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Environmental Security

Economic Sustainability and Environmental Protection in Mediterranean Countries through Clean Manufacturing Methods

Edited by
José Coca-Prados
Gemma Gutiérrez-Cervelló

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Economic Sustainability and Environmental Protection in Mediterranean Countries through Clean Manufacturing Methods

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Series C: Environmental Security

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Preface

Sustainable development has been a key issue in developed countries since 1970. It can be considered as an integration of three factors: environmental, economic and socio-political. Technological advances and new strategies implemented in many industrial activities have been successful in dealing with some major issues, leading to the so called *steady state economy*.

Sustainable development is also a major issue for developing countries, but its implementation is not always compatible with their goals of growth and better living standards. There has been in the last two decades an increasing demand for high quality water mainly because the intensive exploitation of aquifers, primarily in arid zones.

The NATO-Advanced Training Course *"Economic sustainability and environmental protection in Mediterranean Countries through clean manufacturing methods"* was intended to address sustainable strategies and the search of alternative sources and water treatment methods. The course was planned to be held in Sfax (Tunisia), but because of the political events it was postponed and held in Huelva (Spain) on October 3–7, 2012. A selection of presentations is included in this volume.

Membrane treatment of effluents received special attention as a technology to alleviate water shortage, by promoting recycling. Integrated or hybrid systems combining physico-chemical pretreatments followed by membrane treatment are very promising technologies in many arid areas of the world.

The course and this monograph would not have been possible without the generous participation of the speakers and participants interest through stimulating discussions. We acknowledge and thank all of them.

We would like to thank those who contributed with their efforts to the organization of the course (Prof. José Manuel Benito, María Matos, and Emilio Muñoz).

Finally, we acknowledge the support of the NATO Science for Peace and Security Section (NATO-SPS) for granting us the opportunity to host this course in Huelva, the University of Huelva for making available its facilities, and the companies

(CEPSA and J. García Carrion) for letting us to visit their manufacturing plants. And last but not least, we thank Prof. Juan Pedro Bolívar of the University of Huelva for his cooperation, patience and understanding.

José Coca-Prados
Gemma Gutiérrez-Cervelló

NATO ADVANCED TRAINING COURSE: "Economic Sustainability and Environmental Protection in Mediterranean Countries through Clean Manufacturing Methods"

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El Ayni Foued, Centre International des Technologies de l'Environnement de Tunis, Tunisia

List of Contributed Lectures Presented During the ATC:

1. Achieving Sustainability with Clean Manufacturing Methods (S.K. Sikdar)
2. Innovative Technologies for Wastewater Treatment (J.M. Lema)
3. Treatment of Complex Systems – Advanced Oxidation Processes (T.W. Chapman)
4. Recovery and Recycling of Industrial Wastewater by Hybrid Processes (F. Shadman)
5. Activated Carbon Adsorption and Chemical Regeneration in Food Industries (R. Sierka)
6. Cleaner Production in Industry: Capacity Building and Implementation (J.K. Staniskis)
7. Treatment of Oily Wastewaters by Hybrid Membrane Process (J. Coca)
8. New Technologies in Leather Processing Industry (M. Renner)

9. Textil Wastewater Treatment and Recycling (R. Ben Amar)
10. Application of Cross-Flow MBR Technology for the Treatment of High Loaded Wastewater and Landfill Leachates (B. Fitzke)
11. Nutrient Removal and Phosphorous Recovery from Wastewaters (M. Alvarez-Cuenca)
12. Changes in Groundwater Salinity and Nitrate Concentrations Due to a Aquifer Recharge by Treated Wastewater: Korba Case Study (A. Foued)

Contents

Chapter 1
Cleaner Production in Industry: Capacity Building and Implementation

Jurgis K. Staniškis and Valdas Arbačiauskas

Abstract Cleaner production (CP) is a recognised and proven strategy for improving the efficient use of natural resources and minimizing waste, pollution and risks at the source where they are generated. CP is an essential part of any comprehensive environmental management system. Significant reductions in pollution loads can often be obtained at a low cost, and efficient use of resources and reduction in pollution in industrial production are clearly preferable to reliance on the end-of-pipe treatment. CP means a continuous application of an integrated preventive environmental strategy to processes, products and services to increase overall efficiency. This leads to improved environmental performance, cost savings, and the reduction of risks to humans and the environment. CP is achieved by applying know-how, by improving technology, by input substitution, by better process control and/or by changing attitudes. Investments in CP can have attractive economic benefits due to reduction of input costs of materials, energy and water, and reduced expenditures related to waste treatment and disposal. The article is focused on cleaner production concept, CP innovation development and implementation methodology, and the key issues related to cleaner production capacity building activities in a country. In addition to an example of an innovative transdiciplinary education programme, the article provides recommendations concerning the most effective ways to build basic capacity level in cleaner production.

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1.1 Introduction

The concept of resource efficient and cleaner production (CP) was introduced by UNEP as a response to the question of how industry could work towards sustainable development. CP is a recognized and proven strategy for improving the efficient use of natural resources and minimizing waste, pollution and risks at the source where they are generated. CP is an essential part of any comprehensive environmental management system. Significant reductions in pollution loads can often be obtained at a low cost, and efficient use of resources and reduction in pollution in industrial production are clearly preferable to reliance on the end-of-pipe treatment. In many cases, adoption of CP improvements can reduce or even eliminate the need for end-of-pipe investments [1]. Therefore, CP is associated with both environmental and economic benefits. Despite its conceptual simplicity, it took until the late 1980s for CP to become recognized as a valuable approach for achieving the dual objectives of environmental improvement and industrial development. CP is being increasingly recognized as an essential route towards sustainable development [2].

Cleaner production is (in general) diffusing comparatively slowly despite good results achieved [3]. On the other hand, environmental management systems are implemented with a “certificate-oriented” approach whose effectiveness in terms of sustainability performance improvement is low [4]. Even if management systems are implemented with a “performance-oriented” approach, enterprises might not be able to realize their full potential for performance improvement. One of the reasons is lack of motivation to maintain the system after certification [5]. Moreover, enterprises often lack explicit information about their activities, particularly quantitative information on production processes. Existing information is seldom systemized and made available to decision makers in a form suitable for effective decision making. The main reasons for this is lack of knowledge and competence about cleaner production methodology in development of cleaner production innovations, obstacles related to CP implementation (particularly financing) and lack of basic cleaner production capacity in a country.

In terms of competences for cleaner production innovation development and implementation, the starting point for discussion is the fact that enterprises are not sufficiently aware of the environmental impacts of their business activities. Additionally, existing data show that a large part of enterprises tends to underestimate their environmental impacts. Without information about their environmental impacts and associated production inefficiencies, e.g. in energy and natural resource use, enterprises will be neither motivated nor be able to make decisions that would improve their environmental performance. Action is often taken when enterprise has no other choice or possibility to postpone a decision. Decision-makers in enterprises are often “too quick” in finding solutions to particular problems. Seldom real causes of a problem are analysed as solution often seems to be “obvious”, e.g. when new legal requirement concerning emission of particular pollutant is introduced, decision makers are often tempted to go the easiest, but not the most efficient and economically viable way – to look for pollution control technology that would enable to capture pollution. Additional data collection and analysis could help to identify more alternatives to solve the problem, e.g. material substitution to eliminate the pollutant in concern (product innovation), production process modification to reduce pollutant generation, or even better control of the process as a result of non-technical innovation.

One of the key factors affecting behaviour of enterprises in the area of CP implementation is their limited competence level and capacity to adopt approaches of environmentally sustainable industrial development. Enterprises might also have limited financial resources to invest in management and technical solutions that could make their operations more environmentally sustainable. Moreover, in some cases economically feasible cleaner production ideas might be rejected because of incomplete accounting when full environmental costs are not calculated. Sometimes, this contributes to the sceptical attitude enterprises show towards the potential benefits and cost savings associated with environmental improvements. Many enterprises still believe that activities related to environmental protection are costs without any benefits.

Enterprises implement measures aimed at improvement of environmental performance because of various internal driving forces, e.g. opportunities for increasing efficiency of operations, reduction of resource consumption and pollution generation, savings associated with implementation of preventive measures, increased sales associated with improved image, future economic benefits of compliance. However, experience shows that such internal driving forces are not sufficient for enterprises to apply sustainable industrial development tools systematically. Therefore, certain external incentives are needed to ensure broad implementation of cleaner production in industry. This could only be ensured when basic capacity for cleaner production in a country is built.

Objective of the article is twofold: (i) to present cleaner production concept and methodology; and (ii) to discuss key issues related to cleaner production capacity building activities in a country.

1.2 Cleaner Production Concept

Cleaner production means a continuous application of an integrated preventive environmental strategy to processes, products and services to increase overall efficiency. This leads to improved environmental performance, cost savings, and the reduction of risks to humans and the environment.

- In production processes, CP includes conserving raw materials and energy, eliminating toxic raw materials, and reducing the quantity and toxicity of all emissions and waste before they leave the process.
- In products, CP focuses on reducing impacts along the entire life cycle of the product – from raw material extraction to the final disposal of the product.
- In services, using a preventive approach CP involves design issues, housekeeping improvement, and a better selection of material inputs (in the form of products).

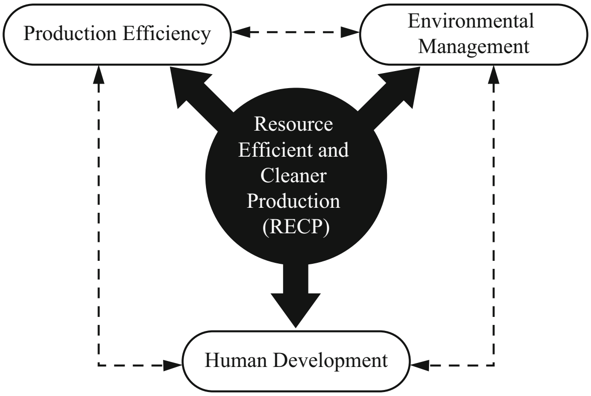

Fig. 1.1 Resource efficient and cleaner production concept (Source: [6])

Other concepts such as eco-efficiency, waste minimization and pollution prevention share a common emphasis on pollution/waste elimination/reduction at the source where it is generated. However, CP strategy includes a well-developed procedure for systematic assessment of pollution/waste generation causes and development of practical options aimed at the solution of concrete problems.

A preventive approach means that environmental problems are addressed before they arise when choices are made concerning processes, raw materials, design, transportation, services, and more. Such an approach effectively addresses the wasting of natural resources since pollution not only leads to environmental degradation but it is also a sign of inefficient production processes or management. In practice, CP means avoiding or reducing the amount of the waste produced; using energy and resources efficiently; producing environmentally sounder products and services; and generating less waste, reducing costs and risks and increasing profits/competitive advantage (Fig. 1.1).

Cleaner production concept relies on the following principles [7]:

- Precaution principle. Precaution is not simply avoidance of being “off law”, it is also assurance that workers are protected from irreversible ill-health and that the plant is protected from irreversible damage. The precautionary principle calls for reduction in anthropogenic inputs into the environment, and this call is essentially a demand for substantial redesign of the industrial system of production and consumption which relies at the moment on the extensive throughput of materials.
- Prevention principle. Prevention is equally important, especially in cases where a product or process is known to cause harm. The prevention principle is to look to changes upstream in the causal network of the system of production and consumption. The preventive nature of CP calls for a new approach to reconsider product design, consumer demand, patterns of material consumption, actually – the entire material basis of economic activity.
- Integration principle. Integration involves adoption of holistic view of a production cycle, and one method of introducing the idea is through the life-cycle analysis.

> One of the difficulties in the preventive approach is the integration of environmental protection measures across the system boundaries. Traditional end-of-pipe regulation generally applies to a specific extent by calling for process-integrated measures to reduce the generation of pollutants. By reducing the need for emission into the environment of such substances, these measures thereby provide for an integrated protection of all environmental media.

CP innovation development and implementation requires application of know-how, improvement of technologies/production processes, and changing attitudes. CP strategy includes the following prevention practices [1]:

1. Good housekeeping: taking appropriate managerial and operational provisions to prevent leaks and spills (such as preventive maintenance schedules and frequent equipment inspections) and to enforce the existing working instructions (through proper supervision, training, etc.).
2. Input substitution: substitution of input materials by less toxic or by renewable materials or by adjunct materials (for instance, lubricants, coolants, cleansing agents, etc.), which have a longer service life-time in production.
3. Better process control: modification of the working procedures, machine instructions and process record keeping in order to run the processes at a higher efficiency and lower waste and emission generation rates.
4. Equipment modification: modification of the (existing) productive equipment and utilities, for instance, through addition of measuring and controlling devices, in order to run the processes at a higher efficiency and lower waste and emission generation rates.
5. Technology change: replacement of the technology, processing sequence and/or synthesis pathway to minimize waste and emission generation during production.
6. Product modification: modification of the product characteristics to minimize environmental impact of the product during or after its use (disposal) or to minimize the environmental impact of its production.
7. Efficient use of energy: energy is a very significant source of environmental impact. Energy use may result in the effects on land, water, air, and biodiversity, as well as in the production of large quantities of solid waste. The environmental impacts resulting from energy use can be decreased by improved energy efficiency and by using energy from renewable sources, such as the sun and wind.
8. On-site recovery/reuse: reuse of waste materials in the same process or for another useful application within the company.

The confluence of global economic and environmental crisis that has occurred in recent years has consolidated the understanding of the interdependence between our economic and environmental systems and provided a new impetus to international efforts to promote the transition towards more sustainable industrial systems and Green Industry. This has required the broadening of the definition of cleaner production to include resource efficiency which is a key element of the transitions towards Green Industry and Green Economy. According to ENEP/UNIDO definition,

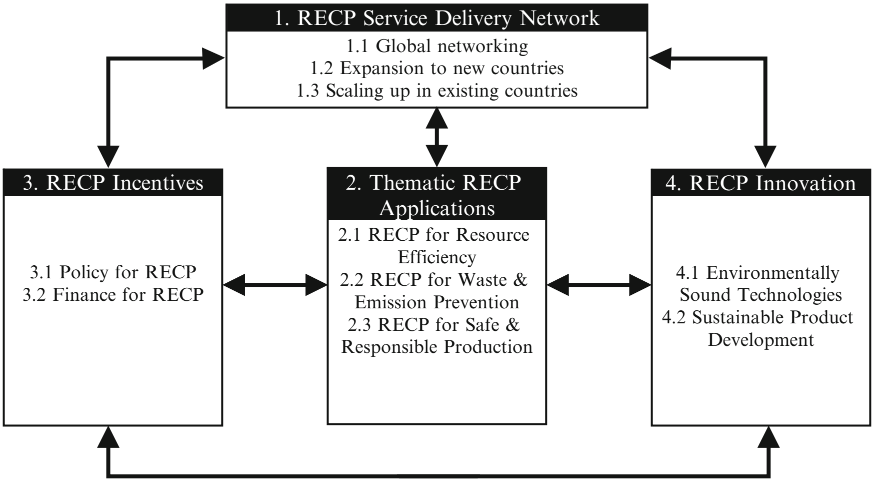

Fig. 1.2 RECP Programme modules (Source: [6])

resource efficient and cleaner production continuously applies integrated and preventive strategies to processes, products and services. This increases efficiency and reduces risks to humans and the environment. RECP specifically works to advance [6] (Fig. 1.1):

- Production Efficiency – through optimisation of productive use of natural resources (materials, energy, water) at all stages of the production cycle;
- Environmental Management – through minimisation of the adverse impacts of industrial production systems on nature and the environment;
- Human development – through minimisation of risks to people and communities, and support to their development.

RECP, therefore, builds upon CP in accelerating the application of preventive environmental strategies to processes, products and services to increase efficiency and reduce risks to humans and the environment. Enterprises and other organisations that adopt RECP increase the efficiency with which they use materials and energy; they improve their productivity and thus their competitiveness. At the same time, through greater efficiency, enterprises reduce the amount of pollution and waste they generate, thus lowering their impact on the environment, including their carbon footprint. As waste and emissions reduce, and hazardous substances are eliminated, the risks of industrial operations to workers, communities and consumers reduce.

The RECP Programme is implemented through four main intervention modules. Each covers several key activities and outputs (Fig. 1.2):

1. RECP Service Delivery Network: expanding, strengthening and further capacitating the network of NCPCs and other RECP service providers. This includes, intensive networking and knowledge management, expansion of

RECP to new countries and supporting existing NCPCs to scale-up their activities and impacts;
2. Thematic RECP Applications: implementation of RECP in enterprises and other organizations and monitoring of results, in particular on resource efficiency, waste and emission prevention and safe and responsible production;
3. RECP Incentives: mainstreaming RECP into government policy and enterprise finance, to further incentivize enterprises and other organizations to implement RECP; and
4. RECP Innovation: strengthening and/or creating national innovation capacities to support the adaptation and adoption of Environmentally Sound Technologies and sustainable product developments that are appropriate in the national industry context.

These components are implemented in flexible combinations to ensure effective support at the national, regional and global levels and further develop of RECP methods, tools, policies and technologies [6].

1.3 Methodology for Development and Implementation of Cleaner Production Innovations

Cleaner production assessment is a systematically planned procedure with the objective of identifying ways to reduce or eliminate the generation of waste and emissions. Generally, an assessment should aim to complete at least one environmental improvement cycle which results in the implementation of particular prevention options and to create conditions for the execution of a new improvement cycle [8]. CP assessment could divided into five phases: (i) planning and organisation; (ii) pre-assessment; (iii) assessment and option generation; (iv) feasibility analysis; and (v) implementation (Fig. 1.3).

CP planning is needed to ensure management commitment for CP and is a systematic method to identify options aimed at resource efficiency/reduction of waste generation. The process ensures the consistency of CP objectives and activities with those identified in the organisation's broader planning process, and facilitates broader investment analysis and decision-making (such as capital budgeting and purchasing). Development of project plan and approval of project team are also essential elements of this phase.

The phase of assessment focuses on the production processes that involve waste streams and is based on examination and re-evaluation of the production processes. The re-evaluation consists of "source identification" followed by "cause diagnosis" and "option generation". For source identification, an inventory is made of the material flows entering and leaving the company with the associated costs. It results in a process flow diagram, allowing the identification of all sources of waste and emission generation.

The use of environmental and resource accounting tools have proliferated and are widely used both as messaging tools for the public to communicate impacts of

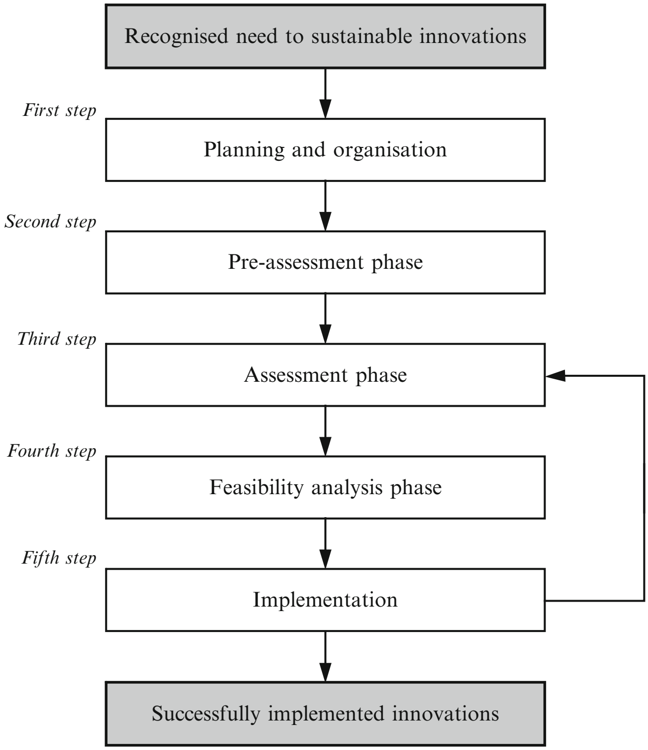

Fig. 1.3 Cleaner production development and implementation algorithm

consumption patterns and also as a valuable indicator for supporting policy-making. Among others, these include ecological foot-printing, water foot-printing and material flow analysis. Of these, material flow analysis (MFA) offers great potential to link with economic and social processes and therefore policy interventions. Literally, material flow analysis is a systems approach to understanding what happens to the materials we use from the time a material is extracted, through its processing and manufacturing, to its ultimate disposition. The methodology can be used in company, commodity performing mass balance study, which follows and quantifies the flow of a single company or commodity through its entire cycle. Such analysis identifies areas where adverse impacts could be minimised through reducing waste at the source where it is generated, improving waste utilization, and enhancing efficiencies. The indicators can be calculated in absolute terms as well as in relation to the product produced and to economic performance. In terms of policy, MFA can be used for early recognition, priority setting, to analyse and improve the effectiveness of measures and to design efficient material management strategies in view of sustainability.

The next step (cause diagnosis) is based on the material and energy balance and investigates the factors that influence the volume and composition of the waste and

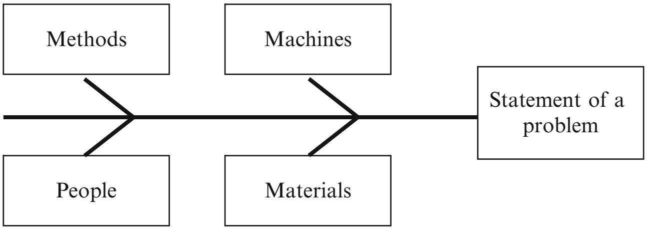

Fig. 1.4 Cause-effect diagram for establishing root causes (Source: [9])

emissions generated. Evaluation of relative importance of each of the possible waste generation causes is performed. The purpose of innovation generation is to create a vision of how to eliminate or control each of the causes of waste and emission generation.

In practice, preventative options can be identified by finding the root causes of the environmental problems. This can be done by posing a number of fundamental questions:

- What caused the loss?
- Why does it exist?
- Where did it start and where did it come from?
- What happens just before the loss occurs?
- Why is it tolerated?

Starting from these questions, a "Cause and Effect Diagram" can be established, which is a practical tool available for systematically identifying root causes (Fig. 1.4).

Feasibility studies have to prove whether each of the innovations is technically and economically feasible and whether each option contributes to the environmental improvement. The level of detail in the feasibility studies needs to be tailored to the nature of the innovation, since they may vary from simple operational improvements, the use of alternative materials to the installation of advanced equipment.

Technical evaluation consists of two interrelated parts. First, it should be evaluated whether the innovation can be put into practice, i.e. a check on availability and reliability of the equipment, the effect on product quality and productivity, the expected maintenance and utility requirements and the necessary operating and supervising skills. Second, the changes in technical specifications can be converted into a projected material balance, reflecting the input and output material flows and energy requirements after implementation of the preventive innovations.

The economic evaluation consists at least of data collection (regarding investments and operational costs, as well as benefits), choice between evaluation criteria (payback period, net present value or internal rate of return) and feasibility calculations. The economic data collection is based upon the results of technical evaluation. To incorporate the CP long-term economic advantages properly, it is highly recommended to apply the total cost assessment (TCA) principles to the economic evaluation (especially for high cost options). It is suggested that all significant environmental costs (and impacts) should be traced up to the responsible product (as opposed to the use of overhead accounts). That is, material tracking could be used for material costs and other related product costs (such as energy, water use, etc.), as well as for waste streams. Where tracking does identify costs, these should be clearly identified with the tasks or processes generating the costs.

The objective of environmental evaluation is to determine the positive and negative impacts of the innovation on the environment. It is of a little value if an option reduces one problem and creates another, potentially a worse one. In order to be comprehensive, an environmental evaluation must take into account the entire life-cycle of a product or service. The following steps can be used:

- Evaluate changes in: (i) quantity and (ii) toxicity of wastes/emissions at all stages in their life-cycle (at least in terms of raw materials, production, use and disposal);
- Evaluate changes in energy consumption throughout the life-cycle;
- Determine whether the environmental effects will be shifted to the other media;
- Determine whether there will be a change in the re-usability of this or other waste streams;
- Determine whether degradability of waste/emissions will be changed;
- Determine the extent to which renewable raw materials can be used;
- Determine the extent to which energy consumption can be reduced.
- Determine the extent to which renewable energy sources can be used.

Depending on resources required for implementation of cleaner production innovations and expected benefits (e.g. pay-back period), selected CP options could be divided into several packages, i.e.: (i) low investment good house-keeping measures; (ii) payback on investment of less than 2 years; and (iii) long-term measures with larger investments which could be considered after options from the first two categories have been exhausted. Systematic environmental, economic and technical feasibility analysis of identified CP options is extremely important in ensuring that the priority options are selected and implemented.

Feasible prevention measures are implemented and provisions taken to assure the ongoing application of CP. The development of such ongoing program requires the monitoring and evaluation of the results achieved by implementation of the first batches of prevention measures. The expected result of this phase is threefold: (i) implementation of the feasible prevention measures; (ii) monitoring and evaluation of the progress achieved by implementation of the feasible innovations; and (iii) initiation of ongoing CP activities. To increase effectiveness of monitoring and evaluation process, a set of performance indicators could be used [10].

In addition to challenges in identification and development of sustainable innovations, companies that have identified cost-effective and technically feasible CP innovations may be unwilling/unable to make necessary investments [11]. Generally, obstacles to financing CP investments could be on both demand and supply sides. On the demand side, enterprises have insufficient experience in preparing CP projects that are systematically evaluated from the environmental, economic and technical perspectives, and in development of applications for the project financing. Lack of knowledge in CP auditing and assessment, evaluating financial aspects of the project efficiency and investments, often blocks implementation of CP projects. Even when the capital is available, CP is one in the range of investment options. On the supply side, there are obstacles in capital markets for lack of environmental expertise and unattractive loan rates to enterprises. Costly administrative requirements result in loan thresholds established by international financial institutions, which sometimes are significantly higher than the costs of CP investments; it is difficult to receive financing for small projects [12, 13].

In some cases, economically feasible cleaner production ideas might be rejected because of incomplete accounting when full environmental costs are not calculated due to use of conventional cost accounting when environmental and non-environmental costs are aggregated in overhead accounts. Thus, environmental costs become "hidden" from management. To identify, assess and allocate environmental costs, and to identify opportunities for cost savings, environmental management accounting (EMA) methodology could be used. Prime examples from the EMA literature are the savings that can result from replacement of toxic organic solvents by non-toxic substitutes, thus eliminating the high and growing costs associated with the use of toxic materials. Many other examples deal with a more efficient material use, highlighting the fact that waste is expensive not because of disposal fees, but because of the wasted material purchase value [14].

To tackle challenges related to idea generation/innovation development and to overcome obstacles related to financing of sustainable innovations, and to increase application of CP in industry, a system for development, financing and implementation of sustainable innovations in enterprises was created by the Institute of Environmental Engineering (APINI), Kaunas University of Technology [15]. The key feature of the system is partnership of industry, academia and financing institution in a cycle that covers all stages from idea generation to innovation implementation and monitoring of results.

Financing is provided in a form of soft loan to commercially viable innovations with secure stream of earnings to repay the loan. The basis for providing a loan is a cash flow of investment and ability of the enterprise to repay the loan over the agreed period. The system is non-profit and seed money is used to finance implementation of sustainable innovations on a revolving basis.

Business development service provider should play a key role in identification, development and implementation of sustainable innovations, i.e.:

- Assistance to companies in identification/development of innovations
- Preparation of a loan application on behalf of the applicant, including assistance in calculation of costs savings and environmental benefits
- Assistance to the financing institution in communication with the applicant
- Development of the project progress and completion reports
- Assistance in the project monitoring/supervision, including the supervision of procurement and project implementation progress/results

Structural model of a system is presented in the Fig. 1.5.

One of the key obstacles for practical application of the system is reactive approach towards sustainable development/environmental issues still prevailing in

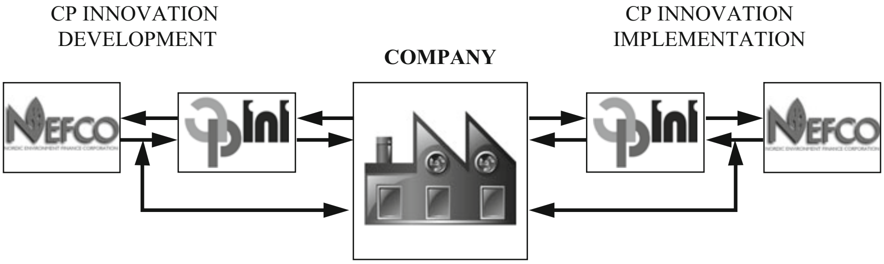

Fig. 1.5 Structural model for development, financing and implementation of cleaner production innovations

many of enterprises. A problem for successful transfer of the system to other countries might be lack of local institution capable to provide effective assistance to enterprises in identification and development of sustainable innovations based on CP methodology.

Success factors of the system for development, financing and implementation of sustainable innovations in enterprises:

- The system is based on preventive strategies;
- The process of innovation generation and development is carried out jointly by researchers and industry from the very beginning;
- Clear and tested methodology is used for identification of improvement options and development of innovations;
- The system is “one stop shop” comprising innovation generation, assessment, financing, implementation, and monitoring stages;
- Local capacity in resource efficient and cleaner production; and
- Availability of a local institution that can support the identification of sustainable production innovation opportunities and the elaboration of loan applications.

1.4 Cleaner Production Capacity Building: Experience in Central and Eastern Europe

Experience accumulated over two decades since activities have been initiated in the area of cleaner production clearly demonstrated that sufficient capacity level is a precondition for broad implementation of cleaner production in a country.

The concept of Basic capacity level (BCL) for CP was introduced by the Organisation of Economic Co-operation and Development (OECD) in 1996. The basic capacity level was defined as the level which is needed for further dissemination of the CP concept and principles throughout industry and society by the host country. Specifically, it involves creating: (i) an active core of CP advisors and trainers; (ii) a set of CP case studies and demonstration projects; (iii) a functioning CP Centre or Centres; (iv) training materials in the local language; (v) cleaner production principles, included in the university course curriculum, and (vi) a monitoring framework and quality assurance [16].

Training programmes are a core of cleaner production capacity building in a country. In principle, two types of training programmes could be used: (i) long-term training programmes and (ii) short-term training programmes.

Experience of CP capacity building programmes in Central and Eastern Europe (CEE) demonstrated that a long-term training programmes emphasising on-the-job training are the most effective way to create domestic professional capacities [12, 13]. Furthermore, the only cost and time efficient way of fulfilling this need is to adopt a train-the-trainer approach. The key factor that ensures effectives of the long-term training programme is integration of theoretical training and practical work in enterprises. The right balance between these two elements can be achieved by interchange of theoretical training sessions and in-company work between the sessions. The programme should result in development of CP innovations ready for implementation in participating enterprises. Prior to receiving their certification, trained experts could be asked to prepare reports which include three types of projects: (i) low investment good house-keeping measures; (ii) payback on investment of less than 2 years; and (iii) long-term measures with larger investments which could be considered after options from the first two categories have been exhausted. Systematic environmental, economic and technical feasibility analysis of identified CP options is extremely important in ensuring that the priority options are selected and implemented.

Such interactive CP capacity building approach covering both theoretical and practical training has been used in five Norwegian – Lithuanian Cleaner Production Programmes, implemented jointly by the Institute of Environmental Engineering (Kaunas University of Technology) and Norwegian Society of Chartered Engineers, and financed by Norwegian Government. The programme consists of a series of theoretical training seminars (including lectures and group work) and practical work in enterprises between the training seminars. The seminars cover the following topics [17]:

1. Cleaner production concept and methodology; practical examples from other countries; CP pre-assessment;
2. Comparative evaluation of cleaner production alternatives; environmental, technical and economic evaluation. Participating enterprises present results of in-company work;
3. Participants present initial cleaner production alternatives and evaluate environmental and economic benefits of selected options;
4. Final seminar is devoted for presentation of the fully developed cleaner production innovations and evaluation of programme results in participating enterprises.

One of the lessons learned from CP capacity building activities in CEE was that education of the company personnel often does not sufficiently include the top management. This issue could be addressed by organising short sessions for senior managers with focus on basics of CP and its benefits as well as obstacles, so that top managers would gain better understanding of the concept to be enabled to facilitate more effectively further work of the enterprise team. Short-term training programmes for staff in authorities is also important for achieving sustainable/wide-scale application of RECP concept. Ministerial staff in particular should be involved in special seminars regarding (i) the role of cleaner production in optimising environmental protection efforts, and (ii) the possibility of developing public policy instruments supporting this approach.

To ensure sustainable application of CP and other modern environmental tools in a country, there is a need to create a pool of specialists having appropriate education in CP, modern environmental management, environmental policy, law and similar subjects. In some countries, educational modules related to CP have been introduced at universities. Some universities have taken further step and established specialised post-graduate educational programmes. An example of innovative integrated M.Sc. programme in cleaner production and environmental management that is based on multidisciplinary and transdisciplinary approaches is presented in the Chap. 5.

The key objective of demonstration projects is to demonstrate potential of CP concept by implementation of pilot projects and subsequently to introduce the concept to a broader number of enterprises. Common practice in implementing demonstration projects in CEE was external financial support for implementation of identified technical options in participating enterprises and extensive involvement of external experts in identification of these options. While these projects had positive effect in terms of quick environmental improvements and in enterprises, long-term effects on environmental performance proved to be limited. Lack of involvement of local experts and lack of follow-up in implementation of selected CP measures generally did not spark expected multiplier effect in other enterprises [18]. Experienced showed that achieving desired objectives requires more than providing cleaner technology hardware.

To ensure sustainability of cleaner production in a country, institutional aspects are also to be considered. To sustain CP programmes, national cleaner production centre could be established. Generally, CP centres provide a variety of services to help overcome barriers to CP implementation within enterprises: training, technical assistance to enterprises, facilitating the financing of CP investments, demonstration projects, policy advice and similar activities. An important activity to promote cleaner production application is information dissemination targeted at specific audiences, mainly industry as well as national and local governmental institutions (seminars, workshops and conferences focusing on information dissemination and experience exchange, training and other printed materials).

While some of the services provided by CP centres are commercially viable once enterprises are willing to pay for them (e.g. audits), others (e.g. education and information dissemination) are public services that require public financing [16]. The contribution of CP centre to achievement of wide-scale CP application in a country depends on many different aspects related to the centre's organisation, range of activities and relations with other stakeholders. Based on experience of CP centres in CEE, the effectiveness of the centres is strongly influenced by several factors: the selection of host institution, the effectiveness of counterpart institutional arrangements, and the relationship with government.

1.5 Innovative Approach to Education in Cleaner Production: A Case Study

To ensure long-term capacity building in the area of sustainable industrial development, a new M.Sc. Programme in Environmental Management and Cleaner Production has been developed in the framework of the BALTECH consortium, which consists of technical universities in the Baltic Sea region. The Programme has been initiated by the Institute of environmental engineering (APINI) and started at Kaunas University of Technology in September 2002. This is a 2–year (120 ETCS Credits) programme suitable for graduates with qualification in many engineering fields such as chemical engineering, energy and electrical engineering, civil engineering, environmental engineering and others. The purpose of the programme is to create an example of effective education for sustainable industrial development on M.Sc. level [19].

Taking into account that number of companies applying different preventive environmental measures is growing, there is an increasing demand for engineers with high competence in technologies for cleaner production and integrated environmental management. Presented M.Sc. Programme enables to satisfy this demand.

The compulsory courses of the Programme cover all basic aspects of the industrial ecology approach. Optional courses are used to discuss these issues in more detail and to provide additional knowledge to ensure that graduates of the Programme will be able to apply industrial ecology approach, i.e. will be capable to conduct systematic analysis of industrial activities and to find optimal solutions for many problems related to sustainable industrial development.

The educational program is structured according to the following main guiding principles:

- Multidisciplinary approach. The environmental field is in its nature multidisciplinary, which is mirrored in the course structure of the Masters course. The programme covers technologies in coping with industrial residues, particularly those technologies aimed at reuse and recycling (course "Environmental Technologies"); identifying, evaluating and implementing technical and managerial options for improvement of environmental and economic performance (courses "Environmental Assessment", "Cleaner Production and Environmental Management"); design of industrial processes and products from dual perspectives of product competitiveness and environmental impact ("Eco-design"), and development of policy framework, which provides appropriate incentives for enterprises to adopt preventive environmental management practices and to increase their efficiency (course "Environmental Policy, Law and Economics"). To summarise, the programme has strong emphasis on engineering, management and policy to make sure that graduates have broad understanding and capability to work with a complex issues of sustainable industrial development.
- Strongly research-connected. Most of the optional courses are treating advanced topics with close research connections. The subject matter as well as the topics of course assignments and projects are closely linked to the research of the department giving the course or to its R&D co-operation with Industry, with

  projects defined by the need for solutions to current environmental or environmental management problems in the industrial company. The connection with the research in particular is ensured in the thesis projects under supervision of active researchers that have extensive experience in transdisciplinary research, i.e. in development of preventive innovations together with enterprises.
- Practical education. Kaunas University of Technology has very strong links to industry and governmental institutions. Institute of Environmental Engineering implemented a number of training programmes for industrial enterprises and assisted a number of enterprises to develop and implement cleaner production projects. M.Sc. students of the Programme in Environmental Management and Cleaner Production have an opportunity to participate in the projects aimed at improvement of environmental performance in industry and to acquire valuable practical experience.
- Integrated programme/transdisciplinary approach. The aim is to provide M.Sc. students a solid theoretical knowledge and hands-on experience in real world. This is achieved by a balanced and integrated theoretical and practical education. M.Sc. students use theoretical knowledge in their practical assignments accomplished in industrial companies that result in practically applicable sustainability performance improvement projects. The contents of the programme are based on industrial ecology approach, i.e. on industry – environment interactions to aid industry in evaluating and minimising impacts to the environment. The programme courses reflect one of the most important concepts of industrial ecology, which is like in the biological system, is rejecting the concept of waste.

The Programme, on the basis of the technical background of the student, enables graduates to integrate preventive managerial and technological tools in achieving a more sustainable development for industry and society; lead and sustain the process of change in industry, academia and other organizations; understand the interdependence of environmental, technical, economic and social sciences, and to perform interdisciplinary research and development. This is achieved by providing the M.Sc. students with skills to identify and assess the effects of human activity on the environment; knowledge of national and international environmental policy and legislation and the management of environmental issues in industrial and service systems; knowledge of technical systems, strategies and technologies for applying the principles of cleaner production in developing products and production systems; and practical experience in implementing preventive environmental measures.

During the last years a special interest has been paid to eco – design of the industrial products. With an active students participation more than 20 products has been redesigned in order to minimize their environmental impact during the whole product life cycle. There is a very wide range of the products: from refrigerator or corner sofa to very small integrated electronic devises. The electric meter shown in the Fig. 1.6 was redesigned by using life cycle assessment method and now it is available on local and international market.

Since 2002, the programme was graduated by 115 M.Sc. students having a very broad perspective for considering environmental issues and understanding the context of sustainability problems and wide range of actions. A balanced combination

Fig. 1.6 Examples of products redesign with active involvement of M.Sc. students

of theoretical and practical education enables to ensure that graduates are capable of accomplishing challenging tasks immediately after graduation and are desirable employees in research organisations, industrial enterprises, consulting companies and governmental institutions.

1.6 Conclusions and Recommendations

- Cleaner production assessment is a continuous process structured in cycles that enables to reduce pollutant generation at every stage of the production process and thus to minimise or eliminate waste that otherwise would need to be treated at the end of the process. This is achieved by applying good housekeeping practices, process modification, technology changes, raw material substitution, and redesign of a product or services. Effluent treatment, incineration, and even waste recycling outside the production process are not regarded as cleaner production, although they remain necessary activities to achieve a low environmental impact. CP is more cost-effective than pollution control. Through pollution prevention at the source, the cost of final treatment and disposal is minimized
- Cleaner production methodology is systematic and clear step-by-step cycle for identification of performance improvement options, development of improvement alternatives and implementation of the most beneficial cleaner production innovations that result in environmental and economic benefits. To ensure continuation of cleaner production activities in an enterprise, cleaner production procedure should be integrated in the overall management system of the enterprise.
- Obstacles to CP are mostly related to human rather than technical factors. Therefore, capacity building activities play a vital role in achieving sustainable/wide-scale application of CP in a country.

- The most effective way to ensure sufficient capacity for cleaner production in a country is use of train-the-trainer approach and integration of CP related education in education programmes, particularly transdisciplinary study programmes at universities with involvement of students in real-life projects.

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Chapter 2
Recovery and Recycling of Industrial Wastewater by Hybrid Processes

Farhang Shadman

Abstract Modern industries demand large quantities of water at purity levels that are unprecedented in industrial applications. Unless water usage is changed, these processes will not be sustainable. The key solution to reducing water usage and wastewater discharge in the ultra-pure water (UPW) plants is the development of suitable technology for water reuse and recycling. In particular, successful water conservation strategies will require innovations in a number of areas.

The ultimate solution to water conservation and sustainability for industrial use lies in some form of reuse and recycling strategy. However, the recycling process is not trivial and involves some challenges. Typically, the success in implementing recycling depends on two major factors:

1. The first requirement would be the availability of robust and low-energy purification processes. This is critical because the environmental issues associated with water usage and wastewater discharge cannot be solved simply by recycling water if the recycling process consumes large amounts of energy. Large energy usage, in addition to being costly, would cancel any environmental gains that may be achieved by water saving. There is no merit in water recycling if for every unit of water recovered and recycled we end up using large amounts of energy. This is particularly important because many of the existing purification methods were not originally developed and optimized to accommodate recovery and reuse. In this article, some novel approaches and technologies based on the use of hybrid systems, their principle of operation and design, as well as the methods for selection and optimization of these promising hybrid systems are presented.

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2. The second requirement is the availability of fast-response, real-time, and on-line sensors, and the associated process control strategies to monitor the quality of purified wastewater and protect the system against any unexpected upsets or surges in impurities. In particular, there is a need for robust metrology methods to prevent potential risks associated with water recycling as well as to demonstrate that recycling, when properly designed and implemented, can save water, reduce cost, and improve water quality. The concept of comprehensive and integrated metrology combined with process control is key in both performance improvement and in cost reduction. The application of sensors and advanced process-control are particularly critical for the operation of the hybrid systems. The available technologies in this area, as well as the remaining challenges that would need further research and development, are reviewed.

2.1 Introduction

There is an ever increasing demand for high purity water in many industries. For example, the water usage in modern semiconductor manufacturing plants easily reach 2–3 million gallons of ultra-pure water per day. The production of ultra-pure water from various feed water sources is a complex process that involves a large number of steps and process units. A generic version of a typical ultra-pure water system is shown in Fig. 2.1.

The feed water goes through three stages of *pretreatment*, *primary treatment*, and *final polishing*. The pretreatment steps typically involve the following steps:

- Softening
- Coagulation
- Sedimentation
- Filtration
- Carbon-bed filtration
- pH adjustment

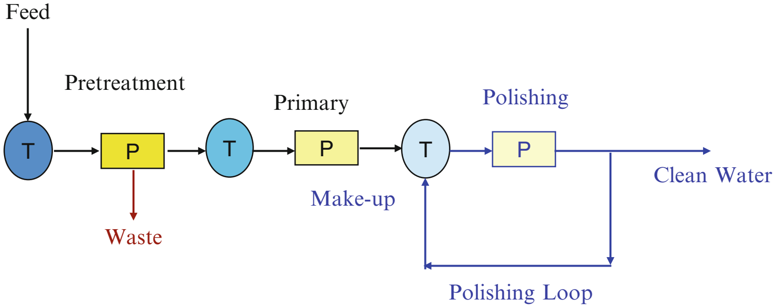


Fig. 2.1 General layout of typical water purification plants

- Chlorination (NaClO)
- Multi-media filtration

The typical feed water has a hardness of 4–110 mg/l and total dissolved solid (TDS) of 10–200 mg/l. The output of the pretreatment stage is conductivity of about 100 μ-siemens/cm.

The primary treatment typically consists of the following steps:

- Ion exchange: cation and then anion, sometimes followed by mixed bed
- RO units
- UV 254 sterilization
- Filtration
- Heat exchange

Front-stage reverse osmosis (RO) units, with typical recovery of about 75–90%, usually are either cellulose acetate, which is a chlorine resistant material, or polyamide thin film composites, with essentially no chlorine resistance. Two arrangements for RO are possible: double pass (product staging) and double stage (reject staging). It should be noted that RO does not remove any low molecular weight organics

Finally, the polishing stage consists of the following unit processes:

- Mixed-bed ion exchange
- Ultra filtration (UF)
- Ultra-violet radiation – UV185 (oxidizer)
- Ultra-violet radiation – UV254 (sterilizer)
- Ozonation

In addition to the above main steps, there are a number of other supplementary treatment processes used in the UPW plants. These include use of additives such as acrylic acid polymers as anti-scaling agents as well as HCl, H_2SO_4, and NaOH during ion-exchange regeneration.

The key solution to reducing water usage and wastewater discharge in the ultra-pure water (UPW) plants is the development of suitable technology for water reuse and recycling. The conservation of water is linked to the usage of chemicals and energy. Consequently, successful water conservation strategies will require innovations in a number of areas. The strategies of decision on recycle or reuse and the overall picture determining the overall environmental impact are shown in Fig. 2.2.

The major factors in design and operation of UPW plants for sustainability are:

- Environmentally-friendly wastewater treatment: This includes lowering both energy and chemical usage.
- Decision on “*reuse*” vs “*recycle*”*:* Cost, environmental impact, and local constraints affect this decision.
- Process control to avoid disturbances and upsets: Sensors and related hardware for recycle control, as well as process control software (process simulator) are key elements of process control.
- Design of recycle configuration: The best use of recycled water

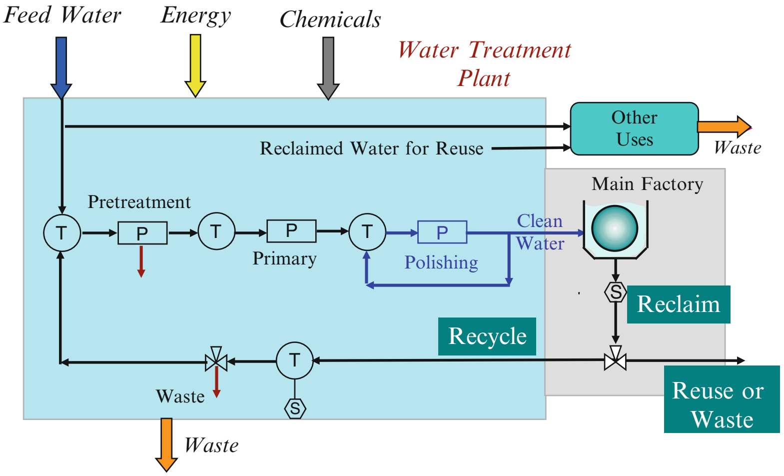


Fig. 2.2 Input, output, and general configuration of UPW systems

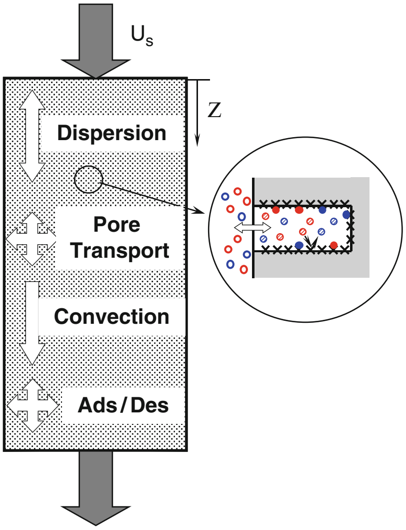
2.2 Issues and Problems in Conventional Water Purification Systems

In this section some of the key issues in purification that require novel approaches and new process innovations will be discussed. For this analysis the treatment processes for removal of organics from water and wastewater can be divided into two categories:

1. Removal by phase separation (capture): The main examples are packed-bed sorption, filters (regular, UF, charge-assisted), and membranes. The main issue for this class of treatment processes is that the impurities removed from water remain in the system.
2. Removal by chemical reactions: The reactions include oxidation, reduction, and decomposition. The main challenge for this class of treatment processes is that these reactions are often slow and require large amounts of energy and chemicals. The fundamentals of impurity removal by capture and the basic equations that form the foundation of any process analysis are shown in Fig. 2.3. Examples of results are shown in Fig. 2.4.

Typically there are four stages in any adsorption bed during the operations:

- Stage 1 is the initial washout period during which bulk flow characteristics and mass transfer effects dominate.
- Stage 2 represents early stages of the operation during which fresh adsorbent exist in some parts of the packed bed.



Adsorbed Phase Conservation:

$$\frac{\partial s_i}{\partial t} = k_{ai}\, p_i \left(\frac{s}{1 + a\, s_i}\right) - k_{di}\left(\frac{s_i}{1 + a\, s_i}\right)$$

Pore Phase Conservation:

$$\varepsilon_p \frac{\partial p_i}{\partial t} + \frac{\partial s_i}{\partial t} = \alpha\, k_{pi}(c_i - p_i)$$

Bulk Fluid Phase Conservation:

$$\varepsilon_b \frac{\partial c_i}{\partial t} + \varepsilon_p (1 - \varepsilon_b)\frac{\partial p_i}{\partial t} + (1 - \varepsilon_b)\frac{\partial s_i}{\partial t} = -U_s \frac{\partial c_i}{\partial z} + D\frac{\partial^2 c_i}{\partial z^2}$$

Sites Conservation:

$$s_o = s + \sum_i s_i$$

Fig. 2.3 Fundamentals of impurity removal by capture

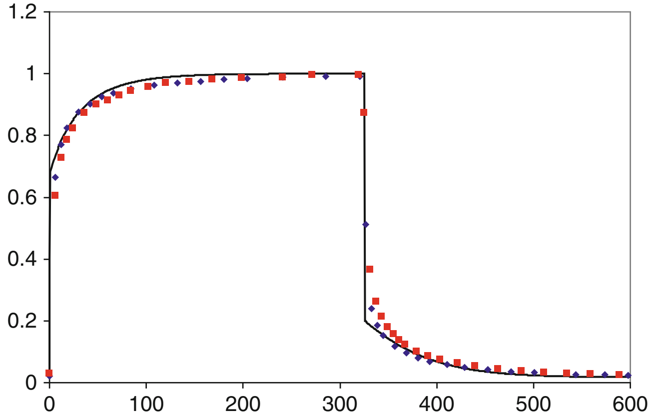


Fig. 2.4 Typical profiles of adsorption and desorption

- Stage 3 is when partial adsorbent deactivation has taken place in all parts of packed bed.
- Stage 4 represents the total bed exhaustion.

These stages are shown in the example illustrated in Fig. 2.5.

One of the key issues in the capture process is the fact that the removal efficiency of the process is highly compound-dependent. For example, Fig. 2.6 shows the difference between the capture efficiency of activated carbon for two

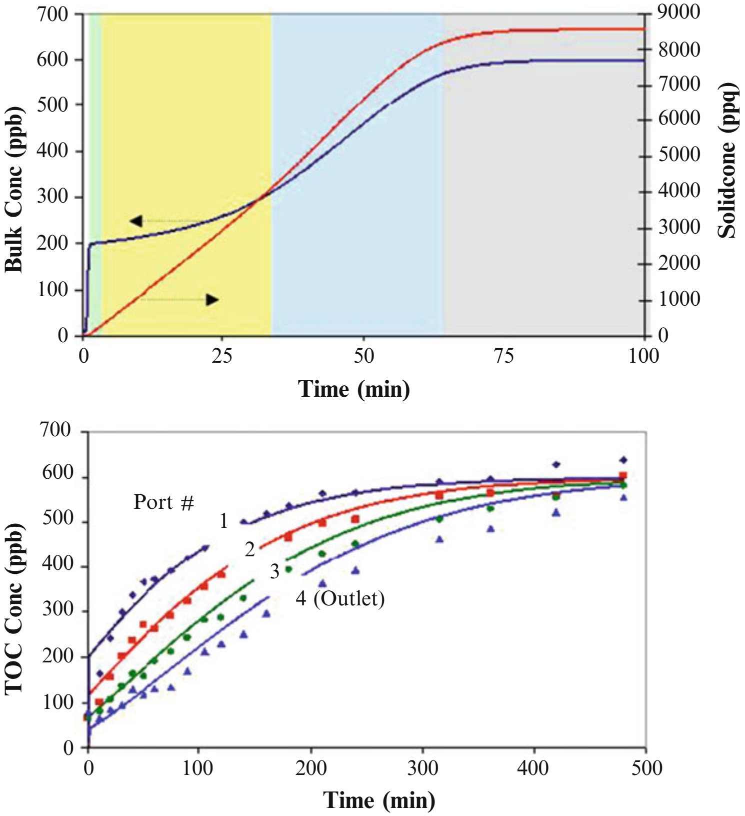


Fig. 2.5 Stages and zones in adsorption beds

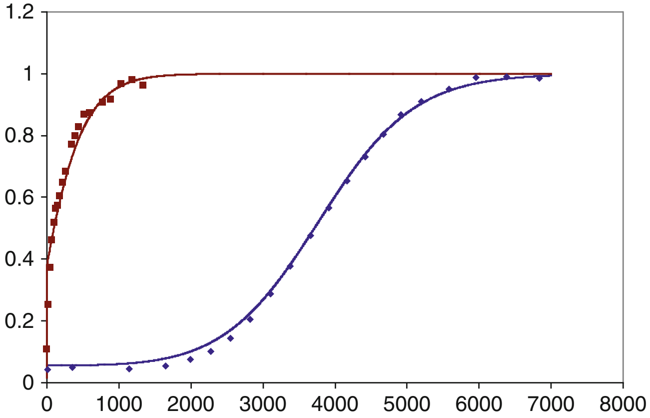


Fig. 2.6 Compound dependence of capture process

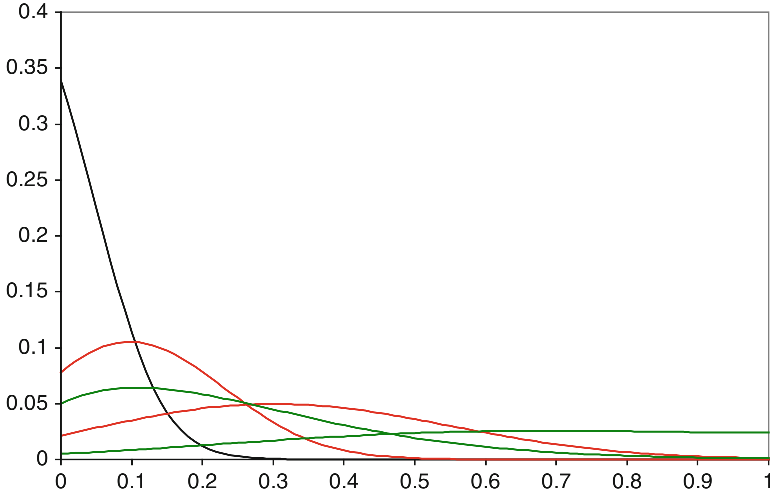


Fig. 2.7 Mobility of captured impurities

organic impurities: isopropyl alcohol (IPA) and chloroform. Multiple beds or multiple sorbents may be required to remove a wide range of impurities present in feed water. The impurities captured in typical adsorption beds are not permanently immobilized. A key issue related to the capture processes is their reversibility of the process and the risk of the release of captured impunity and the re-contamination of water triggered by changes in the operating condition or properties of the feed water. The mobility of impurity in the adsorbed phase is illustrated in Fig. 2.7. This is of particular concern in manufacturing processes where steady and reliable quality of process water is required, and at the same time transient situations causing upsets in the operation are inevitable. An example is shown in Fig. 2.8, where a small change in the water pH due to a spike of pH in water causes the release of organic impurities measured as TOC (total organic or oxidizable carbon).

The other complicating issue is the multicomponent interaction among adsorbates during adsorption of various impurities competing for the sites on the adsorbent. As shown in Fig. 2.9, during the simultaneous adsorption of ethylene glycol and FC-93 on granular activated carbon (GAC); the presence of FC-93 causes the ethylene glycol concentration to overshoot above its equilibrium value.

2.3 Creating Synergy Among Processes by Application of New Hybrid Systems

In this section, examples of new ideas for solving the issues discussed above will be presented. One such idea is the use of a hybrid system, which would combine a number of conventional processes and create more efficient integrated processes

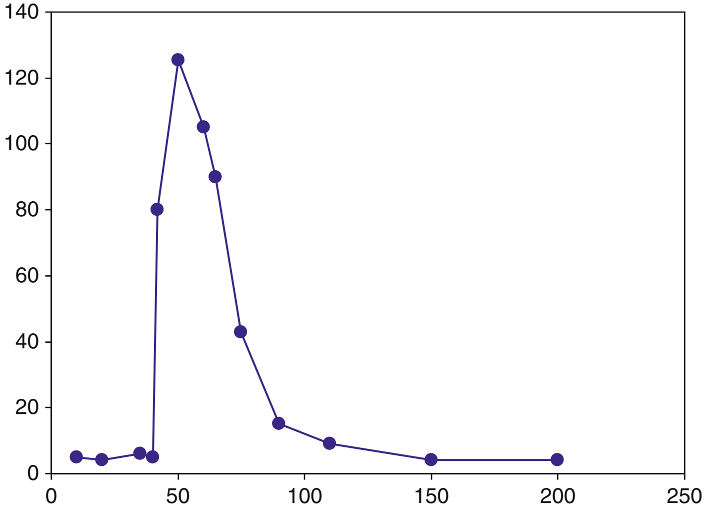


Fig. 2.8 Leakage of impurities from adsorption bed

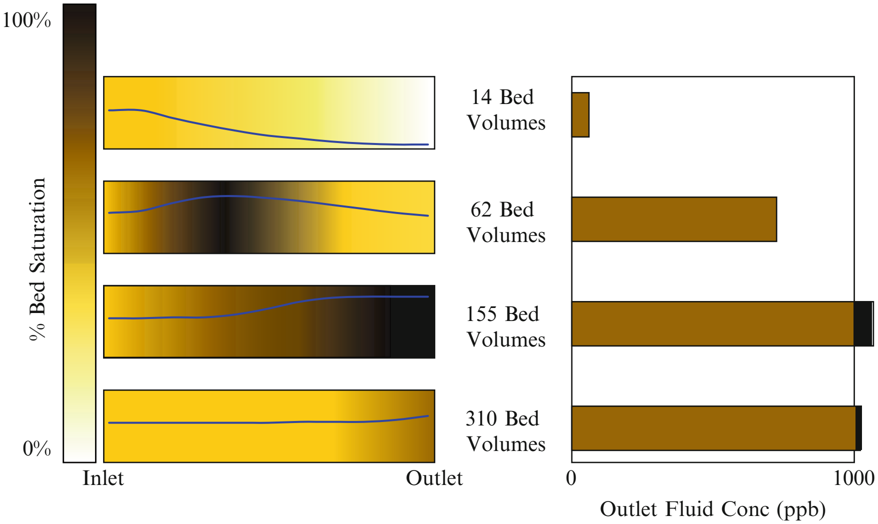


Fig. 2.9 Complex interactions in multi-impurities separation

showing synergistic effects. The synergy basically means that the efficiency of the hybrid combined process is significantly greater than the simple additive effect of individual processes that make the overall system.

In the development of such hybrid processes, the key step is to recognize the primary weaknesses and strength of each conventional unit process. For example,

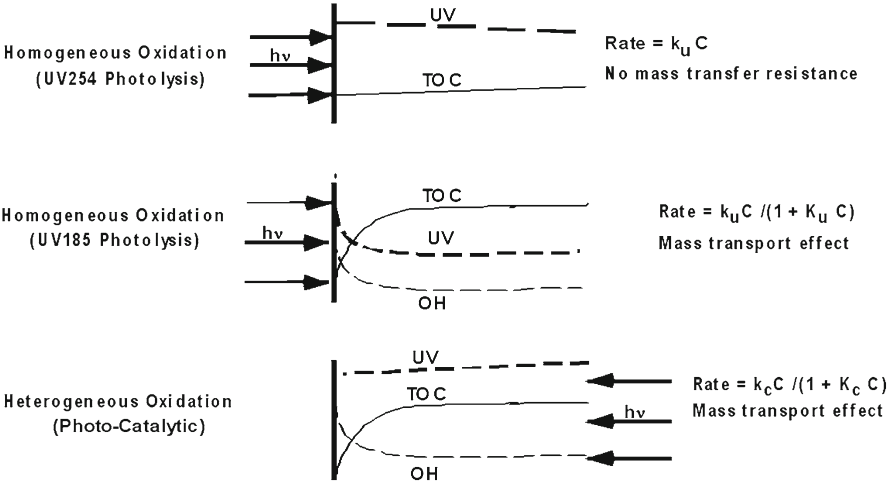


Fig. 2.10 Mechanisms of UV action for TOC removal

considering the removal of total organics (measured as TOC) in water, the removal processes are as follows:

- Capture: Adsorption on packed beds, filters, and membranes.
- Oxidation by ozone: Action through formation of oxidizing radicals causing the lysing of cells.
- Oxidation by other oxidizers: Action through formation of oxidizing radicals.
- Treatment by ultra-violet (UV) radiation: primarily coming in two forms: UV 185 (oxidizer) which causes lysing through radical formation, and UV 254 (sterilizer) which stops cell growth and reproduction. The effect of various forms of UV is illustrated in Fig. 2.10.
- Others: Examples are bio-reactions and reduction reactions.

In general, all options mentioned above fall in two general groups: Removal by capture and removal by chemical reaction. The advantages of removal by capture are fast removal and the availability of well-established unit operations, whereas the disadvantages are the inevitable retention of captured impurities in the system and potential release and re-contamination. The advantages of removal by chemical reactions are possible total removal with no retention of impurities whereas the disadvantages are slow removal rate and potentially higher energy and chemicals consumption.

An example of a hybrid system that combines the advantages of the capture and reaction strategies and essentially eliminates the disadvantages of both is the application of what we call *reactive filtration*. Figure 2.11 shows a specific embodiment of this type of system as a photo-catalytic membrane. In this system the removal process starts with first capture of organics by the membrane, then with complete removal (destruction) of organics by oxidation reaction which takes place on catalytic

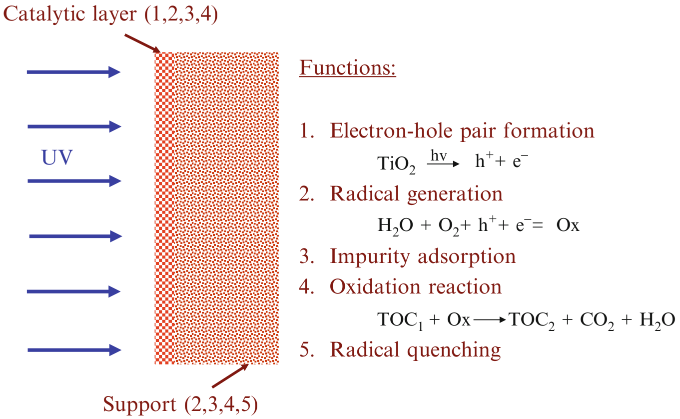


Fig. 2.11 Hybrid system: reactive filtration

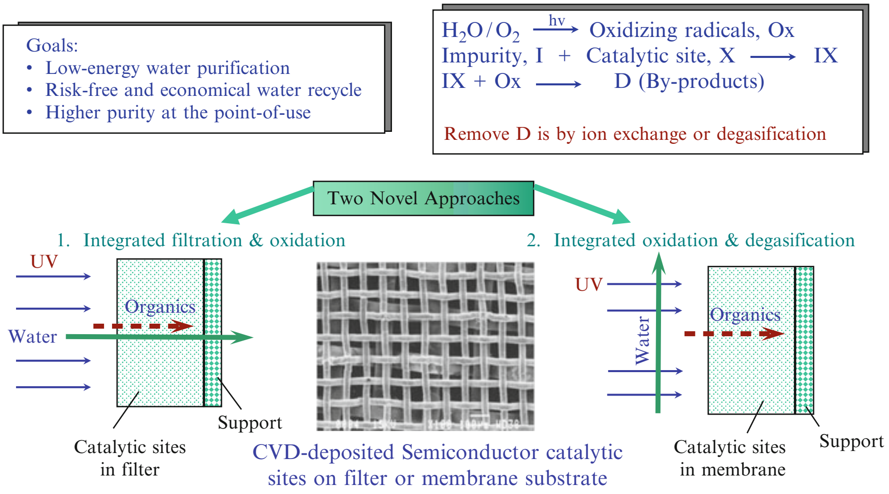


Fig. 2.12 Photo-catalytic membrane

sites incorporated in the membrane and energized by the UV light. A more detailed description of this hybrid system that combines separation and reaction is shown in Fig. 2.12. In this illustration, two flow patterns and configurations are illustrated: one for integrated filtration and oxidation and the other for integrated oxidation and degasification.

Photo-catalytic membranes are a very promising and attractive method of removing low level organics from water in ultra-pure water systems, particularly in the final stages of purification process, as well as for cases where impurities are hard to remove (recalcitrant). Figure 2.13 shows a special experimental setup for testing these membranes used for photo-catalytic oxidation or organics and removal by degasification.

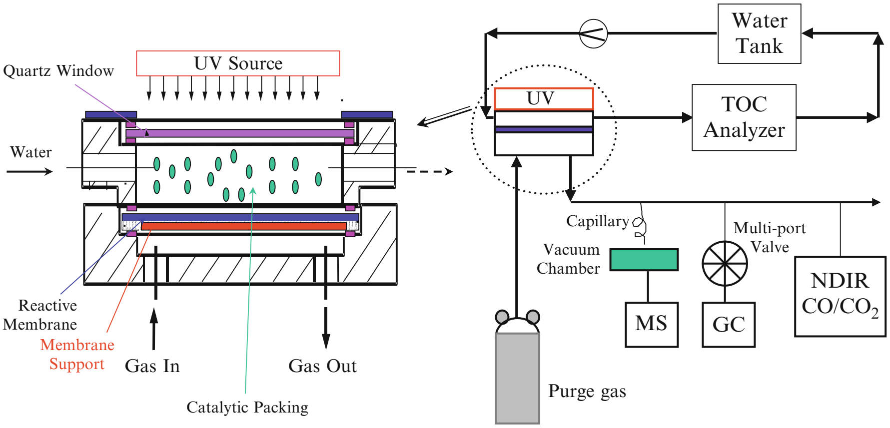


Fig. 2.13 Catalytic membrane test setup

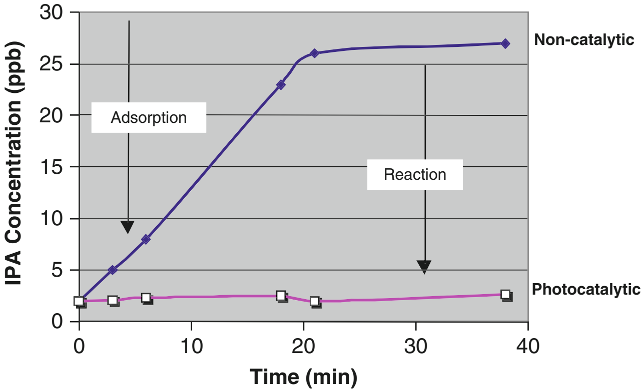


Fig. 2.14 Typical test results for photo-catalytic membranes

The key component of the setup is a test cell which holds the membrane. Figures 2.14 and 2.15 show the test results, using the catalytic membrane for removal of iso-propyl alcohol (IPA) from water. IPA is an organic contamination used in semiconductor fabs which end up in the rinse water discharged from these fabs. It is also a good model compound representing organics with moderate to slow rate of oxidation.

The application of photo-catalytic oxidation for removal of organic from water is an active area of research [5, 8]. In particular, work is going on by a number of research groups to find better catalytic or promoters to enhance the catalytic effect of conventional catalysts such as titanium oxide. A key idea for improvement of catalytic action is the use of promoters. Figures 2.16 and 2.17 illustrate the primary function and mechanism of action of promoters in suppressing the undesirable hole–electron recombination process. As shown in Fig. 2.18, the use of promoters

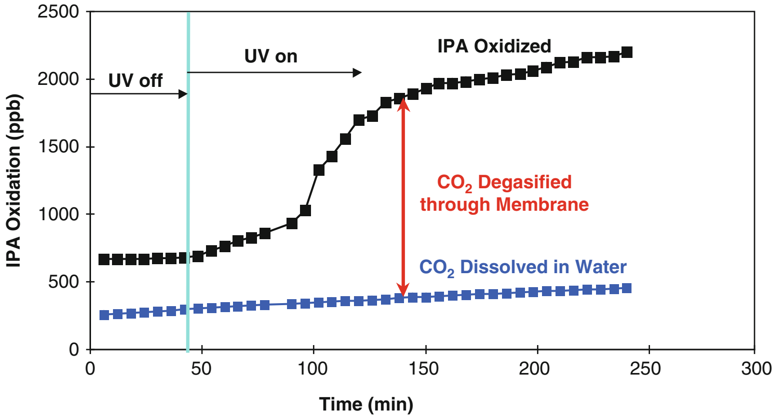


Fig. 2.15 Catalytic oxidation of IPA

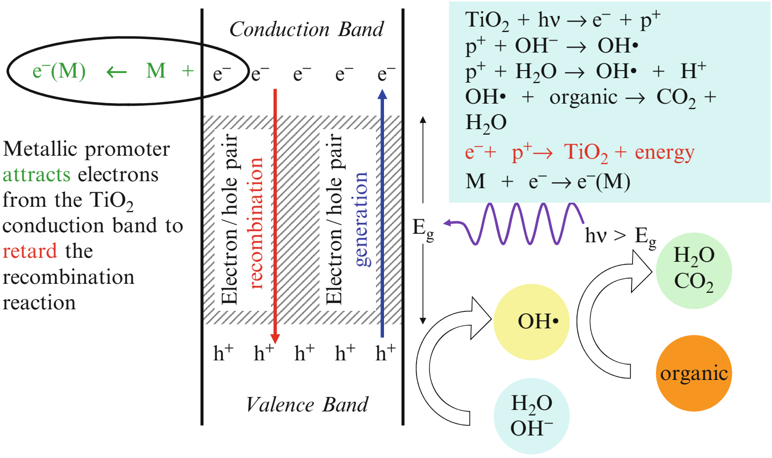
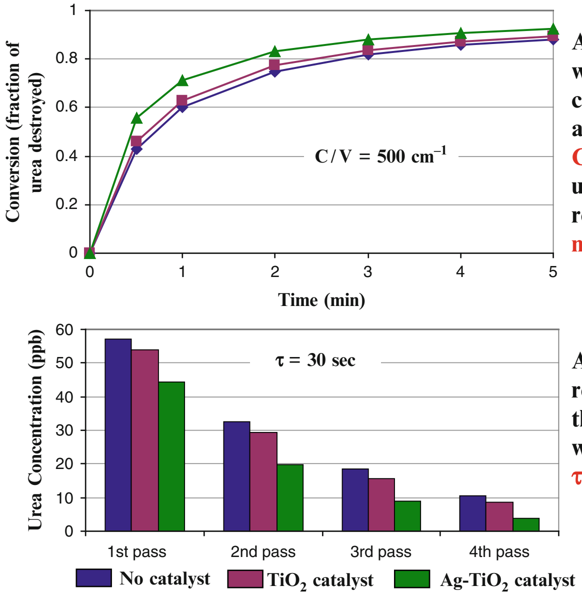


Fig. 2.16 Role of promoters in TiO_2 catalytic oxidation

$TiO_2 + h\nu \rightarrow e^- + p^+$		photogeneration of electron / hole pair
$p^+ + OH^- \rightarrow OH\bullet$		production of radicals
$p^+ + H_2O \rightarrow OH\bullet + H^+$		
$OH\bullet + TOC \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O$		radical oxidation of organic compound
$e^- + p^+ \rightarrow TiO_2 + \text{energy}$	*(undesirable reaction)*	recombination of electron / hole pair
$M + e^- \rightarrow e^-_M$	*(desirable reaction)*	Noble metal, M, attracts free electron slows recombination, and promotes radical generation

Fig. 2.17 Role of promoters in catalytic oxidation



A single pass contact reactor with a Ag - TiO_2 catalyst concentration (catalyst surface area / reactor volume) of $C/V=500\ cm^{-1}$ can achieve a urea destruction of 93% with a reactor residence time of $\tau = 5$ min.

A multiple pass reactor can reduce 100 ppb of urea to less than 5 ppb by the fourth pass with a residence time of only $\tau = 30$ sec.

Fig. 2.18 Comparison of catalytic and non-catalytic oxidation

Deposition of TiO_2 Catalyst

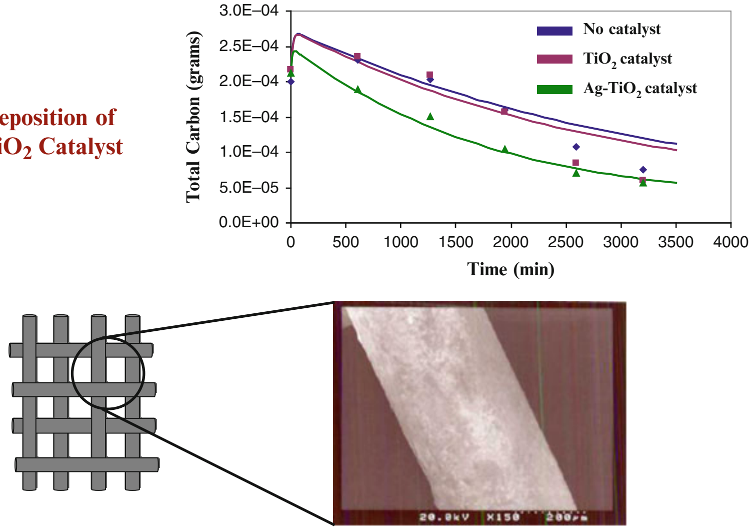
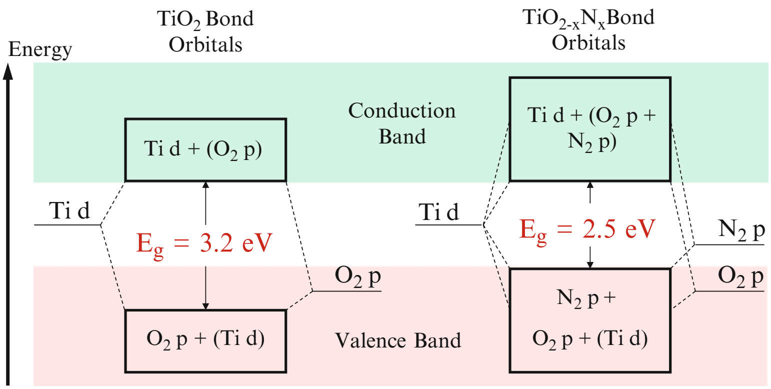


Fig. 2.19 Fabrication of catalytic filters by atomic layer deposition

is a very effective way of enhancing the efficiency of catalytic reactors treating and removing traces of urea (a relatively recalcitrant organic impurity) from water. As shown in Fig. 2.19, these filters can be fabricated by depositing the catalyst using atomic layer deposition (ALD) method.



- Addition of nitrogen increases size of bond orbitals, thus decreasing the energy band gap.

Fig. 2.20 New concepts in TiO_2 catalysis

$$
\begin{aligned}
&O_3 + H_2O \xrightleftharpoons{\text{High pH}} O_2 + 2OH^* \quad \text{pH controlled}\\
&O_3 + OH^* \rightleftharpoons O_2 + HO_2^*\\
&O_3 + HO_2^* \rightleftharpoons OH^- + 2O_2\\
&O_3 + OH^- \rightleftharpoons HO_2^- + O_2\\
&O_3 + HO_2^- \rightleftharpoons OH^* + {}^*O_2^- + O_2\\
&O_3 + {}^*O_2^- \rightleftharpoons {}^*O_3^- + O_2\\
&{}^*O_3^- + H_2O \rightleftharpoons OH^- + OH^* + O_2\\
&OH^*, HO_2^*, {}^*O_2^-, {}^*O_3^-, O_3 + CH_n \longrightarrow CH_m + CO_2 + H_2O
\end{aligned}
$$

Fig. 2.21 Hybrid system: UV – ozone combination

Another approach to enhancing the catalytic effect is by modification of the substrate to lower the band gap energy needed to activate the sites for the hole generation [1, 3, 4, 6]. In case of titanium oxide, the incorporation of nitrogen in the titanium oxide matrix to convert oxide to oxi-nitride has proven to be a promising method to lower the band gap energy; an example of such results is shown in Fig. 2.20.

The hybrid treatment effect can also be obtained by combining the UV with ozone. The combination is shown to be synergistic. The mechanism of this combined synergistic process in shown in Fig. 2.21.

The concept of combining conventional processes to get new integrated systems with synergistic effect can be extended beyond what has been discussed to systems that involve more than two process units [2, 7]. An example of this in a three-stage process is shown in Fig. 2.22. In this three-stage process, the catalytic oxidation is used in stage 1 to completely oxidize (mineralize) some TOC impurities and, at the

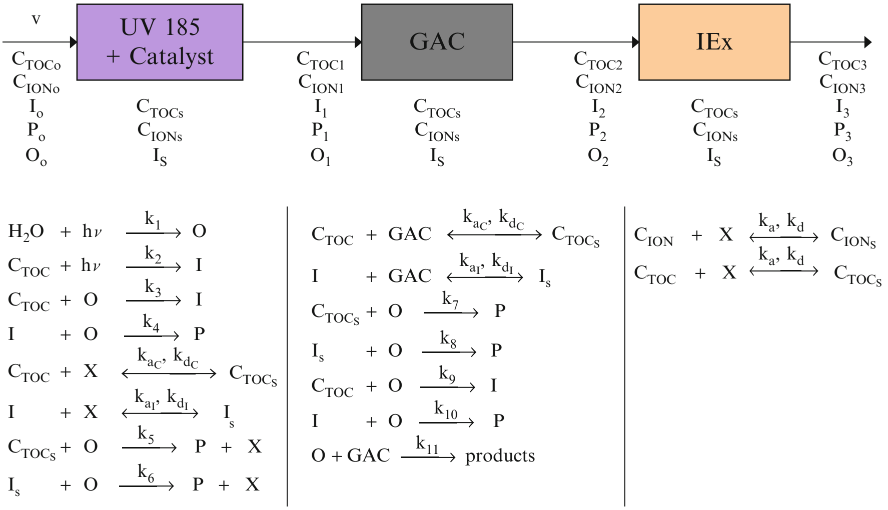


Fig. 2.22 Three-stage hybrid system

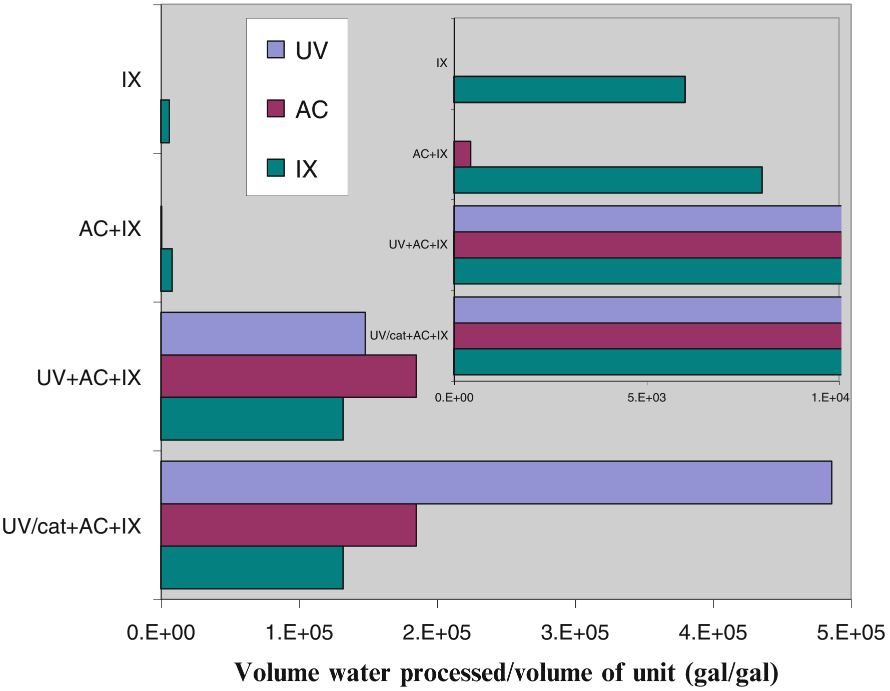


Fig. 2.23 Hybrid purification system performance

same time, partially oxidize or reform other impurities which are recalcitrant to total oxidation. Partial oxidation of these recalcitrant impurities would make them more absorbable on GAC or similar capture process units that follow the first stage. Finally in the third stage, ion exchange is used to remove any ionic impurity that has not been removed in the first two stages and to increase the resistivity of the final ultra-pure water. The role of each unit in this three-stage hybrid process is shown in Fig. 2.23.

2.4 Summary and Conclusions

The key to green technology for water purification is the application of low-energy and low-waste water purification methods. To facilitate this application, novel purification techniques are needed. This does not exclude the conventional processes; in fact, innovative combination of well-proven conventional methods and their usage in hybrid systems can create synergistic efficient processes. The usage of these hybrid new processes can be greatly promoted by the application of a robust metrology method using on-line, real-time, and fast response sensors as well as a process control algorithm.

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Chapter 3
Treatment of Oily Wastewater by Membrane Hybrid Processes

José Coca-Prados, Gemma Gutiérrez, and José Manuel Benito

Abstract Oily wastewaters are usually treated by physical, chemical and biological methods. Most conventional methods (coagulation, sedimentation, centrifugation and filtration) are not efficient in treating stable oil-in-water (O/W) emulsions, especially when the oil droplets are finely dispersed and the concentration is very low. These techniques can reduce oil concentrations by no more than 1% by volume of the total wastewater and cannot efficiently remove oil droplets below 10 µm. Hence, further treatment is needed to meet effluent standards. Membrane processes have found an increasing number of applications in the treatment of complex oily wastewater. However, sometimes it is not desirable or even possible to use a membrane system to carry out the entire separation because of the effluent nature that may cause severe fouling of the membrane. In those situations a pretreatment of the effluent by conventional methods may be suitable for a better process performance. These membrane-based hybrid processes combine a conventional process (mechanical, chemical or thermal) with a membrane separation. In this review lecture the design parameters and performance of conventional processes for the treatment of oily wastewater are summarized and several membrane hybrid processes and chosen examples are presented.

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3.1 Introduction

Oily wastewater comes from many sources and when it reaches the natural environment creates a major ecological problem, often with large impact on human activities. The main sources of oily waters are oil spills from any type of offshore drilling rigs, and the transportation sector (tankers, freighters, barges, and other vessels), and *industrial wastewaters* (petroleum refineries, metalworking industries, etc.).

Most oils spilled into the sea are fuels (48%) and crude oils (29%). The leading cause of oil spills is grounding of vessels (26%), followed by collision (22%), explosion/fire (9%), and tankers (5%), as shown in Fig. 3.1 [24]. It should be noted that half of the oil entering the sea is the run-off of oil and fuel, and oily wastewater from land-based sources.

Refineries generate wastewaters that contain mineral oil and hydrocarbons, often in the form of emulsions, from mechanical operations such as grinding, alkaline degreasing, and transportation. Oily wastewater from metalworking industries has a complex composition containing oil (mineral, vegetable or synthetic), fatty acids, surfactants, extreme pressure agents, biocides, corrosion inhibitors and other chemicals. Food industries generate oily effluents from oil mills (olive, sunflower, palm, cotton seed, and peanut oils). It has been stated that oil waste ending up in sewers and dumps each year is equal to 25 times the amount of crude oil spilled (39,000 t) in the Exxon Valdez accident [24].

Treatment of oily wastewater from any source must be carried out to avoid hazards to aquatic and terrestrial life, and to comply with strict environmental regulations that require a maximum total oil and grease concentration of 10–15 mg L^{-1} in discharge waters. Wastewater generated in oil fields may reach concentrations of oil in the range of 100–1,000 mg L^{-1} [24].

Recycling of process water in the same process or as a replacement for water in another application is a way of saving fresh water supply. Conventional methods for treating oily wastewater will depend on the concentration and physical nature of the oil and the drop size. By analogy with traditional processes in municipal wastewater treatment, methods to treat oily wastewaters can be classified as *primary*, *secondary* and *tertiary*. These methods may not be appropriate for water recycling, as the water chemistry is changed by the treatment process and the presence of heavy metals and dissolved salts makes the water unsuitable for reuse in the process.

Oily wastewater flows are often treated in a three-step process, as shown in Fig. 3.2.

The *primary treatment* is used to remove free oil (D_p >40 μm) and is based on physical separation to settle suspended solids and gravity or centrifugal separation of the broken emulsion. The *secondary treatment* is used to remove the dispersed oil (D_p >20 μm), and it involves coagulation and/or flocculation of the oil drops to break the emulsion, and a change of pH to neutralize the emulsion stabilizers. The dispersed oil is removed by flotation, filter coalescence and membrane filtration. The *tertiary treatment* aims to reduce the concentration of dissolved soluble oil fractions and inorganic salts. Thermal processes (evaporation), reverse osmosis and carbon adsorption are the most common methods used.

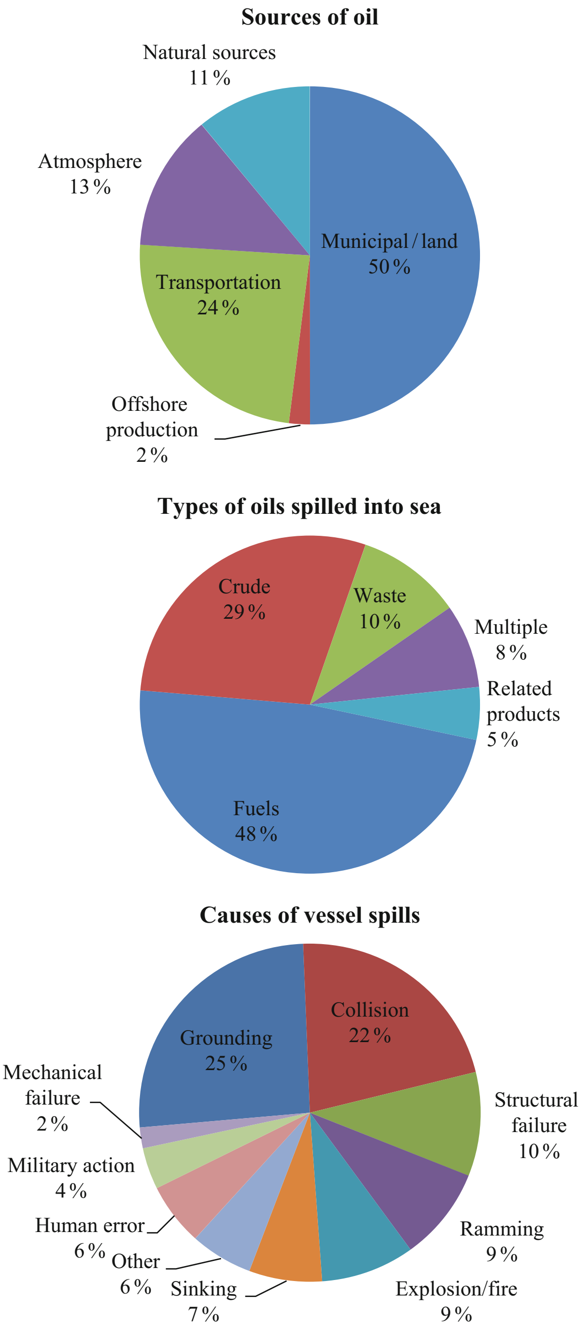


Fig. 3.1 Sources of oil leaked into the seas worldwide [24]

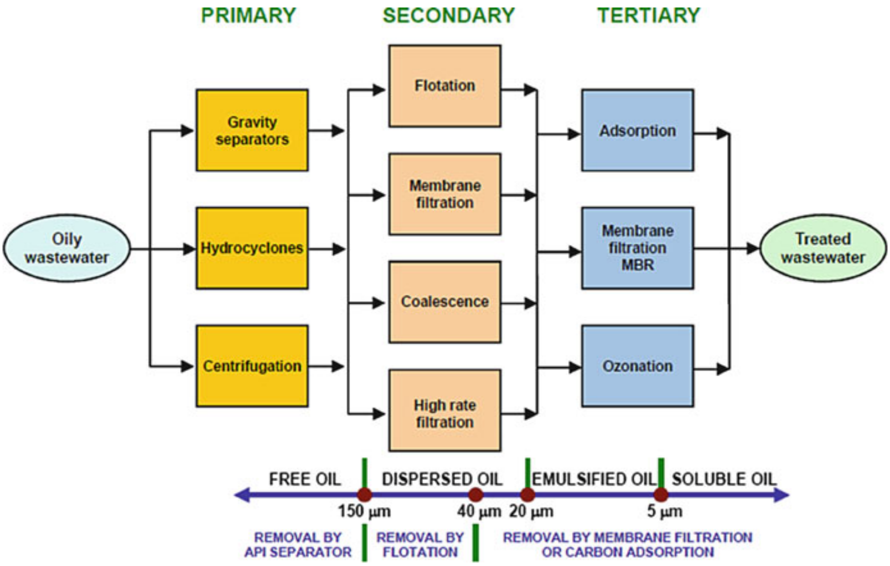


Fig. 3.2 Processes in the treatment of oily wastewater

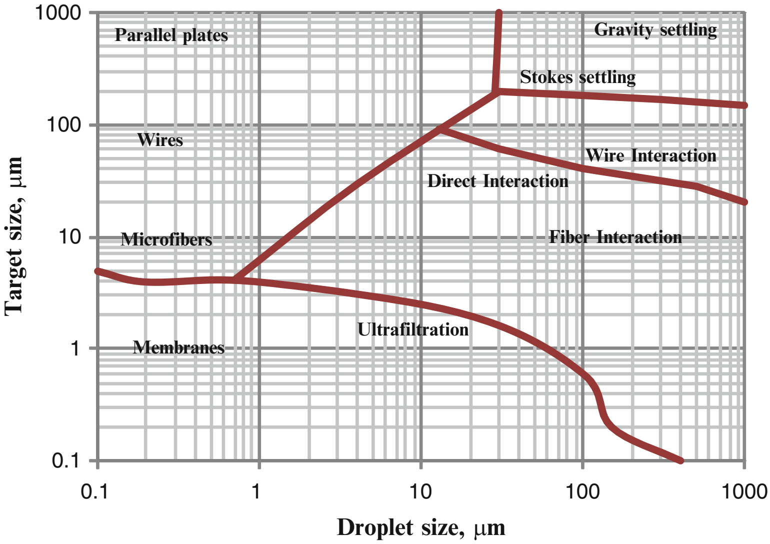


Fig. 3.3 Zones of coalescing mechanisms [4]

Characterization of oil-in-water (O/W) emulsions and their treatment by the aforementioned methods have been discussed in a previous NATO-ATC publication [18]. Figure 3.3 shows the ranges of drop size over which some oily water treatment methods can be applied [4].

Most traditional methods are not efficient for treating stable O/W emulsions ($D_p \leq 20$ µm), especially when the oil droplets are finely dispersed and the concentration is very low. It has been reported that these techniques at the most can reduce oil concentration by 1% by volume of the total wastewater and cannot efficiently remove oil droplets below 10 µm [10, 18]. Hence, further purification is needed to meet effluent standards.

Membrane processes have found an increasing number of applications in the treatment of complex oily wastewater. However, sometimes it is not desirable or even possible to use a membrane system to carry out the entire separation. For example, in some industrial waters, a treatment with membranes may not be practical because of the high osmotic pressures, viscosities, or concentration of the resulting suspended solids. Furthermore, several effluents may cause severe fouling of the membrane, which leads to high energy consumption and high chemical cleaning requirements, and a pretreatment step may be necessary to maintain a high and steady flux through the membrane. In those situations *membrane-based hybrid processes* may be the alternative to obtain a good performance of the process and to extend membrane life. A *membrane hybrid process* is the combination of a conventional treatment process (mechanical, chemical or thermal) with a membrane process. Pretreatment of O/W emulsions prior to membrane filtration is critical for the performance and economics of the process.

The purpose of this chapter is to describe examples of *membrane hybrid processes* for the treatment of oily wastewater. Several industrial case studies of different processes will be described. Finally, some operational parameters and cost analysis will be considered.

3.2 Membrane Filtration

Membranes are a physical barrier to the passage of pollutants in wastewater. They are extensively used for water processing, mainly for water supply treatment (desalination) and wastewater treatment for reuse or disposal. There are four main membrane filtration technologies: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). MF and UF are pressure-driven processes with membranes that typically have pore sizes in the range of: MF (≥0.1 µm, ≥500,000 Da) and UF (0.01–0.10 µm, 1,000–500,000 Da). MF and UF remove particulate matter from a liquid phase, and UF has a high removal capability for emulsions, bacteria and viruses. UF membranes are used for many separations, including oily wastewater treatment. NF (0.001–0.01 µm, 100–1,000 Da) is used to separate materials on the order of nanometers, and is used to remove salts and organic compounds in a wide range of molecular weight. RO (≤0.001 µm, ≤100 Da) removes the salt from seawater, the rejection of NaCl being greater than 95%. Permeation takes place by water diffusion through the membrane while most of the ionic species are rejected. RO is utilized for the production of drinking water or process water (boilers, etc.), and it is used as the final step in the treatment of

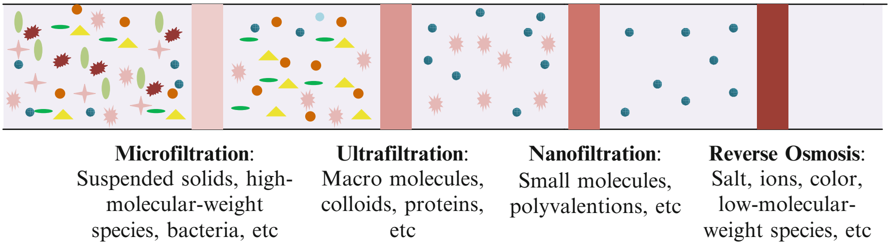


Fig. 3.4 Membrane filtration processes

wastewater, after extensive pretreatment by other methods. Figure 3.4 illustrates the membrane filtration spectrum described above.

MF and UF membranes operate at low transmembrane pressures (ΔP) (MF, ΔP = 2–6 bar and UF, ΔP = 6–10 bar) compared with NF (10–40 bar) and RO (40–60 bar). Lower ΔP extends the useful life of the membrane by reducing membrane compaction. UF membranes may have a service life greater than 8–10 years. However, the main limiting factors for membrane filtration of wastewaters are *concentration polarization* and *fouling*. The existence of a boundary layer of highly concentrated oil next to the membrane (concentration polarization) or the temporary or permanent attachment of colloidal organic and inorganic matter to the membrane (fouling) reduce drastically the permeate flux through the membrane and cause the increase of ΔP. MF and UF provide a good filtration performance, but the membranes become easily fouled.

Membranes can be manufactured from different materials (polymers, ceramic, and metal). They can be electrically neutral, positive, negative or bipolar, which enables membranes to perform different kinds of separations.

3.2.1 Membrane Performance and Interfacial Properties

The membrane treatment of O/W emulsions has been commonly carried out using hydrophilic MF or UF (organic or ceramic) membranes, where the permeating phase was water and any other soluble compounds [2, 14, 26, 75, 89]. The transport mechanism in this case has not been related to any property of the emulsion system.

It is also possible that the permeating phase is oil, instead of water, if hydrophobic membranes are used [81]. The removal of oil (demulsification) exploits the preferential wetting principle, which depends on the interfacial properties of the liquids involved and the membrane. The nonwetting fluid (water) requires a minimum pressure (*breakthrough pressure*) to force it through the membrane, and therefore the demulsification process should be carried out *below* this breakthrough value. The breakthrough pressure for a membrane depends on the pore-size distribution, the interfacial tension between the two liquids, the contact angle of the aqueous (nonwetting) phase on the membrane wetted by the oil (wetting phase) and the size

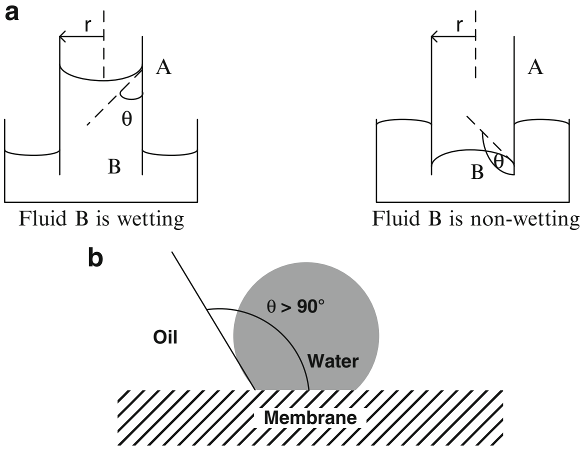


Fig. 3.5 Contact angle at three phase boundaries

and shape of the pores of the membrane. To force a nonwetting fluid through the pores of the membrane, the applied pressure should at least be equal to the pressure drop across the interface, $P_A - P_B$, as given by the Young-Laplace equation:

$$P_{cap} = P_A - P_B = 2\gamma \cos\theta \left(1/r_1 - 1/r_2\right) \tag{3.1}$$

where P_{cap} is the capillary pressure, P_A is the pressure within phase A, P_B is the pressure in phase B, γ is the interfacial tension, θ is the contact angle as measured in phase B (Fig. 3.5a) and r_1 and r_2 are the two radii of curvature for the surface.

The contact angle of a fluid with a solid is a measure of the wettability of the solid by the fluid. The interfacial tension is a liquid-liquid property while the contact angle is a liquid-liquid–solid property. For the two liquid system with a hydrophobic membrane, the contact angle of a water droplet is the angle as measured through the organic phase which is formed at the junction of the three phases (Fig. 3.5b). A contact angle of 0° indicates complete wetting and 180° indicates complete nonwetting.

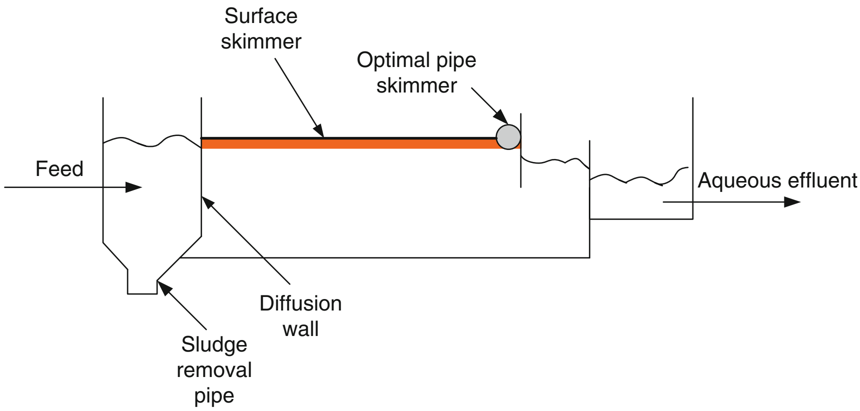
The breakthrough pressure, ΔP_{brk}, for the nonwetting fluid in the pores of a hydrophobic membrane can be obtained by the following equation [43]:

$$\Delta P_{brk} = 2\gamma \cos\theta_{eff} 1/r \tag{3.2}$$

where θ_{eff} accounts for the shape of the pores and was calculated from measurements of the contact angle θ on the membrane surface.

3.3 Primary Treatment: Removal of Free Oil

Oily wastewaters may contain free, emulsified, and dissolved oil. The primary treatment aims at removing the free oils and solids present. The most common methods are *gravity separation* and *centrifugation*. Details on these methods have been described previously [18].



API SEPARATORS	Capacity:100–600 m^3/h		
	Free oil	***Emulsified oil***	***Suspended solids***
Process (chemical/physical)	Physical	Physical	Physical
Addition of chemicals	No	No	No
Removal efficiency (%)	90–95	0	80–95
Effluent quality (oil) (mg/L)	15–20	n.a.	20–30

$$A_H = F\,\frac{Q_m}{v_t} \qquad L = F\,\frac{v_H}{v_t}\,D \qquad A_C = \frac{Q_m}{v_H}$$

A_H: minimum horizontal area
L: length
A_C: minimum cross-sectional area
Q_m: wastewater flowrate
D: oil droplet diameter
v_H: horizontal velocity of the oil droplets
v_t: terminal velocity of the oil droplets
$F = F_1F_2$
$F_1 = 1.2$: short circuiting factor
F_2: turbulence factor

v_H/v_t	F_2
20	1.45
15	1.37
10	1.27
6	1.14
3	1.07

Usually $v_H = 15\ v_t$, but should not exceed 0.91 m min^{-1}

Fig. 3.6 Diagram and design parameters of an API separator [44]

3.3.1 Gravity Separators

API separators. The API separators are often used in refineries, oil terminals and de-ballasting facilities for large flow rates. Separation of oil and water relies on density differences. The oil layer is skimmed off and the bottom sediment layer is removed by a chain and flight scraper and a sludge pump. A diagram of an API separator and the main design parameters and characteristics of API separators are given in Fig. 3.6.

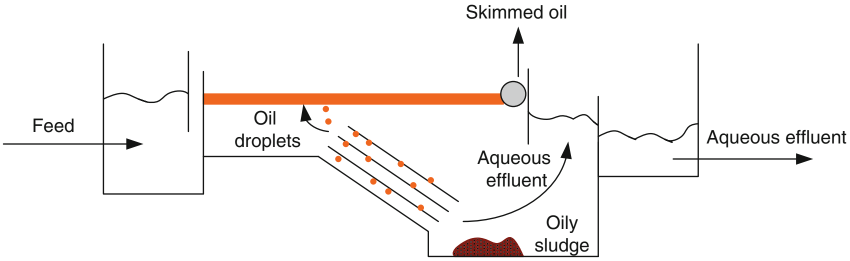


PLATE COALESCERS	Capacity: 15–250 m^3/h		
	Free oil	***Emulsified oil***	***Suspended solids***
Process (chemical / physical)	Physical	Physical	Physical
Addition of chemicals	No	No	No
Removal efficiency (%)	90–95	0 –10	90–95
Effluent quality (oil) (mg / L)	10–15	10 –15	5–10

Fig. 3.7 Diagram and design parameters of a coalescing plate separator [44]

Coalescing plate separators. These are used for oily waste streams with low particulate matter. Coalescing plate separators promote coalescence by passing the oily stream through a set of parallel angled plates. Such device can handle low to medium flow ranges, and for larger flowrates several units operate in parallel. A diagram and some characteristics of a coalescing plate separator are shown in Fig. 3.7.

3.3.2 Centrifugal Separators

Centrifugal separators use centrifugal force, 3,500–6,000 times the force of gravity, to increase the separation rate of oil drops and solid particles. The most common centrifuges used in oily wastewater treatment are the decanter and disc centrifuge and the disc-bowl centrifuge. Some design parameters and particle range application are shown in Fig. 3.8. Because of the moving parts, centrifuges are subject to high maintenance.

Decanter and disc centrifuges. Decanter and disc centrifuges are suitable to separate oily wastewaters containing solids. Two or three phases are formed. Decanter centrifuges may be used for treating fuel oil, bilge water, drain water de-oiling and crude oil dewatering. Flocculation may be carried out upstream by introducing a flocculant into the oily water feed. Capacities are low. A pictorial view and some characteristics of decanter and disc centrifuges are shown Fig. 3.9.

Disc-bowl centrifuges. The disc-bowl centrifuge consists of a rotating bowl and an inner screw conveyor. The bowl acts as the settling vessel for drops and solid particles, and the screw conveyor picks the settled material up and conveys it to the discharge port.

$$D_c = \sqrt{\frac{27Q\,\mu\,\tan\theta}{\pi n \omega^2\,\Delta\rho(r_2^3 - r_1^3)}}$$

D_c: critical droplet diameter
Q: volumetric flow rate
r_2, r_1: distances from the rotating axis to the inlet and outlet of the fluid to the disc
θ: disc half angle
n: number of discs
ω: angular velocity
μ: viscosity of the continuous phase
$\Delta\rho$: difference in densities between the dispersed (oil) and continuous (water) phase

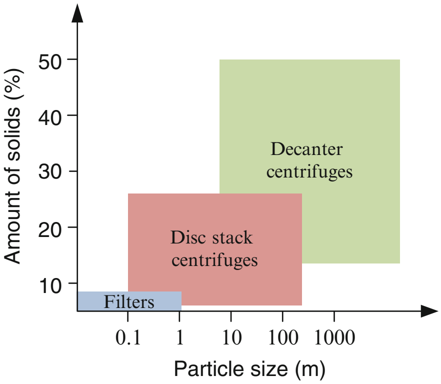
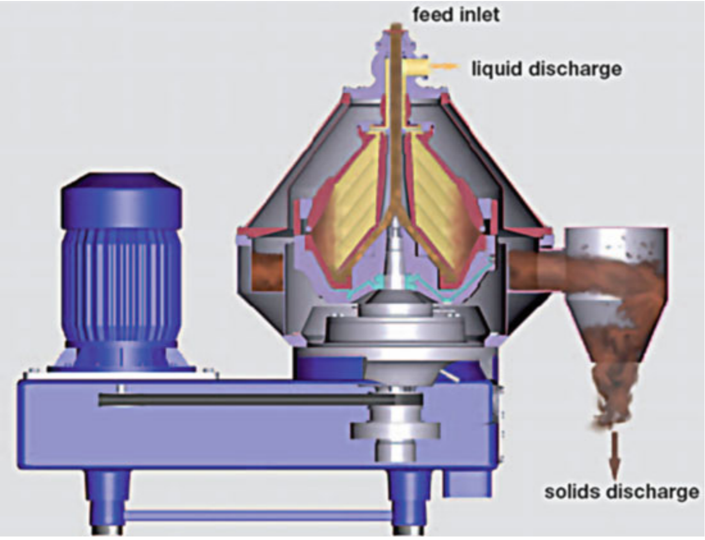
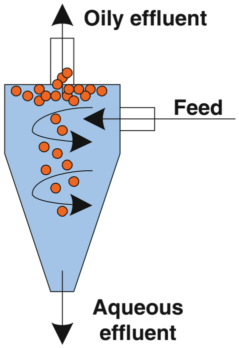


Fig. 3.8 Design parameters and particle range application of centrifuges



DISC CENTRIFUGES	Capacity: 5–10 m^3/h		
	Water from free oil	***Water from emulsified oil***	***Suspended solids from oil***
Process (chemical / physical)	Physical	Chemical/Physical	Physical
Addition of chemicals	Yes	Yes	Yes
Removal efficiency (%)	60–90	40–80	90–95
Processed phases	Water/oil	Water/oil	Water/oil

Fig. 3.9 Pictorial view and some characteristics of decanter and disc centrifuges [44]



HYDROCYCLONES	Capacity: 1–50 m^3/h		
	Free oil	***Emulsified oil***	***Suspended solids***
Process (chemical / physical)	Physical	Physical	Physical
Addition of chemicals	No	No	No
Removal efficiency (%)	80–90	0	90–95
Effluent quality (oil) (mg / L)	20–30	n.a.	5–10

Fig. 3.10 Diagram and characteristics of a hydrocyclone [44]

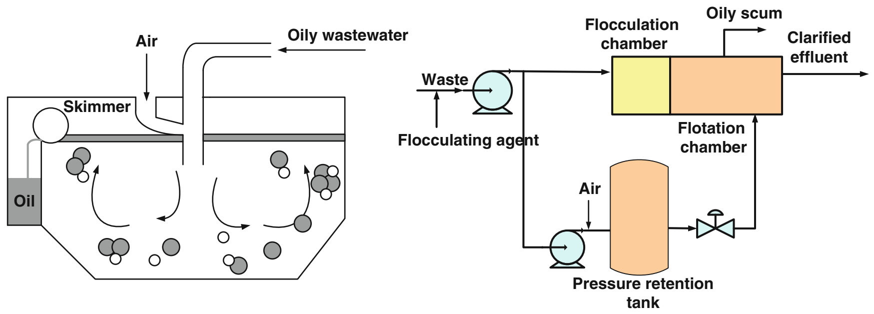
3.3.3 Hydrocyclones

Hydrocyclones can be considered enhanced gravity separators that separate the phases (solids + water) and oil by the spinning-motion forces resulting from the tangential injection of the feed. The separation efficiency is a function of the phase density difference and is usually poor with viscous liquids. Hydrocyclones are often used in the oil industry. Some characteristics of hydrocyclones are shown in Fig. 3.10.

3.4 Secondary Treatment: Removal of Emulsified Oil

The secondary treatment aims at removing emulsified oil. The most common methods are *chemical treatment* (*coagulation* and *flocculation*) and *flotation*. Details on these methods have been described previously [18].

For non-segregated oily wastewaters the secondary treatment process was traditionally a biological treatment (activated sludge or sequencing batch reactors). The final effluent from this process had not the quality of process water, but could meet the effluent requirements to permit direct discharge to the environment.



DAF UNITS	Capacity: 10–500 m^3/h		
	Free oil	*Emulsified oil*	*Suspended solids*
Process (chemical / physical)	Chemical/ Physical	Chemical/ Physical	Physical
Addition of chemicals	Yes	Yes	Yes
Removal efficiency (%)	95–98	95–98	95–98
Effluent quality (oil) (mg / L)	5–10	5–10	5–10

Fig. 3.11 Schematic diagrams and characteristics of DAF processes [44]

3.4.1 Chemical Treatment: Coagulation and Flocculation

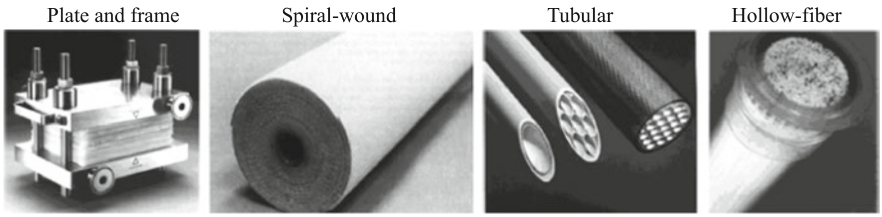
The aim of chemical treatment is to break the emulsion by forming larger flocs that may be subsequently separated by flotation. Coagulants are usually inorganic salts, and organic polymers are used as flocculants.

3.4.2 Dissolved Air Flotation (DAF)

In DAF units air is bubbled into the tank bottom and solids and oil droplets are floated to the top and skimmed off. Optimal performance of DAF requires a preconditioning of the oily feed with the use of coagulants/flocculants. DAF requires a frequent addition of coagulants/flocculants, which is a significant operating cost. Some characteristics of DAF processes are shown in Fig. 3.11.

3.4.3 Membrane Filtration

Membranes have been widely used in laboratory and pilot-plant tests for the secondary and tertiary treatment of oily wastewater. However, they have not been widely used in heavy-duty applications, unless a thorough pretreatment of the oily stream is carried out. Membrane filtration can achieve oil concentrations of 5 mg L^{-1} or less, however fouling and scaling problems lead to poor permeate flux stability. Such procedures are often used on board ships, and therefore they have a low treatment



MEMBRANE FILTRATION	Small unit capacities: 1–10 m^3/h Tailor-made unit capacities: 10–50 m^3/h		
	Free oil	***Emulsified oil***	***Suspended solids***
Process (chemical/physical)	Chemical/ Physical	Chemical/ Physical	In additional pretreatment
Addition of chemicals	Yes	Yes	Yes
Removal efficiency (%)	95–99	95–99	95–99
Effluent quality (oil) (mg/L)	5	5	n.a.
Retentate production (% of flow)	5–10	5–10	5–10

Fig. 3.12 Membrane configurations and characteristics of membrane filtration processes [44]

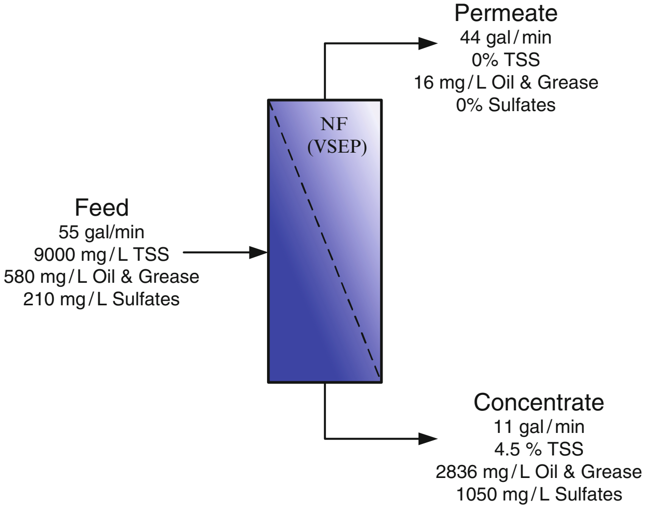


Fig. 3.13 Example of performance with the VSEP system [59]

capacity. Membranes have to be replaced every 3–5 years. Membrane configurations and characteristics of membrane filtration processes are shown in Fig. 3.12.

UF membranes have been commonly used for oily wastewater treatment, but new processes using other membranes have also been developed. A new single-step membrane system, known as *vibratory shear enhanced process* (VSEP) has been used successfully in many applications [58, 59]. It consists of a NF filtration module attached to a torsional vibration mechanism to reduce colloidal fouling and concentration polarization. An example provided by the company is shown in Fig. 3.13.

In this example the total suspended solids (TSS) reduction is over 99%, and the oily waste is concentrated from a starting feed of 1.5–2% to a final concentrate of 10% by weight. The permeate stream can be sewered or reused in the process.

3.5 Membrane Hybrid Processes: Removal of Dissolved Oil

Sometimes it is not desirable or even possible to use a simple membrane system to carry out oil/water separation. For example, in some industrial waters, a treatment with membranes may not be practical because of the high osmotic pressures, viscosities or concentration of the resulting suspended solids. Furthermore, several effluents may cause severe fouling of the membrane and pretreatment is necessary to maintain a high and steady flux through it. In these situations, *integrated-membrane* or *membrane-based hybrid processes* may be a suitable alternative in order to obtain good process performance and to extend membrane life. Membrane processes can easily be integrated into total treatment systems combining several technologies. Nowadays, *membrane hybrid processes* have gained an increasing importance for the treatment of industrial oily wastewaters, combining a membrane separation process with a conventional unit operation (distillation, evaporation, adsorption, solvent extraction, etc.) or with a chemical or biological reaction. The selection of a suitable membrane hybrid process depends on the characteristics of the oily effluent to be treated, and those most commonly used are described in the following sections.

3.5.1 Membrane Hybrid Processes with Mechanical Pretreatment of the Feed

Certain industrial oily effluents may cause severe membrane fouling, and pretreatment is needed to maintain a high, steady flux through the membrane. A typical membrane-based system for oily wastewaters is shown in Fig. 3.14. Usually the process starts with the removal of settleable solids and free-floating oil prior to membrane treatment, mainly UF [38]. This can be accomplished in a tank with free-oil removal equipment, such as a skimmer, or by a rotating brush strainer, a pressure or vacuum filter to remove solids, and a centrifugal separator or a hydrocyclone [80] to remove oil and solids. The remaining oily wastewater is then transferred to a process tank and pumped through the UF unit to remove the emulsified oil. The retentate containing the oil is recycled to the process tank, and the permeate is continuously withdrawn. This process is commonly used in the automobile industry [15]. Up to 98% oil removal efficiency was obtained for a hybrid API separator–UF system [70].

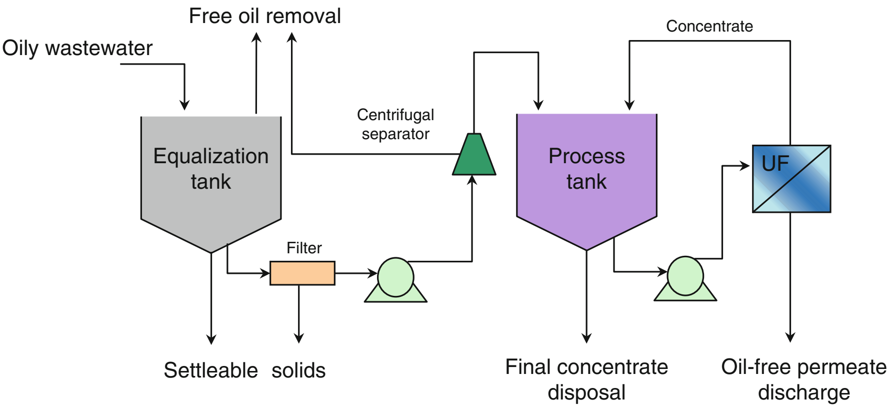


Fig. 3.14 Typical hybrid UF system for oily wastewater treatment

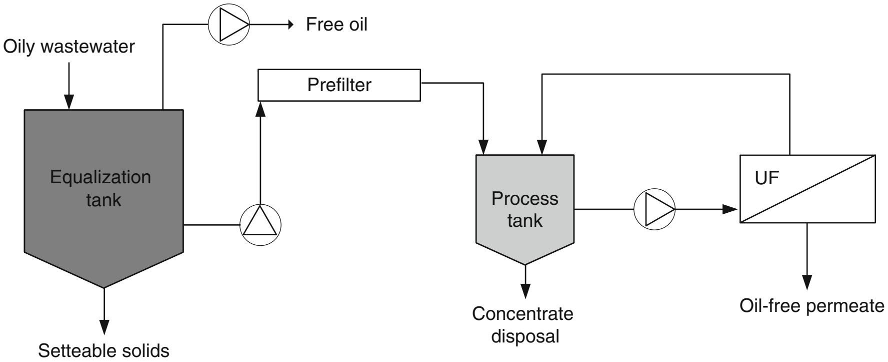


Fig. 3.15 Destabilization/UF hybrid process for oily wastewater treatment [16]

3.5.2 *Membrane Hybrid Processes with Chemical Pretreatment of the Feed*

There are certain processes that use chemical instead of mechanical pretreatment. A common flow diagram of such a process is shown in Fig. 3.15. It consists of a feed tank, a chemical pretreatment stage for O/W emulsion breaking and free oil removal, a UF membrane module and a process tank for retentate disposal. Part of the retentate is recirculated to the UF unit and the permeate is withdrawn continuously. Fresh oily wastewater is added to the feed tank to replace the permeate volume, thus keeping a constant level in the tank. A final concentrate volume is obtained that is only 3–5% of the initial oily wastewater volume. The system is then cleaned until the initial permeate flux is restored. The permeate may require a chemical treatment, after which it can sent to the sewer. An excessive build-up of contaminants must be avoided in the feed/concentrate, since this can lead to mineral scaling on the membrane or irreversible fouling

Coagulation/flocculation is mainly used as a chemical pretreatment [9, 90], being the critical step for the performance of the subsequent membrane stage in order to maintain a high flux and to prevent membrane fouling.

A dissolved air flotation (DAF)–membrane hybrid process is a versatile technology that has been used for the treatment of oily wastewater [7]. A pilot plant test has been scaled up for use in two ferries for bilge water treatment. Results showed that the volume of effluent that has to be treated onshore is reduced six times whereas the regeneration of membrane permeate flux after each cycle is effective, working in continuous operation mode [27].

3.5.3 Sorption/Membrane Processes

Sorption processes involve the use of a material to remove the waste matter (e.g., oil, metals or organics) from wastewater streams and to collect a more purified effluent. Such operation can comprise a filtration process prior to the membrane stage or as a polishing step for the resulting permeate stream.

Filtration has been used widely for the separation of free and emulsified oil. The oily wastewater passes through a filter bed of granular material that either adsorbs oil droplets (deep-bed filtration) or enhances droplet coalescence (filtration-coalescence), so that the purified effluent can be collected at the filter outlet. The oil removal mechanism involves direct filtration, which is based on droplet size, induced coalescence, which promotes the growth of oil droplets, and physical adsorption of the oil onto the filtering material.

Several types of sorbents can be used as filtering material: anthracite coal, sand and gravel, zeolites, cotton fibers, barley straw, hay, peat, vermiculite, polyester, polyvinylidene fluoride, etc. ([3, 5, 17, 20, 36, 42, 50, 53, 57, 62, 92]). Coagulant salt addition to the filtering media helps to promote emulsion breaking and oil coalescence and also to improve waste matter retention [12, 17].

The operating variables that determine the process performance are: the properties of the filter material (porosity, granularity, and composition), feed flowrate, oil concentration and pressure drop through filter media, equipment geometry [3, 5, 12, 20, 47, 49, 67, 71, 79, 85], and properties of the effluent to be treated, mainly pH and temperature [6, 12, 20, 36, 62, 72, 74, 77].

The use of a filtration process as a pretreatment of the membrane stage minimizes membrane fouling and increases removal efficiencies to values higher than 98% [17, 50, 51].

Activated carbon has been extensively used as an alternative for advanced treatment of oily wastewater due to its large specific area and predominant proportion of micropores [93]. Powdered activated carbon (PAC) has the ability to adsorb primarily the lower molecular weight organic compounds, and it shows more affinity

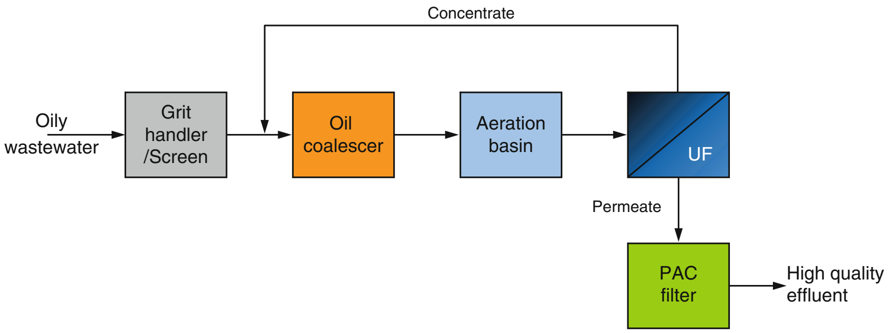


Fig. 3.16 Sorption/membrane hybrid process for oily wastewater treatment in a petroleum refinery

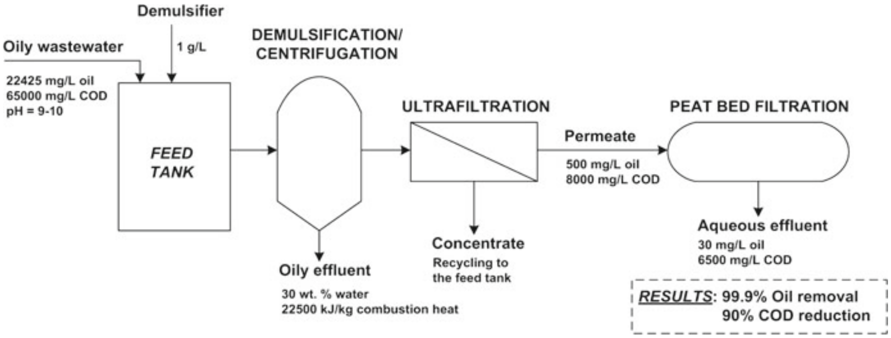


Fig. 3.17 Experimental results for the treatment of a waste metalworking fluid using a hybrid UF process including a chemical pretreatment stage and a peat filtration polishing stage [10, 18]

towards the hydrophobic components. However, activated carbons are expensive and their use may imply activation and reactivation procedures, so they are commonly used in combination with membrane processes.

In some processes PAC is added to the feed circulation loop in order to adsorb the organic compounds and facilitate their rejection by the UF membrane, which lowers the final COD and TOC content of the permeate compared to that obtained by conventional UF or biological treatment. PAC concentration cannot exceed 0.1 vol.% [54]. However, when MF is used instead of UF for O/W emulsion treatment, PAC addition also improves permeate flux and reduces membrane fouling, but it has no obvious effect on TOC removal efficiency [88].

Nevertheless, PAC is commonly used as a polishing step after MF [1], UF [22, 78] or NF [35] treatment in order to obtain a high quality aqueous effluent. Figure 3.16 shows a typical hybrid membrane process configuration for oily wastewater treatment in a petroleum refinery [63].

In some processes, peat filters were used instead of PAC as a polishing stage after UF [10, 11] or NF [58] treatment, as shown in Fig. 3.17.

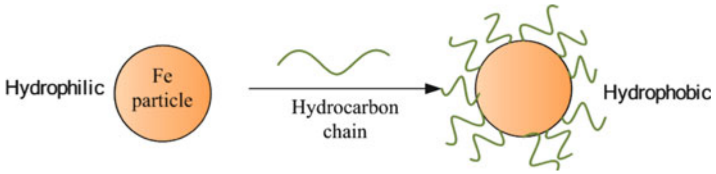


Fig. 3.18 Schematic picture of a Fe particle transformed from hydrophilic to hydrophobic

3.5.4 Magnetic/UF Process

A hybrid magnetic–UF process can be used to remove oil from oil spills. Crude water-in-oil (W/O) emulsions can be treated using surface-modified ferromagnetic particles to remove oil from water and seawater magnetically. Advantages over other mechanical means, such as skimming, dispersants or sorbents, include: (i) the ability to remove oil from a variety of surfaces and from areas difficult to reach (e.g., under piers); (ii) magnetic removal can be employed to remove emulsified oil; (iii) oil-particle mixtures can be easily treated and ferromagnetic particles can be separated from the oil and reused to remove more oil, and (iv) no harmful waste is generated.

The particles, mainly iron (Fe) or iron oxide (Fe_3O_4), can be rendered hydrophobic (Fig. 3.18) by a variety of means (*i.e.* silane functionalization), which allows them to remain in the oil phase.

These functionalized particles must be added to the W/O emulsion under conditions such that the resulting oil-particle mixture remains less dense than the water, but still sufficiently magnetizable so that the oil-particles mixture can be separated with a permanent magnet or an electromagnet [19, 45, 69, 83]. The remaining oil-in-water (O/W) emulsion obtained after crude oil removal by ferromagnetic particles can then be treated by UF to remove the dissolved oil (Fig. 3.19).

3.5.5 Membrane/Thermal Processes

Evaporation is a thermal process used in many industrial applications, including water desalination and wastewater treatment. Evaporation can also be used for the treatment of waste O/W emulsions, yielding a very high quality aqueous effluent which can be reused as process water or for emulsion reformulation. The main problem with this technique is its energy requirements [30, 37], but operation under vacuum conditions helps to reduce operation costs, as it is being used in several wastewater treatment processes [8, 52, 86, 91].

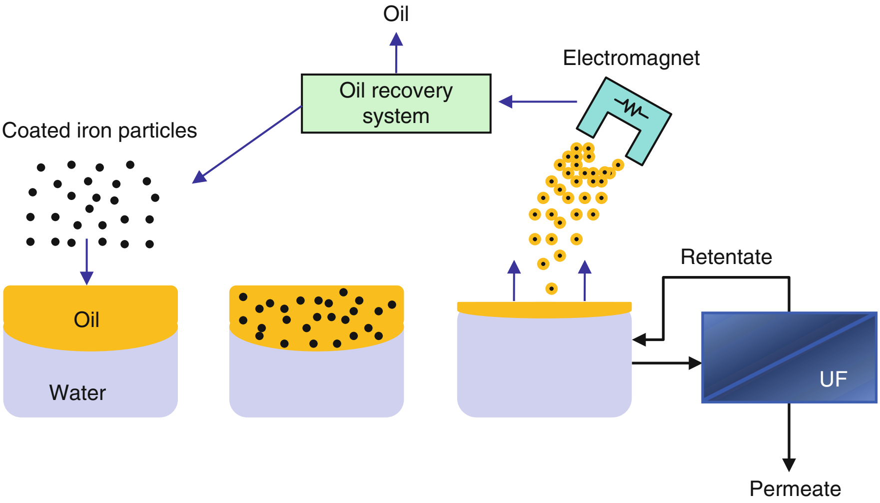


Fig. 3.19 Schematic diagram of hybrid process: magnetic and ultrafiltration treatment

Evaporation is a suitable technique except when the emulsions to be evaporated contain components with volatilities higher or close to water [13]. However, more than 95% oil removal was achieved when treating oily wastewaters using this technique [8, 13, 29–33, 48, 52, 68].

A few examples have been published regarding the effect of operating conditions on evaporation, and it can be concluded that the key operating variables for evaporation are pressure and the heat transferred to the feed [13, 21, 29–32, 48, 52]. As a general rule, an increase in heat transfer increases the evaporation rate but reduces the quality of the evaporated water [29, 68].

Evaporators do not remove the waste oil from the liquid stream; they only reduce the volume of waste, reducing disposal costs. They are easy to operate, they require little space, and the type of oil is not critical. However, cleaning them is labor intensive, and so their use should be considered only when other treatment systems do not work. A coagulation/flocculation pretreatment stage can improve the final aqueous effluent quality and reduce evaporator cleaning cycles [31, 33].

A hybrid process, shown in Fig. 3.20, was proposed for the treatment of a waste O/W emulsion from a copper rolling process. It was a demulsification/centrifugation–ultrafiltration process, where the permeate stream from the UF unit was treated by vacuum evaporation [29, 30]. More than 99.8 % of COD reduction was achieved.

Sometimes the aim is the retentate treatment, not the permeate, especially when used oils can be regenerated. In this case a hybrid UF/distillation or UF/evaporation process was performed [73]. The benefits of these processes are lower energy consumption, since large amounts of water are removed by the membrane unit, which requires less energy than an evaporator or a distillation tower.

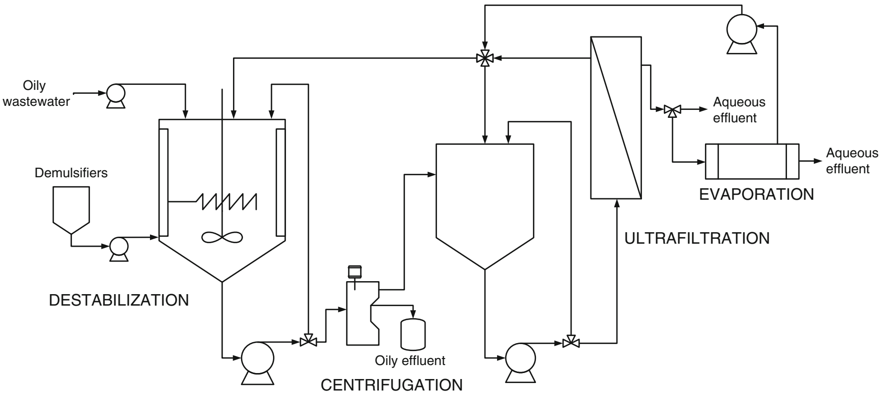


Fig. 3.20 Integrated treatment of a waste O/W emulsion from a copper rolling process

3.5.6 Dual Membrane Processes

Oily wastes can sometimes be treated by a combination of two membrane processes to obtain a high-quality water effluent. Purification of oily wastewaters has been accomplished by a combination of two or more membrane processes. Several oily effluents have been treated by these hybrid processes: oily wastewaters from engine-rooms [40] and from automotive industries [61], metal finishing wastewaters [84], spent O/W emulsions from copper wire drawing [39], waste metalworking fluids [34], crude oil desalting effluent from an oil refinery [60], and bilge water from ships [82].

MF/UF process. Hybrid MF/UF systems have been used for the treatment of bilge water, an oily wastewater that accumulates in the lowest internal part of a ship. Peng and Tremblay [64–66] treated a synthetic bilge water employing a pilot-scale membrane cascade system consisting of a backflushed carbon MF membrane used as a pre-treatment and a polymeric hollow fiber UF membrane. The permeate from the MF membrane was treated by UF as a final polishing step. The system was effective in reducing oil and grease content in the permeate below the allowable discharge limit (15 mg L^{-1}) for coastal waters. Similar results were obtained for bilge water treatment using an UF/photocatalytic process [41], and also for an alternative UF/membrane distillation (MD) hybrid system [28].

UF/NF process. An UF/NF integrated membrane system has been applied to treat a spent copper wire drawing emulsion [39]. The UF process allows complete removal of suspended solids, with 99% of oil and lubricant rejection. After applying the NF process, the content of organic compounds in the permeate, expressed as TOC, was below 1 mg L^{-1}, with a 92% rejection of copper ions. The permeate from this process can be directly reused for fresh emulsion reformulation. The use of UF prior to the NF leads to considerable fouling reduction of the NF membrane and also improves the quality of the final permeate.

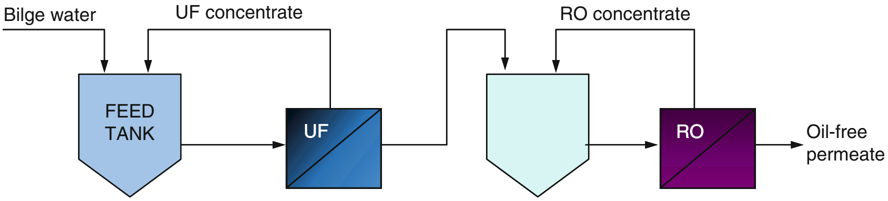


Fig. 3.21 UF/RO treatment of bilge water [82]

UF/RO process. An integrated UF/RO process has also been used for the treatment of bilge water. For instance, Tomaszewska et al. [82] have studied the influence of each stage on the wastewater treatment, concluding that during the first stage 95% of the oil was removed, whereas the RO stage removed more than 99.7 % of turbidity and suspended solids (Fig. 3.21).

Another example is the UF/RO treatment of oily wastewaters from the automotive industry [61]. UF was used to separate and concentrate the oil and suspended material from the O/W emulsions. The permeate goes through RO membranes. This process was performed in two plants: the first was designed to treat 20,000 m^3 of wastewater per year, and had a UF stage with tubular membranes, a RO stage which reduced ten times the waste volume in the UF permeate, and an evaporation stage to reduce the volume of the RO concentrate. The second plant was designed for 15,000 m^3 of wastewater per year, with two UF and one RO stages. The first UF stage consisted of hollow fiber membranes, and permeate then passed through a spiral wound cellulose acetate membrane. The purpose of the second UF stage was to increase the lifetime of the RO membranes and the flowrate of the permeate. The concentrate of this second UF unit was recycled to the first one and the permeate was fed into the first RO stage. This stage was divided into two sequences with a short settling time between them. In the first one, the wastewater was concentrated five times and, after the settling time, the concentrate went back into the RO membranes again and was reduced by half in the second sequence. Removal of 97% COD and 98% BOD was achieved at both plants.

NF/RO processes. The largest source of oily wastewaters originates from onshore and offshore oil and gas production. The waters produced constitute the single largest waste stream from oil and gas exploration and production activities, and their treatment could improve the economic viability of oil and gas fields and lead to water reuse. Total dissolved solids (TDS, mainly inorganic salts) in produced waters can be as high as 360 $g\,L^{-1}$ [23], and their treatment by conventional methods is complex and expensive. An NF/RO hybrid process has been developed for the treatment of produced waters [55, 56] because of its capacity for oil and salt removal. Two commercially available NF plus low-pressure RO thin-film composite membranes have been used to treat three produced waters. Up to 84% of TDS removal was achieved, resulting in a permeate that may be used for various purposes such as livestock and crop watering.

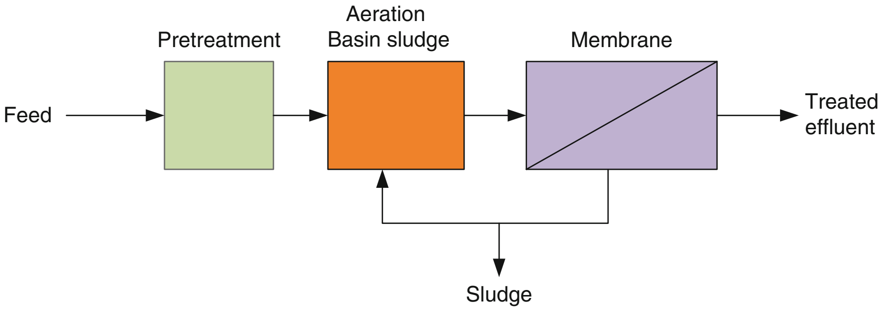


Fig. 3.22 Combined biological and tertiary treatment in the membrane bioreactor process

3.5.7 Membrane Bioreactors

Most methods for physical treatment of oily wastewater do not remove the pollutants completely, but just transfer them to a more concentrated waste, without removing the soluble components. Conventional biological processes have a low efficiency because of the inhibitive effects of toxic substances and hydrophobic nature of oil components.

Membrane bioreactors (MBR) have been widely applied to wastewater treatment in recent years. The MBR process operates as a conventional activated sludge process in which solid/liquid separation is accomplished by a membrane (Fig. 3.22), that replaces the secondary sedimentation tank.

This technology is in operation mainly at automotive plants and uses UF membranes to treat metalworking fluid wastewaters containing toxic and recalcitrant organic compounds. In these plants the UF unit retains oil and grease, which are biologically degraded in the aerobic reactor, obtaining a final effluent with less than 6 mg L^{-1} of oil and grease [46, 76, 87].

MBR characteristics and operation are discussed in another lecture in this volume [25].

3.6 Treatment Costs of Membrane Hybrid Processes

Treatment costs for oily wastewaters depend on the type of oil present, being lower for free oil removal and increasing successively for dispersed, emulsified, and dissolved oil removal. However, it is very difficult to make a cost comparison among the techniques described in this lecture, because treatment costs are not only a function of the technique employed but also of the equipment used.

Compared to other treatment methods, membrane technology results in fairly quick payback periods, operation is simple, effluent quality is consistently good,

Table 3.1 Running cost of typical UF and NF membrane processes

	Cost, \$/m^3 permeate			
	UF 100 L/m^2	UF 120 L/m^2	UF 150 L/m^2	NF 80 L/m^2
Investment	0.17	0.14	0.11	0.21
Power	0.15	0.13	0.11	0.21
Replacement membrane	0.11	0.09	0.07	0.17
Cleaning	0.01	0.01	0.01	0.02
Total running	0.27	0.23	0.11	0.41
Total	0.44	0.37	0.30	0.61

results are usually immediate, and chemical usage can be substantially reduced [16]. However, capital costs are higher than for most of the conventional technologies.

Membranes are more likely applicable to oily wastewater treatment where process volumes are less than 190 m^3 per day. Beyond such a flowrate, and depending on the oil and total solids concentrations in the influent stream, membrane hybrid processes are the most frequently used for the treatment of oily wastewaters at industrial scale and in order to reach the most severe discharge standards, to achieve better oil separation efficiency, and also to reduce total costs. Running costs of typical UF and NF membrane processes (Table 3.1) depend mainly on the type of membrane process and the permeate flux.

3.7 Conclusions

Oily wastewaters are generated in many industrial processes, and fats, oils and greases present have to be removed before the water can be reused in a closed-loop process or discharged into the sewer system. Oil in wastewaters may be of mineral, animal, or vegetable origin, and it is usually classified as free, dispersed, emulsified or dissolved oil. A specific oil–water separation process for each kind of industrial effluent may have to be implemented, depending on the physical nature of the oil present.

Treatment of oily wastewaters can be considered similar to the treatment of municipal wastewaters: the primary treatment is used to remove the free oils from the other oil fractions and the secondary treatment is used to break O/W emulsions and to remove the dispersed oil, whereas finely dispersed, emulsified and soluble oil fractions are removed in the tertiary treatment.

Gravity separation is the most common method used to remove free oil in oily wastewaters. Chemical treatment may be used with oily emulsion wastewater for the removal of suspended or colloidal oil. Membrane processes are used to remove finely dispersed, emulsified (using MF and UF) and soluble oil fractions (using NF and RO).

Treatment costs for oily wastewaters are lower for free oil removal, and they increase for dispersed, emulsified and dissolved oil removal, respectively.

A combination of two or more separation processes (integrated or hybrid) are the most frequently used for the treatment of oily wastewaters at industrial scale. Hybrid membrane processes may reduce total production cost, energy consumption, capital cost, and give a better oil separation efficiency.

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Chapter 4
CUBEN, A Novel Bioreactor for the Removal of Nutrients

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Abstract The applications, management and processing of wastewater have experienced an extraordinary transformation in the last two decades. Methods and terminology once the domain of disciplines like Chemical Engineering or Microbiology, are incorporated in the academic programs of water/wastewater treatment. Terms like “aeration tank”, “tricking filter”, “retention time”, which often denoted simple physical unit operations in Civil Engineering, have been replaced by “reactor”,“fixed bed reactor”, “residence time ” and the concept of “waste” is being replaced by “resource” from where materials, heat or electric power, can be recovered, recycled or transformed. What used to be management and disposal of waste is being replaced by processing of a resources to obtain value added products. In this context, the configuration or topology of a conventional wastewater treatment plant is being replaced by that typical of a chemical engineering processing plant. This article gives a brief description of the evolution of wastewater engineering, and the unavoidable replacement of the horizontal geometry of the “tanks” by vertical reactors. These reactors offer a much smaller construction surface, exhibit a greater operational flexibility than conventional horizontal basins, and deliver equal or superior process performance. CUBEN (US Patent; Publication No. US-2012-0031836-A1) the first vertical nutrient removal bioreactor comes to meet those criteria. Its design allows the successful incorporation of processes like ANAMMOX eliminating one of the disadvantages of ANAMMOX: the presence of low dissolved oxygen concentrations (DO) in the effluent from the secondary

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treatment. The results presented herein show that DO can be virtually 0 mg/L in the anaerobic section, the elimination of nitrates in the anoxic stage exceeds 98% and the concentration of phosphorous in the effluent can be reduced to less than 1 mg/L without the addition of any salt or chemical. Optimization of the process with the optimum process control is underway.

4.1 Introduction

The development of effective technologies for the processing of wastewater began with activated sludge and rotating biological contactors early in the twentieth century in Europe. Only in the last two decades water engineers have begun calling bioreactors what they still call "tanks" and wastewater is increasingly seen as a resource rather than a "waste". Indeed, practicing engineers have started exploring bioreactors other than activated sludge and its versions. The evolution of effective wastewater treatment technologies has been slow and exhibits a pronounced lack of innovation. This is especially truth when compared to far more complex wastewater treatment plants used in the chemical industry where the processing of hazardous wastes or the recovery of valuable "wastes" like proteins, fat and grease, valuable metals from catalysts, steam, heat etc. have been implemented for decades. To the chemical engineer, water/wastewater treatment does not offer any professional challenge that her/his professional background cannot overcome. That is, whereas water engineers from other disciplines must refurbish their professional curriculum with non-trivial additional subjects, chemical engineers are exceptionally well prepared to offer the best possible solutions in water/wastewater engineering. Fundamental subjects like simple chemical nomenclature and formulation, chemical and microbial kinetics, thermodynamics, chemical/biochemical reactor design, etc. are part of conventional chemical engineering programs. This raises some questions as why lack of innovation is so prevalent in the North American (Canada and United States) wastewater industry. This anomaly observed by some worker [1], in Canada and in the USA [2] is confirmed by the data presented in Yale University's Environmental Performance Index (2012 EPI Policymaker Summary). There are multiple causes for the failure to incorporate effective technologies and regulatory processes in the treatment of municipal/domestic wastewater. These are explained below.

In the present article we glance at the processes used in nutrient removal including both conventional denitrification and Anammox process, and phosphorous removal with special emphasis on CUBEN, a novel vertical bioreactor [3].

4.2 Innovation in Wastewater Treatment

Since ancient times, water supply and wastewater disposal have been the domains of Civil Engineering inasmuch as the discipline is associated to the development of the infrastructure of the city (roads, building, aqueducts, sewers, etc.). In this sense, construction played a central role in the management of both water and wastewater management and the main instruments for the management of water and wastewater were sewers and aqueducts. Thus, the effective construction of facilities for both services was of paramount importance since the impact of chemical and biological pollution were minor relative to the availability of water or the unsanitary accumulation of sewage. Furthermore, because of the low scientific development, pollution prevention was in its infancy so that construction was the only option leading to improved sanitary conditions. As urban populations grew and both demand for potable water and disposal of wastewater became a major public health issue, civil works expanded and water and wastewater began to be processed. Thus, at the end of the nineteenth century and beginning of the twentieth appear in Europe the first municipal works leading to the management and treatment of water and wastewater. Early efforts by urban societies (Mediterranean, Mayan, Babylonian, and Indian, among other cultures) are historical testimonies of the vital importance of water treatment and wastewater disposal. By the middle of the twentieth century operations like screening, classical settling, biological treatment based on the activated sludge process, chemical flocculation, sand filtration and chlorine-based disinfection had a widespread use in industrialized societies. However, water supply was based on abundant resources from aquifers and rivers, and wastewater disposal was the only method considered both economically and socially accepted practice. More recently “externalization”, an euphemism used by economists, was the method favored by polluting firms to escape their environmental responsibilities at the expense of the tax-payer. In the 1960s, domestic wastewater and sources of drinking water became increasingly loaded with complex chemicals, pesticides, solvents, etc. of industrial or domestic origin. Their impact became publically unacceptable and newly created environmental agencies issued unprecedented effluent standards, regulations and enforcing policies. At this stage, water engineers were largely civil engineers with experience in civil construction and water works (sewers, filters, tanks, topography, hydraulics, fluid mechanics, etc.). Environmental Engineering in North America became part of the Departments of Civil Engineering with some being part of the Departments of Chemical Engineering. Terms like “trickling filters”, “aeration tanks” or “septic tanks”, “retention time” convey the idea of physical unit operations with no allusion to the main role played by chemical /biochemical processes. Currently, the acronym MBR (membrane bioreactor) is used erroneously by many water engineers as a reactor (exclusively an activated sludge reactor) where a membrane is incorporated to separate the biosolids generated in the secondary and tertiary treatment. Indeed, many of these practitioners think that there is only one type of reactor (Activated sludge).

The recognition of the impact of complex chemicals in domestic wastewater occurred in the 1980s–1990s when many of the methods used in chemical engineering, like reactor analysis, calculation of residence time distributions [4], [5] and gas/liquid mass transfer models [6] were introduced in some texts on the design of wastewater treatment plants.

In the last 20 years water engineering has moved slowly from focusing on solids and BOD removal in secondary treatment to biological nutrient removal, energy recovery, ultrapure water, micro-pollutants removal. These areas are the domain of Chemical/Biochemical Engineering.

The use of innovative technologies in Canada is very unequal. Some provinces, including Ontario, adopt conservative, even obsolete policies and do not create incentives to introduce effective processes and technologies. This is consistent with engineers/decision makers not familiar, or uncomfortable, with technologies outside their conventional experience in civil construction. This outdated knowledge is the basis for the selection of treatment technologies by decision makers, and environmental agencies which have been slow at incorporating innovative methods and technologies. Even European countries with good environmental technologies, like the Netherlands exhibit a poor environmental record in the area of nutrients removal as very high concentrations of nitrates and phosphates gravely affect its soil and surface water [7]. Thus, the causes for this conspicuously slow progress in wastewater engineering include:

1. Human negligence and greed where profits are a higher priority than public health.
2. Engineering practitioners/decision makers unfamiliar with disciplines fundamental in the efficient design of bioreactors, including chemical and microbial kinetics, thermodynamics, chemical reactor engineering, and membranes technology.
3. Political decisions based on electoral criteria rather than on sound engineering and economic principles. For example, the province of Ontario has hundreds of thousands of disabled, polluting septic tanks even though there are available perfectly effective decentralized wastewater treatment technologies.
4. Regulatory barriers and costs prevent the performance evaluation of new technologies in adequate testing facilities. The approval of a promising technology in Ontario demands very high testing costs since Ontario does not have any testing facilities and must rely on distant testing installations (Michigan State, province of Quebec). Thus, to install and obtain certificates of approval, can be a major hurdle in the commercialization of new technologies. These costs and bureaucratic impediments discourage small but innovative firms.
5. Canada is a country with abundant resources including land availability and abundant, if unevenly distributed water resources. The current horizontal configuration of wastewater treatment plants is very wasteful and lacks retrofitting flexibility. Once built in an urban environment, conventional facilities are difficult to expand or modify since they are not modular.

The incoming Wastewater Treatment Plants, now being tested [8] will operate as Chemical Process Industries and new configurations of wastewater treatment plants will exclude or drastically reduce,

- the extensive use of excavation and civil works,
- the massive use of concrete , and
- the large footprints prevalent in the conventional, planar configurations of WWTP.

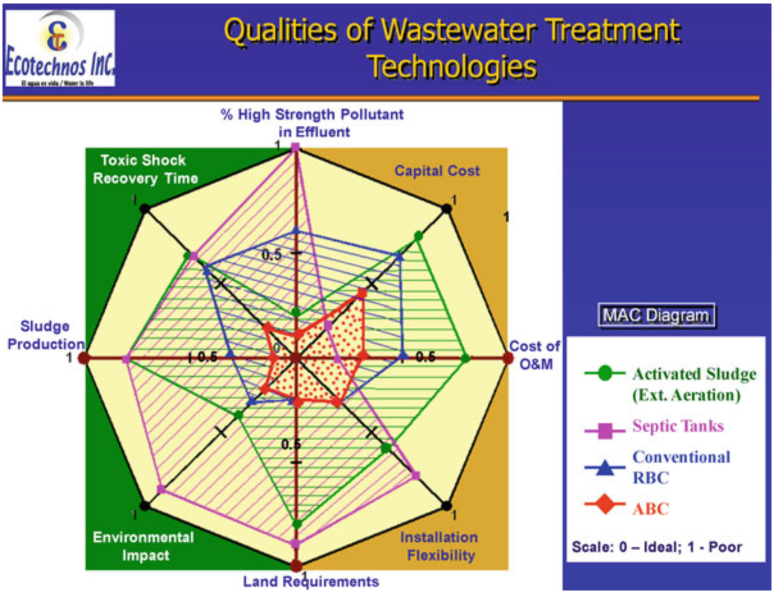
Considering that chemical and biochemical products and reactions are the main source of pollutants and hazardous products, it is easy to understand why the discipline of water/wastewater treatment can only offer effective solutions within the chemical/biochemical framework. That is, within the perspective of a chemical process industry where the feed is wastewater, and the products are energy (heat and power), phosphorous, fertilizers, fat, oil and grease for subsequent processing, etc. Municipal WWTPs are becoming chemical process plants like, say, oil refineries, and wastewater is becoming a feed that can yield value added products. In North America, advanced decentralized WWTP are few and vertical bioreactors, mainly packed columns, have been used with limited success.

4.3 Characteristics of WWTP

Secondary treatment in most of the WWTPs are based on suspended growth technologies that is, Activated Sludge and Sequencing Batch Reactors. The importance of Fixed Film technologies (Rotating Biological Contactors and Fluidized Bed Reactors) has been recognized early but their rigorous design demands an understanding of processes with which water engineering practitioners are seldom familiar and that barrier has not been overcome yet. A number of desirable characteristic define an advanced WWTP. These are:

- High, consistent performance
- Competitive capital costs
- Operation and maintenance costs
- Energy recovery
- Low land requirements
- Low sludge production
- Fast toxic-shock recovery
- Low Environmental Impact
- Installation flexibility and simplicity

It is evident, that many of the wastewater treatment processes do not meet but few of the above features. Furthermore, additional professional, bureaucratic and political barriers multiply the constraints to use effective and advanced technologies. Figure 4.1 [9] shows a comparative diagram of some wastewater treatment technologies and their characteristics. Rigorous analyses of performance can be both time consuming and exceedingly difficult exercises. This is so because the basis for comparison are not standardized and the number of performance variables are numerous including, construction area, superior performance, energy requirements/recovery, capital costs, process consistency and operation simplicity. Thus only qualitative performances based on experienced practitioners can produce useful comparative analysis shown in Fig. 4.1 and Table 4.1. In the diagram numerical weights from 0 to 1 are given to the eight qualities considered more relevant in the evaluation of a technology. The ideal value for a given quality is 0 and the worst value is 1. Thus, activated sludge or the hugely popular rudimentary technology like the septic tank, have large areas whereas fixed film technologies like rotating biological contactors and active biological contactors (RBC and ABC) have low areas



Qualities of Wastewater Treatment Technologies

Fig. 4.1 Comparative evaluation of technologies used in wastewater treatment

and higher performance. In Fig. 4.1, the "ideal" technology would have zero surface area (Represented as a red dot in the center of the diagram). Powerful technologies like three-phase fluidized beds are not represented in the diagram because of insufficient data. Larger areas correspond to more inefficient processes.

Additional performance features of the best known processes are listed below

.

THE IDEAL WASTEWATER TREATMENT TECHNOLOGY

- ✓ Superior performance
- ✓ Competitive prices. Outstanding cost-benefit. Quick ROI
- ✓ Specially suited for high-strength industrial wastewater
- ✓ Modular configuration, compact, flexibility to be compatible with other technologies
- ✓ Low energy consumption and high energy generation
- ✓ Easy installation and maintenance, and low operating costs
- ✓ Superior capacity to overcome toxic shocks
- ✓ Lower sludge production than that by activated sludge processes
- ✓ Low noise and low odor generation

Table 4.1 Comparison of eight selected WWT technologies

Comparative evaluation of technologies									
Secondary waste water treatment technologies for high-strength flows									
Technologies	Land required m^2/person	Environmental impact sludge production	Tolerance of toxic shocks	Residence time of wastewater	Modular configuration	Performance removal % BOD TSS ammoniac	Operation monitoring/ control	Cots	
								Operation and maintenance	Capital
Aquacan Active Biological Contactor (ABC)	Very low 0.25	Very low very low sludge production	Very high housing required	2 days	Yes, easy contruction and expansion	>96 >96 >96	Low, easy to operate	Low energy requirements	Moderate
Activated sludge (Ext. Aeration)	High 1.08	Low high sludge production	High housing require	4 days	No	>96	High sludge recirculation difficult to monitor and control	High	High
SBR (experimental)	Moderate 0.89	Low	Housing require	3 days	No	>94	Very high difficult to monitor and control	High O&M cost	High
Aerated lagoons	Very high 5.95	Very severe Algaes growth See page Evaporation Offensive odours	Weather dependent Raining Freezing	60–150 days	No	Low shortcircuits and very inefficient 30%	Poor process control poor understanding	Low high possibility of losses	Moderate
RBC	Low 0.51	Low Low sludge production	High housing require	3 days	Yes easy construction and expansion	85–90	Low	Low energy requirements moderate O&M	Moderate

(continued)

Table 4.1 (continued)

Comparative evaluation of technologies									
Secondary waste water treatment technologies for high-strength flows									
Constructed wetland	Very high 7.27	Very high High sludge production	Low	5.5 days	No	Low 68–78 30–80	Low	Low	High
Trickling filters	Very low N/A	Very high filter fly Offensive odours	Weather dependent	0.5 day	Yes	40–80	High numerous control problems	High	Moderate
Septic tank + Leaching bed	Not suitable for industrial/domestic; high–strength wastewater, obsolete technology								
Membrane filters	Very expensive. Not suitable for industrial; high–strength wastewater								

A wastewater treatment plant consists of many stages and chemical/biochemical processes. Some of the stages or processes, like gross solids separation, have not experienced great improvements or innovations since their first introductions in WWTP. Others, like nutrient removal, power generation, or membrane applications, have experienced major innovations and are fully commercial.

As a result of excess nutrients in water and their severe economic and social impact, the interest in the removal of nitrates and phosphates from surface waters has acquired a very important dimension in the last two decades. Indeed, most of the process/mathematical models and technologies were proposed in the 1990s and later. All those processes have not offered yet a model that satisfactorily explains their microbial kinetics. Furthermore, all the processes occur in planar basins of very large surface area. In addition, because of it the flows and mixing are difficult to monitor and control, and the use in retrofitting older plants is very limited precisely because of the absence of modularity and large surface area of (BNR) plants.

In the following pages we give a glance at the economic impact of eutrophication, followed by a description of both existing BNR technologies and the novel vertical bioreactor (CUBEN). The performance results are also presented.

4.4 The Environmental Impact of Excess Nutrients

Eutrophication is the most important water quality issue around the world. This is not only an ecological problem but also a serious threat to people's lives as it deteriorates the recreational areas and water resources. Devaluation of real estate, loss of tourism, and water toxicity are examples of societal issues in connection to eutrophication. This environmental problem causes annual economic losses over $3 billion in Europe, North America, and Asia.

The excessive concentration of nutrients such as phosphates and nitrates in surface and ground water is currently one of the major environmental concerns. The high nutrient concentration in lakes, rivers and surface water in general causes severe reduction in water quality and is a serious threat to aquatic life. Eutrophication is the result of excess concentration of nutrients which magnifies the growth of algae and plankton. This in return disrupts the balanced growth of aquatic life. The uncontrolled growth of plankton, algae and other aquatic vegetation depletes dissolved oxygen in water (hypoxia) which is detrimental to fish, marine mammals and many other organisms.

Human induced eutrophication, and subsequent hypoxia, is produced by both agricultural runoff and to incomplete treatment of industrial, municipal and domestic wastewater discharged into lakes and rivers. The phosphorus release from human sources is part of synthetic detergents, food waste, food additives, human fecal matter and other household products. Also, the use of fertilizers in farming increases the phosphorus build up in the soil which is ultimately washed out into the ground water [10].

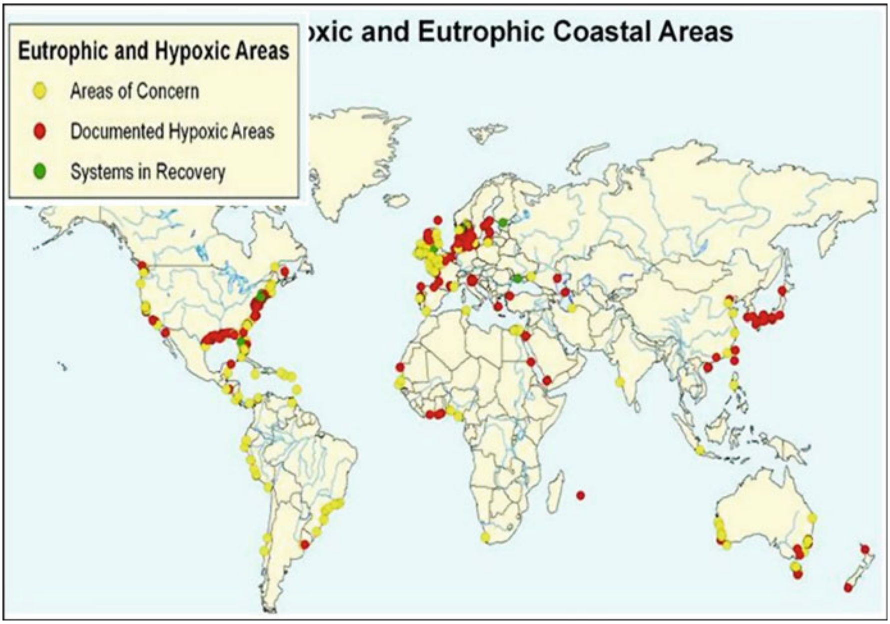


Fig. 4.2 Coastal hypoxic and eutrophic areas of the world [12]

The economic losses due to eutrophication have become a major environmental issue in many countries around the world. The annual economic losses in USA is reported over \$2.2 billion per year [11], and \$105–\$160 million per year in England and Wales. The Netherlands, with the highest number of livestock per head in Europe produce very large amounts of manure. With small land surface and high population soil water pollution is inevitable [7]. Similar phenomena occur in the Baltic Sea and the state of Sao Paulo in Brazil where the economic impact of eutrophication is extremely high [22]. Figure 4.2 highlights and maps 415 eutrophic and hypoxic coastal areas worldwide in which 169 are hypoxic areas, 233 are areas of concern and 13 are areas in recovery from eutrophication [12]. This figure illustrates the dramatic global deterioration of the ecosystems.

The treatment of eutrophic water is a costly and long term process [11]. For example a 50% reduction in total nitrogen and phosphorus concentration of dead zones costs over \$3.86 and 0.436 billion US respectively. Therefore, the best solution to protect water quality is to reduce nutrient concentration from wastewater before it is released into the environment. The world-wide need for the development and deployment of an efficient, reliable, cost-effective and compact technology for nutrient removal is a fundamental issue. A full description of the technology has been filed with the US Patent Office ("Compact Upright Bioreactor for the Elimination of Nutrients" Inventors: M. Alvarez Cuenca and M. Reza, Publication No. US-2012-0031836-A1).

4.5 Biological Nutrient Removal

Ammonia/Nitrate/Organic Nitrogen and Phosphates are major nutrients affecting water quality and threatening the environment. Biological Nutrient Recovery and Removal (BNR) is an important area of water engineering. Chemical removal (by precipitation) of phosphates is an old and very simple method but because of the necessity of chemical salts, it is expensive. Furthermore, the handling of the produced sludge makes chemical nutrient removal a labor intensive process. This process is being utilized when operation simplicity is required or small amounts of chemicals reduce P concentration to regulatory levels after BNR has been used.

Thus, whereas BNR of ammonium and nitrates has clearly shown its superiority over physicochemical methods, biological phosphorous removal is, due to its greater complexity, taking longer to be incorporated as the process(s) of choice in WWTP. We present next a brief look at BNR processes and most frequently used bioreactors for nutrient removal.

4.6 Biological Removal of Nitrogen Compounds

There are two biological processes. One well established; (1) Nitrification-Denitrification and (2) Anaerobic Ammonium Oxidation (ANAMMOX) of most recent development. This process is still under evaluation in demonstration plants or incipient commercial plants.

4.6.1 Nitrification-Denitrification Process

This process involves two sequential biological treatments including aerobic nitrification and anoxic denitrification. Normally, the nitrification process oxidizes ammonia (NH_3) to nitrite (NO_2^-) and this one to Nitrate (NO_3^-). This takes place in the secondary treatment of WWTP after or along with BOD removal. The effluent from the secondary treatment contains mostly phosphate and nitrate since nitrite is very unstable and is quickly oxidized to nitrate. Further removal of nitrate requires an anoxic phase which occurs in the tertiary stage of the wastewater treatment plants. Under anoxic condition, nitrates are reduced by denitrifying bacteria instead of dissolved oxygen, and oxidize the organic matter in water. This process is called Denitrification which can be carried out independently or in conjunction with phosphorus removal.

Denitrification is the reduction of NO_3^- to N_2 by certain heterotrophic bacteria commonly named denitrifiers. The denitrification process requires anoxic conditions with adequate amounts of carbon source. Anoxic conditions refer to the presence of combined oxygen in the form of nitrate, nitrite and sulfate and absence of

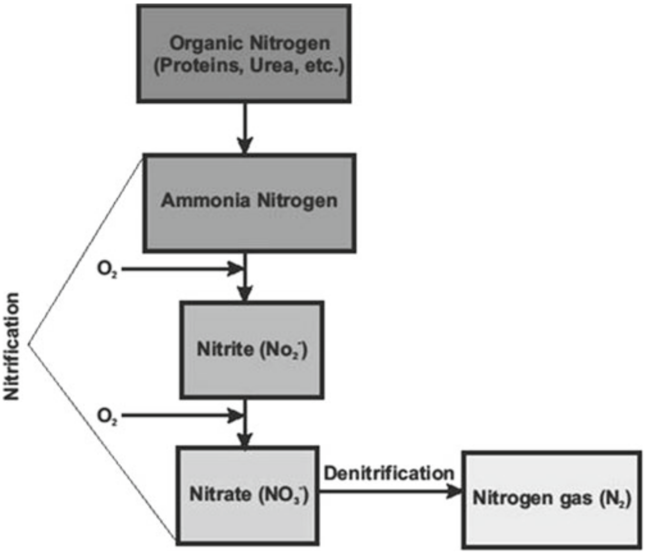


Fig. 4.3 Nitrogen transformation in biological wastewater treatment [14]

dissolved oxygen. A properly designed anoxic zone allows the proliferation of denitrifying bacteria. Denitrifiers use nitrate/nitrites as electron acceptors in the absence of molecular oxygen. There are large numbers of bacterial genera in wastewater capable of denitrification including *Achromobacter, Aerobacter, Alcaligenes, Bacillus, Flavobacterium, Micrococcus, Proteus* and *Pseudomonas*. There is uncertainty regarding the fraction of heterotrophic bacteria that can denitrify in a nutrient removal reactor, however, evidence has shown that the introduction of wastewater into an anoxic stage will give a competitive advantage to denitrifying bacteria over other heterotrophic bacteria community [13].

The following flow diagram shows nitrogen compounds transformations in biological wastewater treatment. As it can be seen from Fig. 4.3, denitrification completes the nitrogen cycle by returning molecular nitrogen (N_2) to the atmosphere.

4.6.2 The Anammox Process

The microorganism responsible for the Anammox process (Anaerobic Ammonium Oxidation Bacterium) was discovered in 1989 in Delft University, the Netherlands. The reaction involves the oxidation of ammonium to molecular nitrogen at anoxic conditions and with nitrite as electron acceptor. Currently there are over five full scale plants in Europe and the US which carry out this process.

The application of the ANAMMOX process consists of two separate processes.

Table 4.2 Advantages and disadvantages of Anammox process

Advantages of Anammox process	Disadvantages of Anammox process
No external carbon source required	Supply of inorganic carbon source for autotrophic bacteria
No oxygen required and lower power consumption	Strictly anoxic conditions (Requires Complete de-oxygenation of feed water)
Much lower CO_2 emissions	Low growth rate
Much lower excess sludge	High processing temperature (30–35°C)
Smaller construction surface	–

The first step is partial nitrification to nitrite of half of the ammonium by ammonia oxidizing bacteria:

$$4NH_4^+ + 3O_2 \rightarrow 2NH_4^+ + 2NO_2^- + 4H^+ + 2H_2O \tag{4.1}$$

The resulting ammonium and nitrite are converted in the Anammox process to molecular nitrogen and almost 15% nitrate (not shown) by Anammox bacteria

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \tag{4.2}$$

Both processes can take place in one reactor where two guilds of bacteria form compact granules. As shown in Table 4.2, the Anammox bacteria demand a virtual elimination of DO in the anoxic stage. That is an important feature that, as opposed to CUBEN, most BNR reactors cannot provide. The ANAMMOX process is still under evaluation.

4.7 Bioreactors for Nitrogen Removal

Biological nutrient removal (BNR) processes provide nitrogen and phosphorus removal by incorporating anoxic, anaerobic and aerobic conditions for microorganisms to carry out cellular metabolism in response to their specific environment. An anoxic stage contains water/wastewater with nitrate (NO_3^-) as electron acceptor. Therefore, this stage is concentrated with NO_3^- and contains very low or no dissolved oxygen (DO) concentration. An anaerobic stage has neither NO_3^- nor DO. In conventional wastewater treatment plants (WWTP), the removal of nutrients occurs after secondary treatment. That is, after the elimination of most of the BOD and ammonia. These processes are followed by both denitrification to eliminate the nitrates, and by phosphate removal. The following reaction shows the conversion of nitrate to free nitrogen.

$$NO_3^- + \text{Organic Matter}(\text{i.e. BOD})N_2(\text{gas}) + CO_2 + H_2O + OH - + \text{New Cells} \tag{4.3}$$

Organic matter is used by denitrifying bacteria as carbon and energy source. The type and amount of organic matter are important factors in the denitrification rate.

The organic compounds that improve the denitrification process include methanol (CH_3OH) and Volatile Fatty Acids (VFA) [15]. Table 4.3 lists some of the common nitrogen removal processes currently being used in wastewater treatment plants.

In all BNR plants in operation, the processes take place in rectangular, horizontal bassins. CUBEN is a major departure from that configuration. CUBEN carries out the following process for nitrate removal with the exception of having an anaerobic stage between anoxic and aerobic stages. This sequence provides a great advantage where both nitrate and phosphate removal processes take place in CUBEN.

4.7.1 Pre-Anoxic Denitrification or Modified Ludzak-Ettinger Process (MLE)

The MLE process is the most common process used for biological nitrogen removal in wastewater treatment plants. The MLE process consists of an anoxic reactor followed by an aerobic reactor where nitrification takes place. Nitrate produced in the aerobic stage is recycled back into the anoxic stage. The organic substrate in wastewater is used for denitrification. The MLE process is called substrate denitrification since no external carbon source is required. The MLE process is also called pre-anoxic denitrification since the anoxic stage precedes the aerobic stage [14]. This process represents one of the simplest systems within which both nitrification and denitrification take place in different stages. In this system, both wastewater and recycled biomass enter the anoxic stage with a very low dissolved oxygen and high nitrate concentration. The internal recycle flow ratio (recycle flowrate/influent flowrate) is in the range of 2–4. In the MLE process, the aerobic stage contains a high dissolved oxygen concentration of approximately 2.0 mg/L (Fig. 4.4).

4.8 Biological Phosphorous Removal

Phosphorus is a macro-nutrient required by all living cells. It is absorbed by microorganisms in the form of orthophosphates to build their cell structure. It is also an important part of Adenosine Tri-Phosphate (ATP) which is the energy supply of all

Table 4.3 Various nitrate removal processes

Nitrate removal processes	Post-anoxic denitrification
	Pre-anoxic denitrification or Modified Ludzak-Ettinger (MLE)
	Four-stage Bardenpho
	Nitrox™
	Bio-denitro™
	Step-feed activated sludge process (SFAS)

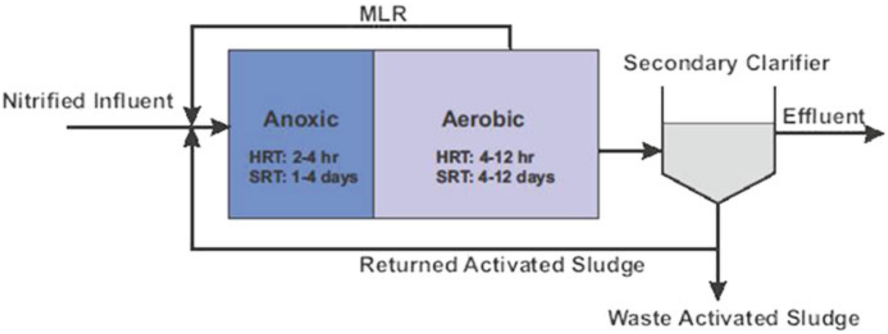


Fig. 4.4 Modified Ludzak-Ettinger process [13]

cells. The phosphate bonds in ATP are high-energy bonds and their formation and hydrolysis is the primary means by which cellular energy is stored and released [16]. Phosphate is also an important component of nucleic acids (DNA and RNA) and phospholipids in cellular membrane. Therefore, scientists could use the concept of phosphate demand in living cells to develop certain biological processes to eliminate the excess phosphorus from the environment particularly from surface water. Wastewater contains phosphorus as either particulate or dissolved matter. Particulate phosphorus is insoluble in water and includes living and dead plankton and phosphorus adsorbed to particulate matters in the water. The dissolved phase includes inorganic phosphorus (orthophosphate, PO_4^{-3}, and polyphosphate) and organic phosphorus. A typical wastewater treatment plant with only secondary treatment removes about one-third of the total influent phosphorus by settling the insoluble phosphorus. Also, small portion of soluble phosphorus is removed during the secondary treatment by normal heterotrophic bacteria for their cellular growth. In order to remove soluble or dissolved phosphorus from wastewater advanced tertiary treatment must be performed. In the tertiary treatment stage, there are two ways to remove dissolved phosphorus and reduce the effluent concentration of phosphorus to meet the discharge limit set and regulated by local governments.

Due to the large number of disadvantages associated to the chemical addition techniques, more attention has been paid in the last two decades towards biological phosphate removal and feasibility and optimization of these processes. Microorganisms use small amounts of soluble phosphorus for their cell function and contain 1.9% phosphorus by weight. However, there are special types of bacteria called phosphorus accumulating organisms (PAOs) that have the ability to store from 5 to 38% by weight phosphorus in their cells when they are subjected to anaerobic and then aerobic conditions. The advantages of biological phosphorus removal include:

- Less sludge production
- No chemical costs
- Good sludge settling due to lower filamentous bacterial growth
- Easier resource recovery

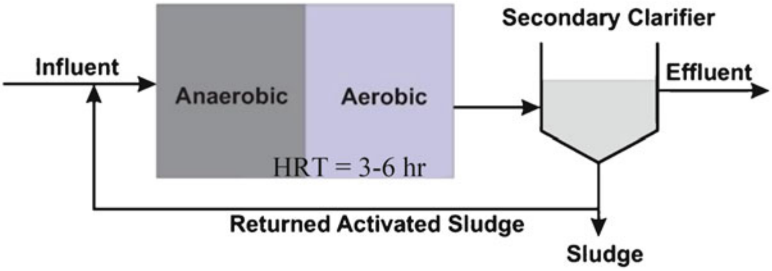


Fig. 4.5 Phoredox (A/O) process [14]

The disadvantages of the biological phosphate removal include high installation costs, complexity of operation and inability to achieve consistently effluent phosphorus concentration lower than 0.5 mg/L. In general, when the Enhanced Biological Phosphorus Removal (EBPR) process is operated successfully, it has relatively lower operating costs and is an environmentally sustainable option for phosphorus removal compared to chemical removal techniques.

The average concentration of phosphorus both inorganic and organic in wastewater is within the range of 5–20 mg/L [17]. To remove the phosphorus, biomass suspended in wastewater must first be subjected to an oxygen and nitrate free environment (Anaerobic) where no electron acceptor is present. Then the suspended biomass passes through an aerobic phase where phosphorus removal takes place. This reactor sequence (anaerobic-aerobic) provides a suitable condition for PAOs to grow and proliferate.

Biological phosphorus removal is a hypersensitive process that is affected by external disturbances such as high rainfall, excessive nitrate loading to the anaerobic reactor and many other important factors such as pH, high or low temperature and lack of carbon source. Therefore, stability and reliability of EBPR must be maintained and monitored through advanced process instrumentation and control (Fig. 4.5).

4.9 Bioreactors for Phosphorous Removal

Over the past two decades, various configurations of biological phosphorus removal have been developed, modified and used in the wastewater treatment industry. They all consist of anaerobic, aerobic stages as well as anoxic stages if phosphorus removal and denitrification are combined. Table 4.4 shows some of the most common biological phosphorus and combined phosphorus and nitrate removal processes.

Some of the above phosphorus removal processes are described below:

Table 4.4 Various phosphorus removal processes

Phosphorus removal	Phoredox (A/O) Phostrip (combined chemical and biological phosphorus removal)
Combined nitrate and phosphorus removal processes (Enhanced biological nutrient removal)	A^2/O process Modified Bardenpho (5-stage) Standard and modified UCT

4.9.1 *Phoredox (A/O) Process*

The term A/O stands for anaerobic and oxic (aerobic) which represent the sequence of these phases in this process. This is the basic process configuration for biological phosphorus removal which was first identified by Barnard in 1974 and then patented by Air Products and Chemicals Inc. This reactor sequence is used in CUBEN.

4.9.2 *Advantages and Disadvantages of the Commercial BNR Processes*

The use of the aforementioned BNR processes in wastewater treatment plants depends on many factors including target effluent quality, influent quality, operators experience and budget. The following tables summarize the advantages and drawbacks of the BNR processes explained herein. The performance of all the BNR processes is site-specific. Thus, the Tables 4.5, 4.6, and 4.7 below provide a general comparison of treatment performance of various BNR configurations.

4.10 The CUBEN Bioreactor

As explained before, in the wastewater industry there are many different commercially available nutrient removal technologies, trying to meet the stringent limits of nutrient discharges. Most of these technologies have various drawbacks which limits their use. These limitations are listed in the Table 4.8.

In addition, current environmental regulations regarding the nutrient discharge limits are becoming increasingly strict in Canada and other industrialized countries. Thus, there are strong social and economic needs for the development of a cost effective, highly efficient, easy to operate and compact, nutrient removal technology.

The Compact Upright Bioreactor for the Elimination of Nutrients (CUBEN) is a bioreactor with unique staging sequence. No vertically-staged configuration exists in BNR reactors. All commercial and experimental BNR plants consist of horizontal,

Table 4.5 Advantages and drawbacks of the biological nitrogen removal processes [13, 14]

Nitrate removal processes

Process	Advantages	Disadvantages
Post-anoxic denitrification	Excellent TN removal Minimum reactor volume	Required upstream denitrification Supplemental electron donor required High energy requirement
Pre-anoxic denitrification (MLE)	Good nitrogen removal Moderate reactor volume Good solid settleability Low oxygen requirement Simple control	Nitrogen removal capability is a function of internal recycle Potential Nocardia growth problem DO control is required before recycle
Bio-denitro™	5–8 mg/L TN is achievable	High construction cost (since two oxidation ditch reactors are required) Complex operation
Nitrox™	Easy and economical to upgrade the system	Nitrogen removal capability is limited by higher influent TKN concentrations Process is susceptible to ammonia bleed-through
4-Stage Bardenpho	Capable of achieving TN level of less than 3 mg/L	Large reactor volumes are required Second anoxic zone has low efficiency

Table 4.6 Advantages and drawbacks of the biological phosphorus removal processes [13, 14]

Phosphorus removal processes

Process	Advantages	Disadvantages
Phoredox (A/O)	Simple operation Low BOD/P ratio Short HRT Good phosphorus removal	Phosphorus removal declines if nitrification occurs Limited process control flexibility
Pho-Strip	Can be incorporated easily into existing activated sludge plants Process is flexible Phosphorus removal performance is not controlled by BOD/phosphorus ratio	Required lime addition for phosphorus precipitation Additional tank capacity required for stripping lime

rectangular cross section bioreactors. CUBEN occupies smaller foot print and has higher nutrient removal efficiency and lower pumping costs than conventional technologies. This new bioreactor requires fewer pumps due to its vertical alignment in which water flows by gravity from one stage to the other (Anoxic-Anaerobic-Aerobic). Thus, CUBEN has two major advantages; A) Because its vertical configuration has a superior flexibility of installation that exploits better hydraulic profiles and lowers pumping costs and B) A smaller foot print and therefore construction costs.

Table 4.7 Advantages and drawbacks of the combined biological phosphorus and nitrogen removal processes [13,14]

Combined biological phosphorus and nitrogen removal processes		
Process	Advantages	Disadvantages
A^2/O	Removes both nitrogen and phosphorus	Nitrogen removal is limited by internal recycle ratio
	Produces good settling sludge	Needs higher BOD/P ratio compare to A/O process
	Simple operation	Moderate phosphorus removal
Modified Bardenpho (5-stage)	Produces good settling sludge	Less efficient phosphorus removal compared with A/O or A^2/O
	Can achieve 3–5 mg/L TN in unfiltered effluent	REQUIRES larger tank volume
Standard and modified UCT	Good nitrogen and good phosphorus removal	
	Produces good settling sludge	More complex operation
	Nitrate loading on anaerobic zone is reduced, thus increasing phosphorus removal	Required additional recycle stream

Table 4.8 Disadvantages of the existing BNR technologies

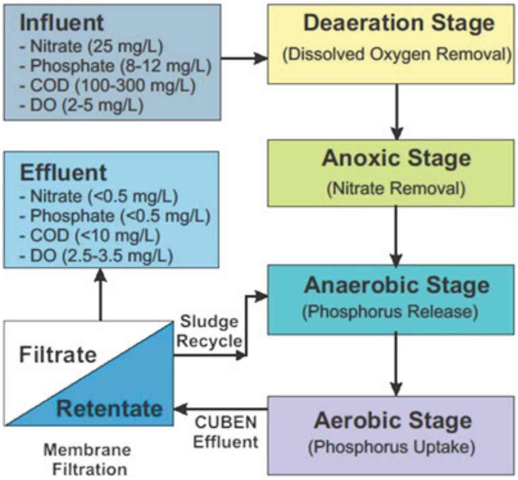
Disadvantages of existing BNR technologies
High capital costs
Control complexity
Excessive sludge recycle
Undesirable sludge production
Long residence time
Provision of excessive carbon source requirement
Moderate pumping

The block diagram Fig. 4.6 shows the arrangement of CUBEN stages and associated processes. The wastewater enters from the top of the column into the Vacuum or Deaeration stage where dissolved oxygen (DO) is rapidly removed from the bulk liquid. Then, the effluent from the Deaeration stage enters the Anoxic stage which is located underneath the Vacuum Deaeration stage. In the Anoxic stage, nitrate concentration is reduced and converted to free nitrogen.

The DO in the effluent of the anoxic stage is lower than 0.1 mg/L and the concentration of NO_{3-} less than 0.5 mg/L. The Anaerobic stage and the subsequent Aerobic stage exhibit a high phosphorus removal performance.

In the Anaerobic stage, PAOs uptake Volatile Fatty Acids (VFAs) and accumulate them in their cells in the form of Poly-hydroxyalkanoates (PHAs). As PAOs take up VFAs and store PHAs inside their cells, they also release phosphorus into the water. Therefore, phosphorus concentration in water increases in this stage. Under aerobic condition, PAOs oxidize the cellular PHAs as a source of energy and uptake

Fig. 4.6 Block diagram of the CUBEN and membrane unit



phosphorus that is already present in the influent to the bioreactor as well as the amount released by the PAOs in the Anaerobic stage. The effluent from the Aerobic stage of CUBEN enters a membrane filtration unit. The collected sludge (membrane's retentate) contains high concentration of PAOs and the membrane's filtrate contains very low concentrations of phosphorus (less than 0.5 mg/L). A portion of the collected sludge (Approximately 80%) is recycled back into the Anaerobic stage to be reused in the phosphorus removal process. Sludge recycling is an important requirement for successful biological phosphorus removal process. Recycled sludge with a large PAO population can highly improve the phosphorus removal efficiency and reduces the COD concentration in the final effluent.

The following table (Table 4.9) shows the feed flow rate and concentration of the constituents of the wastewater used in the design and operation of CUBEN. The CUBEN's influent contains nitrate and phosphorus concentrations typical of a wastewater that has undergone secondary treatment. The wastewater flow rate of 120 (L/day) is considered as the basis for the design of this experimental unit.

The design influent and effluent criteria are similar to many wastewater treatment plants with both secondary and BNR process. The flow was scaled down relative to a commercial plant with the same HRT CUBEN effluent concentrations, once achieved steady state, are set to satisfy the discharge limits regulated by Ontario's Ministry of the Environment (MOE).

In CUBEN, the removal of dissolved oxygen takes place in the Deaeration stage. In the medium and large scale plants, it is very difficult to consistently and reliably remove and control dissolved oxygen. DO removal in water/wastewater can be achieved either physically or chemically. Chemical methods are not used due to the undesirable effects of scavengers such as sulfite or increased sludge content from the chemical addition to the water. Physical methods of oxygen removal from water include thermal degassing, vacuum degassing and nitrogen stripping. Among the above physical methods, vacuum degassing (deaeration) and nitrogen stripping are relatively fast and simple. Vacuum

Table 4.9 CUBEN bioreactor design basis

Parameters	Design influent criteria	Design effluent criteria
Flowrate (L/day)	120	120
BOD_5 (mg/L)	50	<5
COD (mg/L)	100–300	<10
TSS (mg/L)	0–8	<5
NO_3 (mg/L)	25	<0.5
Phosphorus (mg/L)	10–30	<0.9
Dissolved oxygen (mg/L)	4–6	2.5–3.5

stripping has shown to be more economic due to lower maintenance and energy consumption costs ([18], [19]). It has successfully being applied to remove dissolved oxygen in a three-phase fluidized bed. Similarly, vacuum stripping is a method that is used in the deaeration stage of CUBEN for effective and fast removal of oxygen from wastewater. CUBEN is specifically well suited technology for application to the ANAMMOX process since the oxygen dissolved in the secondary wastewater can be reduced to virtually zero very rapidly. The performance of the deaeration stage in CUBEN is very important since it significantly affects the performance of subsequent stages. The lower the oxygen concentration in the effluent leaving the Deaeration stage, the better is the efficiency of Anoxic, Anaerobic and Aerobic stages. Figure 4.7 shows a schematic diagram of CUBEN and its auxiliary units (Fig. 4.8).

4.11 Evaluation of the CUBEN's Performance

The CUBEN operation was tested for about 2 months under varying inlet flowrates (90–300 L/day), phosphorous concentrations (30–10 mg/L) and organic loadings. The unit was started up with synthetic wastewater and was inoculated with actual sludge from the aerobic digesters of the onsite wastewater treatment plant of Conestoga Meat Packers Ltd. in Breslau, ON. During the second month of operations, the unit was inoculated with the sludge taken from secondary treatment stage of the Ashbridges Bay Wastewater Treatment Plant in Toronto, Ontario.

An excellent degree of denitrification was observed throughout the experimental operation. The inlet concentration of nitrate was kept constant at 25 mg/L. Due to the excellent performance of the Vacuum stage, nitrate concentrations were reduced drastically from 25 to less than 1 mg/L in the Anoxic stage and reached less than 0.1 mg/L in the lower stages.

As expected, the phosphorus removal process in CUBEN was difficult to sustain and improve during the first operational period (May to July 2010). This was due to the hypersensitivity and slow growth rate of the PAOs involved in this process. The adequate PAOs concentration largely determines the phosphorus removal capacity of a BNR unit. It practically takes 40–100 days [20] for a bio-

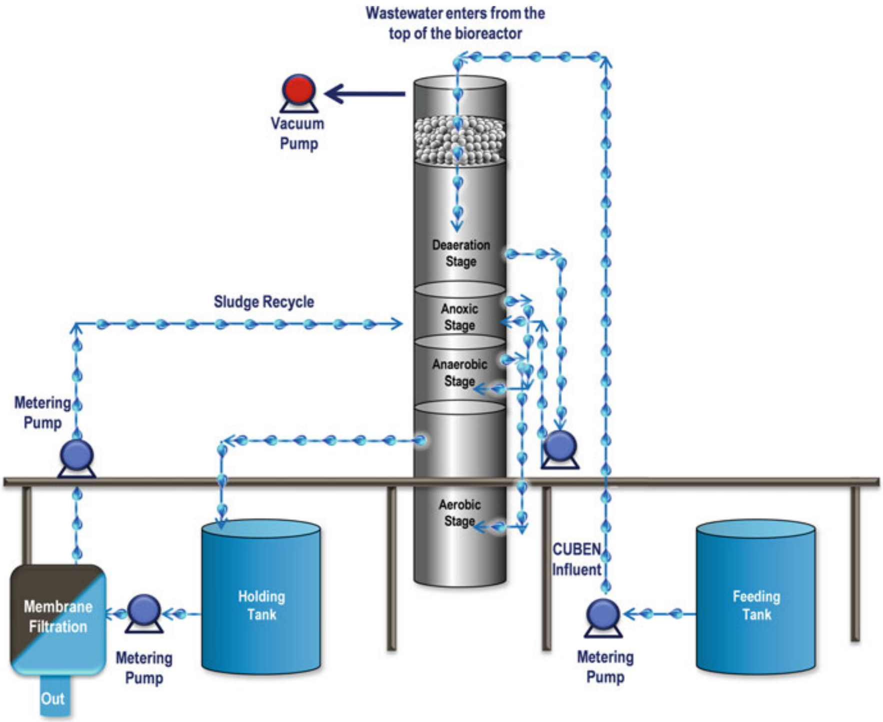


Fig. 4.7 Schematic diagram of CUBEN

logical phosphorus removal process to become stable, consistent and efficient. During the second operational period (April-December 2011), CUBEN's phosphorus removal efficiency was significantly improved. The phosphorus removal performance of over 95% was achieved during the second run. A consistent and stable phosphorus removal required a long operational period. For many researchers, the enhanced biological phosphorus removal process is viewed as a black box whose behavior can only be adjusted and determined after many months of operation. The microbial decay and deterioration of PAOs may occur unexpectedly which consequently results in decline of the biological phosphorus removal.

To improve the phosphorus removal process inside the unit, a series of microbial analyses including identification and quantification tests were performed on the samples taken from the Anaerobic and Aerobic stages of both CUBEN and the original sludge sample. Fluorescence in Situ Hybridization (FISH) analysis with rRNA-targeted probes was conducted on the samples to identify the type of PAOs inside the unit. Furthermore, the quantification of the desired bacteria was performed by image analysis (microscopic) of the hybridized fixed cells.

Fig. 4.8 CUBEN's pH, ORP and DO sensors connected to DAS and lab. View software

4.11.1 *Dissolved Oxygen (DO) Concentration Results*

Dissolved oxygen concentration plays a central role in BNR processes. DO concentrations in all four stages of CUBEN were recorded continuously. Table 4.10 represents the average DO concentrations in all four stages of CUBEN from February until July 2010.

There is a general correlation between DO concentrations, PAO's cellular stored PHA in the anaerobic phase, and their phosphorus uptake in the aerobic phase.

Table 4.10 Dissolved oxygen concentration

Dates	18-Feb (mg/L)	10-Mar (mg/L)	27-Apr (mg/L)	20-May (mg/L)	9-June (mg/L)	9-July- (mg/L)	Objective
Deaeration	1.1	0.78	1.70	0.1	0.28	0.1	0.1
Anoxic	0.17	0.10	1.6	0.06	0.06	0.06	0.1
Anaerobic	0.25	1.5	2.9	0.07	0.07	0.07	0.1
Aerobic	6.5	5.3	8.4	5.5	3.2	2.2	2.5–3.5

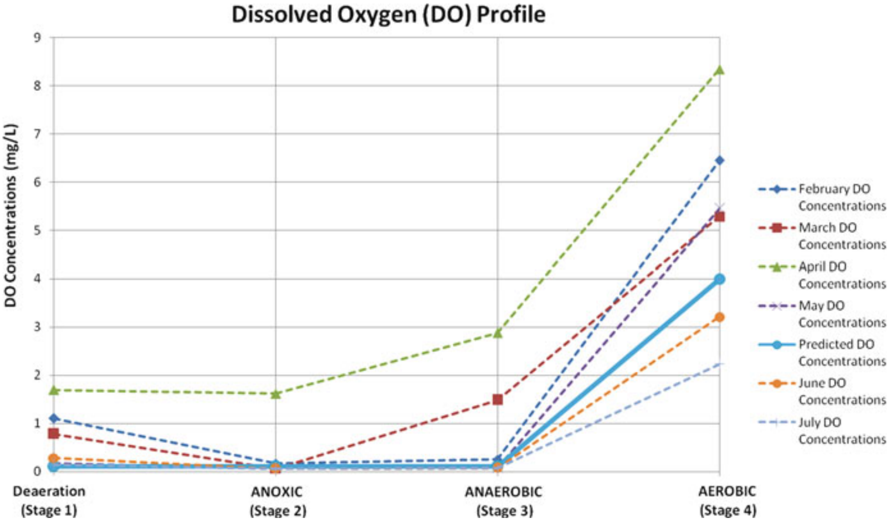


Fig. 4.9 Dissolved oxygen profile in CUBEN

Experience in numerous large plants has shown that very high DO concentrations (4.5–5.0 mg/L) in the aerobic stage results in low phosphorus removal. However, DO concentrations of approximately 2.5–3.5 mg/L have exhibited greater abundance of PAOs and consequently higher phosphorus removal [21]. CUBEN exhibited excellent DO removal results due to high performance in the Deaeration stage. Figure 4.9 illustrates the profiles of dissolved oxygen during February to July 2010. The DO profiles show that the experimental trends met the predicted DO profile over time.

4.11.2 Denitrification Process Results

The influent concentration of nitrate (NO_3^-) was maintained between 24 and 25 mg/L throughout the experimental period. Denitrification process in the anoxic stage (2nd stage) began shortly after starting up the unit operation. The Anoxic stage was inoculated with fresh sludge from a local WWTP . The effluent NO_3concentration

Table 4.11 Nitrate concentrations throughout all stages of CUBEN

Feed (mg/L)	25	25	24	26	25	25	24	25	24	21
Anoxic stage (mg/L)	22	7	14	3.4	2.7	14	0	1.2	0	2.6
Anaerobic stage (mg/L)	7.6	9.8	9.4	2	1.7	4.2	0.7	1.7	0.6	0
Aerobic stage (mg/L)	5.4	0.3	2.8	2	0.2	3.9	0	0.3	0.1	0.3
% Removal	78	99	88	92	99	84	100	99	99	9

at the beginning was about 4–5 mg/L which showed over 80% removal. After 1 week from start-up date, denitrification efficiency reached 98–100% removal. The denitrifiers responsible for the denitrification process showed a remarkable adaptability to the new environment composed of synthetic wastewater, carbon source, temperature and neutral pH. To maintain the high nitrate removal efficiency of the unit, 5 to 10 mL of pure methanol were added directly to the Anoxic stage. Another important factor in the high denitrification rate was the inclusion of packing in this stage. Hydroxyl-Pac media in the Anoxic stage resulted in denitrification via biofilm formation. The attached growth offered several advantages over the suspended growth denitrification. The following advantages of the biofilm development in the Anoxic stage were found to be the key elements in the successful denitrification process in CUBEN.

- Protection against washout of slow growing bacteria under high inlet flow rate or low hydraulic residence time
- Attached microbial species on the surface of the packing have interspecies interaction that is beneficial for the individual denitrifying bacteria
- Presence of packing in the anoxic stage provides higher surface area and consequently increases the concentration of the denitrifiers in this stage
- Maintain the population of denitrifiers in this stage which results in high nitrate removal
- The biofilm formation of denitrifiers on the surface of the packing reduces their flow to the Anaerobic stage thus avoiding the interference of the denitrifiers in the phosphorus removal process
- It provides an extremely cost-effective retrofit solution for future expansion of the unit
- The existence of a high-density population of fixed film bacteria requires less Mixed-Liquor Suspended Solids (MLSS) which consequently reduces the sludge loading generation (Table 4.11)

Figure 4.10 illustrates the nitrate removal profile throughout various stages of CUBEN. It also compares the removal profiles with the predicted nitrate profile which is highlighted with a solid, thick green line. The experimental nitrate removal results represent very well the predicted profile. The inlet concentration of nitrate was varied to investigate the effect of the inlet nitrate concentration on the performance of denitrifying bacteria. Initially, high inlet nitrate concentration decreased the efficiency of the unit. However, denitrifiers quickly adapted to this high concentration and after few days the unit performance experienced a remarkable improvement.

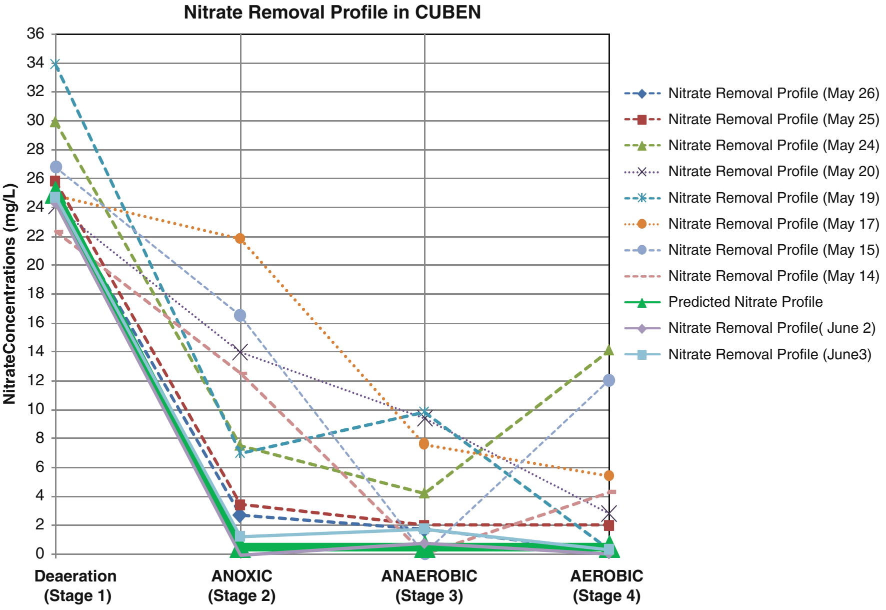


Fig. 4.10 Nitrate removal profile in CUBEN

4.11.3 Phosphorus Removal Results

Biological phosphorus removal in the Anaerobic and Aerobic stages of CUBEN took place several days after the inoculation of the bioreactor with fresh sludge. The phosphorus removal development was much slower than the denitrification since Phosphorus Accumulating Organisms (PAOs) slowly adapt to the new environmental conditions in the Anaerobic and Aerobic stages. The inoculum consisted of a mixed microbial culture. The enrichment of PAOs after bioreactor's inoculation was a long term process. As it was mentioned earlier, biological phosphorus removal process and in particular PAOs responsible for phosphorus removal are highly sensitive and require long term operation to reach steady state. This is due to their slow growth rate of 0.04/day and selective behavior. Many of the environmental parameters such as inlet phosphorus, pH, COD and DO concentration were varied during the commissioning period to enrich the PAOs and improve the overall phosphorus removal.

The inlet phosphorus concentration was increased from 10 up to 30 mg/L to analyze the optimum inlet P concentration relative to the concentration of PAOs. Phosphorus concentration increased in the Anaerobic stage. The phosphorus release by PAOs has a direct relationship with acetate uptake and ultimately intercellular PHA production. The phosphorus release is due to the energy requirement by PAOs for acetate uptake and PHA formation. The energy for this biochemical activity is obtained by breaking down the internal polyphosphate bonds and hydrolysis of ATP

Table 4.12 Phosphorus concentration in CUBEN

Date	TP feed	Eff. TP	Date	TP feed	Eff. TP	Date	TP feed	Eff. TP
8/21/11	31.8	30.3	**10/12/11**	23.3	21.9	**11/13/11**	15	0.7
8/28/11	30	27.9	**10/13/11**	23.51	16.7	**11/14/11**	15	1.5
9/1/11	30	31.6	**10/14/11**	25.09	14.7	**11/15/11**	15	1
9/5/11	27	27.1	**10/15/11**	25	22.9	**11/20/11**	15	0.8
9/8/11	30	39.3	**10/24/11**	25	27.2	**11/20/11**	15	0.5
9/11/11	30	41.5	**10/25/11**	25	31.2	**11/6/11**	15	5.8
9/13/11	38.8	41.8	**10/27/11**	25	21.9	**11/7/11**	15	5.2
9/19/11	35	45.6	**10/28/11**	25	16.8	**11/8/11**	15	4.6
9/24/11	35	48.7	**10/29/11**	25	12.3	**11/10/11**	15	2.8
9/26/11	35	35.9	**10/31/11**	25	9.7	**11/11/11**	15	2.3
9/27/11	31.2	29	**11/1/11**	25	9.3	**11/11/11**	15	1.9
9/28/11	31	20.8	**11/2/11**	15	5.7	**11/12/11**	15	1.8
9/29/11	31	19.2	**11/4/11**	15	7.2	**11/22/11**	15	0.5
10/10/11	31	24.8	**11/5/11**	15	6.5	**11/26/11**	15	0.5

to ADP. Both biochemical processes result in the release of orthophosphate into the liquid phase.

In the Aerobic stage, phosphorus concentration decreased drastically compared to its concentration in the Anaerobic stage. According to our expectations, the Aerobic stages provided the environmental conditions including sufficient dissolved oxygen concentration, neutral pH level and complete mixing. An air diffuser installed near the bottom of the bioreactor provided the oxygen for PAOs to utilize their internal PHAs and consequently uptake phosphorus from the wastewater. The aeration rate could be reduced to meet economic requirements.

The results obtained for the phosphorus removal process reached the target value of 0.5 mg/L or less in the effluent after 8 months of operation. As it can be observed from Graph 4, the inlet phosphorus concentration ranged between 30–10 mg/L throughout the CUBEN's operation period. During the first month of the operation, overall phosphorus removal efficiency was as high as 60%. Ultimately, the P removal efficiency increased to over 95% in the last month of continuous operation. Many parameters were changed to improve the P removal efficiency. These include COD concentration, type of COD mixture (various ratios of propionic, butyric and acetic acid), frequency of inoculation (from twice to three times per week). Table 4.12 shows the concentration of total phosphorus (TP) in both influent and effluent (Fig. 4.11).

4.12 Conclusions

The presence of excessive nutrients, such as nitrates and phosphates in wastewater released into lakes and rivers, is the source of major environmental problems domestically and internationally. The excess of nutrients in water is responsible for two

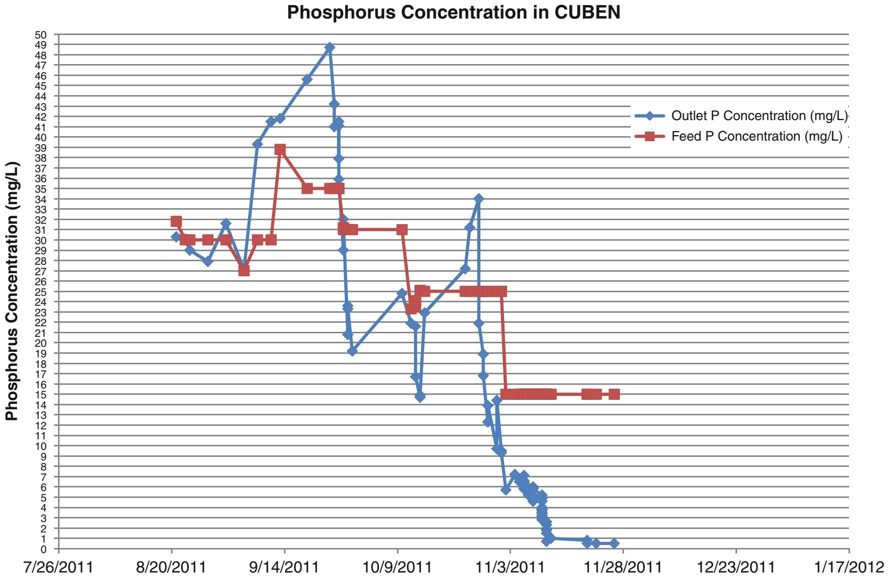


Fig. 4.11 Inlet vs. outlet phosphorus concentration in CUBEN

phenomena: *eutrophication*, which is the unbalanced growth of algae and degradation of aquatic life, and *hypoxia* (oxygen depletion) that reduces the quality of receiving water and the sustainability of reuse. The economic losses of $3 billion annually, loss of recreational capacity, tourist repulsion, and toxicity to both aquatic and human life have imposed increasingly strict nutrient discharge limits. This issue obliges many professionals in the water and wastewater field to propose, design and operate more efficient nutrient removal systems and processes.

The objective of the aforementioned patent and present paper was to construct, operate and demonstrate the viability of a vertical biological nutrient removal reactor which is cost effective and provides high performance efficiency. The CUBEN bioreactor requires a much smaller footprint, lower pumping costs, and has higher removal efficiency than existing conventional systems. Furthermore it can incorporate both conventional and ANNAMOX denitrification.

The Compact Upright Bioreactor for the Elimination of Nutrients (CUBEN) consists of four stages.

- The Deaeration stage where physical removal of dissolved oxygen takes place under vacuum. The DO concentration in the effluent of this stage was less than 0.1 mg/L.
- Anoxic stage where the anoxic conditions (high nitrate concentration and no DO concentration) promote the enrichment of denitrifying bacteria to accomplish denitrification. The effluent concentration of nitrate from this stage approached less that 0.5 mg/L during the experimental period

- The Anaerobic stage where phosphorus accumulating organisms (PAOs) are used to uptake acetates from water/wastewater and form polyhydroxyalkanoates (PHAs) inside their cells. In this stage, PAOs release orthophosphates into the surrounding liquid as a result of breakages of internal polyphosphate bonds to obtain energy, and
- The Aerobic stage where PAOs enriched with PHAs are exposed to oxygen concentration of 2.5–3.5 mg/L. In this stage PAOs utilize reserved PHAs for cellular growth, reconstruction and reproduction. They also have the unique capability to uptake orthophosphates from the water/wastewater and form intracellular polyphosphates, thus removing phosphorus from the liquid phase

CUBEN is designed in compact vertical alignment. This vertical configuration is more flexible than the conventional horizontal basin and allows to optimize hydraulic profiles so that both foot print and pumping energy yield lower costs. Its procurement and construction took 1 year and the bioreactor was commissioned for 2 months using synthetic wastewater, similar to a secondary treatment effluent with 25 mg/L of inlet nitrate concentration and inlet phosphorus concentration of 10–30 mg/L. The unit was inoculated with sludge taken from commercial wastewater treatment plants and was regularly seeded to enhance and maintain the bacterial communities inside the bioreactor. The deaeration stage located at the top section of the column was under continuous vacuum throughout the experimental study. This stage can efficiently remove dissolved oxygen concentration to zero mg/L. The high performance of the Deaeration stage resulted in excellent denitrification in the Anoxic stage with a removal efficiency of 98–100%.

The biological phosphorus removal process in CUBEN successfully met the target value of 0.5 mg/L. The enrichment of PAOs after bioreactor's inoculation was a long term process and was fully accomplished during a 9-month period. In general, biological phosphorus removal process and, in particular, PAOs responsible for phosphorus removal are hypersensitive organisms and require long term operation to reach steady state. Many of the environmental parameters such as inlet phosphorus, pH, COD and DO concentration were changed during the commissioning period to optimize the overall phosphorus removal process. CUBEN can provide proper conditions for the ANAMMOX process due to the superior performance of the Deaeration stage.

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Chapter 5
Activated Carbon Adsorption and Chemical Regeneration in the Food Industry

Raymond A. Sierka

Abstract Approximately 5.2 million pounds (2.36 million kg) of pesticides were used worldwide in 2008. In the United States alone, there are sales of more than 1,055 registered active ingredients found in 16,000 pesticides. There are negative environmental and human health consequences from the use of pesticides.

In the Mediterranean region strawberries and grapes are grown and wines produced with the use of irrigation and pesticides to maximize yields and profits. Pesticide residuals including the metals they contain, have been detected in food, fruit, juices and wines. The organic chemical architecture of pesticides is quite complex and variable. Activated carbon adsorption is the best broad-spectrum treatment available for the removal of pesticides from, fruit, juices wines as well as contaminated irrigation water. Also, activated carbon is employed in wine fining protocols to produce positive quality changes.

Environmental regulations are in place or being promulgated that will necessitate the use of activated carbon treatment in the future. The viability of activated carbon use depends on the economical regeneration of the spent adsorbent. In this paper a Low Energy Chemical Regeneration Process (LECRP) will be described. The process involves the adsorption of contaminants on activated carbon followed by regeneration of the adsorbent via Fenton based oxidations. The operational parameters of the LECRP, adsorbent selection, iron amendment protocol and optimum dose, hydrogen peroxide dose and reaction temperature are discussed.

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5.1 Introduction

Farming practices today in agricultural include irrigation and the employment of organic and inorganic chemicals to maximize crop yields. The use of chemicals in modern farming relies on the use of pesticides. Pesticide is a term that encompasses all chemicals that kill or control pests. Subclasses of pesticides include herbicides, insecticides, fungicides, rodenticides, pediculicides and biocides. [1, 2]. Pesticide residuals including the metals they contain are now found in foods and beverages such as wine, beer and fruit juices. Additionally, pesticides are present in ground and surface waters anywhere modern agricultural practices are employed thereby endangering water supplies for human consumption. Pesticides produce acute and delayed human health problems.

Approximately 5.2 billion pounds (2.36 billion kg) of pesticides were used in the world in 2008. Herbicides accounted for 40 % of pesticides used while insecticides and fungicides totaled 17 and 10 % respectively [3]. There are more than 1,055 registered active ingredients in pesticides employed in the United States. These chemicals are found in 16,000 pesticides sold in the United States alone [4].

The organic chemical architecture of pesticides is generally complex and quite varied and therefore removal from agricultural wastewaters and products such as wines and fresh fruit is complicated. Activated carbon adsorption is the best broad-spectrum treatment available to control these problems.

5.2 Background

In the Mediterranean region, grapes, cork and strawberries and their processed products (e.g. wine and juices) are important to the economic well being of the European Union (EU). Therefore, in an attempt to maximize yield, the most modern of farming techniques are utilized and they include the use of pesticides and irrigation.

5.2.1 Grapes and Wine

Wine has become a universal drink. In 2009, the worldwide the production of wine exceeded 268 million hectoliters (Mhl). European wineries accounted for 68 % of the total production [5]. With a history dating back to the Romans and Greeks, winemaking has undergone many changes, beginning with grape growing and the extensive use of agro-chemicals and irrigation. Environmental impacts of such practices are clearly in focus around the world. Existing regulations as well as new regulations are being promulgated to address these concerns. Likewise, the quality of wine itself has come under new scrutiny.

Table 5.1 Wine production problems solved by fining techniques

Problem	Description	Fining agent
H_2S, Thiols	Rotten eggs	$CuSO_4$ Activated carbon
Polysaccharides	Haze	Enzyme treatment
Proteins	Haze	Bentonite clays Activated carbon
Tannins	Astrigent	Activated carbon
Catechins	Bitter	PVPP
Browning, odor	Off-color, Aroma	Activated carbon

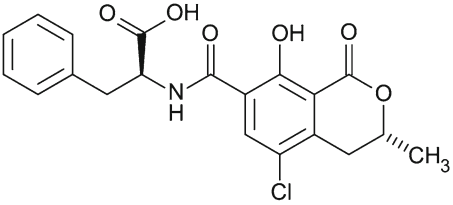

Fig. 5.1 Structure of orchratoxin A

The Pesticide Action Network (PAN) (Europe) has found evidence that wines sold in the EU contain pesticide residues. 100 % of the conventional wines analyzed in the EU revealed 24 different pesticide contaminants. The French Ministry of Agriculture has identified 15 pesticides that transfer from grapes to wine during winemaking processes [6]. A total of 34 pesticide residues have been documented in the United States of America, [7] on grapes from domestic and imported sources and that includes both conventional and organically produced fruit. Human health effects noted are; 4 known or probable carcinogens, 17 suspected hormone disruptors, 10 neurotoxins and 6 developmental or reproductive toxins. Also, 14 honeybee toxins were found.

Wines are a product of many factors including the vineyard and the protocols employed by the winery. *Fining* [8] is a technique to remove or alter chemicals in wine that produce astringency, color, aroma or bitterness or affect clarification (Table 5.1). Activated carbon is employed to decolorize color by adsorbing phenolic compounds. Activated carbon is more often used to decolorize white wines, but also finds utility in removing brown tones or to create red pigment distinctions in red wines.

Another application of activated carbon is the removal of Mycotoxin Ochratoxin A (OTA), a naturally occurring mycrotoxin produced mainly by *Aspergillus ochraceus, Aspergillus carbinarius and Penicillium verrucosum* [9]. Mycrotoxins are highly toxic chemical compounds and represent a particularly serious risk to human health including renal diseases [10]. OTA is a commonly occurring mycrotoxin and is regulated by the EU to a permitted level in wines of 2.0 ug/kg [11]. OTA occurs mainly in sub-tropical and temperate climates. The chemical structure of OTA consists of a chlorine containing dihydroisocoumarin liked through the 7-carboxy group to 1-B-phenylaline (Fig. 5.1).

Research has shown [12] that activated carbon reduced OTA by 90 % from 3 μg OTA/g activated carbon. In another study [13] reported adsorption efficiencies as high as 99.86 % were achieved, depending upon the specific activated carbon employed. White wine samples with 5 μg OTA/ml were successfully treated by 1.0 mg/ml [14]. Many factors affect OTA adsorption by PAC including; molecular size and physiochemical properties of OTA and the properties of the adsorbent, especially pore size and volume distribution, as well as the total charge and charge distribution.

Metals including vanadium, copper, manganese, zinc, nickel chromium and lead have been found in wines [15]. Adsorption by activated carbon has been shown to be a proven technique for removing metals from water [16]. Metal adsorption efficiency is influenced by solution concentration, solution pH and ionic strength. Modification of the adsorbent surface by acid treatment is an effective way to increase adsorption efficiency. Presumably, this improvement is due to the introduction of acidic surface oxides on activated carbon.

5.2.2 *Strawberries*

Strawberries are an important cash crop in the EU. Spain, for example, is the largest exporter of strawberries worldwide and has an estimated value of 400-million (m) euro [17]. The growing of strawberries is not without environmental and human impact.

In a companion study to grapes carried out by USDA, 54 pesticide residues were detected on strawberries. The human health effects noted from the pesticides included; 9 human or probable carcinogens, 24 suspected hormone disruptors, 11 neurotoxins and 12 developmental or reproductive toxins. Nineteen pesticides exhibited toxic responses in honeybees [7].

Methyl bromide has been injected into soils in California for many years before strawberry fields were planted. The Montreal Protocol International Climate Treaty banned the use of methyl bromide due to its ozone depleting action. Suggested alternative pesticides include; 1,3-dichloropropene, methyl iodide, propylene oxide, and di-methyl disulfide among others.

Pesticide residuals in groundwater present a human health hazard. Before producing safe and potable water these residues will require removal. The organic chemical architecture of pesticides is generally complex and quite varied and therefore few single process removal technologies have been successful.

5.2.3 *Cork*

The production of cork is obviously important to the wine industry however contaminated wastewaters are generated in the finishing process. Portugal produces 50 % of the world's cork supply via a two-step process. The initial action is boiling cork bark in water. Approximately 400 l of wastewater per ton of cork, containing phenolic acids (gallic, protocatechuic, vanillic, syringic, ferulic and allegic) and tannic acids, (2,4,6-trichloroanisol and pentachlorophenol) is generated. After boiling, the cork slabs are dried and cut into strips and corks punched out. To remove residual odor and flavor treated from the corks, various bleaching agents [18] are employed. Because of the chemical and physical properties of contaminants in cork wastewater they are amenable to removal by activated carbon.

Fenton based processes have also been proposed for the mineralization of organic pollutants in cork boiling and bleaching wastewaters. Solar photocatalytic processes, TiO_2/UV and Fe^{2+}/H_2O_2/UV, were tested [19] and indicated that when approximately 49 % of the organic matter was mineralized, the remaining organic matter was biodegradable. Advanced oxidation processes that generate hydroxy ($^{*}OH$) radicals and superoxide radicals (O_2^{-*}) are considered to be the reason that the recalcitrant organics were mineralized.

Activated carbon has been derived from cork solid waste products [20, 21]. It has been found that micropore structure of the chemically activated cork was similar to that of commercially available activated carbon, however, preliminary studies indicate special adsorption characteristics that suggests potentially novel applications.

Pesticide residuals have been detected in fruit and their products (e.g. wine, juices) and in ground and surface water resources. The organic and inorganic contaminants from pesticides can be removed from the environment by the use of activated carbon. Economical use of activated carbon suggests that regeneration of the spent adsorbent will play a major role in minimizing treatment costs. In the following portion of this chapter, the concept of adsorption by activated carbon and chemical regeneration of exhausted adsorbents via Fenton driven oxidations will be presented.

5.3 Adsorption by Activated Carbon

Adsorption is the accumulation of a substance at an interface between two phases (e.g. liquid–solid). The material being accumulated is the adsorbate while the accumulating medium is the adsorbent. The surface area, pore size and volume distribution and surface chemistry of the adsorbent affect adsorption efficiency. Maximum adsorption is proportional to the amount of adsorbent surface area within the pores that are accessible to a given adsorbate. Commercially available GACs contain as much as 1,500 m^2/g of total surface area. Distribution of the surface area is in micropores (<2 nm diameter, d), mesopores (2 <d <50 nm) and macropores (d >50 nm). The stoichiometry and kinetics of adsorption are related to the pore size and volume distribution of the adsorbent and the molecular size of the adsorbate. Surface chemistry of GACs also plays a role in adsorption efficiency.

Commercially available activated carbons are produced from carbonaceous substances such as bituminous coal, wood, petroleum coke, bone char, and coconut shells. The activation process, usually carried out in multiple hearth Hershoff Furnaces, follows a three step protocol; (1) input material drying, (2) heating in the absence of air to form a crude pore structure and (3) activation which is carried out between 200 and 1,000 °C temperatures with steam, carbon dioxide or air. It is in the activation step that the extensive pore structure of the carbon is created. The total surface area achieved ranges between 800 and 1,500 m^2/g. Thermal regeneration of spent GAC duplicates the protocol above.

There are two forms of activated carbons produced for use powdered (PAC) or granular (GAC). GAC is sieved in two main size ranges; 1.68–0.42 mm and 2.38–0.59 mm. PAC is general defined as 65–90 % of particles passing a 44 um screen. The choice of form, PAC or GAC is dictated by the application.

All activated carbons have a finite capacity to adsorb molecules. When the adsorbent is exhausted or spent, it is either deposited in landfills or it is regenerated. Two major pathways for spent carbon regeneration are available; (1) thermal and (2) chemical. The former is the more traditional methodology and the latter the latest innovation. The Low Energy Chemical Regeneration Process (LECRP) utilizes two different treatment technologies in a synergistic scenario – adsorption of contaminants onto GAC and their subsequent oxidation via Fenton Chemistry driven reactions.

5.4 Low Energy Chemical Regeneration Process

A LECRP has been developed through combined research efforts at the United States Environmental Protection Agency (USEPA) Kerr Research Laboratory and the University of Arizona Department of Chemical and Environmental Engineering to regenerate exhausted activated carbon. A schematic representation of LECRP is depicted in Fig. 5.2. The initial step consists of filling a contactor with virgin

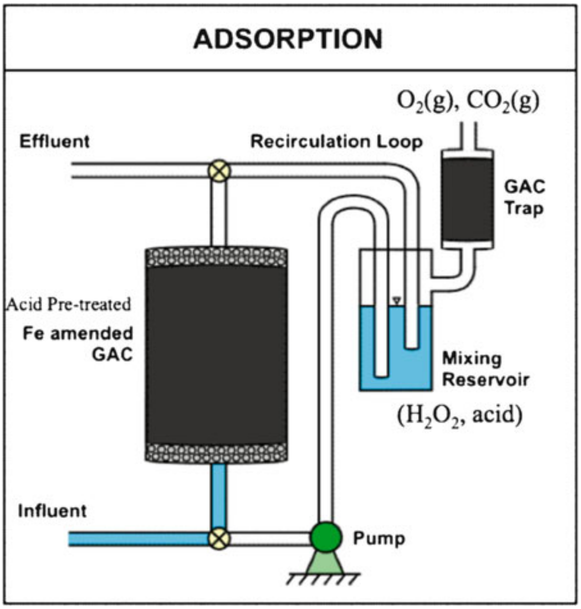

Fig. 5.2 Low energy chemical regeneration process

activated carbon and for purposes of illustration it is assumed this will be granular activated carbon (GAC). The adsorbent is then wetted with an aqueous acidic solution to decrease its zero point charge (ZPC). Following acidification, an iron solution is admitted to the column at a pH above the pH_{zpc} to impregnate iron on the external and internal pore structure of the GAC. At this point, the column is operational. Contaminated wastewater is passed through the column and contaminant adsorption takes place until the adsorbent is saturated and no further adsorbate is removed. The chemical regeneration of spent GAC commences as H_2O_2 is pumped through the column reacting with Fe immobilized on GAC surfaces to produce free radicals, via Fenton based chemistry. Free radicals oxidize adsorbates regenerating the spent GAC. Gaseous emissions from the Fenton reactions, for example volatile organic chemicals and oxidation gases, are removed by a separate activated carbon trap residing at the top of the contactor. During GAC regeneration, H_2O_2 is decomposed and the small volume of aqueous solution now contains partially oxidized oxygenated compounds that are biodegradable and can be safely added to community wastewater systems.

The objectives of LECRP are to transform adsorbates into less toxic by-products, re-establish the sorptive capacity of spent GAC for target contaminants and increase the treatment life of the GAC.

LECRP is an in-situ process, that is, adsorption and chemical regeneration are carried out in the same contactor. Since LECRP is carried out on-site, at ambient or slightly elevated temperatures it minimizes energy requirements. Also, the need for carbon handling, off-site transport and thermal reactivation at high temperatures (>1,000 °C), all conditions of the thermal regeneration process, are eliminated. In thermal regeneration of spent activated carbon, mass loses by particle attrition and incineration are, approximately 10 % per regeneration cycle, while in the LECRP mass loss is negligible, also pore size and volume distribution changes are negligible. Another important advantage of LECRP is that chemical and physical properties of regenerated activated carbon are essentially unchanged unlike those seen in thermal regeneration. LECRP is a "green" process with a minimal carbon footprint. For the past 10 years, research has been conducted by the USEPA and the University of Arizona to determine the optimum design and operating conditions for the LECRP. The parameters of the LECRP, iron concentration [22], reaction temperature [23], GAC particle size [24] and iron type [25] have been thoroughly researched in the laboratory and pilot scale experiments.

5.4.1 LECRP Process Parameters

5.4.1.1 Adsorbent Selection

GAC selection for CRP must fulfill two major criteria; (1) maximum adsorption of the target contaminant and (2) minimization of ingredients in the adsorbent that lead to non-productive reactions with H_2O_2, that is a reduction in the production of free radicals.

The adsorptive properties of activated carbon, principally, specific surface area, pore size and volume distribution as well as the chemical nature of the surface affect the capacity and kinetics of adsorption. The size of the adsorbate pore must exceed the adsorbate molecular size for adsorption to take place. The distribution of the pores will determine the degree and rate of contaminant accumulation on the adsorbent. Because surface chemistry of a carbon causes interaction between adsorbates and surfaces, it likewise plays a role in adsorption efficiency and rate. Pore size and volume distribution as well as surface chemistry of an activated carbon are influenced by the choice of carbonaceous starting materials and the manufacturing protocols especially temperature and the use of different oxidants in the activation step.

Commercially available activated carbons contain an array of metals. One transition metal, manganese (Mn), cycles between oxidation states in Fenton type reactions with H_2O_2 in a fashion similar to iron [26]. The major difference is that $^*OH$ is not produced and H_2O_2 is not productively utilized. The concentration of metals in activated carbons is primarily a function of starting raw material for activated carbon. Commercial activated carbon manufacturers have successfully minimized H_2O_2 reactivity with activated carbon metals by special designed steam activation protocols. (R. Hayden, Calgon Corporation, 2001 personal communication).

5.4.2 Pre-Acidification and Zero Point Charge

The pH at the point of zero charge (pH_{pzc}) occurs when the when positive and negative surface charges are equal and the GAC has a net charge of zero. Acidic pretreatment of GAC alters the surface chemistry of the adsorbent by increasing carboxylic and lactonic surface oxide functional groups, increasing the cation exchange capacity and lowering pH_{zpc}. Acidification reduces the repulsive forces between Fe^{2+} and Fe^{3+} in solution and positively charged surface sites of the GAC. Application of the iron solution at a pH above the pH_{pzc} lowers the electronic repulsion that in turn permits deeper penetration and dispersion of iron on the GAC. Dispersion of iron throughout the interior of a GAC particle produces favorable Fenton reaction conditions [23].

Iron, amended to GAC without pre-acidification, is immobilized within a short transport distance (18 um) within the adsorbent particle [22]. With pre-acidification, iron penetrates deeper into the particle (Fig. 5.3). Consequently, more volume within the adsorbent pore structure contains all of the elements necessary for spent GAC regeneration; iron, H_2O_2 and target contaminant.

5.4.3 Iron Concentration

The background concentration of Fe in a given GAC is related to the starting raw material and the process used to activate the adsorbent. Coal based activated carbons (e.g. lignite, bituminous) contain the highest amounts of Fe followed by wood and

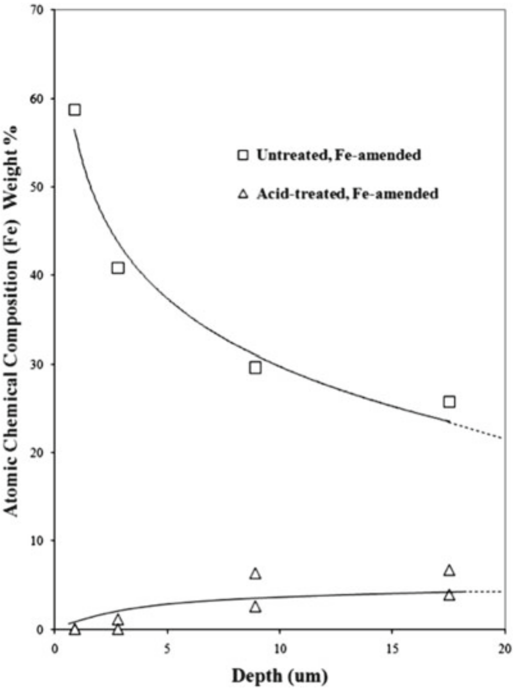

Fig. 5.3 Atomic chemical composition of Fe in acid treated and untreated Fe amended GAC. Measurements were by SEM/EDS

Table 5.2 Fenton and related chemical reactions

1) $H_2O_2 + Fe^{2+} >>>> Fe^{3+} + {}^* OH + OH^-$
2) $H_2O_2 + Fe^{3+} >>>> Fe^{2+} + {}^* O_2^- + 2\ H^+$
3) ${}^*O_2^- + Fe^{3+} >>>> Fe^{2+} + O_2(gas) + 2\ H^+$
4) $*OH$ + target contaminants >>>> reaction by-products
5) ${}^*OH + H_2O_2 >>>> {}^*HO_2 + H_2O$
6) $2\ H_2O_2 >>>> O_2 + 2H_2O$

natural shell (e.g. coconut) materials. If strong chemical oxidants, (e.g. phosphoric acid) are employed in the activation process, Fe leaching will occur reducing background Fe. Insufficient iron is present on commercial GAC's to maximize Fenton oxidations and therefore external additions are required.

The classic Fenton reaction (Table 5.2) involves the reaction between H_2O_2 and ferrous iron (Fe^{2+}) yielding the hydroxyl radical (${}^*OH$) and Fe^{3+} and the hydroxyl ion (OH^-). Fe $^{3+}$ reacts with H_2O_2 (reaction 2) or the superoxide ion (${}^*O_{2-}$) (reaction 3) yielding Fe^{2+}. This sequence of reactions proceeds until the H_2O_2 is used up.

${}^*OH$ has an unpaired electron and therefore is a highly reactive non-specific oxidant (reactions 4 and 5). Steady state concentrations of ${}^*OH$ in Fenton systems are quite low (10^{-14}–10^{-16} M) [27–29]. Due to extremely rapid reaction rates of ${}^*OH$, their transport distances are limited to a few nanometers. Thus, Fe, ${}^*OH$ and target contaminant must be in close proximity. This is the central feature of the LECPR.

Table 5.3 MTBE destruction (%) as a function of temperature, iron concentration and amendment protocol

Temp.(°C)	% MTBE destroyed Fe-un-amended GAC	% MTBE destroyed Bulk Loaded Fe GAC	% MTBE destroyed Acid treated Fe GAC
25	27.2	35.1	49.4
35	31.9	38.9	54.6
45	32.6	49.8	62.5
55	34.4	51.4	68.2

Non-productive reactions, that is reactions that do not produce $^*OH$, are represented by the disproportionation reaction 6.

The optimum amount and deposition of Fe on GAC has been investigated [22] in terms of Fenton driven chemical oxidation of methyl *tert*-butyl ether (MTBE) on spent GAC. Fe concentration was varied from 1,020 mg/kg (background concentration of the GAC) to 25,660 mg/kg. MTBE degradation in Fe-amended GAC experiments increased by an order of magnitude over the Fe un-amended GAC case. It was also found that 99 % of the H_2O_2 reacted, was attributable to GAC bound Fe within the pores of the adsorbent. The optimum Fe concentration was 6,710 mg/kg. At lower than 6,710 mg/kg of Fe concentration, MTBE destruction was Fe limited. At higher (>6,710 mg/kg) concentrations of Fe, reduction of MTBE oxidation efficiency was thought to be due to iron deposition reducing pore surface area. Pore blockage limited H_2O_2 diffusive transport.

5.4.4 H_2O_2 Concentration

Kinetic analysis of the H_2O_2/Fe reaction [22] on GAC indicates a non-linear relationship between total iron and pseudo first order H_2O_2 degradation rate constant. At high Fe concentrations, H_2O_2 was somewhat limited by iron concentrations. Three mechanisms have been cited as potential reason for this response; (1) Fe blockage of H_2O_2 transport in the GAC, (2) unavailable iron and (3) the effect of fast H_2O_2 reaction rates on H_2O_2 diffusive transport. In summary, these mechanisms limited contact on the GAC surface of H_2O_2, Fe and the adsorbate.

5.4.5 Temperature Effects

The LECRP was designed to minimize energy expenditure and this is accomplished by carrying out Fenton based oxidations of spent activated carbon at ambient temperature. However, the decomposition of H_2O_2 in GAC beds is an exothermic reaction and reaction temperatures will rise. Laboratory scale investigations into the effect temperature have been conducted [23] on GAC saturated with MTBE. The data indicate that MTBE destruction increased with reaction temperature (Table 5.3), Fe-amendment and pre-acidification. When acidification preceded iron amendment on the GAC, MTBE destruction increased from 49.4% at 250°C to 68.2% at 550 °C.

Pilot scale experiments have also been conducted (Huling et al., Fenton Based Chemical Regeneration of MTBE Spent Activated Carbon – A Pilot Plant Study, submitted to J. Haz Mat, 2011 in review) at a pump and treat facility where GAC was saturated with MTBE. Spent GAC regeneration performance of the LECRP was tested by varying iron amendment protocols and temperature. Iron amendment concentration (~6 g/kg) was constant for the three columns employed, however ferrous iron was amended to the GAC in two columns without pre-acidification while the third column was pre-acidified before ferrous iron amendment. GAC regeneration was carried out under ambient thermal conditions (21–27 °C) or enhanced thermal conditions (50 °C). Significant removal of MTBE was achieved with a constant H_2O_2 amount of \$0.6 H_2O_2/lb GAC. The application method of H_2O_2 (semi-continuous or continuous) was also investigated. Continuous H_2O_2 addition proved to be more efficient based on required reaction time. For the columns employing iron addition without pre-acidification, MTBE removals ranged from 62–80% at ambient thermal conditions and increased to 78–95 % at enhanced thermal conditions (50 °C). Thermally enhanced (50 °C) pre-acidified GAC showed even greater MTBE removals (92–97 %). Isotherm testing of regenerated GAC showed no loss in MTBE sorption capacity.

5.5 Summary

Modern day agriculture is dependent upon extensive use of irrigation and pesticides. There are negative environmental and human health consequences of these practices, for example, the contamination of underground and surface water supplies for human consumption. Pesticide residues, both organic and inorganic, have also been identified in fruit and food products including wine. Pesticide chemical architecture is complex and varied. Legislation to control pesticide contamination has been passed or is being promulgated and this will necessitate the employment of efficient and economically viable treatment systems. Activated carbon appears to be the best broad-spectrum approach for the solution of pesticide contamination scenarios.

The economic viability of activated carbon use depends on the economical regeneration of spent the spent adsorbent. A Low Energy Chemical Regeneration Process (LECRP) is capable of meeting the demands of controlling pesticide environmental pollution. The LECRP employs two well-understood processes, the adsorption of contaminants on activated carbon followed by regeneration of the spent adsorbent via Fenton based oxidation involving the production of free radicals from hydrogen peroxide. The operational parameters of the LECRP, adsorbent selection, iron amendment to activated carbon, the optimum dose of hydrogen peroxide and iron and the reaction temperature have been identified.

5.6 Acknowledgements

Dr. Scott Huling of USEPA Kerr Research Laboratory has continued to conduct research on the LECRP and is responsible for the majority of results presented. Professor Robert G. Arnold of the University of Arizona likewise contributed to these studies and together with the author were the inventors of the LECRP. Jeanne M. Sierka served as reviewer for this author's paper.

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Chapter 6
Hybrid Processes for the Treatment of Leachate from Landfills

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Abstract Sanitary landfilling is the most common way to eliminate solid urban wastes. An important problem associated to landfills is the production of leachates. Because of its characteristics and because of its occurrence at remote locations, leachate needs to be treated separately from municipal or other wastewater. In this paper, the main technologies for the treatment of leachate from landfills are presented with special attention to hybrid processes, combining biological and physical treatment steps to fulfil the future demand on save, reliable and economic landfill leachate treatment. The technologies shall be grouped according to outlet requirements and inlet pollution load, pointing out the main advantages and disadvantages of each technology. This paper will summarize WEHRLE's 25 years of experience in treating leachate in Europe, Asia and North Africa.

6.1 Introduction

For several decades it has been acknowledged that leachate from landfill sites imposes a severe and detrimental impact on the environment. Focal parameters are COD, BOD_5, NH_4-N, heavy metals and salts (especially chloride or sulphate). In the past, the adverse effect of leachate on waterbodies and wastewater treatment works very often was heavily underestimated due to its comparably low volumetric flows.

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In recent years it has become accepted that leachate even in small amounts is a very harmful liqueur, because its loadings on hazardous and toxic pollutants can exceed the loadings in municipal wastewater by approximately two to three orders of magnitude.

It has now been widely recognized that leachate needs to be treated and needs to be treated separately. Yet for all the different types of wastewater, throughout one country the same effluent standards have to be met. This means that there is no such thing as the leachate treatment but from a range of technologies the most appropriate has to be chosen in accordance with leachate characteristics, effluent requirements and technical prerequisites at the site.

This paper will concentrate on those forms of treatment that are most commonly used in Europe, Asia and North Africa, giving a brief overview on their advantages and disadvantages. This introduction will be based on the experience of more than 25 years WEHRLE Umwelt GmbH has in the field of treatment of landfill leachate.

6.2 Leachete from Landfills

The importance of good health requires the deposition of domestic and industrial solid waste in landfills, often located at remote areas. But the decomposing of the waste within these landfills creates major environmental problems: Emissions such as the landfill generated greenhouse gases methane and carbon dioxide as well as a liquid known as leachate are of major concern.

Landfill leachate originates from water contained in the discharged waste and from infiltration water that seeps through the body of the landfill. The so generated leachate is highly polluted due to a high content of ammonium ions and organic compounds. In most cases it is toxic, acidic and rich in halogenated hydrocarbons. It has a high buffer capacity, possesses a high amount of inorganics (salts) and usually shows an unbalanced COD to NH_4-N ratio. Furthermore, the COD often consists of lots of non-biodegradable COD, the so called “hard COD”.

The leachate can contain elevated values of chloride and sulphate ions as well as a high concentration of common metal ions especially iron or even heavy metals (see Table 6.1).

In some European countries new pollutants like pharmaceuticals, pesticides or fluoro-surfactants and even nanoparticles have come into public focus recently and are discussed on expert levels and among authorities. It cannot be ruled out that these pollutants will be introduced to discharge limits in the future.

However, the composition of waste as well as specific regulations on waste disposal have an impact on the leachate produced. Also the location of the landfill site has an influence: Different climates, different lifestyles, different waste collection systems etc. have an effect on the leachate amount and its composition.

Moreover, the composition of leachate varies over the years: Leachate from an “aged” municipal landfill site in the methane phase has a very different composition

Table 6.1 Constituents in leachates from municipal solid waste landfills

	Unit	Leachate from MSW landfills [1]				Leachate from MSW landfills [2]					
		Acid phase		Methanogenic phase		Acid phase		Intermediate phase		Methanogenic phase	
Parameter		Range	Medium	Range	Medium	Range	Medium	Range	Medium	Range	Medium
pH-value	–	4.5–7	6	7.5–7	8	6.2–7.8	7.4	6.7–8.3	7.5	7.0–8.3	7.6
COD	mg/l	6.000–60.000	22.000	500–4.500	3.000	950–40.000	9.500	700–28.000	3.400	460–8.300	2.500
BODs	mg/l	4.000–40.000	13.000	20–550	180	600–27.000	6.300	200–10.000	1.200	20–700	230
TOC	mg/l	1.500–25.000	7.000	200–5.000	1.300	350–12.000[2)]	2.600[2)]	300–1.500[2)]	880[2)]	150–1.600[2)]	660[2)]
AOX	µg/l	540–3.450	1.674	524–2.010	1.040	260–6.200	2.400	260–3.900	1.545	195–3.500	1.725
org. N[1)]	mg/l	10–4.250	600	10–4.250	600						
NH_4-N1_[1)]	mg/l	30–3.000	750	30–3.000	750	17–1.650	740	17–1.650	740	17–1.650	740
TKN[1)]	mg/l	40–3.425	1.350	40–3.425	1.350	250–2.000	920	250–2.000	920	250–2.000	920
NO_2-N1)[1)]	mg/l	0–25	0.5	0–250	0.5						
NO_3-N[11)]	mg/l	0.1–50	3	0.1–50	3						
SO_4	mg/l	70–1.750	500	10–420	80	35–925	200	20–230	90	25–2.500	240
Cl	mg/l	100–5.000	2.100	100–5.000	2.100	315–12.400	2.150	315–12.400	2.150	315–12.400	2.150
Na[1)]	mg/l	50–4.000	1.350	50–4.000	1.350	1–6.800	1.150	1–6.800	1.150	1–6.800	1.150
K[1)]	mg/l	10–2.500	1.100	10–2.500	1.100	170–1.750	880	170–1.750	880	170–1.750	880
Mg	mg/l	50–1.150	470	40–350	180	30–600	285	90–350	200	25–300	150
Ca	mg/l	10–2.500	1.200	20–600	60	80–2.300	650	40–310	150	50–1.100	200
tot. P[1)]	mg/l	0.1–30	6	0.1–30	6	0.3–54	6.8	0.3–54	6.8	0.3–54	6.8
Cr[1)]	mg/l	0.03–1.6	0.3	0.3–1.6	0.3	0.002–0.52	0.155	0.002–0.52	0.155	0.002–0.52	0.155
Fe	mg/l	20–2.100	780	3–280	15	3–500	135	2–120	36	4–125	25
Ni[1)]	mg/l	0.02–2.05	0.2	0.02–2.05	0.2	0.01–1	0.19	0.01–1	0.19	0.01–1	0.19
Cu[1)]	mg/l	0.004–1.4	0.08	0.004–1.4	0.08	0.005–0.56	0.09	0.005–0.56	0.09	0.005–0.56	0.09
Zn	mg/l	0.1–120	5	0.03–4	0.6	0.05–16	2.2	0.06–1.7	0.6	0.09–3.5	0.6
As[1)]	mg/l	0.005–1.6	0.16	0.005–1.6	0.16	0.0053–0.11	0.0255	0.0053–0.11	0.0255	0.0053–0.11	0.0255
Cd[1)]	mg/l	0.0005–0.14	0.006	0.0005–0.14	0.006	0.0007–0.525	0.0375	0.0007–0.525	0.0375	0.0007–0.525	0.0375
Hg[1)]	mg/l	0.0002–0.01	0.01	0.0002–0.01	0.01	0.000002–0.025	0.0015	0.000002–0.025	0.0015	0.000002–0.025	0.0015
Pb[1)]	mg/l	0.008–1.02	0.09	0.008–1.02	0.09	0.008–0.4	0.16	0.008–0.4	0.16	0.008–0.4	0.16

[1] parameter more or less independent from the biochemical degradation phase

[2] is referred to the econd reference

Table 6.2 Regional differences in the leachate characteristics

Region	COD range (mg/l)	NH_4-N range (mg/l)
Northern Europe	<5.000	<1.200
Southern Europe	<15.000	<2.000
Turkey	<20.000	<2.500
Northern Africa	<70.000	<2.500
Asia	<25.000	<3.000

Table 6.3 Regional differences in the leachate discharge limits

	COD			NH_4-N		
	Leachate (mg/l)	Discharge Indirect (mg/l)	Direct (mg/l)	Leachate (mg/l)	Discharge Indirect Removal	Direct (mg/l)
Germany (northern Europe)	<5.000	400	200	<1.200	up to 95 %	10
Spain (southern Europe)	<15.000	1.500	160	<2.000		
China (Asia)	<25.000	1.000	100	<3.000		

The table reflects the main and easy determinable pollutants. Generally, there are many other parameters to be met like NO3-N, TN, AOX, heavy metals, which are part of different local discharge consents

than that from a "young" municipal landfill site in the acid phase or a landfill site containing industrial waste or mining waste.

This can lead to distinct differences in the characteristics. As an example, the main pollutants (COD and NH_4-N) of leachate from different origins are shown in Table 6.2.

When leachate moves downwards through the landfill-body it washes out all contaminants from the discharged waste and gets loaded with all components that are soluble in water. To avoid infiltration to the soil or even to the groundwater landfills are equipped with a bottom sealing, preventing the leachate from entering the environment.

The amount of leachate generated by a landfill can be quite different and it occurs discontinuously. The amount is mainly governed by the moisture content of the discharged waste, the climate (amount of rainfall) and the existence of a top cover of the landfill. For landfills it is significant that the occurrence of leachate can be observed for decades. Therefore, the landfills are commonly equipped with a piping systems installed above the liners as leachate collection and discharge system. From this system the leachate is pumped out and treated before discharging to the environment.

Treating leachate can be difficult because of its complex and heterogeneous nature and because of its discontinuous occurrence. Additionally, regional differences in legislation for the leachate discharge are defining different demands on the treatment technology and the discharge limits as shown in Table 6.3.

When discharging leachate it is important to define to where it is to be discharged:

indirect discharge: discharge to the sewer
direct discharge: discharge to the watercourse

There are also special forms of leachate such as the Asian bunker water (leachate from fresh municipal waste containing a very large proportion of organic matter that needs to be dewatered before being incinerated) or water from mechanical-biological waste treatment (MBT) plants which are not accounted for in this paper.

6.3 Leachete Treatment in Accordance with Inlet Concentrations and Outlet Requirements

In summary it can be stated that there is no typical process for landfill leachate treatment existing. In fact, there are very different leachate treatment processes available and applied to meet the different requirements and to handle the different types of leachate.

The focus of this paper will be on aerobic technologies in combination with filtration techniques as principal means to treat landfill leachate successfully. Table 6.4 depicts the most appropriate concepts depending on influent contamination and effluent requirements.

There are also physico-chemical processes which can be used to treat leachate, for example chemical oxidation, flocculation/precipitation, evaporation, stripping, ion exchange. However, since none of them has proven successful as a sole treatment technology or has an elevated demand on chemicals and energy, they are not dealt with here; they may be used as additional pre- or post-treatment steps, though.

Anaerobic treatment is not used in Europe because COD concentrations are far too low and also because nitrogen removal is required and not achievable with an anaerobic treatment. In Asia, anaerobic treatment is often used as a first treatment step e.g. when bunker water with COD concentrations up to 70.000 mg/l needs to be

Table 6.4 Decision support matrix for leachate treatment processes

	Discharge to sewer COD < 400 mg/l	**Discharge to water course** COD 100–200 mg/l	**Discharge to water course** salt reduction
Lowly loaded COD < 1.500 mg/l NH4-N < 500 mg/l	SBR, optional with sand filter + AC	MBR + Activated carbon	Reverse osmosis (RO)
Medium loaded COD < 5.000 mg/l NH4-N < 1.500 mg/l	MBR + Activated carbon (AC)	MBR + Nanofiltration (NF) Option: concentrate treatment with activated carbon (AC)	
Highly loaded COD < 20.000 mg/l NH4-N < 3.000 mg/l			MBR + Reverse osmosis

Fig. 6.1 SBR “Rosenheim”, Germany

treated but one has to consider the tendency to huge problems with precipitation of inorganics when this process is applied to treat leachate with its high salt content. Since bunker water is a special form of leachate and not focus of this paper, anaerobic processes will not be dealt with hereafter.

6.3.1 Low Outlet Requirements: BOD_5 and NH_4-N Reduction in a Sequencing Batch Reactor (SBR)

If only reduction of BOD_5 and NH_4-N (no explicit COD and TN reduction) is desired, the most cost-effective form of treatment is the sequence batch reactor (SBR) (see Fig. 6.1), a form of activated sludge treatment. Traditional activated sludge plants utilise an aerobic/biological tank followed by a settlement chamber. Solids/sludge separation is carried out by gravimetric settlement, where solids are settled to the bottom of the vessel. The supernatant liquid is removed as clean/treated leachate and the remaining solids are recycled to the aerobic/biological tank for reuse.

The SBR combines several process steps in a single unit tank (Fig. 6.2). Raw leachate is fed to the reactor and the aerated biological stage is timed to operate for a specified period. After this, the aeration system is shut down and an anoxic phase with intensive mixing is following. Finally the mixing is shut down and the solids are allowed to settle to the bottom of the reactor. The supernatant (in equal volume to the initial raw leachate feed) is removed and discharged (to sewer or watercourse) and the cycle starts again with a new batch of raw leachate. When necessary a proportion of the suspended solids will be removed as excess sludge.

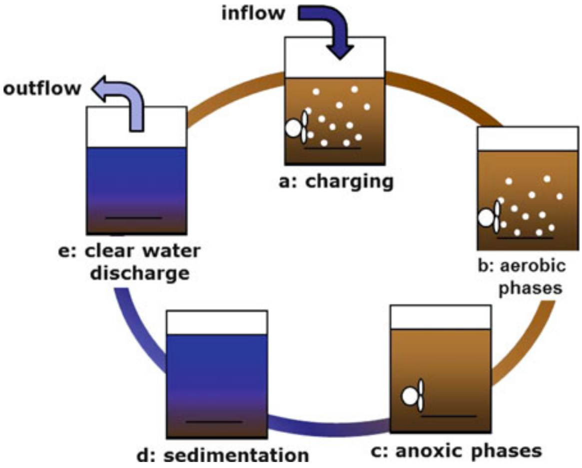

Fig. 6.2 Principle of the SBR concept

In case a SBR reactor is applied for the treatment of leachate with high NH_4-N concentrations, one has to be aware of the complex control mechanisms which are required in order to maintain the pH value and with it to keep the biological process stable. This is necessary as the pH in a SBR is subject to great variations.

Outlet requirements of NH_4-N <100 mg/l and BOD_5 <50 mg/l are easily fulfilled. However, depending on the local (cold!) climate and nitrogen removal requirements, large reaction volumes, i.e. large basins are required. Yet large basins imply large surfaces which enhances the cooling effect and, as a consequence, leads inevitably to a decrease of biological activity and thus to a loss of process stability. Only a sound insulation of tanks and perhaps heating of bioreactors can avert these problems.

Recently, the deammonification a combination of partial nitrification and anaerobic ammonium oxidation (ANAMMOX) is being applied in SBR plants (also ANAMMOX directly could be applied). Deammonification is a process where the oxidation of NH_4-N is purposely kept incomplete as NH_4-N is only oxidized to NO_2-N. The incomplete oxidation results in a decreased oxygen consumption, i.e. less air is required and accordingly less energy for the aeration. The advantage of less energy demand appears to be convincing, but the drawback of this incomplete oxidation is an elevated remaining load of pollutants (COD, NH_4-N, NO_2-N, NO_3-N), which makes this technology very risky when low discharge limits have to be met. Moreover, when the discharge consents are even stricter and additional treatment is required to purify the deammonification (and ANAMOX) effluents, higher post treatment costs have to be expected.

The sales argument for these processes is the lower energy uptake of the aeration system compared to conventional systems, which is claimed to be about 50%. However, one has to keep in mind that the reduction in energy uptake only refers to reduced NH_4-N oxidation whereas the oxidation of organic compounds (BOD and COD, respectively) remains unchanged. Where leachate is concerned, the bulk of the oxygen uptake (= energy requirement) results from the oxidation of the COD, therefore the application of the deammonification or ANAMOX process would not have a substantial effect on the overall energy uptake.

Moreover, these processes are rather sensitive which requires a well-adapted, specialized community of microbes (biocenosis). Thus, all boundary conditions in the reactor, such as temperature, oxygen concentration and pH have to be kept within a very narrow range. Especially the stabilization of the pH requires an increased dosing of caustic soda. This usually results in increased costs for caustic which may well equal the savings from the reduced energy uptake of the aeration system.

Because of the highly specialized microbes, the adaptation process and with the start-up phase of such a plant is prolonged compared to a biological process where NH_4-N is fully oxidized.

6.3.2 Medium Outlet Requirements: Nitrogen and COD Reduction Required

When requirements on the leachate treatment become somewhat tighter, the focus usually is on nitrogen (NH_4-N <10 mg/l and/or total nitrogen reduction of >90 %) and COD removal. Then a SBR needs a more sophisticated process design and consequently the investment costs increase substantially – and still it often fails to meet outlet requirements. This again makes an additional treatment step obligatory. But since the effluent contains high concentrations of suspended solids, a subsequent treatment becomes difficult and expensive. In this case, a Membrane Bioreactor (MBR) is an excellent key-technology, which might be applied either exclusively or in combination with other treatment steps.

6.3.2.1 Membrane Bioreactor (MBR)

A MBR consists of two main units: A biological system and an ultrafiltration (UF) (see Fig. 6.3). The ultrafiltration separates the biomass from treated effluent and replaces the settling tank. The activated sludge is being pumped through external tubular membrane modules and during the passage of the modules, treated effluent is being separated from the biomass. As the pore size of an ultrafiltration membrane lies around 0.02–0.05 μm, no activated sludge is lost, i.e. biomass and suspended matter are retained in the biological system.

The complete retention of biomass is a distinctive feature compared to conventional treatment systems and SBRs which two main beneficial effects:

1. The concentration of adapted bacteria can be kept at a high level,
2. Partical-associated contaminants remain in the system, which improves effluent quality.

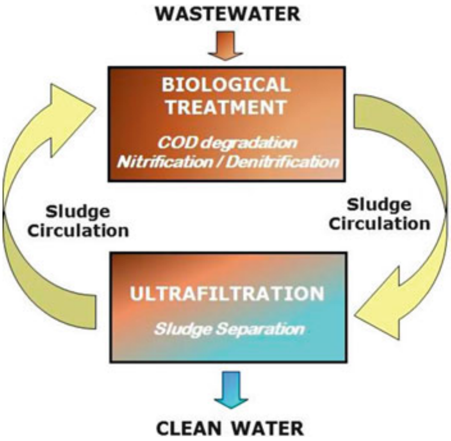

Fig. 6.3 Operation principle of a MBR

Table 6.5 Comparison of MBR systems with submerged or external membranes

MBR with submerged membranes	MBR with external membranes
⊕ Lower energy consumption	⊕ High net flux (up to 150 l/(m²h))
⊕ Many references in municipal applications	⊕ Less membrane surface area required
∅ Low net flux (up to 15 l/(m²h))	⊕ Low membrane replacement costs
∅ High membrane replacement costs	⊕ Easy to clean (CIP)
∅ Difficult to clean (on air)	⊕ Many references in industrial applications and leachate treatment
	∅ Higher energy consumption

A MBR achieves more complete biodegradation compared to other aerobic systems because of high MLSS-concentrations in the reactors (10–25 g/l) and a very high sludge age (20–60 days).

Some countries, such as Great Britain, set target values for TSS in the outlet. These requirements cannot be fulfilled by an SBR alone. Therefore, in most cases it is more cost efficient to build an MBR system than equipping an SBR with a subsequent solid retention step.

There are two different classes of MBR systems, which differ in the way the ultrafiltration membranes are installed. They are referred to as “MBRs with submerged membranes” and “MBRs with external membranes”, respectively. Each of these classes has its individual pros and cons; the most significant ones are listed in Table 6.5.

MBRs with external membranes are very robust, reliable and fully automated systems. The easy CIP cleaning, the low membrane replacement costs and the modular and flexible operation (especially with varying leachate quantities and qualities) are the main arguments that make the MBR technology most suitable in landfill leachate treatment. In Fig. 6.4 a schematic diagram of a MBR-Process is shown. Figure 6.5 shows the largest European installation of a MBR to treat landfill leachate.

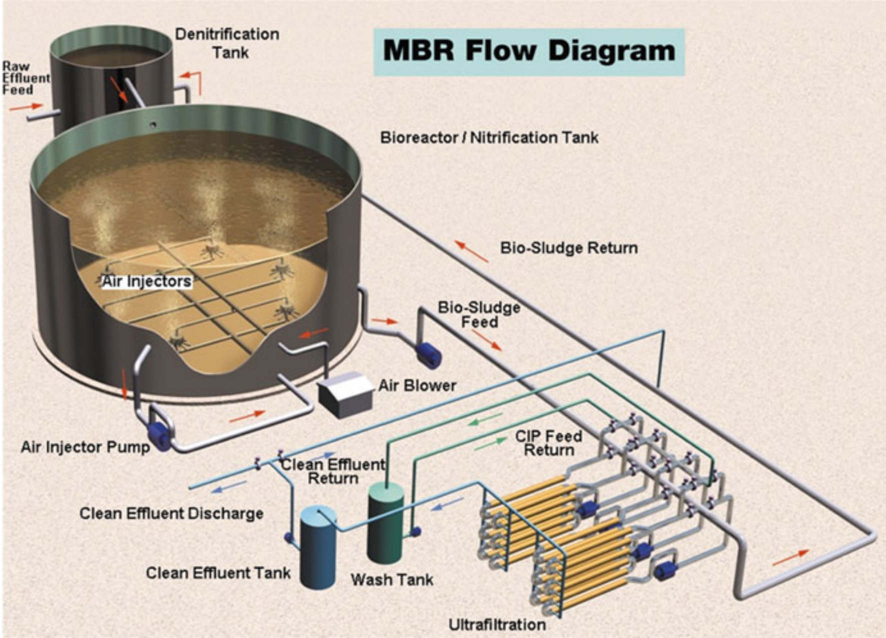

Fig. 6.4 Schematic diagram of a MBR

Fig. 6.5 Leachate treatment plant Bilbao, Spain, built by Wehrle Umwelt

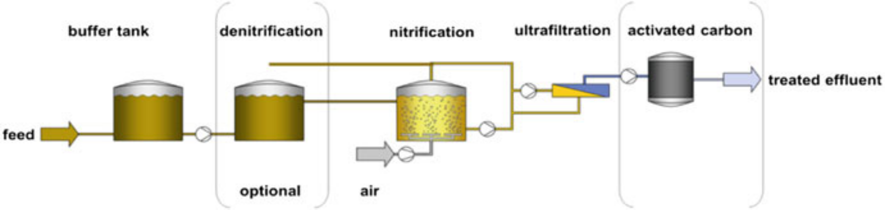

Fig. 6.6 Scheme of MBR/AC configuration

Fig. 6.7 MBR reactor with denitrification/nitrification and AC (Pedret, Spain)

6.3.2.2 MBR + Activated Carbon (AC)

Although in a MBR a substantial COD reduction is achieved, the outlet COD requirements often cannot be met because COD in leachate contains a lot of the so called “hard COD” which is difficult to digest – the readily digestible fraction has often already largely been removed during the passage through the landfill itself. In these cases, a physical-chemical treatment such as activated carbon (AC), chemical oxidation or flocculation/precipitation is included to complete the leachate treatment.

The application of a subsequent AC step is an effective means to bring down COD effluent concentration, as COD is absorbed and retained. Figure 6.6 depicts schematically the configuration of a MBR system with external membranes with a subsequent activated carbon absorber. Figure 6.7 shows an installed system according to this process sceme in Pedret, Spain.

The significant advantage of this configuration over an SBR is apparent: The effluent is free of solids (<5 mg/l) and the biodegradable COD is removed completely. Moreover, the footprint of the installation is significantly smaller. On the other hand, this improved technology is more expensive with respect to CAPEX and OPEX.

The discharge limits for the treated leachate require a biological treatment to meet the nitrogen limits, and an activated carbon system to ensure compliance with the limits for non-biodegradable COD and AOX in the effluent of the plant. Particular requirements for salinity are not provided. The activated carbon is loaded with COD and AOX until the effluent concentration reaches the discharge limits; after this, the activated carbon has to be replaced. The loaded activated carbon is regenerated in special furnaces of the supplier and can then be reused. With this concept, the only residual material to be disposed of is the excess sludge that is produced in the bioreactor.

6.3.2.3 MBR + Nanofiltration

Whereas the combination MBR/AC is appropriate for lower loads of contaminants, this set-up is not economically viable for larger volumes, as the frequent regeneration of activated carbon would result in elevated operational costs. In this case, a subsequent nanofiltration (NF) is the more adequate process.

Due to its unique properties between ultra-filtration (UF) and reverse osmosis (RO) membranes, NF has found a place in the removal of recalcitrant organic compounds and heavy metals from landfill leachate. This treatment process has the ability to remove particles with a molecular weight of higher than 300 Da as well as inorganic substances through electrostatic interactions between the ions and membranes. The significance of this membrane lies in its surface charges, which allow charged solutes smaller than the membrane pores to be rejected, along with bigger neutral solutes and salts.

As a pressure driven (3–20 bar) cross-flow filtration technology with membrane pore sizes of 1–10 nm, NF is able to hold back molecular substances, such as dissolved organic compounds and bivalent ions, which pass an UF membrane. Monovalent ions such as chloride or sodium, which would increase the osmotic pressure, pass through the membrane and leaving the system with the treated leachate. Due to these two characteristics of a NF membrane, the nanofiltration process is ideal as a secondary treatment after MBR.

When using membrane filtration units for the treatment of leachates, two outputs are produced: a concentrate and permeate.

The **permeate** as the clean effluent is usually very low polluted. The average pollutant concentration is far below discharge limits and the permeate as the treated effluent can be discharged directly into the watercourse.

The **concentrate** containing the dissolved organic fraction as well as the bivalent ions is considered as liquid waste. Therefore it requires further treatment before it is discharged or sent back to the landfill as waste.

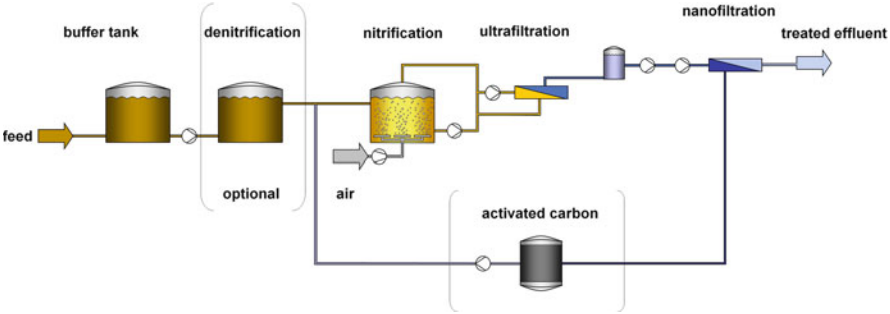

Fig. 6.8 Schematic depiction of the BIOMEMBRAT® plus process

Thus concentrates from the NF need to be treated furtherly. Treatment options are activated carbon, oxidation or flocculation/precipitation. Costs for the operation of a NF and for the subsequent treatment of NF concentrates are still far lower than costs for the direct treatment of the MBR effluent with physical-chemical means. This is because of the high COD concentrations in the NF concentrate that makes secondary treatment much more effective. This concept of concentrate treatment is an economic alternative to either burning or evaporation.

6.3.2.4 MBR + Nanofiltration + Activated Carbon (BIOMEMBRAT® plus)

The MBR technology combined with a nanofiltration unit allows strict effluent conditions to be met. However, this concept has a handicap if it is not possible to return the concentrate to the landfill or if the disposal costs are too expensive.

Wehrle Umwelt GmbH has developed a low residues production process technology for the leachate treatment, combining not only MBR and nanofiltration technology, but also a sustainable solution for the concentrate treatment: the BIOMEMBRAT® *plus* Process (Fig. 6.8).

The process combines three of three different processes:

- The biological treatment in the MBR, which reduces nitrogen concentration, BOD and biodegradable COD.
- A Nanofiltration Unit (NF) as post-treatment for the permeate coming from the MBR, where the slowly biodegradable COD, or the non-biodegradable COD are removed. In this step the wastewater is separated into two streams: A high loaded concentrate and a clean permeate. Depending on the type of membrane used for the NF, the COD of the permeate can reach values lower than 100 mg/l. Still, it is required that all the nitrogen is removed in the biological treatment as the NF is not capable of retaining monovalent ions. This is the advantage of having the combined biological process. Chloride and sulphate are partially retained by the NF. An assessed mass balance ensures that the amount of chloride and sulphate

Table 6.6 Concentrations of the Winnenden LTP

		Inlet	Outlet
COD	mg/l	2.800	<200
BOD	mg/l	400	<10
NH4-N	mg/l	1.200	<10
NO2-N	mg/l	<1	<2
NO3-N	mg/l	<1	<70
AOX	mg/l	1.5	<0.5

discharged is equal to the values in the inlet, assuring no toxicity for the bacteria concerning the sulphate. Compared to Reverse Osmosis, the Nanofiltration has also the advantage that less concentrate is produced, being capable of coping with the discharge limit values, and hence providing very efficient leachate treatment.

- An adsorption step with Activated Carbon (AC), where the concentrate coming from the NF will be treated. This concentrate can contain up to 8,000 mg/l of non-biodegradable COD. This COD will be then adsorbed on the AC bed. The costs of an AC-treatment are related to the maximal load possible before regeneration and the invest costs of the AC. This means that the maximal load allowed at the surface area of the AC is proportional to the COD concentration in the wastewater. By concentrating the load on the concentrate side of the NF treatment, the amount of required AC is reduced, and hence a more economically efficient process is achieved. If the wastewater would be treated directly after the MBR (without the NF step), such a high load of the AC could not be reached and, consequently, the required AC quantity would be higher.

Usually in a Reverse Osmosis plant (see Sect. 6.3.3.1) both chlorides and sulphates are retained. This means that these salts will stay in the concentrate and since they are not adsorbed by the activated carbon, they will stay in the system. By using nanofiltration membranes the concentrate produced is more organic, because the monovalent ions mainly pass the NF membranes and therefore the NF permeates salts content is lower, and thus the efficiency that can be achieved at the AC reactor is much higher. The NF membranes are tough enough to cope with the discharge limit values.

In the BIOMEMBRAT® *plus* process, only the excess sludge of the biological treatment has to be disposed of. The treated concentrate after the AC-treatment is sent back to the inlet of the plant and the permeate leaving the NF-unit can be directly discharged into the surface water bodies. The salts contained in the raw wastewater are discharged with the permeate. The AC can be regenerated by the supplier and can be reused again for the removal of organic matter from the wastewater.

The leachate treatment plant in Winnenden (Stuttgart, Germany) (Fig. 6.9) is an example for the successful implementation of this process. It was designed for the following inlet and outlet concentrations (Table 6.6):

The leachate amount treated in this plant is approx. 75.000 m³/a. The treated leachate is directly discharged into a river. In Europe there are four more plants working with this procedure.

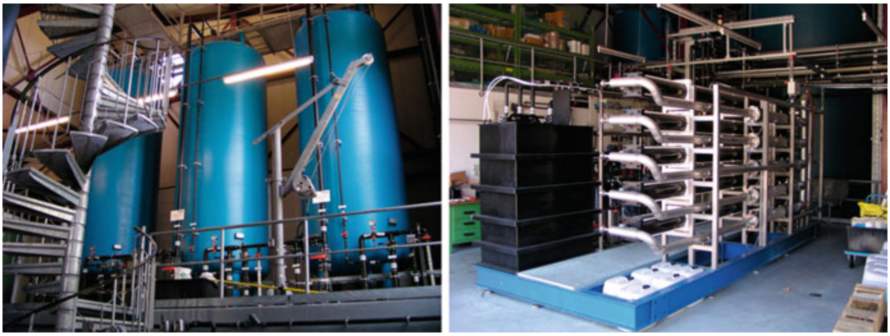

Fig. 6.9 Winnenden LTP (*left: Bioreactors; right: NF-unit*)

The BIOMEMBRAT® *plus* process can not only be a solution for leachate treatment, but also for industrial wastewater treatment, where the production of lower residues is important.

6.3.3 High Outlet Requirements = Direct Discharge to Rivers

When a direct discharge of the effluent to a river is envisioned, high demands on the treatment regarding COD and nitrogen removal are made. In Europe, COD has to be lowered to 200 mg/l and in Asia even as low as 100 mg/l. NH_4-N has to be lowering than 10 mg/l and denitrification as far as possible is demanded. Furthermore, some countries even ask for a distinct salt removal from the leachate before discharge to the watercourse. Environmental agencies survey inlets to rivers very closely; therefore the technique used for the leachate treatment has to fulfil high standards and has to be very reliable.

6.3.3.1 Reverse Osmosis

When stringent effluent quality parameters and especially low salinity/conductivity is demanded, the use of the reverse osmosis (RO) might be an adequate option for the treatment of landfill leachate. Figure 6.10 shows a schematic flow diagram of the process.

A pre-treatment, typically by filtration, is always needed to remove suspended solids. Moreover, if the NH_4-N concentration in the leachate is high, a pre-treatment like a stripping unit is strongly recommended, to reduce the ammonium content before the leachate is pumped to the RO-unit, since strict NH_4-N effluent limits cannot be met with high RO inflow ammonium levels when using single or two step RO systems. Some chemicals, such as sulphuric acid or antiscaling products, are added to prevent scaling on the RO membranes.

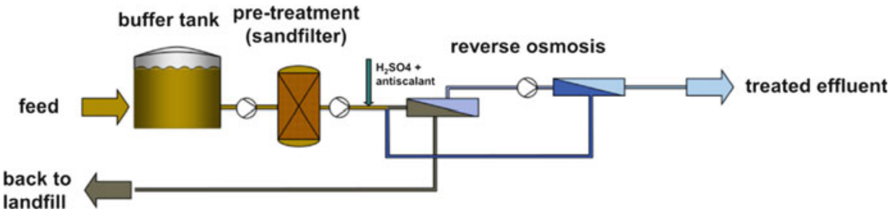

Fig. 6.10 Schematic depiction of a reverse osmosis plant for the leachate treatment

The reverse osmosis process is usually designed with at least two stages, where the permeate of the first stage is further treated in a second stage to fulfil the strict discharge limit requirements. The concentrate of this second stage is returned to the first stage, whereas the concentrate of the first stage has to be disposed of. This concentrate is usually a 20–40 % of the total inlet volume and its disposal becomes a problem. As it will be described later, in many cases the concentrate is returned to the landfill, although this practice is nowadays forbidden in many countries. The only alternative is the external disposal by a waste management company, which leads to high operational costs. In this way, it has to be pointed out that the reverse osmosis is just a concentration process, which is not meant to degrade the pollutants but only to reduce volume of wastewater.

Although the RO permeate has a good quality (COD <100 mg/l, no solids, low salt content), the RO process has a reduced reliability compared to other treatment techniques, mainly because of its troublesome operation, involving high operation costs (membrane replacement due to scaling/biofouling, chemicals consumption, etc.) and due to changes in the leachate composition which varies with the seasons of the year. In addition, the investment costs for large installations make this process a real alternative only in certain conditions: Low leachate volume (batch operation) and low pollutant concentration in the inlet.

6.3.3.2 MBR + Reverse Osmosis

As previously described, the treatment of landfill leachate by reverse osmosis implies a tough operation and expensive treatment costs, but a good quality effluent. The main problems of the RO process are related to the membrane performance. Landfill leachate contains many compounds, which are prone to affect the membrane, reducing the membrane flux by (bio)fouling, scaling or chemical damage. Most of these compounds may be removed or reduced in a MBR process, so the combination of MBR and reverse osmosis has achieved good performance in the treatment of landfill leachates, especially under direct discharge conditions, where high quality in the effluent is required.

The UF permeate from the MBR process is herein pumped into the RO unit, where the non-biodegradable COD and salts are removed. The reduced content in pollutants in the RO inlet leads to the installation of only one RO stage which is,

Fig. 6.11 Ultrafiltration and reverse osmosis units in a MBR + RO plant in a landfill of Girona, Spain, built by Wehrle Umwelt

moreover, operated at lower pressure. As a result, the concentrate volume and the amount of chemicals added are lower compared to the sole reverse osmosis process: The nitrogen compounds, as well as the biodegradable COD, are removed in the biological step by the combined nitrification/denitrification process, so there is no need of additional stages or treatments to remove NH_4-N.

Figure 6.11 shows UF and RO units in a MBR/RO plant for the treatment of landfill leachate in Girona, Spain.

6.3.3.3 RO Concentrate Management: Back to the Landfill?

As previously mentioned, the management of the RO concentrate has become a problem because of its high degree of pollution, especially in the case of a direct RO treatment, where all the pollutants contained in the leachate are concentrated in a lower volume. In some countries it is a common practice to return this concentrate back to the landfill. The aim is to try to deposit and fix in place some of the pollutants in the landfill bed once again, such as bivalent ions (carbonates, sulphates) or long-chained organic molecules. However, the monovalent ions, such as ammonium or chloride, are barely or not at all retained in the landfill, leading to a re-concentration of these compounds in the leachate.

Figures 6.12 and 6.13 shows the evolution of concentration of COD and ammonium and the conductivity of the leachate, after the disposal of the concentrate back to the landfill. Obviously, there is a significant increase in these parameters once the

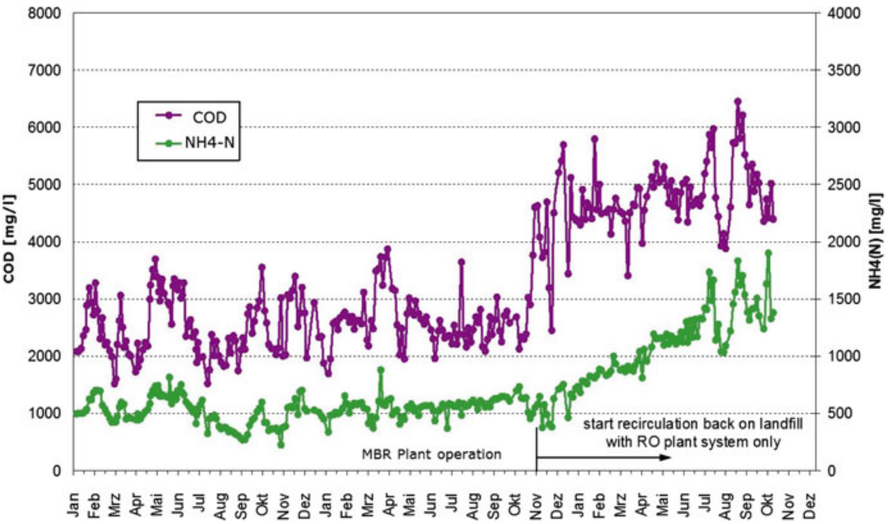

Fig. 6.12 Evolution of COD and ammonium concentration in the leachate after the disposal of RO concentrate back to the landfill

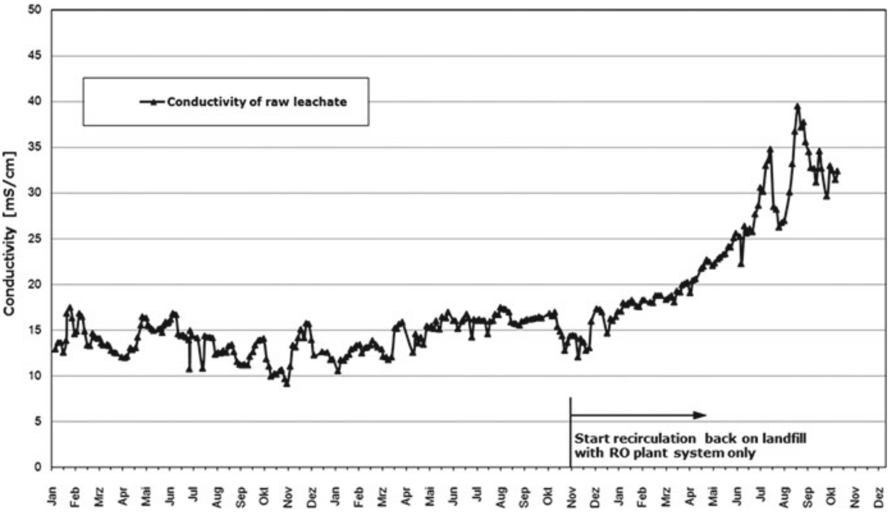

Fig. 6.13 Evolution of conductivity in the leachate after the disposal of RO concentrate back to the landfill

client decided to return the concentrate back to the landfill, which has after a short time a notable effect on the leachate treatment in terms of treatment costs (increased demand on chemicals and energy, more concentrate production) and in terms of effluent quality, that is influenced negatively by increasing pollutant concentrations.

As the recirculation of RO concentrates results in a notable decrease of leachate quality and hence in plant performance, this is not at all a sustainable approach. As a consequence, several evaporation plants have been installed lately in landfills of Europe to reduce the waste volume of concentrates before they are disposed of externally. In some plants the concentrated phase from the evaporation, the so-called superconcentrate, is even processed in a so called inertisation step, whose end-product may be returned to the landfill as it fulfil strict elution tests.

As a matter of fact, all these post-treatments increase the operation costs and it is up to the client to take a decision about the concentrate management, depending on local circumstances.

6.4 Conclusion

Aerobic processes for the treatment of leachate are very effective and more economical compared to the direct treatment of leachate with physico-chemical technologies. Throughout Europe and Asia, aerobic processes are the leading technology for leachate treatment. When effluent requirements exceed the pure reduction of BOD_5, a Membrane Bioreactor (MBR) is an excellent means because it reaches maximal COD reduction and an effluent free of suspended solids. In combination with subsequent NF/RO, even very high outlet requirements can be met without the drawbacks that come along with a reverse osmosis as exclusive treatment process such as reduction of yield and deterioration of the overall treatment process performance due to constant salt enrichment.

To fully reduce the negative impact on the environment optimal leachate treatment is today's challenge. But, the complexity of the leachate composition makes it very difficult to formulate general recommendations on the proper treatment technology. Variations in leachates, in particular their variation in flow at a single landfill site as well as the variation in load and pollution at a single site and when different landfills are compared means that the most appropriate treatment should be universal and adaptable. In many cases the conventional biological or physical treatment alone is not suitable to reach the requested level of purification and thus more complex "hybrid" treatment processes are demanded.

The various methods presented in the previous sections offer individual advantages and disadvantages with respect to certain facets of the problem. Suitable treatment strategies depend on two major criteria:

1. The final requirements given by local discharge water standards
2. The leachate characteristics such as COD, BOD, NH_4-N, heavy metals, salts which vary with the age of a landfill

The knowledge of these specific parameters may help to select the most suitable treatment processes, according to the decision support matrix presented as Table 6.4.

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Chapter 7
Textile Wastewater Treatment and Recycling

Raja Ben Amar and Gazza Masmoudi

Abstract Textile industry consumes huge quantities of fresh water (100–150 l/kg of cotton for direct dye). During various stages of textile processing, wastewater is charged with substantial amounts of chemical pollutants. Direct discharge of these effluents into the environment causes irreversible ecological problems. Effluents coming from the different steps of dyeing cycle can be collected separately for a further treatment at source or simultaneously to be treated using a traditional treatment process. Various technologies are developed to reduce environmental damage. The most used technologies are Conventional Activated Sludge (CAS) and coagulation-flocculation (CF). However, color and salt removal from textile wastewater by means of these technologies still a major problem. Membrane processes represents a better alternative for the treatment and reuse of such wastewaters due to their capability to produce a water quality, in conformity with the more and more strict legislation in place. Microfiltration and Nanofiltration used separately or combined together have been found to be the most successful treatment methods. Various aspects will be discussed regarding the methodology and process adopted to enhance the efficiency of the treatment including the treatment at source which can be a good alternative. Also, several examples will be given.

7.1 Textile Wastewater

Industrial textile process includes several operations such as pretreatment, dyeing, washing, neutralizing and softening. Some operations are followed by one or more rinsing step. Dyeing is an essential step in the production cycle of finished textile.

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DOI 10.1007/978-94-007-5079-1_7,

It is a combined process of coloring, finishing and washing. Different operations accomplishing the dyeing cycle require the input of wide range of chemicals (salts and auxiliaries) and dyestuffs which are generally organic compounds of complex structure. Reactive dyes are especially used for dark colors dyeing; they are soluble in water and have affinity to cotton and cellulosic fibers. [1] cited that 1 kg of cotton requires an average of 70–150 L of fresh water, 0.6 kg of NaCl and 40 g of reactive dye. Almost 20–30% of the applied dyes are not fixed on the substrate and will be found in the effluent.

Therefore, textile industries generate voluminous quantities of complex effluents which in turn cause irreversible environmental degradation when they are directly discharged into the environment.

7.2 Textile Wastewater Treatment Processes

Due to the complexity of produced effluents, the treatment may needs more than one step. The current trends in the treatment of textile wastewater include CF, CAS and membrane processes.

7.2.1 Coagulation/Flocculation (CF) Performances

CF is the most commonly used as main or pre-treatment process due to its low capital cost but it's unable to reduce the conductivity and to eliminate completely the color mostly for soluble dyes [2].On the other side, large quantities of chemicals are needed to achieve completely color removal producing large volume of sludge which constitutes the main limitation of this process. The CF efficiency depends widely on the effluent quality regarding salinity, pH and color intensity; therefore the effectiveness of the coagulation process can be enhanced by the optimisation of initial pH, coagulant and flocculant's doses and settling time. The coagulation process was generally performed using the aluminium sulphate reagent $Al_2(SO_4)_3$, 16 H_2O as coagulant. Different hydrolysis species can be formed depending on pH, salinity and coagulant dose such as Al_3^+, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$ and $Al(OH)_4^-$. All these species can interact with different types of pollutants, achieving or preventing their removal from the wastewater. Thus, zeta potential variation under different conditions should be determined taking into account the fluctuation of the effluent quality.

To investigate the effect of pollution content fluctuation on treatment process performances, a model effluent should be used. The optimal dose of coagulant is usually determined by Jartests under different conditions of salinity, pH and stirring. Figures 7.1 and 7.2 illustrates experiments with model effluent using reactive blue Bezactiv S-GLD150 dye showing turbidity and color removal as well as the variation of zeta potential with pH when different doses of coagulant were used. It can be

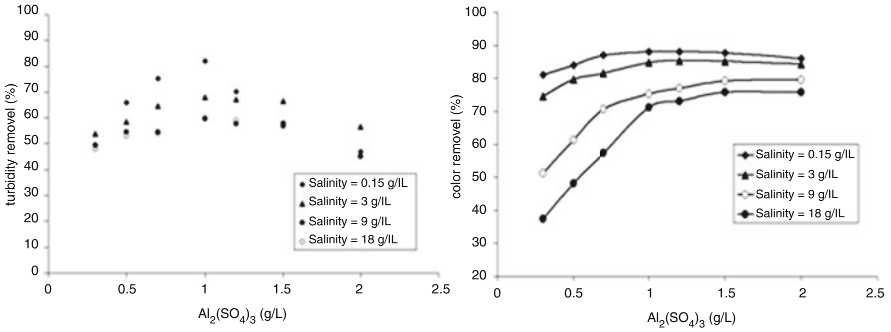

Fig. 7.1 Variation of color and turbidity removal versus coagulant dose for model effluents

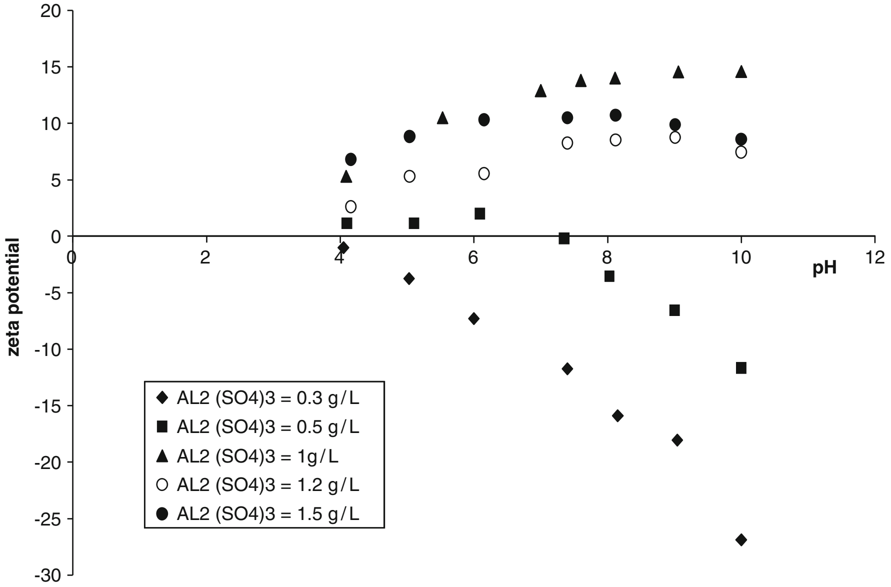

Fig. 7.2 Effect of pH on zeta potential distribution at different dose of coagulant (salinity = 3 g/l) ([3])

seen that an optimal value of coagulant dose can be determined; in this case it is of almost 1 g/l.

On the other hand, if we analyze the surface charge of the coagulated colloids, it appears that the colloidal charge may be very different when coagulant dose and pH vary which affect coagulation performances.

Figure 7.3 illustrates the variation of the zeta potential and color removal when real effluents having different characteristics were used. In this case, the zeta potential remains constant over a coagulant dose of 0.5 g/l. It is negative for real effluent and

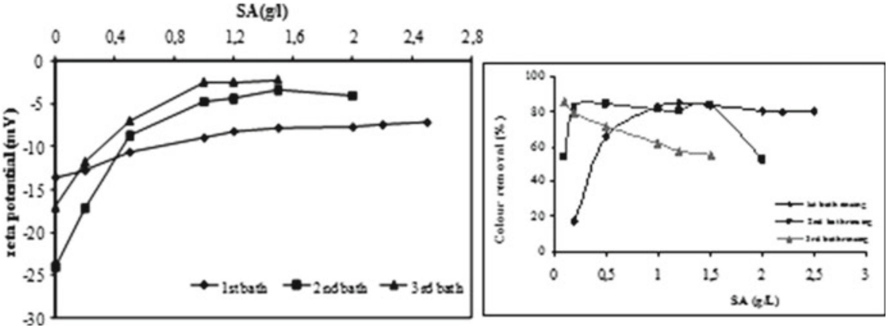

Fig. 7.3 Zeta potential and color removal results with real effluents [3]

positive for model effluent. The optimal dose of coagulant is between 0.5 and 1 g/l. Thus, it appears that the charge distribution depends on the ionic matrix, ionic strength and concentration of the pollutants.

7.2.2 Biological Treatment Performances

Notes in this section are taken from [4]. Usually, the biological treatment can be achieved by different experimental approaches such as Conventional Activated Sludge (CAS), Aerobic Sequencing Batch Reactor (SBR) and enzymatic treatment using commercial laccase.

When biological treatment is considered, the sludge production during the run should be stable and relatively low. However, values above the mean fixed can be obtained which shows that during the period of treatment, the biomass loses its characteristics of good settling; this strongly suggests the addition of nutrients for a good bacterial growth. On the other hand, mixture culture composed of a wide range of micro-organisms including bacteria, fungi, yeast and algae have been found suitable to distain and degrade several classes of dyes (Fig. 7.4).

At low organic loading rates (from 350 to 400 mgCOD/gMLVSS.d), high COD removal efficiencies were obtained and were in the range of 96–98 %. About 95 % COD removal efficiency was obtained at organic loading rates of about 420 mgCOD/gMLVSS.d .

Due the relatively low biodegradability of most of the textile effluents, (COD/BOD$_5$ value between 2.5 and 3), biological treatment by traditional methods such as activated sludge does not always meet with great success. Nowadays, the main biological treatment for a specific need for recycling strategy is membrane bioreactor (MBR). MBR is commonly understood as the combination of membrane filtration and biological treatment using activated sludge where the membrane primarily serves to replace the clarifier tank in the waste water treatment system (Figs. 7.5 and 7.6).

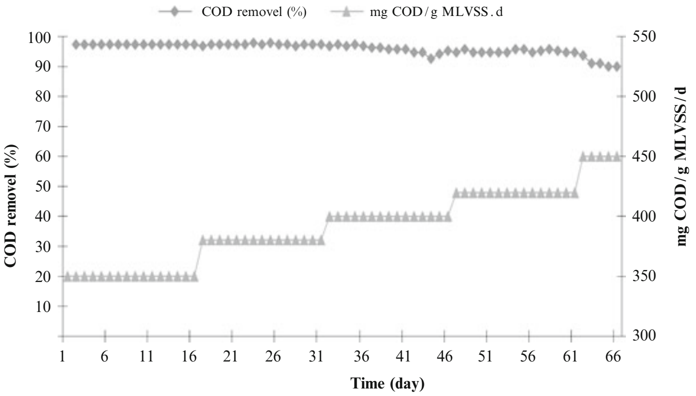

Fig. 7.4 Typical results with CAS treatment

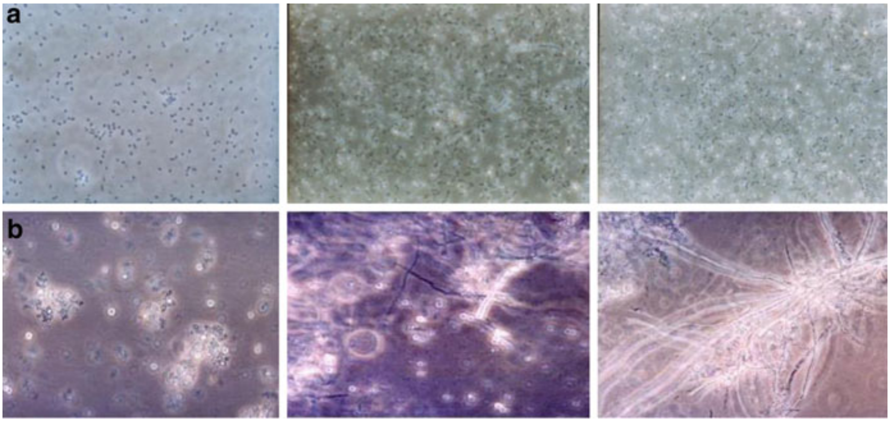

Fig. 7.5 Microbial flora forming the bacterial consortium 'Bx' during MBR treatment (**a**) and SBR treatment (**b**)

The microbial flora resulting from biological treatment of a textile reactive Blue Dye solution using mixed bacteria consortium has different aspects depending on the biological process used: flocculated aspect for SBR treatment and dispersed aspect for MBR treatment. Indeed, the use of MBR induces significant modifications in sludge morphology such as: decrease in flocks size, densification of aggregates, and development of non-flocculating organisms which explain the enhancement of the quality of the treated water.

The MBR allows adaptation of a microbial community towards toxic or recalcitrant compounds which is very useful to improve the decolourization performances and COD degradation. In the same time, membrane separation allows a total removal of suspended matter.

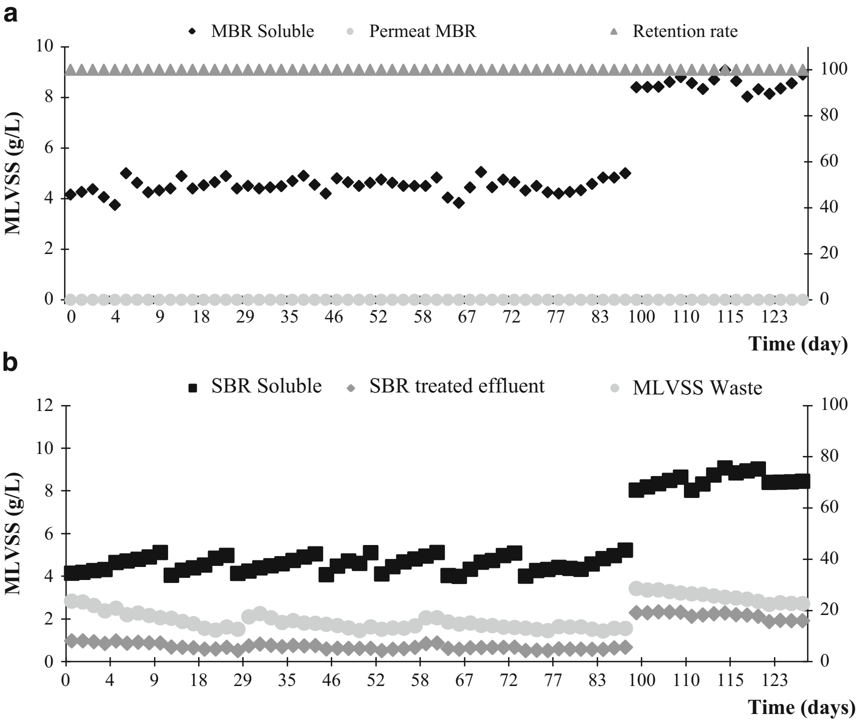

Fig. 7.6 Comparison between MBR (**a**) and SBR (**b**) performances: MLVSS variation

7.3 Membrane Processes

Membrane separation technologies are potentially able to reduce the load of polluted effluents from industrial wastewaters. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) represent different scales of membrane filtration. Regarding the pore size, MF (>0.1 μm) is almost used as pretreatment, UF (0.1–0.01 μm), NF (0.01–0.001 μm) and RO (<0.001 μm) assume a finalization role and are essential for effluents reuse.

In the treatment of textile effluents, membrane technology can be applied following two approaches; hybrid treatment in which membrane technology is coupled with another process (Coagulation-flocculation or biological treatment) or membrane combination processes.

7.3.1 Hybrid Treatment

To enhance the performances of CF or biological treatments, membrane processes can be added as post-treatment for the purpose of a possible effluent reuse.

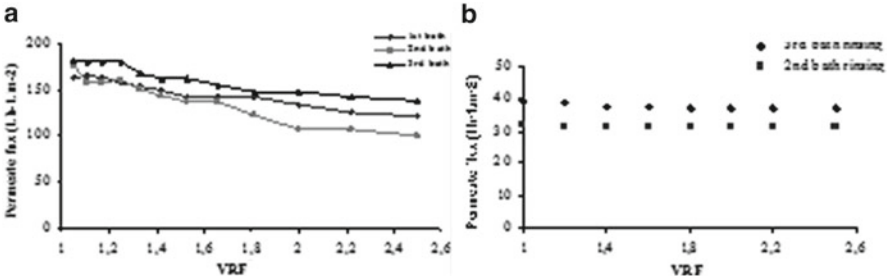

Fig. 7.7 Variation of the permeate flux for UF (**a**) and NF (**b**) versus VRF for different baths

Table 7.1 Performances of different treatment schemes for different effluents

Bath	Treatment	Color removal (%)	Salinity removal (%)	Turbidity (NTU)
1st bath	CF/NF	99.4	47	0.6
	CF	85	0	8
	CF/UF	90	20	0.86
2nd bath	CF/NF	99.6	51	0.4
	CF	85	0	6
	CF/UF	88	22	0.7
3rd bath	CF/NF	99.6	58	0.36
	CF	86	0	3.1
	CF/UF	90	24	0.62

7.3.1.1 Coupling of C-F with Membrane Process

UF and NF membranes were often used after CF treatment. This combination enhances the quality of purified water and minimizes the membrane fouling.

From permeate flux values, turbidity and color removal measurement, it is possible to evaluate the performances of the treatment. The following results taking into account the fluctuation of the quality of the effluents (baths) show that the performances in term of permeate flux as well as treated water quality can be almost maintained constant independent of the initial effluent quality. Therefore, to enhance the performances of the CF treatment and following the goal of the treatment (clarification, desalination or decolourisation), UF and NF can be successfully used as post-treatment (Fig. 7.7), (Table 7.1).

7.3.1.2 Coupling of Activated Sludge with Membrane Processes

Although the treatment by conventional activated sludge (CAS) is among the most common processes used in the treatment of textile effluents, it remains inefficient in salts and some dyes removal. To enhance the CAS efficiency, membrane process

Table 7.2 CAS/NF treated effluent at different transmembrane pressure (TMP) and pollutant concentration (VRF): TMP = (Pi + Pe)/2–Pp When Pi is the inlet pressure; Pe is the exit pressure and Pp is the permeate pressure, usually $Pp = P_{atm}$; VRF is Volume Reduction Factor/VRF = Vi/Vr where Vi and Vr are respectively the initial and the retentate volumes5

Parameters	TMP = 8 bar	TMP = 10 bar	TMP = 12 bar	TMP = 14 bar
VRF	3.2	2	2	2
R Color (%)	100	100	100	100
R Salinity (%)	50	50	65	61
R COD (%)	63	68	83	62
J (l/h.m²)	10.5	9.5	18	18.7
RHCO3(%)	31.4	53.4	71.1	71.8
R Cl^-(%)	11.2	23.7	32.3	19.8
RNO_3^-(%)	58.2	60	61.9	40
RSO_4^{2-}(%)	98.6	99.2	99	99
R Ca^{2+} (%)	90.4	99	96.8	95.5
R Mg^{2+} (%)	90.6	94.8	97	97.5
RNa^+ (%)	41.7	66	62.5	64.5
RK^+ (%)	38.3	70.4	63.7	65.8

The best performances regarding permeate flux and pollutant retention rate were obtained at 12 bar. A total retention of color was achieved [5]

such as MF or NF can be added in post-treatment to biological treatment. Table 7.2 illustrates the results obtained from NF used in post treatment to CAS system applied to textile industry waste water treatment.

7.3.2 Combination of Membrane Processes

In this approach, two or more membrane processes have to be used. MF has been gaining a wider acceptance as pretreatment because it is more economically feasible than conventional methods. The use of combination of MF and NF for the treatment of textile effluents allows complete removal of COD and color. In the same time, the removal of salt can reach important values mostly for the bivalent.

Two approaches were considered in the treatment of textile effluents using combined membrane processes; treatment of global effluent where all baths are collected and treated by the same way and the treatment at source which seems to be a good alternative to minimize pollution released by the dyeing bath produced in small volumes, compared with other operations, but with substantial concentration of pollution.

7.3.2.1 Treatment of Global Effluent

The global effluent involves different wastewater coming from different textile operations like dyeing, bleaching and washing. As it can be seen on Fig. 7.8, a comparison between MF and CF performances as pretreatment for NF in the treatment of global effluent showed that MF gives the better performances than CF [6]

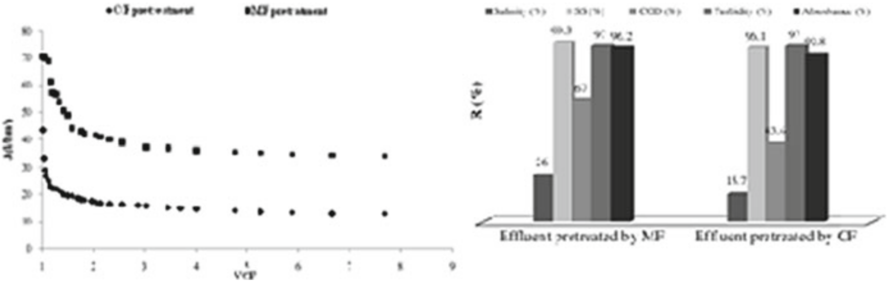

Fig. 7.8 Comparison between MF/NF and CF/NF performances

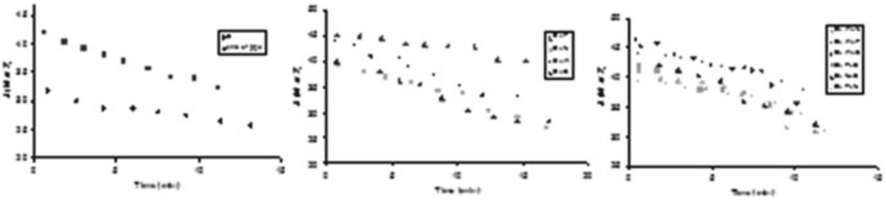

Fig. 7.9 NF permeate flux after MF pretreatment versus time for all realized configurations

7.3.2.2 Treatment at Source

The treatment at source of textile effluents for reuse is a recent treatment scheme. It seems to be a good alternative for the treatment of the dyeing bath producing small volumes, compared with other operations, but with substantial amounts of pollution.

The dyeing process comprises different operations, beginning with preparation (P), then dyeing (D), neutralizing (N), washing (W) and finally softening (S). However, the dyeing effluent is the most charged with pollution. Many combinations considering the dyeing bath and other effluents can be achieved allowing dilution of and favorable reactions between different baths components. A combined treatment coupling MF and NF was generally used also (Fig. 7.9). The presence of surfactant in some bathes such as P, W and S can make micelles in which dye particles are locked. Then, pollutant size increases allowing easily retention by the membrane [7].

The high quality of NF permeate produced showing total retention of all pollution parameters (color, turbidity and COD) expected for salinity which did not exceed almost 50 %, allows its reuse as a process water for dyeing step under two possible conditions which are only NF permeate as well as a mixture of NF permeate and soft water.

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Chapter 8
Changes in Groundwater Salinity and Nitrate Concentrations Due to Aquifer Recharge by Treated Wastewater: Korba Case Study

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Abstract The overexploitation of Korba aquifer mainly for irrigation purposes at a rate of 103 % caused a decrease in aquifer level in addition to its deteriorating water quality. Since July 2008, treated wastewater from Korba plant has been used to artificially recharge the aquifer at a site close to the treated wastewater plant. The purpose of this project is to develop a new sustainable water resource, to improve the groundwater bad quality and raise the piezometry of the coastal groundwater in this region.

Before starting the recharge, both groundwater and treated wastewater were monitored for their quality. The resulting mixture of groundwater and infiltrated treated wastewater is monitored since then. The changes in water quality before and

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after 3 years of recharge are followed for two significant parameters throughout the whole study zone: salinity and nitrates concentration, in an area of about 9 km^2 including both the recharge site and the treatment plant. There is no clear difference introduced by the recharge on nitrates very high concentrations as 90 % of the studied waters contain more than 50 mg L^{-1} NO_3 unchanged and classified as bad or very bad quality waters. For salinity there is a slight decrease especially around the recharge area. In the light of these results, this ambitious project already shows positive effects for water and environmental management in the region.

8.1 Introduction

Groundwater, which represent an important source of water in Tunisia, is overexploited at a rate exceeding 103 %, essentially for agriculture that consumes 80 % of the available freshwater. Additionally, the use of various fertilizers has damaged qualitatively and quantitatively the groundwater resources [7]. This conjunction leads to a decrease in piezometric levels, seawater intrusion and high nitrates and salts levels. By the same time, as salty groundwater is used for irrigation, agricultural field salinity is increased, reducing and sometimes even stopping productivity [4]. High bacteriological, salt and/or nitrate contaminations of Tunisian ground waters make them useless for drinking purposes [3]. Considering these facts and the high occurrence of water scarcity in the southern shore of Mediterranean sea [2] the reuse of treated wastewater (TWW) in Tunisia has been used since 1965 as a solution to water shortage. This reuse has been applied in direct irrigation of authorized fruit tree growing, green spaces and golf courses. Presently, the reuse of TWW is beginning to be applied to groundwater remediation by the recharge of deteriorated aquifers using infiltration basin systems.

Many experiments has been conducted elsewhere for the recharge of aquifers by treated wastewater. For example, in 1985 at El Paso (Texas, USA) wastewater was treated by tertiary treatment operations serving dual purposes: the reuse of the wastewater and the restoration of groundwater [9]; in Dan region (Israel) tertiary treated wastewater was used for the recharge of an aquifer during a 300 days experiment, the resulting water was true to irrigation standards with non restrictive use as no bacteriological contamination was found in the aquifer [6]. On the other side, irrigation with water from wells refilled by TWW for agriculture can decrease fertilization use and costs due to the nutrients that it contains [5] and its reuse for recharging the aquifer would help struggling water scarcity and braking marine intrusion.

The aim of the present paper is to investigate the impact of recharging the aquifer by tertiary treated wastewater in a semi-arid region in Tunisia (Korba) in its first 3 years phase, especially on groundwater salinity remediation. The results would allow the evaluation of the effects of TWW on the local groundwater in order to suggest adequate solutions to water scarcity, destruction of the regional aquifer and solving the problem of TWW safe elimination.

8.2 The Study Area

The study area is located in Korba region, in Tunisia (Africa) (Fig. 8.1). Geologically, the region (Pliocene-quaternary) is mainly composed by sandstones, conglomerates and clay. The dominant economic activity is agriculture with some agro-industries, textile industries and tourism. The population of this region is about 100,000 inhabitants [8] and the region is situated in a moderate pluvial zone with an annual rain average between 450 and 500 mm year^{-1}. In order to respond to the increased water demand in this region, the aquifer was highly solicited since the seventies conducting to a decrease in piezometric levels and generating a degradation of the groundwater quality essentially because of seawater intrusion. This bad situation was worsened by to the multiplication and deepening of the wells as well as their electrification in order to increase the volume of pumped groundwater. This situation results in marine intrusion, depriving the plio-quaternary aquifer of any contribution of subsoil water.

Fig. 8.1 Location of the studied area (Korba -Tunisia)

Fig. 8.2 Korba wastewater treatment plant (© 2009 Google)

8.3 Project Description

8.3.1 Treated Wastewater Plant

Reclaimed water used to feed the project is provided by the treatment plant which begins its work in July 2002, close to the infiltration basins (Fig. 8.2). It is dimensioned for 7,500 m^3 of wastewater per day and actually receives about 5,000 m^3 per day and can provide 1,500 m^3 day^{-1} to the recharge site.

The treatment process consists of three successive steps: pre-treatment, secondary then tertiary treatments. The pre-treatment removes large solid wastes. The secondary treatment is performed by an oxidation channel process and allows the development of bacterial flocs while the tertiary treatment allows clarified water to move towards the maturation ponds. This process allows the reduction of the organic content without artificial ventilation or mixing.

8.3.2 Infiltration Basins Plant

The retained site for the case of Korba project is situated close to the treated wastewater plant. In the feasibility study, it was dimensioned to receive 1,500 m^3 day^{-1} of treated wastewater and proposed according to the hydro-geological conditions of the site.

Fig. 8.3 Photography of one of the infiltration basins

The characteristic of the recharge basins (Fig. 8.3) are as follows:

- infiltration capacity of 0.5 m day^{-1}
- number of basins: 3 with 4,500 m^2 of total surface
- TWW collecting reservoir: 300 m^3
- pipe diameter for basins feeding is 400 mm

The sustainability of the infiltration process needs an alternately use of the infiltration basins to allow the non-saturated zone aeration and the basins cleaning in order to re-establish and maintain infiltration capacity of the basins. The advantage for the infiltration basins technique is the promotion of the soil purification as an additional treatment of the water. Bad points are the use of a big surface area and the high costs of maintenance to ovoid clogging risks. The clogging is a phenomenon frequently observed in aquifer recharge with treated wastewater. It can become a barrier against infiltration process.

8.4 Sampling, Preparation and Analyses

Samples are collected from 23 piezometers and surface wells three times: before the recharge start the 15 January 2008 and two times after starting recharge operation. The TWW is sampled directly from the outlet of the treatment plant by using an auto-sampler to study TWW over a day and over a year. For the day study, the TWW was sampled each 30 min during 24 h in June 2008. For the year study, five instantaneous samples were collected monthly from January to September 2008. A GPS is used to identify the exact location of each sampling point (Fig. 8.4).

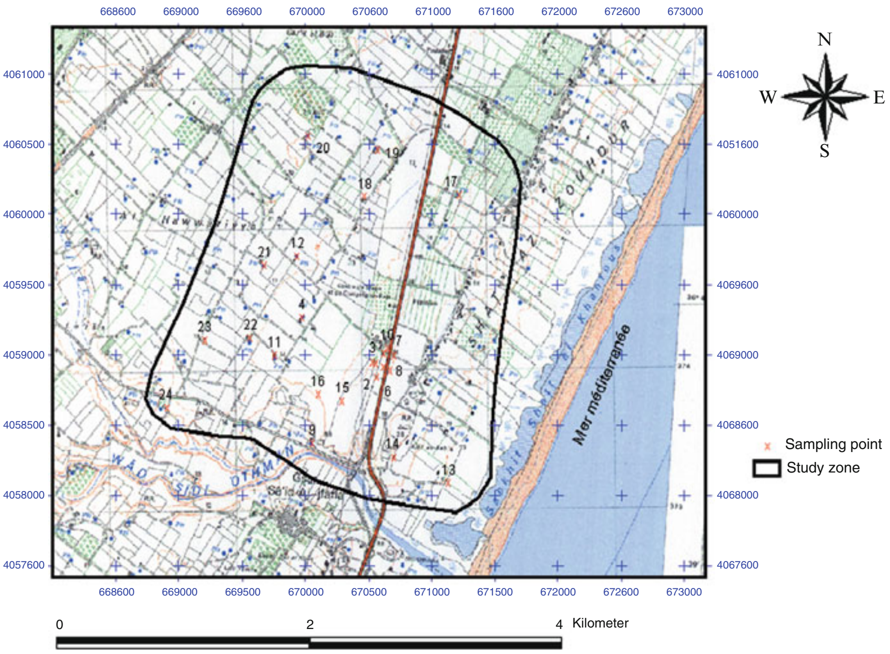

Fig. 8.4 Sampling location (*red crosses*)

The analysis of salinity were performed by electrochemistry according to the NF EN 27–888. The analysis of nitrates concentrations were performed by ion chromatography according to NF EN ISO 10304–1.

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8.5 Treated Wastewater Quality

Two main parameters are focused for their influence on aquifer recharge (Table 8.1): salinity and nitrate concentrations. Some fluctuations are observed in salinity that varies from 1.8 to 5.4 $\mathrm{g\,L^{-1}}$ (August). The latter is the only to exceed the NT 106.03 Tunisian standards for treated waste waters reused in agriculture. Salinity fluctuations show instability of the quality generated by this treatment plant. This can be due to the evaporation phenomena that increases in summer especially in the anaerobic lagoons for tertiary treatment, besides the summer industrial activities of the region mainly tomatoes conservation factories. Nitrates levels are high only in summer months with a maximum of 6.6 $\mathrm{mg\ L^{-1}}$.

Table 8.1 Quality of six TWW samples regarding salinity and nitrate concentrations

Sampling date	Salinity (mg L^{-1})	NO_3 (mg L^{-1})
28-Jan	2.2	<0.11
13-Mar	2.3	<0.11
05-Apr	2.2	<0.11
27 June [a]	1.8	2.3
14 Aug	5.4	5.8
14-Sept	2.7	6.6

[a] 24 h sample

Eleven other main parameters were measured to control physical and chemical as well as bacteriological quality of the TWW samples: pH, temperature, total suspended solids, ammonia, orthophosphates, potassium, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand after 5 days (BOD_5), total coliform, thermotolerant coliform and Escherichia Coli [3]. They show high levels of ammonia and bacteriological contaminants that could cause problems if used directly in irrigation, rejection in the maritime environment or aquifer recharge. It appears that except in summer, the quality of this TWW can be considered tolerable for irrigation use for some crops and excellent for the aquifer recharge with infiltration basins as original aquifer water in this region has salt concentrations that can reach salinities of 7 g L^{-1}.

8.6 Aquifer Quality Before and After Three Years of Recharging by Treated Wastewater

In order to evaluate the impact of the recharge of the aquifer by the treated wastewaters, two significant parameters are studied by following their evolution in the aquifer before and after 3 years of the recharge operation: salinity, and nitrate concentrations. The display of the informations uses Arcview/GIS software combined with Groundwater quality evaluation system (SEQ groundwater).

8.6.1 Aquifer Salinity Remediation

Salinity is the principal parameter characterizing the quality of groundwater. Two charts were drawn concerning the salinity distribution in the study region: the first one (Fig. 8.5) before starting the recharge and the second one (Fig. 8.6) after 3 years of aquifer recharge. While referring to the chart of the distribution of salinity in 2008 (Fig. 8.5), we note that the Northern and South-western part site is strongly salted, the recorded concentrations exceed the 2.5 g L^{-1} and reach 7 g L^{-1} in the extreme North. One well even see its salinity at 10.4 g L^{-1}. The South-eastern part

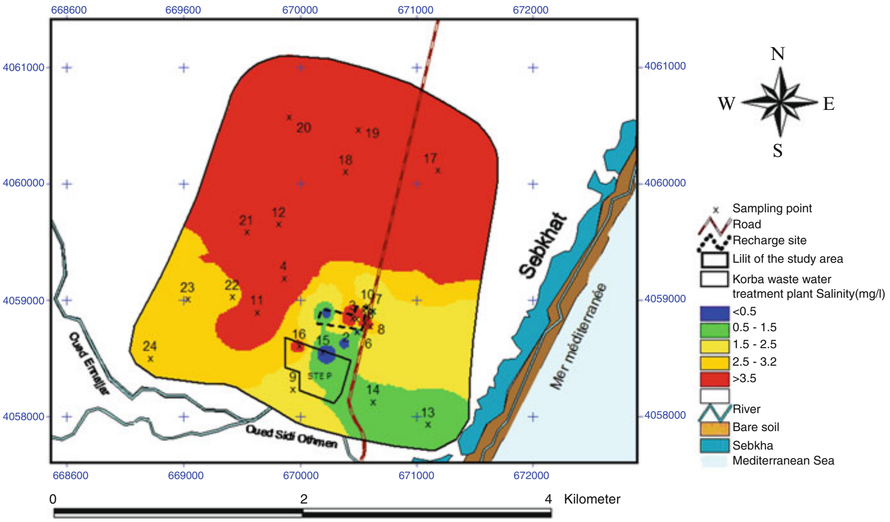

Fig. 8.5 Salinity distribution in the recharging site in 2008 (Before recharge)

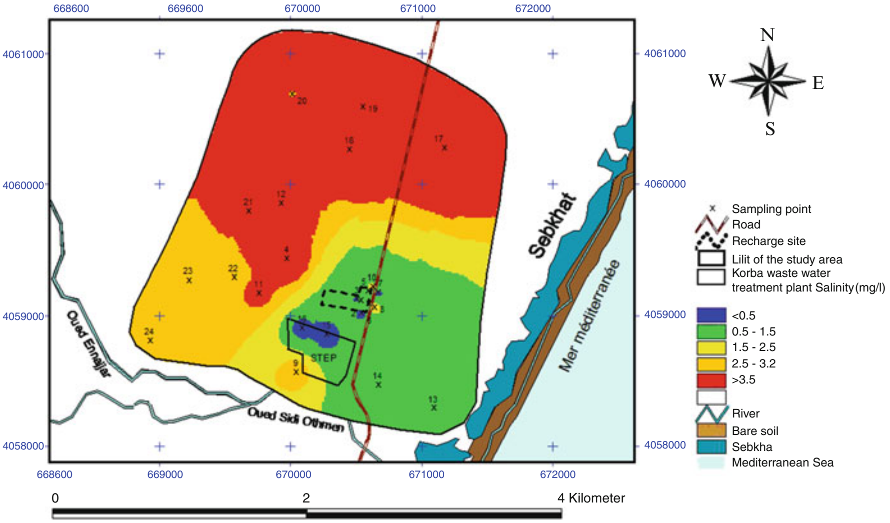

Fig. 8.6 Salinity distribution in the recharging site in 2011 (After 3 years of recharge)

has relatively good quality regarding salinity that varies between 0.5 and 2.5 g L^{-1}. On the whole, more than 50 % of the groundwater in the studied region are of bad quality in terms of salinity. These high levels of salts are ascribable to several origins. The progression of bevel salted due to the multiplication of pumpings and the reduction of the refill to the aquifer remains the principal origin of the aquifer salinity [1].

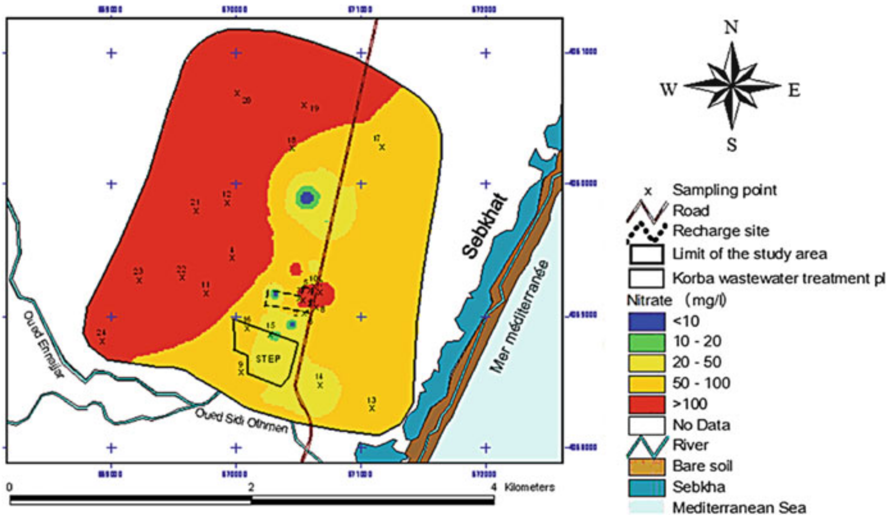

Fig. 8.7 Nitrates distribution in the recharging site in 2008 (Before recharge)

After 3 years of recharging the aquifer with treated wastewaters (Fig. 8.6), changes in salinity levels had occurred in almost all points close to the recharge plant (dashed line). The chart of the distribution of salinity in 2011 reveals a lowering of groundwater salinity around the recharging site and in the South-eastern part of the studied area. The recorded concentrations range between 0.5 and 1.5 $g L^{-1}$ and water of good quality in term of salinity gains space with a light progression towards Northern part.

8.6.2 Evolution of Nitrates in the Aquifer

Likewise salinity display, two charts were drawn (Figs. 8.7 and 8.8) in order to view the nitrates distribution in the study region and to demonstrate the impact of the recharge of the aquifer on groundwater quality.

The chart of the nitrates distribution in 2008 (Fig. 8.7), before recharge, reveals values higher than the standard SEQ of the groundwater (20 mg NO_3 L^{-1}) on almost the totality of the study zone. The most polluted points were identified in the Western part where the contents of nitrates exceed 100 mg NO_3 L^{-1} and reach a maximum value of 300 mg NO_3 L^{-1}. Approximately 90 % of these waters are of poor quality regarding nitrates and cannot be used as drinking waters. These high values are primarily due to the frequent use of the artificial fertilisers in the intensive agriculture of this region, Korba, but also to the common use of septic tanks. The high concentration of nitrates recorded near the wastewater treatment plant are probably due to the infiltration of water from maturation basins having high nitrogen pollution to the

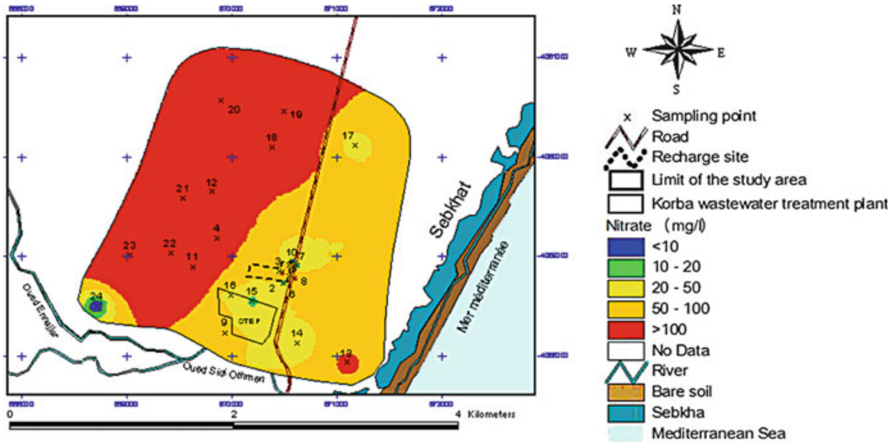

Fig. 8.8 Nitrates distribution in the recharging site in 2011 (After 3 years of recharge)

aquifer. As long as the contents nitrates do not exceed the 450 mg NO_3 L^{-1}, these waters can be used with an increased monitoring for adult resistant animals like cattle and sheep. No restriction was indicated for their use in irrigation regarding nitrates.

There is no net global improvement of the nitrates distribution through the studied area after 3 years of artificial recharge of the aquifer (Fig. 8.8). Some points in the south western part of the study area see a lowering in nitrate concentrations that need to be explained by local geographical and geological characteristics. Some other local points see higher nitrate levels, like the one in the north of the recharge area, probably due the homogenization of the concentrations because of the transverse diffusion phenomena, from the recharge area through the aquifer. The high spot in the south eastern part can hardly be due to recharge but more probably to local pollution.

8.7 Conclusions

The groundwater quality of the studied region shows high nitrates and salts concentrations. Salinity has reached 10.4 gL^{-1} in some wells and nitrates exceeded 300 mg L^{-1} in some others. These results in addition to other analysis concerning bacteriological quality make this groundwater useless for drinking or irrigation uses. Despite this fact, as farmers in this region do not have access to freshwater, they have no other choice than use this salty and polluted groundwater to irrigate their crops particularly in summer dry season when no rainfall occurs.

The analysis of the water from the outlet of Korba TWW plant has shown that it if used safely it can be beneficial in arid and semi-arid countries like Tunisia, which is suffering from the increasing scarcity of water resources making precious all alternative water resources like TWW.

The monitoring of water quality evolution of the Korba aquifer during 3 years of recharging operations using infiltration basins since its establishment in 2008 until 2011 showed the effectiveness of the project to cure high salinity levels. The site also played the role of a hydraulic barrier to mitigate the problem of marine intrusion and to limit its geographical expansion. This evolution reveals the interest of the project not only by limiting the intrusion of bevel salted but also by mobilizing a non conventional water resource and avoiding the residual impacts related to the rejection in the receiving domain.

Nevertheless, the pollution by nitrogen and bacteria still remains a major problem of the aquifer and allowed the use of these waters only for agricultural purposes. Their use for human or animal drinking is unsafe. It should be also pointed that the spurred agricultural activities in Korba highly contributed to the deterioration of the quality of its groundwater because of the irrational use of the artificial fertiliser.

As the operations of recharge are continuing, it would be interesting to follow the evolution of the quality of the aquifer further through the years. For a more precise knowledge of the tendencies to come and the capacity to simulate the various scenarios of management of water, a modelling with adequate software should be built up in order to better understand the impact of the artificial recharge by treated wastewater and the evolution of chemical and bacteriological quality of the groundwater.

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Index

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