation obtained by HPLC-ICP-MS (with EDTA as a commonly used preservative when applying this method) and with field speciation by solid phase cartridges.

2. Experimental

Water samples were obtained from 31 wells operated by electronic pump. The depth of the wells ranged from 30 to 170 m.

2.1. TOTAL AND DISSOLVED ARSENIC ANALYSES

To determine total arsenic concentration, samples were acidified by SupraPur HNO_3 (1/100 v/v) without filtration. Samples for the determination of dissolved As were filtered with 0.2-µm pore size filters (Whatman) and acidified by SupraPur HNO_3 (1/100 v/v). Field sampling method using filters of 0.45 µm could overestimate the dissolved arsenic concentrations due to the presence of suspended submicron-sized particles ranging from 0.2 to 0.45 µm.[21] Arsenic analyses were performed by HG-ICP-OES. The on-line HG method was used in order to achieve a lower detection limit (<1 µg/L). The sample was mixed on-line with 3N HCl, followed by mixing with 1.5% $NaBH_4$ solution in 0.1% NaOH for the generation of arsine gas, which was introduced into the plasma torch after gas–liquid separation.

2.2. FIELD SEPARATION OF ARSENIC(III) AND ARSENIC(V)

Field speciation was performed using a SPE strong anion exchange cartridge (Elut bond, Varian). Membrane filter of 0.2 µm pore size (Wathman) and strong anion exchange cartridge were connected in tandem. In the field, 5 mL of the filtered sample were passed through the cartridge, then 15 mL of deionised water were passed and the effluent was acidified with HNO_3 SupraPur (1/100 v/v). As(III) as uncharged As species remains in the sample solution and is eluted from the cartridge, whereas charged species (As(V), DMA, and MMA) are retained on the cartridge. As(III) in the effluent was analyzed by HG-ICP-OES as described earlier for As_{tot}.

2.3. PRESERVATION OF ARSENIC SPECIES AND ITS DETERMINATION BY HPLC-ICP-MS

A volume of 500 µL of 0,25 M EDTA were added to 10 mL of the sample previously filtered through 0.2-µm pore size filters. All samples were stored at 4°C until further analyses. The analyses were performed in the Laboratory of Hydrosciences, Montpellier, France so sample storage time was prolonged (≥30 days).

The Hamilton PRP X100 HPLC column (25 cm × 4.1 mm i.d.) with VARIAN ProStar solvent delivery system was used for laboratory As speciation and an ICP-MS (Thermo X7 Series) was used for on-line detection of the separated species. Separation of As(III) and As(V) was achieved in 10 min using a 30-mM ammonium phosphate buffer at pH 8.0. A gradient program was used for simultaneous determination of As(III), As(V), MMA and DMA) using two ammonium phosphate buffers: (i) Sol A, 5 mM and pH 4.7, and (ii) Sol B, 30 mMand pH 8.0. From 0 to 4.1 min, Sol A was pumped then from 4.1 to 10.1 min Sol B. Sol A was pumped again from 10.1 to 20.0 min in order to equilibrate the column before further analysis. The flow rate through the column was maintained at 1 mL/min.

3. Results and Discussion

3.1. TOTAL AND DISSOLVED ARSENIC CONCENTRATIONS

Analyses of the total (dissolved + particulate) and dissolved arsenic concentrations in the groundwater show similar results, except for one point (Figure 1). This indicates that there is no considerable amount of particulate arsenic present in the tested well water. Similar results were found in the groundwater in southeastern Bangladesh,[22] while other contaminated groundwater showed variable percentages of particulate arsenic fraction[23,24]; for example in the Inner Mongolia, particulate arsenic accounts for 39 ± 38% of total arsenic.[25] The amount of the particulate arsenic depends on the chemical conditions in the water such as pH, ionic strength, the amount of particulate matter and the concentration of competing ions.[1,2] The results presented here have important implications in the choice of appropriate technology for arsenic removal because dissolved arsenic is harder to remove than particulate arsenic using filtration.[26]

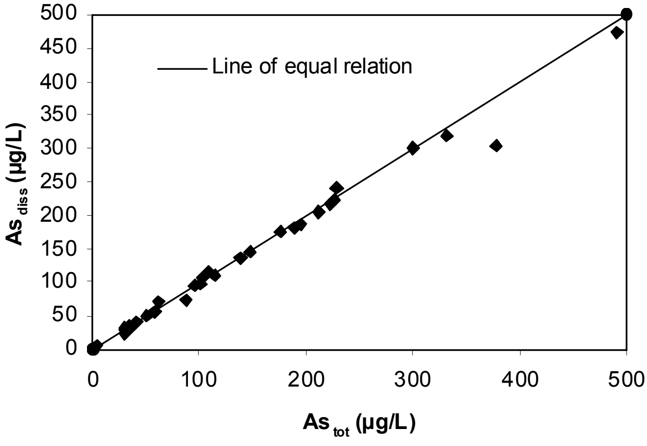

Figure 1. Correlation between total and dissolved arsenic concentrations measured by HG-ICP-OES in the tested groundwater

3.2. ARSENIC SPECIATION

Linear regression analyses and the two-sample paired for means t-test were used to evaluate whether the results of the determinations of As(III) concentration obtained by the two methods (HPLC-ICP-MS and field-speciation, shown in Figure 2) were significantly different. The slope (0.78 ± 0.02) and y-intercept (1.05 ± 3.45) coefficients from the linear regression of As(III) results indicate no significant difference between the two data sets at the 95% confidence interval. However, field method gave higher results, especially when the As(III) concentrations were higher. The paired two sample for means t-test with p-value <0.0001 shows that there is significant difference between tested methods.

Such discrepancy may be related either to As(III) oxidation or to the removal of As(III) from the aqueous phase during storage prior to analysis by HPLC-ICP-MS. Results for total dissolved As obtained by HPLC-ICP-MS (As(III) + As(V)) were lower than those obtained by HG-ICP-OES, which suggests that As was removed from the aqueous phase during storage. Such removal may be associated with the presence of high concentrations of Fe(II) (from 82.4 up to 3466 μg/L) in the groundwater samples. Fe(II) is rapidly oxidized upon contact with oxygen at near-neutral pH values and Fe(III) precipitates in the form of Fe-oxyhydroxides that have the ability to scavenge As(V), but also As(III).[27] The addition of EDTA in mine water samples has been shown to prevent Fe precipitation.[11] However, according to Gault et al.,[14] the preservation of arsenic species with EDTA is not sufficient when Fe(II) prevails since Fe(II) does not form stable complex with EDTA. A weak correlation ($R^2 = 0.32$) was found between the proportion of arsenic measured in the laboratory and in the field as a function of the Fe dissolved concentrations (Figure 3), which suggested that Fe concentration in the groundwater was not the only parameter affecting the preservation of arsenic species with EDTA. Samanta and Clifford[9] showed that preservation with EDTA alone is insufficient for maintaining the distribution of arsenic species in synthetic groundwater even in the absence of Fe(II). It was shown that no preservative tested could maintain the As(III/V) speciation when samples had been exposed to UV light.[9] As samples were not preserved in opaque PP bottles to eliminate/minimize the influence of the UV light, this influence cannot be completely negligible. Calcium and magnesium in groundwater may compete with iron for complexation with EDTA and decrease the efficiency of this preservation agent.[14] However, no correlation has been found between the proportion of

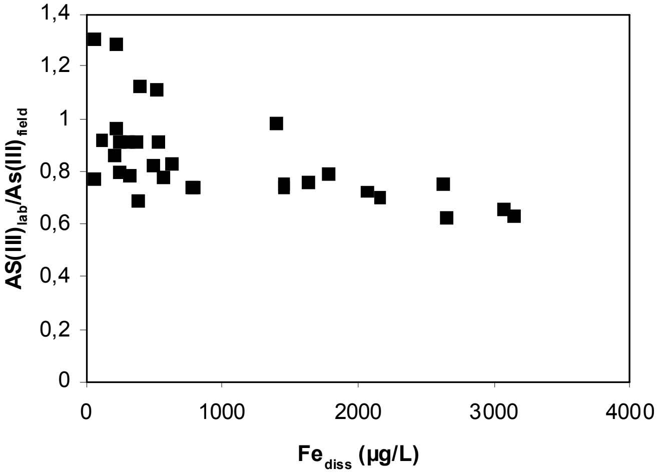

Figure 2. Correlation between As(III) measured in the laboratory by HPLC-ICP-MS and As(III) determined from field-speciated groundwater samples

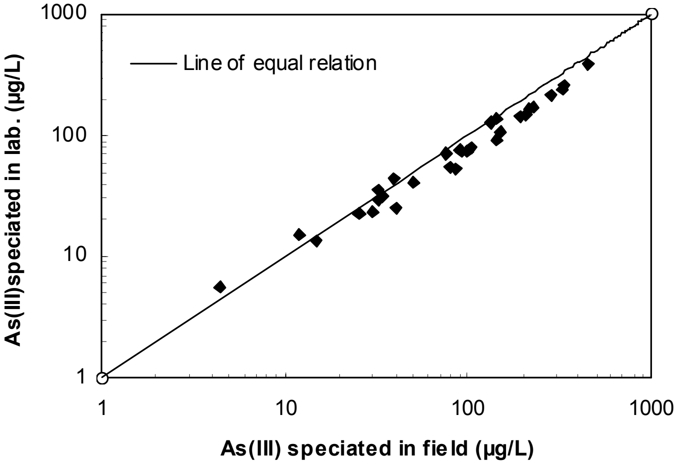

Figure 3. Correlation of the proportion of arsenic measured in the laboratory and in the field-speciated samples as a function of the dissolved Fe concentrations

the As(III) measured with the used methods and calcium concentrations (Figure 4). Thus, the impact of calcium on the preservation of As species seems to be negligible in groundwaters from Eastern Croatia.

Two samples preserved with EDTA were analyzed for MMA and DMA and none of these methylated arsenic species was found. As Roig-Navarro et al.[28] did not find any conversion of DMA or MMA into other species over 15 days of storage without any preservative; we can presume that these species were definitely not present in our groundwater samples.

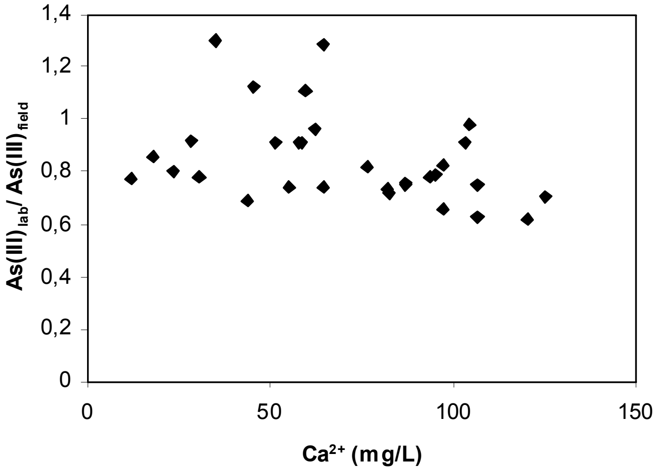

Figure 4. Correlation of the proportion of arsenic measured in the laboratory and in the field-speciated samples as a function of the Ca concentrations

3.3. ARSENIC DISTRIBUTION

Total arsenic concentrations in 31 investigated wells were between 4.3 and 490.8 μg/L. Croatian drinking water limit (50 μg/L) and WHO recommended value (10 μg/L) were exceeded in 22 and 30 groundwater samples, respectively. Whatever the speciation method, As(III) is predominant species in the tested groundwater. The proportion of dissolved arsenic occurring as As(III) ranged from 35% to 109% (median 95.1%) according to field speciation data.

Variation of the arsenic total concentrations with depth is shown in Figure 5. It can be seen that higher concentrations were observed in deeper wells. However, the correlation between the well depth and As concentration is weak. This may be due to the fact that the aquifers in the area are generally multilayered and usually one single well drains water from different layers located at different depths. Moreover, arsenic has not been detected in samples from private shallow wells (up to 15 m) in Osijek-Baranya County.[29]

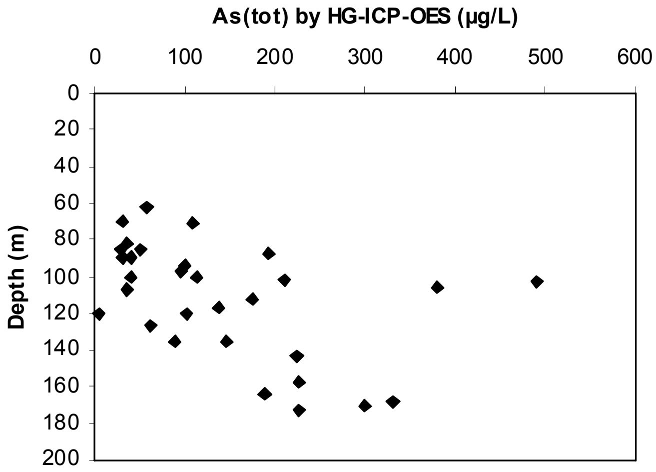

Figure 5. Variation of the arsenic total concentrations with well depths

Water supply at 11 locations relies on the raw groundwater without any treatment. Groundwater as it is has been supplied to the residents even without disinfection. Thus, samples were taken at wellhead and at residents tap to examine As speciation in the distribution system. Results for As_{tot} and As(III) for raw groundwater samples and corresponding residents' tap are shown in Table 1. It can be seen that in most cases As total concentrations were lower at tap water than at the corresponding raw groundwater. However, higher As total concentrations were observed at residents' tap at few locations. This shows that the process of As accumulation in the distribution system solids (corrosion byproducts, precipitated solids (e.g. MnO_2, $Al(OH)_3$, $Fe(OH)_3$, $CaCO_3$), suspended matter) can occur, as well as its release back into the water, as it was shown by Lytle et al.[30] Iron-based solids accumulated in the water distribution system can accelerate rates of arsenic oxidation. Probably as a consequence, As(V) prevails at residents' tap water, while As(III) prevails in raw groundwater (Table 1). In some cases oxidation was complete, e.g. at locations 8 and 10. The rate of As(III) oxidation probably depends on water retention time in the distribution system since these samples were taken at residents' homes at the end of the distribution system. Lytle et al.[30] also found As(III) as a predominant species in the majority of source (raw) water; however, they could not perform As speciation in the distributed water since almost all utilities involved chemical oxidation. The arsenic accumulation and/or release from the solids depend on water chemistry, pipe material and age, flushing procedures and frequency, solid retention and exposure time.[30] The same factors seem to have an impact on the rate of As(III) oxidation in the distribution system.

TABLE 1. As(III) and As(V) concentrations at tap water and the corresponding raw groundwater. Concentrations are expressed in μg/L. Analyses were performed by HG-ICP-OES, and As(III) was done from in situ speciated samples

Location ID	As_{tot} – raw	As(III) – raw	%As(III) – raw	As_{tot} – tap	As(III) – tap	%As(III) – tap
1	29.9	14.8	49.4	23.7	1.7	7.2
2	51.0	50	98.0	23.6	3 9	16.5
3	34.6	34.1	98.8	53.8	22.2	41.3
4	29.2	25.3	86.6	22.4	3.9	17.4
5	102.3	90.9	88.9	93.8	55.5	59.2
6	490.8	444.1	90.5	561.1	210.8	37.6
7	379.2	332.9	87.8	409.7	247.2	60.3
8	94.7	76.6	80.9	65	<1	0
9	58.1	39.5	68.0	42.5	31.6	74.4
10	30.1	32 1	106.5	19.7	<1	0
11	227.6	216.4	95.1	262.5	187.2	71.3

4. Conclusions

Two analytical approaches were used to study arsenic distribution and speciation in the raw groundwater from 31 wells used for public water supply in Esatern Croatia. Groundwater arsenic concentrations obtained by laboratory (HPLC-ICP-MS) and field speciation methods were correlated quite well; however, the laboratory method gave lower results, even with samples preserved with EDTA. The observed differences could be explained by As(III) oxidation during storage and As coprecipitation with Fe-oxyhydroxides. However, it seems that Fe concentration was not the only parameter affecting the preservation of arsenic species. Although sample preservation with EDTA is preferred for determination of As(III), As(V), MMA and DMA by HPLC-ICP-MS, it seems to be insufficient preservative at least for long (≥30 days) sample storage periods. Thus, field speciation data were considered reliable.

Shallow aquifers were not contaminated by arsenic, while deeper aquifers were generally more affected. In the tested groundwater, arsenic was present mainly in the dissolved form. Predominant species was As(III), a more toxic and hard to remove one.

Arsenic speciation analyses were performed in residents' tap water at 11 locations where groundwater is used for water supply without any treatment. As(V), a less toxic species, was predominant. Different processes can occur in the distribution systems, such as arsenic accumulation in the solids, its release back into the water column, and changes in As oxidation state. These processes seem to depend on water chemistry, water retention in the distribution system as well on pipeline characteristics and its maintaining. These results could have important effect on the protection of public health as well on the choice of a cost-effective arsenic removal technology.

Acknowledgements This research was done as part of Croatian-French Program "Cogito", project "Arsenic in the Groundwater of Eastern Croatia". The authors thank colleagues from water supply companies in Osijek-Baranya and Vukovar Srijem Counties as well the residents for permitting sampling of their wells and tap waters. The corresponding author thanks colleagues from Croatian National Institute of Public Health, Water Department for their help with the analyses, sampling and their constant support during this work. Many thanks go to Ivica Lausic for help with sample collection; T. Ignjatic-Zokic and M. Habuda-Stanic for their help with arsenic speciation analyses as well to colleagues from Hydroscience Montpellier for their cooperation. Dr. M. Kosicek is gratefully acknowledged for discussion about statistical data analyses and M. Miljkovic for English proofreading.

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OXYANIONS IN WASTE: OCCURRENCE, LEACHING, STABILISATION, RELATION TO WASTEWATER TREATMENT

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Abstract This paper describes the leaching and stabilization of oxyanion forming elements, mainly As, Se and Sb from solid wastes (sludge, fly ash, bottom ash). It is argued that knowledge of the leaching behaviour of oxyanions from waste is of high importance relative to wastewater treatment. Experiments and modelling demonstrate that immobilization of the oxyanions is mainly due to precipitation with Ca and to adsorption and solid solution formation with minerals such as calcite, gypsum, ettringite, HFO and AAM.

Keywords: Oxyanions; leaching; stabilization; waste; adsorption; precipitation; solid solution; arsenic; selenium; antimony

1. Introduction

Several elements (metals, metalloids) form oxyanions in solution at all pH values. Important examples are: As, Cr, Mo, Sb that lead to such anions as $AsO_3^{3\bullet}$, $AsO_4^{3\bullet}$, $CrO_4^{2\bullet}$, $MoO_4^{2\bullet}$, $Sb(OH)_4^{\bullet}$ and $Sb(OH)_6^{\bullet}$. The situation differs from that for amphoteric elements, e.g. Zn, that lead to anions at high pH, precipitate as hydroxide at lower pH and occur as cations at low pH. Different oxidation states may behave differently, e.g. Cr(III) forms cations, whereas Cr(VI) forms $CrO_4^{2\bullet}$ oxyanions. Oxyanions may be mononuclear or polynuclear, but at low metal concentration and high pH, polynuclear species predominate.

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

As (EPA number 1 priority hazardous substance) and Cr are since long recognized as priority pollutants, Mo, Sb, Se, V, W, are only recently on the environmental agenda. These emerging pollutants occur usually in trace concentrations in the environment and have moderate to high toxicity. Interest in these oxyanions relative to landfilling and recycling is growing. The European Directive 1999/31/EC on landfilling of waste has been complemented by the Council Decision 2003/33/EC establishing criteria and procedures for the acceptance of waste at landfills. The European leaching criteria include limit values for As, Cr, Mo, Sb and Se. Table 1 gives leaching limit values relative to landfilling and recycling of oxyanion forming elements. This paper focuses on the oxyanions of As, Se, and Sb. As occurs in the oxidation states –III, 0, +III and +V, Se in the oxidation states –II, 0, +IV and +VI, and Sb in the oxidation states –III, 0, +III and +V, similar to As.

TABLE 1. European, Flemish[a] and Dutch[b] leaching limit values (mg/kg) for landfilling of hazardous and non-hazardous waste

	Non-hazardous			Hazardous		
Test	L/S 2	L/S 10	L/S 0.1	L/S 2	L/S 10	L/S 0.1
As	0.4	2–10[a]	0.3	6	25–10[a]	3
Cr	4	10–5[a]	2.5	25	70 – 5[a]	15
Mo	5	10	3.5	20	30	10
Sb	0.2	0.7	0.15	2	5	1
Se	0.3	0.5	0.2	4	7	3
V	–	–	–	–	20[b]	–
W	–	–	–	–	0.5[b]	–

[a]Flemish limit values (VLAREM)

[b]Dutch limit values (Dutch Landfilling Decree)

Many waste materials contain high concentrations of oxyanion forming elements:

- Wastes originating from high temperature processes: fossil fuel combustion products (bottom ash, fly ash, flue gas desulphurisation residue), solid waste incineration residues (bottom ash, boiler ash, fly ash, and air pollution control residues) and solid residues from ferrous and non-ferrous industries (blast furnace slag). All these wastes are usually alkaline.
- Wastewater treatment sludge.

We carried out several studies on the leaching and stabilisation of oxyanions from solid waste[1–10] and a comprehensive review on the subject[11] was prepared. This paper gives an overview of some findings of these studies. The results of these studies are of interest relative to water treatment, as in water treatment very often sludge or other waste with high concentrations of oxyanions is obtained, which much eventually be stabilised and landfilled; leaching of oxyanions may be at the origin of water pollution, e.g. around landfills; phenomena that govern leaching of waste (precipitation, adsorption, etc.) are also relevant in water treatment: precipitation and adsorption/solid solution formation may be used to remove oxyanions from wastewater.

Oxyanion leaching may be controlled by formation of a slightly soluble compound with a (very) low solubility product. Ca is a cation that occurs in high concentrations in many alkaline solid wastes. Table 2 gives some examples where precipitation with calcium has been suggested to be the main mechanism that controls oxyanion leaching in alkaline solid wastes.

TABLE 2. Studies on alkaline solid wastes where calcium metalates control the leaching of oxyanion forming elements

Element	Mineral	Waste type	Reference
As(V)	$Ca_3(AsO_4)_2.xH_2O$	Cement matrix	[8,12,13]
Cr(III)	$Ca_2Cr_2O_5.6H_2O$	Cement matrix	[14]
	$Ca_2Cr_2O_5.8H_2O$	Cement matrix	[15]
Mo(VI)	$CaMoO_4$	Bottom ash	[16–18]
		Fly ash	[19]
		Cement matrix	[20]
V(V)	$Ca_3(VO_4)_2$	Steel slag	[21]
W(VI)	$CaWO_4$	Bottom ash	[16]
		Cement matrix	[20]

Formation of a slightly soluble compound alone does often not explain the low concentrations obtained when leaching several waste types. Leaching may also be controlled by surface adsorption (ion plus counter ion sorbed on a mineral) or solid solution (mixed crystal) formation (one of the ions in a crystal lattice is replaced by an ion of another element with the same charge and a similar size).

In this paper the following three topics will be addressed:

- Leaching of As and Se from sludge from water treatment of NF metal production
- Immobilization of As in fly ash from the Cu industry
- Leaching of Sb from MSWI bottom ash

2. Leaching of As and Se from Sludge from Water Treatment of NF Metal Production

A sample of water treatment sludge from NF metal production was obtained at a site where lime was added to sulphuric acid wastewater, until a pH between 10.5 and 11.5, along with polyelectrolyte. Table 3 gives the main properties of the studied filter cake that is classified as a hazardous waste according to European legislation (Table 1).

TABLE 3. Total concentrations of the most important elements in the water treatment sludge of NF metal production and leaching characteristics (liquid-to-solid ratio = 10)

Ca	6.11 mol/kg	Porewater pH	11.1
As	0.899 mol/kg (6.7 wt %) of which 3.7% is As(III)	As leaching	38.3 mg/kg
Se	0.036 mol/kg (0.29 wt %) of which 21.3% is Se(IV)	Se leaching	19.5 mg/kg
Fe	0.248 mol/kg		
Al	0.232 mol/kg		
S	4.16 mol/kg		

The As and Se concentrations are very high. Figure 1 shows the XRD pattern of the original and washed filter cake. Originally the main minerals are gypsum and calcite, after washing most gypsum dissolves and calcite and rauenthalite, $Ca_3(AsO_4)_2.10H_2O$, appear more clearly.

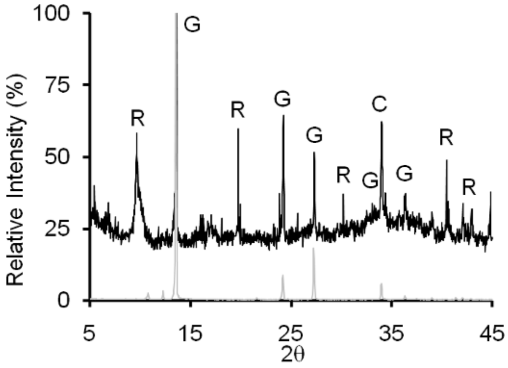

Figure 1. XRD pattern of original (gray) and washed (L/S = 500) sludge

Table 3 also shows the leaching value (L/S = 10) for the considered waste. As the standards in Table 1 are exceeded for both As and Se, a study of the leaching behaviour in function of pH is in order.

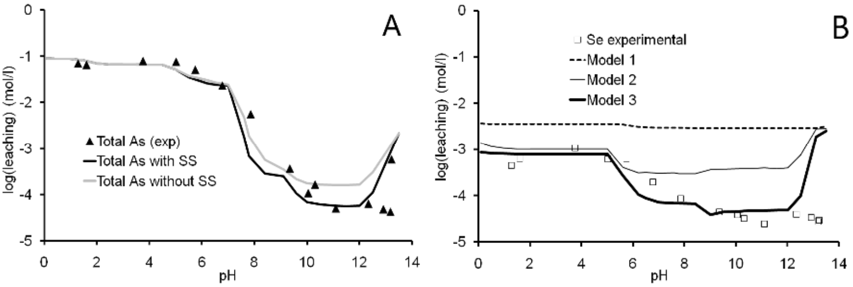

Figure 2. Experimental and modeled pH-dependent leaching behaviour of A) total As (As(V) + As(III)) and B) total Se (Se(IV) + Se(VI)) in water treatment sludge of NF metal production

Figure 2 gives the pH-dependent leaching behaviour of As and Se in the sludge and also shows the results of model calculations. These models were developed in PHREEQC[22] to find possible explanations for the behaviour of As(V), As(III), Se(VI) and Se(IV). A detailed discussion of model development can be found in Cornelis.[10] In the case of As, speciation was dominated by As(V) (Table 3). A first model for the leaching behaviour of As(V) ("without SS") considered precipitation of rauenthalite only. When ideal solid solution formation of rauenthalite with gypsum was considered, model predictions improved slightly. The behaviour of As(III) (results not shown) appeared to be controlled by $CaHAsO_3$ formation. In the case of Se, speciation was mixed Se(VI)/Se(IV) (Table 3). Three model calculations are shown in Figure 2B for the leaching behaviour of total Se (Se(IV) + Se(VI)). Model 1 only considered precipitation of $CaSeO_4$ and $CaSeO_3$ but overestimates total Se leaching by several orders of magnitude. Model 2 considered adsorption of Se(IV) to calcite and non-ideal solid solution formation of $CaSeO_4$ with gypsum. This approach improved predictions relative to model 1, but only in case of Se(IV). Se(VI) leaching was still overestimated by model 2 (results not shown). Model 3 considered adsorption of Se(IV) as in model 2 and ideal solid solution formation of $CaSeO_4$, gypsum and calcite. PHREEQC is not capable of calculating non-ideal solid solutions of more than two components.

Table 2 already suggested that calcium arsenates are relatively stable solids that can explain the often low As concentrations found in leachates of alkaline matrices, but in the case of Se(IV) and Se(VI), calcium metalates are much more soluble.

3. Immobilisation of As in Fly Ash from the Cu Industry

We also studied[1–4,6,8] the case of immobilization of As in fly ash from the copper industry containing As (40% w/w) in the As(III) oxidation state. The waste is produced in large quantities. Moreover, as useful applications of arsenic are limited in volume, recycling is not a valid waste treatment option for all this waste. Therefore it was attempted to develop a treatment method allowing controlled landfilling of the waste, complying with the leaching limits for landfilling. Two ways to achieve this were investigated:

- Direct solidification/stabilization
- Solidification after oxidation with H_2O_2

Direct solidification/stabilisation was applied according to a process with lime and cement addition. Per 10 g of waste material 8 g of lime, 10 g of cement and 20 mL water were added, and the mixture was allowed to solidify. It appeared, that the addition of lime was essential. Adding a sufficient amount of lime allowed to reduce the As-leaching from ca 3,000 mg/L to ca. 5 mg/L. This could be explained by formation of a $CaHAsO_3$-precipitate in the presence of an excess of $Ca(OH)_2$. The leaching value still exceeded the Flemish limit value (Table 1), but permission was obtained to apply the method in view of landfilling in “salt cell conditions”.

Oxidation of As (III) to As (V) gives lower leaching of As (0.5 mg/L) than without pre-treatment[6] with H_2O_2.Table 4 gives the calculated solubility at a pH of 12.5 for pure $CaHAsO_3$, $CaHAsO_3$ with an excess of $Ca(OH)_2$, pure $Ca_3(AsO_4)_2$ and $Ca_3(AsO_4)_2$ with an excess of $Ca(OH)_2$. These values are in good agreement with experimental data. It appears that pretreatment with H_2O_2 followed by stabilisation with $Ca(OH)_2$ and cement allows to comply with the 1 mg/L leaching limit for As.

TABLE 4. Calculated As concentration in equilibrium with pure calciumarsenate or arsenite with or without the presence of an excess of $Ca(OH)_2$ at pH = 12.5

Compound(s)	[As] mg/L
$CaHAsO_3$	65.4
$Ca(OH)_2 + CaHAsO_3$	5.4
$Ca_3(AsO_4)_2$	30.3
$Ca(OH)_2 + Ca_3(AsO_4)_2$	0.465

4. Sb in Municipal Solid Waste Incinerator Bottom Ash

As indicated in Table 1, Sb is recognized as a toxic element. The sand fraction (particle size 0.1–2 mm) of municipal solid waste incinerator (MSWI) bottom ash contains ca. 150 mg/kg of Sb, mainly originating from flame-retardants, Sb-alloys, brake linings and pigments. The recycling potential of this waste may be limited by the leaching of Sb. The leaching of Sb in the sand fraction of bottom ash regularly exceeds the relevant standards. In addition, the pH of a bottom ash will change due to weathering and this greatly affects Sb leaching. We therefore decided to study the mechanisms that control Sb leaching from this material.[9]

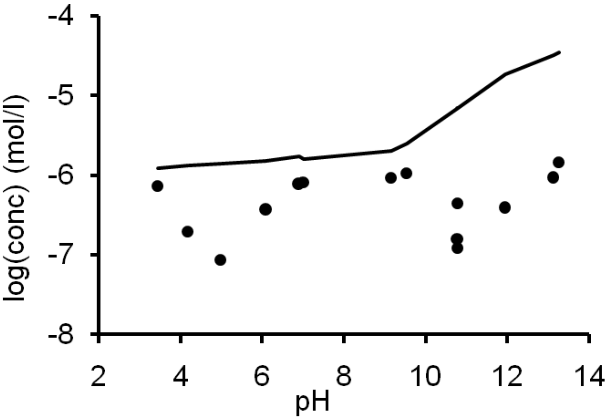

Figure 3. The pH dependent leaching behaviour of Sb in MSWI bottom ash (sand fraction) compared to saturation of calcium antimonate (full line)

Figure 3 shows the pH-dependent leaching behaviour of Sb in a mildly weathered MSWI bottom ash batch with a pore water pH of 11.8. From speciation analysis with HPLC-ICP-MS it appeared that the predominant soluble Sb species at the natural pH was antimonate ($Sb(OH)_6^{\bullet}$). Figure 3 shows that antimonate concentrations in bottom ash are lower than the curve calculated based on equilibrium with $Ca[Sb(OH)_6]_2$. For this calculation, the lowest solubility product found in literature[23] was applied (pK_{sp} = 12.55). The curve is, however, approached at pH = 3 and around pH = 8.

At pH < 7, Sb-leaching is believed to be controlled by adsorption to hydrous ferric oxides (HFO) and/or amorphous aluminium minerals[24] (AAM). It is however not known which mechanism controls Sb-leachability at the "natural" alkaline pH (11–12) of fresh or mildly weathered bottom ash. It is assumed that ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$) plays an important role due to its high abundance in bottom ash[25] and its high affinity for many other trace oxyanions.[10] Other minerals with affinity for oxyanions, such as calcite, portlandite and gypsum, also occur in large amounts in bottom ash, and can possibly also influence Sb leaching.

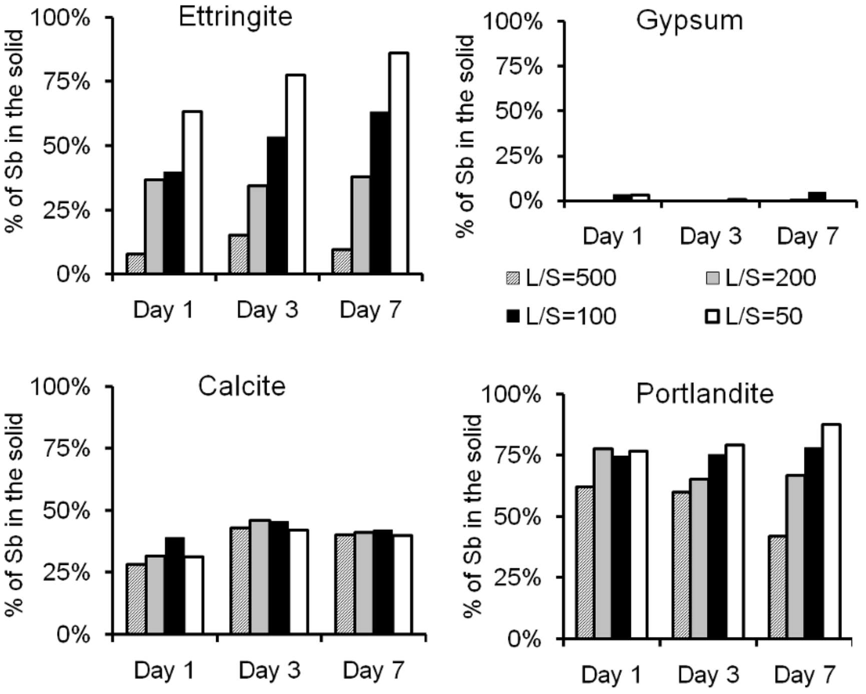

Figure 4. Adsorption of 100 ppb Sb(V) in ettringite, portlandite, calcite and gypsum suspensions at different liquid-to-solid ratios and as a function of equilibration time

Figure 4 shows the adsorption or solid solution formation of $Sb(OH)_6^{\bullet}$ in suspensions of ettringite, portlandite, calcite, and gypsum as a function of time and of liquid-to-solid ratio (L/S). The suspensions were allowed to reach full equilibrium before Sb addition. Sb concentrations were at all times well below the equilibrium concentration with calcium antimonate. The interaction with calcite is not clear because a relation with the L/S should exist if a solid solution or adsorption phenomenon occurred. Ettringite and portlandite both show significant uptake of Sb. Especially the interaction with ettringite is important. This mineral dissolves and is converted to gypsum and $Al(OH)_3$ as pH is lowered below 10.5. Gypsum has no affinity for Sb (Figure 4). Figure 3 shows that Sb indeed dissolves and approaches equilibrium with $Ca[Sb(OH)_6]_2$ as the leachate pH is gradually lowered below 10.5. This suggests that at the natural pH of MSWI bottom ash, Sb is controlled by adsorption or solid solution formation to ettringite. This is important in the context of weathering, as a pH decrease below 10.5 as a result of the reaction with atmospheric CO_2 will result in an increase in Sb leaching.

5. Conclusion

The leaching of the oxyanions of As, Se, and Sb from waste materials (sludge from wastewater treatment of NF metal production, solidified/stabilised fly ash from the Cu industry, MSWI bottom ash) is studied. The existence of slightly soluble Ca metalates often determines the solubility (As in all cases considered). Ca selenite and selenate are more soluble, so that adsorption and solid solution formation to e.g. calcite and gypsum had to be considered. Although for some pH values Sb leaching from MSWI bottom ash approaches the equilibrium value with $Ca[Sb(OH)_6]$, at $pH < 7$ Sb leaching is controlled by adsorption to HFO and AAM. At the natural pH of fresh bottom ash (11–12) adsorption to ettringite predominates.

Geochemical modelling is of great help in understanding these phenomena.

The information obtained may be of help in stabilizing oxyanion-containing materials, such as sludges or other wastes obtained in wastewater treatment, in view of landfilling. Moreover it allows understanding the origin of some cases of water pollution and it may help in designing water treatment for oxyanions based on precipitation or adsorption/solid solution formation.

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TRACE ELEMENTS SPECIATION IN MINING AFFECTED WATERS

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Abstract The trace element species distribution in the waters of Maresh and Luda Yana Rivers flowing the region of Cu–Mo Asarel-Medet mine, Bulgaria, were determined during a high-flow May 2007 by a combination of monitoring studies and a thermodynamic modeling. The mining activities, the weathering and the oxidation processes in the East dump were found to affect strongly the composition, physico-chemical characteristics and behaviour of trace elements in the whole water system. High levels of $SO42^{-}$, Cu, Mn, Fe, Al and acidity were determined in the affected stations. In the reference and mining affected waters different species were calculated. Cu^{2+} and $CuCO_3^{o}$ species (1:1) existed in the reference waters and Cu^{2+} and $CuSO_4^{o}$ species (1:1) in the polluted and affected waters. Cu^{2+} species was dominating downstream. Hydroxy species $Fe(OH)_2^{+}$, $Al(OH)_n^{3-n}$ ($n = 2–4$) (responsible for the formation of a suspended phase) and Me^{2+} ions followed by sulphate species $MeSO_4^{o}$ (Me = Mn, Zn, Cd and Pb), and carbonate species $PbCO_3^{o}$ and $PbHCO_3^{+}$ were predominant in the system. Some more sulphate species, such as $MeSO_4^{+}$, $Me(SO_4)_2^{-}$ (Me = Fe, Al), $Me(SO_4)_2^{2-}$ (Me = Zn, Cd, Pb), $Me(SO_4)_3^{4-}$ (Me = Zn, Cd) and $Cd(SO4)_4^{6-}$ also appeared in mining polluted and affected waters. Although the trace elements concentration decreased downstream However, the quota of their free metal species, which are more toxic, increased.

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

Keywords: Copper mining pollution; river waters pollution; inorganic chemical species; trace metals; thermodynamic modeling

1. Introduction

Nowadays the natural waters are under the influence of industrial (especially ores leaching and mineral processing), agricultural and daily human activities. In the waters of polluted areas the trace element contents are increased, but the monitoring studies that are regularly performed still produce data on the total trace metals content only, and not on the chemical species which are responsible for the metal toxicity and bioavailability. The thermodynamic approach and computer programs (e.g. PHREEQCI,[1] MINTEQA,[2] etc.) enable us to model chemical processes in river waters[3,4] by calculation of chemical species, their changes and distribution.

The purpose of this study was to calculate the trace metals species and their distribution in the waters of Maresh and Luda Yana Rivers, affected by Cu–Mo Asarel-Medet mine, Bulgaria by the use of monitoring analytical data and thermodynamic modeling.

Asarel-Medet, an open pit Cu–Mo mine with its two branches – Asarel and Medet, is the major producer of pyrite and copper concentrates in Bulgaria and is one of the largest in Europe. The deposits of Asarel and Medet mines are porphyry copper variably enriched in Au and Mo. Under atmospheric conditions, the ores undergo oxidation processes resulting in environmental pollution. For the minimization of pollution impacts, the acidic drainage waters from the East dump are collected and treated in purification plants. Generally the treatment procedures applied are effective but from time to time some problems arise and negative impact still exists.

Two rivers, the Maresh and the Luda Yana, and a few streams flow in the area (Figure 1). The Maresh is a small river (~10 km). It springs near the East Dump and flows in a mountainous area to the Luda Yana River in Panagiurishte city. The Luda Yana (~70 km long, 685 km^2 catchment area) is one of the biggest tributaries to the Maritsa River that discharges through Greece and Turkey (Evros River) to the Aegean Sea, where an ecologically important wetland is formed (the Evros Delta).

2. Experiments

The sampling stations were chosen to cover reference positions (Mr1 and Mr2 at both branches of Maresh River, and LYa1 at Luda Yana River), the main pollution source Ba1 (small lake with East dump drainage waters)

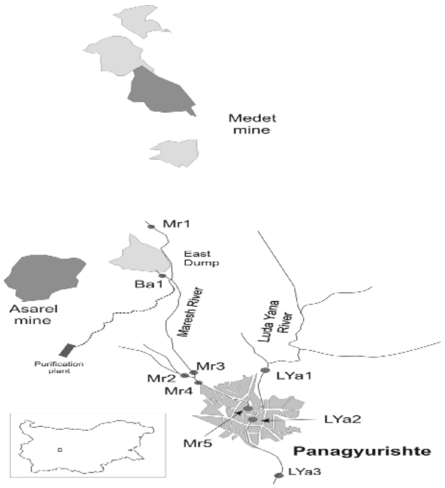


Figure 1. Maresh and Luda Yana Rivers sampling stations

and affected positions (Mr3, Mr4, Mr5, LYa2 and LYa3) (Figure 1). The study was carried out in May 2007 during the high-flow period and heavy rainfalls (102 L/m^2 for 2 weeks).

The chemical analysis of major elements, trace elements, nutrients as well as physicochemical measurements and samples preservation were described elsewhere.[5] Physico-chemical data and trace elements under considerations are only given (Table 1).

3. Thermodynamic Modelling

A thermodynamic ion-association model, PHREEQCI computer program, version 2.14.3 was used for simulating the dissolved inorganic species in the river waters studied. The model uses Debye–Hückel expressions to account non-ideality of aqueous solutions. Experimental data on the total content of the investigated elements were utilized in the calculations. An enriched thermodynamic database *sst2008.dat*[6] with thermodynamic constants K^0 of possible complexes in polluted natural waters was used for the calculations.

The redox processes (Fe^{2+}/Fe^{3+}; Cu^{+}/Cu^{2+}; $Mn^{2+}/Mn^{3+}/ Mn^{4+}/Mn^{6+}/Mn^{7+}$) in the system were predicted using the redox couple O^0/O^{2-}. The latter one is applied to modeling of well-oxygenated surface waters.[7]

TABLE 1. Physicochemical characteristics and trace elements content in Maresh and Luda Yana Rivers waters

	Reference stations			Drainage	Mining affected stations				
Stations	Mr1	Mr2	LYa1	Ba1	Mr3	Mr4	Mr5	LYa2	LYa3
				Physicochemical characteristics					
T, °C	17.7	18.5	16.2	17.5	18.7	18.4	18.3	17.1	16.4
pH	8.80	5.84	7.00	3.10	3.82	4.10	3.85	4.40	6.70
Eh, mV	-125	63	-19	206	164	150	159	129	21
Conductivity, µS/cm	302	716	129	4700	2170	1674	1185	454	247
Alkalinity, mg/L	43	<10	48	10	<10	<10	<10	<10	<10
O_2, mg/L	7.2	7.8	8.6	8.1	8.0	7.2	8.4	8.8	8.4
				Macro components					
Cl, mg/L	11.9	6.5	3.5	6.6	6.5	5.7	6.2	3.9	4.9
SO_4^{2-}, mg/L	67	410	45	5500	2000	1230	900	290	100
SiO_2, µmol/L	314.48	316.6	235.43	1179.35	645.15	510.13	474.73	294.95	270.75
				Trace elements – dissolved					
Al, mg/L	<0.10	<0.10	<0.10	431	110	91.4	68.4	16.5	<0.10
Fe, mg/L	<0.2	<0.2	<0.2	21.9	0.68	0.43	3.8	0.96	<0.2
Mn, mg/L	0.01	2.42	0.01	36.9	15.1	8.64	4.08	1.44	0.41
	Reference stations			Drainage	Mining affected stations				
Cu, mg/L	<0.03	2.19	0.13	274	100.3	61.6	43.9	11.7	2.14
Stations	Mr1	Mr2	LYa1	Ba1	Mr3	Mr4	Mr5	LYa2	LYa3
Zn, mg/L	0.01	0.36	0.01	6.66	2.46	1.65	1.04	0.30	0.09
Pb, µg/L	<1.0	<1.0	<1.0	1.41	<1.0	3.65	<1.0	1.0	<1.0
Cd, µg/L	<0.1	3.66	<0.1	85.0	25.6	25.2	10.9	3.06	0.89
				Trace elements – particulate					
SPM, mg/L	0.80	5.3	5.0	4.40	32.7	7.2	25.2	45.4	18.0
Al, mg/L	0.02	0.30	0.38	0.24	3.27	0.49	0.84	2.14	4.58
Fe, mg/L	0.03	0.25	0.20	0.13	0.89	0.32	1.77	0.79	1.04
Mn, mg/L	0.01	0.01	0.04	0.02	0.04	0.03	0.02	0.02	0.01
Cu, mg/L	<0.002	0.03	0.02	0.05	1.93	0.04	0.06	0.04	0.63
Zn, mg/L	0.001	0.002	0.002	0.002	0.016	0.002	0.003	0.004	0.006
Pb, µg/L	<0.01	0.02	<0.01	0.21	0.06	0.01	0.02	0.01	0.02
Cd, µg/L	0.18	0.48	0.49	0.21	2.29	0.50	1.09	1.31	1.89

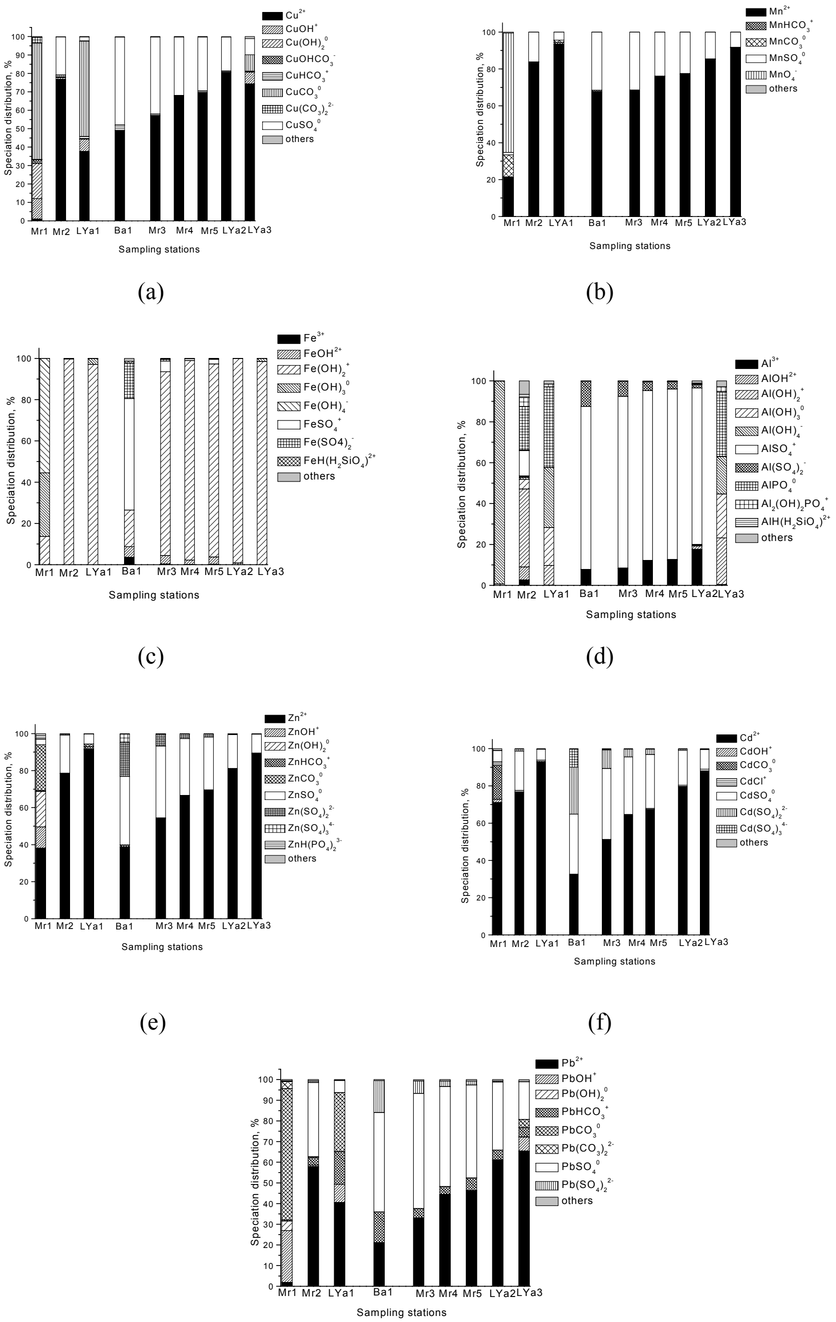
	Trace elements distribution Dissolved/particulate								
Al, %	82/18	25/75	21/79	100/0	97/3	99/1	99/1	89/11	2/98
Fe, %	26/74	4/96	23/77	100/0	55/45	73/27	68/32	60/40	22/78
Mn, %	66/34	99/1	20/80	100/0	100/0	100/0	100/0	99/1	98/2
Cu, %	100/0	99/1	89/11	100/0	98/2	100/0	100/0	100/0	77/23
Zn, %	94/6	100/0	84/16	100/0	99/1	100/0	100/0	99/1	93/7
Pb, %	0/100	0/100	0/100	100/0	83/17	89/11	0/100	43/57	0/100
Cd, %	99/1	100/0	99/1	100/0	100/0	100/0	100/0	100/0	98/2

4. Results and Discussion

The geological character and mining activities of the Asarel-Medet copper mine was found to strongly influence the composition, chemical speciation and physico-chemical characteristics of Maresh and Luda Yana River waters during high rainfalls (Table 1). Station Ba1 was a source of large pollution. High levels of SO_4^{2-}, Cu, Mn, Fe and Al were determined in the affected stations, which decreased downstream in the sequence Al≈Cu>>Mn>Fe>Zn>Pb>Cd.

The thermodynamic modeling showed a great variety of trace metal species depending on the composition, pH and redox potential of the waters. It is due to the ability of Me^{n+} ions in water solutions to coordinate predominantly with some of the existing anions. The calculations have only included Fe^{3+} and Cu^{2+} element states, which dominate in ore-dressing areas[3] and not Fe^{2+} and Cu^{+} because of their very low concentrations. Mn^{3+} and Mn^{7+}, which are not stable in natural surface waters were also included in the calculations. It was because in slightly acidic waters the Mn^{2+} ions are easily oxidized to Mn^{3+} and Mn^{7+}. Despite the fact that $[Mn^{7+}O_4]^-$ species are quickly reduced to Mn^{2+} in acid waters and to MnO_2 in neutral and alkaline waters, the latter was not taken into account in the calculations because of data absence.

Free Cu^{2+} ions followed by $CuSO_4^0$ species were the main pollutants of the studied waters (Figure 2a). In the polluted and affected stations they were in almost equal ratios (1:1), whereas downstream Cu^{2+} species were dominating. In the reference stations LYa1 and Mr1 $CuCO_3^0$ species were calculated as dominant followed by $Cu(OH)_n^{2-n}$ (n = 1,2) species. The latter determined the presence of copper in the suspended materials in these stations (Table 1).



(a) (b) (c) (d) (e) (f) (g)

Figure 2. Trace metals speciation distribution in the waters of Maresh and Luda Yana Rivers: (a) Cu; (b) Mn; (c) Fe; (d) Al; (e) Zn; (f) Cd; (g) Pb

Free Mn^{2+} ions were dominant in all the studied waters (Figure 2b). In the polluted and affected waters $MnSO_4^0$ species increased up to 35–38%. In the reference station Mr1 the non-stable MnO_4^- species was calculated as dominant, followed by Mn^{2+} and $MnCO_3^0$ species in equal concentrations (Figure 2b).

Contrary to copper and manganese, iron did not exist as free Fe^{3+} species in the studied system. Four hydroxy species, $Fe(OH)_n^{3-n}$ (n = 1–4), responsible for the formation of suspended phase and two sulphate species, $Fe(SO_4)_n^{3-2n}$ (n = 1–2), were calculated as typical of these waters. $Fe(OH)_2^+$ was the dominant species along the whole system, excepting the Ba1 and Mr1 stations. Two dominant species, $Fe(OH)_4^-$ and $Fe(OH)_3^0$, were found in the reference station Mr1. $FeSO_4^+$ and $Fe(SO_4)_2^-$ species were calculated in addition to a small amount of free Fe^{3+} ions and $FeH(H_2SiO_4)^{2+}$ species in the pollution Ba1 station (Figure 2c).

Dominant sulfate species $Al(SO_4)^+$ and $Al(SO_4)^{2-}$ and free Al^{3+} ions were calculated in the polluted and affected waters (Figure 2d). Hydroxy species $Al(OH)_n^{3-n}$ (n = 1–4), phosphates species $AlPO_4^0$ and $Al_2(OH)_2PO_4^+$ and $AlH(H_2SiO_4)^{2+}$ species were calculated in the reference stations (Figure 2c).

Free Me^{2+} ions (Me^{2+} = Zn (Figure 2e), Cd (Figure 2f) followed by sulphate species $MeSO_4^0$, $Me(SO_4)_2^{2-}$ and $Me(SO_4)_3^{4-}$ were found as dominant in the pollution and affected waters (Figure 2e).

Free Pb^{2+}, $PbCO_3^o$, $PbHCO_3^+$ and $Pb(OH)^+$ species were found in the reference stations. Sulphate species $PbSO_4^o$ and $Pb(SO_4)_2^{2-}$ were dominant in the polluted and affected waters. Their concentrations decreased downstream at the expense of free Pb^{2+} ions (Figure 2g).

The self-cleaning water ability increased by pH and followed the sequence Fe>Al>Mn>Cu>Pb>Zn>Cd.

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EFFECT OF ELECTROLYTES ON THE ELECTROCHEMICAL OXIDATION OF SYNTHETIC DYES

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Abstract Textile industries produce large quantities of wastewaters containing significant amounts of toxic organic substances (mainly synthetic dyes) and other pollutants. The impact on the environment is large and strict limits have been applied recently. Most of the currently available treatment methods cannot treat effectively wastewaters containing synthetic dyes. Methods that are based on the production of solids are ineffective due to the high solubility of synthetic dyes. Even when solids are produced the final solid residue is toxic and should be handled with care. One alternative method is electrochemical oxidation, which has the potential to destroy the toxic organic dyes to less toxic or smaller ones that are biodegradable. In this work it has been applied on commercially available synthetic reactive dyes (blue, orange and red) at various initial concentrations (100, 200, 500 and 1,000 mg/L) and promising results were obtained. The kinetics of the process was studied for each of the above dyes; 50% of the color was removed after 20 min for all dyes and the final concentrations after 60 min were similar. The effect of the type of electrolyte was also studied. Analytical solutions of $NaNO_3$, Na_2SO_4 and NaCl were used under similar conditions (electrolyte concentration, pH, applied Voltage and current intensity) and the results were compared. It was found that NaCl was much faster in colour removal for all three dyes used; 20 min were enough to remove the dyes when NaCl was used. However, the final

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

concentrations of the dyes after 60–90 min were similar. Even high initial concentrations of the dyes (i.e. 1,000 mg/L) were treated fast and effectively. The method was proved effective for the removal of synthetic dyes from model solutions.

Keywords: Synthetic dyes; electrochemical oxidation; electrolyte effect; decolouration

1. Introduction

Textile industry and its wastewaters is one of the main sources of severe pollution problems worldwide. In particular, the release of coloured effluents into the environment is undesirable, not only because of their colour, but also because many dyes from wastewater and their breakdown products are toxic and/or mutagenic to life.[1]

This wastewater has serious negative impact not only on underground and surface water bodies and land in the surrounding area but also has an adverse effect on the aquatic ecological system.[2]

Today nearly 1 million metric tones of dye is annually produced in the world of which azo dyes (R1–N=N–R2), represent about 70% on weight basis. The largest consumer of these dyes is the textile industry accounting for two thirds of the market. Recent estimates indicate that 12% of the synthetic textile dyes used yearly is lost to wastewater streams. Approximately 20% of these enter the environment through effluents from wastewater treatment plant.[3]

The increased colour intensity is the most serious problem of the wastewater provided by the textile industries because many of the commercial azodyes can produce hazardous aromatic amines, as well as other highly toxic by-products through metabolic processes in plants and animals or directly after the disposal in lakes, rivers or sea. Moreover, azodyes which are synthetic products, show rather low biodegradability, firstly because of lack of natural biodegradation paths and secondly because of stereochemical interferences concerning the accession of the reductant or oxidant molecule to the azo-group.[4]

Textile industry wastewater is usually treated by conventional methods such as adsorption, chemical oxidation or reduction and biological degradation. Adsorption does not solve the pollution problem, but shifts it into solid waste disposal problem, while chemical treatment produces final wastewater contaminated with significant quantities of chemical reagents.

Biological treatment, which is the main procedure used, causes sludge formation and additionally it is not able to degrade the pollutants completely, since it is known that huge organic molecules with many phenyl rings are hard to biodegrade, mainly due to stereochemical interferences.[5]

Due to the large variability of the composition of textile wastewater, most of the traditional methods are becoming inadequate. Among advanced oxidation processes, the electrochemical treatment has been receiving greater attention in recent years due to its unique features, such as versatility, energy efficiency, automation and cost effectiveness.[6]

It's an effective method for colour removal; there is little or no consumption of chemicals and degradation of recalcitrant pollutants can be achieved, including polyaromatic organic compounds like anthraquinone-based compounds.[7]

The purpose of this research was to explore the effectiveness of electrochemical decolourisation of model solutions of azodyes at different concentrations comparable with dye content from industrial textile effluents, using $NaNO_3$, Na_2SO_4 and NaCl as electrolytes and commercially available Ca/Pb electrodes.

2. Materials and Methods

Three commercial purity azodyes (Remazol gelb 3RS 133% CI 176 (Yellow), Remazol Brillantrot 3BS CI 236 (Red) and Remazol CI 19 (Blue), all manufactured by DyStar) were used. Model solutions were prepared by dissolving appropriate amounts of the respective dye in deionized water. The concentrations examined were 100, 200, 500 and 1,000 mg/L. The electrochemical oxidation experiments were performed in an electrochemical cell constructed from Plexiglas with places for electrodes at 1 cm distance. One anode and two cathodes, placed on each side of the anode, were used. The anode was made from niobe/synthetic diamond doped with boron[5] and the cathodes were commercially available Ca/Pb battery electrodes.

All the experiments were carried out at room temperature. For each experiment a model dye solution was prepared of a certain concentration. The pH was adjusted with NaOH to 10.0 ± 0.2, which is an average value for textile effluents. A certain volume (500 mL) of the solution was transferred to the electrochemical cell, a small amount (4 mL) of electrolyte ($NaNO_3$, Na_2SO_4 or NaCl) was added and potential was applied. The current intensity was kept constant during the experiment. The current density applied during experiments was ~15 mA/cm^2. An air pump was supplying air at the base of the cell. Samples of 10 mL were taken at various time intervals. Colour concentration was determined by measuring absorbance peak at the wavelength corresponding to each dye using a Hitachi 2000 UV-Vis spectrophotometer.

3. Results and Discussion

Textile wastewaters contain significant amounts of dyes, which colorize the water streams. Removal of colour from these streams by sorption or membrane processes just shifts the problem from the liquid to the solid phase. The best way to remove the colour is to destruct it. The aim of this work was to investigate if electrochemical oxidation would be able to remove the colour from model solutions containing medium (i.e. 100 mg/L) and relatively high concentrations (i.e. 1,000 mg/L) of synthetic dyes. Initially, model solutions made from synthetic reactive dyes (yellow, red and blue) were tested at initial dyes concentrations 100 mg/L. The pH of the solution was adjusted to 10.0 with NaOH. A small concentration (4 mL of 1M electrolyte in 500 mL of solution) of three different supporting electrolytes ($NaNO_3$, Na_2SO_4 and NaCl) was added. The results are given at Figures 1, 2 and 3 respectively. As the electrolytes had a common cation (Na^+) what was actually tested was the effect of the anions on the electrochemical oxidation.

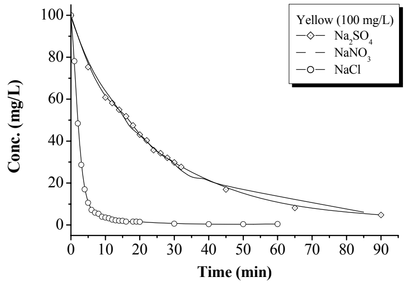

Figure 1. Effect of electrolyte on yellow colour (CI 176) removal: pH 10.0

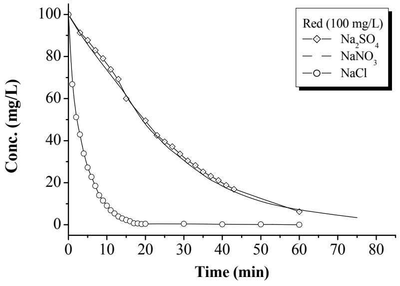

Figure 2. Effect of electrolyte on red colour (CI 236) removal: pH 10.0

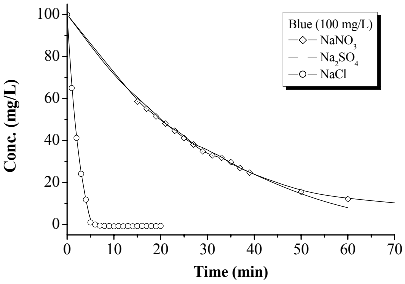

Figure 3. Effect of electrolyte on blue colour (CI 19) removal: pH 10.0

The effect of $NaNO_3$ or Na_2SO_4 on each colour was very similar. The curves were almost identical. Colour degradation was continuous with time. Half of the colour was removed at 20 min and equilibrium was obtained at 80 min with almost complete decolouration. The effect of NaCl was much more pronounced than the other two electrolytes. The kinetics of the process was significantly faster for each of the colours. The NaCl curves were initially very steep; in 5 min around 80% of the colour was removed from all three colours studied. Equilibrium was obtained in 10, 15 and 5 min for yellow, red and blue colour respectively. This clearly shows that chlorides played an important role while nitrates and sulphates did not participate in decolouration reactions. A good criterion for reaction rate comparisons is the half-life of the dye. The half-lives of the three dyes for the three supporting electrolytes are given in Table 1.

TABLE 1. Comparison of half-lives for various electrolytes

Dye	$NaNO_3$	Na_2SO_4	NaCl
Yellow	16.6	15.5	2.04
Red	19	19.6	2.2
Blue	19.5	19.8	1.5

It is clear that NaCl was affecting significantly the kinetics of decolouration of all three colours studied, as the half-lives are almost eight to nine times smaller. For further experiments NaCl was chosen as the supporting electrolyte.

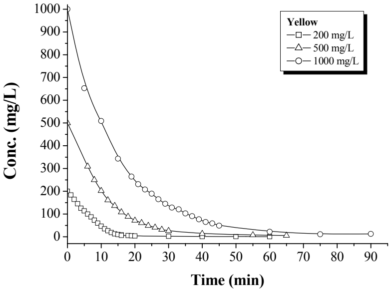

Figure 4. Yellow colour (CI 176) degradation with time: pH 10.0

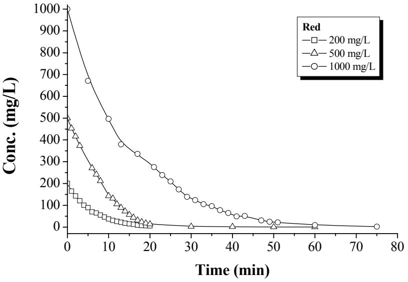

Figure 5. Red colour (CI 236) degradation with time: pH 10.0

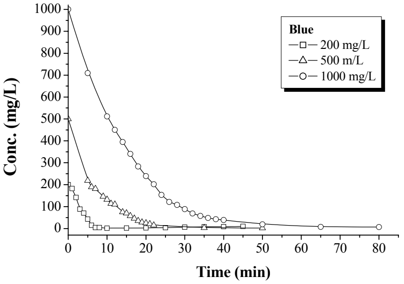

Figure 6. Blue colour (CI 19) degradation with time: pH 10.0

Decolouration of concentrated solutions is even more important than decolouration of solutions of low dye concentrations. As the synthetic dyes, which are used today, are toxic, the best solution is to degrade them to harmless or easily biodegradable products. Most other methods that simply remove dyes from wastewaters produce small to medium quantities of highly concentrated and toxic dyes that should be disposed off properly. It would be much better if those highly concentrated dyes could be degraded. For this reason, the effectiveness of electrochemical oxidation was examined on solutions of the three dyes with initial concentrations 200, 500 and 1,000 mg/L. The results are given in Figures 4, 5 and 6 for yellow, red and blue dye respectively. NaCl was used as electrolyte and the pH was adjusted to 10.0 with NaOH. The current density for all experiments was 15–16 mA/cm^2. The corresponding half-lives are given in Table 2.

TABLE 2. Comparison of half-lives for various concentrations with NaCl as electrolyte

Conc. (mg/L)	200	500	1,000
Yellow	5.3	8.0	10.1
Red	4.2	6.5	9.7
Blue	2.9	4.6	10.4

A fast decolouration was observed for all studied dyes. The time needed for the degradation of the dyes increased proportionally with the initial dye concentration. For initial concentrations 200 and 500 mg/L the blue colour showed faster kinetics than the other two; the time for half-life was smaller. For 1,000 mg/L initial conc. all dyes showed a similar rate (half-lives around 10 min). A complete decolouration was achieved for all dyes in ~30 min, being much faster for blue (10 min) at 200 and 500 mg/L. Solutions of 1,000 mg/L needed a longer time of treatment to obtain the same results. Almost complete decolouration could be achieved after 75 min for red and blue, and 90 min for yellow.

Under these conditions, the rate of dye degradation is controlled by mass transfer limitations. The dye molecules should approach the electrodes, react there and the reaction products should leave the electrode's area. As the concentration increases the diffusion rate is not enough to replenish the electrode area with unreacted molecules. The electrochemical reaction rate is much higher than the diffusion rate, thus making the degradation rate proportional to the bulk concentration.[8]

The drastic effect on chlorides on dye's degradation rate can be explained if the electrolysis of NaCl is considered. It is well known that the electrolysis of NaCl results in some very strong oxidants, such as free chlorine (Cl_2) at the anode with subsequent formation of hypochlorite anions (ClO^-). Subsequently, the oxidation of the dye is achieved.[8,9] The whole decolouration proceeds mainly via direct redox reactions on the electrodes, enhanced by indirect redox reactions by the produced oxidants or reductants. The stronger the oxidants or reductants are, the better enhancement they can achieve. Consequently, the dye molecules can more easily be degraded in aquatic media containing chloride anions (Cl^-).[4]

4. Conclusions

Electrochemical oxidation is a fast and effective method for decolouration of synthetic reactive dyes from medium and high initial concentration water solutions (100–1,000 mg/L). Chloride anions (introduced as NaCl) play a very important role increasing drastically the decolouration rate. Chlorides participate in redox reactions with the dye molecules through the formation of free chlorine (Cl_2) at the anode with subsequent formation of hypochlorite anions (ClO^-). Complete decolouration of solutions of yellow, red and blue reactive dyes with initial concentrations 100, 200, 500 and 1,000 mg/L was obtained. During electrochemical treatment synthetic azodye's molecules were destroyed to smaller colorless products, which are more biodegradable.

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HEAVY METAL CATIONIC WASTEWATER TREATMENT WITH MEMBRANE METHODS

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Abstract Nanofiltration (NF) and low-pressure reverse osmosis (RO) for the removal of zinc ions from wastewaters have been studied. Influence of co- and counter-ions concentration in feed water on zinc removal by NF, RO was analyzed and described. The effect of the pH on the Zn removal has shown that RO could not be recommended for acidic cationic wastewater treatment due to high osmotic pressure. The isoelectric point of nanofiltration membrane (pH ≈ 5.4) has been defined.

Keywords: Nanofiltration; reverse osmosis; wastewater treatment; heavy metals; co-ions; counter-ions

1. Introduction

Wastewaters containing heavy metals are discharged to the environment by variety of industries, such as galvanic, metallurgical, electronic, etc. The removal of heavy metals from wastewaters is of critical importance due to their high toxicity and tendency to accumulate in living organisms. Moreover, heavy metals can not be degraded or destroyed.[1]

Various heavy metal cationic wastewater treatment methods have been developed in recent years. Use of effective wastewater treatment technologies allow the industrial facilities to create water recycling systems, saving discharge fees and freshwater supply payment. Membrane filtration processes are prevailing methods in cationic wastewater treatment due to the number

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

of their advantages, among them: high rejection, low footprint of equipment, low reagent consumption.

The most applicable are following pressure-driven membrane processes:

Microfiltration (MF) is based on the sieving mechanism. Particles with a higher size than the membrane pore dimension are retained whereas smaller particles pass through the membrane. MF can be applied for removal of dispersed heavy metal hydroxides or for separation of adsorbent powder with adsorbed cations.[2]

Ultrafiltration (UF) is based on the adsorption-sieving mechanism and applied for separation of macromolecules or colloidal particles from liquid.

Reverse Osmosis (RO) demonstrates a high heavy metal rejection, compared to ion exchange, but it is operated in a continuous flow mode and has considerably lower reagent consumption. RO technique of heavy metal cationic wastewater treatment can provide potable-grade water or high purity water for technological operations.

Nanofiltration (NF) is the separation process, using specially designed membranes with electrically charged surface.

The pore size of NF membranes is of 20–50 Å, corresponding to a molecular cut off value of 200–500 g/mol.

The electrostatic interaction between surface and corresponding ions, as well as steric and Donnan effects, plays the main role in separation of ions with different valences.

It is important to note that the general theory of nanofiltration is not yet developed due to the variety of factors affecting this process. The main of them is a membrane selective layer composition corresponding with its electrostatic charge properties, membrane structure and pores characteristics.

Analysis of the data published in various sources[3–6] and our own experience showed, that low-pressure RO and NF demonstrate very prospective parameters- high rejection and flux as well as low energy and material consumption for wastewaters purification.

In previous studies the effect of heavy metals cations concentration and temperature on the main characteristics of separation process – permeate flux and rejection were determined[7,8]. It was shown that the rejection data for these cations (copper, nickel, zinc, cadmium) are of important values reaching 98.0% for NF and 99.3% for RO. However, all results were obtained from model solutions, having only one metal cation and corresponding anion. Real wastewaters usually contain greater number of ions and their mutual interaction should influence the process itself. The main goal of this study was to reveal the influence of co- and counter-ions concentrations (in feed water) on zinc removal and corresponding mechanism of membrane recharging.

2. Experimental

The investigations were carried out using commercial NF spiral-wound ERN-B-45-300 Vladipor, and GE Osmonics spiral-wound RO thin film TFM-75 membrane elements. The modules were placed in standard housings.

The membrane filtration unit (Figure 1) consists of feed water tank, rotary pump, two cartridge filters (activated carbon for tap water chlorine removal and microfilter-5 μm for fine particles retention), two parallel membrane modules, valves and instruments. Valves V1-4 were used for feed pressure adjustment; pressure gauges 1–2 to measure pressure drop on cartridge filters, and gauges 2–3 to check transmembrane pressure; two flow meters 4–5 controlled concentrate and permeate flow rates.

Permeate and retentate were recycled to the feed tank in order to keep the feed concentration constant. Samples of permeate were collected at a given time interval, to measure the observed salt rejection (R) and permeate volume flux (Jv).

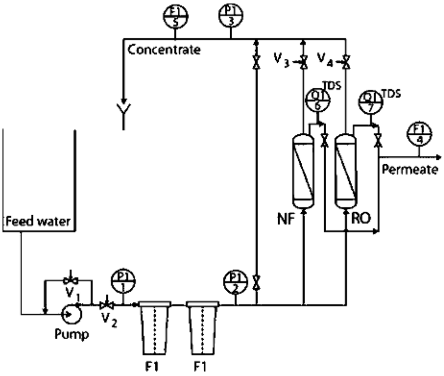


Figure 1. Process and instrumentation diagram of NF/RO unit

At given experimental conditions, steady state regime was reached after approximately 30 min. Feed pressure was P = 4 bar, the experiments were carried out at 25 ± 2°C.

Model solutions of wastewater were prepared by adding required amounts of zinc, cadmium, potassium, calcium, magnesium chloride and zinc sulphate to distilled water.

Feed concentration of basic cation (zinc) was 10 ppm. The zinc ion concentrations were measured by an atomic absorption spectrophotometer according to standard methods. Feed pH value (5.5 ± 05) was in the region of supposed isoelectric point of NF membrane.

3. Results and Discussion

In first series of experiments the effect of co-ions concentration on zinc rejection for NF and RO was analyzed (Figures 2 and 3).

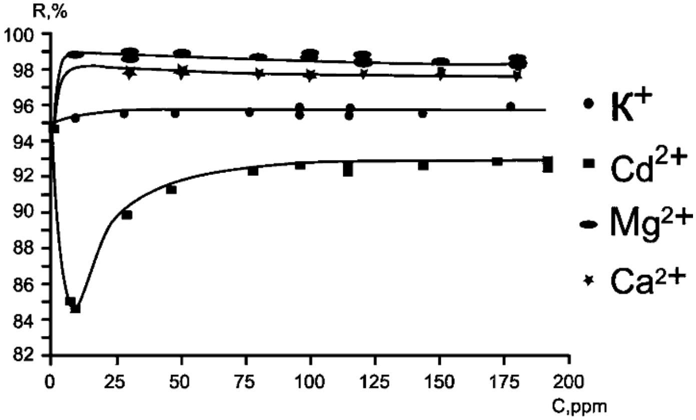


Figure 2. NF zinc rejection vs. feed co-ions concentration

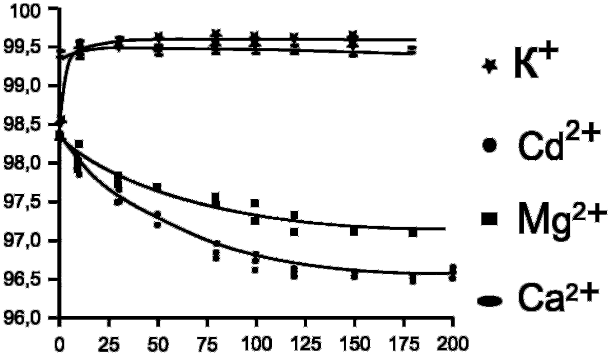


Figure 3. RO zinc rejection vs. feed co-ions concentration

The results obtained while examining co-cations (K^+, Mg^{2+}, Ca^{2+}) concentration influence on NF zinc rejection showed that there are no significant changes. In contrary, the effect of cadmium concentration on zinc rejection for NF membrane is quite different- local minimum was observed. Evidently, that in this region of pH values cadmium-ion is hydrolyzed. The relationship between cadmium-ion and membrane pore surface has specific character.

Figure 3 shows that increasing of magnesium and cadmium concentration diminishes RO zinc rejection due to increasing osmotic pressure and value of concentration polarization. The effect of potassium and calcium cations on RO zinc rejection can be explained by increasing of penetration rate of these ions through so-called "stagnant water" layer.

In second series of experiments, we studied influence of feed counter-ion (SO_4^{2-}, Cl^-) concentration on RO and NF zinc rejection. The results are presented in the Figure 4.

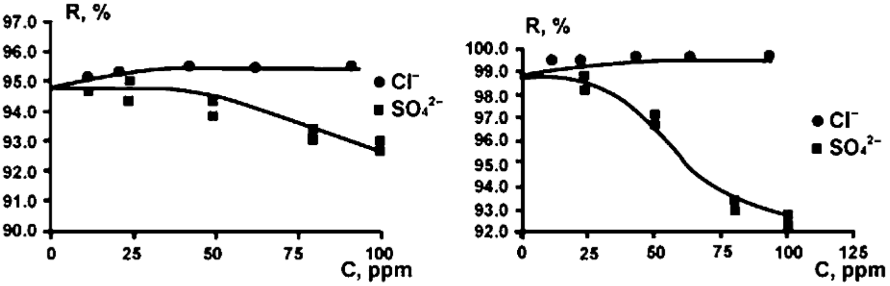
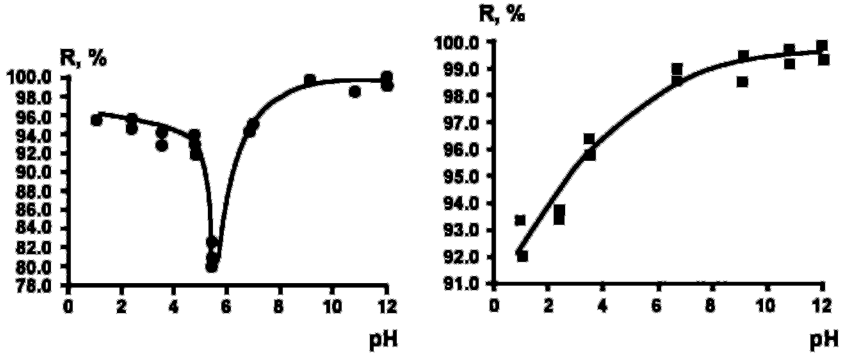


Figure 4. NF/RO zinc rejection vs. feed counter-ions concentration

Figure 4 shows that the influence of feed sulphate-ion concentration on RO is greater than on NF. It can be explained with lower value of concentration polarization in NF process than in RO process (in equal conditions).

In third series of our development the dependence of NF and low-pressure RO zinc rejection on feed pH value was analyzed.



(a) nanofiltration (b) reverse osmosis

Figure 5. NF/RO zinc rejection vs. feed pH value

As presented in Figure 5 RO rejection was drastically decreased at pH < 4 due to the increase in feedwater osmotic pressure (pH was decreased step-by-step with addition of sulfuric acid; concentrate and permeate were fully recycled to feedwater tank), which means that RO could not be recommended to acidic cationic wastewater treatment due to high-osmotic pressure.

Dependence between pH values and corresponding rejection data has the local minimum. This phenomenon could be explained by membrane recharging and, obviously, at pH = 5.4 the point of zero charge was observed.

At present, investigation on NF mechanism and its influence on heavy metal separation characteristics are being carried out.

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SEPARATION OF CESIUM-137, STRONTIUM-90 AND ACTINIDES FROM WATERS AND WASTEWATERS: A SHORT REVIEW OF THE MATERIALS AND PROCESSES

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Abstract The presence of ^{137}Cs, ^{90}Sr and actinides in waters is mainly connected with the nuclear power production and the development and testing of nuclear weapons. Minor amounts of U and Th, and their decay products, are also associated with the U-mining and milling, the production of phosphate fertilizers and the coal burning for power production. This contribution is going to present the principle ways of removing ^{137}Cs, ^{90}Sr and actinides from natural waters and effluents of the nuclear industry.

Keywords: Cesium-137; strontium-90; actinides; waters; wastewaters; sorption; extraction; precipitation

1. Fission Products and Actinides in the Environment

The presence of fission products and actinides in the environment is directly connected with the nuclear power production or the development and testing of nuclear weapons. Pollution of the environment by the naturally occurring U- and Th-isotopes is also due to uranium mining and milling, production of phosphate fertilizers and coal burning in conventional power stations.[1] In global terms the uranium mining represents the major health and environmental hazard of the nuclear industry.[2]

The release of radioactive materials by the nuclear industry under normal operating conditions is relatively small. Severe environmental contamination has only been observed in cases of nuclear reactor accidents, explosions in

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

nuclear waste storage facilities and in the surroundings of nuclear fuel reprocessing plants.[1, 3–5]

Among the fission products released by the nuclear industry and the weapon testing, ^{137}Cs ($T_{1/2}$ = 30.1 years) and ^{90}Sr ($T_{1/2}$ = 28.8 years) are, because of their high fission yield and their half-life, of long-term environmental importance. On the other hand, Np-, Pu-, Am- and Cm-isotopes are the most abundant transurans produced during the operation of nuclear reactors and the atmospheric or underground nuclear explosions.

All fission products and actinides injected to the environment become involved in a series of chemical, geochemical and biogeochemical processes and are finally transferred through different pathways to man.[6]

1.1. BEHAVIOR OF CESIUM-137, STRONTIUM-90 AND ACTINIDES IN THE AQUATIC ENVIRONMENT

Radioactive Cs-isotopes released in natural waters can primarily be found in cationic form, adsorb to suspended solids and are ultimately deposited in sediments. Cesium is also bioconcentrated and bioaccumulated in terrestrial and aquatic food chains.[7]

Strontium-90 is present in aquatic systems in the form of mobile compounds of low molecular weight and appears to be removed by outflow and radioactive decay. Only small fraction of ^{90}Sr entering the aquatic system is bound to the bottom sediments. Strontium also shows a high bioconcentration tendency.[8] The concentration of Ca in the water inversely influences the strontium bioaccumulation.

The actinide of primary importance for the nuclear industry is uranium whereas thorium can gain importance in the future. Transmutation and decay in U-fuelled reactors generate large amounts of Np-, Pu-, Am- and Cm- as well as smaller amounts Bk and Cf. In the case of direct disposal of the used fuels to a repository, the uranium with the rest actinides and the fission products remain together until an eventual failure of both cladding and containment allows gradual leaching by groundwater. If the fuel is reprocessed, most uranium and plutonium are separated whereas the long lived fission products and the minor actinides are left in the waste also containing some small amounts of Pu-isotopes and some uranium. The mixture is solidified and disposed in the same way as the intact fuel. Concerning the release of radioactivity apply the same considerations. The reprocessing of nuclear fuel also leads to the production of liquid waste requiring further treatment.[9] Besides the waste of the civil nuclear production industry, large volumes of waste remained from early military plutonium production programs. The management of these, in underground tanks stored, waste is imperative and would be much facilitated if the cesium, strontium and actinides were separated. Finally, the control of the pollution caused by U-mining and by the uncontrolled disposal of the residues of several other industrial activities is of great importance for the protection of the aquatic environment.

The actinide elements exhibit many oxidation states and therefore show a complex chemistry.[9,10] The prediction of the actinide behavior in an aqueous systems is very difficult and requires extensive information about the geologic environment, the temperature, the pressure, the pH, the redox potential (Eh), the ligand concentration as well as about the presence of organic matter and microorganisms. In general, the solubility of actinides in most natural waters is very low. The actinides in the V oxidation state show the highest solubility, whereas those in the IV oxidation state, the lowest. Neptunium, the only actinide favoring the V oxidation state, shows the highest solubility, whereas plutonium, favoring the IV oxidation state in many natural waters, a quite low one.

2. Materials and Processes for the Separation of Cesium, Strontium and Actinides from Aqueous Streams

Ion-exchange using natural and synthetic sorbents, solvent extraction and precipitation are the main processes that have been used for many years for the removal of ^{137}Cs, ^{90}Sr and actinides from aqueous solutions. Among the natural sorbents the zeolites early gained attention and were utilized for decontamination and nuclear waste treatment purposes.[11] These natural aluminosilicates possess high ion-exchange capacity and selectivity. Organo-modified zeolites were also tested as sorbents for anionic forms of fission products and actinides[12] (e.g., $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$).

High ion-exchange capacity and selectivity also characterizes the clay minerals but their small grain size does not especially favor their direct use in separation columns. However, the clays find, as the zeolites, applications as backfill materials in underground repositories retarding the migration of fission products and actinides in the environment and as decontamination agents for soils and water basins.[13–15] Locations rich in natural zeolites and clays (e.g. Yucca Mountains) were also proposed as potential repositories for high level radioactive waste (HLW).[16]

In addition to zeolites and clay minerals, a number of other inorganic and organic sorbents, extractants and precipitants have been investigated and applied in different processes to the removal of radioactive Cs- and

Sr-isotopes and actinides from nuclear waste streams.[9,17–19] Generally, the inorganic materials mainly find application where extreme selectivity and radiation-, heat- and chemical resistance are important.

Among the investigated inorganic materials for the removal of ^{137}Cs and ^{90}Sr from nuclear waste streams the metal hexacyano-ferrates have a profound position possessing high selectivity and ion exchange capacity for Cs-isotopes but, on the other hand, limited stability at enhanced pH environments.[20] Composite and newly developed insoluble granular transition metal hexa-cyanoferrates (e.g. CsTreat® [21]) combine the extreme selectivity with the wide operational pH range.

Ammonium molybdophosphates (AMP) also found extensive applications to the removal of cesium from acidic aqueous solutions. However, the small particle size of the material made large-scale column application quite difficult. The embedment of AMP in polyacrylo-nitride matrices (AMP-PAN) resulted in granular sorbents with good performance in acidic environments suitable for column applications.[22]

Studies on crystalline (CST) and semicrystalline silicotitanates indicated that these materials exhibit strong retention ability for cesium in both acidic and basic environments, but limited stability at highly alkaline solutions.[20,23–27] Their maximum cesium binding ability was observed in the pH range 2–6. The silicotitanates can be vitrified and disposed but not regenerated. The Cs-selectivity of the silicotitanates is based on the control of its lattice spacing (<0.8 nm) excluding larger hydrated ions (e.g. Na-ions). High Na-concentrations in the solution significantly interferes on the cesium uptake. The selectivity for cesium can be enhanced, on the cost of the ion-exchange capacity, by substitution of Nb^{5+} ions for Ti^{4+}.[21] The optimization CST can also lead to materials able to adsorb Sr and actinides.[25–27] Mono-sodium titanate (MST), sodium nonatitanate and pharmacosiderites also show enhanced strontium sorption ability. The MST can also effectively remove limited amounts of uranium, neptunium, plutonium and americium but does not pose criticality concerns. Recent research presented in the literature indicated the peroxo-titanates show improved kinetics, selectivity and capacity for Sr and actinide (especially Pu) separations.[27]

Silicotitanates are commercially available under different trade names (e.g. IONSIV by UOP Molecular Sieves, SrTreat® by Selion). The comparison of IONSIV IE-911 with AMP-PAN as Cs-sorbents indicated that second one is more effective than the first one for the Cs-removal from acidic solutions. However, the disposal of Cs-loaded IONSIV IE-911 may be more straightforward than the AMP-PAN, because its inorganic matrix is less sensitive to radiation.[28] Generally, the strontium selectivity of the most sorbents is rather poor in the presence of calcium in the solution. SrTreat®, a commercial strontium silicotitanate sorbent was found to possess high selectivity against Na ($k_{Sr/Na}$=200,000) but rather limited operational pH range (above 9) and calcium sensitivity.[21,29]

Raw,[30–32] composite[33] and Fe(III) hexacyano- ferrate(II)-modified[34] Ti- and Zr-phosphates were also investigated and found to remove efficiently ^{137}Cs, ^{90}Sr and actinides from aqueous solutions.

Organic ion exchange resins, such as the resorcinol-formaldehyde (RF), Duolite® CS-100, Diphonix-CS™, and SuperLig® 644, have been tested and used among others for the cesium separation from civil and weapon nuclear waste.[35–37] Especially, the SuperLig® 644 resin has high selectivity for Cs in alkaline solutions because it is based on a crown-ether attached to an organic substrate. The basis of the selectivity is the size of the opening in the crown ether, which is sized to accept Cs and reject the larger hydrated Na-ions. Analogous products based on crown ethers have also been developed for the separation of Sr, Tc and actinides.[38]

Tributyl-phosphate dissolved in kerosene or dodecane is the main extractant used for the separation of uranium and plutonium from used nuclear fuels. The separation of plutonium from uranium takes place in a second stage by reduction of plutonium by excess of U^{4+} to Pu(III), which remains in the aqueous phase (PUREX procedure).[39] A number of other extractants has also been tested and proposed for the separation of actinides. These extractants include monoamides ($R\ CONR'_2$), which were also proposed as an advantageous alternative to TBP, mono- and polyfunctional organophosphorous extractants, diamides ($(RR'NCO)_2CHR''$) as well as soft nitrogen- and sulfur-donor ligands.[17–19,40] Especially interesting is the development of specialized anion receptors for the separation of actinide anions (e.g. $Pu(NO_3)_6^{2-}$, negatively charged actinyl-complexes).[41]

Solvent extraction of Cs and Sr has also been reported using large hydrophobic organic anions, neutral extractants and hydrophobic organic acids. Dicarbollide dissolved in organic solvents, crown ethers and combinations of crown ethers with calixarenes as well as functionalized calixarenes were also effectively applied to extraction of cesium isotopes from acidic solutions.[20,42,43] Crown ethers alone have shown stability problems.[20] The recent use of combinations of extractants (e.g. chlorinated cobalt dicarbollide, polyethylene glycol, and diphenyl-*N,N*-di-n-butyl-carbamoyl-methyl-phosphine oxide) increases the effectiveness of the decontamination removing simultaneously Cs- and Sr-isotopes, actinides and lanthanides from aqueous solutions (e.g. UNEX process[39]).[44]

Precipitation and co-precipitation processes are only applied in combination with more advanced techniques for the separation of fission products and actinides. These techniques are, in many cases, not especially selective and lead to low purity precipitates. Co-precipitation processes have been generally used for separations from low concentration solutions. For example, coprecipitation by in-situ formed magnetite can efficiently remove Pu(IV) and Np(V) along with Sr(II) from alkaline nuclear waste solutions achieving decontamination factors 2–3 orders of magnitude higher than those obtained using MST.[45,46]

Biosorption and bioaccumulation processes can also remove radioactive Cs- and Sr-isotopes from waters.[47–49]

Finally, the purification of uranium mining and milling waste waters can be decontaminated using co-precipitation procedures (e.g. using $BaSO_4$ from the removal of Ra-isotopes, chemicals for the reduction of U(VI) to (U(IV)) and ion exchange utilizing natural and synthetic sorbents. The use of microorganisms can also play an important role to the purification of mining wastewaters and to the remediation of the polluted environment.

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Mo, Sb AND Se REMOVAL FROM SCRUBBER EFFLUENT OF A WASTE INCINERATOR

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Abstract Common physicochemical treatment of industrial wastewater is not very efficient regarding the removal of the oxyanion forming elements selenium, molybdenum and antimony. An industrial case is described where effluents from the wet treatment of flue gases from a rotary kiln for the incineration of industrial waste, contain variable amounts of the elements mentioned. The effluent of the scrubbers is neutralized, coagulated and flocculated. Mercury is removed by precipitation with TMT. The installation shows satisfactory results, complying with the regulations for common cations. The effluent of the settling tank still contains variable concentrations of selenium, molybdenum and antimony and the overall removal efficiency is not reproducible for these elements. Laboratory experiments are presented for the removal by co-precipitation and the results are discussed. Possible treatment methods are selected and evaluated in a matrix that may help in the selection of methods for the simultaneous removal of oxyanion forming elements.

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

Keywords: Oxyanions; industrial wastewater; waste incineration; antimony; molybdenum; selenium

1. Introduction

Increasing environmental health concern leads to lower acceptable quality standards for surface water and drinking water for the elements Mo, Sb and Se.

Numerous reviews[1–6] and articles are written about the removal of the oxyanion forming elements Mo, Sb and Se from drinking water supplies, mining waters, effluents from oil refineries etc. Table 1 gives an overview of possible treatment methods.

TABLE 1. Possible water treatment for removal of Mo, Sb and Se

	Mo	Sb	Se
Lime precipitation	$CaMoO_4$ pKsp = 8.64	$Sb(OH)_3$ $Ca(Sb(OH)_6)_2$ pKsp= 12.55.	$CaSeO_4$: pKsp= 4,77 $CaSeO_3$: pKsp= 7.76.
Adsorption/ coprecipitation HFO	< pH 8, e.g. 100 mg Fe(III)/l at pH 4, also with ferric sulphate : 11 ppb possible[7]	Sb(III) (insoluble $Sb(OH)_3$) adsorbs at high pH, < pH 8: also Sb(V)[8,38] 200 ppb possible after reduction	SeO_4^{2-} has lower affinity than SeO_3^{2-} < pH 10 (optimally 4–6) adsorption of Se(IV) Reduction : e.g. Green Rust, Zn, $Fe/FeSO_4$, $Fe(OH)_2$ < pH 7.5: also Se(VI)[9–12,24] ppb range possible
Sulphide precipitation	–	Max solubility 200 ppb as Sb_2S_3 and Sb_2S_5 (not TMT)[38]	>92% removal efficiency[13]
Bariumsulfate	BaMoO4 pKsp = 6.96		Coprecipitation when treating high sulfate waters with $BaCl_2$[23] $BaSeO_4$, pKsp = 7.3 $BaSeO_3$, pKsp = 6.57
Electrocoagulation	coagulating sedimentation generating calcium molybdate [14] 6 ppb possible[16]	?	Adsorption/ coprecipitation with iron hydroxide generated by electrocoagulationfollowed by ceramic microfiltration, 98.7 %[15] removal

Chemical	(catalytic) cementation	Not promising	?	Reduction of selenate followed by adsorption of selenite to HFO
	Zerovalent iron[18,22] nanoparticles			Fe/Cu and Fe/Ni couples 50 ppb possible [14] Immobilisation[17] as elemental Se[19] Bimetallic nanoparticles NiFe powder[23]
	Microbial reduction (metalloids as e^- acceptors) MBR	?	?	Aqueous selenate is efficiently bioreduced under sulfate reducing, methanogenic conditions Selenite under denitrifying conditions[20,25,26,27,32]
	Algal volatilisation Constructed wetlands[29,33]	?	?	Reduction pond, algal high rate pond harvested with DAF
Biological	Phytoremediation[30,31,32] Rhyzofiltration Reduction pond	? ?	? ?	Immobilisation into sediments and plant tissues, 10–30% volatilisation 10^4 × upconcentration
	Membrane treatment and ion exchange[3]	Not considered	Not considered	Not considered because of the high salt concentration (1.5 g SO_4^{2-}/L,13 g Cl^-/L, 12 g Ca/l….) leading to fouling, saturation
Physical	Adsorptive media fixed-bed filters iron-based: GFH[36], goethite, hematithe, zeolites	Hydrocalumite, ettringite[35,36]	+ [42]	Hydrocalumite, ettringite[35,36,39–41]

In the existing installation (Figure 1) the treatment of flue gases from incineration of dangerous waste is performed by several scrubbers. The effluent of the scrubbers is neutralised, coagulated and flocculated and mercury is removed by adding TMT. Every step is performed at pH = 8.7. After settling, the effluent is filtered by sand-filtration.

This treatment removes most common metals, as shown in Table 2. The effluent may still contain oxyanion forming elements such as Mo, Sb and Se, in case of incineration of highly contaminated waste.

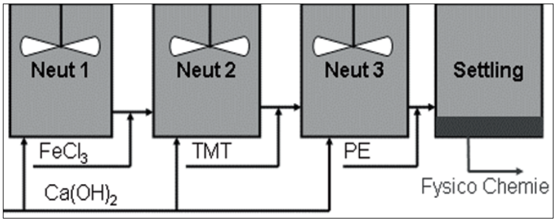

Figure 1. Neutralisation, coagulation, TMT precipitation, flocculation and settling in current installation

TABLE 2. Typical concentrations of influent and effluent

		Influent	Effluent			Influent	Effluent
pH		1,1	10,3	Sb	ppb	1,420	81
redox	mV	320		Se	ppb	175	<10
Al	ppb	9250		Sn	ppb	170	<10
As	ppb	75	<10	Tl	ppb	<10	<10
Ba	ppb	700	130	V	ppb	110	<10
Cd	ppb	153	<10	Zn	ppb	1,360	220
Co	ppb	13	<10	Fe	ppm	19	nm
Cr	ppb	111	<10	Ca	ppm	11,600	nm
Cu	ppb	360	<10	Mg	ppm	160	nm
Mn	ppb	3,110	26	F	ppm	350	8
Mo	ppb	950	460	Cl	ppm	36,300	13,000
Ni	ppb	120	11	Br	ppm	400	390
Pb	ppb	350	<10	SO_4	ppm	4,000	1,500

Research is now done to develop a subsequent treatment for the removal of Mo, Sb and Se to the ppb level. A target value estimate for effluent concentration of Mo is 70 ppb. The existing quality standards for surface water are 10 ppb for both Sb and Se.

2. Experiment

A mixture of scrubber effluents (pH 1, 19 ppm Fe, see Table 2) is spiked to obtain concentrations of 9.2 ppm Mo(VI), 11.2 ppm Sb(III) and 6.7 ppm Se(IV). Neutralisation with lime (8%) to a pH around 4, 7 and 10 is followed by addition of $FeCl_3$ (30%) to obtain total Fe-concentrations of 122 and 277 ppm, respectively. The pH is raised again to 4, 7 and 10. Samples are taken after each step, filtered and analysed by ICP-AES.

3. Results and Discussion

3.1. ANTIMONY

Figure 2 shows the concentration of Sb at different pH and Fe values. The decreasing Sb concentration with increasing Fe concentration appears to be caused by adsorption to Ferri(hydr)oxide.

The adsorption/coprecipitation of Sb(III) ($Sb(OH)_3$) on HFO is seen over a wide pH-range.[43] A value of 300 ppb is reached at pH 9.7.

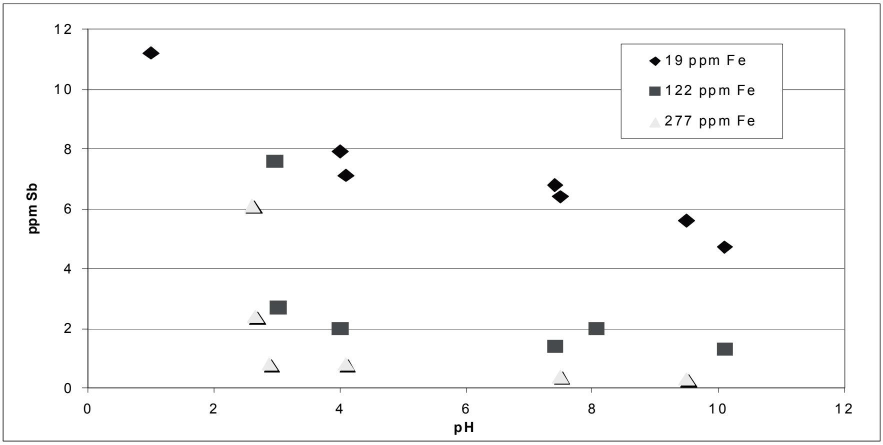

Figure 2. Sb concentrations in the spiked scrubber effluent solution at the start (19 ppm Fe), after adding Fe and after neutralizing

3.2. MOLYBDENUM

Figure 3 shows the concentration of Mo at different pH and Fe values. The optimum around pH 4 (<100 ppb Mo at pH 2.4–4.7), the decreasing Mo concentration with increasing Fe addition and the increasing Mo with increasing pH (competition of OH^-) clearly show that the Mo removal is due to adsorption to Ferri(hydr)oxide. The redox state is Mo(VI) as MoO_4^{2-}.

Apparently, Mo cannot be removed by $CaMoO_4$ precipitation (pKsp = 8.64).

Precipitation as calcium metalate is however theoretically possible. The solubility product of about 10^{-9} and the calcium concentration of about 0.3 M suggest a few ppb Mo in solution.

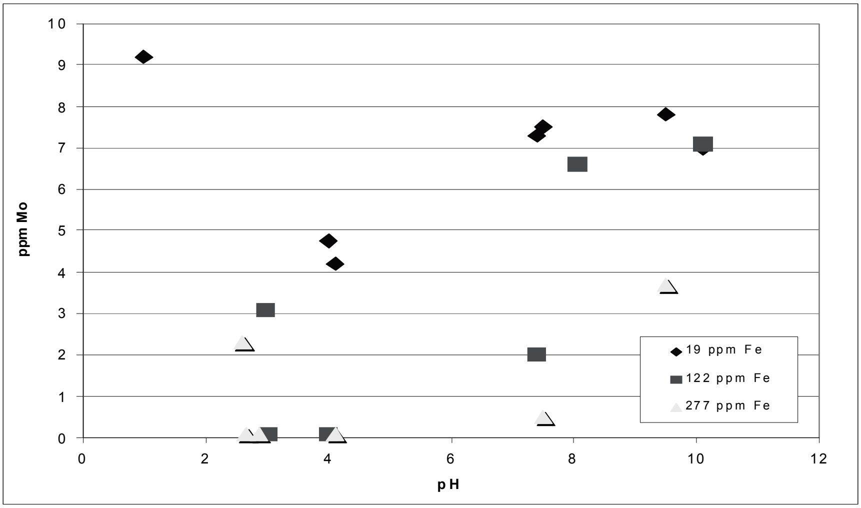

Figure 3. Mo concentrations in the spiked scrubber effluent solution at the start (19 ppm Fe), after adding Fe and after neutralizing

3.3. SELENIUM

Figure 4 shows the concentration of Se at different pH and Fe values. The decreasing Se concentration with increasing Fe concentration indicates that Se(IV) adsorbs slightly to HFO without obtaining sub-ppm concentrations.

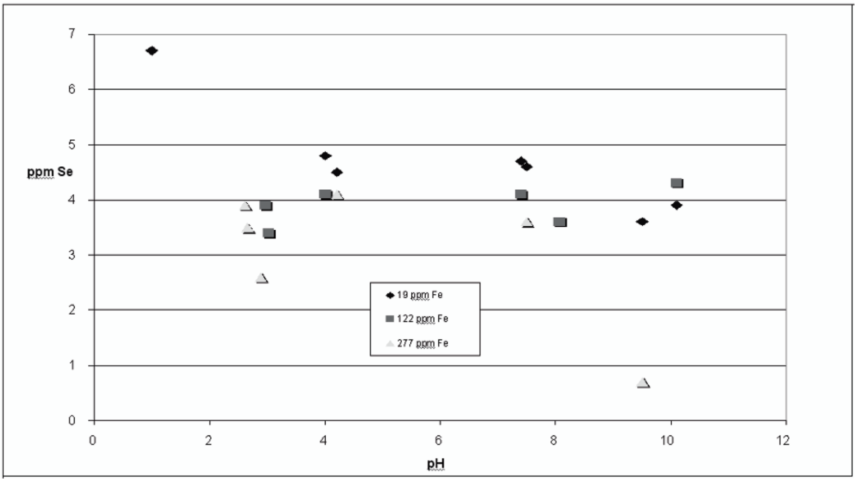

Figure 4. Se concentrations in the spiked scrubber effluent solution at the start (19 ppm Fe), after adding Fe and after neutralizing

4. Conclusions

A mixture of Mo, Sb and Se in ppm-level was spiked to the scrubber of effluent of a waste incinerator at various pH values and Fe additions in a laboratory experiment.

The results show that it will not be possible to sufficiently remove Sb, Mo and Se by lime precipitation, coagulation, flocculation and adsorption/coprecipitation at the pH 8.7 and Eh conditions in the current installation.

Although, in principle these elements could also be precipitated as Ca-metalate, our experiments indicate that this is not the main removal mechanism.

Therefore a post-treatment before sand-filtration (preferably in one step) will be tried out.

Biological methods are not yet considered due to lack of space at the site and lack of experience.

Membranes and ion exchange resins are also not considered because of the high salt concentration leading to fouling, saturation.

Lime precipitation is theoretically capable to reduce the concentrations to the ppb level.

Sulphide precipitation is not capable to reduce the concentrations to the ppb level.

Therefore, for the simultaneous removal of Mo, Sb and Se we intend to continue investigation of physico-chemical alternatives like

- Adsorptive media fixed-bed filters
  - For example, the iron-based GFH (granulated Fe(hydr)oxide), goethite, hematite
  - Hydrocalumite and ettringite
- Reducing media like zerovalent iron, nanoparticles
- Electrocoagulation

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EQUILIBRIUM MODELING OF Cu REMOVAL FROM AQUEOUS SOLUTIONS: INFLUENCE OF IONIC STRENGTH

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Abstract The effect of ionic strength on the removal of Cu cations from aqueous solutions by natural sorbents (zeolite, bentonite, slovakite) has been studied. The ionic strength has been adjusted using the $NaNO_3$ electrolyte (0.001–1 M). Equilibrium data were obtained by batch experiments. Increasing the $NaNO_3$ concentration the Cu sorption was negatively affected in the case of zeolite sorbent, while in the case of bentonite and slovakite, the maximum sorption capacity was increased. The influence of $NaNO_3$ on the sorption of Cu by zeolite was negative, while in the case of slovakite the effect was positive. The effect of $NaNO_3$ on Cu sorption onto bentonite was lower.

Keywords: Copper; sorption; zeolite; bentonite; slovakite

1. Introduction

This study deals with the influence of ionic strength[1,2] on the equilibrium copper concentration when removing by natural zeolites from aqueous solutions. The selective and quantitative separation of metal ions from aqueous solutions has been extensively investigated by applying several techniques.[3] Metal ions in low quantities are difficult to remove from aqueous solutions. One of the possible solutions for such situations is the adsorption. Nowadays, a number of low cost adsorbent materials are available to remove metal ions, e.g. zeolites, chitosan, chitin, sawdust, green algae, and others.[4,5]

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

2. Equilibrium Modelling

Isotherm models provide an adequate description of metal adsorption equilibrium on wide range of adsorbent materials.

Equilibrium data, used for designing adsorption isotherms, are used for estimation of adsorption system. Three adsorption models were used to describe the equilibrium between adsorbed copper ions on the adsorbents zeolite, bentonite and slovakite (q_{eq}) and copper ions in solution (c_{eq}) at a constant temperature and pH (Table 1).

TABLE 1. Units for sorption

Symbol	Quantity	SI
b_L	Adsorption constant defined by Langmuir isotherm (1)	m^3/g
b_R	Adsorption constant defined by Redlich–Peterson isotherm (3)	m^3/g
c_0	Initial metal concentration in solution	m^3/g
c_{eq}	Concentration of metal in solution in equilibrium	m^3/g
d_{32}	Sauter mean particle diameter (4)	m
d_{50}	Mean particle diameter at 50%	m
d_i	Mean particle diameter in the interval *i*	m
k_F	Adsorption constant defined by Freundlich isotherm (2)	m^3/g
k_R	Adsorption constant defined by Redlich–Peterson isotherm (3)	m^3/g
n	Adsorption constant defined by Freundlich isotherm (2)	–
n_i	Number of particles in the interval *i*	–
q_{eq}	Relative amount of metal adsorbed at given concentration per unit amount of dry adsorbent in equilibrium	mg/g
q_{max}	Maximum relative amount of adsorbed metal per unit amount of dry adsorbent	mg/g

2.1. LANGMUIR ISOTHERM

The Langmuir equation[6–8] that is valid for monolayer sorption onto a surface is given by equation

$$q_{eq} = q_{\max} \frac{b_L c_{eq}}{1 + b_L c_{eq}} \tag{1}$$

2.2. FREUNDLICH ISOTHERM

The Freundlich expression[7–9] is an exponential equation and therefore assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases.

The empirical Freundlich equation based on sorption onto a heterogeneous surface is given by equation

$$q_{eq} = k_F c_{eq}^{\frac{1}{n}} \tag{2}$$

2.3. REDLICH–PETERSON ISOTHERM

The Redlich–Peterson isotherm (R–P),[8,10] contains three parameters unlike the Langmuir and the Freundlich isotherms that contain two parameters. The form of R–P equation includes features of the Langmuir and Freundlich isotherms and is given by equation

$$q_{eq} = \frac{k_R c_{eq}}{1 + b_R c_{eq}^{\beta}} \tag{3}$$

3. Materials and Methods

3.1. PARTICLE SIZE DISTRIBUTION

The particle size distribution of adsorbents was estimated by a particle analyser Analysette 22 (Fritsch, D). The Sauter mean diameter of particles is defined by equation

$$d_{32} = \frac{\sum_{i=1}^{m} n_i d_i^3}{\sum_{i=1}^{m} n_i d_i^2} \tag{4}$$

3.2. SORBENTS

3.2.1. *Zeolite*

Zeolite used for the experimental study is from the Nižný Hrabovec (SK) locality, where the principal part is composed by clinoptilolite.[11]

The Sauter mean diameter of zeolite particles, defined by Eq. 4 is d_{32} = 2.170 µm. The mean diameter of zeolite particles at 50% is d_{50} = 1.415 µm.

3.2.2. *Bentonite*

Bentonite is a sorbent of generally impure clay consisting mostly montmorillonite. There are a few types of bentonites and their names depend on the dominant elements, such as K, Na, Ca, and Al.[12]

The Sauter mean diameter of zeolite particles, defined by Eq. 4 is d_{32} = 2.284 µm. The mean diameter of zeolite particles at 50% is d_{50} = 1.890 µm.

3.2.3. *Slovakite*

Slovakite is a mixture of natural raw materials: dolomite, diatomite, smectite, basaltic tuff, bentonite, alginite and zeolite. The exact composition is a trade secret and is protected by European patent No. EP 1098851 B1.

The Sauter mean diameter of zeolite particles, defined by Eq. 4 is d_{32} = 3.200 µm. The mean diameter of zeolite particles at 50% is d_{50} = 2.162 µm.

3.3. BATCH ADSORPTION EQUILIBRIUM STUDIES

A series of flasks containing 200 mL of copper solution of different concentrations prepared from copper sulphate (with pH fixed to 5) and a fixed dosage of sorbent (1 kg/m^3) together with a fixed dosage of $NaNO_3$ (10^{-3}, 10^{-2}, 10^{-1} and 1 mol/L) were agitated for 3 h in a rotary shaker at 200 rpm, with a temperature control at 25°C, which was sufficient for the copper adsorption to reach an equilibrium. After equilibration and sedimentation of suspensions, Cu was determined by atomic absorption spectrometer Perkin Elmer 3100 with deuterium correction background, and uptake q_{eq} was calculated from the difference between initial and equilibrium concentration.

4. Results and Discussion

The experimental data of copper adsorption on zeolite, bentonite and slovakite for all doses of $NaNO_3$ were fitted using Eqs. 1–3, respectively.

4.1. ZEOLITE

According to the results presented in Figure 1, there is a significant decrease of copper adsorption in the presence of $NaNO_3$ compared to the adsorption without $NaNO_3$ added.

The maximum sorption capacity was achieved for solutions without $NaNO_3$ added (0.026 mg/g) in comparison with the maximum equilibrium capacity for adsorption with $NaNO_3$ added (in the range from 14 to 19 mg/g). This represents a 60% decrease of the maximum equilibrium capacity.

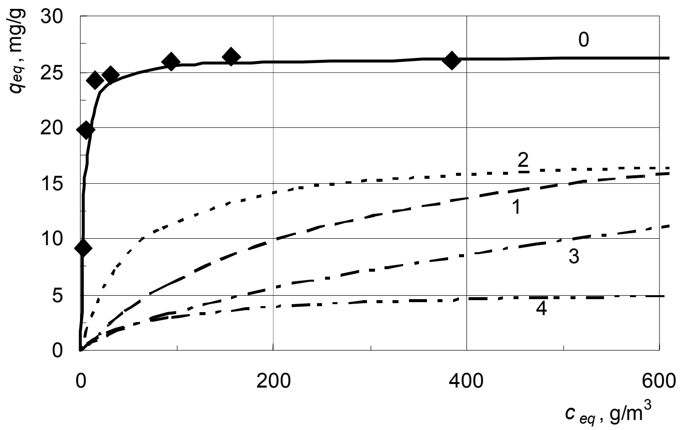

Figure 1. Adsorption isotherms of copper on zeolite (Ionic strength: 0 – 0 M $NaNO_3$ [Langmuir isotherm], 1 – 0.001 M $NaNO_3$ [Langmuir isotherm], 2 – 0.01 M $NaNO_3$ [Langmuir isotherm], 3 – 0.1 M $NaNO_3$ [R–P isotherm] and 4 – 1 M $NaNO_3$ [Langmuir isotherm])

4.2. BENTONITE

According to the results presented in Figure 2, adsorption is partly influenced by the presence of $NaNO_3$ compared to the adsorption without $NaNO_3$ added. There is no significant influence on the maximum capacity for $NaNO_3$ concentrations 0.001 and 0.01 mol/L.

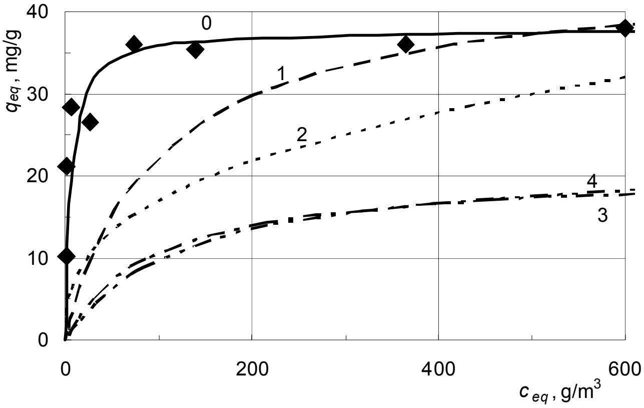

Figure 2. Adsorption isotherms of copper on bentonite (ionic strength: 0 – 0 M $NaNO_3$ [R–P isotherm], 1 – 0.001 M $NaNO_3$ [R–P isotherm], 2 – 0.01 M $NaNO_3$ [Freundlich isotherm], 3 – 0.1 M $NaNO_3$ [Langmuir isotherm] and 4 – 1 M $NaNO_3$ [Langmuir isotherm])

The maximum equilibrium capacity for adsorption without $NaNO_3$ added is 38 mg/g and for $NaNO_3$ concentrations 0.001 and 0.01 mol/L is 34 and 40 mg/g, respectively. There is a significant decrease of copper adsorption in the presence of $NaNO_3$ compared to the adsorption without $NaNO_3$ added for $NaNO_3$ concentrations 0.1 and 1 mol/L. The maximum equilibrium capacity for $NaNO_3$ concentrations 0.1 and 1 mol/L is 20 and 22 mg/g, respectively. This represents a 50% decrease of the maximum equilibrium capacity.

4.3. SLOVAKITE

According to the results presented in Figure 3, there is a significant increase of copper adsorption in the presence of $NaNO_3$ compared to the adsorption without $NaNO_3$ added that is in contrast to adsorption on zeolite.

The maximum equilibrium capacity is higher for adsorption with $NaNO_3$ added (in the range from 163 to 230 mg/g) in comparison with the maximum equilibrium capacity for sorption without $NaNO_3$ added (93 mg/g). This represents a 50% increase of the maximum equilibrium capacity.

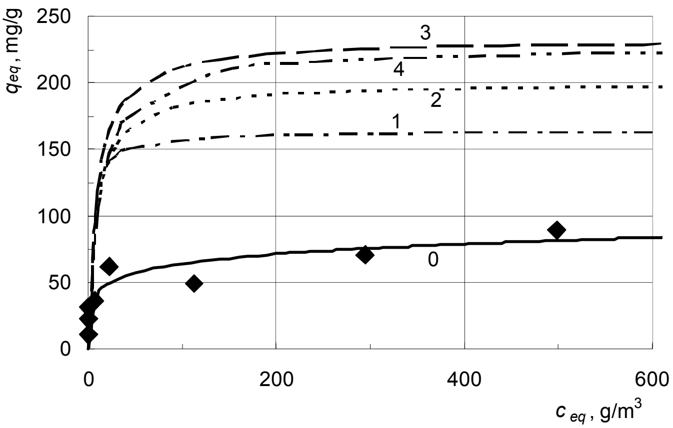

Figure 3. Adsorption isotherms of copper on slovakite (ionic strength: 0 – 0 M $NaNO_3$ [R–P isotherm], 1 – 0.001 M $NaNO_3$ [Langmuir isotherm], 2 – 0.01 M $NaNO_3$ [Langmuir isotherm], 3 – 0.1 M $NaNO_3$ [Langmuir isotherm] and 4 – 1 M $NaNO_3$ [Langmuir isotherm])

5. Conclusion

The influence of ionic strength represented by added $NaNO_3$ is different for various sorbents. The copper sorption on zeolite is negatively influenced by the added $NaNO_3$ and the maximum sorption capacity of zeolite for Cu is decreased by about 60%.

On the contrary the copper sorption on slovakite is positively influenced by the added $NaNO_3$ and the maximum capacity of slovakite for Cu is increased by about 60%. The effect of $NaNO_3$ on the removal of copper by sorption onto bentonite is lower comparing to other materials. There is no significant influence on the maximum sorption capacity of bentonite for Cu for 0.001 and 0.01 mol/L $NaNO_3$ added, but the maximum capacity of bentonite for Cu for 0.1 and 1 mol/L $NaNO_3$ added is decreased by about 50%.

Acknowledgements This work was supported by the Scientific Grant Agency of the Ministry of Education of Slovak Republic under the grant No. 1/4184/07. This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0068-07.

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ADSORPTION CHARACTERISTICS OF COBALT(II) AND NICKEL(II) ONTO DIATOMITE AND AMBERLITE 252 ZU RESIN FROM AQUEOUS SOLUTIONS

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Abstract Many industrial facilities such as metal plating, mining operations, fertilizer industry, tanneries and textile industries discharge heavy metals via their waste effluents. The disposal of these effluents into natural water resources causes damage to the aquatic environment and in humans some of these metals, even in small amounts can cause severe physiological and health effects. In this study, the adsorption conditions of Co(II) and Ni(II) metal ions onto a strong cation-exchange resin, Amberlite 252 ZU and diatomite have been studied. The different variables affecting the sorption capacity such as pH of the solution, adsorption time, initial metal ion concentration, adsorbent amount have been investigated. Also, for investigation of exchange equilibria different amounts of ion exchange resin and dolomite were contacted with a fixed volume and concentration of a heavy metal bearing solutions. Sorption data have been interpreted in terms of Langmuir and Freundlich equations.

Keywords: Ni(II); Co(II); diatomite; ion exchange resin; adsorption

1. Introduction

Heavy metals are not biodegradable and tend to accumulate in biological systems, posing health hazards if their concentrations exceed allowable limits. Inorganic micro-pollutants are of considerable concern because they

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

are non-biodegradable, highly toxic and have a probable carcinogenic effect.[1,2]

The discharge of heavy metals into aquatic ecosystems has become a matter of concern over the last few decades. They are extremely toxic elements, which can seriously affect plants and animals and have been involved in causing a large number of afflictions. Increased knowledge about toxicological effects of heavy metals on the environment is well recognized and therefore, it is inevitable to search for different methods to reduce water pollution. The major sources of heavy metal contaminations are the industrial effluents. Industries, such as metal plating, mining, painting, car manufacturing, smelters and metal refineries are major sources of heavy metal pollution.[3] There are several methods to treat the metal contaminated effluent such as precipitation, ion exchange and adsorption, etc., but the selection of the wastewater treatment methods is based on the concentration of waste and the cost of treatment. Ion exchange and adsorption is one of the most popular methods and has been widely practiced in industrial wastewater treatment processes for the removal of heavy metals from wastewater. Adsorption is one of the few promising alternatives for this purpose, especially using low-cost natural sorbents such as agricultural wastes, clay materials, zeolite, biomass, and seafood processing wastes.[4–11]

In this study, as a low cost adsorbent, diatomite's performance for removal of Co(II) and Ni(II) was investigated against a strongly cationic resin Amberlite 252 ZU.

2. Materials and Methods

2.1. MATERIALS

A strong cation-exchange resin, Amberlite 252 ZU (Rohm & Haas Company) in hydrogen form and diatomite were used for the removal of cobalt(II) and nickel(II). For conditioning of resin, after three preliminary recycling of the resin in column system with 1 M HCl and NaOH solutions to remove eventual chemicals residues (solvents, functionalizing agents) trapped in the resins' matrixes during their preparation, the samples were finally converted in hydrogen forms by 1 M HCl. The properties of Amberlite 252 ZU are given at Table 1. Chemical composition of the diatomite sample was first identified by x-ray diffraction, differential thermal and IR spectrophotometric analysis. Chemical analysis of the sample was carried out on GE-SPG 7, x-ray fluorescence spectrophotometer. The results are summarized in Table 2. Diatomite was washed thoroughly with double distilled water to remove the dirt and other foreign matter and dried at 40°C for a period 4–5 h. The samples were 200 mesh particle size.

TABLE 1. Properties of Amberlite 252 ZU

Data	Amberlite 252 ZU
Matrix	Styrene
Functional group	Sulphonic acid
Particle size	0.6–0.8 mm
Max. temp.	100°C
pH range	0–14
Total capacity	1.8 eq/L

TABLE 2. Chemical analysis of natural diatomite

Component	%
SiO_2	78
Al_2O_3	5.1
Fe_2O_3	1.6
CaO	3.0
MgO	0.8
Na_2O	0.6
K_2O	0.8
TiO_2	1.0
L.O.I[a]	9.5

[a] L.O.I: Lost on ignition

2.2. METHODS

2.2.1. *Determination of Optimum Conditions*

The adsorption of Co(II) and Ni(II) on Amberlite 252 ZU and diatomite samples was studied by a batch technique. The parameters for sorption as pH, adsorbent amount, contact time and concentration were studied with the aim to find the optimal conditions. The batch adsorption experiments were carried out by shaking known amounts of Amberlite 252 ZU and diatomite with 100 mL aqueous metal solutions of 5–100 mg L^{-1} concentration at various pHs (1–8) and at room temperature (20 ± 2°C) in several stoppered bottles for retention times varying from 5 to 60 min. The study of adsorbent doses was carried out by varying the amount of adsorbent (0.1–1 g). The batch adsorption experiments were also conducted at different pH levels (pH: 1–8) and solution pHs were adjusted by adding 0.1 N

NaOH and HCl solutions. The pHs of the solutions were adjusted before adding ion exchange resin and diatomite. The stirring speed was 250 rpm during all of the batch experiments. Diatomite samples were well dispersed in aqueous metal solutions. At the end of the pre-determined time interval, the adsorbent was removed by the filtration (the supernatant solution was filtered through 0.45 μm microporous membrane filter) and the final concentration was determined in the filtrate by atomic absorption spectrophotometry using an air-acetylene flame (Varian Spect AA 220). Optimum conditions were determined for both metals.

3. Results and Discussion

In this study, adsorption properties of Co(II) and Ni(II) on diatomite has been studied by using batch technique and the results were compared with Amberlite 252 ZU, strong cationic resin. Equilibrium experiments were done and adsorption isotherms were obtained. Sorption data have been interpreted in terms of Langmuir and Freundlich equations.

Optimum conditions were found at a concentration of 20 mg/L, pH 5, contact time 30 min, and amount of adsorbent 0.5 g.

The sorption data have been subjected to different sorption isotherms, namely, Freundlich and Langmuir. The results are given in Figures 1 and 2.

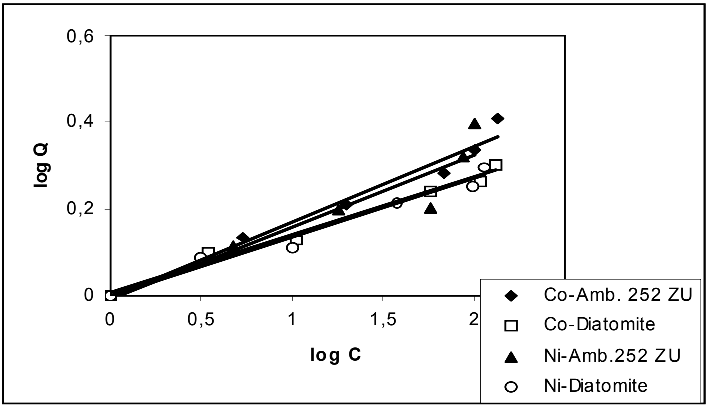

Figure 1. Freundlich sorption isotherm of Co(II) and Ni(II) ions by Amberlite 252 ZU and diatomite

The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, usually fits the experimental data over a wide range of concentrations. As can be seen in Figure 1, $\log Q$ vs log C curves give straight lines according to the Freundlich isotherm equation. Both K_f and n are empirical constants, being indicative of the extent of adsorption and the degree of nonlinearity between solution and concentration, respectively. For favorable adsorption, $0 < n < 1$.

In order to ascertain whether the adsorption is chemisorptive in nature with chemical forces binding Co(II) and Ni(II) ions to the surface of the clay adsorbents, the experimental data are also tested with respect to Langmuir isotherm. As seen in Figure 2 from the linear relation between C_e/Q_e and C_e, the adsorption equilibrium constant b and maximum adsorption capacity Q_0 of adsorbents were calculated and these are also shown in Table 3. The adsorption isotherm of Co(II) and Ni(II) exhibit Langmuir behavior, which indicates a monolayer adsorption.

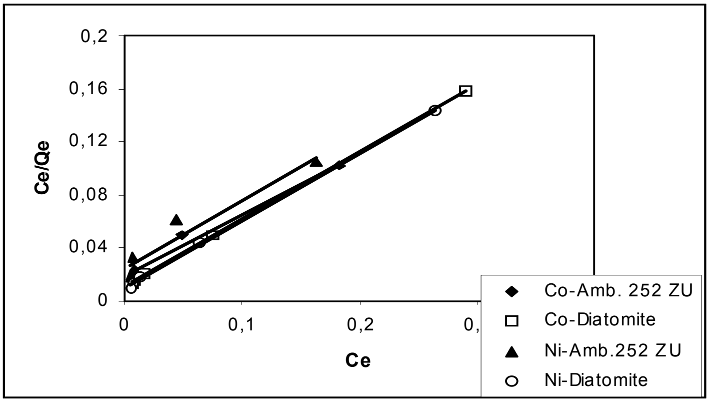

Figure 2. Langmuir sorption isotherm of Co(II) and Ni(II) ions by Amberlite 252 ZU and diatomite

The plots have good linearity in both cases (Freundlich plots, R = 0.91–0.97, Langmuir plots, R = 0.88–0.99) at room temperature. The values of the adsorption coefficients, computed from these plots are given in the Table 3. The values of the adsorption coefficients indicate the favorable nature of adsorption of Co(II) and Ni(II) on the clay and resin.

TABLE 3. Parameters of Langmuir and Freundlich isotherms for sorption of metal ions

Metal ion	Langmuir isotherm method			Freundlich isotherm method		
	b	Q_0 (meq/g)	R^2	K_f (meq/g)	n	R^2
Co-Amb.252 ZU	0.4724	0.0178	0.9790	0.1733	0.0032	0.9713
Ni-Amb.252 ZU	0.5213	0.0229	0.9242	0.1674	0.0075	0.8804
Co-diatomite	0.5106	0.0108	0.9997	0.1329	0.0059	0.9846
Ni-diatomite	0.5060	0.0093	0.9994	0.1333	0.0013	0.9702

4. Conclusion

In this study, the effects of parameters such as pH, amount of adsorbent, contact time and concentration on removal of cobalt and nickel metal ions from aqueous solutions. According to these experimental results and all previous works with cationic resins and natural zeolites,[6,12–14] it was demonstrated that Amberlite 252 ZU is a strong cation-exchange resin and diatomite have good capability and efficiency for the removal of these heavy metals from aqueous medium.

Optimum conditions were found at a concentration of 20 mg/L, pH 5, contact time 30 min, and amount of adsorbent 0.5 g.

The adsorption is supported by Freundlich and Langmuir isotherms and the adsorption coefficients indicate favorable adsorption.

As a low cost adsorbent, diatomite can be preferable for removal of heavy metals from water and wastewaters.

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REMOVAL OF HIGHLY TOXIC WASTEWATER POLLUTANTS WITH EXCESSIVE ACTIVE SLUDGE

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Abstract A possibility of the some toxic compounds elimination using the excessive active sludge (EAS) from the wastewater biotreatment stage has been investigated. The sludge exhibits high adsorptive ability and can capture and firmly fix large amounts of various toxic compounds. On the other hand, high proteins content in EAS allows its utilization as part of the cementing composition at concrete construction blocks and the pavement slabs production. Determined results show that addition of 5–10% of EAS provides the account small loss of the products mechanic durability. Therefore, this technology can be used for the ecologically safe utilization of the sludge with the adsorbed toxicants.

Keywords: Active sludge utilization; xenobiotics removal; concrete blocks production; pavement slabs production

1. Introduction

Biotreatment is a key stage of various wastewater treatment technologies. However, many xenobiotics do not undergo biodestruction and survive after the biological treatment. Most part of such compounds can be adsorbed by EAS, which captures relatively large amounts of heavy metals, cyanides, benz(a)pyrene, phenols, synthetic detergents, surfactants, pesticides, oil-products, medicals, pathogenic microbes etc. Account on this EAS is transformed into toxic material. Municipal wastewater treatment plants produce large amount of the toxic EAS, which requires the treatment. Annual

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

discharge of organic and mineral wastes can be assessed as 25–30 kg/year for a one standard inhabitant resulting in total annual production of about 3 million tons of EAS in Ukraine.[1,2] Current amount of EAS waste collected in Ukraine assessed as 5 billion tons.[3]

Our work was oriented on the possibility of the EAS utilization as the additional component at the production of concrete blocks. This way of utilization was reported before[4,5] however, without the investigation of the influence of the EAS addition on the blocks mechanic durability.

2. Active Sludge Composition

We investigated the EAS that was collected from the secondary settlers output at the Chernivtsi municipal wastewater treatment plant (Ukraine). Various heavy metals ions were identified in the sludge (see Table 1).

TABLE 1. Heavy metals content in the active sludge from the secondary settlers of Chernivtsi municipal wastewater treatment plant

Pollutant	Pollutant content in the active sludge (mg/kg)	Maximum permissible concentration (mg/kg)[6]
Cu	104	65
Zn	393.6	130
Pb	100	20
Mn	145.6	150
Ni	41	32
Cr	10.1	6

The sludge was dewatered in centrifuge at 3,500 rpm and a grey-black suspension was received. It contents 9.5% of a solid residue (the rest of the composition was water). Consequently this suspension was added to various cement blocks together with sand (as the filler) and the cement of M-200 brand (as the binder).

3. Influence of EAS on Mechanic Durability of Various Cement Products

The first series of the blocks was made with the constant binder-to-filler ratio 1:4 and the various EAS addition, which substituted part of cement. Results of the mechanic durability determination are shown in Table 2. These results show the small loss of the durability in the case of the 0–10% EAS addition. Therefore, we can conclude that the adding up to 10% of

EAS as a part of binder non-effects of the decline of the blocks mechanic quality. This effect can be caused by relatively high protein content in EAS, which also binds the cement compounds.

The second series of the blocks was made with the constant content of the cement (20%) and the various content of the EAS that substituted part of filler. Results of the mechanic durability determination for this series are documented in Table 3. They show that up to 10% of EAS weren't observed the significant loss of the durability. Moreover, the addition 5% of EAS gives the higher durability. Only the addition 20% of EAS causes the serious drop of the blocks mechanic quality.

Table 3 proves that partial substitution of sand with EAS is even favourable, because 10% of EAS can be utilized in the concrete blocks causing higher mechanic durability of the final product.

TABLE 2. Influence of EAS content (total binder-to-filler ratio is 1:4) on the concrete blocks mechanic durability. EAS addition substitutes binder (cement)

Block series	Cement content (%)	EAS suspension content (%)	Average mechanic durability (kgf/sm^2)	Relative error (%)	EAS effectiveness[a] (%)
1	20	0	12.30 ± 0.87	7.07	0
2	17.5	2.5	12.83 ± 0.96	7.48	+4.31
3	15	5	11.50 ± 0.91	7.91	−6.50
4	10	10	11.20 ± 0.47	4.17	−8.94

[a] EAS effectiveness calculated as relation between an EAS-containing and EAS-free samples durability referred to EAS-free sample durability (for the sample 2 it is (12.83 – 12.30)/12.30 = 0.0431 = 4.31%

TABLE 3. Influence of EAS content (total binder-to-filler ratio is 1:4) on the concrete blocks mechanic durability. EAS addition substitutes filler (sand)

Block Series	Sand content (%)	EAS suspension content (%)	Average mechanic durability (kgf/sm2)	Relative error (%)	EAS Effectiveness (%)
5	80	0	12.30 ± 0.87	7.07	0
6	75	5	13.07 ± 0.62	4.77	+6.26
7	70	10	12.70 ± 0.60	4.72	+3.25
8	60	20	3.63 ± 0.40	11.02	−70.49

Next stage of our project was investigation of the possibility of EAS utilization in more complex production such as pavement slabs, which consist of various filler kinds: sand and small gravel fractions. In this case we could substitute EAS for at least three compounds: cement, sand and gravel. Final slabs then were tested for the mechanical durability as well as compliance with appropriate standards, which regulate rest of the consumer qualities.

It was found that by substitution the part of cement with EAS we can ensure much better quality of the pavement slabs comparing to EAS-free products (see Table 4) while 10 and more percents of EAS addition result in inappropriate quality drop of the slabs.

The substitution a part of the sand and gravel with EAS we can not achieve better mechanic durability of the product although its quality remains good until EAS concentration reaches 10%. Table 5 shows an example of the product characteristics for the slabs with the constant cement content and the partial substitution of gravel with the EAS.

Also we investigated if toxic compounds adsorbed by EAS can be fixed in the cement products. The prevention of their washout is very important characteristic of any technology of the toxic waste utilization. Atom-adsorption analysis of the long-term washout water after contacting

TABLE 4. Dependence of the pavement slabs characteristics on the EAS content. EAS addition substitutes binder (cement)

Slabs series	Cement content (%)	EAS suspension content (%)	Average mechanic durability (kgf/sm2)	Relative error (%)	EAS effectiveness (%)	Standard compliance
9	25	0	258.00 ± 18.2	7.05	0	Yes
10	22.5	2.5	346.66 ± 17.7	5.10	+34.36	Yes
11	20	5	248.66 ± 3.5	1.40	−3.62	Yes
12	15	10	157.33 ± 5.3	3.36	−39.02	No

TABLE 5. Dependence of the pavement slabs characteristics on EAS content. EAS addition substitutes filler (gravel)

Slabs series	Gravel content (%)	EAS suspension content (%)	Average mechanic durability (kgf/sm2)	Relative error (%)	EAS effectiveness (%)	Standard compliance
13	25	0	337.33 ± 16.8	4.98	0	Yes
14	22.5	2.5	319.00 ± 6.3	1.97	−5.43	Yes
15	20	5	220.66 ± 4.8	2.17	−34.59	Yes
16	15	10	174.66 ± 4.2	2.40	−48.22	No

with EAS-containing products showed no detectable traces of Cd^{2+}, Cu^{2+}, Pb^{2+} and Ni^{2+} ions. Therefore, we can consider the proposed utilization technology as ecologically safe.

4. Conclusion

The results summarization of our investigation can conclude that EAS can be safely utilized at the concrete blocks or pavement slabs production and its concentration in the cement products composition can reach up to 10%. The EAS addition brings some amount of water, which reduces the fresh water consumption for the blocks and slabs production. Using EAS can ensure saving of cement with even higher mechanic durability of the products. The addition of 2.5% of EAS instead of cement is worthwhile for the pavement slabs production because such product reveals much higher mechanic durability and other quality characteristics. Harmful heavy metal ions are fixed in the blocks and slabs firmly and cannot be washout even after long-term contacting with water. Therefore, such technology provides opportunity for a safe and economically expedient utilization of excessive active sludge formed at the municipal wastewater plants.

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ANALYSIS OF INFLUENCE OF THE THERMAL POWER PLANT WASTEWATERS DISCHARGE ON NATURAL WATER OBJECTS

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Abstract The influence of the wastewater discharge on local water bodies has been analyzed for Ladyzhyn thermal power plant (Ukraine). Main negative factors of this discharge have been identified and complex actions have been proposed to improve the water body's condition.

Keywords: Thermal power plant wastewater; discharge to natural water bodies; complex improvement actions

1. Introduction

Water pollution and water shortage become one of the most acute problems in the environment protection policy of Ukraine and many other countries. Energy generating plants consume large amount of water and discharge thousands of cubic meters of wastewater, which leads to significant negative environmental effects. Such plants can influence the river water balance and quality,[1] and/or cause temporal or constant water warming leading to numerous consequences: river freezing changes, changes in the winter water regime, atmospheric precipitation level, fogging, local air warming and others.

Artificial cooling ponds as well as the influence level and quality of the river flow, change living conditions of fishes and plankton provokes higher seismicity, underflooding and waterlogging in the surrounding area. All these effects result in the microclimate changes, which affect hydrosphere, lithosphere and atmosphere.[2]

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On the other hand, thermal and nuclear power plants produce the most part of electricity in Ukraine and many other European countries. The negative impact of the thermal power plants is significantly higher comparing to the nuclear power plants.[2]

2. General Description of the Ladyzhyn Thermal Power Plant and Its Wastewater Categories

The Ladyzhyn thermal power plant is one of the biggest in Ukraine. It is located at the in-channel basin of the Pivdennyi Buh River. The power plant operates 6 power-generating units. Average annual electricity production is of $11{,}250\cdot\times 10^6$ kWh. The energy production is based on combustion of black coal or heavy oil.

Ladyzhyn thermal power plant produces different types of wastewater: heat exchanger water, transport water from the hydraulic ash and slurry removal system, storage and regeneration water from the chemical water treatment system, rainwater and gray wastewater. The wastewater from heat exchanger and drainage can be classified as the most dangerous for local water bodies.

In-channel basin is the main source of the power plant water supply. It is being used for cooling of the power station as well as auxiliary equipment of the plant. Then used warm water is transported back to the basin through a 3.5 km long open manifold equipped with a built-in sprayer-cooler. The manifold has two discharge points: an intermediate (in 2.5 km) and the final (in 3.5 km). Another 0.5 km auxiliary manifold is not equipped with any cooling units and is intended for the sludge ice removal only.

Part of the warmed water is being utilized for the boilers make-up. This water should be previously treated chemically and then piped into the boilers pipeline to compensate losses due to water evaporation.

The total water consumption at the plant is five to six times higher than natural inflow. However, this unbalance can be increased 16–18 times during the dry summer period. Therefore, the plant's in-channel basin transforms into an integral part of the recycling water plant, which supplies technological water and also cools down plant's warmed wastewater.

The sprayer-cooling unit should ensure necessary cooling of the wastewater during its discharge through the manifold keeping temperature raise in the basin under extra 3°C for the summertime. Wastewater should be cooled down about 5–6°C in the manifold in order to meet this requirement. Direct discharge of the wastewater is absolutely unfavorable, especially during the summer period.

3. Analysis of Influence of the Thermal Power Plant Wastewater Discharge

Discharge of the turbine condenser cooling water does not cause any direct chemical pollution. However, it causes warming of the natural water, which results in shifting of the carbon dioxide balance. This can lead to additional hardness salts deposition and/or accelerated corrosion, which would bring additional iron ions to the basin.

One of the condensers operates using oil-containing parts, which can cause contamination of the water by oil substances.

Composition of the turbine condenser wastewater is shown in Table 1 (see water discharge points 1, 1′ and 3).

TABLE 1. Composition of the Ladyzhyn power plant wastewater at discharge points

Pollutant (water quality parameter)	Concentration (mg/L) at discharge point				
	1, 1′, 3	2, 4	5	6, 8	7
COD	28.7	32.5	48.6	72.9	42.3
BOD_5	5.9	10.35	8.06	13.6	5.3
Suspended particles	11.92	21.4	58.4	17.7	6.5
Ammonium	0.39	2.37	0.8	1.23	0.42
Nitrites	0.14	0.04	0.12	0.88	0.11
Nitrates	3.59	1.55	3.2	20.5	3.15
Phosphates	0.13	0.14	0.17	2.19	0.27
Chlorides	47	68	46	62	42.3
Sulfates	56	51	55	57.3	154.7
Solid residue	488	306	376.5	518	552
Surfactants	–	0.128	–	0.13	0.003
Phenols	–	0.001	–	0.00042	0.001
Oil-products	0.05	0.08	0.063	0.011	0.122
Iron (total)	0.52	0.18	–	0.28	0.32
Aluminum	–	–	0.35	–	–
Hydrogen sulfide	–	–	–	0.0001	–

Comparison of the water quality parameters for wastewater discharge points (1, 1′, 3) and river water (see Table 2) proves that the turbine condenser cooling water brings almost no additional chemical contamination.

Another type of the wastewater comes from a system of hydraulic ash sluicing. Technological flowchart has been designed, with mechanical coal feeding and hydraulic ash removal with a system of two-stage dredging pumps installed between the boilers. Ash removal system is 7.6 km long, with the water pumping height difference of 26.5 m. The ash pulp is being transported to the ash/slag dump, then it is partially dehydrated, and the separated transport water is recycled afterwards.

Other industrial wastewaters (chemical water treatment post, black-oil, coal and chemical storage wastewater, pumps and fans bearing cooling water and boiler purging water) are also being delivered to the ash removal system. This type of wastewater brings some additional pollutants.

Chemical water treatment post wastewater contains suspended compounds, cation and anion filter regeneration agents, eliminated water hardness ions (Ca^{2+}, Mg^{2+}, Fe^{2+}, SO_4^{2-}, CO_3^{2-}) and excessive water softening ions (Cl^-, Na^+). Other industrial wastewaters (except boiler purging) contain some amounts of oil compounds and suspended particles. Boiler purging wastewater can be considered as relatively pure.

The ash/slag dump area is located between two hills with upper and lower confining dams. Dams were initially built of clay in order to ensure filtration-proof protection. Then the dams were increased using dried slag in order to increase the ash/slag dump area capacity. Possible infiltration of the drainage water through the increased dam part was taken into account and a drainage channel was built along the dam. Then the drainage water is collected in a main pipe and directed to the water discharge point at the Silnitsa River.

Calculated infiltration water annual volume is 108×10^3 m^3 and its composition is shown in Table 1 (see discharge point 7). This water can be conditionally classified as pure.

The ash/slag dump area is almost completely filled up and its surface area has reached about 100 ha and thickness of the collected slag is about 25 m. This industrial object makes strong and multiform negative influences to the environment. This influence can be felt through the drainage water discharge, disturbance of the underground water circulation, and their contamination with products of the sulfur-containing compounds bio-destruction. All these aspects result in bogging of wide areas outside the ash/slag dump and in other negative consequences. Therefore, a system of the control land holes should be arranged in order to control and prevent such effects.

Grey waters from the power plant together with the city sewage are transported to the biotreatment installations, which include initial collecting chamber, plain sand traps, two-stage and vertical settlers, aeration tower, vertical secondary settler, landfills, sand damp areas, excessive active sludge areas, sludge pumping post and hydroelevators pumps.

Biotreatment installations provide quite good cleaning efficiency estimated to 92–95%. However, discharged water does not meet required standards.[3,4]

The detailed analysis of the biotreatment installation shown that aeration of the sewage water presents the weakest point, which does not provide necessary cleaning. Mechanical pre-treatment was found effective, however biosedimentation may not work effectively due to insufficient aeration. It is believed that this is the main reason of insufficiency of the Ladyzhyn power plant sewages. However, some other potential problems should also be taken into account. The power plant sewage treatment plant works also with the city grey water, which has unstable and very complex composition. Moreover, their composition is different comparing to the power plant's sewage. Naturally, such different sewage would require different treatment methods and intensity. Most aeration facilities were built in the late of 1960s and still use passive tower aeration units, which do not meet today's standards and should be replaced with aeration tanks or other more effective equipment with forced aeration.

Therefore, we can propose following mitigation ways:

- To ensure effective work of the sand traps sediment hydrodischarge system in order to avoid overshooting of the suspended particles to the settlers.
- To normalize work with sediments in the two-stage settlers. Current chaotic sediment unloads without proper control of its mineralization ratio or settlers overfilling also cause overshooting of the suspended and floating particles to the settlers.

Proper mechanical cleaning can lower workload on the aeration filters and increase their capacity. This would also lower workload on the biosettlers and improve quality of the outgoing wastewater. Present composition and quality parameters of the wastewater are shown in Table 1 (see discharge points 6 and 8).

Discharge point 5 relates to the chemical water treatment post sewages. It shows sewage water parameters for the worst possible case – blowing-cleaning of the chemical treatment equipment.

Discharge points 2 and 4 relate to the rainwater collecting system. It collects rain and snow melting water all over the plant's territory and roofs of the building. Total water collection area is about of 117 ha. There is no water cleaning equipment installed to treat rain or snow melting water. As it is evident from the Table 1, this water can be classified as weakly contaminated. Complete separation of all black oil equipment, coal and reagent storage facilities from this sewage system maintains low contamination of rain/snow melting water.

4. General Consequences of the Power Plant Sewage Discharge and Recommended Water Protection Measures

The power plant is located between the junction point of two rivers: the Pivdennyi Buh and the Silnitsa. The dam is built at the Pivdennyi Buh and discharge points 1, 1′, 2, 3 and 4 are directed to the in-channel basin and discharge point 5 is directed to the river below the dam. Discharge points 7 and 8 are directed to the Silnitsa and discharge point 6 is directed to the Pivdennyi Buh lower the junction point.

Background water quality parameters of the both rivers are shown in Table 2.

TABLE 2. Background water quality parameters for the Pivdennyi Buh and the Silnitsa Rivers

Pollutant/water quality parameter	Concentration (mg/L)	
	Pivdennyi Buh	Silnitsa
COD	26.7	23.83
BOD_{full}	2.92	4.73
BOD_5	2.02	3.55
Suspended particles	12.8	3.5
Ammonium (salt)	0.41	0.08
Nitrites	0.12	0.002
Nitrates	3.2	2.25
Chlorides	35.4	45.6
Sulfates	33.3	296.9
Dry residue	371.0	657
Oil products	0.01	0
Surfactants	0.06	0.003
Iron	0.23	No data
Aluminum	0.08	No data
Hydrogen sulfate	0	0
Phosphates	0.13	0.42
Phenols	0	0

Data of Table 2 prove that water of the Pivdennyi Buh has a moderate level of pollution with organic substances. Nitrogen can be found in various forms in concentration from 2 to 5 mg/L. This concentration of nitrogen provides enough feeding for eutrophication and water blooming processes in the summertime. So, water in the Pivdennyi Buh can be classified as a household water source, it fails to meet requirements for the fishery water sources.

Pollution level of the Silnitsa water is also moderate but it is lower than in the Pivdennyi Buh. Data in Table 2 show lower content of various nitrogen and phosphorus forms and this river still can be classified as a household water source.

Generalizing data related to all discharge points we can propose following recommendation to improve water management at the power plant.

Wastewater quality at discharge points 1, 1′ and 3 is almost similar to the long-term background water quality parameters in the Pivdennyi Buh. There are no additional chemical pollution sources at these points and no additional wastewater treatment measures are needed.

Water quality at discharge points 2 and 4 does not meet maximum contaminant level of BOD, oil compounds and surfactants content. These points discharge mainly rain and melted snow water, which is known to have relatively high pollution level for initial portions and much lower pollution for next water portions. Therefore, a simple oil-pollution cleaning system should be installed at these points in order to catch and treat first mostly polluted water portions and let next portions to run through.

Discharge point 5 operates with water treatment and filtration post sewage and its quality is close to the background water quality except periodical massive slurry discharges from the water treatment equipment. These discharges should be caught and directed to existing wastewater treatment facilities to improve the situation.

Wastewater quality at discharge point 6 meets requirements but corresponding biotreatment equipment was found working practically at its limit capacity. This is a threatening situation because any small fault or increased work load may cause significant outbreak of insufficiently treated wastewater. Related aeration filters have low and insufficient oxidation efficiency and it is rather difficult to control them. General treatment level is so far satisfactory (BOD_5 = 13.8 mg/L and suspended particles content = 17.7 mg/L) but we can recommend some measures in order to increase the cleaning capabilities limits. First of all, improved mechanical cleaning of the wastewater is needed in order to lower workload of the biotreatment equipment and its clogging. Biotreatment dumps should also be cleaned from the mud collected in order to expand their volume. However, it is necessary to emphasize that more intensive reconstruction of the biotreatment equipment is unavoidable in longer perspective.

This reconstruction should increase total effectivity of the biotreatment equipment and mitigate the danger of their overloading.

TABLE 3. Proposed environment protection measures and their assessed effects

Mitigation measure	Wastewater quality parameter	Concentration			
		Before		After	
		mg/L	tons/year	mg/L	tons/year
Discharge point 5. Equipment reconstruction to eliminate periodical massive slurry discharges	BOC$_{\text{full}}$	6.89	3.772	6.29	3.444
	BOC$_5$	6.06	3.318	4.98	2.727
	Suspended substances	58.4	31.974	31.47	17.230
	COD	32.42	17.750	28.58	15.648
Closing of discharge point 8		Elimination of all discharges is expected			
Discharge point 6. Improving of the wastewater mechanical cleaning	BOC$_{\text{full}}$	18.06	46.143	10.76	31.419
	BOC$_5$	13.6	34.748	8.0	23.360
Discharge point 6. Alternate cleaning of the biosettlers from excessive mud	BOC$_{\text{full}}$	10.76	31.419	6.53	19.068
	BOC$_5$	8.0	23.260	4.84	14.133
	COD	72.9	212.678	56.73	165.652
	Suspended particles	22.0	64.240	15.6	45.552
	Phosphates	5.2	15.184	2.19	6.395
Discharge point 2. Installation of the initial water portions cleaning equipment	BOC$_{\text{full}}$	4.76	0.332	3.13	0.218
	BOC$_5$	4.61	0.321	2.6	0.181
	Suspended particles	21.4	1.492	13.46	0.938
Discharge point 2. Installation of the initial water portions cleaning equipment	BOD$_{\text{full}}$	4.11	0.669	3.01	0.490
	BOD$_5$	4.2	0.683	2.27	0.369
	Suspended particles	21.4	3.482	13.08	2.128
	Surfactants	0.128	0.021	0.105	0.017
	Oilproducts	0.122	0.020	0.055	0.0089

Wastewater discharge point 8 is temporary and discharges excessive wastewater after the biotreatment stage. This point will be stopped and closed after completion of the sewage pumping post construction. This post will catch the excessive wastewater and direct it the main discharge collector.

Wastewater quality at the discharge point 7 does not meet relevant requirements. However, there is no real measure to improve this situation. This discharge point works with the ash dump drainage waters, which come from a very wide area and are very hard to be collected and adequately treated. Therefore, we recommended constant water control measures in order to investigate possible negative impact of this discharge point.

The above-mentioned can be summarized as follows.

The Ladyzhyn thermal power plant provides significantly influence on hydrological and hydrochemical characteristics of the Pivdennyi Buh and the Silnitsa rivers. It is caused by construction of the in-channel basin and intense use of its water for the equipment cooling needs, supplying of drinking and technological water. This "technological" influence is intensified by parallel discharge of various warmed, rain, industrial, household and other wastewater.

The basin water is subjected to excessive heat load and chemical pollution, which causes accumulation of the pollution agents, water warming, insufficient oxygen balance, eutrophication and summer water blooming.

Our mitigation recommendation and their effects are summarized in Table 3.

To achieve recommendations would ensure better quality of the power plant's wastewater and bring its parameter closer to the values recommended by Ukrainian legislation. Assessed funding for all these reconstruction works is about of 0.5–1.0 million Ukrainian hryvnya but total annual ecological–economical effect is about of 0.3–0.6 million hryvnya. Therefore, direct reconstruction investments should be returned within 2–3 years.

5. Conclusion

Operation of the Ladyzhyn power plant causes numerous negative environmental effects. The most of them are caused by insufficient effectiveness of the water biotreatment equipment. Part of the discharge points provides bearable contamination level while others deliver wastewater with excessive pollution.

We recommend a complex solution and reconstruction plan that can significantly improve power plant's wastewater quality and decrease its anthropogenic load. Approximate evaluation shows that main investments can be returned within 3 years.

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EXTRACTION OF NICKEL AND COPPER IONS FROM WASTE TECHNOLOGICAL SOLUTIONS

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Abstract New methods of chemical and electrochemical extraction of nickel and copper ions from the wasted solutions of chemical nickeling and copper etching have been proposed. These methods combine deep level of Ni and Cu elimination and easy recycling of the metals. The technology does not require expensive reactants, nor new sophisticated equipment. A new membrane electrolyser has been developed to ensure ecologically safe elimination of the metals. It prevents emission of highly toxic chlorine gas, which can form in traditional electrochemical extraction technologies during treatment of the chloride-containing solutions of nickel or copper salts. Our technology effectively prevents contamination of the natural waters with toxic Ni and Cu ions. Original membrane electrolyser and the technology have been protected by the Ukrainian patent.

Keywords: Extraction of nickel and copper ions; waste technological solutions; electrochemical decontamination

1. Introduction

Nickel and copper compounds can be found in various waste technological solutions for nickel or copper alloys etching, electrochemical and chemical plating. Both metal ions are highly toxic and their maximum contaminant level (MCL) for the fish-growing water objects is limited by 0.01 mg/L.[1] This value is lower than MCL for lead ions (0.1 mg/L) or even cyanide compounds (0.05 mg/L). Nickel and copper ions are dangerous for all

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

warm-blooded organisms and may cause serious intoxications of human body. Some mutagenic activity of copper and carcinogenic activity of nickel is reported.[2,3] An average mortality at the nickel production plants is 1.2–3 times higher comparing to the control value. Nickel mostly provokes lung and thyroid cancer and influences the nerve system. Therefore, effective technologies for nickel and copper compounds extraction are vital for development safer schemes of electrochemical and other related production plants.

2. Existing Technologies of Nickel and Copper Elimination and Their Shortcomings

There are some well-known technologies for elimination of Ni and Cu compounds.[4,5] These compounds can be eliminated both electrochemically (cathodic reduction, electrodialysis) or chemically (transformation into low soluble nickel or copper compounds: carbonates, hydroxides). They are relatively inexpensive but the resulting elimination slurry can be hardly recycled. Complex solutions produce slurry, which contains a mixture of various metal compounds. Separation and reuse all individual metal compounds is still much more expensive comparing to use of the primary metals. That is why such slurry is mostly being collected at the industrial waste storage area. Acid rains attack the slurry gradually washing-out heavy metal ions contaminating soils and ground waters.

Electrochemical methods can produce relatively pure individual metals however, they can not be applied to any of widely used chloride-containing solutions. Electrochemical treatment of such solutions would release highly toxic chlorine gas.

These problems should be resolved in the ecologically friendly technology of economically worthwhile elimination of Cu and Ni compounds from technological wastewater and solutions.

3. Reagent-Catalytic Nickel Extraction from the Waste Chemical Nickeling Solution

We propose a method of chemical destabilization of the waste chemical nickeling solution, which results in catalytic reduction of Ni ions forming metal nickel powder. This powder is relatively pure and can be easily recycled.

Chemical reduction of nickel includes two stages[6]: one anodic (Eq. 1) and three cathodic reactions (Eqs. 2–4). This process runs according to the electrochemical mechanism and can be classified as an auto-catalytic.

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + H^+ + H_{ads} + e^- \quad (1)$$

$$Ni^{2+} + 2e^- \rightarrow Ni \quad (2)$$

$$H^+ + H_{ads} + e^- \rightarrow H_2 \quad (3)$$

$$H_2PO_2^- + e^- \rightarrow P + 2OH^- \quad (4)$$

Resulting process (Eq. 1 + Eq. 2) is very slow without a catalyst but even small amount of the metal nickel powder significantly accelerates the process rate. Increasing the pH and temperature also causes higher Ni reduction rate (see Figure 1). Figure 1 illustrates this effect showing the final Ni^{2+} concentration achieved after 1,800 s of treatment under various temperature and pH values. Initial content of Ni^{2+} was 3.8 g/L.

It was found that potential of the steel electrode is oscillating with the nickel reduction (see Figure 2). Figure 2 shows these oscillations for an electrode made of St-3 brand steel and for the solution containing 10 g/L of $NiCl_2{\cdot}6H_2O$, 15 g/L of $NaH_2PO_2{\cdot}H_2O$ and 20 g/l of $CH_3COONa{\cdot}3H_2O$ at 328 K.

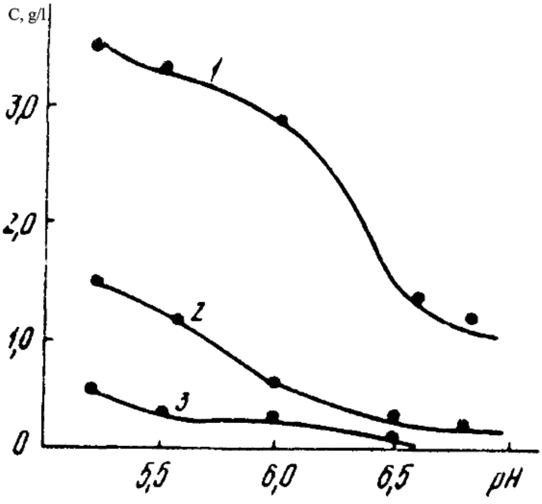

Figure 1. Influence of pH and temperature on the nickel residual concentration. Temperature was 313 K for the line 1, 323 K for 2 and 333 K for 3

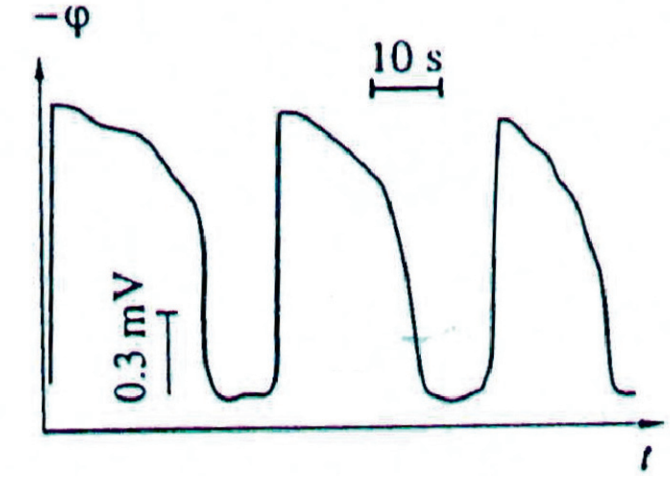

Figure 2. Steel electrode potential (φ) oscillation at nickel deposition

We can recommend following regime for the most effective nickel elimination: T = 338–343 K, pH = 6.5–7.0 in presence of the nickel powder as a catalyst. This regime ensures decreasing Ni^{2+} concentration below 0.01 mg/L. The final product consists of some phosphorus amount due to sodium hypophosphite decomposition (Eq. 4) however, this fact does not prevent easy and inexpensive nickel recycling.

This original technology has been secured by the Ukrainian patent. It is necessary to emphasize that it ensures elimination of the metallic nickel unlikely to other elimination technologies, which suppose elimination of Ni as its hydroxide, salts, etc. This is an evident advantage of our technology because pure metallic nickel can be recycled much easier than any compound of this metal.

4. Environmentally Friendly Electrochemical Method of Copper Elimination from Waste Chloride Solutions

Copper etching stages are widely used for surface cleaning, dimensional processing at radio-electronic and other similar production plants. Copper salts content in waste copper etching solutions is very high and such solutions require treatment before discharge or reuse. Current reagent methods of the waste solutions treatment are mostly wasteful because extracted copper or its compounds are rather hard and expensive to be recycled.

We investigated an electrochemical method of copper extraction from the waste etching solutions in an original two-chamber membrane electrolysis cell. The electrolyte should be placed in the cathodic part of the cell while chloride-free salt solution is placed in its anodic part.[7]

Fresh copper etching solution consists of $CuCl_2 \cdot 2H_2O$ (160–200 g/L), KCl (250–300 g/L) and HCl (9–12 g/L). Copper ions content in the waste solution can reach 70–90 g/L. Excessive amount of the ions should be extracted from the solution, which can be reused afterwards. Cu^{2+} is present in the fresh solution in form of various aqua-chloride complex ions: $[CuCl_3(H_2O)_3]^-$, $[CuCl_2(H_2O)_4]^0$ and $[CuCl(H_2O)_5]^+$. Waste solution contains also Cu^+ compounds (for example, K_2CuCl_3), which can be gradually oxidized in the acid media by oxygen to Cu^{2+} compounds[8,9]: $4CuCl + O_2 + 4HCl \rightarrow 4CuCl_3 + H_2O$. Simultaneous reproportionation process transforming Cu^+ into Cu^0 and Cu^{2+} is also possible[8]: $6Cu^+ + O_2 + 4H^+ \rightarrow 5Cu^{2+} + Cu^0 + 2H_2O$.

So, waste copper etching solutions is a complex composition of various complex compounds of Cu(I) and Cu(II).

Regeneration regimes were investigated for the current densities of 1–25 A/dm^2. It was found that the copper dissolution rate in the acid waste solution is higher than electrochemical copper deposition rate for the current densities below 5 A/dm^2. Increasing this parameter one can achieve copper deposition on the cathode. Current density of 6–8 A/dm^2 ensures obtaining dense, light-colored and well-associated deposits. Random embedded dark-colored Cu crystals can be seen for the current densities of 6–8 A/dm^2 and dendrites start to appear if this parameter reaches 10–12 A/dm^2. Finally, powdered poorly-associated copper deposits were formed under current densities of 12–25 A/dm^2.

This regeneration process should be carried out until excessive copper concentration lowers to its initial value. Excessive copper is eliminated as metal copper powder with a grain size of 50–200 μm (depending on the current density).

It is necessary to emphasize that there is no chlorine gas emission during this regeneration because the anodic part consists of chloride-free solution separated from the chloride solution in the cathodic part.

Then the regenerated solution effectiveness was compared to effectiveness of the fresh etching solution. It was found that the fresh solution reveals the etching rate of 0.49 g/(min·dm^2) and the regenerated one reveals 0.48 g/(min·dm^2). Therefore, this regenerated solution can be effectively used for new copper etching.

This original membrane electrolytic device has been secured by the Ukrainian patent. There are no other references related to such method of the copper etching solutions regeneration. Similar technology has been described for regeneration of the iron etching solutions but its chemical mechanism and scheme are absolutely different.

5. Conclusion

Using the proposed technological schemes one can develop ecologically friendly and effective methods for nickel and copper elimination from the waste chemical nickeling and copper etching solutions. These methods ensure both effective elimination of dangerous heavy metals from waste technological solutions and their inexpensive recycling back to the same production schemes. No additional harmful compounds are formed with these technological schemes.

These solutions can effectively prevent contamination of water with highly toxic copper and nickel ions and secure the human and animals nutrition chains.

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COMPOSITE IRON-BASED COAGULANT SYNTHESISED BY INORGANIC POLYFERRIC SULPHATE AND ORGANIC, NON-ANIONIC POLYMER

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Abstract Currently, research is focused on the synthesis of new composite coagulants, which are constituted of both inorganic and organic materials, so as to utilize within one reagent the advantages of both inorganic and organic components and increase their efficiency in treating water and/or wastewater. In this paper, the development of such reagents is investigated by combining an inorganic pre-polymerised coagulant (polyferric sulphate, PFS) with an organic, non-anionic polymer (polyacrylamide, PAA) under different [PAA]/[Fe] (mg/L) ratios. The results show that they possess improved properties than the conventional, non-modified reagents. Coagulation experiments suggested that the new coagulants exhibit a very good coagulation performance, thus enabling to consider their application in treating real and more loaded wastewaters, investigating their efficiency in removing possible toxic pollutants.

Keywords: Coagulation; composite coagulants; toxic pollutants; polyacrylamide; polyferric sulphate

1. Introduction

Effective coagulation reagents, such as the Inorganic Polymeric Flocculants (IPFs) have been developed, which have recently become the main water and wastewater treatment reagents with production and application on a large scale across the world. However, despite their efficiency, IPFs are

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

still inferior to the organic polymeric flocculants. Currently, research is focused on the synthesis/improvement of new composite coagulants, either by optimising the preparation conditions or, mainly, by adding appropriate additives with desired properties, such as polysilicic acid, organic polymers etc.[1,2] Under this framework, the synthesis of new composite coagulants, which are constituted of both inorganic and organic materials (mainly used as flocculant aids,[3,4] so as to utilize within one reagent the advantages of both inorganic and organic components and increase their efficiency in treating water and/or wastewater, has been attracted increasing attention. Possible additives may be classified into three categories as follows:

- Cationic: e.g. polydimethyldiallylammonium chloride (PDMDAAC)
- Anionic: e.g. polyacrypamide co-polymers with acrylic acid
- Non anionic: e.g. polyacrylamide

In this paper, the development of such reagents is investigated by combining an inorganic pre-polymerised coagulant (polyferric sulphate, PFS)[5] with an organic, non-anionic polymer (polyacrylamide, PAA) under different [PAA]/[Fe] (mg/L) ratios. Polyacrylamide is a synthetic polymer, which has been widely used in water treatment applications for more than four decades. These applications include use as a coagulant/flocculant aid for water and wastewater clarification and filtration and thickening of coagulant sludge.[6] The coagulants were characterised in terms of typical properties, such as the degree of polymerisation, pH, conductivity, ζ–potential, turbidity, density etc. Finally, coagulation experiments (jar tests) enable the assessment of coagulants efficiency, when treating model kaolin–humic acid suspensions.

2. Materials and Methods

2.1. PREPARATION OF PFS-PAA

Firstly, the preparation of the inorganic pre-polymerised polyferric sulphate under two r = OH/Fe molar ratios i.e. 0.25 and 0.5 was accomplished. The preparation procedure was based, in general terms, on the method proposed by Jiang and Graham.[7] Then, to prepared PFS-PAA composite coagulants with different r and PAA/Fe ratios, a predetermined amount of water-based polyacrylamide solution was injected into PFS stock solution at a rate of 0.4 mL/min under magnetic stirring at temperature of 50°C to prevent the formation of insoluble products.

2.2. COAGULATION EXPERIMENTS

The coagulation experiments were carried out using a jar test apparatus with six paddles. The aqueous solution to be treated was kaolin–humic acid model suspension (5 mg/L of both kaolin and humic acid), dosed with the appropriate amount of coagulant. The properties of the test suspensions are summarised in Table 1. Finally, a supernatant sample (100 mL) was collected for further analysis.

TABLE 1. Typical properties of kaolin–humic acid model suspension

pH	Turbidity (NTU)	Conductivity (mS/cm)	zeta-potential (mV)	Absorbance at 254nm	Alkalinity (mg $CaCO_3$/L)
7.98	9	0.616	–29.0	0.092	280

3. Results and Discussion

3.1. PREPARATION OF PFS-PAA

Table 2 shows the typical properties of the reagents produced in the laboratory. The measurements were conducted after 24 h aging at room temperature.

TABLE 2. Typical properties of the prepared coagulants

[PAA]/[Fe] (mg/L)	Fe_{tot} (mol/l)	Fe_{pol} (%)	pH	NTU	Conductivity (mS/cm)	r = OH/Fe	Density (g/L)
0 (PFS)	0.71	10	1.69	4.5	57.2	0.25	1,149.7588
0.02	0.14	14	2.00	2.8	21.8	0.25	1,031.1859
0.05	0.14	20	2.03	2.0	21.5	0.25	1,035.1156
0.10	0.14	23	2.06	7.0	19.5	0.25	1,031.2311
0.20	0.14	26	2.08	8.2	19.7	0.25	1,031.9899
0.30	0.14	29	2.1	9.5	19.7	0.25	1,033.1206
0.40	0.14	31	2.09	10.0	19.4	0.25	1,032.2914
0.50	0.14	30	2.09	16.0	19.2	0.25	1,032.0653
0 (PFS)	0.74	15	1.78	2.0	38.3	0.50	1,120.7085
0.02	0.14	20	2.22	2.5	12.8	0.50	1,024.1206
0.05	0.14	24	2.23	3.0	12.7	0.50	1,024.0452
0.10	0.14	23	2.22	3.5	12.8	0.50	1,024.2563
0.20	0.14	34	2.22	9.0	12.8	0.50	1,024.7789
0.30	0.14	31	2.22	7.5	12.9	0.50	1,024.9749
0.40	0.14	34	2.23	18.0	12.7	0.50	1,024.5478
0.50	0.14	37	2.23	16.0	12.8	0.50	1,025.3919

3.2. STABILITY OF PFS-PAA

Table 3 demonstrated the effect of time (after 45 days of aging) on the values of selected properties of coagulation reagents, serving as an evidence of their stability. It is concluded (through the comparison with Table 2) that the values of the parameters remain relatively steady especially for the reagents with r = 0.25. For the reagents with r = 0.5, the turbidity values increased, however without compromising the properties of the coagulants.

TABLE 3. Stability of PFS-PAA

	r = 0.25			r = 0.50		
[PAA]/[Fe] (mg/L)	Fe_{pol} (%)	pH	NTU	Fe_{pol} (%)	pH	NTU
0 (PFS)	12	1.65	2.5	18	1.90	14
0.02	16	2.11	2.0	24	2.39	21
0.05	23	2.12	2.5	27	2.38	44
0.10	31	2.15	6.0	31	2.38	14
0.20	30	2.15	6.0	33	2.38	13
0.30	33	2.16	10.0	31	2.38	16
0.40	30	2.15	9.0	30	2.38	21
0.50	33	2.18	9.5	30	2.38	12

3.3. COAGULATION EFFICIENCY OF PFS-PAA

Colloids destabilization is a crucial step of coagulation process especially for the removal of highly charged colloids. The changes in the zeta (ζ) potential values of colloid microflocs are used to evaluate the destabilization ability of coagulation reagents (Figure 1). It is demonstrated that as the PAA/Fe ratio increases the destabilization ability is respectively increased.

The coagulation efficiency of PFS-PAA reagents on treating a kaolin–humic acid suspension was evaluated by measuring residual turbidity (Figure 2). It is illustrated that the PFS-PAA exhibits significantly better performance than PFS and as the PAA/Fe ratio increases the efficiency is similarly improved.

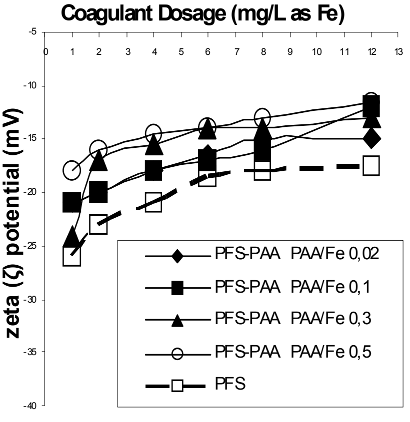

Figure 1. Effect of coagulant dosage and PAA/Fe molar ratio on the zeta (ζ) potential of kaolin–humic acid colloids

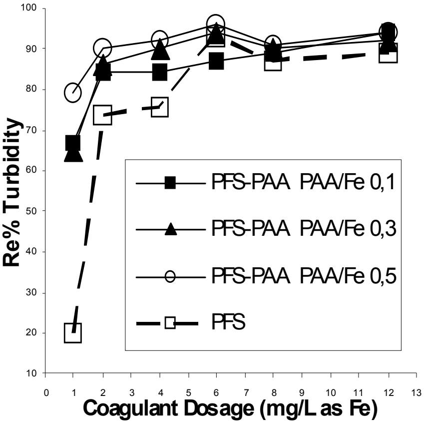

Figure 2. Comparison of coagulation performance of PFS-PAA and PFS

4. Conclusions

Overall, the results show that a preparation of a novel coagulation reagent of PFS-PAA is possible as it is emphatically shown that they possess improved properties than the conventional, non-modified reagents. The PAA/Fe ratio significantly affects the properties and the efficiency of the reagents. Coagulation experiments suggested that the new coagulants exhibit a very good coagulation performance compared to the non-modified coagulants. Finally the stability of PFS-PAA is satisfactory.

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CHARACTERIZATION AND APPLICATION OF NOVEL COAGULANT REAGENT (POLYALUMINIUM SILICATE CHLORIDE) FOR THE POST-TREATMENT OF LANDFILL LEACHATES

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Abstract Relatively "old" (stabilized) landfill leachates are a special category of wastewaters, which are difficult to treat further, mainly due to their bio-refractory organic content (humic substances). In this study, coagulation–flocculation was examined as post-treatment method for the biologically pre-treated stabilized leachates. The purpose was to examine the coagulation performance of alternative coagulant agents, i.e. the composite coagulant polyaluminium silicate chloride. Composite coagulants with different properties were prepared and characterized by means of aluminium species distribution, pH and turbidity. Their coagulation efficiency was evaluated by monitoring turbidity and parameters strongly correlated with the presence of organic matter, such as UV absorbance at 254 nm, COD and color.

Keywords: Polyaluminium silicate chloride; post-treatment; stabilized leachates; humic substances; coagulation

1. Introduction

Landfill leachates can cause considerable environmental problems, mainly by polluting the nearby underground or surface waters and therefore, collection and efficient treatment of them before discharge is necessary.

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The operational age of a landfill indicates the treatability of produced leachate. As the landfill matures, the organic fraction in the leachate becomes dominated by refractory (non-biodegradable) compounds, such as humic substances (HS).[1] The "old" (stabilized) leachates are more difficult to be treated due to the presence of HS, and in particular the biological processes are not anymore applicable. Regarding that the HS content can vary from 30% up to >70% of leachate DOM,[2,3] the need for an effective treatment method becomes obvious.

Polyaluminium silicate chloride is the outcome of polymerized silica addition into polyaluminium chloride (PACl) coagulant. It is a relatively new coagulant agent, developed in order to improve the coagulation performance of PACl. In particular, the introduction of silica chains into the structure of PACl has proved increases in the molecular weight (MW) of the coagulants,[4] thus leading to enhanced aggregating power and bigger and denser flocs' formation.[5]

In this study, coagulation-flocculation was applied as the post-treatment method of biologically pre-treated stabilized landfill leachates. The properties and coagulation efficiency of several polyaluminium silicate chloride coagulant reagents with different Al/Si molar ratios and preparation methods was investigated and compared with the coagulation efficiency of alum and PACl reagents.

2. Materials and Methods

2.1. SYNTHESIS OF COMPOSITE COAGULATION REAGENTS

The novel coagulants preparation procedure was recently described.[5] The prepared coagulants exhibit the following properties: OH/Al = 1, Al/Si = 10 or 15, and were prepared with two polymerization methods, i.e. co-polymerization (product denoted as PASiC) and composite polymerization (PACSi). Overall, four different novel coagulants were prepared with a final Al concentration of 0.2 M. The coagulants are referred in the text as PASiC 1/10 or PACSi 1/10, where 1 corresponds to OH/Al molar ratio and 10 to Al/Si molar ratio. PACl with OH/Al 1 (referred as PACl-1) was also prepared, under the same procedure, but without the addition of silicates.

2.2. CHARACTERIZATION METHODS – COAGULATION EXPERIMENTS

Aluminium species distribution was determined with the application of Al-ferron timed spectrophotometric method.[6]

The pre-treatment stage included the biological treatment of leachates in a Membrane Sequencing Batch Reactor (MSBR). The properties of the pre-treated leachates sample were: pH 8.5, turbidity 4.5 NTU, Abs UV_{254} 2.74, COD 450 mg/L, ortho-phosphates 18.2 mg/L, and the color 1813 ADMI values. The coagulation efficiency of the prepared coagulants was evaluated with common jar-test experiments with the following experimental conditions (500 mL sample volume): initial rapid mixing at 200 rpm for 3 min, followed by slow mixing at 40 rpm for 30 min and final sedimentation for 45 min. The flocculant aid (anionic polyacrylamide) was introduced just 15 s before the initialization of the slow mixing period. The concentrations of coagulants are expressed as mg Al/L for the case of PACl or alum, and as mg (Al + Si)/L for the case of PASiC or PACSi samples. The monitored parameters were measured according to standard methods.[7]

3. Results and Discussion

3.1. CHARACTERIZATION OF THE PREPARED COAGULANTS

Table 1 displays the properties of the examined coagulants. Silica addition results in an increase of composites coagulants turbidity, indicating a possible increase of the coagulant components size. Turbidity increases with silica content, whereas the coagulants prepared with the co-polymerization technique (i.e. PASiC) are more turbid than those prepared with the composite technique (i.e. PACSi). pH seems to be unaffected by the addition of silica.

Aluminium species distribution strongly correlates with the coagulation performance of an Al coagulant. With the use of ferron reagent, the Al species can be categorized into three main fractions; Al_a which corresponds to monomeric Al species, Al_b which corresponds to medium sized Al polymers and Al_c which corresponds to large Al polymeric species. From table 1 it can be seen that the addition of polysilicates results in a decrease

TABLE 1. Physicochemical properties and Al species distribution in the prepared coagulants

Coagulant	Physicochemical properties		Al species distribution		
	Turbidity (NTU)	pH	Al_a	Al_b	Al_c
PACl 1	1.8	3.76	58	37	5
PASiC 1/10	48	3.74	48	32	20
PASiC 1/15	41	3.72	50	34	16
PACSi 1/10	31	3.73	51	33	16
PACSi 1/15	26	3.71	53	33	14

of Al_a and Al_b and an increase of Al_c. The increase of the large polymeric species content confirms the observations made regarding the turbidity, as it is evident that silica increases the size of the composite coagulants components. The effect that this increase exhibits in the coagulation performance was evaluated with the respective coagulation experiments.

3.2. COAGULATION EXPERIMENTS

The percent removal efficiencies of monitored parameters with increasing coagulants dosages are given in Figure 1. Regarding turbidity, absorbance at 254 nm and COD removal (Figures 1a–c) it can be seen that for almost all concentrations the composite coagulants are more efficient than alum or PACl. The reduction in turbidity was over 80% in almost all cases, corresponding to turbidity values lower than 1 NTU, and the highest removal (93%) was achieved with PASiC 1/10. The greatest Abs UV_{254} removal of 75% was achieved with the PACSi 1/15 (for 300 mg/L initial concentration). Moreover, COD reduction under 200 mg/L (i.e. the respective legislation limit for the discharge of treated wastewaters) is accomplished almost for all examined coagulants at the dosage of 200 mg/L. The greatest

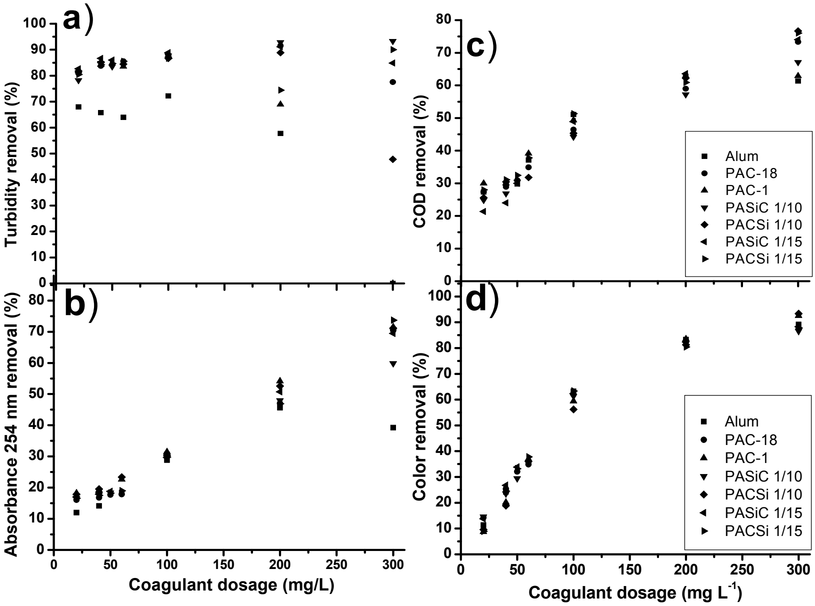

Figure 1. Coagulation experiments

removal efficiency was achieved with the coagulant PACSi 1/10 (77%, final COD value 105 mg/L), by using 300 mg/L of coagulant. Finally, for those examined parameters it can be observed that with increasing coagulant dosages over 200 mg/L, the performance of alum (or PACl) deteriorates, indicating the negative effect of overdose.

Color removal seems to be quite efficient with all the examined coagulants (fig. 1d). Removal efficiencies can reach over 90% (ADMI values <300) for the highest dosage applied, and visual decolorization can be observed for the treated sample at the high level dosages. Particularly, the highest colour removal was obtained by using 300 mg/L of PACSi 1/10 (94%, ADMI final value 120).

4. Conclusions

Coagulation–flocculation has proved to be an efficient process for the tertiary treatment of biologically pre-treated stabilized landfill leachates. Moreover, the treatment results can be significantly improved by the application of alternative coagulation reagents, i.e. by the silica-based coagulants. This improvement can be attributed to the alteration of the coagulants composition, and in particular in the increase of coagulants components size, thus resulting in bigger flocs formation. However, specific attention has to be given to the specific properties of the composite coagulants applied, i.e. the silica content and the preparation method.

Acknowledgements Thanks are due to the Greek Ministry of Development (General Secretariat for Research and Technology), which supported this research through the PENED program (25%) and to the European Union, which co-founded this program (75%). This research is part of the Ph.D. thesis of N.D. Tzoupanos.

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APPLICATION OF CARBON NANOPARTICLES FOR WATER TREATMENT

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Abstract Aqueous dispersions of carbon nanoparticles have been obtained in the range of 1–100 nm, concentration of 150–400 ppm and pH of 2.8–3.1 using a novel synthesis technique. Due to functional carboxyl groups the ion exchange capacity of carbon colloids obtained is very high – 7.4 mmol/g for a monovalent cation. The synthesized carbon nanoparticles are proved to be effective in removal of metal ions (Zn, Ni, Cu, Sb, Co, Cd, Cr, etc.) from contaminated water samples.

Keywords: Carbon; nanoparticle; water treatment; remediation

1. Introduction

Use of metals and chemicals in process industries has resulted in the generation of large quantities of effluent containing high levels of toxic heavy metals; meanwhile mining and mineral processing operations also generate toxic liquid wastes.[1] The presence of different organic and heavy metal contaminants in groundwater has a large environmental, public health and economic impact. Most of the traditional technologies such as solvent extraction, activated carbon adsorption, biological degradation and common chemical oxidation, whilst effective, very often are costly and/or time-consuming.[2] Over the last decade usage of nanoparticles, structures from 1 to 100 nm in size have been studied in this regard due to their large surface areas and high surface reactivity.[3] For instance, nanoscale iron particles have been considered as a new generation of environmental

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remediation technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems.[4]

This paper deals with synthesizing carbon nanoparticles; it also discusses their usage for the extraction of pollutants from industrial wastewater. The colloidal carbon with functional groups such as carboxyl, hydroxyl and keto-groups can be particularly useful being applied jointly with micro and ultra-filtration processes for conducting separations not achievable by microporous activated carbons. The commercially available activated carbons are heterogeneous in nature; hence new carbons with well-defined chemical groups are required.

Although it is not possible to form colloids of unoxidized carbon, colloids of oxidized graphite or graphite oxide are widely known.[5] Nitric acid, hypochlorite and ammonia are usually used for surface modification of carbon. Here, we describe an electrochemical oxidation method to produce aqueous solutions of carbon nanoparticles with sufficient stability without mixing nitric acid with a surfactant. The capability of carbon nanoparticles in removing metal ions and radionuclides from water is also discussed.

2. Materials and Methods

High-density isotropic graphites are used as an anode and a cathode. The dimensions of electrodes are chosen as follows: 65 mm (W) × 30 mm (H) × 15 mm (Th). The distance between electrodes immersed in a distilled water bath is able to be varied from 10 to 120 mm in the current density range 0.1–3 mA/cm^2. The electric power applied to the electrodes is 60 V (DC). Two anodes and one cathode between anodes are used to increase the surface of working electrodes and to decrease dimensions of the device. Total working area of the anodes is 24 cm^2. The constructed apparatus includes an electrolytic cell 120 mm (W) × 140 mm (H) × 105 mm (Th) made of plastic. The cell contains distilled water as an electrolyte and three carbon electrodes immersed into the electrolyte. Deionized water is most preferable for cost-effective production of pure carbon colloids. The electrolytic cell is installed on a magnetic stirrer. The electrolyte is passed between the electrodes to provide the electrolyte with carbon particles and discharge the gas generated via electrolysis from the electrodes.

The process of the device operation consists of two stages. The first stage is the electrolysis during 10 min. The second stage is the electrolyte stirring during 60 s. This process is executed automatically. Twin timer ST-T (Korea) is used to control the process.

The radionuclides used as the label of ions during the study of water purification process are given in Table 1; they were produced by irradiating salts of ions in nuclear reactor of the Institute of Nuclear Physics (Tashkent, Uzbekistan). Ge(Li) detector with a resolution of about 1.9 keV at 1.33 MeV and the 4096-channel multichannel analyzer were used to detect g-quantum from radionuclides. Areas under g-peaks of radionuclides were measured to calculate the amount of ions.

TABLE 1. Radionuclides used as labels ($T_{1/2}$ is the half-life of the radionuclides, E_γ is the energy of the γ-peaks)

Elements	Radionuclides	$T_{1/2}$	E_γ , MeV
Cr(VI)	^{51}Cr	27.73days	0.320
Co(II)	^{60}Co	5.27 years	1.17, 1.33
Ni(II)	^{65}Ni	2.5 h	1.480
Cu(II)	^{64}Cu	12.7 h	0.511
Zn(II)	^{65}Zn	244.1 days	1.115
Sr(II)	^{89}Sr	50.5 days	0.909
Cd(II)	^{115}Cd	53.5 h	0.336
Sb(II)	^{124}Sb	60.2 days	1.691
Cs(I)	^{134}Cs	2.07 years	0.605

The exchange capacity Q, mmol/g, was calculated as follows:

$$Q = (A_0 - A_e)/(A_0 - A_B) \cdot B/W \tag{1}$$

where B is amount of carrier (mmol); W is weight of exchanger (g); A_0 is a count rate of the original solution, A_e is a count rate of the solution at equilibrium, A_B is a background count.

The distribution coefficient K_d and the percent adsorption P were calculated by Eqs. 2 and 3:

$$K_d = ((A_0 - A_B)/(A_e - A_B) - 1) \cdot V/W \tag{2}$$

$$P = 100 \cdot (1 - (A_e - A_B)/(A_0 - A_B)) \tag{3}$$

where V is a total volume of the solution (mL).

3. Carbon Nanoparticle Synthesis Technique

The electrolysis is executed by two stages: activation of the anode and the carbon nanoparticles generation. At the first stage the electrolyte has low conductivity, value of electric current is small, about 0.1–0.2 mA/cm^2 and the oxidization reaction is slow. Duration of this stage is about 50 h and depends on the quality (density) of graphite. At this stage a voltage between electrodes can be high, about 60–100 V.

As the reaction proceeds, the conductivity of the electrolyte is abruptly increased, electric current can increase up to 10 mA/cm^2 and higher and the oxidization reaction is activated. As a result, the carbon is finely split, and then is covered by the carboxyl group. At the second stage the electric current between electrodes must be about 3–4 mA/cm^2. If current density values are greater than 8–10 mA/cm^2, the rate of oxygen evolution is greater than the rate of its diffusion through the electrode; hence there is a pressure build-up within the electrode causing the electrode to disintegrate. Carbon colloids are not stable, in 2–3 weeks their precipitation is observed. Similarly, at current density less than 3–4 mA/cm^2 the rate of oxygen evolution is such that, although some pressure builds up in the electrode, the gas is able to diffuse out of the electrode before disintegration occurred, small pieces of carbon broke off in the process to form colloidal carbon and very small amount of slurry. Carbon nanoparticles are stable during 150 days at least. The rate of diffusion of hydrogen at the cathode is such that little or no pressure built up within the electrode and therefore no colloid is produced at this electrode. The colloidal carbon is produced only at the anode and remains within the vicinity of the electrode, indicating that the carbon is negatively charged. Reversal of the electrode polarity results in the surrounding carbon migrating slowly to the new anode.

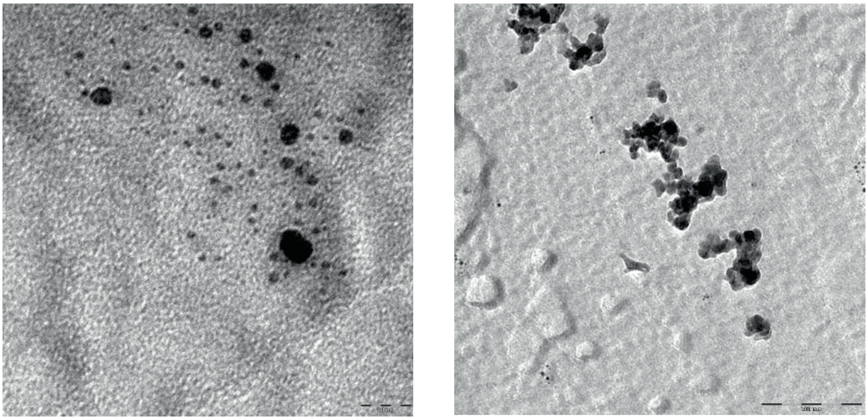

Figure 1. TEM images of carbon nanoparticles obtained (the scale is 20 and 200 nm respectively)

Carbon nanoparticles are removed from the anode during the electrolyte stirring stage. pH of the solution is 2.8–3.1 and depends on the concentration of carbon nanoparticles; concentration of carbon nanoparticles is 150–400 ppm and depends on duration of the process; ion exchange capacity is 7.4 mmol/g for a monovalent cation. The typical TEM images for carbon colloids obtained using various process parameters are shown on Figure 1.

4. Water Decontamination by Carbon Nanoparticles

The removal of heavy metal ions (Zn, Ni, Cu, Sb, Co, Cd, Cr, etc.) from water was studied. The pH of the aqueous dispersion of carbon colloids was 2.8 and the concentration of carbon nanoparticles was 250 ppm. The distribution coefficient K_d for different ions at pH = 7.1 of the solutions is presented in Table 2. The results given there demonstrate high ion-exchange potential of the colloidal carbons. In real water samples containing different ions, the colloidal particles are coagulated within some time depending on the concentration of salts. Before and during coagulation process the nanoparticles as the ion exchangers react with cations. After the coagulation water can be easily filtered from particles with attached cations. Thus the colloidal particles are quite effective for removal of the metal cations and may provide a useful alternative for example to method of flocculation of metal hydroxides and oxides.

TABLE 2. Distribution coefficient K_d (mL/g) and percent adsorption P (%) for different ions (concentration of ions C_0 = 10 mg/L, V = 50 mL, W = 0.5 g, pH = 7.1, contact time 1 h).

Elements	P	K_d, 10^5
Cr(III)	>99	140
Co(II)	>99	170
Ni(II)	>99	1,300
Cu(II)	>99	1,400
Zn(II)	>99	4,000
Sr(II)	>99	3,800
Cd(II)	>99	100
Sb(II)	>99	400
Cs(I)	60	0.6

5. Conclusion

The described method allows production of carbon nanoparticles with concentration of 150–400 ppm and pH of 2.8–3.1. The concentration of nanoparticles depends on the duration of the process and the pH of the colloidal solution depends on the concentration of carbon nanoparticles. The ion exchange capacity of carbon nanoparticles due to functional carboxyl groups is very high, 7.4 mmol/g for a monovalent cation. The obtained carbon nanoparticles can be used for effective removal of metal ions (Zn, Ni, Cu, Sb, Co, Cd, Cr, etc.) from contaminated water.

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SORPTION OF COPPER AND ZINC CATIONS BY BIO-MODIFIED BROWN COAL

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Abstract Knowledge on the mechanism of microorganisms participation in the elements cycle and their role in the environmental equilibrium establishment that leads to new generation of environmental biotechnologies evolution is significantly growing. Biotechnological methods have wide application area in the remediation of heavy metals from wastewaters. We studied bio-modification of brown coal sorption materials with the aim to enhance its sorption properties. The micromycetes (*Aspergillus niger, Aspergillus clavatus, Penicillium glabrum and Trichoderma viride*) have been selected for biological activation of coal samples. The quantitative maceral composition and specific surface of prepared sorbents has been investigated. The sorption of copper(II) and zinc(II) ions from aqueous solutions by this unconventional sorbents was studied. It was found that, for each sorbent the equilibrium establishing time was about 1 h. The Langmuir adsorption model was applied to describe isotherms and isotherm constants. The isotherms studies revealed that prepared sorbents exhibited relatively high capacity for the metals removal.

Keywords: Brown coal; micromycetes; heavy metals; sorption

1. Introduction

Numbers of studies of metal accumulation from the metal recovery and/or removal of metal from aqueous solutions have been launched due to a

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

great awareness of the ecological effects of toxic metals released into the environment.

Conventional methods of heavy metals removal from aqueous solutions include chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, electrochemical treatment, membrane technologies, and evaporation technology.[1,2] These processes may be ineffective or extremely expensive, especially when the metals occur in low concentrations (1–100 mg/L).[1]

In recent years, numerous low-cost natural materials have been proposed as potential source of commercial synthetic sorbents.[3] Natural low-cost materials that have been studied include leaves, mould, peat moss, green algae, fungi, activated carbon fibers, coconut waste, etc.[4–10] However, new economical, easily available and highly effective sorbents are still needed. Although the adsorption capacities of low-rank coal are lower than of synthetic ion-exchange materials, the substantially lower costs shows great potential for the use of low-rank coal for removing heavy metal ions from wastewater.[4]

Knowledge of the porous structure of different coal types is of relevance if the organisms involved are sufficiently small to penetrate part of the structure. This might mean that the surface area available for reaction is considerably increased and could indicate, which coal type would be more susceptible to bio-attack. Considering the possibility of in situ coal conversion in deep streams by either conventional gasification or microbial action, knowledge of the physical and chemical properties of the coal under the prevailing conditions is essential. The fact that microorganisms can be developed in fine pores was reported within the research on the aerobic microbial conversion of phenols adsorbed on active carbon.[11]

Micromycetes belong to soil microorganisms, which take part in decomposition processes in the soil. Micromycetes are saprophytes, sponges and live in commensalisms. They attack plastics, glass, the walls of buildings, etc. Micromycetes can decompose the organic matter of vegetable and animal origin in the nature.[12–15] In accordance with theoretical knowledge there was an effort to choose microorganisms for the biological activation of coal samples, of which bearing on the coal matrix was not studied so far. Finally, four types of microorganisms were chosen for bio-activation of brown coal samples, such as *Aspergillus niger*, *Aspergillus clavatus*, *Penicillium glabrum* and *Trichoderma viride*. Studied brown coal was after its bio-activation applied as sorbent in removal of Cu(II) and Zn(II) from water solutions.[16]

2. Experimental

2.1. BROWN COAL

A sample of Slovak brown coal from Novaky deposit (Hornonitrianske mines, Prievidza), with diameter under 1 mm was selected for an activation by microorganisms. The chemical analysis of the sample showed Ash^d 20.88%, W^a 24.56%, Fe^d_{dat} 1.44%, S^d 3.00%, As^d 380 ppm, HA^{dat}_{total} 12.94%.

The quantitative maceral analysis was performed using the NU 2 microscope by Carl Zeiss-Jena in oil immersion with the refraction index 1.515, at 20°C and wave length 564 nm. Samples of the investigated coal were embedded in to the epoxy resin and were prepared as polished specimen in accordance with ISO 7404-2.

2.2. SORBENT PREPARATION AND ADSORPTION EXPERIMENTS

The cultures of selected micromycetes were grown in Sabouraud agar medium (SAB – mycological peptone, maltose, agar, distilled water). Suspension was injected (5 mL) of every 14-day-old culture spores in SAB to the 10 g of brown coal mixed with 10 ml of SAB medium. The cultivation was executed in the dark at ambient temperature.

The leaching process took 7 weeks. After leaching, the suspensions were filtered, washed with distilled water, dried and prepared for adsorption experiments.

Stock solutions of each metal: Cu(II) containing 30–300 mg/L and Zn(II) containing 30–300 mg/L were prepared by dissolving $CuSO_4.5H_2O$ and $ZnSO_4.H_2O$ of analytical grade in distilled water.

All the adsorption experiments were conducted at ambient temperature in a laboratory shaker. Metal solutions of known concentrations were introduced into the glass Erlenmeyer bottles (25 mL) containing defined amounts (10 g/L) of the adsorbent. The bottles were shaken horizontally and the adsorbent was removed by filtration after 1 h adsorption.

The equilibrium concentrations of heavy metals were determined by atomic adsorption spectroscopy (Varian Spectr AA-30) and the metal uptake was calculated from the difference.

The Langmuir adsorption isotherms have been constructed and the maximum adsorption capacity of the adsorbents has been determined. The pH measurements were carried out with a laboratory pH meter GPRT 1400 A-GL. For Cu(II) sorption the pH reached 5, as Cu(II) ions undergo hydrolysis reactions in water and form insoluble aqueous complexes with increasing pH. Zn(II) sorption experiments were performed at pH 7 for the same reason as in case of Cu(II) adsorption. The surface characteristics of prepared adsorbents were measured by the BET method using the Micrometrics Gemini 2360 apparatus and the surface morphology was studied using the Scanning Microscope TESLA BS 300.

3. Results

Specific surface area of brown coal was determined by the BET method before and after the activation by microorganisms and the results are shown in the Table 1.

TABLE 1. Specific surface area of brown coal sorbents activated by different species of microorganisms

Sample	S_1	S_2	S_3	S_4	S_6
Microorganism	*Aspergillus niger*	*Aspergillus clavatus*	*Penicillium glabrum*	*Trichoderma viride*	–
Specific surface (m^2/g)	4.94	3.60	3.93	4.34	3.23

The Figures 1 and 2 present the scanning electron micrographs of the samples S_1 and S_3. SEM micrographs were taken using the Tesla BS 340 electron microscope. Scanning electron micrograph of modified brown coal shown in Figure 1 presents sample S_1, which was treated by Aspergillus niger, while Figure 2 presents the S_3 modified by *Penicillium glabrum*. From both figures is obvious that the aggregates were developed.

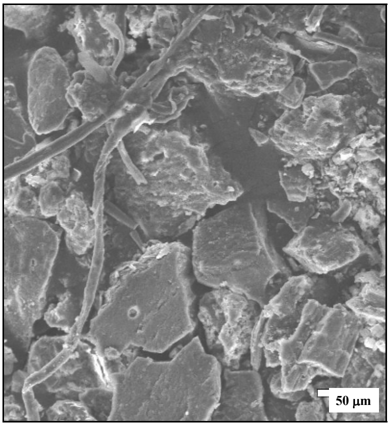

Figure 1. SEM micrograph of brown coal treated by *Aspergillus niger* – sample S_1

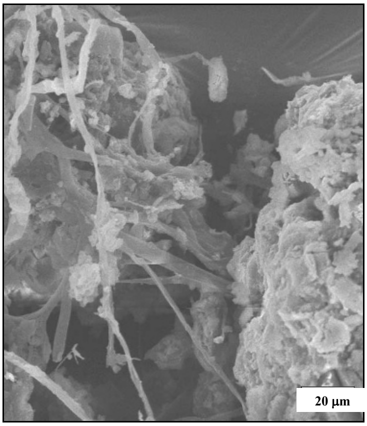

Figure 2. SEM micrograph of brown coal treated by *Penicillium glabrum* – sample S_3

The microscopical evaluation confirmed that the investigated sample is brown coal. Maceral groups of huminite were hardly gelified (Figure 3). According to the intensive colouring of liptinite maceral group (dark brown) we can state that this represents a coal rank with low coalification. The content of inorganic materials as well as of clay minerals, sulphides (Figure 4), carbonate minerals etc., was very high, because the polished specimens were prepared from the original non-washed samples.

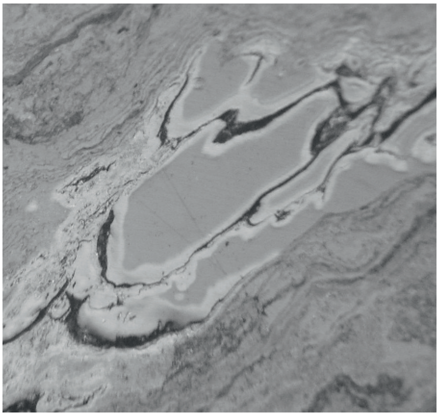

Figure 3. Effect of *Aspergillus clavatus* influence on the humotelinite; oil immersion, reflected light: ×400

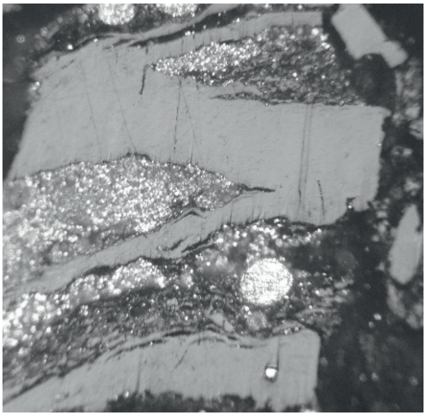

Figure 4. Syngenetic pyrite in the coal sample; oil immersion, reflected light: ×400

Table 2 shows the results of maceral analysis of coal affected by different micromycetes species. The results are corrected to the clear coal mass. From the results of maceral analysis we can say that the most notable changes in maceral composition were in the sample affected by microorganisms from the species *Penicillium glabrum.*

TABLE 2. Maceral analysis of coal samples affected by different micromycetes species

Sample	HT (%)	HK (%)	HD (%)	L (%)	I (%)
Coal	28.0	57.6	1.0	11.3	3.1
Coal + *Aspergillus niger*	17.7	57.8	10.2	8.6	5.7
Coal + *Aspergillus clavatus*	19.2	58.4	8.4	11.3	2.7
Coal + *Penicillium glabrum*	1.9	63.2	10.9	19.8	4.2
Coal + *Trichoderma viride*	4.2	62.8	24.0	2.6	6.4

HT – humotelinite, HK – humocollinite, HD – humodetrinite, L – iptinite, I – inertinite

Figures 5 and 6 present adsorption isotherms of copper and zinc adsorption by bio-modified adsorbents. Experimental data were fitted by Langmuir equation. The correlation coefficient ranged from 0.96 to 0.99.

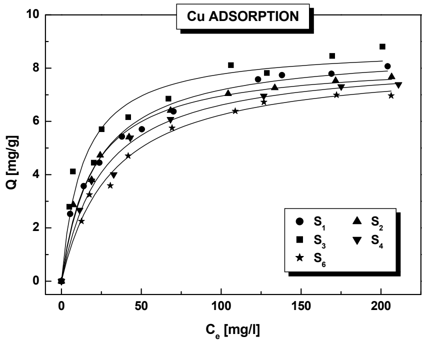

Figure 5. Langmuir adsorption isotherms of Cu adsorption on brown coal treated by different microorganisms (samples S_1–S_6)

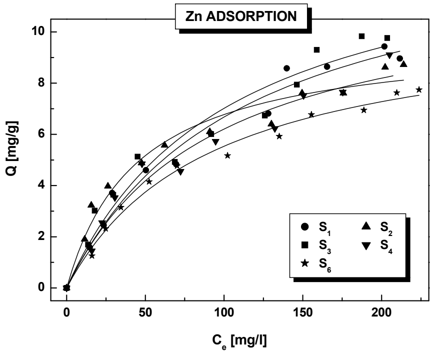

Figure 6. Langmuir adsorption isotherms of Zn adsorption on brown coal treated by different strains of microorganisms (samples S_1–S_6)

Experimental results showed that maximum increase of metals uptake for biologically activated brown coal was achieved by the activation by *Penicillium glabrum* (sample S_3), i.e. 8.8 mg Cu(II)/g of sorbent and 14.3 mg Zn(II)/g of sorbent.

4. Conclusion

The micromycetes evoked certain changes in maceral composition of coal. The most notable changes were influenced by *Penicillium glabrum*. The results of maceral analysis can be used only as orienting as they are strongly influenced by inorganic material in the original non-washed sample of coal from Novaky deposit, hence all results can be referred only to used coal sample.

The results of adsorption experiments showed that selected type of sorbent preparation had positive influence on sorption properties of activated material and prepared sorbents had good affinity to selected metals.

The results confirmed that there is a possibility to prepare the sorbents by new non-conventional methods and the obtained results appear as promising for the research and development in utilisation of non-energetic coal.

Acknowledgements This work was supported by the Slovak Research and Development Agency under the contract No. APVV-51-017104.

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APPLICATION OF BACTERIALLY PRODUCED HYDROGEN SULPHIDE FOR SELECTIVE PRECIPITATION OF HEAVY METALS

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Abstract The generation of acid mine drainage (AMD) and its discharge into the environment surrounding abandoned mines is likely to cause serious environmental pollution. Numerous techniques are available for neutralization and removal of metals and sulphates from AMD. One of the best available technologies for the removal of metals from AMD is the application of the sulphate-reducing bacteria (SRB). This process is based on the production of biogenic hydrogen sulphide by SRB, which consequently reacts with metal ions in the water forming sparingly soluble metal sulphides. The main objective of this work was to study the process of the heavy metals precipitation from AMD by bacterially produced hydrogen sulphide combined with intermediate steps of metals precipitation by sodium hydroxide at various pH values. The experiments were conducted with AMD coming from the abandoned and flooded deposit of Smolník (Slovak Republic). This process is able to sequentially precipitate Cu^{2+}, Zn^{2+} and Fe^{3+} in the form of sulphides, Al^{3+}, Fe^{2+} and Mn^{2+} in the form of hydroxides.

Keywords: Biogenic hydrogen sulphide; selective precipitation; acid mine drainage

1. Introduction

Acid mine drainage (AMD) is the phenomenon of acid production from mining tailings. It is the most critical environmental problem created

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

mainly by the mining industry of the sulphide minerals. The process of AMD generation is well understood.[1] AMD contains sulphuric acid, dissolved heavy metals, sulphates, iron precipitates and their pH can be very low about 1.5–2.0. High acidity and presence of toxic metals in AMD waters degrade soil, air, and water quality, and detrimentally impact vegetation and aquatic life. Consequently, mine waste waters, prior to being released into the environment, must be treated to meet government standards for the amounts of metal and non-metal ions contained in the water.

AMD represents a major environmental problem and has been a long-standing major concern to scientists, engineers, industry, and governments, both in Slovakia and throughout the world.[2] Numerous techniques are available for the neutralization and removal of metals and sulphate from AMD[3,4]. The first experimental solution to AMD was simply to neutralize the mine wastewaters with lime or limestone with further aeration. This method precipitates the iron, which is the most abundant metal in AMD waters, but other metals present are difficult to precipitate out and are not removed by this treatment. Also, remobilisation of the contaminants can occur as well. Other methods have treated mine waste waters with ionic surfactants to control the bacterial population and, thereby inhibit the oxidation of ferrous iron to ferric iron. This strategy, however, has not been successful as many other factors are involved in controlling AMD, which this attempted solution does not take into account.

Nowadays the attention is paid to physical, chemical and biological methods for selective recovery of metals from AMD.[5–8] These methods have the potential to recover metals in a suitable form for commercial use. One of the best available technologies for the removal of metals from AMD is precipitation resulting in metal sulphides. Furthermore, due to the different pH values of metal sulphide precipitation, selective recovery of valuable metals (like copper, nickel, cobalt, zinc etc.) from AMD can be achieved by hydrogen sulphide.[9] However, chemical sulphide precipitation has not been generally used probably due to the high costs of reagents. Sulphates already exist in AMD and should be removed. A good way to obtain this is to reduce the sulphates to hydrogen sulphide by sulphate-reducing bacteria (SRB) and to use the biologically generated hydrogen sulphate to precipitate the AMD metals. As there are certain metals in AMD that do not precipitate as sulphides, an extra step of hydroxide precipitation is needed.

The main objectives of the present work were to study the AMD outflowing from the shaft Pech of the deposit Smolník (Slovak republic) and to set up a flow sheet for its successful treatment by combined chemical and biological methods. The specific objectives of this research can be outlined as follows: to develop several stages of process consisting of separate

SRB bioreactor system for sulphate-reducing activity and production of biogenic hydrogen sulphide to be used in the subsequent metal precipitation and biorecovery system and to achieve high recoveries and metal precipitate purities, while producing water suitable for discharge to the environment.

2. Materials and Methods

2.1. ACID MINE DRAINAGE

A sample of AMD from the abandoned and flooded deposit of Smolník (the shaft Pech) was used in this study. The average values of the major metal concentrations, pH and Eh of aforementioned AMD are reported in Table 1.

TABLE 1. Comparison of AMD major metal concentrations and pH with limits according NV SR č. 296/2005 Z.z. (AMD sample from the shaft Pech, deposit Smolník, Slovak republic)

Parameter	pH	SO_4^{2-} (mg/L)	Fe (mg/L)	Mn (mg/L)	Cu (mg/L)	Zn (mg/L)	Al (mg/L)
Value	3.7	2 938	307	26	5.3	10.8	77
Limits	6–8.5	250	2	0.3	0.02	0.1	0.2

2.2. MICROORGANISMS

For the experiments the cultures of SRB (genera *Desulfovibrio*) were used, which were isolated from a mixed culture obtained from the potable mineral water (Gajdovka spring, Kosice-north, Slovak republic). The SRB were selected from the mixed cultures grown on plates and in agar shake tubes containing modified Postage's medium E[10] The isolation was performed by the modified dilution method.[11]

2.3. SELECTIVE SEQUENTIAL PRECIPITATION

The experiments of the heavy metals selective sequential precipitation from AMD sample was performed in two interconnected reactors with a capacity of 1,000 mL (the first bioreactor) and 250 mL (the second bioreactor), which operated at the semi-continuous conditions. This method contains several process steps, which could be grouped in two main stages:

- *Biological hydrogen sulphide production*. In this stage SRB using organic matter (sodium lactate) convert the sulphate to hydrogen sulphide.

- *Selective heavy metals precipitation by the bacterially produced hydrogen sulphide.* In this stage the previously produced H_2S in the first bioreactor is continuously transferred by N_2 to the second reactor, which was filled by sample AMD. There the pH is adjusted to suitable values (three different steps for Cu, Zn and Fe; see Figure 1) and selective precipitation of metal sulphides is observed.

The solid produced in each step is separated from the dispersion by filtration. Intermediate steps of metal hydroxide precipitation by 1M NaOH take place (three in total at various pH values; see Figure 1). The solids produced in each step are also removed by filtration. The pH values used for heavy metals precipitation were assigned on the ground of our previous works and enumerations.[12]

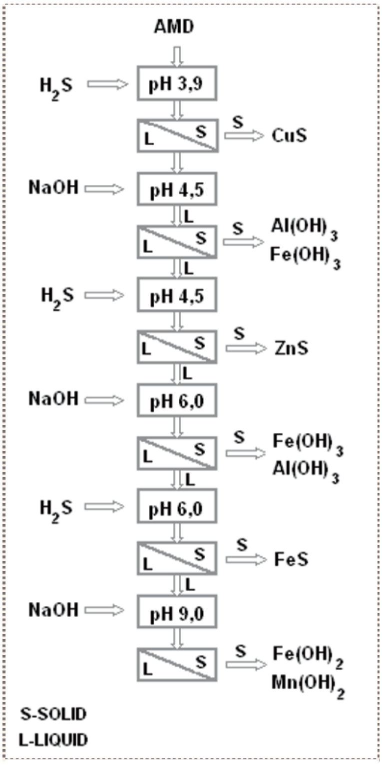

Figure 1. Scheme of the six-step precipitation process studied for recovery of metals from acid mine drainage

2.4. ANALYTICAL PROCEDURES

A turbidimetric method was used to measure the concentration of sulphate ion concentrations. The concentration of metals was determined by atomic absorption spectrometry (AAS) using Spectrometer AA-30 Varian (Australia) instrument. A glass pH electrode combined with the reference Ag/AgCl electrode was used to measure pH. Digital pH-meter GPRT 144 AGL (Germany) was used. The qualitative analysis of precipitates obtained by biologically produced hydrogen sulphide and by sodium hydroxide was done by energy dispersive spectrometry (EDS) analysis using instruments, which consisted of a scanning electron microscope BS 300 (Tesla, Czechoslovakia) and an x-ray microanalyser EDAX 9100/60 (Philips, Holland). Samples of precipitates were dried and coated with carbon before the EDS analysis.

3. Results and Discussion

The flow sheet of the six-step precipitation process for the selective sequential precipitation of heavy metals form AMD sample is given in Figure 1. The solids separated from each precipitation step were analysed by SEM-EDS and the results are given in the following Figures 2–7.

After the first precipitation the suspension of precipitates was filtered and analysed. The data (Figure 2) show clearly that the precipitate is CuS. The pH of the filtrate was adjusted to 4.5 with 1 M NaOH (step 2 of precipitation process) and the solid precipitated was separated and analysed. The results are presented in Figure 3 and show clearly that the precipitate is mainly Al hydroxide with some Fe hydroxide. The filtrate was returned into the second reactor and was submitted to the effect of the bacterially produced hydrogen sulphide again. The solid produced was separated and analysed as well (step 3 of precipitation process) and the results are given in Figure 4. It consisted of pure zinc sulphide. In a similar way steps 4 to 6 were realized. The solid from the fourth step of precipitation was a mixture of Al and Fe hydroxides (Figure 5). The solid from the fifth step was a mixture of Fe sulphide and Fe hydroxide (Figure 6). The solid from the sixth step of precipitation was a mixture of Mn and Fe hydroxides. The above procedure recovered CuS and ZnS in pure form, while Al, Fe and Mn were recovered but not in pure form. Fe was precipitated as Fe(III) in steps 2 and 4 and as Fe(II) in step 6.

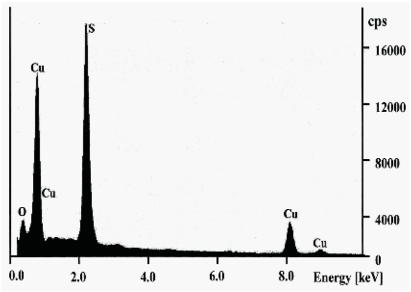

Figure 2. EDS qualitative analysis of precipitates from step 1. Precipitating agent: bacterially produced H_2S; pH: 3.9 – initial pH of AMD

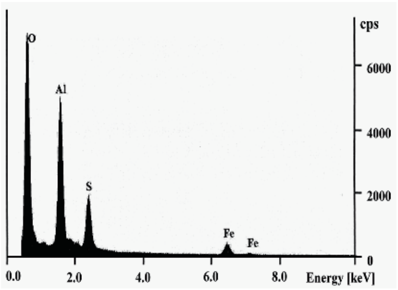

Figure 3. EDS qualitative analysis of precipitates from step 2. Precipitating agent: 1 M NaOH; pH 4.5

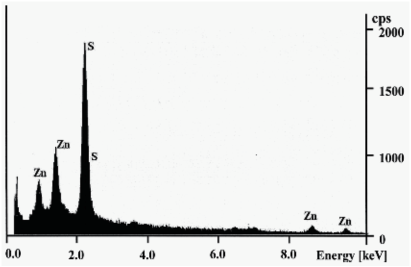

Figure 4. EDS qualitative analysis of precipitates from step 3. Precipitating agent: bacterially produced H_2S; pH 4.5

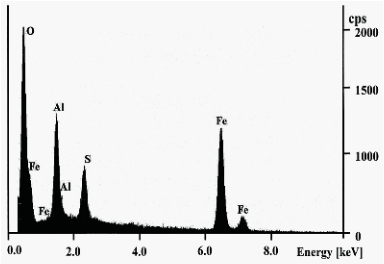

Figure 5. EDS qualitative analysis of precipitates from step 4. Precipitating agent: 1M NaOH; pH 6.0

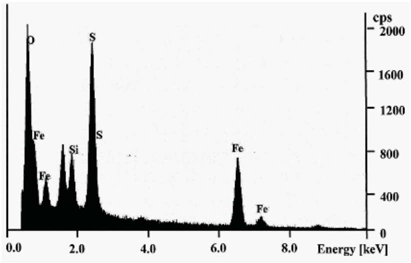

Figure 6. EDS qualitative analysis of precipitates from step 5. Precipitating agent: bacterially produced H_2S; pH 6.0

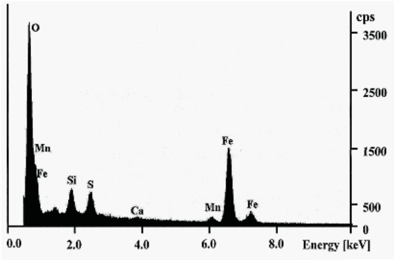

Figure 7. EDS qualitative analysis of precipitates from step 6. Precipitating agent: 1 M NaOH; pH 9.0

4. Conclusions

The selective sequential precipitation and bio recovery of metals from AMD from the deposit of Smolník – shaft Pech was studied. A six-step process was realized with a combination of metals precipitation by bacterially produced hydrogen sulphide (Cu(II), Zn(II), Fe(III)) and metals precipitation by sodium hydroxide at various pH values. The suggested procedure was able to sequentially precipitate of Cu^{2+}, Zn^{2+} and Fe^{3+} in the form of sulphides, Al^{3+}, Fe^{2+} and Mn^{2+} in the form of hydroxides. Cu and Zn were obtained in pure form.

Acknowledgements This work was supported by the Slovak Research and Development Agency under the contract No. APVV-51-027705.

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MORPHOLOGY CONTROL OF ORDERED POROUS SILICA ADSORBENTS

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Abstract Peculiarities of template synthesis of ordered porous silicas with spherical morphology of particles were investigated in alkaline and acidic media. Obtained silicas were characterized by nitrogen adsorption–desorption measurements, x-ray diffraction, scanning and transmission electronic microscopies.

Keywords: Ordered mesoporous silicas; morphology control; template synthesis

1. Introduction

Functionalized mesoporous silica matrices of MCM-41 type with hexagonal ordered porous structure possess high adsorption capacity and specificity for certain contaminants and can be used for the removal of toxic heavy metal cations and anions, radionuclides and organic solvents.[1,2] However, particle morphology of MCM-41 materials is one of the primary factors for their application in sorption and separation techniques. That is why the ability of the macroscopic control and improve of pore structure are the important trends in the field of template synthesis of ordered mesoporous materials.[3,4] In this paper the influence of media type on pore structure and particle morphology of obtained silicas was studied.

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

2. Experimental

Syntheses were carried out in alcohol-ammonia media by modified Stober method[5] in ethanol and isopropanol with use of tetraethoxysilane (TEOS) as silicas precursor and cethyltrimethylammonium bromide (CTAB) as supramolecular template with a molar ratio of the components 1TEOS: XCTAB: 11NH_3: 144H_2O: 58ROH, where X = 0.1, 0.2 and 0.3. Synthesis in acidic media was done using the TEOS, CTAB with a molar ratio of components 1TEOS: 0.1CTAB: 0.45HCl: 100H_2O.

3. Results and Discussion

3.1. SYNTHESES IN ALKALINE MEDIA

Nitrogen adsorption–desorption isotherms of silicas synthesized in ethanol-ammonia media with different surfactant/TEOS molar ratios (Figure 1) are type IV isotherms in the IUPAC classification[6] and characterize MCM-41 type silicas. The isotherms have a sharp raise at the relative pressure of $0.3 < p/p_0 < 0.4$, which is characteristic for capillary condensation within mesopores, the sharpness of these reflections testifies to uniformity of the mesopores diameter. Specific surface areas of the synthesized silicas were 700–1,200 m^2/g (by BET-equation). The BJH pore size distribution curves have marked peaks in the range of pore size 2.5-3.0 nm.

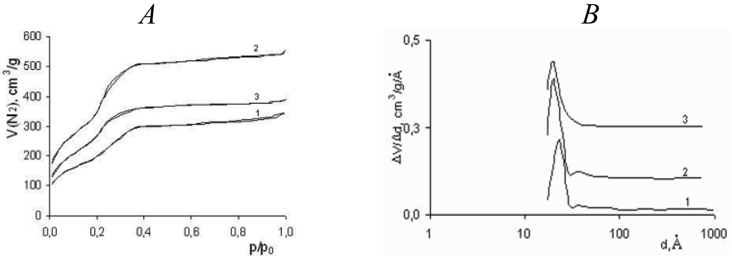
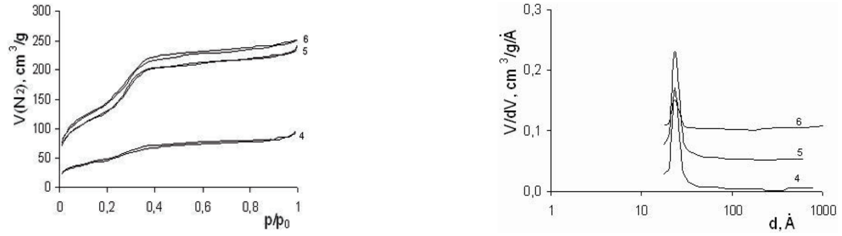


Figure 1. Nitrogen adsorption–desorption isotherms (a) and pore size distributions (b) of silicas synthesized in ethanol–ammonia media with different molar CTAB/TEOS ratios: 0.1 (1), 0.2 (2), and 0.3 (3). Here and at Figures 2 and 3 curve number corresponds to sample number in table

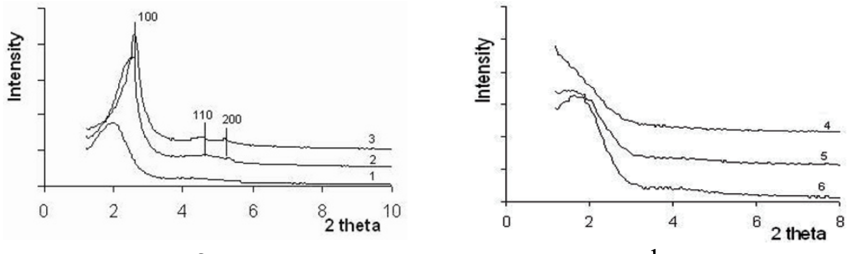
Nitrogen adsorption–desorption isotherms of silicas, synthesized under alkaline conditions with use of isopropanol (Figure 2) at molar CTAB/TEOS ratios equal to 0.2 and 0.3, are also type IV isotherms with expressed ranges of capillary condensation at relative pressures p/p_0 = 0.2–0.4. Specific surface area of synthesized samples is 400–500 m^2/g. The nitrogen adsorption isotherm for silica synthesized in the system with a molar ratio of CTAB/TEOS = 0.1 has a weakly marked range of capillary condensation and low specific surface area (170 m^2/g). Maximum in the pore size distributions curves correspond to pores sizes in the range of 2.5–3.0 nm.

Diffractograms of silicas synthesized in ethanol with molar ratios of TEOS/CTAB = 0.3 and 0.2 show three low-angle Bragg peaks in the range of 2θ = 2.5–7.0° with indexation (100), (110) and (200) for a hexagonal lattice and characterize the structure of MCM-41 materials.[7] The x-ray diffraction patterns of silicas synthesized in ethanol with molar ratios of TEOS/CTAB = 0.1 and silicas synthesized in isopropanol with molar ratios of TEOS/CTAB = 0.3 and 0.2 have only one weak peak (Figure 3) characteristic for a weakly ordered pore structure.



a b

Figure 2. Nitrogen adsorption–desorption isotherms (a) and pore size distributions (b) of silicas synthesized in isopropanol with different CTAB/TEOS molar ratios: 0.1 (4), 0.2 (5), and 0.3 (6)



a b

Figure 3. X-ray diffractograms of silicas synthesized in ethanol (a) and isopropanol (b) with different CTAB/TEOS molar ratios: 0.1 (1, 4), 0.2 (2, 5), and 0.3 (3, 6)

The lattice parameter a_0 (the distance between the nearest centers of cylindrical mesopores) was determinated using a formula $a_0 = 2d_{100}/3^{0.5}$ for the hexagonal symmetry, where d_{100} is the interplanar distance of (100) planes. The thickness of pore walls h was calculated from $h = a_0 - d_p$, where d_p is pore diameter determined by the BJH-method. Structural-adsorption characteristics of silicas synthesized in alcohol-ammonia media are presented in Table 1.

TEM-photos (Figure 4) in combination with x-ray diffraction results demonstrate an ordered uniform pore arrangement of MCM-41 silica synthesized in ethanol–ammonia media with a molar ratio of CTAB/TEOS = 0.3.

Scanning electron microscopy results clearly show that silica synthesized in ethanol–ammonia media with a molar ratio of CTAB/TEOS = 0.3 consists of homogeneous spherical particles with a diameter 0.5 μm (Figure 5a). Synthesis of mesoporous silica matrices with use of isopropanol with a molar CTAB/TEOS ratio of 0.3 yields silicas that consist of particles with less marked spherical granulation (Figure 5b).

TABLE 1. Adsorption-structural characteristics of silicas synthesized in alkaline media

N	CTAB/TEOS, molar ratio	Alcohol	Structure of pores	a_0, nm	d_p, nm (by BJH)	Surface area, m^2/g
1	0.1	Isopropanol	Disordered	–	3.4	166
2	0.2	Isopropanol	Disordered	–	3.0	505
3	0.3	Isopropanol	Disordered	–	3.1	458
4	0.1	Ethanol	Slightly ordered	5.2	3.0	701
5	0.2	Ethanol	Hexagonal ordered	4.0	2.7	1227
6	0.3	Ethanol	Hexagonal ordered	3.9	2.5	946

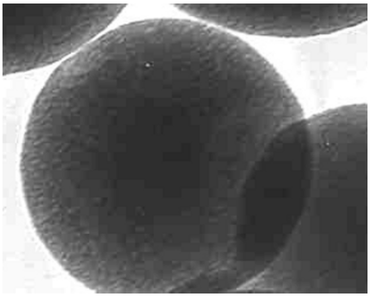
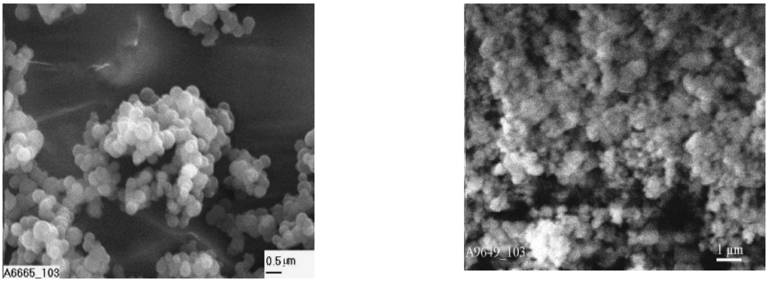


Figure 4. TEM-photo of MCM-41 synthesized in ethanol-ammonia media with a molar ratio of CTAB/TEOS = 0.3



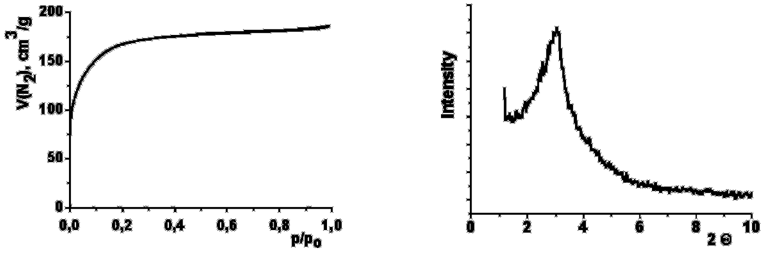
A B

Figure 5. SEM-photos of silicas synthesized in alcohol–ammonia media with molar ratios of CTAB/TEOS = 0.3 with use of ethanol (a) and isopropanol (b)

3.2. SYNTHESIS IN ACIDIC MEDIA

The nitrogen adsorption–desorption isotherm of silica synthesized in acidic condition (Figure 6a) is of type I isotherm according to the IUPAC classification and clearly shows no mesopores but the presence of micropores. Specific surface area of the synthesized silica calculated by the BET-equation was 600 m^2/g. X-ray diffraction results of obtained silica demonstrate one expressed peak at 2θ = 3°, which are characteristic for a weakly ordered pore structure (Figure 6b).

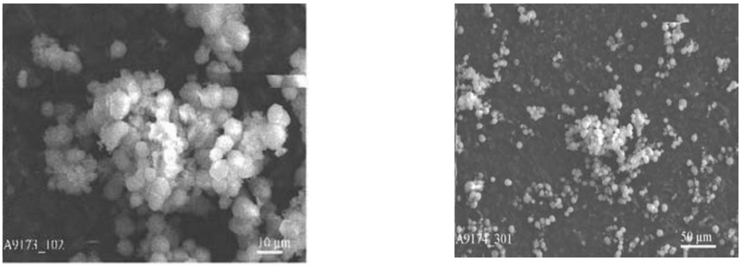
Mesophase formation of silicas synthesized under acidic conditions is possible due to the influence of halogen anions, which act as counterions arranged around the positive charged micellar aggregates and thereby electrostatically coordinate positively charged silicate oligomers. It can be assumed that such weaker bonding provides less ordered pore structure. In alkaline media, formation of an ordered pore structure is realized due to direct interactions between negatively charged silica macroanions and positively charged head micelles of CTAB.



A B

Figure 6. Nitrogen adsorption–desorption isotherm (a) and x-ray diffractogram (b) of silica synthesized under acidic conditions

The final particle size of silicas synthesized in acid and alkaline conditions depends on the rate of hydrolysis of the silica precursor and further condensation of silicate macroanions. In alkaline media the hydrolysis and condensation rate is rather high and uniform spherical particles of silica have been obtained after 2 h of stirring. The condensation rate of silicate species in acid media is slow and after growing for ten days under calm conditions (without stirring) silica spheres with larger size (10 µm.) were formed (Figure 7).



A B

Figure 7. SEM-micrographs of silica synthesized under acidic conditions

4. Conclusion

In alcohol–ammonia media, the mesoporous silicas with a pore diameter about 25–35 Å and a specific surface area of 450–1,200 m^2/g have been obtained. It was established that silicas with monodisperse spherical granulation of particles were formed using ethanol with molar ratios of CTAB/TEOS = 0.2 and 0.3. For many applications it is desirable to obtain spherical silica particles of a larger size. In acidic media, the uniform spherical particles of microporous silicas have been synthesized up to a size of 10 µm. Moreover they shown lower specific surface area (600 m^2/g) and weakly ordered pore structure.

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CHEMICAL MODIFICATION OF SILICA SURFACE BY IMMOBILIZATION OF AMINO GROUPS FOR SYNTHESIS OF SILVER NANOPARTICLES

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Abstract The particular features of the formation of silver nanoparticles on the surface of fumed silica aerosil A-300 type with grafted amino groups were studied. The conditions of the formation of silver nanoparticles and their structural and optical properties have been investigated.

Keywords: Silica; modified surface; amino groups; silver; in situ reduction

1. Introduction

Antibacterial properties of metallic silver and its compounds are known from time immemorial. In small concentrations, silver is safe for human cells but lethal for the majority of bacteria and viruses and hence widely used in disinfection of water and food in everyday life and in the infection control in medicine.[1–4] Nanoparticles of silver exhibit a high antibacterial effect due to their well-developed surface, which provides the maximum contact with the environment. Moreover, they are sufficiently small and capable of penetrating through cell membranes to affect intracellular processes from inside. Therefore elaboration of the new approaches of synthesis of silver nanoparticles is of great interest.

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

For the preparation of silver nanoparticles aerosil A-300 silica with grafting amino groups was used in this work. An elaborated approach allows the reduction of the complexes of metals immediately in a place of attaching of reducer NH_2 groups and, thus ensure immobilization of the formed nanoclusters.

2. Experimental

With the aim of grafting of amino groups fumed silica was modified with gamma-aminopropyltriethoxysilane (A-300-NH_2). Then the modified silicas was impregnated with silver nitrate solutions for 24 h at room temperature (sample A-300-Ag-20) and dried for 2 h in an oven at 120°C (sample A-300-Ag-150).

Presence of amino groups grafted to the silica surface was confirmed by FTIR spectroscopy data (NEXUS FT-IR). Nanoparticles of silver were identified by the transmission electron microscopy (JEM-1OOCXII). UV-Vis spectra of metal-containing composites were recorded on Carl Zeiss Jena spectrophotometer.

3. Results and Discussion

Silicas with amino groups in the grafted modifying layer were used for synthesis of noble metal nanoparticles. Chemisorption of gamma-aminopropyltriethoxysilane on silica surface is confirmed by appearance of 1,068 cm^{-1} band of ≡Si–O–Si≡ grouping forming in result of reaction between silanol and ethoxy groups. Furthermore 3,650 cm^{-1} band is appeared, which corresponds to weak hydrogen bond between grafted amino group and unreacted silanol groups of silica. Chemical interaction of gamma-aminopropyltriethoxysilane with silica surface can be realized with use of one or two ethoxy groups of silane molecule. Interaction of three ethoxy groups with silanol groups of silica is unlikely due to steric hindrances.

Interaction between modified silicas with silver nitrate solution (samples A-300-Ag) is accompanied by appearing of absorption band 1,382 cm^{-1} relating to symmetrical stretching vibrations of nitro groups causing by oxidation of amino groups during formation of silver nanoparticles. (Figure 1, curve 3).

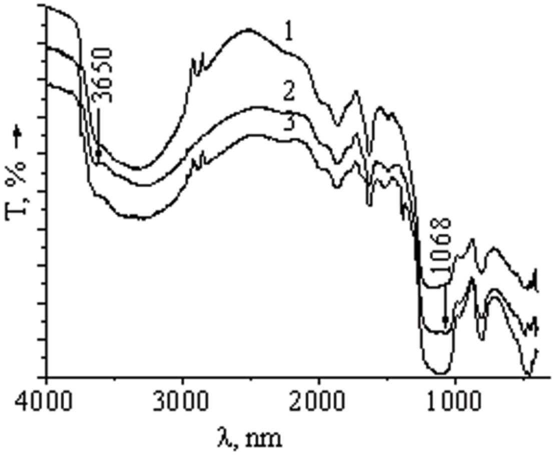

Figure 1. FTIR spectra of aerosil: (1) initial silica matrices, (2) silica with grafted NH_2 groups, (3) silica with reduced nanoparticles of silver

To detect the silver nanoparticles the silver-containing silicas were treated with potassium hydroxide solution for dissolution of silica matrices. Presence of surface plasmon band in UV-VIS spectra provides evidence for the occurrence of nanoparticles of silver in solution. Comparing of the spectra of silver-containing silicas reduced in room temperature (A-300-Ag-20) and calcined at 120°C (A-300-Ag-120) we could conclude that calcinations promote the formation of silver nanoparticles (Figure 2).

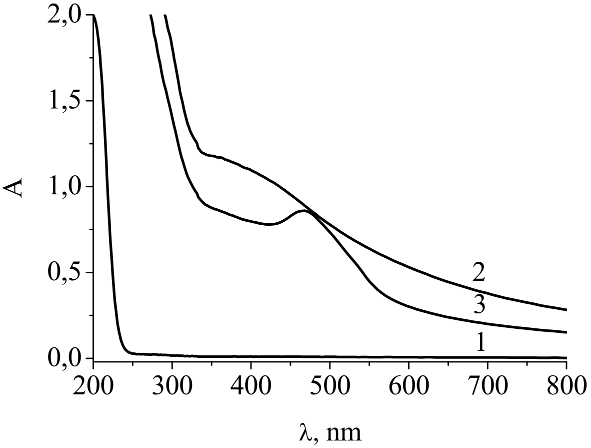

Figure 2. UV-VIS spectra of colloidal silver obtained after dissolution of the silica matrices modified with gamma-aminopropyltriethoxysilane A-300-NH2 (1) after interaction for 24 h with AgNO3 solutions (2) and calcinated for 2 h at 120°C (3)

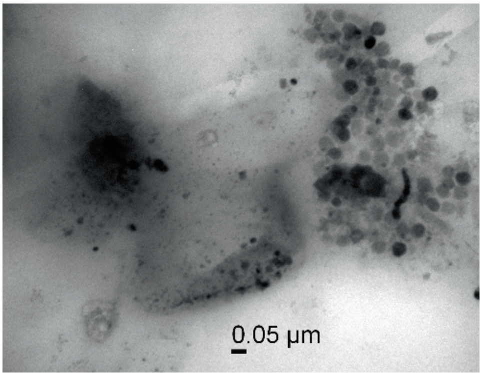

Figure 3. TEM images of the silver-containing silicas before dissolution

Formation of silver nanoparticles is confirmed by TEM data (Figure 3).

It is possible to regulate the sizes of the metal particles by varying the concentration of the silver nitrate solution. The formation of nanoparticles with smaller sizes is accompanied by visible changes of the color of the metal-containing composites in UV-VIS spectra. A blue shift of the surface plasmon band (Figure 4) is observed as a result of the gradual decrease of the concentration of $AgNO_3$ from 11.25 to 1.25 mmol.

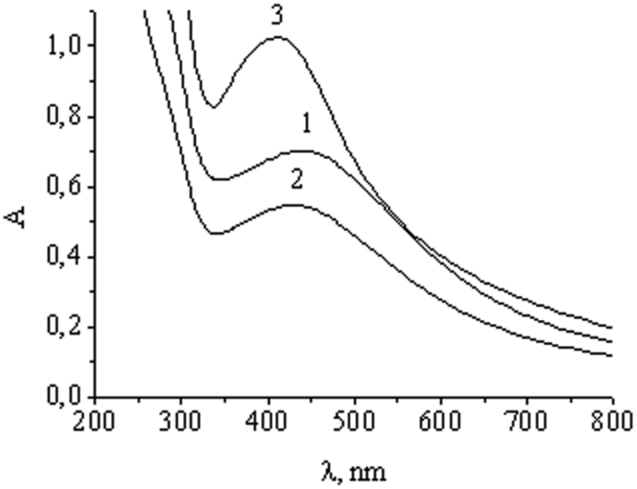

Figure 4. UV-VIS spectra of colloid silver obtained after dissolution of the silica matrices modified with gamma-aminopropyltriethoxysilane after interaction for 24 h with AgNO3 solutions with concentrations of (1) 11.25 mmol/L, (2) 3.75 mmol/L, (3) 1.25 mmol/L

4. Summary

Method of synthesis of silver-containing silicas was presented. It is possible to control the sizes of the metal particles by varying the concentration of the metal salt taken for the reduction, and the temperature of calcination.

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REMOVAL OF NICKEL BY NATURAL AND MAGNETICALLY MODIFIED BENTONITE

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Abstract Bentonite with its unique structural properties is a valuable material for environmental application. Its sorption properties are usually improved by different ways of modification. In this work, the modification by iron oxide particles was used with the aim to prepare a magnetic sorbent with enhanced sorption properties. The removal of nickel from aqueous solutions by the natural and magnetically modified bentonite was studied in batch adsorption-equilibrium experiments. The initial concentration of nickel in model solution was in the range 5–1,000 mg/L. Sorption experiments were carried out at pH 5.5, the sorbent concentration of 2 g/L and at the ambient temperature (25°C). The quantity of element in model solution was determined after the equilibrium time of 24 h by the atomic absorption spectroscopy (AAS). The experimental data were fitted with Langmuir, Freundlich and Redlich–Peterson isotherms. The sorption capacities of the natural and modified bentonite were compared.

Keywords: Bentonite; modified bentonite; adsorption; adsorption isotherm

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

1. Introduction

Some naturally occurring clay minerals may serve as cost-effective sorbents for the removal of heavy metals. While their sorption capacity is usually less than those of synthetic sorbents, these materials could provide an inexpensive substitute for the treatment of heavy metal waste waters. To enhance the sorption capacity, the clays are modified in various ways.[1]

Magnetic nanoparticles and their composites are suitable in water treatment for the coagulation of sewage or for the complete elimination of contaminants from drinking water sources such as heavy metals[2] and can be subsequently removed from the medium by a simple magnetic process.[3]

In this work the bentonite/iron oxide composite was prepared and its sorption capacity of nickel in comparison to natural and treated bentonite was studied.

2. Experimental

2.1. MATERIALS AND CHEMICALS

The natural bentonite originated from the locality Jelšový potok was treated by sedimentation method to obtain monomineral fraction of montmorillonite with the particle size below 20 μm. The treated bentonite was modified by iron oxide particles by the method of coprecipitation from the solution of ferric and ferrous salts. The bentonite/iron oxide weight ratio was 3:1 and the temperature of the synthesis was 85°C. Inorganic chemicals were supplied as analytical reagents and deionized water was used. Solution of nickel was prepared by using nitrate salt, $Ni(NO_3)_2.6H_2O$.

2.2. METHODS

Powder x-ray diffraction (XRD) patterns were collected using a Philips PW1820. The JCPDS PDF database was used for the phase identification. Mössbauer spectroscopy measurements were carried out with a ^{57}Co/Rh γ-ray source at room temperature. The velocity scale was calibrated relative to ^{57}Fe in Rh. Recoil spectral analysis software was used for the quantitative evaluation of the Mössbauer spectra.

The sorption of nickel from model aqueous solutions by the natural, treated and magnetically modified bentonite was carried out using batch-type equilibrium experiments in a rotary shaker for 24 h at constant ambient temperature (25°C). Sorption experiments were realized at pH = 5.5 and the initial total metal ion concentration range was 1–1,000 mg/L and sorbent concentration was 2 g/L. The quantity of elements in solution has been determined both before the introduction of sorbent and after the equilibrium time of 24 h by atomic absorption spectroscopy (AAS using a Varian 240 RS/2402). Sorption isotherms have been fitted with Langmuir, Freundlich and Redlich–Peterson equation.[4]

3. Results and Discussions

3.1. XRD ANALYSIS AND MÖSSBAUER SPECTRUM OF TREATED SAMPLES

The XRD analysis of the treated bentonite showed the presence of montmorillonite phase (Figure 1). The diffractions of iron oxide were observed in composite sample C85. It was difficult to differentiate between magnetite and maghemite phase because of strongly overlapping of diffractions. Therefore the Mössbauer spectroscopy was used to characterize the iron oxide in composite.

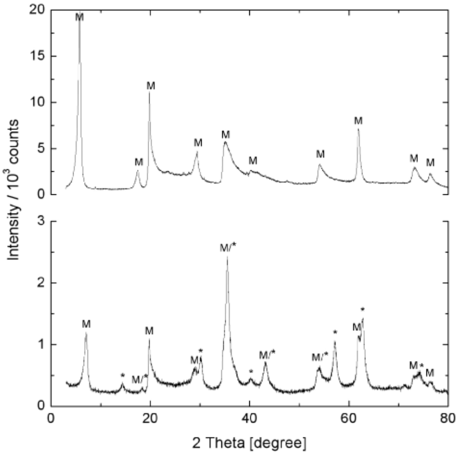
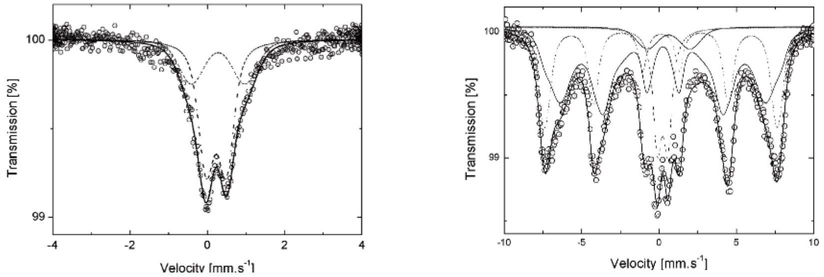


Figure 1. XRD pattern of treated bentonite and composite C85 (M – montmorillonite, * – iron oxide)

The Mössbauer spectrum of the treated bentonite consists of two spectral components with hyperfine parameters: isomer shifts $IS_1 = 0.28$ mm/s, $IS_2 = 0.23$ mm/s; quadrupole splittings $QS_1 = 1.39$ mm/s, $QS_2 = 0.52$ mm/s; relative intensities $I_1 = 33.7$ %, $I_2 = 66.3$ % (Figure 2a). It can be stated that iron cations in the natural bentonite are trivalent. The bentonite/iron oxide composite spectrum is complex consisting of the paramagnetic doublet and one sextet. Fitted parameters for C85 sample (Figure 2b), indicate the Fe^{3+}

in maghemite (RA = 81.4 %; average hyperfine magnetic field, $B^{\mathrm{Oct}} = 38.5$ T, IS = 0.25 mm/s, RA = 50.9 %, $B_{\mathrm{hf}}^{\mathrm{Tet}} = 46.6$ T, IS = 0.13 mm/s, RA = 30.5 %) and two paramagnetic positions of Fe^{3+} in bentonite. Only the presence of γ-Fe_2O_3 phase was confirmed in composite.



(a) (b)

Figure 2. Fitted Mössbauer spectrum of (a) treated bentonite; (b) composite sample

3.2. ADSORPTION ISOTHERMS

The adsorption of Ni^{2+} onto different sorbents as a function of its concentration was studied at 25°C by varying the metal concentration from 1 to 1,000 mg/L while keeping all other parameters constant. The adsorption isotherms, which are the most suitable to fitting the adsorption processes on sorbents are shown on Figure 3. The isotherm analyses

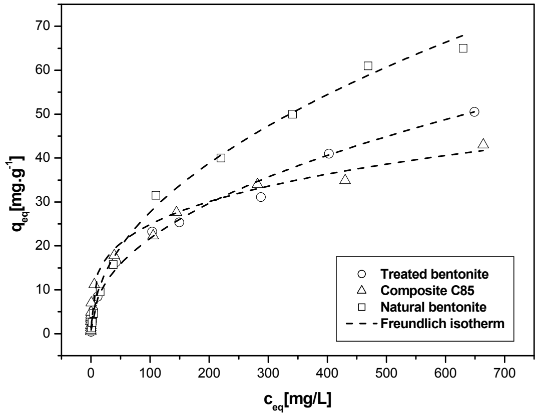


Figure 3. Adsorption isotherms of Ni^{2+} on natural bentonite, treated and composite C85

showed different adsorption behaviour for Ni^{2+}. Figure 3 presents that the sorption capacity of sorbents was not expended even by the highest initial concentration of metal ion in solution, adsorption still shows an increasing trend at higher equilibrium concentrations.

Figure 4 shows adsorption capacity on selected sorbents in low concentration range. Best sorption capacity in low range of concentrations which is characteristic for environmental weight, was obtained in the following order: composite C85 > treated bentonite > natural bentonite.

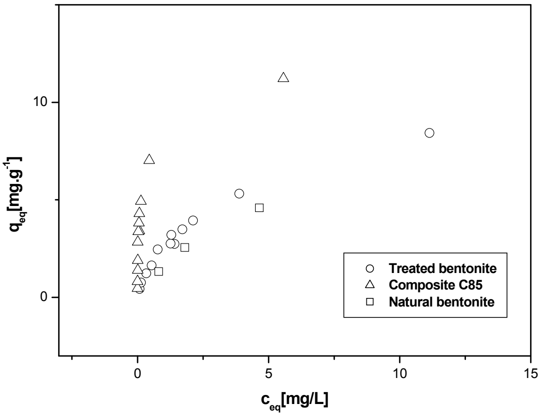


Figure 4. Adsorption of Ni^{2+} in low range of concentrations

4. Conclusion

The present study showed that the composite C85 and treated bentonite were effective in removing Ni^{2+} ions from aqueous solutions compared to the commercial bentonite from the locality Jelšový potok. The results showed that the composite C85 was the most effective in adsorption process. It showed that the selectivity sequence of metal ions by the adsorbents was dependent on the system employed, and was mainly dependent on the initial concentrations of the metal ions in the solution.

Acknowledgements The authors are thankful for financial support of VEGA grant G-6189 and APVV grant 0728-07 and APVV-51-035505.

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EFFECT OF MAGNETIC MODIFICATION ON THE SORPTION PROPERTIES OF NATURAL BENTONITE

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Abstract Bentonite, due to its physical and chemical properties, is considered to be one of the most promising candidates for decontamination and disposal of high-level heavy metal wastes. Magnetic particles and their composites are also extremely suitable in water treatment. Therefore, the possibility to enhance the sorption properties of natural clay rock bentonite by its magnetic modification was investigated. The bentonite/iron oxide composites were prepared in different weight ratios at two selected temperatures 20°C and 85°C. The surface and pore changes of natural bentonite after magnetic modification was studied by nitrogen adsorption measurements. It was found that the composite prepared in weight ratio 1:1 of bentonite/iron oxide at 85°C, denoted as A85, showed the highest increase in total pore volume (0.216 cm^3/g) and the specific surface area from the value 39.4 m^2/g of the natural bentonite to 82.8 m^2/g of A85. The natural bentonite and composite materials were characterized by powder x-ray diffraction (XRD) analysis in order to quantify the structural changes. The magnetic properties were measured by superconducting quantum interference (SQUID) magnetometer and the morphology of the investigated samples was observed by scanning electron microscopy (SEM). The natural bentonite and composites A85 and E20 were chosen to study the sorption of cadmium from model solutions.

Keywords: Bentonite; iron oxide; composite; structural properties; adsorption

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

1. Introduction

Large specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity have made the clays excellent adsorbent materials. Use of natural bentonite in treating aqueous waste containing heavy metals and organic matter has been previously reported in many works.[1,2] If the physical and chemical properties of natural bentonites are improved by a special modification process the adequate supplies for environmental purposes can be obtained.[3]

There is a great interest in the decontamination by various iron-based sorbents. Uptake of arsenate by an alginate-encapsulated magnetic sorbent was studied by Lim et al.[4] Based on the surface morphology study, the microstructure and the element constitution of the sorbent, as well as the binding characteristics between arsenate and magnetic sorbent, a conceptual model for the adsorption of arsenate was proposed to illustrate the mechanism. Peng et al.[5] prepared montmorillonite-Cu(II)/Fe(III) oxides magnetic material and studied its efficiency in the removal process of humic acid from water. Thermal regeneration of magnetic sorbent after adsorption process showed enhancement of saturation magnetization and good adsorption capacity as the as-prepared sorbent. Removal of contaminants from water by clay–iron oxide magnetic composites was also described by Oliveira et al.[6] The adsorption isotherms of metal ions Ni^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} from aqueous solutions onto the composites also showed that the presence of iron oxide cause the increase of the adsorption capacity of the bentonite.

In this work the natural bentonite was modified by the magnetic particles and its sorption affinity to cadmium was studied.

2. Experimental

2.1. MATERIALS

The natural bentonite originated from the locality Jelšový potok, was treated by the special sedimentation method to obtain particle size below 20 µm.[7] The composite materials were prepared from the solutions of ferric and ferrous salts, where bentonite was added before the iron oxide precipitation. The bentonite dosage was adjusted in order to obtain different bentonite/iron oxide weight ratios 1:1, 5:1 denoted as A, E, respectively. The modification process was realized at two selected temperatures 20°C and 85°C.

2.2. METHODS

The nitrogen adsorption experiments were realized with Micrometrics ASAP 2400 apparatus. Powder x-ray diffraction (XRD) patterns were collected using a Philips PW1820. The JCPDS PDF database was used for the phase identification. The value of magnetization of the samples was determined by the superconducting quantum interference device (SQUID) magnetometer measurement (in Germany) at the maximum field of 50 kOe. The scanning electron microscopy (SEM) analyses were made in JEOL JSM-6400.

The sorption of cadmium from model aqueous solutions by the natural and magnetically modified bentonite was carried out using batch-type equilibrium experiments in a rotary shaker for 24 h at constant ambient temperature. Sorption experiments were realized at pH = 5, the initial total metal ion concentration range was 1–50 mg/L and sorbent concentration was 1 g/L. The final metal concentration was determined by atomic absorption spectroscopy (AAS using a Varian 240 RS/2402 and the metal uptake was calculated. Sorption isotherms have been fitted with Langmuir equation.

3. Results

The values of BET surface area values of external surface and pore volume are included in Table 1. The higher values of the specific surface area of the composites and increasing values of total pore volume should be explained by the secondary pore structure formation on the bentonite surface during the iron oxide precipitation.

TABLE 1. Structural parameters of the samples

Sample	S_{BET} [m^2/g]	V_a (cm^3/g)	V_{micro} (cm^3/g)	S_t (m^2/g)
Bentonite	39.4	0.096	0.005	27.6
A20	73.7	0.216	0.004	64.2
E20	90.7	0.187	0.002	83.9
A85	82.8	0.251	0.004	73.7
E85	84.8	0.183	0.003	77.5

S_{BET} – specific surface area, V_a – pore volume, V_{micro} – volume of micropores, S_t – external surface area

The XRD analysis of the composites confirmed the presence of montmorillonite and Fe oxidized phase belong to maghemite. Except of it, goethite in the samples synthesized at 20°C was observed too (Figure 1).

The value of magnetization of the composites increases in dependence on the increasing maghemite content in the samples. The highest value was measured for the composite A85 (46.22 emu/g) and the lowest value was obtained for the composite E20 (6.85 emu/g). The magnetization of the composites prepared at 20°C was lower than for composites prepared at 85°C that should be caused by the goethite presence in their structure.

Figure 2 shows the morphology of the sample A85 observed by SEM in Compo mode. The white spots belong to maghemite particles creating agglomerates on the bentonite surface.

The sorption experiments of cadmium were realized on the natural bentonite and composite materials. From all obtained results of previous studies two samples were interesting from the sorption point of view. A85 showed the highest value of pore volume and magnetization, E20 had the largest specific surface area. Therefore both were chosen for the sorption experiment. The pH dependence of sorption capacity, as well as the stability of iron oxide in composite sample E20 was studied in the range 2–9. The composite material was stable in solutions with pH = 4 and higher. At lower value of pH, the iron was loosened in to the solution.

The effect of metal ion concentration on cadmium adsorption was investigated over the concentration range 1–50 mg/L at room temperature. The obtained sorption isotherms are shown in the Figure 3a.

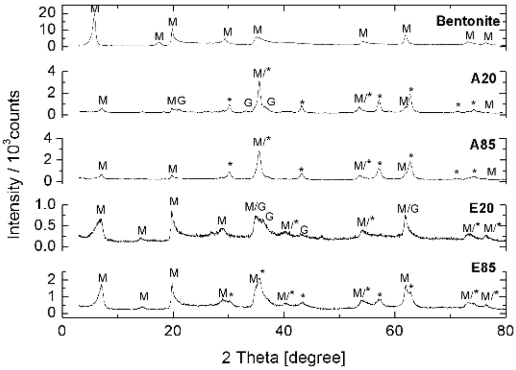

Figure 1. XRD pattern of the investigated samples (M – montmorillonite, G – goethite, * – maghemite)

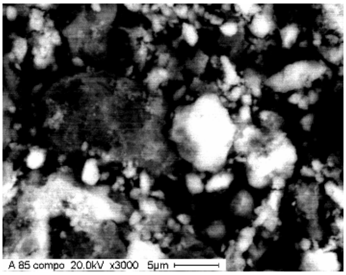

Figure 2. Image of A85 composite observed by SEM in Compo mode

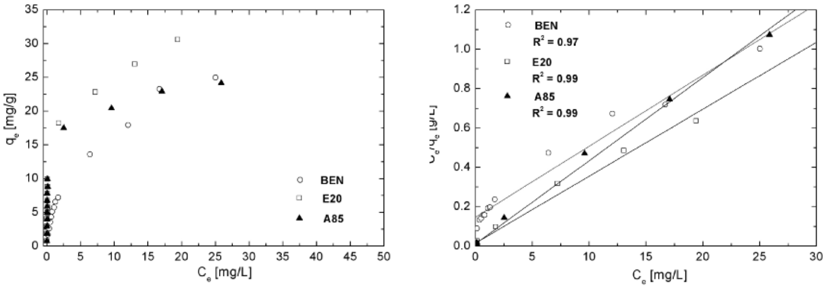

Figure 3. Sorption isotherms (a) and linearized form of Langmuir sorption isotherms (b) of Cd^{2+} ions by the natural bentonite and composites samples

It can be observed that the instantaneous adsorption capacity increases with metal concentration. The sorption capacity of bentonite and composite sample E20 was not reached in the chosen initial metal ion concentration range. In spite of that, linearized Langmuir model, Figure 3b, was more convenient for fitting the experimental data of sorption than Freundlich model, the values of correlations coefficients obtained from the linearized Freundlich isotherms were worse. The maximum sorption capacity of bentonite, A85 and E20 calculated from the slope of the plot was 27.7 mg Cd/g, 23.7 mg Cd/g and 29.4 mg Cd/g, respectively. Comparing the efficiency of the natural and modified bentonite towards cadmium cations it seems that in low range of metal concentration, the composite materials could be more convenient for sorption from solutions or waste waters.

4. Conclusion

The natural bentonite was modified by iron oxide particles and its improved properties were studied. The BET surface area of the composite materials was twice higher in comparison to the natural bentonite. The total pore volume had the increasing tendency in dependance on the content of iron oxide in the composite materials because of textural porosity created between the iron oxide particles.

The composites exhibited the magnetic properties, which were confirmed by the magnetization measurements. Maghemite particles observed by SEM were nonhomogenously distributed on the bentonite surface, creating agglomerates.

The experimental data of sorption on E20 and A85 were fitted by the Langmuir type model. The composite sample E20 showed higher adsorption capacity of Cd^{2+} over investigated concentration range comparing to the natural bentonite. The composite sample A85 had higher sorption capacity of Cd^{2+} in low range of concentration 1–30 mg/L.

It follows from these results that magnetically modified bentonite seems to be a suitable sorbent, especially in the solutions with lower concentration of heavy metals and its magnetic properties could be used for its easy separation and recovery.

Acknowledgements The authors are thankful for financial support of VEGA grant G-6189 and APVV grant 0728-07.

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NEW CHEMICAL SENSORS FOR FAST AND RELIABLE ANALYTICAL CONTROL OF Sn^{2+} AND Pb^{2+} IONS IN WATER AND WASTE WATER

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Abstract Chemical sensors selective to Pb^{2+} and Sn^{2+} ions were developed on the base of chalcogenide glasses (ChG) from the $GeSe_2$-PbSe-PbTe and $GeSe_2$-Sb_2Se_3-SnSe systems. All-solid-state sensors of the 'coated wire' type were designed consisting of inner Ag/AgCl reference electrode uniformly coated with composite mixture of binding polymer and Pb- and Sn- ChG powder. Pb(II)- and Sn(II)-sensors were tested in aqua solutions with respect to their basic analytical characteristics: stability, linearity and slope of the calibration function, working pH-range, limits of detection, response time and selectivity. The proposed sensors guarantee reliable analytical performance for water and waste water control with detection limits of the order of 10^{-6} mol/L, selectivity and chemical stability in aggressive media.

Keywords: Chemical sensors; heavy metals; ion-selective potentiometry; water control

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

1. Introduction

Recently, the problems arising from the environmental contamination with heavy metals and the increased necessity for ecological and health risk assessment and pollution prevention require new opportunities for extremely fast, reliable and economy control. Potentiometric chemical sensors give possibilities for rapid detection, but the main restrictions for their wide practical application originate from the insufficient chemical durability and selectivity.

Chalcogenide glasses (ChG) are advanced membrane materials for chemical sensors, microsensors and multisensor systems for water solution measurements, because of their better chemical durability in acidic and redox media, better selectivity and reproducibility of the analytical characteristics, and longer time of life as compared with liquid and polycrystalline membranes.[1,2]

Multicomponent glasses on the base of $GeSe_2$-glass-former, containing heavy metal chalcogens have attracted our interest as promising membrane materials for chemical sensor devices.[3,4]

2. Experimental

ChG bulk glasses from the $(GeSe_2)_x(PbSe)_y(PbTe)_z$ and $(GeSe_2)_x(Sb_2Se_3)_y(SnSe)_z$ systems, where $x + y + z = 100$ mol%, were synthesized by a conventional melt-quenching technique. The glass-formation in the pseudo-ternary $GeSe_2$-PbSe-PbTe and $GeSe_2$-Sb_2Se_3-SnSe systems, as well as the main physicochemical properties of the glasses have been studied preliminarily. The compositions selected as membrane materials are given in Table 1.

The all-solid-state Pb(II) and Sn(II) selective sensors of the "coated wire" type were constructed as homogeneous mixture of a binding polymer and 2 mass% ChG powder (with a particle size up to 63 μm) was coated onto Ag/AgCl electrodes. This constructional design ensures reliable electric contact between the membrane and the inner reference electrode, as well as eliminates the drawbacks arising from the insufficient mechanical durability of the ChGs.

The electrode functions and the basic analytical characteristics of the Pb(II) and Sn(II) potentiometric sensors were measured using the following standard electrochemical cell (Figure 1).

Hg, Hg_2Cl_2	KCl (saturated)	Measured solution	Ion-selective composite membrane	Ag, AgCl

Figure 1. Scheme of standard electrochemical cell

The tested sensors were calibrated in standard solutions in the concentration range 10^{-6}–10^{-1} mol/L $Pb(NO_3)_2$ and $SnCl_2$, respectively. The potential of the electrochemical cell was measured in sequence of progressively increasing concentrations under constant magnetic stirring (200 rev/min).

Before each series of measurements, conditioning of Pb(II) and Sn(II) sensors was carried out in 10^{-3} mol/L solution of the potential determining ion for stabilization of the electrode functions.

3. Results and Discussions

Analytical performance of the suggested potentiometric sensors was evaluated by the following analytical characteristics: slope (S, mV/dec) and linear range (L, mol/L) of the electrode functions, limits of detection (LD, mol/L), response time (τ_{95}, s), working pH-range and cross-sensitivity (selectivity coefficients).

The best results obtained for the analytical characteristics of the Pb(II) and Sn(II) potentiometric sensors based on multicomponent ChG are summarized in Table 1.

TABLE 1. Membrane compositions and analytical characteristics of the Pb(II)- and Sn(II)-sensors

		Membrane composition, mol %			Analytical characteristics		
Pb(II)-sensors	Labels	$(GeSe_2)_x(PbSe)_y(PbTe)_z$			L, mol/L	S, mV/dec	LD, mol/L
		x	y	z			
	I	56	24	20	10^{-5}÷10^{-1}	25.8	5.2×10^{-6}
	II	54	6	40	10^{-5}÷10^{-1}	19.0	3.5×10^{-6}
Sn(II)-sensors		$(GeSe_2)_x(Sb_2Se_3)_y(SnSe)_z$			L, mol/L	S, mV/dec	LD, mol/L
		x	y	z			
	I	54	36	10	10^{-5}÷10^{-1}	56.5	2.79×10^{-6}
	II	36	24	40	10^{-5}÷10^{-1}	56.0	2.88×10^{-6}

The measured calibration curves are characterized with a slope closed to the theoretical Nernstian values for one-valence (S_{theor} ~59 mV/dec) and two-valence (S_{theor} ~29.5 mV/dec) anions for the Sn(II) and Pb(II) sensors, respectively.

Working pH range for the tested sensors was established in the regions $1 < pH \leq 3$. All of the investigated devices work reliably in strong acidic media with pH = 1.5–2.5 without distortion of the selective membranes. At pH > 3 sedimentation of $Pb(OH)_2$ and $Sn(OH)_2$ takes part into the solution.

Response time (τ_{95}), which is the time for the establishment of the equilibrium potential, was measured of the order of 5–20 s depending on the concentration of the potential determining ions in the analyzed solution.

The cross-sensitivity of the suggested sensors was investigated in the presence of ions, which commonly accompany Pb^{2+} and Sn^{2+} ions in the analytical media.

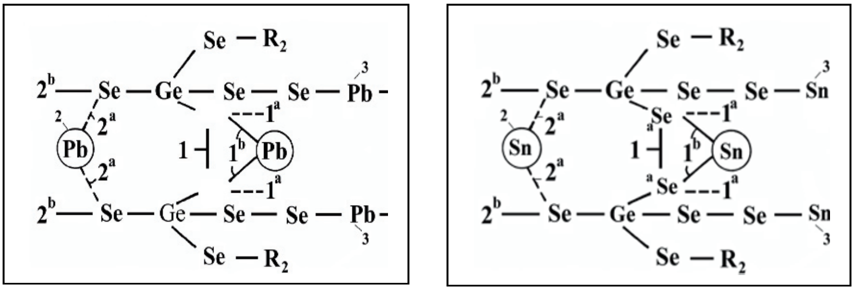
The obtained values for the selectivity coefficients ($K^{pot}_{i,j}$) are summarized in Table 2.

The general concepts for the potential-generating mechanisms at the chemical sensors with ChG membranes are based on the model for the formation of modified active layer on the membrane surface (MSL).[5] The ion exchange on the MSL/analyzed solution interface takes place on different schemes depending on the ChG membrane composition.[1] Taking into account our observations on the peculiarities in the analytical performance of selective to heavy metal ions chemical sensors with multicomponent ChG membranes, we have considered that the ion-exchange between the membrane and the measured solution, i.e. $Me(II)_{solution} \leftrightarrow Me(II)_{glass}$, where Me = Pb, Sn, takes part in Me-containing charged defect centers, which exist in the structural glassy networks.

TABLE 2. Selectivity coefficients of Sn(II) and Pb(II) sensors at concentration of the interfering ions 10^{-3} mol/L

Sample	Selectivity coefficients, $K^{pot}_{i,j}$					
	Pb^{2+}	Ni^{2+}	Zn^{2+}	Cd^{2+}	Cu^{2+}	Al^{3+}
Sn(II)-I	2.5×10^{-2}	4.0×10^{-2}	3.2×10^{-2}	4.0×10^{-2}	6.3×10^{-2}	3.2×10^{-3}
Sn(II)-II	2.0×10^{-2}	3.2×10^{-2}	2.0×10^{-2}	2.0×10^{-2}	1.6×10^{-2}	2.5×10^{-3}
Pb(II)-I	–	–	1.0×10^{-7}	7.9×10^{-7}	5.0×10^{-7}	6.6×10^{-6}
Pb(II)-II	–	–	5.6×10^{-7}	4.9×10^{-7}	35×10^{-6}	2.8×10^{-6}

The structure of such defect centers for the glasses from both investigated systems are illustrated in Figure 2 a, b.



a) b)

Figure 2. Structure of negatively charged defect centers in the ChGs form the: (a) $GeSe_2$-PbSe-PbTe and (b) $GeSe_2$-Sb_2Se_3-SnSe systems

For the as-prepared ChG membranes, the exchange process takes place between the metal atoms from position 3 (Figure 2) and the potential determining ions in the measured solution. After conditioning, the permanent working regime of the sensors is ensured by the continuous repeating of the consecutive occupation and liberation of the active positions 1 and 2 in the defect centers from the Pb^{2+} and Sn^{2+} ions from the solution. This ion-exchange process is accomplished by the bond break between the bridged Se atoms in positions 1 and 2, forming (1^a and 2^b) and connecting (1^b and 2^a) unsaturated bonds.

This model of potential generating mechanism explains some common peculiarities observed in the analytical behavior of potentiometric sensors based on multicomponent ChGs with $GeSe_2$-glass-former and reversible to heavy metal ions, concerning anion slope of the calibration functions and the changes in the slope values after the membrane conditioning.

4. Conclusion

All-solid state chemical sensors of ‘coated wire’ type selective to Pb^{2+} and Sn^{2+} ions were designed on the base of multicomponent chalcogenide glasses from the $GeSe_2$-PbSe-PbTe and $GeSe_2$-Sb_2Se_3-SnSe systems. The suggested sensors are characterized with reliable analytical performance and allow controlling concentration levels of the order of 10^{-6} mol/L of the potential-determining ions in complex water solutions. The sensors preserve excellent characteristics in strong aggressive media.

Acknowledgements The authors are grateful to the Technical University of Sofia for the financial support by a grant 08048si-2 and NATO support under CBP.EAP.RIG 981850.

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EXPRESS UV-PHOTOMETRY METHOD FOR DETERMINATION OF THE OIL-COMPOUNDS CONTENT IN WATER

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Abstract A new UV-photometry method is proposed for express determination of the oil-products content in water. It does not require long samples preparation and expensive lab equipment but still ensures accurate determination of the dissolved oil-products content. The method is based on the characteristic pattern of the oil-product–water spectra and the peak wavelength. We suppose that the oil-product–water solution has spectrum that corresponds to the spectrum of 1,3,5-trimethylbenzene. A calibration equation connecting optical density of the oil-product–water solution and its concentration has been proposed.

Keywords: Oil-products; water contamination; UV-photometry; express analytical method

1. Introduction

Oil-products are very dangerous and toxic pollutants of water. Annual world discharge of oil-products reaches 1.5–2.5 million tons.[1] They contaminate river, sea and ocean water and come from various industrial wastewater discharges, tanker ballast waters exchange and other anthropogenic sources.[2] Accurate assessment of negative effect of the oil-products contamination is impossible without reliable and accurate methods of analytical determination of the oil-products concentration. There are many known analytical methods but they require long and complicated sample preparation (like

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

infrared photometry or fluorescence methods) and/or some expensive and rather large lab equipment, which can be used only in a stationary laboratory (like gas or gas–liquid chromatography).[3–5]

Here we propose an express method for analytical determination of the oil-products content in water. It requires quite simple lab equipment and does not involve extensive samples preparation operations.

2. Oil–Water Mixtures: Solubility, Composition and Spectrophotometry Investigation

Most of oil products and water are slightly soluble in each other. Gasoline, oils, grease and diesel fuel form thin film that spread on the water surface. However, there are some classes of relatively well-dissoluble compounds (phenols, alcohols) in the oil products.[3,6] These compounds can dissolve in water and influence deep-water ecosystems as well as surface ones.

It is known that most phenols actively absorb UV-light.[7] This fact can be used for the UV-spectrophotometry determination of their concentration in water. UV spectra of the diluted water–gasoline mixtures were registered in order to check this assumption. Solutions of 95 gasoline in water with concentration ranging from 0.03 to 0.35 g/L were made. All the spectra were recorded immediately after preparation of the solutions using a standard SF-26 spectrophotometer. Typical UV spectrum of the gasoline-water system can be seen in Figure 1.

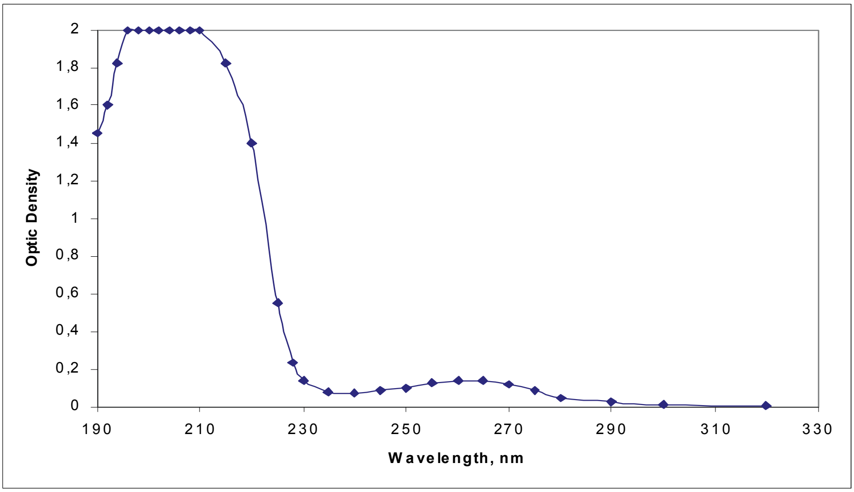

Figure 1. UV spectrum of the gasoline–water system

One can see a band of very intense light absorption located at a wavelength of 230 nm and further to the shorter-wave part. Another absorption band is located between 240 and 280 nm. The first band was found to be very intense and almost independent from the gasoline concentration (non-analytic absorption peak). Intensity of the light absorption within the second band was found to be dependent on the gasoline concentration (analytic absorption peak). This absorption band is enlarged in Figure 2.

It is seen that the maximum light absorption is registered at a wavelength of 260 nm. This peak can be used to build a calibrating diagram connecting the optical density of a solution (D) and concentration of gasoline (c). This dependence was found to be linear and the corresponding calibrating equation is $D = 0.315 \cdot c + 0.0112$. It fits experimental values with the a correlation coefficient of 0.97 or higher along all above mentioned range of the gasoline concentrations, and thus it can be used for the UV-spectrophotometry determination of the gasoline content in water.

Then the water-gasoline spectrum pattern was compared to typical spectra of various aromatic phenols. We found a spectrum, which pattern appeared very similar to our experimental spectra. It was the spectrum of 1,3,5-trimethylbenzene (see Figure 3).

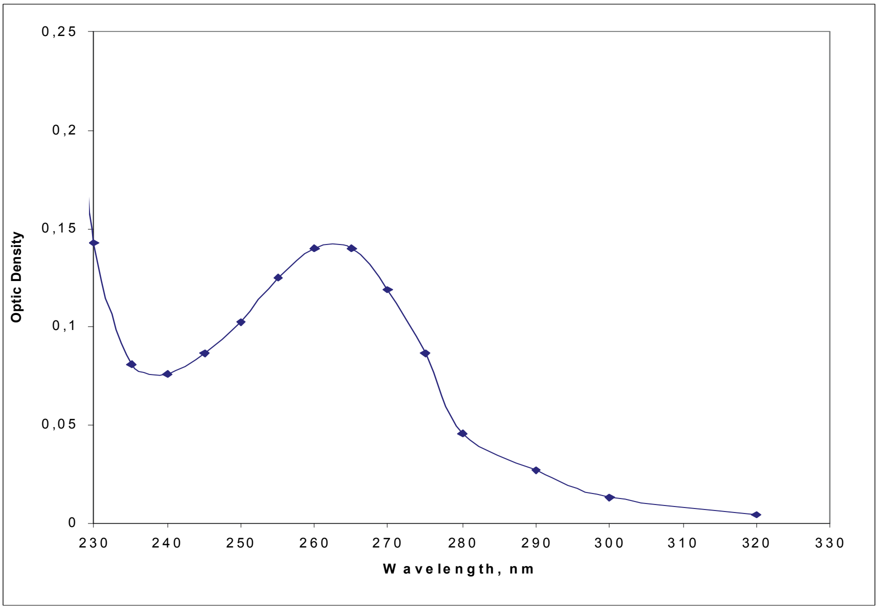

Figure 2. Part of the gasoline-water UV spectrum with the analytical adsorption peak found

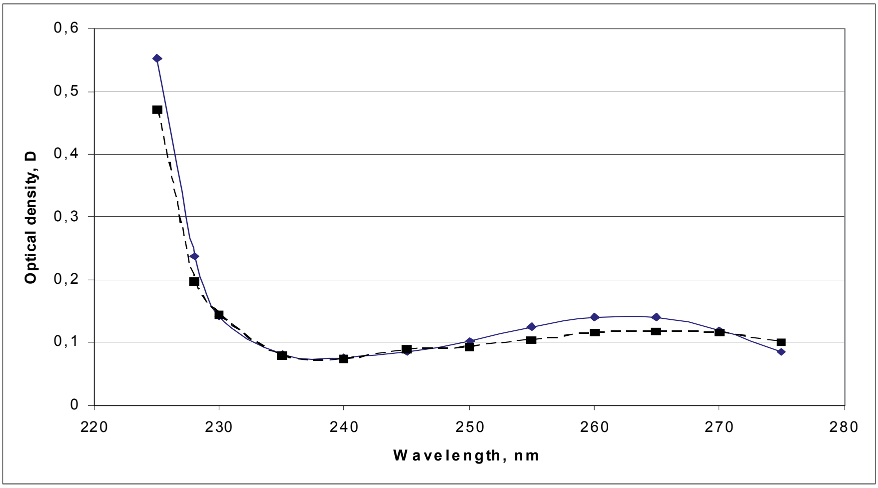

Figure 3. UV spectra of the gasoline-water solution (solid line) and 1,3,5-trimethylbenzene (broken line).[7]

Therefore, we suppose that 1,3,5-trimethylbenzene is a close homolog of well-dissolved gasoline compounds, forming the same pattern of the analytical absorption peak of the water-gasoline mixtures. It is also known that aromatic compounds determine higher octane number of the high performance motor fuel and in fact they are present in the high-octane gasoline.

3. Conclusion

The above mentioned original UV-spectrophotometry method can be recommended for the test determination in order to investigate its reliability in analytical determination of the oil contamination of water. It is more simple and less expensive comparing to other analytical methods. However, its usage is limited by high-octane motor fuels containing 1,3,5-trimethylbenzene or its homologs. These compounds are in fact registered through the 260 nm UV light absorption.

Another investigation is required in order to find the characteristic light absorption peaks for other types of the motor fuel (e.g. diesel) or other oil contamination agents (grease, raw oil, etc.). Then this analytical method can be expanded to wider range of the water pollutants.

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OPTIMAL SYNTHESIS OF SYSTEM FOR THERMAL TREATMENT OF CHLORINE WATER

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Abstract In the design and operation of energy intensive systems the problem of improving its efficiency is very important. The main way for solving this problem is optimization. This paper describes a general approach for the thermoeconomical optimization systems with a linear structure. The suggested method is based on building and analysing special graphs of thermoeconomical expenditure. The method is illustrated by an example concerning the system optimization for thermal treatment of chlorine water.

Keywords: Optimization; linear systems; graphs; thermoeconomic; chlorine water

1. Introduction

Processes that take place in complex energy intensive systems are characterized by the mutual transformation of quantitatively different power resources. The fast growth and development of modern technologies requires a thermodynamic analysis and optimization of such systems, based on the application of the laws of thermodynamics, and it is best done an exergy approach.[1,2] Exergetic methods have an universal nature, and allow the estimation of the energy fluxes and the development of energy balances

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

for every element of the system using a common criterion of efficiency. Therefore, they are meaningful both in analysis of the system and calculations made on it.

Despite its usefulness, the benefits of the exergetic approach were not fully realized until recent years. One reason for this situation is the sub-estimation of the power of using exergetic functions for mathematical modeling, synthesis, and optimization of flow sheets. Another reason is the mathematical difficulty of the exergetic approach in thermodynamic analysis. Moreover, the increasing complexity of optimization problems requires more effective and powerful mathematical methods. Hence, during the last years, many papers with different applications of exergetic methods have been published.[3–7]

The above referenced papers, as well as the author's earlier investigations[8–13] show that one of the most effective mathematical methods used for exergetic analysis and optimization is graph theory.[14–15] The benefit of graph models can also be demonstrated by its flexibility and its wide variety of possible applications.

Possible exergy topological methods include the sole use or combination of exergy flow graphs, exergy loss graphs, and thermoeconomical graphs.[3–7]

Systems with linear structure are often used in energy technology as well as in other branches of industry. For that reason it is necessary to study the problem of linear structures systems optimization separately from the systems of arbitrary structure.

2. Method Optimization of Linear System

First, let us consider a homogeneous system that contains **n** different elements of one type (as shown in Figure 1).

In this system one flow $h_{j,}$ $j = 1$ interacts successively with flows C_i, $I = 1,2,\ldots n$. In the problem of optimal synthesis, this can be reformulated in the following form. It is necessary to distribute the multitude of flows

$$C = \{C_1, C_2, \ldots, C_i, \ldots, C_n\}$$

along the flow h_j ($j = 1$) and as a result of interaction between the streams and the optimization procedure, the parameters of interest of flow h_j at system outlet of system will conform to the required constrains and the thermoeconomical criteria will be minimized.

$$\sum_i \sum_j Z_{ij} = Z_\Sigma^{\min} \tag{1}$$

where Z_{ij} is the thermoeconomical expenditure at i-element ($j = 1$).

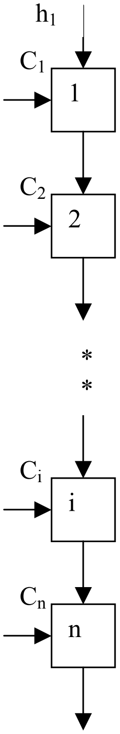

Figure 1. Linear system

As it is known[16] thermoeconomical criteria include the investment and operation costs as well as any energy expenditures calculated via appropriate exergy losses in each element.

For solving this type of problem, it is necessary to build the graph of thermoeconomical expenditure.[8] In our case this graph will be a tree *Z = (N, D)*, where the multitude of nodes *N* display the possibility of distribution of flows in the system, and the multitude of arcs *D* display the possible meanings of thermoeconomical expenditures.

The governing equations, which represent those levels, are:

$$N_p = \left\{C_1^{(p)}, C_2^{(p)}, \ldots, C_{i_p}^{(p)}, \ldots, C_{[n-(p-1)]}^{(p)}\right\}$$

$$N_p = \left\{C_1^{(p)}, C_2^{(p)}, \ldots, C_{i_p}^{(p)}, \ldots, C_{[n-(p-1)]}^{(p)}\right\} \tag{2}$$

$$p = 1,2,\ldots,k; i_p = 1,2,\ldots,[n-(p-1)]$$

where

$$N_p \subset C, p = 1,2,...,k,$$

$$p = 0 \Rightarrow |N_0| = 1$$

$$p = 1 \Rightarrow |N_p| = |C|, C - N_p = \varnothing \tag{3}$$

$$1 \leq p \leq k \Rightarrow |N_p| \leq |C|$$

$$\forall\left(C_{i_{p-1}}^{(p-1)}, C_{i_p}^{(p)}\right) \in D \Rightarrow \left(C_{i_{p-1}}^{(p-1)}, C_{i_p}^{(p)}\right) = Z_{i_p}^{(p)} \tag{4}$$

$$\forall\left(C_{i_{p-1}}^{(p-1)}, C_{i_p}^{(p)}\right) \notin D \Rightarrow \left(C_{i_{p-1}}^{(p-1)}, C_{i_p}^{(p)}\right) = \infty \tag{5}$$

where symbol ∞ shows that arcs of this type are absent.

The flow h_j in graph $Z(N, D)$ is described as node $C_0^{(0)}$, as shown in Figure 2. Then to fulfill conditions (1) it is necessary to find an optimal path that

$$\overline{C} = \left(C_0^{(0)}, C_1^{(1)}, ..., C_{i_p}^{(p)}, ..., C_{[n-(p-1)]}^{(k)}\right) \qquad \overline{C} \subset N \tag{6}$$

so that

$$\sum_{i_p} \sum_{p} Z_{i_p}^{(p)} = Z_{\Sigma}^{min} \tag{7}$$

The algorithm of Belmann–Kalaba is usually used for seeking the optimal way in graphs without contours. This algorithm is based on the matrix of thermoeconomical expenditure.[8,9]

In our case the graph of thermoeconomical expenditure is successive:

$$\Gamma_p N_p = N_{p+1} \tag{8}$$

where Γ_p is a display of set N_p, and the restraint imposed by Eq. 4 will be valid for elements of matrix (Figure 3), which are located in the intersection of columns $C_{i_p}^{(p)}$ and lines $C_{i_{p-1}}^{(p-1)}, p = 1,2,...,k;$ $i_p = 1,2,...,[n-(p-1)]$. This feature of graph of thermoeconomical expenditure allows one to simplify the matrix of expenditure and to reduce the number of variants analysed.[8,9] Based on features of the thermoeconomical expenditure graph, we recommend that the algorithm of searching optimal variant should be used.

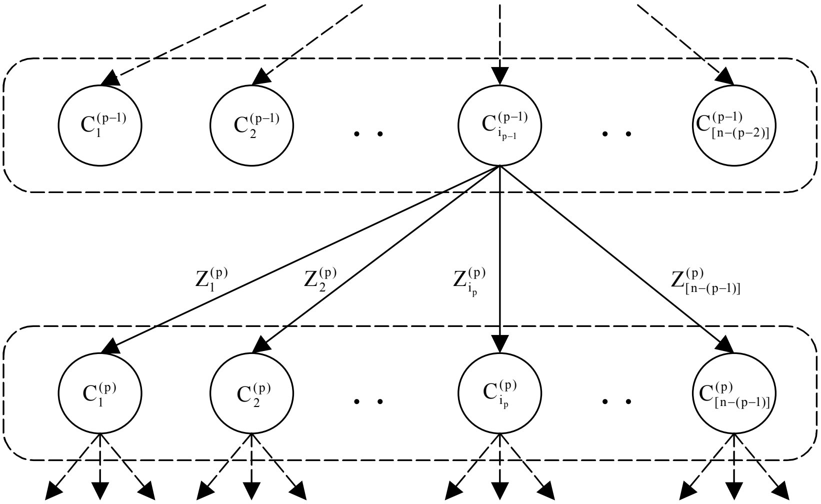

Figure 2. (P − 1) and P – levels tree of thermoeconomical expenditure

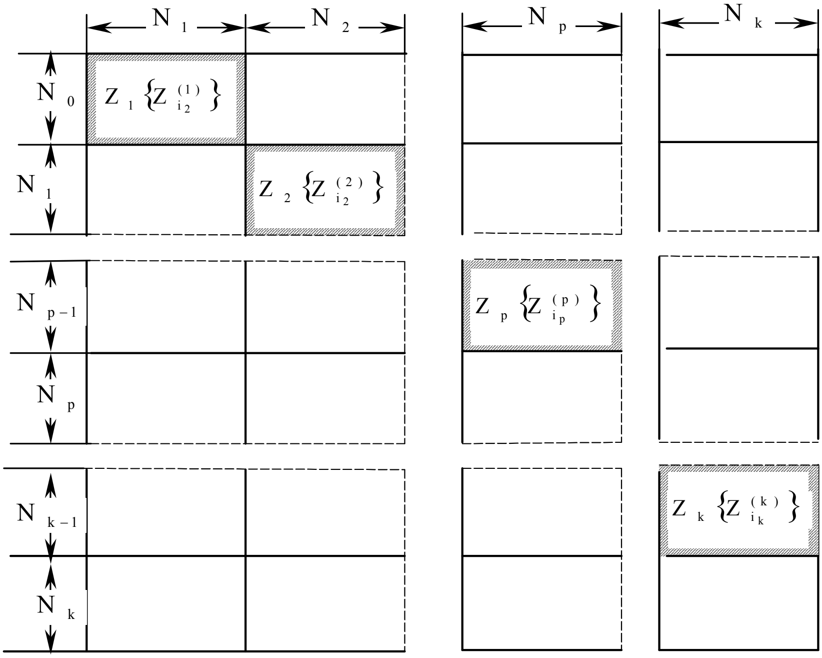

Figure 3. Matrix of thermoeconomical expenditure

Each step of seeking an optimal variant is successively compared with thermoeconomical expenditure $Z_{i_p}^{(p)}$ and $Z_{min}^{(p)}$. Thus, $Z_{\Sigma}^{\min}$ can be found (see Eq. (7)). Then, applying the procedure of seeking $Z_{min}^{(p)}$ to all k steps, we will find the optimal flow distribution, that verifies the constraints imposed by Eq. (1).

In the case of inhomogeneous linear systems optimization, the main idea of this approach will be retained. Since inhomogeneous elements are able to change the characteristics of flow h_j, it is necessary to consider not only the *p*th-step but also previous steps for system's optimization. Consequently, the method of dynamic programming has to be changed to a branch and bound method. On this approach at each step we seek and then save expenditure $Z_{\Sigma}^{(p)min}$, where $Z_{\Sigma}^{(p)}$ is the sum of thermoeconomical expenditure for all the p steps of variant considered. Then expenditure $Z_{\Sigma}^{(p)min}$ will be compared with the analogous sums for the previous steps $(p-1),(p-2),\dots,1$.

Then the variant corresponding to the following equation has to be developed:

$$Z_{\Sigma}^{min} = min\left[Z_{\Sigma}^{(l)min} \right], l = 1,2,\dots,p \tag{9}$$

Then elements for the next step of optimization have to be taken from the multitude N_{p+1}, which corresponds to Eq. 8.

3. Optimal Synthesis of Chlorine Water Refrigeration

The systems of chlorine water refrigeration usually have a linear structure, and can be described by Figure 1. In this case the flow h_1 will be the flow of refrigerated chlorine water and C is the set of flows which refrigerate the flow h_1. The set of flows C include flows of industrial water and cooled water. If industrial water is used, the surface of heat exchangers and appropriate expenditures will be bigger than in the case of using cooled water. But using the cooled water requires an additional cost for its cooling. So the question is to find the variant of system of chlorine water refrigeration with minimum expenditure:

$$Z_{\Sigma} = \sum_{i=1}^{n} Z_i^{min} \tag{10}$$

$$Z_i^{min} = min\{(Z_i^A + Z_i^{iw}),(Z_i^A + Z_i^{cw})\} \tag{11}$$

where:

Z_i^A is the year investments cost (for surface, repairing, salary of personal etc.) for heat exchanger i,

Z_i^{iw} is the year expenditure for industrial water

Z_i^{cw} is the year expense of cooled water

$$Z_i^{cw} = P_i^{cw} E_i^{cw} \tau \tag{12}$$

where:

P_i^{cw} is the price of one kJ cooled water

E_i^{cw} is the exergy of cooled water which can be calculated as exergy of a heat flow entered to heat exchanger **i**

$\boldsymbol{\tau}$ is the period work of the system during a year

$$Z_i^{iw} = P_i^{iw} m_i^{iw} \tau \tag{13}$$

where P_i^{iw} is the price of 1 kg of industrial water (as the difference between parameters of industrial water and environment are very little we can assume that exergy of industrial water equal zero) for heat exchanger **i,** m_i^{iw} is the mass flow of industrial water for heat exchanger **i.**

As an example, a typical line of chlorine production was taken (the mass flow of chlorine is 2.53 kg/s) with mass flow of chlorine water 10.9 kg/s. The working time during a year is $\tau = 7{,}200$ h. The temperature of chlorine water at inlet of system is 50°C the required temperature at outlet of the system is 15°C. The heat exchangers for such scheme are titanium refrigerators with a surface area each of 60 m^2 with a heat transfer coefficient of 700 $W/(m^2\ K)$. The initial temperature of the industrial water is 20°C. The initial temperature of cooled water is 5°C. The year investment cost for the heat exchanger is 0.0666 USD for 1 m^2 of surface. Price of exergy of cooled water is 0.0038 USD/MJ, price of industrial water is 0.065×10^{-6} USD/kg.[17]

Application of the procedure described above for optimisation of this system gives the tree of solution shown in Figure 4. The left branch of the tree displays variants of using cooled water, and the right branch-industrial water. Each level of tree (excluding level zero) has two nodes with appropriate temperature of chlorine water and thermoeconomical expenditure. To further develop the tree at each level taken (as it was described above), the node with a minimum of $\boldsymbol{Z_\Sigma}$ was selected.

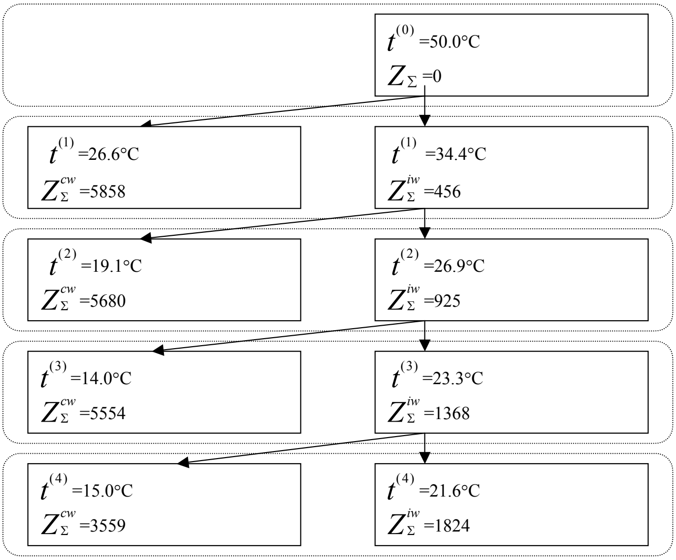

Figure 4. Tree of possible thermoeconomical expenditure of the system of chlorine water refrigeration

It is seen that on the first three levels the variant chosen uses industrial water and only on the last one cooled water. Therefore, optimal system of chlorine water refrigeration will include three-heat exchangers with industrial water and one with cooled water.

The optimal meaning of thermoeconomical expenditure for this system is 3,559 USD per year.

4. Conclusion

The problem of optimisation linear systems has to be solved separately from the problem of optimisation of systems with arbitrary structure. On base of features linear systems it is possible to build the effective procedure of optimisation. The suggested method based on developing and analyses of graph of thermoeconomical expenditure. It allows one to find the optimal variant for homogeneous systems as well as for systems with different tips of elements. The method is illustrated by an example of chlorine water refrigeration system optimisation.

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RESEARCH IN THE INSTITUTE OF GEOTECHNICS SAS – WATER TREATMENT TECHNOLOGIES

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Abstract The paper presents a short overview of the research focused on the water treatment in the departments of the Institute of Geotechnics of Slovak Academy of Sciences.

Keywords: Institute of Geotechnics; water treatment technologies; sorption of heavy metals

1. Introduction

The Institute of Geotechnics of the Slovak Academy of Sciences has a dominant position in Slovak Republic within the basic and applied research in the field of rock disintegration, mineral processing, mechanochemistry, mineral biotechnologies and environmental protection. The institute is divided into five scientific departments:

- Department of destructional and constructional geotechnics, here the research is aimed at the study of the interaction rock – tool, monitoring and optimization of the rock disintegration processes.
- Department of mineral biotechnologies, where the application of mineral biotechnologies in contaminated soils and waters are studied.
- Department of physical and physico-chemical mineral processing methods is focused on the complex mineral processing, including recycling of secondary-raw materials, using the microwave energy in extraction processes and the influence of selected physical fields on the

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M. Václavíková et al. (eds.), *Water Treatment Technologies for the Removal of High-Toxicity Pollutants*,

synthesis. The interaction of the magnetic sorbents with toxic species in aqueous media is studied as well.

- Department of mechanochemistry, where the possibilities of minerals pre-treatment by mechanical activation and synthesis of new-advanced materials are studied.
- Department of environment and hygiene in mining engineering, aimed at the study of pollutants emitted by mining and manufacturing industry.

2. Research Groups Contributing to the Environmental Problems

The Institute has overcome general problems connected with the damping of mining activities and found its new position in mineral and material science. In three of these departments the research activities are focused to the environmental problems related to the waste waters treatment:

2.1. DEPARTMENT OF MECHANOCHEMISTRY

The mechanical activation of minerals was used for modification of their sorption properties:

2.1.1. *Modification of Calcite*

The mechanical activation of mineral was performed in a planetary mill Pulverisette 6, changing the time of grinding in range 0.6–60 min. The activated minerals were used for Zn removal from model water solution.

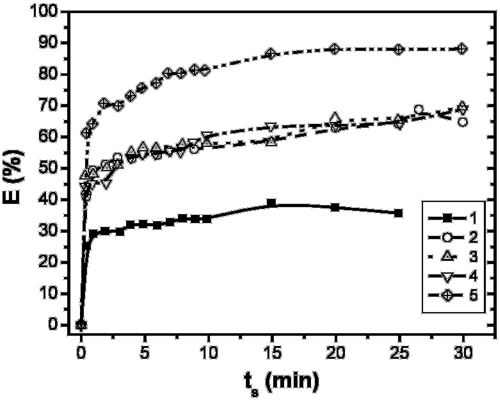


Figure 1. Efficiency of Zn sorption vs. sorption time of mechanically activated calcite: 1 – 0 min, 2 – 0.6 min, 3 – 3 min, 4 – 15 min, 5 – 60 min

It followed from the experiments that for the calcite[1] sample mechanically activated for 60 min, an increase of sorption efficiency from 35% to 88% was observed (Figure 1). In the next stage, the influence of temperature of mechanical activation on sorption efficiency of Zn was studied; the maximum efficiency was observed for calcite activated for 15 min at 50°C.

2.1.2. *Adsorption of As and Zn on Mechanically Synthesized FeS*

Pyrrhotite, synthesized in the planetary mill by mechanochemical reaction of pyrite with elemental Fe was used for As(III) and Zn(II) sorption[2] from model solution, where the ion concentration 25–400 mg/L and sorbent concentration 5 g were used (Figure 2).

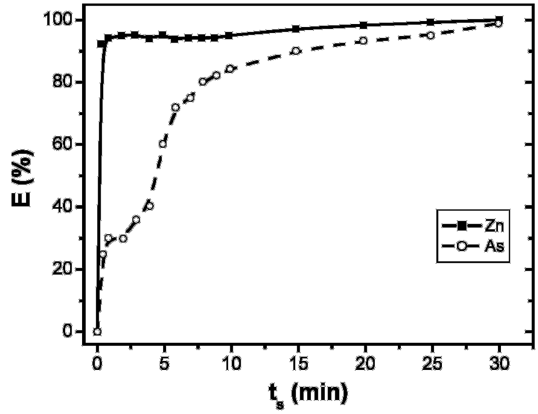


Figure 2. Efficiency of As sorption on the mechanochemically activated sample of FeS_2+ Fe vs. sorption time

2.2. DEPARTMENT OF MINERAL BIOTECHNOLOGIES

2.2.1. *Biological Activation of Coal Based on Interactions of Bacteria with Mineral Surface*

Adsorption of Cu and Zn ions from aqueous solutions on biologically activated brown coal sludge was investigated.[3] Four groups of adsorbents were prepared by microorganism’s activity: microscopic fungi such as *Aspergillus niger*, *Aspergillus clavatus*, *Penicillium glabrum* and *Trichoderma viride* were used. The maximum sorption capacity of activated sorbents *Aspergillus Niger* used for sorption Cu and *Trichoderma viride* for Zn sorption were twice as high as of the non-activated coal sludge.

2.2.2. *Selection of Packing Material for Biofilter Development*

Biofiltration is a potential process for treatment of large volume of wastewaters containing low concentration of heavy metals. In order to find the appropriate packing material,[4] sorption experiments using zeolite, bentonite, calcite and magnezite samples activated with bacteria were studied.

The experiments were carried out in Erlenmeyer flasks, where 10 g of mineral sample and 100 mL medium were inoculated with bacteria *Bacillus cereus and Bacillus megaterium.* The flasks were incubated under dynamic conditions for 3 h at 25°C. The liquid phase contained metals in forms $ZnSO_4$, $CuSO_4$ and $Pb\ CO_3$.

The removal of Zn, Cu and Pb were analysed and the sorption experiments showed that the minerals activated with bacteria should be used as packing material for biofilter, considering increasing the bacterial amount in packing filter.

Other technologies available for removal of metals from acid mine drainage (AMD) by sulphate reducing bacteria were presented on the conference NATO ARW 2008.

2.3. DEPARTMENT OF PHYSICAL AND PHYSICO-CHEMICAL METHODS OF MINERAL PROCESSING

2.3.1. *Sorption of Metal Ions by Red Mud*

Red mud, a solid byproduct of the alumina production industry, was found to be an environmentally suitable sorbent in removing cadmium, zinc, lead and copper from model aqueous solutions.[5] The best removal efficiency was observed at removal of zinc (133 mg/g) at pH 7 in the presence of 0.01 M $NaNO_3$. Cadmium was also satisfactorily removed at pH 6 and 0.01 M $NaNO_3$ with maximum removal capacity equal to 68 mg/g. Copper and lead were due to precipitation effect almost completely removed at pH values 6 and 7.

2.3.2. *Sorption of Metal Ions by Magnetic Particles*

The method of magnetic particles[6] synthesis is in this department well known since the production and application of magnetic fluids in various areas of mineral processing have been realized and studied.[7]

Synthesized magnetic particles were used for removal of Cu, Cd and Pb ions from model solutions, where the concentration of ions was in range 20–400 mg/L, sorbent concentration 2 g/L, and the pH suitable for removing of Cu, and Pb was equal to 4.5 and for Cd removal equal to 5.

It followed from the sorption experiments, that the synthetic magnetic oxides were found to be the effective sorbents of selected cations with maximum sorption capacity for Cd equal to 65 and 54 mg/g for Pb.

Using the synthetic akagenite for arsenic removal from aqueous solution with initial concentration of arsenic 20–200 mg/L and sorbent concentration 2 g/L, yielded to the maximum sorption capacity equal to 49.97 mg/g.[8]

2.3.3. *Sorption of Metal Ions by Natural Zeolite*

Natural zeolite of Slovak provenience was studied as a sorbent of Pb(II) and Cd(II) ions from model aqueous solutions, changing the ionic strength.[9] The initial concentration range was 20–400 mg/g and sorbent concentration 2 g/L. The best sorption capacity has been observed with no electrolyte or a small electrolyte concentration and was found to be equal 65 mg/g for Pb and 30 mg/g for Cd.

2.3.4. *Modification of Natural Zeolite by Iron Oxide Particles*

Trying to enhance the sorption capacity of natural zeolite its modification by magnetic particles in zeolite: iron oxide ratio 5:1 at selected temperatures was studied. The magnetic sorbent prepared by precipitation of iron oxides was used for removal of Pb(II) from model solution. The concentration of the sorbent was 2 g/L and the initial ion concentration range was 20–400 mg/L. The maximum sorption capacity calculated from the Langmuir model was 73.25 mg/g.[10–12]

The surface and pore properties of zeolite modified by iron oxides were studied by low nitrogen adsorption measurements. Analysis of measurements showed that the precipitated magnetic nanoparticles are forming an aggregated structure on the surface of zeolite, increasing thus the values of surface area and total pore volume (Table 1). Adsorption and desorption isotherms showing the adsorbed pore volume are in Figure 3.

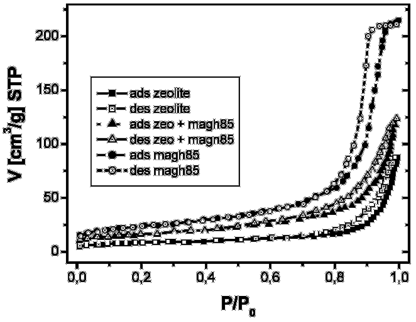


Figure 3. Adsorption and desorption isotherms of natural zeolite, modified zeolite and pure iron oxide

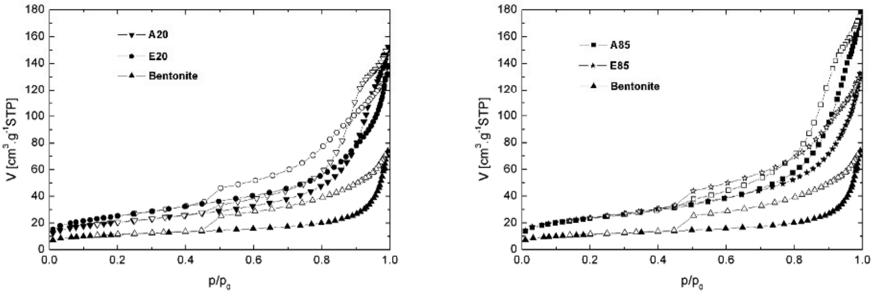
TABLE 1. Structural characteristics of zeolite samples

Sample	S_{BET} (m2/g)	V_a (cm^3/g)	V_{micro} (cm^3/g)	S_t (m^2/g)
Natural zeolite	27.3	0.108	0.003	20.8
Iron oxide composite 85	55.5	0.174	0.003	47.8
Pure iron oxide	81.3	0.331	0.003	71.5

2.3.5. *Sorption of Metal Ions on Natural Bentonite and Composite with Iron Oxide*

For further study, the clay mineral bentonite, treated by a sedimentation method to obtain a fraction <20 μm, has been used. The composites were prepared at two selected temperatures 20°C and 85°C in different weight ratios of bentonite and iron oxides. It follows from the nitrogen sorption measurements (Figure 4) that the shape of isotherms differs in accordance with the used weight clay/iron oxide ratio. The temperature of composite synthesis caused the shifting of the plots of isotherm to the higher values of adsorbed gas volume. Analysing the values of specific surface area, as well as the total pore volume, being the decisive factors at sorption experiments, the composites A85 (prepared at 85°C and ratio 1:1) and E20 (20°C and 5:1) were chosen to realize the sorption of zinc, nickel and cadmium from model solutions.[13]

The sorption experiments have shown, when using the initial metal ion concentration in range 10–100 or 1–50 mg/L, that the modified clays assign to higher sorption capacity as natural bentonite, especially in cases of lower concentration range.



a) b)

Figure 4. Adsorption and desorption isotherms of bentonite samples prepared in different weight ratios A- 1:1, E- 5:1 at different temperatures (a) 20°C, (b) 85°C

Moreover, selected results on sorption of arsenic under dynamic conditions were presented on the conference NATO ARW 2008.

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INDEX

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1
2
3

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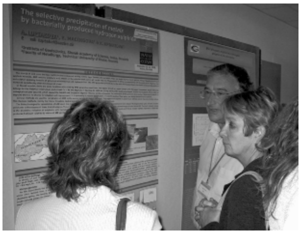
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