NATO Science for Peace and Security Series - C:
Environmental Security

Water Purification and Management

Edited by
José Coca-Prados
Gemma Gutiérrez-Cervelló

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Water Purification and Management

NATO Science for Peace and Security Series

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Series C: Environmental Security

Water Purification and Management

edited by

Prof. José Coca-Prados
University of Oviedo,
Department of Chemical Engineering
and Environmental Technology,
Oviedo, Spain

and

Gemma Gutiérrez-Cervelló
University of Oviedo,
Department of Chemical Engineering
and Environmental Technology,
Oviedo, Spain

Springer

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PREFACE

Water plays a crucial role in industry, agriculture and human life. Its use has increased ten-fold between 1900 and 2000. On a global scale, about 70% of clean water from available sources is used for agricultural purposes, primarily irrigation, with the remainder used for domestic and industrial purposes. Given demographic and economic trends, it is expected that two-thirds of the world population will live in water-stressed countries by 2025 and the world will need 40% more water by then.

Degradation of the environment and pollution of water resources by human activity is taking on greater importance. The world is already facing water shortages in many countries, and nearly 90 developing countries, containing close to one-half of the world's population, already experience water deficits, with resulting constraints on human and ecosystem health as well as on economic development.

One of the major challenges to our society is to find viable solutions to the growing shortage of clean water. Urgent steps to be taken are: saving water and finding cost-effective methods for treating wastewater, recycling it, and thus increasing the water supply.

The course on which the present volume is based, *"Water Purification and Management in Mediterranean Countries"*, held in Oviedo on November 15–21, 2009, dealt with the challenges that water scarcity and water quality are imposing on many countries around the world, and particularly on many arid Mediterranean areas, and threatening their economic and social development.

It was stated in 2006 in a United Nations Development Program report that "*…unclean water is an immeasurably greater threat to human security than violent conflict"*. A positive sign, though, is that new developments in membrane filtration, sorption technologies, membrane bioreactors, and disinfection/oxidation methods, as well as in water management, utilizing remote monitoring and control capabilities, will help to reduce that threat. Chemical Engineering will play an important role in many of the critical advances involving water-treatment processes.

The present volume contains a several presentations from the NATO Advanced Training Course held in Oviedo. The complete titles of all the lectures and posters presented are also listed here.

The authors of this volume are to be thanked for their contributions as are all the lecturers and participants for their cooperation in setting high standards and ensuring the success of the course. Speakers and attendees had the opportunity to meet and discuss numerous topics dealing with technical developments, industrial applications, and academic research in the areas of water treatment, recycling, and management.

We are indebted to those who contributed to the organization of the course for their efficient and unobtrusive efforts (Prof. Ken Jolls, María Matos, Emilio Muñoz, and David Allende).

The support of the NATO Science for Peace and Security Section (NATO-SPS) for granting us the opportunity to host this meeting in Oviedo, of the local sponsors (University of Oviedo, City Hall of Oviedo, Ficyt, and CajaAstur), and of CADASA in the person of Dr. Antonio Marcos, for allowing us to visit one of his company's plants, is gratefully acknowledged.

José Coca-Prados
Gemma Gutiérrez-Cervelló

NATO ADVANCED TRAINING COURSE: "WATER PURIFICATION AND MANAGEMENT IN MEDITERRANEAN COUNTRIES"

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LIST OF CONTRIBUTED LECTURES PRESENTED DURING THE ATC:

- Issues about sustainable protection and development of water resources (S.K. Sikdar)

- Parameters of water quality and their measurement (C. Vandecasteele)

- Reuse/recycle water opportunities and challenges using membrane technology (H.S. Muralidhara)

- Membrane processes in the production of drinking water (P. Aimar)

- Water saving in industry by cleaner production (J.K. Staniskis)

- Physico-chemical treatment methods (S. Ordóñez)

- Treatment of complex systems (T.W. Chapman)

- Metals removal from industrial effluents (D.E. Akretche)

- Oily wastewaters treatment (J. Coca)

- Reuse/recycle water opportunities and challenges using membrane technology: food/bio-processing industry (H.S. Muralidhara)

- Membrane bioreactors for treatment of drinking water sources (J.G. Crespo)

- Process synthesis strategies in water management (S. Luque)

- Purification, reclaim, and recycling in industrial water and wastewater plants (F. Shadman)

- Energy from waste biomass (A. Atimtay)

- Solid disposal from effluents treatment (J. Coca)

- Overview of NATO SPS Programme for cooperation in Civil Science (J.K. Staniskis)

- Removal of micropollutants from wastewaters in STPs (J.M. Lema)

- Membrane bioreactors in wastewater treatment (J.R. Álvarez)

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TREATMENT OF OILY WASTEWATER

JOSÉ COCA*, GEMMA GUTIÉRREZ
Department of Chemical Engineering and Environmental Technology, University of Oviedo, Oviedo (SPAIN)

JOSÉ M. BENITO
Department of Chemical Engineering, University of Burgos, Burgos (SPAIN)

Abstract. Oily wastewaters are generated in many industrial processes, such as petroleum refining, petrochemical, food, leather and metal finishing. Fats, oils and greases (FOG's) present in these wastewaters have to be removed before the water can be reused in a closed-loop process or discharged into the sewer system or to surface waters. These oily waters are mainly in the form of oil-in-water (O/W) emulsions that pose a great problem in facilities attempting to stay in compliance with discharge limits. Emulsion breaking and oil removal require a basic understanding of the physical properties and chemical composition of O/W emulsions. Several properties playing a key role in the stability of an O/W emulsion should be measured for the selection of the appropriate separation process. Only those of industrial relevance will be discussed here, specifically, surface and interfacial tension, contact angle (wetting), zeta potential and droplet size distribution. Treatment of oily wastewaters is performed by a variety of methods and the degree of oil removal depends mainly on the concentration and physical nature of the oil present and its droplet size. The purpose of this work is to study oil/water system characteristics and properties, and techniques for removing oil and grease from industrial wastewaters in analogy with sewage treatment processes. These techniques include gravity and centrifugal separations, chemical treatment, flotation, filtration, membrane processes, evaporation, activated carbon adsorption, biological treatment, and integrated or hybrid processes. Operating parameters, equipment design, treatment costs, range of operation, and the possibility of O/W emulsion reformulation before treatment will also be covered.

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* E-mail: jcp@uniovi.es

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1. Introduction

Wastewaters containing oil-in-water (O/W) emulsions are generated in many industrial processes such as those in the metallurgical, petroleum refining, petrochemical, food, leather and metal finishing industries (Table 1.1). Sources of such wastewaters include cooling lubricants in metalworking processes (metal rolling, metal cutting, and wire drawing), scouring baths for cleaning metal parts, and waste from car washes. Fats, oils and greases (FOG's) in wastewaters are often classified as hazardous waste and have to be removed before water is reused in closed-loop processes or discharged into sewer systems or to surface waters. Oily waters are usually in an emulsified form that poses a great problem in facilities attempting to stay in compliance with discharge limits. Typical limits for oil and grease discharges range 10–15 mg/L for mineral and synthetic oils and 100–150 mg/L for those of animal and vegetable origin (The World Bank Group 1999). Emulsion breaking and removal of oil require a basic understanding of the emulsion, *i.e.* its physical properties and chemical composition.

In this review the relevant physico-chemical properties of oil-in-water emulsions and techniques for their determination will be described, along with conventional methods for oily water treatment.

TABLE 1.1. Sources of oily effluents (Patterson 1985)

Industrial process	**Oil concentration (mg/L)**
Petroleum refining	20–4000
Metal processing and finishing	100–20000
Aluminum rolling	5000–50000
Copper wire drawing	1000–10000
Food processing (fish and seafood)	500–14000
Edible oil refining	4000–6000
Paint manufacturing	1000–2000
Cleaning bilge water from ships	30–2000
Car washing	50–2000
Aircraft maintenance	500–1500
Leather processing (tannery effluents)	200–40000
Wool scouring	1500–12500
Wood preservation	50–1500

2. Oil in Wastewaters

2.1. TYPES OF OIL PRESENT IN WASTEWATERS

Oil in wastewaters may be of mineral, animal, or vegetable origin. The oil content is usually classified into four categories according to its physical form (Table 1.2):

1. *Free (floating) oil*: it rises quickly to the water surface under quiescent conditions.
2. *Dispersed oil*: it is an array of fine droplets stabilized by their electrical charges without presence of surfactants.
3. *Emulsified oil*: it has a similar distribution as dispersed oil, but its stability is enhanced because of the interactions with emulsifiers (mainly surfactants) present at the O/W interface.
4. *Dissolved oil*: the oil is not present as visible droplets, but truly dissolved chemically or dispersed in extremely fine droplets.

TABLE 1.2. Droplet size in O/W mixtures

Type of oil	**Droplet diameter, D_p (μm)**
Free oil	≥150
Dispersed oil	20–150
Emulsified oil	≤20
Dissolved oil	≤5

Sometimes oily wastewaters are classified based on their mean drop size as:

- *Primary dispersions* ($D_p > 50$ μm).
- *Secondary dispersions* ($D_p = 3$–50 μm).
- *Mechanical emulsions* ($D_p < 3$ μm).
- *Chemical emulsions* ($D_p < 2$ μm).
- *Dissolved hydrocarbons*.

Treatment of oily wastewaters is performed by a variety of methods and the degree of oil removal depends on the physical nature of the oil present and its droplet size.

2.2. ANALYSIS OF OILY WASTEWATERS

In the discharge of oil (or any organic material), the amount that can be safely absorbed by the receiving body of water is defined by its effect on the dissolved oxygen (DO) level of the water. The saturation value of DO is 8–15 mg/L, depending on temperature and salinity. Organisms in water use the organic matter as a food source. During the biochemical reaction DO is consumed. If the oxygen consumed is not replaced by natural or artificial methods, the DO level drops, leading to the death of fish and other aquatic life.

Organic compounds in water are normally measured as *chemical oxygen demand* (COD) or *biochemical oxygen demand* (BOD). The COD is a measure of the amount of oxygen needed to chemically oxidize the wastes in a specific time and temperature by a specific oxidizer (such as $KMnO_4$). The COD does not distinguish between ability of microorganisms to degrade the waste and the chemical oxidation of inert organic matter. The BOD is the amount of oxygen required by microorganisms to oxidize organic wastes aerobically under specified conditions of time and temperature. BOD is expressed in milligrams of oxygen required by a liter of wastewater (mg/L) or the equivalent in g/m^3. An aerobic decomposition in simplified form is given as:

$$\text{Organic matter} + O_2 \xrightarrow{\textit{microorganisms}} CO_2 + H_2O + \text{New cells} + \text{Stable products}$$

BOD has traditionally been the most important measure of the strength of organic pollution. It is standard practice to report BOD as BOD_5, which is the total amount of oxygen per liter consumed by the microorganisms during the first 5 days of biodegradation at 20 ºC.

There is a variety of methods available to determine oil and grease concentration in waste. The most common is solvent extraction of the oil from the effluent sample with an organic solvent (e.g. hexane). The resulting organic phase is separated, and the amount of oil and grease is measured and expressed either as mg/L or mg/kg, depending on whether the sample is liquid or solid (Kvernheim et al. 1999, U.S. EPA 1999). A scheme of the experimental procedure is shown in Figure 1.1.

Infrared spectroscopy is generally accepted as the most accurate and reproducible technique for measuring oil in the solvent (Farmaki et al. 2007, Romero and Ferrer 1999).

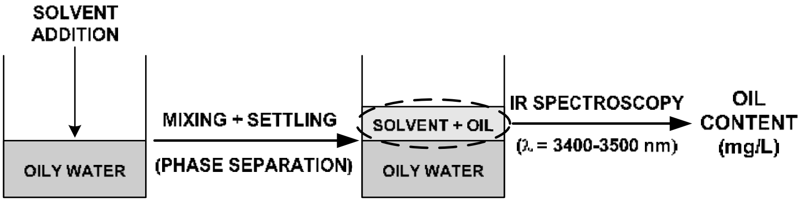

Figure 1.1. Oil analysis in oily wastewaters by the extraction method.

2.3. O/W EMULSIONS

An emulsion is a macroscopically homogeneous mixture of two (or more) kinds of immiscible liquids. In fact, it is a heterogeneous system, consisting of at least one immiscible liquid, the *internal phase*, dispersed as droplets in another *external* or *continuous phase*. In an O/W emulsion the oil droplets are dispersed in a continuous water phase (>30% water), and in a water-in-oil (W/O) emulsion a continuous oil phase contains droplets of water (<25% water). Emulsions are not stable in the thermodynamic sense, and they can be formed only in specific ranges of temperature, pressure, and composition. The type of emulsion formed is a function of the viscosity, dielectric constant, relative concentration, and specific gravity of both phases, while the type of any emulsifier (*surfactant*) present and the pH of the aqueous phase will also have an influence.

2.3.1. *Surfactants*

Mixtures of water and oil will normally separate into two layers. If the amount of oil in the sample is not sufficient to form a distinct layer, the oil will remain as tiny droplets suspended in water. To form a stable O/W or W/O emulsion a surfactant has to be added to the O/W mixture. Surfactants are long organic molecules that, in small amounts, lower the surface tension of the liquid. Surfactant molecules have a water soluble (*hydrophilic*) head and a water insoluble (*hydrophobic*) hydrocarbon chain, as shown in Figure 1. 2. They can adopt different conformations, depending on their concentration in the aqueous phase. The hydrophilic group is ionic or strongly polar and has a solubilizing functionality in polar solvents as a result of hydrogen bonds or electrostatic interactions (Falbe 1987, Porter 1994). The hydrophobic part is usually a linear or branched hydrocarbon which shows only weak solute-solvent interactions, such as London dispersion forces. This molecular structure determines the surfactant behavior and its physico-chemical properties in solution.

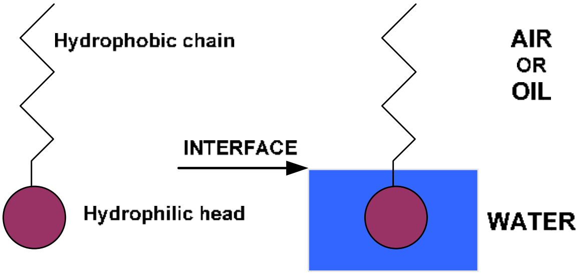

Figure 1.2. Molecular structure of a surfactant and its orientation at the interface.

Surfactants are mainly used in aqueous solutions, their classification being based on the nature of the hydrophilic group:

- *Anionic surfactants* have a negatively charged head, usually based on sulfate, sulfonate or carboxylate anions. Biodegradation of such surfactants can lead to nonylphenol, regarded as a potent endocrine disruptor. Sodium dodecyl sulfate (SDS) is the most commonly used anionic surfactant.
- *Cationic surfactants* have positively charged heads, usually based on quaternary ammonium ($[RN(CH_3)_3]^+$) or phosphonium ($[RP(CH_3)_3]^+$) groups, such as cetyl trimethyl ammonium bromide (CTAB).
- *Amphoteric surfactants* contain both positive and negative ionic groups, and their properties in aqueous solution may change depending on the characteristics of the medium. They are mainly sulfobetaine and betaine esters, such as cocamido propyl betaine.
- *Non-ionic surfactants* have a water-soluble fragment, a hydrophilic portion of the molecule such as polyether instead of a charged head. They solubilize inorganic materials in organic solvents, often through cation chelation. An example is ethoxylated lauryl alcohol.

The key characteristic of a surfactant is that it establishes a higher concentration at the interface than in the bulk liquid. This is known as *adsorption* and depends upon the concentration of surfactant. At very low concentrations, there is no orientation, and the surfactant molecule lies flat on the interface. As the concentration is increased, the molecules start to orient themselves, and this orientation depends upon the nature of the hydrophilic group and the interface. When the concentration increases to a certain value, the number of molecules available is enough to form a unimolecular layer at the interface. This concentration is known as *critical micelle concentration* (CMC). If the concentration increases further, the additional surfactant molecules tend to aggregate and form ordered, three-dimensional structures, known as *micelles* (Figure 1.3). The surfactant can thus form a layer around suspended oil droplets, preventing them from colliding and coalescing. The structure and shape of a micelle depends upon temperature, type of surfactant and its concentration, and upon the presence of other ions and water-soluble organic compounds in solution. Depending on these conditions, micelles can form spherical, rod-shaped or lamellar shapes.

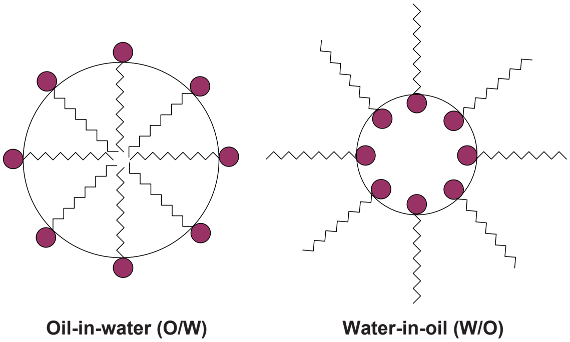

Figure 1.3. Surfactant stabilized micelles.

An important parameter of a surfactant is the *hydrophilic-lipophilic balance* (HLB), which correlates surfactant structures with their effectiveness as emulsifiers. The HLB for a surfactant, calculated from its chemical structure, is given by (Griffin 1949, 1954):

$$\mathrm{HLB} = \frac{20\,M_h}{M} \tag{1.1}$$

where M_h and M are the molecular mass of the hydrophilic portion and of the whole surfactant molecule, respectively. The HLB value is given on an arbitrary scale of 0 to 20. An HLB = 0 corresponds to a completely hydrophobic molecule and HBL = 20 would correspond to a molecule made up completely of hydrophilic components: the higher the HLB number the more hydrophilic is the surfactant. Figure 1.4 shows the classification of surfactants based on HLB.

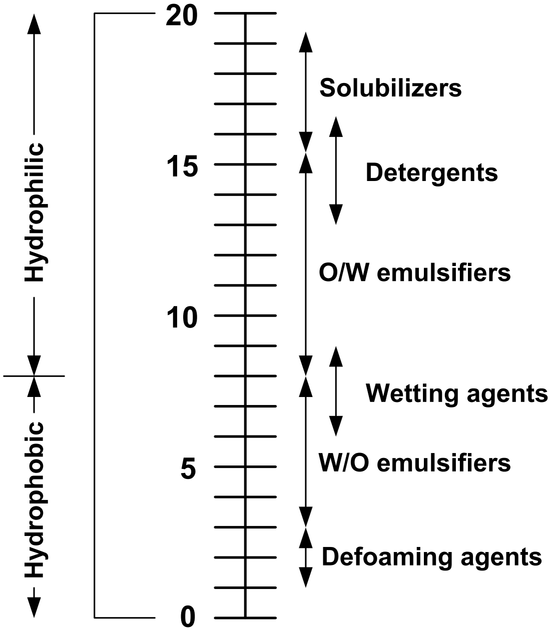

Figure 1.4. Types of surfactants according to their HLB value.

Bancroft's rule (Bancroft 1913, Tadros and Vincent 1983) suggests that the type of emulsion formed depends on the type of emulsifier, which should be soluble in the continuous phase. According to Bancroft's rule, O/W emulsions are produced with a hydrophilic surfactant (high HLB), and W/O emulsions are generated by a hydrophobic surfactant (low HLB). This rule states that, contrary to common sense, what makes an emulsion either O/W or W/O is not the relative percentages of oil or water, but the phase where the emulsifier is more soluble.

Emulsions are generally unstable because they have a large interfacial/ surface area and a high interfacial/surface energy, which is proportional to this area. A change in the system that reduces the total surface energy will bring the system into a more stable state. The total surface energy is reduced if the emulsion droplets coalesce. One way surfactants promote the stability of emulsions is by reducing the total surface energy of the system (Dean 1948). The presence of surfactants can make FOG's in wastewater extremely difficult to clean up, due to the enhanced solubility of the emulsified oil.

2.3.2. *Properties of O/W Emulsions*

Several properties playing a key role in the stability of an O/W emulsion have to be measured in order to analyze potential separation processes. Only those of industrial relevance will be discussed here, specifically, surface and interfacial tension, contact angle (wetting), zeta potential and droplet size distribution (Hrudey and Kok 1987).

2.3.2.1. *Surface and Interfacial Tension*

The surface or interfacial tension (γ) of a liquid is often defined as the force acting at right angles at any line of unit length on the liquid surface or, more precisely, as the work required to increase the area of a surface isothermally and reversibly by a unit amount (Shaw 1992). Both terms refer to the boundary between two phases: if one of them is a gas phase then the term *surface tension* is used, whereas *interfacial tension* is used for boundaries between two non-gas phases.

In an O/W emulsion the presence of surfactant will reduce significantly interfacial tension, and this will lead to stable emulsions. Measurements of the surface and interfacial tensions provide information on the influence of any surfactant present. Common techniques used for measuring the surface/interfacial tension of O/W emulsions are: (a) du Noüy ring, (b) Wilhelmy plate and (c) drop-weight methods. For very low surface/interfacial tensions (d) the pendant drop and (e) spinning drop techniques provide more accurate results.

The Du Noüy ring and the Wilhelmy plate are the methods most used to determine surface/interfacial tension. The Du Noüy ring method utilizes the interaction of a platinum-iridium alloy ring with the liquid interface being tested (Figure 1.5). The ring is submerged below the interface and subsequently raised upwards. As the ring moves upwards it raises a meniscus of liquid.

The force required to detach the ring from the interface is related to the surface or interfacial tension by the following expression:

$$\gamma = \frac{\beta F}{4\pi R} \tag{1.2}$$

where F is the detachment force, R is the mean radius of the ring and β is a correction factor which depends on the dimensions of the ring and the nature of the interface.

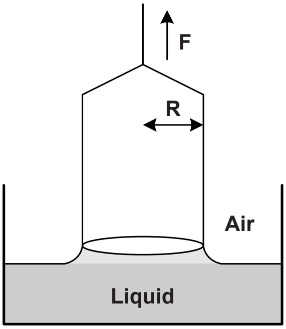

Figure 1.5. Du Noüy ring method for surface/interfacial tension measurement.

The Wilhelmy plate method utilizes the interaction of a platinum plate with the liquid interface being tested. The calculations for this technique are based on the geometry of a fully wetted plate in contact with, but not submerged in, the liquid (Figure 1.6).

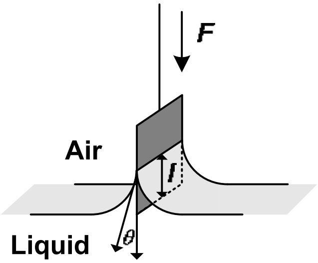

Figure 1.6. Wilhelmy plate method for surface/interfacial tension measurement.

The force acting on the plate due to wetting (F) is measured and used to calculate the surface/interfacial tension by the Wilhelmy equation:

$$\gamma = \frac{F}{2l\cos\theta} \tag{1.3}$$

where l is the wetted length of the plate and θ is the contact angle between the liquid phase and the plate. In most cases a complete wetting is assumed ($\theta = 0$). Due to uncertain wetting behavior, the plate can only be used for interfaces under certain limitations.

As shown in Figure 1.7, surface tension measurements can be used to determine the CMC of surfactant solutions, due to abrupt changes that take place in the observed values around this concentration value.

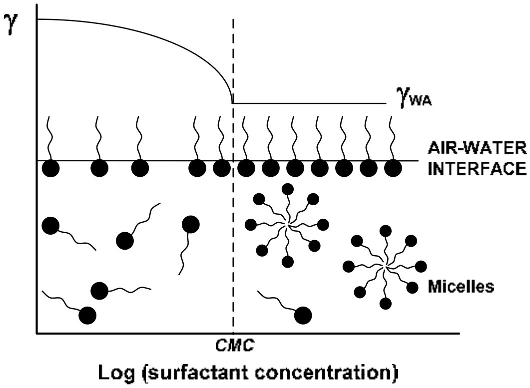

Figure 1.7. Surfactant CMC determination by surface tension measurement.

2.3.2.2. *Contact Angle (wetting)*

Contact angle (θ) is a quantitative measure of the wetting of a solid by a liquid. As shown in Figure 1.8, it is defined geometrically as the angle formed by a liquid at the three-phase boundary where a liquid, gas (or a second liquid phase), and solid intersect. Low values of θ indicate that the liquid wets well, while high values correspond to poor wetting. The best O/W emulsions, in the case of cutting fluids, will be those that present a good wettability for a metal surface. A decrease in wettability indicates emulsion destabilization due to oil contamination or degradation.

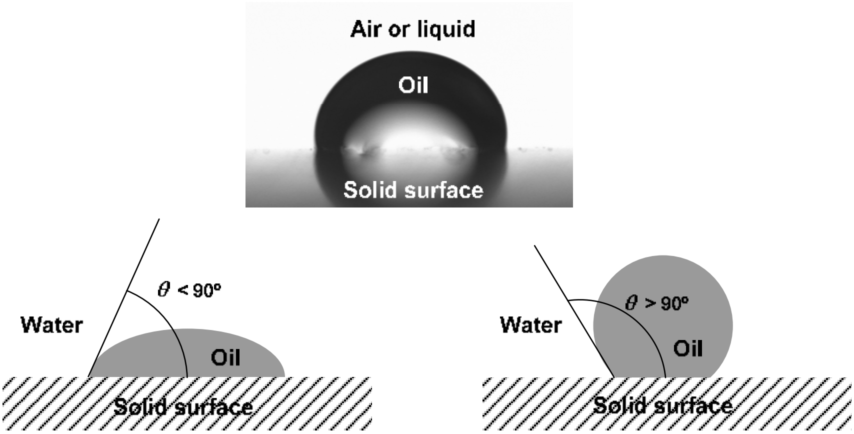

Figure 1.8. Wettability and contact angle.

2.3.2.3. *Zeta Potential*

Zeta potential (ζ) provides information on O/W emulsion stability and is determined by measuring the velocity of charged droplets or colloids in an electrical potential field of known strength. Large values of ζ (positive or negative) increase emulsion stability and indicate difficulty for coalescence of droplets, but ζ is usually pH-dependent, and other relevant factors have to be considered for prediction of coalescence.

Oil droplets in an O/W emulsion exhibit a net charge at the droplet surface. It is usually a negative charge, and as described by the *Helmholtz theory* of the electrical double layer, the negative charges are aligned or closely bound to the interface. These charges attract counter ions from the bulk solution which give rise to a zone of opposite sign, forming an electrical double layer that causes oil droplets to repel one another. Moving away from the oil surface into the water phase, the electrostatic potential drops, as shown in Figure 1.9.

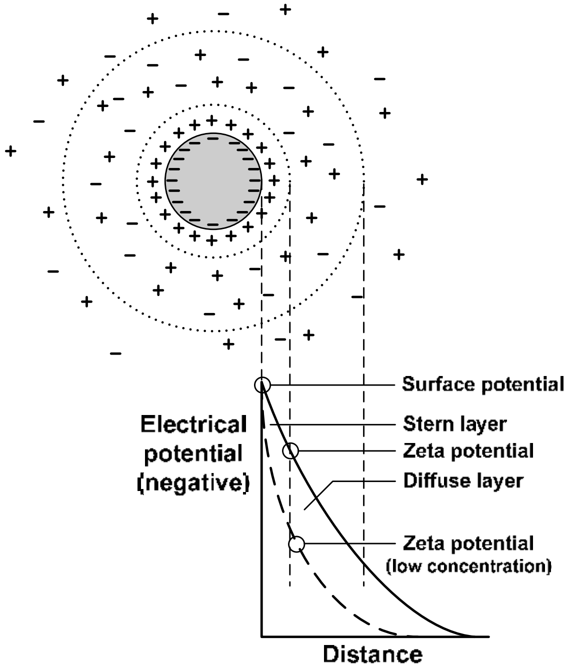

Figure 1.9. Electrical double layer around a negatively charged oil droplet and the distribution of electrical potential around it.

O/W emulsions are primarily stabilized by electrostatic repulsions between the oil droplets. In this model a distinction is made between tightly bound counter ions and diffuse counter ions in solution, which are weakly associated with the droplet. The inner layer is the so-called *Stern layer* and the electrostatic potential at the Stern later is called the *zeta* or *electrokinetic potential*, which is largely responsible for emulsion stability.

In practice the zeta potential of a particle (or a droplet) in solution is defined as the value of the electrostatic potential at the shear plane, *i.e.* the plane at which the ions are no longer dragged along with a moving (or diffusing) droplet. It is determined by measuring the electrophoretic mobility (υ) of oil droplets in an applied electric field and related then to ζ potential at the interface using the Smoluchowski equation (Hunter 1981, Plegue et al. 1986):

$$\zeta = \frac{\upsilon \eta}{\varepsilon_0 \varepsilon_r} \tag{1.4}$$

where ε_r and ε_0 are the relative dielectric constant and the electrical permittivity in vacuum, respectively, and η is the emulsion viscosity.

Stability arises from a balance between repulsive forces of charges on the droplets surface and the attractive forces (van der Waals forces) that normally act between particles or droplets. The net forces arising from those two interactions result in a profile of the potential energy of interaction (Figure 1.10).

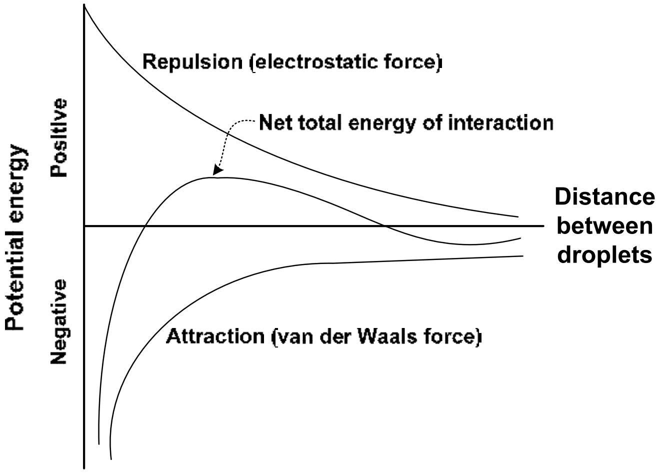

Figure 1.10. Potential energy of interaction between oil droplets in water.

Surfactants are largely responsible for high ζ values, high interfacial-shear viscosity, and relatively low interfacial tension. If polyvalent ions are added with charge opposite to that on the emulsion droplets, the electrically repulsive forces will be neutralized, ζ tends to zero and coalescence can occur (Lissant 1974).

2.3.2.4. *Droplet Size Distribution*

Droplet size distribution (DSD) as a function of time is an indicator of emulsion stability and is an important factor in the performance of oil removal processes such as sedimentation/flotation, membrane filtration and coalescence/adsorption. The most common DSD techniques are microscopic observation and light transmission/scattering.

Microscopic techniques are the most direct approach to droplet size analysis, but they are tedious and suffer from operator errors. Fixing the emulsion by addition of gelatin or agarose provides more accurate results (Churchill and Burkhardt 1976, Ríos et al. 2002). In spite of some limitations counting based on light scattering is the most common approach used for O/W emulsions, as either the traditional Coulter Counter technique or laser light scattering (Tadros and Vincent 1983, Wiacek and Chibowski 1999). Droplet size distribution of an O/W emulsion depends on the method of emulsification. As a general trend, the smaller the droplet size, the more stable is the O/W emulsion.

2.3.3. *Emulsion Breaking: Demulsification*

Emulsion breaking, or demulsification, is the separation of a dispersed oil from the aqueous phase in which it is suspended. The aim of demulsification is to remove the surfactant-stabilized interface and drive the surfactant to either the oil side or the water side, allowing the oil droplets to coalesce and rise to the surface. It can be enhanced by decreasing water phase viscosity, increasing oil viscosity, increasing the diameter of oil droplets, or by lowering the oil density.

The process follows sedimentation laws, based on a density difference, and as a gravity-controlled process, Stokes' law will apply. As shown in Figure 1.11, the three main forces acting on an oil droplet are: gravity (F_g), buoyancy (F_b) and kinetic or drag force (F_d).

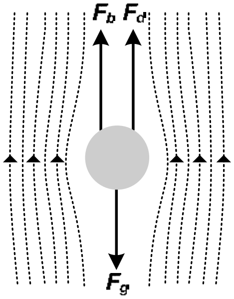

Figure 1.11. Forces acting on an oil droplet during demulsification.

The buoyancy of an oil droplet is proportional to its volume, and the drag force is proportional to the projected area of the droplet:

$$\frac{4}{3}\pi R^3 \rho_o g = \frac{4}{3}\pi R^3 \rho_w g + 6\pi \mu R v_t \tag{1.5}$$

Gravity force = Buoyancy force + Kinetic (drag) force

Solving this steady-state equation for the terminal upward velocity, v_t:

$$v_t = \frac{2}{9}\frac{R^2(\rho_o - \rho_w)}{\mu} \tag{1.6}$$

where g is the gravity constant, R is the droplet radius, μ the viscosity of the emulsion, and ρ_o and ρ_w the density of oil and water, respectively.

Stokes' equation is valid for a spherical droplet in a surfactant free system, under laminar flow conditions. Stokes' law applies up to a Reynolds number ($\mathrm{Re} = D\, v_t\, \rho / \mu$) of about 0.1. According to Eq. (1.6), large droplets will rise (if $\rho_o < \rho_w$) or fall (if $\rho_o > \rho_w$) faster than small ones, and droplets will move faster in a lower viscosity liquid.

3. Methods for Removing Oil and Grease from Industrial Wastewaters

Removal of oil and grease from wastewaters will depend mainly on the concentration and physical nature of the oil present and the droplet sizes.

It must be recognized that, particularly in metalworking operations, the organic phase of the emulsion contains besides the oil a wide variety of additives: emulsifiers, corrosion inhibitors, extreme pressure agents, biocides, antifoam compounds, etc. (John et al. 2004, Zimmerman et al. 2003).

These emulsions may undergo chemical changes over time due to high shear stress and operating temperatures and may become contaminated during use by tramp oils (mainly hydraulic oils from engines or other parts of the industrial process), solids (metal chips) and other products, losing their functional properties and suffering a decrease in performance (Eppert et al. 2003, Greeley and Rajagopalan 2004). A large volume of oily wastewater is produced that must be treated before disposal to obtain an aqueous effluent free of oil and the other additives.

As in the treatment of municipal wastewaters (MWW), a combination of techniques is often needed for the treatment of oily wastewaters (OWW), as shown in Figure 1.12, with a main water-treatment line and a line for handling sludge or oily wastes. As for the main treatment line, the objective is to obtain a pollutant-free effluent that can be either disposed of or recycled to the process.

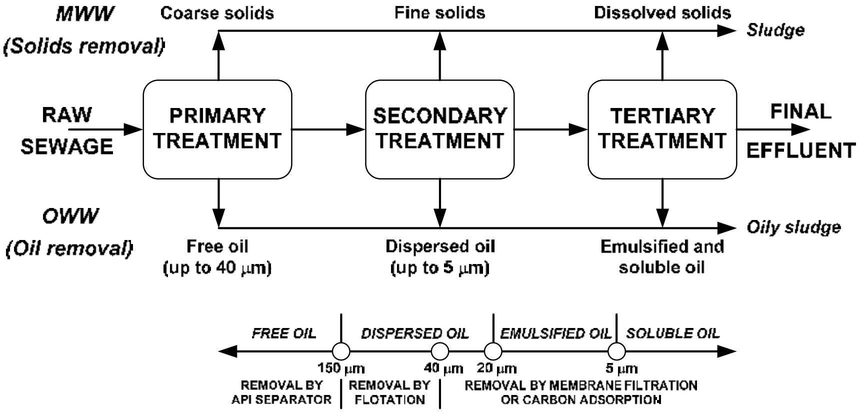

Figure 1.12. Process similarity between the treatment of municipal sewage (MWW) and oily wastewaters (OWW).

The *primary treatment* consists of physical separation steps to settle suspended solids though sedimentation. For oily wastewaters the first step is used to remove free oils, including tramp oils, from the emulsion or suspension. Common techniques used are gravity and centrifugal separations.

The *secondary treatment* is aimed to reduce the organic load that remains after the primary treatment. It consists of a biological treatment followed by secondary sedimentation. In OWW the secondary treatment is used to break O/W emulsions and to remove the dispersed oil. Common techniques for this step are chemical treatment, flotation, filter coalescence and membrane filtration (microfiltration and ultrafiltration).

Tertiary treatment is a physicochemical process to reduce the levels of dissolved organic and inorganic compounds. This process is used with OWW to remove finely dispersed, emulsified and soluble oil fractions. Evaporation, reverse osmosis and activated carbon adsorption are the main treatments used.

3.1. PRIMARY TREATMENT

This step is mainly used to remove free oil and some of the solids present, such as metal chips, and is based on density differences.

3.1.1. *Gravity Separation*

This is the cheapest and most common method used to remove the free oil ($D_p \geq 150$ μm) in oily wastewaters. It is based on the density difference between the two gross phases, oil and water. The oil rises to the surface of a tank and then is skimmed off. The key parameters governing separation can be ascertained from Stokes' law, Eq. (1.6), *i.e.* density difference, droplet size, and viscosity. The efficiency of a gravity separator depends upon proper hydraulic design and the wastewater retention time.

There are several kinds of equipments for implementing gravity separation. Their design tries to avoid turbulence in the system while promoting coalescence of the oil droplets. The major commercial systems are: (a) API separators, (b) plate coalescers and (c) flotation units.

3.1.1.1. *API Separators*

The design of API separators, used in the petroleum refining industry for oily wastes that contain solids, is specified by the American Petroleum Institute (API). This separator consists of a rectangular clarifier with a surface skimmer for oil and a bottom rake for solids (Figure 1.13). Typically, the oil layer is skimmed off and subsequently re-processed or disposed of, and the bottom sediment layer is removed by a chain and flight scraper (or similar device) and a sludge pump (American Petroleum Institute 1959, Simmons et al. 2002).

The oil separation efficiency depends on factors such as the type, concentration and viscosity of oil, feed flowrate, and presence of contaminants, especially particulate matter and surfactants. The design of an API separator is based on the removal of all free oil droplets larger than 150 μm.

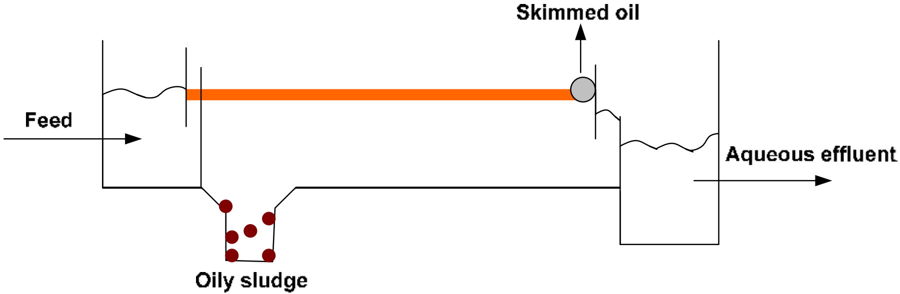

Figure 1.13. Schematic diagram of an API separator.

The basic design principle of the API separator is that the cross section of the tank should allow sufficient time for the oil droplets to reach the surface. The equations for the minimum horizontal area of the separator (A_H), its required length (L), and minimum cross-sectional area (A_C) are given by:

$$A_H = F\frac{Q_m}{v_t} \tag{1.7}$$

$$L = F\frac{v_H}{v_t}D \tag{1.8}$$

$$A_C = \frac{Q_m}{v_H} \tag{1.9}$$

where Q_m is the wastewater flowrate, D is the oil droplet diameter, v_H and v_t are the horizontal and terminal velocity of the oil droplets, respectively, and $F = F_1 F_2$, where $F_1 = 1.2$ is a factor to compensate for short circuiting, and F_2 compensates for turbulence. Table 1.3 shows values of F_2 given as a function of v_H/v_t. Usually $v_H = 15\ v_t$, but should not exceed 3 ft/min. It is essentially the average velocity of the main stream through the separator.

API separators are of simple design and are used when the demands of separation are low, costs must be minimal and enough space is available for the unit. Treated effluent leaving an API separator may have oil droplets smaller than 30 μm and often oil concentrations less than 200 mg/L.

TABLE 1.3. F_2 values as a function of v_H/v_t

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

3.1.1.2. *Plate Coalescers*

Plate coalescers are similar to API separators but they promote oil coalescence by passing the stream through a set of parallel angled plates (also known as parallel packs). The plates, usually made of oleophilic polypropylene and with various designs (Figure 1.14), provide high surface area on which suspended oil droplets can coalesce into larger aggregates (globules).

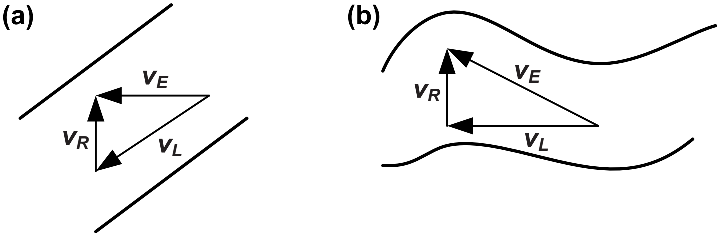

Figure 1.14. Inclined parallel (a) and horizontal corrugated (b) plate designs, where v_R, v_E and v_L are the rise velocity vector, the effective path of removed oil and the liquid velocity vector, respectively.

As shown in Figure 1.15, the influent passes through the entrance chamber in which large oil droplets immediately rise to the surface. Smaller droplets are carried with the aqueous stream to the plate pack. Within the pack, the aqueous stream is in laminar flow, and the lighter oil droplets rise in the narrow flow channels until they reach the plate immediately above. At that point they form a continuous oil film that continues to rise up the plate to the top of the pack. At the top of the plates the large oil globules are released and move to the top of the oil compartment where they are skimmed or pumped away. Particulate matter tends to fall to the bottom of the plate pack and can be collected by a hopper as an integral part of the unit (Stewart and Arnold 2008).

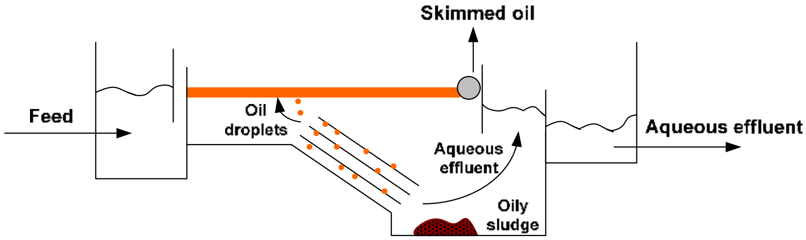

Figure 1.15. Diagram of a parallel plate coalescer.

Parallel plate coalescers require significantly less space than a conventional API separator to achieve the same degree of oil separation. Removal efficiency for oil droplets in the range of 20–50 µm is close to 100%. Treated effluent quality depends on the feed conditions, but often it will be in the range of 10–60 mg/L of free oil. The main drawback of plate coalescers is the possibility of plugging of the plate packs by solids present in the wastewater, and therefore poor separation efficiency is achieved for effluents containing an oily sludge or with a high content of emulsified oil (Stewart and Arnold 2008).

3.1.2. *Centrifugal Separations*

These are also based on the density difference between the two phases (oil and water), but the separation process is improved by applying a centrifugal force using centrifuges or hydrocyclones. They might be also employed within the secondary treatment processes as they may be used with coagulant addition for breaking O/W emulsions (Cambiella et al. 2006a, Curtis 1996).

3.1.2.1. *Centrifuges*

Centrifugation is a very efficient method compared to gravity settling because less space and operating time are required, and it is especially suitable for small workshops. Centrifugation allows treating large volumes of wastewater at low operating cost. In centrifuges, the liquid flows in a circular path due to the rotating motion of the device: the heavier water phase is thrown to the outer region by centrifugal force, whereas the lighter oily phase is collected near the vortex core and is subsequently removed (McCabe et al. 2005).

Batch or *bottle centrifuges* are commonly used for laboratory work, where samples are placed in tubes, and phases are separated after a certain time.

Continuous centrifuges are used for pilot plant and industrial applications. The most common types are the following:

- *Tubular centrifuge*. The centrifugal force is provided by rotating a bowl at high speed, and oily wastewater (feed) enters from a nozzle placed at the bottom. The centrifugal force acts on the feed, separating the two phases according to their density difference: the lighter phase (oil) forms the inside layer and the heavier phase (water) forms the outer layer. Since the oily wastewater is entering continuously into the bowl, two phases are discharged continuously from two separate outlets provided at the top of the bowl. Solids accumulated inside the bowl can be also removed.
- *Disc-stack centrifuge*. This type of equipment (Figure 1.16a) has a high efficiency for liquid-liquid and solid-liquid separations. The oily effluent is fed at the top, close to the axis of the bowl, and is accelerated by a radial vane assembly before entering the disc stack, where separation occurs (Maybury et al. 1998). The rotating bowl contains generally 30–50 closely spaced conical disks in the form of truncated cones. Each disc has several holes spaced uniformly to provide a continuous upward passage for the lighter phase. The oil flows up the discs and is collected from the centre of the centrifuge, whilst the water leaves at the top from the outer region of the centrifuge. The critical droplet diameter (D_c) for a disc-stack centrifuge, corresponding to the minimum oil droplet size that can be separated from the continuous phase, is given by (Cambiella et al. 2006a):

$$D_c = \sqrt{\frac{27 Q \mu \tan\theta}{\pi n \omega^2 \Delta\rho \left(r_2^3 - r_1^3\right)}} \tag{1.10}$$

where Q is the volumetric flow rate, r_2 and r_1 are the distances from the rotating axis to the inlet and outlet of the fluid to the disc, respectively (Figure 1.16b), θ is the disc half angle, n is the number of discs, ω is the angular velocity of the centrifuge, μ is the viscosity of the continuous phase, and $\Delta\rho$ is the difference of densities between the continuous (water) and dispersed (oil) phase.

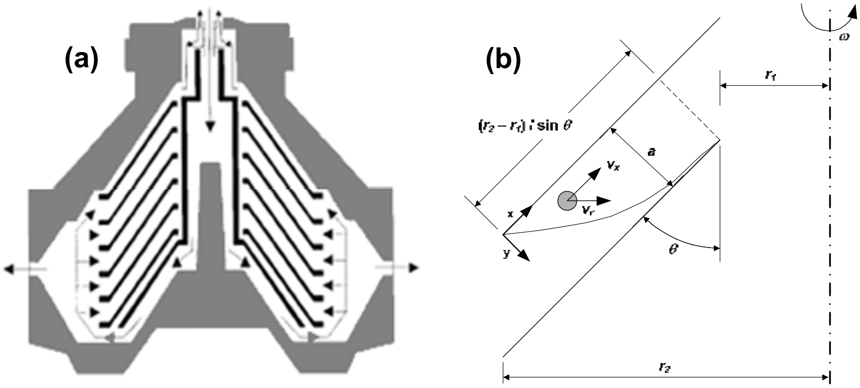

Figure 1.16. Schematic diagrams: (a) disc-stack centrifuge and (b) single disc gap in a disc-stack centrifuge.

3.1.2.2. *Hydrocyclones*

In these devices the liquid feed is forced into a circular motion by injecting it tangentially against the circular configuration of the hydrocyclone. The heavier water phase moves towards the walls and is removed at the bottom of the unit, while the lighter oil phase is collected at the top, as shown in Figure 1.17.

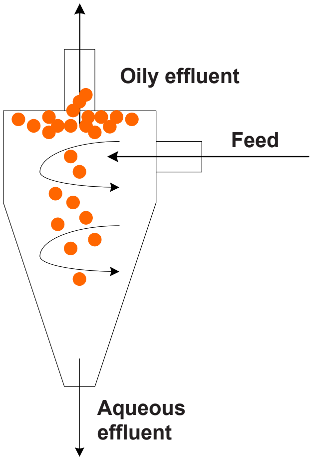

Figure 1.17. Schematic diagram of a hydrocyclone.

There are pressurized hydrocyclones, in which the oil droplets are drawn into the low-pressure central vortex and, by applying a backward-pressure to the water outlet, upward flow is achieved in order to remove the oil at the upstream outlet orifice.

Dimensionless correlations for hydrocyclone design have been reported that involve Stokes (Stk), Reynolds (Re) and Euler (Eu) numbers (Antunes and Medronho 1992, Svarovsky 2000):

$$\text{Stk Eu} = 0.0474\left[\ln\left(\frac{1}{R_f}\right)\right]^{0.742} e^{8.96C} \tag{1.11}$$

$$\text{Eu} = 371.5\,\text{Re}^{0.116}\, e^{-2.12C} \tag{1.12}$$

$$R_f = 1218\left(\frac{D_u}{D}\right)^{4.75} \text{Eu}^{-0.30} \tag{1.13}$$

where R_f is the underflow-to-throughput ratio (flow ratio), C is the feed oil concentration (fraction by volume), D_u is the underflow diameter and D is the hydrocyclone body diameter.

Hydrocyclones have been used widely in the metalworking industry, as they render a good performance in the separation of free oil and solid particles. They require less space and hence less capital cost than gravity separators and yield a sludge with a lower oil content.

3.2. SECONDARY TREATMENT

The aim of this step is to break O/W emulsions and to remove the dispersed oil. These operations can be broadly classified as chemical, physical or electrical methods. Chemical methods, mainly coagulation and flocculation, are the most frequently used and may also enhance mechanical treatments. Physical methods include filtration and membrane separations. Air flotation can be considered as a mechanical method, but it usually requires the utilization of chemicals. Electrical techniques are mainly used for W/O emulsion treatment, and they will not be discussed in this work.

3.2.1. *Chemical Treatment: Coagulation and Flocculation*

Chemical treatment may be used with oily wastewater for the removal of suspended or colloidal oil. The chemical dosing to oil-water systems does not generate separation by itself but may lead to better performance of the physical separation equipment by generating larger oil droplets. Oil droplets in an aqueous medium carry a surface charge, and as two droplets approach each other, electrostatic repulsion prevents them from forming larger aggregates. Using chemical additives destabilizes the dispersed phase by reducing the charge on the surface of oil droplets, serving to break the emulsion and promote droplet coalescence.

Dispersed phase (oil) collection can be accomplished by two mechanisms: *coagulation* and *flocculation*, which in most cases are complementary; these processes use inorganic salts and organic polymers, known as *coagulants* and *flocculants*, respectively.

The addition of coagulants (salts of high valence cations: $AlCl_3$, $FeCl_3$, $CaCl_2$, $FeSO_4$, etc.) to an O/W emulsion has two main effects: to depress the effective width of the double layer around oil droplets and to reduce the surface charge on the oil droplets by cation addition. This leads to a reduction of the zeta potential, and droplet aggregates (flocs) start to form. Addition of inorganic species such as acids or salts (aluminum sulfate, ferric salts) increases the conductivity of the continuous phase (water), thus reducing the surface charge of the droplets and increasing coagulation.

Polyelectrolytes and organic polymers are often used for flocculation of the oil droplets. They either change the surface charge of the oil droplets (polyelectrolytes) or form aggregates by bridging mechanisms (polymers), but they are substantially unaffected by pH.

In all cases, chemical treatment promotes coalescence of oil droplets, which can then be removed mechanically by several techniques.

3.2.2. *Flotation*

This may be considered as a physico-chemical method for emulsified oil removal. It is effectively an enhanced gravity separation that may be used to enhance oil removal where the oil-water density differential is not sufficient to separate oil and oil-wetted solids. Fine air bubbles are introduced into the wastewater, and their adhesion to the oil droplets or even to light solids in suspension makes these more buoyant. The oil or solids can then rise more quickly to the surface of the tank where it is skimmed off as aerated foam. Flotation usually requires the use of chemicals, which mainly act as coagulants or flocculants. The interaction mechanism between air bubbles and oil droplets is shown in Figure 1.18 and follows these steps (Bennett 1988, Vrablik 1959):

a. Collision and attachment of fine air bubbles to the surface of the oil droplets.

b. Collision between gas-attached droplets with the formation of agglomerates.
c. Entrapment of more gas bubbles in the flocculated structure of oil droplets as it rises.
d. Upward rise of floc structures in a sweeping action called *sweep flocculation*.

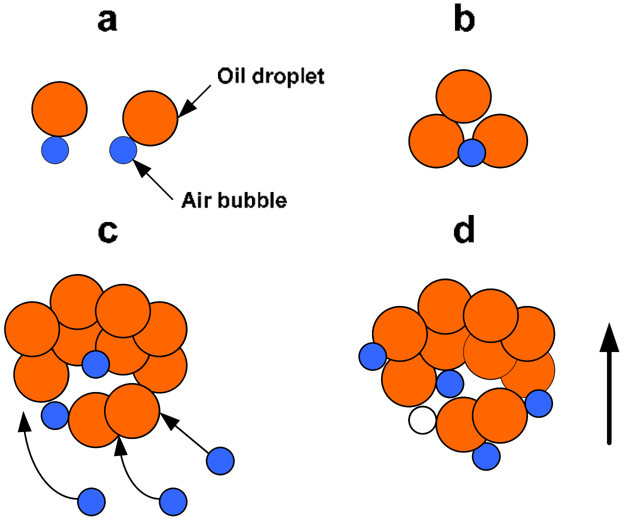

Figure 1.18. Interaction mechanism between gas bubbles and oil droplets during flotation.

There are two major types of commercial flotation processes:

- *Induced air flotation (IAF)* is a process where the air and the liquid are mechanically mixed to induce bubble formation in the liquid. For this process, bubbles are generated and discharged into the liquid by high-speed rotating impellers, by diffusers, or by recycle of a slip stream through venturi nozzles to entrain air into the wastewater. IAF units (Figure 1.19) are usually rectangular and incorporate four or more air flotation stages in series. Diffusers or submerged turbine aerators create bubbles much too coarse for good droplet flotation performance.

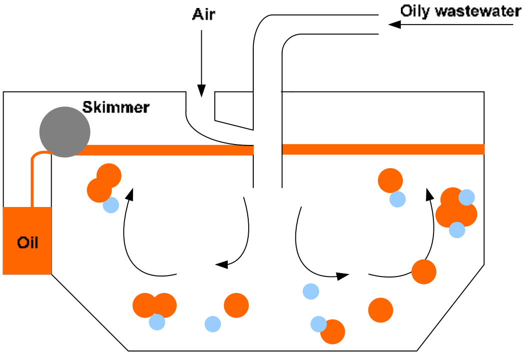

Figure 1.19. Schematic diagram of an IAF unit.

- *Dissolved air flotation (DAF)* uses compressed air that is dissolved in the liquid under pressure and comes out from solution as very fine gas bubbles when the pressure is reduced. The gas bubbles rise to the surface carrying attached oil and suspended solids. DAF units commonly employ rectangular tanks but circular units are also available, resembling a primary clarifier or thickener. The feed stream, often treated with flocculating agents, enters the inlet mixing chamber as does the recycle stream, which is supersaturated with air. The stream then enters the flotation zone, where the oil/solids/bubble assemblies migrate to the surface and are mechanically skimmed, as shown in Figure 1.20.

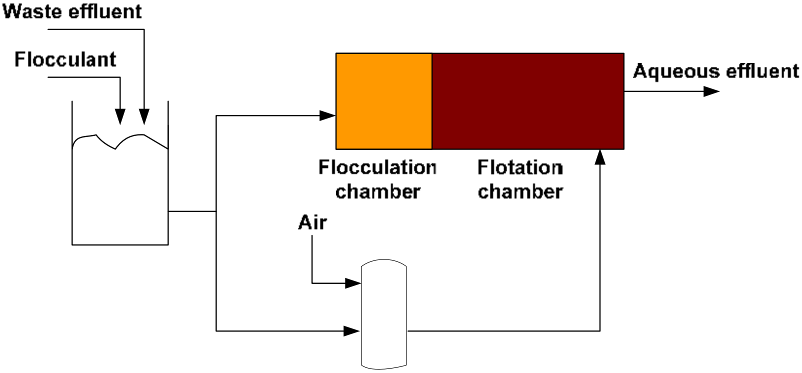

Figure 1.20. Diagram of a DAF unit.

The significant differences between IAF and DAF are the bubble size and mixing conditions. In DAF, the bubbles are about 50–60 µm in diameter, whereas IAF bubbles are an order of magnitude larger.

The main components of a flotation system are: the pressurizing pump, an air injection system, a retention tank, a back pressure control device, a pressure reducing valve, and a flotation tank. The pressurizing pump creates a high pressure (at about 4–6 bar) to increase the solubility of air, which is added through an injector on the suction side of the pump. The air and liquid are mixed in a retention tank with a residence time of 1–3 min. The primary variables affecting flotation performance are: air pressure, recycle ratio and flow rate, oil droplet and bubble size distributions, feed oil concentration, and liquid residence time.

The design equation for a flotation system provides the determination of the air/oil dimensionless ratio (*G/O*), using the equation:

$$\frac{G}{O}=\frac{kS_aR(fP-1)}{QS_o} \tag{1.14}$$

where k is a constant (approximately 1.3), S_a is the air solubility at standard conditions (mL/L), R is the recycle rate (gal/min), f is the air saturation efficiency (usually 0.5–0.8), P is the operating pressure (atm), Q is the wastewater flow rate (gal/min), and S_o is the suspended oil in influent wastewater (mg/L).

Optimum operation of a flotation unit requires maintaining the proper *G/O* ratio. Polymers, emulsion breakers and surfactants are used in air flotation to destabilize emulsions and increase the efficiency of the air bubbles. Flotation is able to produce a cleaner effluent than do coalescers. Plate separators may be used to remove large quantities of free oil and some suspended solids before entering the flotation unit.

For a common waste stream containing about 50 mg/L free oil with suspended solids and a 10000 mg/L COD, typical DAF removal performance is: oil (80–90%), suspended solids (65–75%), and COD (60–70%).

3.2.3. *Filtration: Deep-Bed Filtration and Filtration-Coalescence*

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.

The operating variables that determine the process performance are: the properties of the filter material (porosity, granularity, composition), feed flowrate, oil concentration and pressure drop through filter media. A decrease in fiber or granule size of the filter medium improves the overall efficiency of the process (Ahmad et al. 2005, Cambiella et al. 2006b, Cheremisinoff 1995, Kenneth 1983, Khan et al. 2004, Mysore et al. 2005, Soma and Papadopoulos 1995, Yang et al. 2007). Feed flowrate should be low: high flowrates reduce filter efficiency because of the lesser residence time of oil components in the filter bed. There is a critical flowrate in filtration-coalescence above which no coalescence is observed (Davies and Jeffreys 1969, Menon and Wasan 1985). However, sometimes a high feed flowrate can increase the removal efficiency of deep-bed filtration because of oil drag and its adsorption on the lower saturated zones of the filter bed. A compromise in flowrate should be found to guarantee a high quality aqueous effluent and an efficient use of the filter media.

In the filtration process, the pressure drop tends to built up with time due to accumulation of solids and oil. In some cases, a constant value of the oil concentration in the effluent has been observed (Pushkarev et al. 1983). Some authors have considered this phenomenon to be similar to a breakthrough curve (Menon and Wasan 1985, Viraraghavan and Mathavan 1990), which may indicate that the filtration cycle has ended. The bed must then be backwashed or the filter material renewed.

3.2.4. *Membrane Treatment: Microfiltration and Ultrafiltration*

Membrane processes have found an increasing number of applications, mainly in the treatment of complex industrial wastewaters (Drioli and Romano 2001, Pereira and Peinemann 2006). A membrane is a structure separating two phases and/or acting as an active or passive barrier to the transport of certain species between the phases adjacent to it. Membranes can be classified into two groups (Bhave 1991, Cheryan 1998, Ho and Sirkar 1992): (i) *Organic membranes*, made of polymers: cellulose acetate, polysulfone, polyvinylidene fluoride, etc., and (ii) *Inorganic membranes*, which are made of inorganic materials: ceramics, glasses, carbon and metals.

Membrane filtration is most successful in separating emulsified and dissolved oil, as all the other kinds of oily wastes can be removed readily by some of the mechanical separations previously described. Typical pressure-driven membrane specification ranges are listed in Table 1.4. A typical pressure-driven membrane process is shown in Figure 1.21: solutes larger than the membrane pore size are retained by the membrane in the *concentrate* or *retentate* stream, whereas solvent and smaller molecules will pass through the membrane to the *permeate* stream.

TABLE 1.4. Pressure-driven membrane processes

Membrane process	**Mean pore size (μm)**	**TMP (bar)**
Microfiltration (MF)	10–0.1	0.5–1
Ultrafiltration (UF)	0.1–0.01	1–10
Nanofiltration (NF)	0.01–0.001	10–30
Reverse osmosis (RO)	<0.001	30–50

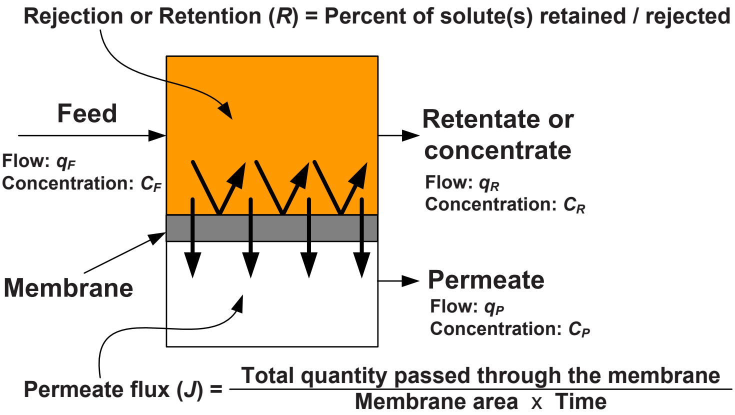

Figure 1.21. Pressure-driven membrane process.

Besides permeate flux, defined in Figure 1.21, membrane processes are also characterized by the following parameters: retention or rejection (R), recovery (S), volume reduction (VR), and volume concentrate ratio (VCR):

$$R = 1 - \left(\frac{C_P}{C_F} \right) \tag{1.15}$$

$$S = \frac{q_P}{q_F} \tag{1.16}$$

$$VR = \frac{q_F}{q_R} \tag{1.17}$$

$$VCR = \frac{V_F}{V_R} \tag{1.18}$$

The development of membrane manufacturing over the last 50 years has led to applications in emulsion processing. The most common membrane separation methods for the treatment of O/W emulsions are MF (Hlavacek 1995, Hu and Scott 2007, Hua et al. 2007, Koltuniewicz et al. 1995, Mahdi and Sköld 1991a, Nazzal and Wiesner 1996) and UF (Bailey 1977, Belkacem et al. 1995a, Bhattacharyya et al. 1979, Chakrabarty et al. 2008, Dick 1982, Lee et al. 1984, Lipp et al. 1988, Mahdi and Sköld 1991b, Nyström 1991, Rezvanpour et al. 2009, Sköld 1991), while NF (Jönsson and Jönsson 1995, Park and Barnett 2001) is not so widely used. RO is considered a tertiary treatment and will be discussed later.

The major drawback in membrane processes is the decline in permeate flux with time, mainly because of concentration polarization, membrane fouling – due to surfactant or oil adsorption on the pore walls – gel layer formation or pore blocking by oil droplets. There is not a clear demarcation between MF and UF for the treatment of O/W emulsions, since the formation of an oil gel layer on the membrane surface modifies the membrane selectivity, and a MF membrane may behave as a UF membrane (Cheryan 1998, Mulder 1991). MF membranes give higher permeate fluxes but have a higher risk of oil permeation. UF membranes, which have tighter pores, have been selected in most applications to ensure steady permeate quality.

The complete membrane process comprises membrane modules, pressure vessels, pumps and control instruments. There are basically four types of membrane modules: plate and frame, spiral, tubular and hollow fiber (Cheryan 1998, Koros 1991, Mulder 1991).

A typical UF-based system for oily wastewaters consists of a feed tank, a pre-treatment stage to remove particles and free oil, a prefilter, a process tank, and the membrane module (Figure 1.22). The membrane unit is operated in a semi-batch recycle mode. The retentate containing the oil is recycled to the process tank and the permeate is withdrawn continuously. Fresh oily wastewater is added to the process tank, thus keeping a constant level. The final concentrate volume may be only 3–5% of the initial oily wastewater volume. The system is then cleaned until the initial permeate flux is restored.

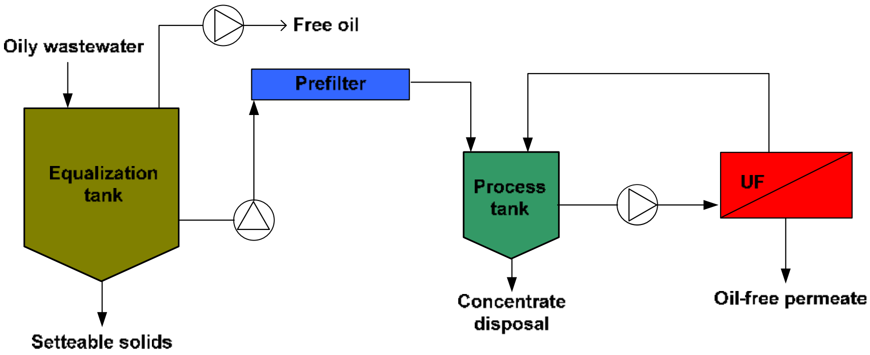

Figure 1.22. UF process for oily wastewater treatment.

An alternative treatment process consist of a process holding tank, a small tank for addition of coagulant, a UF membrane module and a retentate tank to dispose of the oil. The permeate may require a chemical treatment, but then it can be sent to the sewer. An excessive build-up of contaminants in the feed/concentration stream must be avoided since this can lead to mineral scaling on the membrane or irreversible fouling. This treatment (hybrid process) will be explained in more detail in Section 5.

MF or UF processes cannot remove dissolved oil components from the water. If this is required, other methods, such as RO, must be used. The key factor determining the economics of membrane operations is clearly the filtered liquid throughput rate. The choice of membrane material is also important: inorganic membranes are chemically robust and expensive, whereas polymeric membranes have lower resistance to aggressive feeds, but they are considerably cheaper.

The use of membranes for oily wastewater treatment leads to lower energy costs compared to thermal treatment and good filtrate (permeate) quality. However, membrane processes do have some limitations:

- Scale-up is almost linear above a certain size, and investment costs for large effluent volumes may be high. As a rule of thumb, the cost of a membrane installation can be estimated by multiplying by five the price of the membrane.
- Membrane life, especially for polymeric ones, is a function of fouling and degradation with use. They may have to be replaced frequently, which increases the operating costs.

3.3. TERTIARY TREATMENT

This final stage is not always needed. It may be required to improve the quality of the final aqueous effluent, reducing its COD, inorganic salts content and dissolved metals, if it is intended to be reused for reformulation of fresh O/W emulsions or discharged to sewers. The principal technologies applied in this stage are described in the following sections.

3.3.1. *Evaporation*

Liquid evaporation is a heat transfer process that produces a phase change of at least one of the components in a liquid mixture. It is used for the recovery of a volatile liquid from a mixture, and the residual product could be a liquid or a solid or a combination of both. Evaporators are suitable for low volumes of waste because of the large amount of energy required.

There are several types of evaporators available depending on the heat transfer mechanism. The most commonly used at industrial scale are those in which steam is the heating fluid (Bishop and Arlidge 1979, McCabe et al. 2005, Perry and Green 2007), as shown in Table 1.5.

TABLE 1.5. Common types of industrial evaporators

Evaporator type	**Characteristics**
Horizontal tubes evaporator	Low cost. Suitable for low viscosity liquids
Short vertical tubes evaporator	Easy to clean. Appropriate for liquids that could deposit solids on the tubes surface
Long vertical tubes evaporator	
- Rising film evaporator	Useful for evaporation of liquids that have a high foaming capacity
- Falling film evaporator	Appropriate for heat-sensitive liquids and for viscous liquids
Forced circulation evaporator	The liquid is pumped through the tubes. Suitable for heat-sensitive liquids, viscous liquids, liquids with a high salinity content and/or high foaming capacity
Agitated film evaporator	It is a modification of the falling film evaporator. Recommended for viscous liquids
Multiple-effect evaporator	Designed to minimize energy consumption
Vapor compression evaporator	The vapor generated is compressed and used to heat the feed stream

The main variables used for evaporator characterization are the capacity – the mass of solvent evaporated per unit time – and the economy – the ratio of solvent mass evaporated to steam fed to the unit.

The capacity depends on the heat transfer rate (q) through the heating surface (A) of the evaporator:

$$q = UA\Delta T_{VL} \tag{1.19}$$

where ΔT_{VL} is the temperature difference between vapor and liquid, and U is the overall heat transfer coefficient. Among all parameters involved in Eq. (1.19), the heating surface (A) is the only one that depends on evaporator size, whereas the others depend primarily on the effluent to be treated.

The overall heat transfer coefficient (U) depends on the evaporator design, its operational behavior, and fluid properties; it can be expressed as:

$$U = \frac{1}{R_v + R_{do} + R_w + R_{di} + R_l} \tag{1.20}$$

That is, the overall heat transfer coefficient, U, is the inverse of the overall resistance to heat transfer, which is the sum of several local heat transfer resistances-in-series, those due to the water vapor condensate (R_v), to the fouling of external (R_{do}) and internal surfaces of the tubes (R_{di}), to the tube wall (R_w) and to the boiling liquid (R_l). In Table 1.6 typical U values are listed for several types of evaporators as a function of the operational mode and the feed viscosity.

TABLE 1.6. Overall heat transfer coefficients for several types of evaporator (McCabe et al. 2005)

Evaporator type	***U* (W/m^2 °C)**
Long-tube vertical evaporator	
– Natural flow	1000–3000
– Forced flow	2000–5000
Agitated film evaporator (newtonian liquid, viscosity)	
– 1 cP	2000
– 1 P	1500
– 100 P	600

Oily wastewaters are not heat-sensitive feeds, but their salinity and foaming tendency can be high so their treatment by evaporation is mainly performed in rising film evaporators, which have the additional advantages of a relatively low capital cost, ease of maintenance and good heat transfer efficiency. Moreover, in order to reduce energy costs, vacuum evaporation is increasingly used for the treatment of O/W emulsions in some existing plants. However, its performance has not been studied fully, and only scarce information can be found in the literature (Cañizares et al. 2004, Gutiérrez et al. 2009).

The main factors that affect the water evaporation from an O/W emulsion are as follows (Aranberri et al. 2002, 2003):

a. Electrostatic repulsion forces between oil droplets. High repulsion forces could cause a significant reduction in evaporation rate.
b. Progressive water evaporation causes a water concentration gradient in the emulsion bulk, affecting viscosity and perhaps vapor pressure.
c. Oil droplets tend to coalesce during the evaporation process, creaming to the surface of the emulsion stream and forming a thick oil layer. It remains separated from the vapor phase by a thin water film, but the oil film reduces the water evaporation rate, as shown in Figure 1.23.

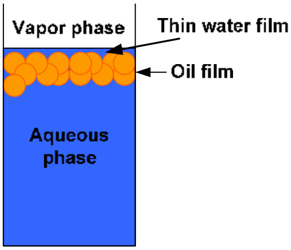

Figure 1.23. Schematic process of evaporation when oil droplets coalescence occurs.

O/W emulsion evaporation can be described as a three-step process:

- The first step consists of water transport to the top of the liquid sample, a process controlled by mass transfer. Repulsive forces between oil droplets, droplet size and interfacial tension are important in this step.
- The second step is water transport through a thin layer of a secondary phase formed by oil and is also controlled by mass transfer, a process influenced by stability and interfacial tension (Aranberri et al. 2002, 2003, 2004). This step does not happen for O/W emulsions that retain high stability throughout the entire evaporation process.
- The third step is vapor transfer from the top of the liquid phase, or from the thin layer of a secondary phase, into the vapor phase. This

depends on emulsion properties such as surface tension and viscosity, which may enhance or hinder the transfer rates.

The evaporation rate (E), expressed as the mass of water evaporated (m) per unit time (t) is given by (Beverley et al. 1999, Aranberri et al. 2002, 2003, 2004):

$$E = -\frac{dm}{dt} = \frac{MA_L D_v P_v z}{hRT} \tag{1.21}$$

where M is the molecular weight of water, A_L is the surface area of the liquid sample, D_v is the water diffusion coefficient in the vapor phase, h is the height of vapor phase, P_v is the vapor pressure of water, R is the ideal gas constant, T is the absolute temperature and z is a correction factor.

The vapor pressure (P_v) of water from the films between the oil droplets depends on the disjoining pressure or repulsive force per unit of film area (Π):

$$P_v = P_{vo} \exp\left(\frac{-\Pi v}{kT}\right) \tag{1.22}$$

where P_{vo} is the vapor pressure of water in the feed emulsion bulk, v is the water molar volume, T is the absolute temperature and k is the Boltzmann constant.

According to Eqs. (1.21) and (1.22), repulsive forces between oil droplets will lower the vapor pressure of the water located between them, so the evaporation rate will be reduced.

Stabilizers and additives used for O/W emulsion formulation have a huge impact on the evaporation process. The composition of the emulsion, the type of emulsifiers (mainly surfactants), and their concentrations influence the evaporation process. High surfactant concentrations may decrease the evaporation rate, especially for emulsifiers containing a long hydrophobic chain (Friberg et al. 1997, Gavril et al. 2006, Lunkenheimer and Zembala 1997, Sefiane 2006). Furthermore, foam formation induced by emulsifiers will provide more air/water interfacial area, enhancing the water evaporation rate (Kibbey et al. 2001). Foaming may result, however, in some organic entrainment into the vapor and the condensate. For the same oil, nonionic surfactants retard water evaporation more than ionic surfactants because electrostatic repulsion between oil droplets in ionic surfactant-stabilized emulsions thicken the water film relative to those emulsions stabilized by non-ionic surfactants (Aranberri et al. 2002, 2004).

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 their cleaning is labor intensive, and so their use should be considered only when other treatment systems do not work.

3.3.2. *Activated Carbon Adsorption*

This technique is based on the adsorption of the contaminants onto an activated carbon bed. Activated carbon can be used to polish effluent from oily wastewater treatment plants to remove residual dissolved organic compounds remaining after primary and secondary treatments (Rozada et al. 2003). The main disadvantages of this process are that activated carbons are expensive, and their use may require activation and reactivation procedures.

To reduce the high cost of the adsorption process, sewage sludge has being considered as a potential raw material for the production of activated carbon for wastewater treatment (Rozada et al. 2005). In recent years, chemical modification of ordinary adsorbents is frequently done by introducing functional groups onto the matrix of the absorbent to obtain a better adsorption capacity and selectivity for specific organic compounds.

3.3.3. *Biological Treatment*

The growing use of synthetic or semisynthetic metalworking fluids, which have low or no oil content, often requires the removal of their organic components when those spent solutions are treated. Biological treatment is being adopted increasingly for metalworking fluid treatment due to significant cost saving although the main drawback is the maintenance in a stable state of the microbial population present in activated sludge plants (Van der Gast and Thompson 2004).

Temperature and pH are very important parameters in biological treatment to achieve high efficiency of the process. Optimum values have been found around 40ºC and pH 6–7. The feed/microorganism (F/M) ratio should be in the range of 0.22–0.63 for the treatment of O/W emulsions (Cheng et al. 2005).

3.3.4. *Reverse Osmosis*

As it was explained in the discussion of secondary treatments, reverse osmosis (RO) is one of the pressure-driven membrane processes and is characterized by its low membrane pore size (less than 0.5 nm) and high operating pressures (30–50 bar). RO allows salt removal that cannot be attained by MF or UF processes. Moreover this is the best technology available for separating total dissolved solids (TDS), and more than 95% removal rates can be reached (Norouzbahari et al. 2009).

As with other membrane processes, the main drawback is permeate flux decline due to membrane fouling. RO is commonly applied as a final stage in a hybrid process in order to obtain good quality effluents.

4. Treatment Costs

Treatment costs for oily wastewaters depend on the type of oil present: they are lower for free oil removal and increase successively for dispersed, emulsified and dissolved oil removal. However, treatment costs are not only a function of the technique employed but also of the equipment used, so it is very difficult to make a cost comparison among the techniques described in Section 3. Figure 1.24 shows a qualitative comparison of relative operating costs of several techniques used for oily wastewater treatment.

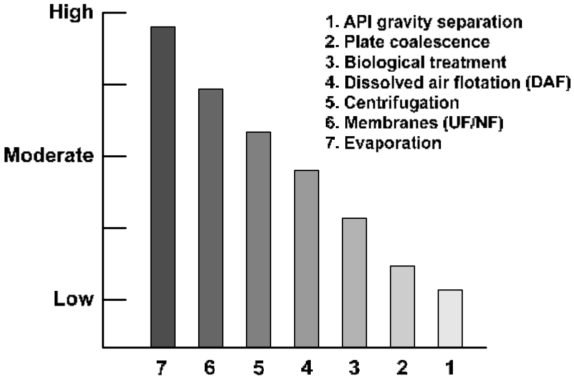

Figure 1.24. Relative operating costs of technologies used for oily wastewater treatment.

Nowadays, a combination of two or more separation processes (integrated or hybrid processes) and specially hybrid membrane processes are the most frequently used for the treatment of oily wastewaters at industrial scale in order to reach the most severe discharge standards, to reduce total costs and to achieve better oil separation efficiency.

5. Trends in the Treatment of Oily Wastewaters

5.1. INTEGRATED OR HYBRID PROCESSES

Many of the above-mentioned treatment methods effectively reduce the amount of oil present in wastewaters, but in most cases a combination of two or more separation processes (*integrated* or *hybrid process*) is required to reach the most severe discharge standards. Integrated processes may reduce total production cost, energy consumption, and capital cost, and give better oil separation efficiency (Cheryan 1998, Mulder 1994). The selection of a suitable integrated or hybrid process depends on the characteristics of the oily effluent to be treated, and the most commonly used are described in the following sections.

5.1.1. *Membrane Hybrid Processes*

Sometimes it is not desirable or even possible to use a simple membrane system to carry out oil/water separation. 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, hybrid membrane 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.

Membrane hybrid processes for the treatment of oily wastewaters can be classified as follows:

A. *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. Usually the process starts with the removal of settleable solids and free-floating oil prior to membrane treatment, mainly UF (Jönsson and Trägårdh 1990). 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 (Teckentrup and Pahl 1996) 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, obtaining a permeate which can be discharged continuously into the sewage system. This process is commonly used in the automobile industry (Cheryan 1998).

B. *Membrane hybrid processes with chemical pretreatment of the feed*. There are certain processes that use chemical instead mechanical pretreatment, which consists mainly of a process tank where a coagulation/ flocculation (Benito et al. 1999, Zhang et al. 2008) and/or a DAF operation (Al-Zoubi et al. 2009, Ghidossi et al. 2009) takes place prior to the membrane treatment. Coagulation/flocculation of the emulsion is a critical step for the performance of the membrane in order to maintain a high flux and to prevent membrane fouling.

C. *Membrane hybrid processes with purification of the permeate or concentrate*. The main purpose here is to meet discharge standards and/or to provide treatment of the retentate for reuse by post-treatment polishing of the permeate after a membrane separation removes the bulk of the contaminants with relatively low energy consumption. Combining UF with a photocatalytic process results in a hybrid process capable of purifying bilge water by decomposition of residual oil and conversion of the organic pollutants into inorganic materials (Karakulski et al. 1998). In some processes activated carbon particles (PAC) are added to the feed circulation loop in order to adsorb the organic compounds and facilitate their rejection by the membrane, lowering the final COD and TOC content of the permeate compared to that obtained by conventional UF or biological treatment (Mohammadi and Esmaeelifar 2005). Retentate treatment is of interest when used oils can be regenerated, employing an UF process followed by distillation or evaporation (Specht 1997). 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.

D. *Combination of two membrane processes*. Oily wastes can sometimes be treated by a combination of two membrane processes to obtain a high-quality water effluent for its further use for several purposes. Purification of oily wastewaters has been accomplished by a combination of UF/NF or UF/RO processes. Several oily effluents have been treated by these hybrid processes: oily wastewaters from engine-rooms (Karakulski et al. 1995) and automotive industries (Olsson and Lindskog 1995), metal finishing wastewaters (Von Mylius 1992), spent O/W emulsions from copper wire drawing (Karakulski and Morawski 2002), waste metalworking fluids (Hilal et al. 2004), crude oil desalting effluent from an oil refinery (Norouzbahari et al. 2009), and bilge water from ships (Tomaszewska et al. 2005).

E. *Membrane reactors*. Membrane reactors are novel systems for wastewater treatment that combine the use of membrane separation technology with biological or chemical reaction processes. The use of *membrane chemical reactors* has been studied for the treatment of metalworking wastewaters (Belkacem et al. 1995b). The process is based on a coupling of MF or UF with a chemical reaction consisting of a partial chemical destabilization of the oil droplets by $CaCl_2$ addition, in two consecutive steps: coagulation and coalescence. *Membrane biological reactors* or *membrane bioreactors* (MBR) have been used as an alternative to the conventional activated sludge process for wastewater treatment. The MBR process consists of a suspended growth biological reactor combined with a membrane process, mainly MF or UF. In this process, pollutants are degraded by the activated sludge, and the clean effluent is obtained by filtering it through a membrane under pressure (Rosenberger et al. 2002, Stephenson et al. 2000). Membranes act as a barrier to the microorganisms and suspended solids, and therefore the final effluent is of better quality than that produced by a conventional biological treatment plant. This MBR process has been applied to the treatment of oily wastewater at several plants of General Motors automotive industry in USA and Canada using UF membranes (Sutton et al. 1994). The UF unit retains oil and grease while it is biologically degraded in the aerobic reactor, obtaining a final effluent with less than 6 mg/L of oil and grease. MBR processes have also been used for the treatment of synthetic wastewater containing fuel-oil or lubricating oil plus surfactants (Scholz and Fuchs 2000) and also for oil refinery wastewater (Pankhania et al. 1999).

5.1.2. *Other Integrated Processes*

All known methods for oily wastewaters treatment consist of a combination of emulsion disruption and the separation of the demulsified oils from water. The principal integrated processes which have found industrial use are the following:

A. *Integrated processes with chemical breakdown of the emulsified oil*. These are the most commonly integrated processes for the treatment of oily wastewaters. They involve an emulsified oil breakdown stage, such as chemical breaking, coagulation and flocculation, followed by secondary clarification and purification of the water phase. Several integrated processes have been developed for the treatment of different industrial oily effluents, such as: treatment of metal finishing wastewaters by chemical precipitation followed by coal adsorption or selective ion exchange (Von Mylius 1992), a coagulation/flotation stage followed by sludge filtration to remove oil and grease present in wastewater (Iida et al. 1996), and a destabilization/evaporation process for the treatment of oily wastewaters generated in copper wire drawing (Gutiérrez et al. 2008, 2009).

B. *Integrated processes with a DAF stage*. Dissolved air flotation (DAF) has been used for emulsified oil removal in effluent streams from the steel industry with subsequent treatment of the effluent leaving the DAF unit by carbon adsorption (Rees and Williams 1997), treatment of hydrocarbon loaded rain runoff by coagulation/flotation and DAF (Bernard et al. 1995), and a coagulation/DAF process for the removal of emulsified oil recovered from petroleum wastewater by API separators (Luthy et al. 1978).

C. *Integrated processes with a biological treatment stage*. Flocculation/biological processes have been reported for the treatment of metalworking fluids with 99% of oil removal (Zhang et al. 1994). Also biological treatment of high-strength bilge water and aqueous petroleum waste was done by an extended aeration sludge process to reduce BOD followed by a post-treatment of the resulting effluent with O_3/H_2O_2 to reduce COD and TOC values (Hulsey et al. 1995).

5.1.3. *Case Study: Integrated Process for the Treatment of Waste O/W Emulsions*

Cutting fluids or metalworking fluids (MWFs) are used in metalworking operations where cooling, lubrication and rust control are important at the tool-workpiece interfaces, in operations such as cutting, grinding or rolling. MWFs help to improve the life and function of the tool and may account for up to 15% of the machining process cost. These fluids may be classified into three broad categories (Figure 1.25):

- *Oil-in-water (O/W) emulsions*. Commonly called "water soluble oils" (although the oils are not truly soluble in water), which are obtained by mixing a mineral oil with an aqueous phase containing an emulsifier (surfactant). They also contain additives to improve their lubricating properties. They have a milky white appearance, with base oil concentrations ranging between 1 and 10 wt % in water, providing good lubrication.
- *Synthetic fluids*. Sometimes referred to as "chemical fluids", which contain no mineral oil, these comprise mixtures of several water-soluble compounds, such as emulsifiers, anti-corrosion agents or defoamers. They form a clear or translucent solution in water and often provide the best cooling performance among all MWFs.
- *Semisynthetic fluids.* These are a combination of O/W emulsions and synthetic fluids and have properties common to both types.

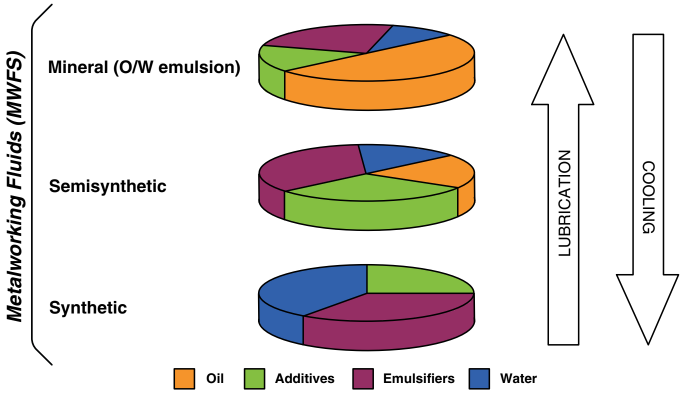

Figure 1.25. Classification of MWFs and their composition before being dispersed in water.

After being used for some time, these fluids are degraded and eventually have to be discarded (Benito et al. 2010, Greeley and Rajagopalan 2004), generating an emulsion waste stream. Spent MWFs constitute one of the largest volumes of oily wastewaters found in metalworking industries. They may contain inorganic, organic and biological contaminants, presenting a difficult waste treatment problem because of their diverse composition and concentration, which vary from one industrial source to another. As a result it is not easy to identify a general treatment suitable for all different types of MWFs.

The design and construction of a modular pilot plant for the treatment of oil-containing wastewaters, which offers the possibility of combining different treatments, were carried out for the following process parameters:

feed capacity 300 L/h, oil content 0.1–10 vol % and suspended solids 500–1000 mg/L (Benito et al. 2002). This plant, shown in Figure 1.26, consists of magnetic and mesh filters for solids removal (mainly metal filings), a 1000-L stainless-steel feed holding tank to store the oily wastewater and operate in continuous mode, a demulsification/centrifugation stage for emulsion breaking and removal of free and demulsified oil, a ceramic membrane UF stage (50 nm pore size, 1.7 m^2 membrane area) to remove the remaining oil in the aqueous phase from demulsification/centrifugation, and a peat bed filter which could be used for the treatment of spent synthetic MWFs (no oil content) or if the permeate obtained in the UF stage has an oil content higher than the limiting standards.

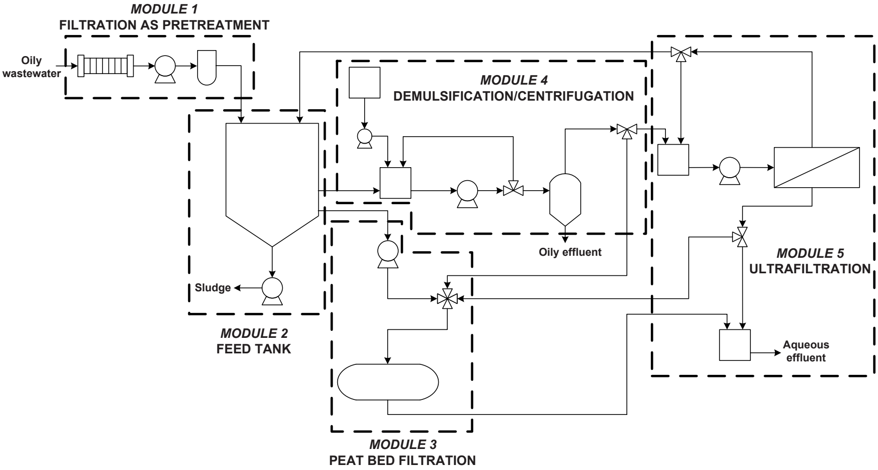

Figure 1.26. Schematic diagram of the modular pilot plant for the treatment of oil-containing wastewaters.

A large volume (1600 L) of oily wastewater, generated during the manufacture of metal components for pumps in a local company, was treated in order to study the performance of this plant (Figure 1.27). Its characteristics are the following: 30 g per ton of metallic filings, 22425 mg/L of oil (excluding free-floating oil, which can be easily removed), 65000 mg/L COD, and pH = 9–10. This waste emulsion was first passed through the filters to remove the metallic filings. The pretreated emulsion was then pumped into the feed storage tank, where it was mixed with 1000 mg/L of the demulsifying agent. Afterwards, it was fed to a centrifuge, and the characteristics of removed oil in this stage were: 30 wt % water, 2 wt % chlorine, and 29500 kJ/kg as combustion heat. The aqueous phase obtained at this point (1500 mg/L oil, 9000 mg/L COD) was fed to the UF unit, where the permeate stream obtained had the following characteristics: 500 mg/L oil and 8000 mg/L COD. These high values of COD and oil content can be explained by the fact that the original oily waste was a mixture of the three types of MWFs available in the market (mineral, semisynthetic and synthetic). To obtain a final effluent suitable for discharge, the next treatment stage was filtration using mixed beds of peat and calcium sulfate. The final effluent had an oil concentration of about 30 mg/L and 6500 mg/L COD.

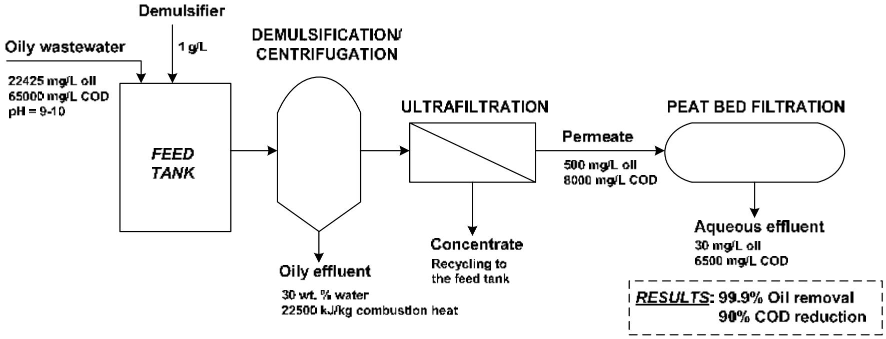

Figure 1.27. Experimental results for the treatment of a waste MWF using the modular pilot plant shown in Figure 1.26.

The effluent had a dark brown color because the high pH of this type of fluid caused the decomposition of the peat material (humic acids). This decomposition gives the effluent a high COD concentration, but the low oil concentration value indicates an adsorption of contaminants and a change in the nature of the organic matter dissolved in the liquid. More than 99.9% of oil removal and 90% of COD reduction were achieved using this integrated treatment. The resulting final effluent is suitable for discharge into the sewage system for subsequent treatment in a conventional wastewater treatment plant as the pollutants that could cause operational problems had been removed.

Another similar process, shown in Figure 1.28, was proposed for the treatment of a waste O/W emulsion from a copper rolling process (67000 mg/L COD). It was a demulsification/centrifugation–ultrafiltration process, but in this case the permeate stream from the UF unit was treated by vacuum evaporation (Gutiérrez et al. 2007, 2008). The best results were obtained when demulsification was performed by the addition of 0.05 mol/L $CaCl_2$; the final aqueous effluent after vacuum evaporation stage had a COD of 104 mg/L, with more than 99.8% of COD reduction.

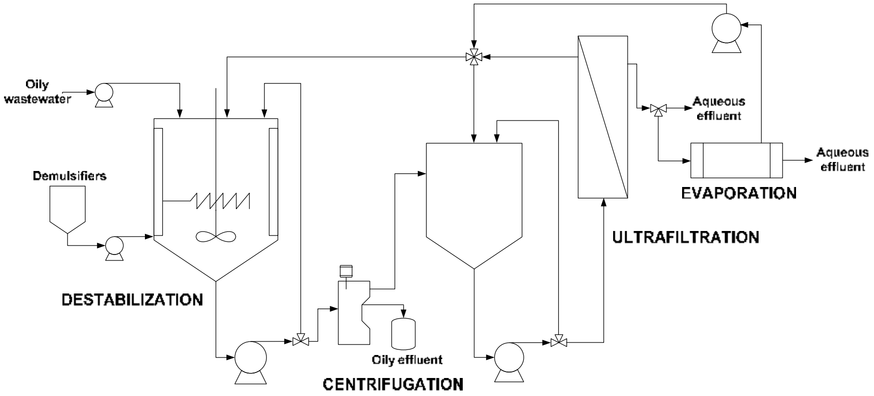

Figure 1.28. Integrated treatment of a waste O/W emulsion from a copper rolling process.

Evaporation is more effective than the other processes for the treatment of water-based synthetic and semisynthetic emulsions because of their low oil concentrations. The energy consumption for the industrial treatment of 1 m^3 of a waste O/W emulsion with the same previous demulsification stage has been calculated (Gutiérrez et al. 2008) for three techniques. It was 70 kWh for a vacuum evaporation treatment, whereas it was only 18 and 5 kWh for UF or centrifugation treatment, respectively. Nevertheless, evaporation is attractive because the quality of the aqueous effluent obtained is much higher with vacuum evaporation than with the other treatments. Moreover, the waste oil recovered from vacuum evaporation has low water content and may be burned for energy production.

5.2. O/W EMULSION REGENERATION

Disposal of waste metalworking fluids is expensive because they are classified as hazardous wastes, being relatively toxic to aquatic organisms. The organic components in oily wastes can either be in a free, emulsified or dissolved state. As it was mentioned above, the treatment to remove the emulsified and dissolved oil is generally complex and expensive, and often emulsion breaking is needed before the oil can be successfully removed (Gutiérrez et al. 2007, Benito et al. 1998, 1999, 2002, 2010). Hence, it would be desirable that MWFs should be formulated for each specific operation and always keeping in mind the disposal problem.

To function effectively a MWF should have the following characteristics: (1) good lubricating properties, (2) good cooling action, (3) effective anti-adhesion properties, (4) low viscosity, (5) good wetting, (6) corrosion inhibition, (7) good emulsion or solution stability, (8) non-toxic and non-flammable, and (9) economical in use and disposal.

At present, efforts are being undertaken to develop MWFs that provide the aforementioned characteristics, but most of the commercial MWFs contain many components that are not disclosed by the manufacturer. The main drawback in using MWFs in industrial processes is the environmental impact that the waste emulsions can cause once they are exhausted. This fact has lead to new formulations that take into account the emulsion life-cycle. A proper formulation of a MWF extends tool life, improves piece finish and reduces energy consumption. Furthermore, a properly formulated MWF is also easily regenerated and is more efficient and less expensive to treat prior to ultimate disposal (Benito et al. 2010). The stability of MWFs along their expected lifetime can be related to interfacial properties (Ríos et al. 1998). Emulsion properties can be monitored easily and the emulsion upgraded with emulsifying agents or replaced when its characteristics are no longer suitable for a given operation.

As an example, the stability of two O/W emulsions used in an industrial copper rolling process was studied along time (Fernández et al. 2005). O/W emulsions were provided by a company manufacturing copper products that uses several processes in its continuous-casting plant. First, copper cathodes with a copper purity higher than 99.9% are loaded into a shaft furnace and melted by natural gas burners (*smelting*). The liquid copper is fed between a water-cooled hollow casting wheel and belt and is transformed into a continuous 80 mm×60 mm rod (*casting*). This rod passes through a rolling mill which progressively reduces its diameter to an 8 mm copper wire rod (*rolling*). The rod then undergoes a *pickling* treatment with isopropyl alcohol to prevent coil oxidation. Afterwards, the 8 mm wire rod undergoes a *smoothing* process to produce 2 mm wire, which is subsequently processed in a *wire drawing* machine to obtain copper wire of 0.25 mm diameter. The resulting wire is processed in an *annealing* furnace to improve product quality.

Emulsion samples were withdrawn from the industrial plant in separate closed circuits of the copper rolling process: the *smoothing emulsion* is used in the first part of the process, and the *finishing emulsion* is used in the final step of copper rolling. These emulsions have a very similar composition: 0.5–1 vol % of a commercial concentrate (a base oil with nonionic surfactants, mainly glycols, and other additives) in demineralized water. Isopropyl alcohol is added to the finishing emulsion in order to improve the further pickling process. The emulsion flowrate is about 200 m^3/h for each circuit, and the operation temperature is 40–45ºC for both emulsions, with a pH of 9–9.5. Each circuit includes a Hoffman band filter to remove metallic copper particles and other impurities present to improve the emulsion lifetime. Emulsion properties were measured over a time span of two months, and four parameters related to emulsion stability were determined: droplet size distribution, zeta potential, surface tension and contact angle. Furthermore, the possibility of regenerating spent *finishing emulsion* was studied. Seven nonionic surfactants, similar to that used in their original formulations, were tested by adding each to emulsion samples at a concentration slightly higher than the measured CMC.

Experimental results showed that the selected parameters (droplet size distribution, surface tension, zeta potential and contact angle) are appropriate to determine emulsion stability over time in a copper rolling process. The most relevant conclusion is that zeta potential (ζ) is the main indicator of emulsion stability: for ζ values more positive than −10 mV the emulsion is completely destabilized, and it is not suitable for the rolling process. The presence of small copper particles is also very important for emulsion stability, especially for the *finishing emulsion*. It was also found that periodic addition of nonionic surfactants improved wettability and emulsion lifetime. Furthermore, surfactant addition and emulsion replacement can be related to zeta potential monitoring during the copper rolling process. By measuring zeta potential of the samples withdrawn from the industrial plant, it was concluded that regeneration is possible only for zeta potentials around −20 mV. Similar behavior was observed in *finishing emulsion* regeneration experiments for all nonionic surfactants studied with respect to droplet size distribution and zeta potential: zeta potential could be lowered to values around −40 mV in all tests, close to the zeta potential of the fresh emulsion. Accordingly, zeta potential can be selected for monitoring emulsion performance in a copper metalworking industry. In addition, such monitoring would increase emulsion lifetime by guiding correct reagent additions (i.e., periodic additions of surfactant or antifoam agents) or even to predict the optimum time for emulsion replacement.

The feasibility of using ultrafiltration permeates to reformulate O/W emulsions was also evaluated using a commercial MWF (Matos et al. 2008). The MWF was reformulated using the permeate obtained at optimum UF operating conditions, and its properties (surface tension, contact angle, zeta potential, droplet size distribution, stability and foamability) were compared with those of the fresh emulsion.

The permeate obtained after UF treatment of the MWF with tubular zirconia membranes (20 or 100 nm pore size) was almost free of oil and might be discharged into the sewage system. However, it contained water-soluble components present in the original O/W emulsion, mainly surfactants, which were not retained by the membrane, and these might cause problems in wastewater treatment plants (i.e. foam formation). A potential option would be to reuse the permeate to reformulate the O/W emulsion with properties similar to the commercial mixture. Properties such as contact angle, surface tension, zeta potential, etc., were used to evaluate emulsion reformulation.

First, the optimum operating conditions for each membrane were determined, and then 3-L permeate samples were collected from UF concentration experiments performed at these optimum conditions. Five different emulsions were reformulated with the collected permeates, two of them taking into account their surfactant concentration, and their properties were compared. Comparison of emulsion properties indicate that the UF permeates can be used to reformulate the original O/W emulsion, but it is necessary to take into account the amount of surfactant that permeates through the membrane. Even though the presence of surfactants seems to improve emulsion wettability, since contact angle decreases, foam power and migration velocity increase. Foam formation and emulsion destabilization are not desired in metalworking processes. Moreover, emulsions reformulated with permeate from UF using a 20 nm membrane show properties closer to the original emulsion, especially zeta potential. Hence, it seems a better option to use the 20 nm UF membrane for emulsion recycling, in spite of the lower amount of surfactants reused and the slightly higher pumping costs.

6. Conclusions

Oily wastewaters are generated in many industrial processes, and fats, oils and greases (FOG's) 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 is usually classified as free, dispersed, emulsified and 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.

These oily waters are mainly in the form of O/W emulsions, so emulsion breaking and oil removal requires a basic understanding of physical properties and chemical composition. Several properties that play a key role in the stability of an O/W emulsion (mainly surface and interfacial tensions, droplet size distribution and zeta potential) should be measured in order to provide information on emulsion stability and thus guidance for the selection of the appropriate treatment for oil removal.

Treatment of oily wastewaters can be described similarly to the treatment of municipal wastewaters. A primary treatment is used to remove the free oils from the waste stream. A secondary treatment is used to break O/W emulsions and to remove the dispersed oil, whereas finely dispersed, emulsified and dissolved oil fractions must be removed by a tertiary treatment process.

Gravity separation is the most common method used to remove free oil ($D_p \geq 150$ μm) in oily wastewaters. It is based on the density difference between oil and water. The oil rises to the surface of a tank and is then skimmed off. API separators, plate coalescers and flotation devices (DAF and IAF) are mainly used in this operation. Chemical treatment may be used with oily emulsion wastewater for the removal of suspended or colloidal oil. The use of chemical dosing to oil/water systems by addition of coagulants or flocculants does not accomplish separation in itself, but it may lead to better performance of physical separation equipment by generating larger oil droplets. Membrane processes are used to remove finely dispersed, emulsified (MF and UF) and soluble oil fractions (NF and RO).

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

Nowadays, a combination of two or more separation processes (in integrated or hybrid processes) is required in order to reach the most severe discharge standards. Specifically hybrid membrane processes are the most frequently used for the treatment of oily wastewaters at industrial scale. Integrated processes may reduce total production cost, energy consumption, capital cost, and give better oil separation efficiency.

Regarding to O/W emulsions, and especially metalworking fluids (MWFs), efforts are being undertaken currently to develop formulations designed to enhance their functional properties as well as to improve emulsion life-cycle. The stability of MWFs during their expected lifetime can be related to interfacial properties, which can be easily monitored, and the emulsion can be upgraded with emulsifying agents or replaced when its properties are no longer suitable for a given operation.

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PHYSICO-CHEMICAL TREATMENT METHODS: FUNDAMENTALS AND DESIGN GUIDELINES

SALVADOR ORDÓÑEZ*, EVA DÍAZ
Department of Chemical Engineering and Environmental Technology, University of Oviedo, Oviedo (SPAIN)

Abstract. This chapter is focused on the main physicochemical methods used in the treatment of waste- and ground-waters. The bases, selection rules, and the main guidelines for the design of distillation-evaporation, adsorption-ion exchange, air stripping, chemical precipitation and chemical reduction/oxidation processes are briefly summarized in the present work. In order to systemize this study, these physico-chemical processes were classified according to their controlling mechanism: phase equilibrium (adsorption), chemical equilibrium (precipitation), kinetics (reduction and oxidation processes), or mass transfer (desorption, distillation). The selection of the most appropriate physicochemical treatment for a given water treatment problem – in terms of matrix properties, degree of depuration and economics – has been afforded in this work through several industrial examples. The main calculations needed for each treatment, (equilibrium, stoichiometry, pumping and mixing requirements) are also summarized. Although most of these operations are well-known within the field of the Chemical Engineering, their application to water treatment presents additional difficulties, such as the complexity of the matrix, the higher conversion levels usually needed, or the difficulty for parameter estimation. Therefore, the use of approximate rules (rules of thumb) is usually needed for preliminary design of physicochemical operations. Finally, a reference to updated available information on this issue in Europe (BREF documents) and United States (EPA resources), is provided in order to advise the reader into the selection of a physico-chemical treatment for a given water treatment problem.

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* E-mail: sordonez@uniovi.es

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1. Introduction

Physico-chemical treatments are among the most widely used methods in both water treatment and conditioning. Processes included in this large group cover from the sedimentation to the disinfection process, as well as metal precipitations or adsorptions. Many unit operations, such as coagulation, flocculation, and sedimentation, are used in both water and wastewater treatment whereas other unit operations are limited to one field – process or waste water. Most of these unit operations have many variants, a systematic study of them being desirable. This chapter provides an overall and systematic view of these unit operations, summarizing their fundamentals, and providing the main design guidelines.

The degree of depuration depends on the raw water quality and the desired quality of the treated water (depending on the application), whereas for wastewater, the treatment degree depends on the required effluent quality. The degree of treatment required in each case determines the number and types of operations employed, thus many variations in the process flowsheet can be found. In a conventional treatment plants physical, chemical and biological methods coexist. Most of the times, at least in the case of waste waters, biological treatments are preferred to physico-chemical plants due to their lower costs. However, it is very often to make preliminary physical treatments to remove the largest solid objects carried by the water stream. Likewise, the most common municipal wastewater treatment plants are divided in three parts: primary, secondary and ternary treatments. Primary treatments consist of removing a substantial amount of suspended solid from the wastewater. This group includes physico-chemical treatments, being the sedimentation the most usual. The collected solids must be further treated before the proper disposal. Secondary treatments consist of biological process where the remaining organic suspended solids and the organic solved solids are oxidized. However, and especially with industrial wastewater, secondary treatment can consist of physico-chemical treatments (coagulation-flocculation). And, ternary treatment consists of further treatment to increase the quality of the effluent, and this objective is reached usually by physico-chemical treatments. Several examples of these treatments are lime coagulation, flocculation, sedimentation, ammonia stripping, recarbonatation, filtration, adsorption, and disinfection. Therefore, physico-chemical treatments are essential in wastewater management, being even possible treatment schemes based only on these treatments.

Concerning the process water plants, the needed operations depend on the source of the water and the final use of the purified water (tap water,

water for industrial or agricultural uses, etc.). Plants using surface waters as raw material usually consist of sand filtration and lime-soda softening plants; whereas groundwaters are less demanding on the elimination of suspended solids, but need additional air-stripping treatments.

The physical-chemical methods, object of the present chapter, can be classified in three groups according to their mechanicistic fundamentals (using the current Chemical Engineering strategies):

(1) Momentum-transport unit operations, treatments that involve a relative movement of the solids in the liquid.
(2) Mass-transfer unit operations, in which the water is depurated by change of phase of the component to be removed. In these cases, the chemical nature of the pollutant does not change. Therefore, these methods are also called “Transference methods”.
(3) Chemical processes, where a chemical reaction allows the removal of the pollutant. In this case, the pollutant is transformed into less pollutant compounds (CO_2, water, etc.). By this reason, this kind of methods is also known as “Transformation methods”.

Momentum-transport unit operations include mainly physical operations in which components of mixture that are already in two different phases are separated. Sedimentation and decanting are easily accomplished with simple equipment. In many cases, flotation, filtration or centrifugation are used to improve the separation. The development of these processes depends on the physical properties of the water and the particles to be removed; these properties include aggregation state, or density. The mass-transfer unit operations include evaporations of components of a mixture and further condensation (distillation), retention of a component of the water on the surface of a solid (adsorption), separation of the volatile components of a water by partitioning the more volatile to a gas phase (air stripping), transference of a component of the water to another liquid phase (extraction), or selective passage of a solute through a thin membrane (membrane processes). These operations depend upon the physico-chemical properties of the materials under consideration, such as solubility in water or organic solvents, volatility, boiling point, melting point, or Henry constant. The applicability of chemical treatments to waters depends upon the chemical properties of the constituents. These properties include acid-base, oxidation-reduction, precipitation, reactivity, corrosivity or flammability. Several treatments are based on these chemical properties: neutralization, precipitation, coagulation-flocculation, emulsion or redox treatments.

The physico-chemical processes described in this chapter include technologies that can be employed both for waste water and process water treatment. Each section presents a description of a technology, and the procedure for the physical design to apply this methodology.

2. Momentum-Transport Unit Operations

Momentum-transport unit operations treatments include the processes for removal of suspended solids from water by sedimentation, flotation, and filtration. Operations for sludge treatment, such as solids thickening and dewatering by gravity, sedimentation, flotation, centrifugation, and filtration, are also included among these techniques. Selection of the specific process or processes for removal of suspended solids from water depends on the characteristics of the solids, their concentration, and required quality. Often, the particulate matter in waters is of colloidal size, of the order of a micrometer or even less. The treatment of particulate matter is complicated since particle sizes of two or more orders of magnitude can be found. The approximate relationship of particle size to the S/L separation devices used in water treatment is shown by Figure 2.1.

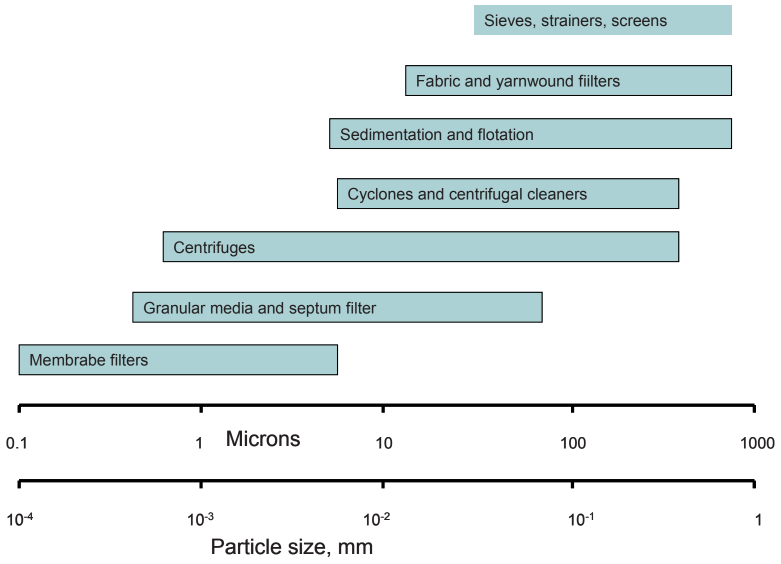

Figure 2.1. Orientative chart of solid/liquid separation devices in water treatments (adapted from Kemmer 1987).

2.1. SEDIMENTATION

Sedimentation is the simplest and least expensive treatment that can be applied to a water stream. Gravity sedimentation is the method by which most suspended matter is removed from waste-water during the course of treatment. There are three modes by which particles undergo the sedimentation process: discrete (type I), flocculent (type II), and zone (type III) settling, Figure 2.2.

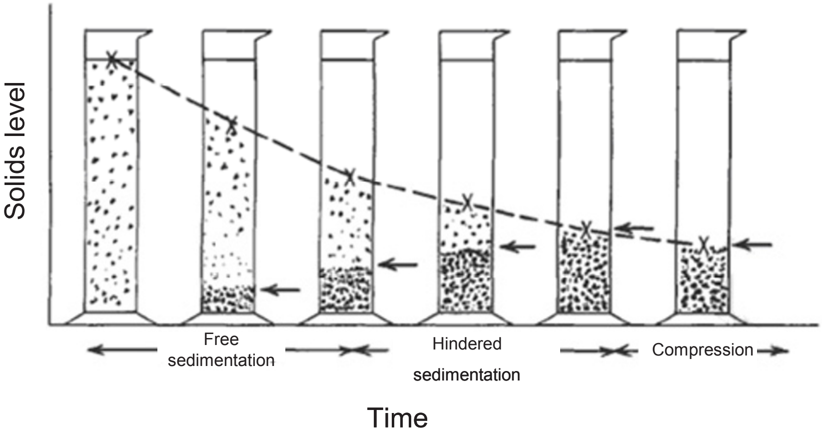

Figure 2.2. The steps in sedimentation of particles in water: particles at first fall free through the water. As they come closer together, their rate of sedimentation is restricted, and the sludge volume increases. In the final stages, compaction or compression becomes slow (adapted from Woodart 2006).

Discrete settling is that process by which individual particles proceed at a steady velocity, governed principally by the specific gravity of the particle and the viscosity of the wastewater, toward the bottom of the settling device. Stokes's law can be used to calculate the settling velocity, v_t, of this type of particle (assumed spherical shape):

$$v_t = \left[\frac{4\,g\,d_p(\rho_p - \rho_f)}{3\,c_D\,\rho_f} \right]^{1/2} \tag{2.1}$$

where: ρ_p, particle density; ρ_f, liquid density; d_p, particle diameter; c_D, drag coefficient, and g, gravitational constant. The drag coefficient, c_D, may be calculated from:

$$c_D = \frac{24}{\mathrm{Re}_p}(1 + 0.14\,\mathrm{Re}_p^{0.7}) \tag{2.2}$$

When Reynolds numbers are less than 1, Eq. (2.1) can be expressed as:

$$v_t = \left[\frac{g\,d_p^2(\rho_p - \rho_f)}{18\,\mu}\right] \tag{2.3}$$

where μ is the dynamic viscosity of the liquid (the dynamic viscosity of water at 20°C is 0.001 N/m^2·s). Because Reynolds number increases with increasing turbulence of the fluid, it is seen that the settling velocity, analogous to the rate of clarification, increases with decreasing turbulence. The settling of sand in water is an example of discrete settling (grit chambers).

Flocculant settling is undergone by particles, often organic, that agglomerate to larger, faster-settling particles as the settling process takes place over time. The settling of activated sludge in the upper several feet of a secondary clarifier (a clarifier that follows, hydraulically, an activated sludge aeration tank or a fixed growth treatment process) is an example of flocculent settling. Often, a given industrial wastewater will contain a mixture of solids; some settle as discrete particles and others undergo flocculent settling. When sufficient particles reach the lower portion of the clarifier, the accumulated mass ("sludge blanket") undergoes zone settling. Normally, either discrete or flocculent settling predominates in the upper portion of the clarifier and, therefore, becomes the basis for design. Those gravity clarification devices that combine the processes of primary sedimentation and sludge thickening are called "clarifier-thickeners." For these devices, the thickening characteristics of the settled sludge are also a basis for design.

Zone settling is typically undergone by a suspension of relatively concentrated solid particles (sludge) as it concentrates even more. The vertical distance that an individual particle moves decreases with increasing depth in the sludge mass itself. The overall objective of any physical wastewater treatment device, including clarifiers, is to remove as much solid material as possible, as inexpensively as possible, with a resulting sludge that has as low water content as possible. The final residuals of the treatment processes must undergo final disposal, and it is usually that the cost of final residuals disposal is proportional to the water content. Kynch, Talmage and Fitch, Behn and Liebman, and Edde and Eckenfelder have developed various methods for predicting the performance of thickeners based on results of laboratory bench-scale tests. These thickening tests have the common procedure of using standard two-liter graduated cylinders, which are filled with primary clarifier sludge, and then determine the rate of downward progress (under the influence of gravity) of the sludge-water interface. More information about these methods can be found in the literature (Woodart 2006).

2.1.1. *Equipment and Design*

Sedimentation equipments are usually constructed of reinforced concrete and may be circular, square, or rectangular. Circular tanks, frequently caller clarifiers, may be from 5 to 95 m of diameter, and from 2 to 5 m of depth. Square tanks have widths from 10 to 60 m, and depths from 2 to 6 m. Rectangular tanks usually have three types of sludge rake mechanism: (1) sprocket and chain-driven rakes, (2) rakes supported from a traveling bridge, and (3) tandem scrapers built for square basins. Rectangular tanks with sprocket and chain drivers have widths from 2 to 6 m, lengths up to 75 m, and depths greater than 2 m (Reynolds and Richards 1996).

Several factors affect the sedimentation tank design (ASCE Manual 1982):

- Scale-up: the range of scale-up factors reflects the influence of flow variation, wind, and temperature gradients. Thy hydraulic overflow rate generally varies from 0.5 to 0.65 of the settling rate of the particles or suspension to be removed. Design retention time is generally from 3 to 4 times the detention determined from laboratory tests.
- Tank-size: in large size tanks (over 30 m) the effect of wind on the surface of the tank can cause light particles to rise to the surface causing mixing.
- Flow variation: without any equalization, all sedimentation tanks are subject to the wide short-term variations in flow that occur, especially in small plants. Usually, it is safe to use the maximum 24 h flow for sizing the equipment.
- Inlet design: the inlet to a sedimentation tank must be an effective arrangement to achieve horizontal and vertical distribution of the incoming flow across the entire cross-sectional flow-through area, while minimizing short circuiting and turbulence factors. Inlet velocities should be kept as low as possible.
- Density currents: This effect is evidence by violent boiling to the surface of masses of liquid with entrained solids. This can occur when

the temperature suddenly increases 1–2°C with light flocculant type solids. The control over such effect is to ensure that any temperature change is slow, not over 1–2°C over a period of 1 h.

- Depth: It has no influence on liquid solids separation, however, the design should consider and appropriate depth for storage of settled solids. Excessive depths are not desirable as long as retention of settled solids will cause anaerobic conditions; moreover, density currents appear to occur more readily in deep, rectangular tanks.
- Outlet design: typical overflow rates are between 200 and 250 $m^3/m^2 \cdot d$.
- Solid loadings: in primary treatment without coagulants, 50–60% of suspended solids and 30–35% of colloidal solids are removed. In biological secondary treatment, most of the soluble BOD is removed and converted to biological solids.

2.2. FLOTATION

Solids can also be removed from water using an air-flotation clarifier. In this unit, light solids are floated to the surface by air bubbles and skimmed off while heavier solids are settled and removed in the normal way. In flotation clarification, the waste flow is usually pressurized and supersaturated with air. When the pressure is released, air comes out of solution, forming microbubbles, which float the solids to the surface. In some cases, instead of pressurizing the influent, a portion of the effluent is recycled through an air-saturation tank to meet the feed stream. Another possibility consists of saturating the water with air at atmospheric pressure, so a reduction of pressure (vacuum) will create the appropriate conditions to form the bubbles.

In treating wastes containing solids which tend to float, air flotation may be so effective that it may reduce clarification time to 15 or 20 min of retention time, compared to the several hours typical of gravity sedimentation. As with gravity clarifiers, it is often necessary to add coagulant or flocculant chemicals, such as ferric chloride and alum to flotation units to aid in floe formation, using lime if needed for pH adjustment. Polyelectrolytes have been gaining popularity for this application, and in almost all cases, they increase the efficiency of a flotation clarifier (Woodart 2006).

The efficiency of an air flotation system depends mainly on the ratio air volume/amount of solids; typical values go from 0.005 to 0.06, and can be calculated from (Metcalf & Eddy 1972):

$$\frac{A}{S}=\frac{1.3\,s_a\,(f\,P-1)}{S_A} \tag{2.4}$$

where *A/S*, ratio air/solids, mL/mg; s_a, air solubility, mL/L; *f*, fraction of air dissolved at pressure *P* (usually 0.8); *P*, pressure, atm; S_a, solids concentration, mg/L.

If only the recycled portion is air-saturated:

$$\frac{A}{S}=\frac{1.3\,s_a\,(f\,P-1)\,R}{S_A\,Q} \tag{2.5}$$

where *R*, recirculation flow rate, m^3/d; *Q*, inlet flow rate, m^3/d.

Since the net specific gravity of the air-solid or air-liquid particles is less than that of water, they rise to the surface. There, they consolidate to form a float, which can be removed by mechanical skimmers. The clear subnatant is withdrawn from the bottom of the unit. Usually the size of a flotation unit is selected on the basis of solids loading on the bottom, expressed as mass per hour per square foot of floor area. Depending on the nature of the solids, the bottom loadings range from 2.5 to 25 kg/h/m^2. The hydraulic loadings and inlet solids concentration must be balanced to arrive at an acceptable bottom loading.

2.3. FILTRATION

Filtration is a solid-liquid separation in which the liquid passes through a porous medium or other porous material to remove as much fine suspended solids as possible. It is used in water treatments to produce a high-quality drinking water; whereas in wastewater, to filter untreated secondary effluents, or chemically treated secondary effluents.

Filters are physical treatment devices, removal mechanisms including one or more of the following steps: physical entrapment, adsorption, gravity sedimentation, impaction, straining, interception, and flocculation. If the filtration takes place slowly in a sand filter, only the first few millimeters of depth from the surface of the sand are used. However, for deep bed granular filters a larger part of the filter medium is implied in the process. Likewise, there are two distinct operations that characterize any granular filter: the filtering phase and the cleaning phase. With respect to these two phases, operation may be continuous or semicontinuous. In continuous operation, the filtering of wastewater and the cleaning of the filter medium or media take place at the same time. In semicontinuous operation, these steps take place in sequence.

Filters used in the filtration operations can be also classified according to the types of media used:

- Single-medium filters: only one type of medium, usually sand.
- Dual-media filters: two types of media, usually crushed anthracite and sand.
- Multimedia filters: three types of media, usually crushed anthracite, sand, and garnet.

Filters can be of downflow type, in which a considerable portion of removal takes place on the surface of the filter medium as well as in the initial few inches, or in the upflow mode, in which the filter bed is expanded, or fluidized, and the initial part of filter medium is not as significant to overall removal. In fact, the primary removal mechanism involved in an upflow filter application is likely quite different from that involved in a filter operated in the downflow mode. For upflow filtration, there is no widely accepted mathematical model for its design. Experience has shown that filter performance is a function of the filtration rate; the concentration and characteristics of the particles to be removed; and the size, surface characteristics, density, and other characteristics of the filter media. An extensive pilot program is always required to develop reliable design parameters.

In the downflow mode, particles that are smaller than the sizes of the pores and passageways between filter medium granules are carried down into the depths of the filter until they contact, and are adsorbed onto, one of the granules of filter medium. Many of the larger particles are intercepted and removed by sieve action at the surface of the filter bed. Also, to some extent, these particles bridge across each other and form their own filter, which further filters out new particles brought to the filter surface.

In downflow filters, as well as up-flow, filtration rate is a critical parameter (Reynolds and Richards 1996). In the case of downflow filters, too low filtration rate will result in too much removal of solids in the upper layers of the filter. The head loss will become too high for further operation before the deeper portions of the filter are used. Too high filtration rates, on the other hand, will result in flushing too many solids through the filter, causing the filtrate to be unacceptable. Head loss is a major operational factor in the case of downflow granular filters, since it is hydraulic head, or pressure, that causes flow through the filter. Both parameters are related by Bernouilli's equation, between points 1 and 2:

$$\frac{V_1^2}{2g} + \frac{p_1}{\gamma} + Z_1 = \frac{V_2^2}{2g} + \frac{p_2}{\gamma} + Z_2 + H_L \tag{2.6}$$

where: V, velocity, m/s; p, relative pressure, m^2/kg; Z, elevation heads, m; γ, specific weight water, m^3/kg; g, gravity, m/s^2; H_L, head loss, m.

Granular media filtration is generally applicable for removal of suspended solids in the 5–50 mg/L range, where an effluent of less than 1 JTU (Jackson turbidity unit) is required. Sand filters have been used for many years as a final polishing step in municipal and industrial water plants where the clarifier effluent contains 5–20 mg/L of suspended solids. Typical single medium filters operate downflow at 0.8 L/min/m^2 of bed area in potable water service, and up to 1.2 L/min·m^2 in industrial filtration. The filter bed is 60–90 cm deep, supported on several courses of graded gravel. In a typical dual media bed, 60 m of anthracite is placed above 30 cm of sand. The coarse anthracite allows deeper bed penetration and provides longer filter runs at higher filter rates. The finer sand polishes the effluent. Under normal conditions, this dual media can produce acceptable effluent at flow rates up to 25 L/min per square foot of bed area (Woodart 2006).

3. Mass-Transfer Unit Operation

Mass-transfer operations treatments include the processes for the separation of a component of the water by selective transfer to another phase; these operations involve changes in composition of the solutions. The most common mass-transfer operations are those in which two immiscible phases are contacted, being differently distributed the components between the phases. This change of phase can be obtained by different methods depending on the receptor phase. In this way, phase change to a gas or vapor phase involves either a thermal treatment (distillation) or higher affinity for the gas phase (air stripping); to a solid phase, adsorption forces to retain the component on the surface (adsorption); or to another liquid phase, where the higher affinity of the compound to separate for an specific liquid phase allows the separation (extraction). Mass-transfer operation could even involve the selective passage of a solver or solute through a thin membrane (membrane technology). The last one was developed in Chapter 1.

3.1. DISTILLATION

Distillation consists of the selective evaporation of several components of liquid mixture, followed by a condensation of this fraction. Thus, separation of volatile materials can be optimized by controlling both the evaporation-stage temperature (and pressure) and the condenser temperature. Distillation separates miscible organic liquids for solvent reclamation and for waste volume reduction. The heavier fraction, recovered in the bottoms, is usually the residual fraction to separate from water (toxic metals from ink, paint pigments, etc.). Distillation is a thermal treatment technology that is also applicable to the treatment of wastes containing organics that are volatile enough to be removed by the application of heat.

The basis of the distillation is the principle of vapor-liquid equilibrium. When a liquid mixture of two or more components is heated, the vapor phase becomes more concentrated in the more volatile constituents (those having higher vapor pressures). The vapor phase above the liquid phase is then removed and cooled to yield a condensate that is also more concentrated in the more volatile components. The degree of separation of components depends on the relative differences in the vapor pressures of the constituents; the larger the difference in the vapor pressures, the more easily the separation can be accomplished.

Two major types of distillation processes are batch distillation and continuous fractional distillation (Treybal 1968, Noyes 1994). If the difference between the vapor pressures is extremely large, a single stage operation or flash vaporization may achieve a significant separation of the constituents. In such cases, batch distillation or thin film evaporation would be used. If the difference between the vapor pressures of volatile components is small, then multiple equilibrium stages are needed to achieve effective separation. In practice, the multiple equilibrium stages are obtained by stacking “trays” or placing “packing” into a column. Essentially, each tray represents one equilibrium stage. In a packed steam stripping column or fractionation column, the individual equilibrium stages are not discernible, but the number of equivalent trays can be calculated from mathematical relationships. The vapor phase from a tray rises to the tray above it, where it condenses; the liquid phase falls to the tray below it, where it is again heated and separated. The vapor-liquid equilibrium of the waste components can be expressed as relative volatility, which is the ratio of the vapor-to-liquid concentrations of a constituent divided by the ratio of the vapor-to-liquid concentrations of another constituent:

$$\alpha = \frac{y^*(1-x)}{x(1-y^*)} \tag{2.7}$$

where α, relative volatility; y^*, equilibrium mole fraction of the most volatile component to separate in the vapor; x, mole fraction of the most volatile compound in the liquid.

The relative volatility is a direct indicator of the ease of separation. If the numerical value is 1, then separation is impossible because the constituents have the same concentrations in the vapor and liquid phases. When the relative volatility is 1, the liquid mixture is called an azeotrope. Separation becomes increasingly easier as the value of the relative volatility becomes increasingly different from unity.

Although distillation is effective in recovering solvents and other organic compounds for recycle and reuse, distillation is not a widespread wastewater treatment technology because effluent levels that are acceptable for recycle and reuse are generally too high for wastewater discharge. In addition, this operation is very energy-consuming, especially for relatively diluted mixtures (as the case of wastewater).

3.2. AIR STRIPPING

Stripping is a process of separating volatile components from less volatile ones in a liquid mixture by the partitioning of the more volatile materials to a gas phase of air or stream. Air stripping is one of the most commonly used processes for treating ground water, since it allows to remove volatile organic compounds, or another undesirable compounds of waters such as H_2S or CO_2. There is an important distinction between oxygen and nitrogen, on the one hand, and carbon dioxide, on the other. The former do not ionize in water, so these molecules produce a gas pressure in solution; carbon dioxide forms carbonic acid, which ionizes in water, so only the unreacted part can exert a gas pressure. At a pH below about 4.5, all of the CO_2 dissolved in water is present as a gas; above about 8.5, all of it is ionized. Other common ionizing gases are H_2S, HCN, and NH_3 (Noyes 1994). In all these cases, the pH values are the main variable to be controlled in order to guarantee an adequate treatment.

The air stripping operation can be performed by using packed towers, tray towers, spray systems, diffused aeration, or mechanical aeration. The most usual one, the packing column, is depicted in Figure 2.3. Typical packing materials consist of plastic shapes that have a high surface/volume ratio and provide the necessary transfer surface to allow volatile components to move from the liquid stream to the air stream. The air stream leaves the column at the top; the water stream at the bottom. The mass balance equation can be written as:

$$Q_W\left[C_{in} - C_{out}\right] = Q_A\left[p_{out} - p_{in}\right] \tag{2.8}$$

where Q_W, water flow rate, m^3/s; C, concentration in water of the contaminant, $kmol/m^3$; Q_A, air flow rate, m^3/s; p, concentration in air of the contaminant, $kmol/m^3$.

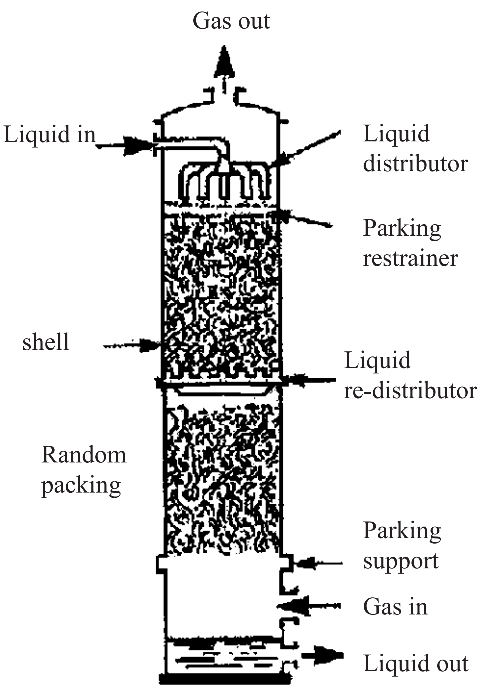

Figure 2.3. Packed tower for air stripping.

The concentration of the contaminant in the effluent air, p_{out}, can be determined by Henry's law. This law establishes that the amount of gas dissolved in water is directly proportional to the partial pressure of that gas in the vapor space above the water/gas interface.

$$p_{out} = H' C_{in} \tag{2.9}$$

where H' is the Henry's law constant. This theoretical relationship is true for ideal equilibrium and perfect stripping. The expression $R=H'(Q_A/Q_W)$ is called stripping factor. Values of this factor should be greater than one for efficient stripping.

Another important consideration of gas solubility is Dalton's law, which states that the total pressure of a mixture of gases is made up of the individual pressures of those gases, and these are in direct relationship to their molar or volume ratios in the vapor space. Temperature is an important factor in gas solubility; solubility decreases as temperature increases. This is because the increasing temperature results in an increasing vapor pressure of the water itself, so that escaping water molecules at the liquid-gas surface force away other gas molecules.

A final factor important to the solution of gases in water is the diffusion of the gas molecules through water. The rate of diffusion increases with increasing temperature as molecular activity increases and the viscosity of the water decreases. In the removal of gas from water, the mass transfer principles that apply to the process are analogous to the principles of heat transfer. Under steady conditions, the flux of the diffusing component is proportional to the difference between the bulk concentration and the concentration at the gas-liquid interface. This flux is constant though the gas and the liquid films:

$$N_A = k_G(p - p_i) = k_L(c_i - c) \tag{2.10}$$

where p is the partial pressure of the transferring component in the bulk of the gas stream; p_i the partial pressure at the interface; c_i, the concentration at the interface; c, the concentration in the bulk of the liquid, and k_G and k_L are the gas and liquid film mass transfer coefficients, respectively.

As interfacial concentrations are difficult to determine experimentally, overall coefficients, which account for the total diffusional resistance present in both phases, can be defined and used in mass transfer correlations and calculations, and Eq. (2.10) can be rewritten for such purposes as:

$$N_A = K_G(p - p^*) = K_L(c^* - c) \tag{2.11}$$

where p^* is the equilibrium partial pressure of solute over a solution having the same concentration c as the main liquid stream; and c^* is the concentration in a liquid solution which would be in equilibrium with the solute partial pressure existing in the main gas stream.

The overall mass transfer coefficients K_G (with pressure units) and K_L (with concentration units) can be determined experimentally and used directly in design equations. For dilute solutions, where Henry's law is valid:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{k_L} \tag{2.12}$$

and

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{Hk_G} \tag{2.13}$$

In separation equipment, such as packed or spray towers, the effective interfacial area for mass transfer cannot be accurately determined. For this reason, it is a common practice to report experimental rates of mass transfer in terms of transfer coefficients based on a unit volume of the packing, rather than on a unit of interfacial area. Such volumetric coefficients are designated as K_Ga, k_La, etc., where a represents the interfacial area per unit volume of packing (or drops in spray systems). Overall volumetric coefficients are thus related to the individual volumetric coefficients as follows:

$$\frac{1}{K_Ga} = \frac{1}{k_Ga} + \frac{H}{k_La} \tag{2.14}$$

and

$$\frac{1}{K_La} = \frac{1}{k_La} + \frac{1}{Hk_Ga} \tag{2.15}$$

It should be noted that usually in the chemical engineering literature, the stripping factor is defined as:

$$R = H'(G/L) \tag{2.16}$$

where, H', is the Henry's law constant (dimensionless); G, the molar flow rate of air kmol/h; and L, the molar flow rate of water, kmol/h.

For a packed tower, if a is the interfacial area per unit of packing volume, S is the tower cross-section, and Z is the height of the tower packing:

$$dA = aSdZ \tag{2.17}$$

And the mass balance, Eq. (2.8), is written as:

$$G_S Y + L_S X_1 = L_S X + G_S Y_1 \tag{2.18}$$

where X and Y are the solute molar ratios are; G_S is the molar flow rate of the pollutant free gas phase, and L_S is the molar flow rate of the liquid phase. The subscript 1 refers to a lower limit corresponding to the bottom of the tower, and no subscript refers to an upper limit corresponding to an arbitrary tower height.

The molar ratios X and Y can be correlated with the partial pressures and concentrations of Eq. (2.8) by:

$$Y = \frac{p}{P - p} \qquad \text{and} \qquad X = \frac{c}{c_T - c} \tag{2.19}$$

where P is the total pressure of the system, and c_T, the (moles pollutant + moles solvent)/volume liquid.

Combining Eqs. (2.14), (2.15) and (2.17):

$$\begin{aligned} d(G_S Y) &= N_A dA = k_G a(p - p_i)SdZ = k_L a(c_i - c)SdZ \\ &= K_G a(p - p^*)SdZ = K_L a(c^* - c)SdZ \end{aligned} \tag{2.20}$$

Integration of Eq. (2.20) gives the height of the tower in terms of either gas or liquid phase parameters:

$$Z = \frac{G_S/S}{K_G a} \int_{p_1}^{p_2} \frac{dp}{(P - p)(p - p^*)} \tag{2.21}$$

$$Z = \frac{L_S/S}{K_L a} \int_{c_1}^{c_2} \frac{dc}{(c_T - c)(c^* - c)} \tag{2.22}$$

When the limiting resistance to mass transfer resides in the liquid phase (stripping of very insoluble gases), it is more appropriate to use Eq. (2.22) than Eq. (2.21). The right sides of Eqs. (2.21) and (2.22) must usually be evaluated by numerical or graphical integration. The volumetric mass transfer coefficients $K_G a$ and $K_L a$ should be obtained from pilot plant experiments in the same kind of equipment.

For design purposes it is convenient to write Eqs. (2.21) and (2.22) in terms of the overall heights of transfer units (H_{OG}, H_{OL}, first terms on the right side) and the number of transfer units (N_{OG}, N_{OL}, the corresponding integrals on the right side of these equations) as:

$$Z = H_{OG}N_{OG} = H_{OL}N_{OL} \tag{2.23}$$

Several dimensionless correlations for use in estimating mass transfer coefficients and heights of overall mass transfer units are available in the published literature.

In practice, striping towers have diameters of 0.5–3 m and heights from 1 to 15 m. The air-to-water ratio rages from as low as 5 to several hundred and is controlled mainly by flooding and pressure considerations. As the air flow in a tower is increased, it will hinder the downflow of the water and cause flooding of the tower. Channeling occurs when water flows down the tower wall rather than through the packing. Distribution plates should be placed approximately every 5 diameters to avoid this. Furthermore, using smaller size packing will also reduce the trend to channeling. The pressure drop in a tower should be between 200 and 400 N/m^2 per meter of tower height to avoid flooding (Kemmer 1987).

3.3. EXTRACTION

Solvent extraction is the process in which a substance is transferred from solution in one solvent (water) to another solvent (usually an organic one) without any chemical change taking place. The basic principle of operation in extraction technologies is that constituents are removed from a waste by mixing the wastewater with an extraction fluid (solvent) that will preferentially dissolve the waste constituents of concern from the waste. In the simplest extraction systems, two components are mixed: (a) the waste stream to be extracted, and (b) extraction fluid. The extraction fluid and waste stream are mixed to allow mass transfer of the constituent (the solute) from the waste stream to the extraction fluid. Except for the waste constituents that are to be extracted, the waste must be immiscible in the extracted fluid, so that after mixing, the two immiscible phases can physically be separated by gravity.

The extraction fluid, which now contains the extracted contaminants, is called the extract; the extracted waste stream from which the contaminants have been removed is called the raffinate. The extract can be either the heavy (more dense) phase or the light (less dense) phase. In theory, the maximum degree of separation that can be achieved is provided by the selectivity value, which is the ratio of the equilibrium concentration of the contaminants in the waste. The solvent extraction process can be either batch or continuous. A typical extraction process is shown in Figure 2.4. The feed enters in the middle of the extraction column and the solvent enters at the top. Two streams exit the column: extract and raffinate. The extract is fed to a distillation column to separate the solute and the solvent. This solvent is recycled to the extraction column. Solvent and solute should differ in their boiling point, otherwise the solvent recovery process may be costly.

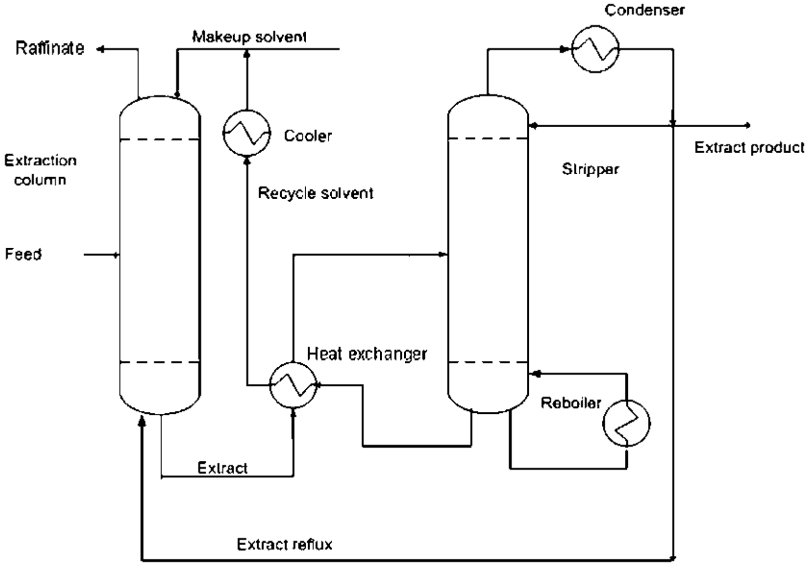

Figure 2.4. Typical continuous liquid-liquid extraction process (from Coca et al. 2007).

In liquid-liquid extraction, as in gas absorption and distillation, two liquid phases must be brought into good contact with the primary goal of promoting turbulence and high interfacial area between the phases. In absorption and distillation, the mixing and separation are easy and fast. In extraction, however, if the two phases have comparable densities, the energy available for mixing and separation – if gravity flow is used – is small, and special problems may arise when some components are easily emulsified. Extraction equipment can be classified into two broad categories: stagewise and differential contactors. The contacting/separation process is typically carried out in the following devices: mixer-settlers, column and centrifugal contactors, and membrane extractors.

Although solvent extraction has excellent potential for the treatment of hazardous wastes, it has not been widely used fro that purpose. The major application in waste treatment has been in the removal of phenol from byproduct water produced in coal coking, petroleum refining, and chemical synthesis that involve phenol (Manahan 1990).

3.4. ADSORPTION

Adsorption is the selective transfer of one or more solutes from a fluid phase (in our case a liquid) to the surface of solid particles. The usual selectivity of a sorbent between solute and carrier flow or between different solutes allows performing the separation. Adsorption involves (in the most general case) the accumulation of solute molecules at an interface, leading to an unsteady-state process.

Although adsorption has been used as a physical-chemical process for many centuries, it is only over the last four decades that the process has developed to a stage where it is now a major industrial separation technique. Nowadays, adsorption may be equally effective in removing or recovering trace components from a liquid phase: it may be used either to recover components or simply to remove noxious substances from gaseous and liquid industrial effluents.

In spite of this, its unsteady character is an important drawback, since it leads to discontinuous operation. In the general case, the adsorbent has to be removed at intervals from the process and regenerated, that is, restored to its original condition. For this reason, adsorption units were considered in early industrial applications to be more difficult to integrate into continuous processes. Another constraint for these processes is the difficulty to manufacture adsorbents with identical adsorptive properties from batch to batch. In several cases, such the removal of trace organics, adsorbent saturation can spend long time periods, leading to a "pseudo-continuous" process.

Adsorbents are available as irregular granules, extruded pellets, or formed spheres, depending on the technology used. Although there are many kinds of adsorbents (alumina, zeolites, silica-gel), most of the adsorbents used nowadays are activated-carbon-based. These adsorbents are manufactured by pyrolysis of carbonaceous materials (coal, wood, and fruit bones and shells) followed by physical or chemical treatments devoted to increase the surface area of the material.

The two key issues for the design of adsorption units are the study of the adsorption equilibrium and operation in continuous fixed-bed reactor.

3.4.1. *Adsorption Equilibrium*

Knowledge of adsorption equilibrium is necessary to estimate the maximum capacity of the adsorbent, as well as to characterize the molecular forces involved in these processes. Adsorption equilibrium is a dynamic concept achieved when the rate at which molecules adsorb onto a surface is equal to the rate at which they desorb. The physico-chemical phenomena taking place are complex and not easy to model. However, there are few single models that can predict adsorption equilibrium at a given temperature (the so-called adsorption isotherms).

In the case of liquid-phase adsorption, the two most frequently used models for equilibrium are the Langmuir isotherm and the Freundlich isotherm.

The Freundlich isotherm is an empirical equation, although it has thermodynamic justification, which can be expressed as a power-law relation between the equilibrium concentrations of adsorbate in the solid phase and the liquid phase:

$$C_s^{'} = \alpha \, (C^*)^{1/n} \tag{2.24}$$

where: C'_s is the mass of adsorbed solute per unit mass of adsorbent
C^* is the concentration of solute in solution at equilibrium
α and n are empirical constants, normally $n > 1$

A particular case of this equation is the Henry equation or linear isotherm. In this case $n = 1$ (note that in this case the equilibrium law is similar to Henry's law for gas-liquid systems). Unfortunately, linear isotherms are not common in adsorption processes and are accurate only at very low surface coverage.

The other model, the Langmuir isotherm, arises from the basic theory of adsorption. So, as adsorption proceeds, the number of adsorbed molecules increases to a point at which further adsorption is hindered by the lack of space on the adsorbent surface. So, the rate of adsorption then becomes proportional to the empty surface available, as well as to the fluid concentration. At the same time that molecules are adsorbing, other molecules will be desorbing if they have sufficient activation energy. Equilibrium is reached when the rates of both processes are equal.

From this mechanism it is possible to obtain the governing equation, taking into account the following assumptions:

1. There are no interactions between adjacent molecules on the surface.
2. The energy of adsorption is the same on all the surface.
3. Molecules adsorb at fixed sites and do not migrate over the surface.

The resulting equation will be as follows:

$$\frac{C_s^{'}}{C_{sm}} = \frac{k\,C^*}{1 + k\,C^*} \tag{2.25}$$

where C_{sm} is the maximum solute concentration in the solid phase (for saturation of the adsorbent).

The Langmuir isotherm is useful in the characterization of adsorption of mixtures, as well as in the interpretation of catalytic reactions, but is not so used for design purposes.

Adsorption equilibrium is affected by the temperature. So, a Van't Hoff dependence could be established. It must be understood that adsorption is an exothermic process, and hence increasing the temperature will hinder this process.

For rough designs, the amount of adsorbent is calculated considering the adsorption capacity at the equilibrium, adding a small percentage (10%) as safety margin. However, mass transfer effect must be considered in the rigorous design of adsorption units.

3.4.2. *Fixed Bed Adsorption*

Because of the inconvenience of continuously transporting solids, as required in steady-state operations, it is frequently more economical to pass the liquid to be treated through a stationary bed of solid adsorbent.

The most critical aspect of the scale-up of the adsorption involves characterization of the effluent concentration profile as a function of throughput (volume or time). This profile, commonly referred to as the breakthrough curve, represents the specific combination of equilibrium and rate factors that control process performance in a particular application. The breakthrough curve can be obtained by passing through an adsorption column a feed containing the solute and monitoring the concentration of the outlet as a function of either volume of effluent or time.

The modeling of the shape of the breakthrough curve is very complex. This profile depends both on adsorption equilibrium and mass transfer. Heat transfer is not considered so important, since liquid-phase adsorption is normally carried out with dilute solutions, and energy changes associated to this process are lower than the corresponding to chemical transformations. Liquid velocities must be carefully selected in order to avoid excessive pressure drops, adsorbent entrainment (both at too high liquid velocity) or laminar flow (at too low surface velocity). Typical surface velocities for these applications are between 0.05 and 0.5 m/min. From the actual flow rate and the recommended surface velocity, the cross section area of the adsorbent bed can be calculated. The height of the bed must be calculated from mass-transfer considerations.

Figure 2.5 depicts the way in which adsorbate is distributed along the bed during an adsorption cycle. During the adsorption cycle, the zone of the bed most closes to the inlet will be saturated, whereas the zone more close to the outlet will be free of adsorbate (since it is in contact with clean fluid), between both zones, there is a transition zone, where a profile of solute both on liquid and solid phase is observed. As the adsorption proceeds, the free zone will shrink, and when this zone completely disappear (t_3, called breaking point, t_b), the liquid leaving the adsorbent bed will have significant concentrations of the pollutant. If the operation proceeds further, the transition region also disappears, and the concentration of pollutant at the outlet will be the same that the corresponding to the inlet.

The shape of the transition zone is given by mass-transfer effects, and determines the adsorption performance. Therefore, the adsorption cycle must be stopped just before the breakpoint, since after this point, the outlet concentration of solute increase sharply.

A general mass balance to the solute in a differential element of the column (*dz*) gives the following expression:

$$u\,A\,\varepsilon\,C-\left[u\,A\,\varepsilon\,C+\frac{\partial(u\,A\,\varepsilon\,C)}{\partial z}dz\right]=\frac{\partial(u\,A\,\varepsilon\,C)}{\partial t}+\frac{\partial(u\,A\,(1-\varepsilon)\,C_s dz)}{\partial t} \qquad (2.26)$$

$$\text{INPUT} - \text{OUTLET} = \text{ACCUMULATION} + \text{LOSS BY ADSORPTION}$$

where u is the liquid velocity, A the cross section, ε the bed porosity, C the liquid phase concentration of solute, and C_s the corresponding solid phase concentration.

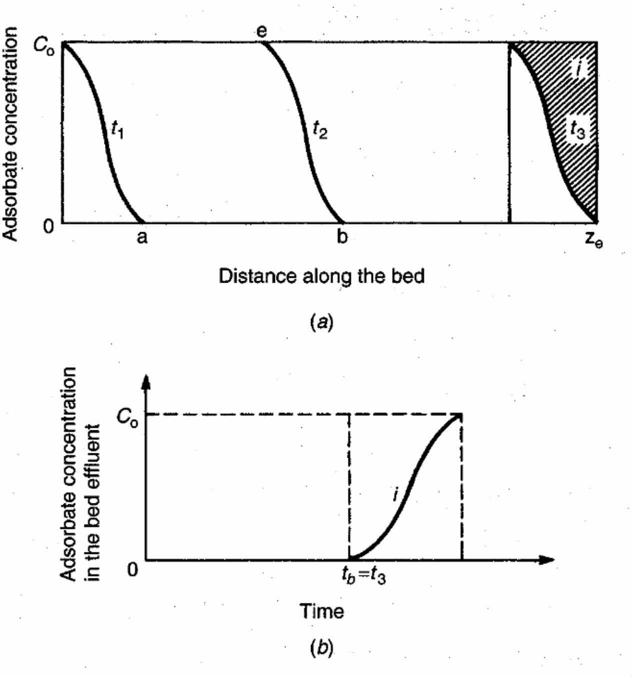

Figure 2.5. The distribution of adsorbate concentration in the fluid phase through a bed: (a) development and progression of an adsorption wave along the bed (b) Breakthrough curve (adapted from Reynolds and Richards 1996).

The complexity of this equation is increased if it is considered the possibility of axial dispersion. The solution of this equation depends on the nature of the equilibrium and the mass transfer conditions. One of the most common solutions, valid for equilibrium limited operation, was the proposed by Levenspiel and Bischoff (1963). The equation expresses the concentration of solute in the liquid at a given position in the column (z) and at given time (t) as:

$$\frac{C}{C_0}=\frac{1}{2}\left\{1+erf\left[\left(\frac{u\,z}{4\,D_L}\right)^{1/2}\frac{(t-t_{\min})}{(t\times t_{\min})^{1/2}}\right]\right\} \tag{2.27}$$

where C_0 is the solute concentration in the feed, u is the fluid velocity, D_L is the axial dispersion coefficient (note that the adsorption is limited by equilibrium when working with low flow rates, and in this cases axial dispersion effects are important), and t_{min} is a characteristic time give by the following expression:

$$t_{\min} = \left(1 + \frac{(1-\varepsilon)}{\varepsilon} \frac{C_{s\infty}}{C_0}\right) \frac{z}{u} \tag{2.28}$$

where $C_{s\infty}$ is the concentration phase in equilibrium with C_0.

The applicability of this technique depends on the regenerability of the adsorbent. Depending on the solute and the adsorbent, regeneration could be carried out by increasing temperatures (steam regeneration is the most common way to do this) by variation of pressures (in the case of volatile solutes, normally using vacuum), or by chemical treatments (e.g., variation of pH).

The design of adsorption units requires column test that simulate the actual operation of full scale units. In the laboratory, small diameter (e.g., 5 cm diameter) columns are filled with the adsorbent to test and the water to treat run through the columns. From the data obtained in this way, the parameters for the larger column are obtained.

4. Chemical Processes

Chemical methods of water treatment take advantage of two types of properties: (1) the chemical characteristics of the pollutants, regarding their trend to react with, or interact with, treatment chemicals, and (2) the chemical characteristics of the products of reaction between pollutants and treatment chemicals, regarding their solubilities, volatilities, or other property that relates to the inability of the product to remain in water solution or suspension. In general, several chemical processes can be used to remove substances from wastewater: reaction to produce an insoluble solid (precipitation); reduction of surface charge to produce coagulation of a colloidal suspension (coagulation-flocculation); or, oxidation or reduction to produce a substance that can be removed more easily by one of the previous methods (redox treatments).

4.1. NEUTRALIZATION

The equalization of flow to give a relatively constant flowrate is a common practice for both process and waste water treatment strategies. Equalization can be of two types: flow equalization and constituent equalization (neutralization). Flow equalization refers to mixing different streams in order to get steady-state flow rates, since most of the treatments cannot deal with sharp variation in flowrates. Constituent equalization refers to the concentration of the target pollutants in the waste stream. Some amount of constituent equalization always takes place during flow equalization. In fact, it is common practice to design for flow equalization and then operate to attain the degree of constituent equalization needed to achieve treatment objectives.

Frequently, industrial wastewaters may be acidic or basic and may require neutralization prior to subsequent treatments or release. Acidic wastewaters may be neutralized by passage through limestone beds, by the addition of slaked lime, $Ca(OH)_2$; caustic soda, NaOH; or soda ash, Na_2CO_3. Limestone beds may be of the up-flow or down-flow type; however, the up-flow type is the most common, since the products of the reaction, such as CO_2, are removed more efficiently. Limestone beds should not be used if the sulfuric acid content is greater than 0.6%, because the $CaSO_4$ produced will be deposited on the crushed limestone and, as a result, neutralization will cease. Alkaline wastewaters may be neutralized with a strong mineral acid, such as H_2SO_4 or HCl, or with CO_{2-} frequently from flue gases – (Reynolds and Richards 1996).

Neutralization usually takes place in two or three agitated vessels in series. Each vessel has a pH sensor that controls the slaked lime feed rate.

4.2. PRECIPITATION

Chemical precipitation is a physicochemical process whereby a substance in solution is transformed into a solid phase and driven out of solution. Precipitation occurs altering the chemical equilibrium affecting the solubility of the hazardous component by either adjusting the pH of the solution, or by adding a substance that will react with the dissolved substance to form a less soluble product (as sulphides for Cd removal of Ca for fluorides removal). In this way, it should be noted that the solubility is very dependent on pH, such that a simple pH adjustment is enough for precipitating and therefore more readily removed. Figure 2.6 presents relationships between pH value and solubility for six common heavy metals and the importance of correct pH. Notice that Figure 2.6 shows that chromium and zinc exhibit optimum pH values of 7.5 and 10, respectively, while iron, copper, nickel, and cadmium show continuous decreasing solubility with increasing pH (Noyes 1994, Woodart 2006).

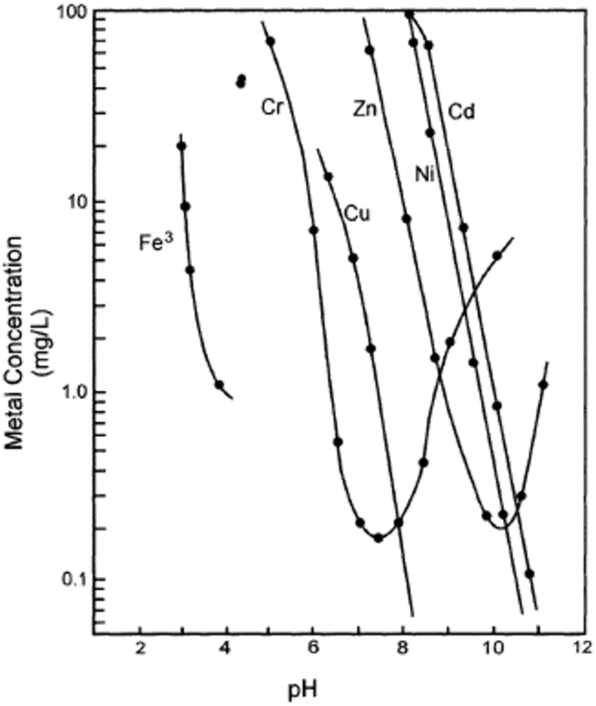

Figure 2.6. Precipitation of heavy metals as hydroxides (from Lanouette 1977).

Precipitation is applied mainly for waste streams containing hazardous solids which can be – after precipitation – sedimented and removed from the solution. There are many factors which affect the efficiency of precipitation (pH, nature and concentration of hazardous substances in water, precipitant dosage, temperature, water turbulence, etc.). In practice, the optimum precipitant and dosage for a particular application are determined by a "trial and error" approach using jar tests. This operation can be followed by coagulation and flocculation – as it will be discussed later – in order to enhance sedimentation.

This technology is used mainly to treat aqueous wastes containing metals, as well as other inorganic substances such as fluorides. These precipitates are settled, clarified, and/or filtered out of solution, leaving a lower concentration of metals and inorganics in the wastewater. The principal precipitation agents used to convert soluble metal and inorganic compounds to less soluble forms include lime [$Ca(OH)_2$], caustic (NaOH), sodium sulfide (Na_2S), and, to a lesser extent, soda ash (Na_2CO_3), phosphate (PO_4^{3-}), and ferrous sulfide (FeS) (Rodríguez and Irabien 1999).

- **Precipitation of Heavy Metals**

  - *Hydroxide precipitation*. It is the most common method to remove heavy metals. Precipitation of many heavy metals is accomplished by adjusting the pH of the wastewater to alkaline, which causes the soluble metal ions to form insoluble metal hydroxides. This pH adjustment is usually achieved by the addition of caustic (sodium hydroxide), limestone (calcium carbonate) or lime (calcium hydroxide). Recently, the usage of magnesium oxide (MgO) and magnesium hydroxide has increased [$Mg(OH)_2$] because they generate lower sludge volumes and are more effective in treating low metal-concentration (<50 ppm) effluents. For metal hydroxide species, the solubilities are known to increase with both rising and falling pH values outside the 7–10 pH range.
  - *Sulfide precipitation*. This process is used as an alternative to hydroxide precipitation. It is used to remove metal ions such as cadmium, silver or mercury, since sulfides are more insoluble than hydroxides. Two different processes are used for sulfide precipitation: (1) the soluble sulfide process, and (2) the insoluble sulfide process. The soluble sulfide process uses sodium sulfide as the treatment reagent, whereas the insoluble sulfide process uses ferrous sulfide as the reagent. The insoluble sulfide process generates a larger volume of sludge than does hydroxide precipitation because of the liberation of ferrous ions during treatment and the subsequent conversion of these ions to ferrous hydroxide. For effective metals removal, the pH of the wastewater must be maintained within the neutral to slightly alkaline range. Contact with acidic wastewaters will result in poorer removal and can cause the emission of hydrogen sulfide (H_2S) gas.
  - *Carbonate precipitation*. Carbonate precipitation with soda ash (sodium carbonate) or calcium carbonate has proven to be an effective process for removal of cadmium, lead, nickel, and zinc. Precipitation as insoluble carbonates tends to occur at more neutral pH conditions than with hydroxide precipitation. Carbonate solubilities tend to be less than those of the corresponding hydroxide. The carbonate-based reaction mechanism, however, proceeds at a slower pace than the hydroxide-based system. The solubility of soda ash also limits its use because a chemical feed of only 20% by weight can be maintained at room temperature without recrystallization.

- **Precipitation of fluorides**. It is a common method applied to waters with a high content of fluorides (>200 mg/L). Fluorides precipitate as calcium salt, using lime as calcium source. If calcium chloride is used with the lime, the precipitation will be enhanced. The optimum pH for the precipitation of calcium fluorides is 8–9 or higher than 12.
- **Precipitation of phosphates**. Two types of precipitation can be considered for phosphates compounds. For acid waters, precipitation with lime and, depending on the initial acidity two possible reaction could take place:

$$2H_3PO_4 + Ca(OH)_2 \rightarrow Ca(H_2PO_4)_2 \downarrow + 2H_2O \ at\ pH\ 6-7$$
$$2Ca(HPO_4)_2 + Ca(OH)_2 \rightarrow Ca_3(PO_4)_2 \downarrow + 2H_2O \ at\ pH\ 9-12$$

For no-acid waters, precipitation with Fe or Al salts is used, forming metallic phosphates. $AlPO_4$ and $FePO_4$ are very insoluble salts that precipitate as colloids.

The equipment and instrumentation required for chemical precipitation vary depending on whether the system is batch or continuous. Both systems are discussed below. For a batch system, chemical precipitation requires a feed system for the treatment chemicals and a reaction tank where the waste can be treated and allowed to settle. When lime is used, it is usually added to the reaction tank in a slurry form. The supernatant liquid is generally analyzed before discharge to ensure that settling of precipitates is adequate. For a continuous system, additional tanks are necessary, as well as the instrumentation to ensure that the system is operating properly. In this system, wastewater is fed into an equalization tank, where it is mixed to provide more uniformity, thus minimizing the variability in the type and concentration of constituents sent to the reaction tank.

4.3. COAGULATION-FLOCCULATION

The processes of coagulation and flocculation are employed to separate suspended solids from water whenever their natural sedimentation rates are too slow to provide effective clarification. Chemical coagulation and flocculation are terms often used interchangeably to describe the physicochemical process of suspended particle aggregation resulting from chemical additions to wastewater. Technically, coagulation involves the reduction of electrostatic surface charges and the formation of complex hydrous oxides. Coagulation is essentially instantaneous in that the only time required is that necessary for dispersing the chemicals in solution. Flocculation is the time-dependent physical process of the aggregation of wastewater solids into particles large enough to be separated by sedimentation.

The process can be grouped into two sequential mechanisms:

1. Chemically induced destabilization of the repulsive surface-related forces, thus allowing particles to stick together when contact between particles is made.
2. Chemical bridging and physical enmeshment between the non-repelling particles, thus allowing for the formation of large particles.

The purpose of coagulation is to overcome electrostatic repulsive surface forces (Figure 2.7) and cause small particles to agglomerate into larger particles, so that gravitational and inertial forces will predominate and affect the settling of the particles. The model colloidal particle used for this figure has a negatively charged surface. This negative charge could have arisen from one or more of several electrochemical activities undergone by the particle when placed in the suspending medium, or simply from the adsorption of OH^- or other anions because of the greater affinity of the suspending medium for cations. The negatively charged particle attracts a layer of positive ions, which may originate either from dissociated electrolytes present in the suspending medium or from dissociated groups on the particle itself. These ions, oppositely charged to the inherent charge of the colloidal particle, are called "counterions." This layer is relatively rigid and does not entirely neutralize the charge on the colloid; the excess charge gives rise to a diffuse layer of co– and counterions, intermingled, but having a higher density of counterions close to the colloid and a higher density of co-ions at the outer reaches of the layer. When the suspended colloid shown in Figure 2.7 is placed in an electric field, it will migrate toward the positive pole. A plane of shear is developed at a certain distance from the surface of the colloid, and this plane of shear defines the boundary between the rigid and diffuse layers. Below the colloid particle in Figure 2.7 is a graphical representation of the electrical potential at increasing distance from the surface of the colloid. The potential decreases linearly between the surface of the particle and the inner periphery of the layer of counterions. After that, the potential drops at a decreasing rate – this potential is called "zeta potential".

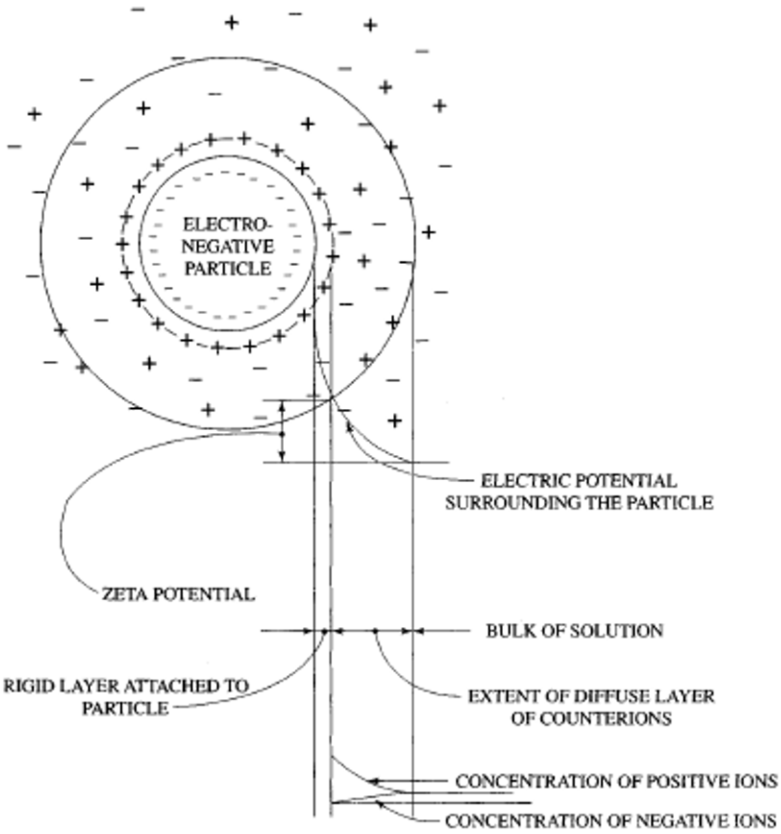

Figure 2.7. Layers surrounding a negatively charged colloid (adapted from Woodart 2006).

There are three different types of coagulants: inorganic electrolytes, natural organic polymers, and synthetic polyelectrolytes. Inorganic electrolytes are salts or multivalent ions such as alum (aluminum sulfate), lime, ferric chloride, and ferrous sulfate. The inorganic coagulants act by neutralizing the charged double layer of colloidal particles and by precipitation reactions. Natural organic polymers derived from starch, vegetable materials, or monogalactose act to agglomerate colloidal particles through hydrogen bonding and electrostatic forces. These are often used as coagulant aids to enhance the efficiency of inorganic coagulants. Synthetic polyelectrolytes are polymers that incorporate ionic or other functional groups along the carbon chain in the molecule. The functional groups can be either anionic (attract positively charged species), cationic (attract negatively charged species), or neutral. Polyelectrolytes function by electrostatic bonding and the formation of physical bridges between particles, thereby causing them to agglomerate.

The particles formed by the agglomeration of several colloids may not be large enough to sedimentate or dewater at the desired rate. A flocculant gathers together different particles in a net, bridging from one surface to another and binding the individual particles into large agglomerates. Alum, iron salts, and high molecular weight polymers are common flocculants. Flocculation is promoted by slow mixing, which brings the agglomerates gently together; too high a mixing velocity tears them apart these floccules. Flocculation not only increases the size of particles, but it also affects their physical nature. Sludges and slurries, when flocculated, dewater at faster rates on sand beds and in mechanical dewatering equipment because their less gelatinous structure.

Processes, coagulation and flocculation, are very different, thus each system, containing the chemically treated solids, has its own physical constraints. To adjust the chemical reaction (alkalinity and pH) for improved coagulation, it is sometimes necessary to first add soda ash, hydrated lime, quicklime, or sulfuric acid. For the control of coagulation, jar tests are made in the laboratory to determine the approximate dosage of the chemicals (not laboratory grade) used, at the actual water temperature, that appear to produce the best results. The best pH and coagulant are also determined. Then, with this as a guide, the chemical dosing equipment, dry feed or solution feed, is adjusted to add the desired quantity of chemical proportional to the flow of water treated to give the best results. The dosages may be further adjusted or refined based on actual operating conditions.

The type of devices usually used to furnish the agitation required for rapid mixing and flocculation can be classified as: mechanical agitators, pneumatic agitators, and baffle basins. The first step is rapid and the second is slow mix. Rapid mix is a violent agitation for a few seconds, not more than 30 s, and is usually accomplished by a mechanical agitator. Slow mix (flocculation) is accomplished by means of baffles or a mechanical paddle mixer to promote formation of a floc and provide a detention of at least 30 minutes. The flocculated water then flows to the settling basin designed to provide a retention time of 4–6 h. The velocity through the basin should not exceed 0.15 m/min. Cold water has a higher viscosity than warm water, hence the rate of particle or floc settling is much less in cold water (Salvato et al. 2003).

The degree of mixing, for both coagulation and flocculation, is based on the power imparted to the water, which is measured by the velocity gradient. The equation for the velocity gradient for mechanical or pneumatic agitation is:

$$G = \sqrt{\frac{P}{\mu V}} \tag{2.29}$$

where G is the velocity gradient, s^{-1}; P, the power imparted to the water per unit volume, Nm/sm^3; V, basin volume, m^3; and μ, the absolute viscosity of the water, Ns/m^2.

The G factor usually recommended for most coagulation units is about 900 s^{-1} for a 30 s mixing time, varying inversely with time. The recommended G factor for flocculation is lower, varying from about 50 s^{-1} for a cold, carrying a very fragile floe, to about 200 s^{-1} for a solids contact lime softener on warm river water (Kemmer 1987).

4.4. REDOX TREATMENTS

Oxidation and reduction can be used to detoxify waters by adding and reducing or oxidizing agent to chemically transform waste components. This is a well established technology that is capable of destroying a wide range or organic molecules, such as phenols, mercaptans, and inorganics such as cyanide, sulfurs and chromates.

Oxidation and reduction reaction occur in pairs to comprise an overall redox reaction. The power of oxidizing or reducing agent is measured by is electrode potential. An indication of how a reaction will proved can be determined fro the free energy consideration. The free energy of a reaction, ΔG^o, is related to the standard electrode potential, E^o, and the equilibrium constant, K, by:

$$\Delta G^o = -nFE^o = -RT \ln K \tag{2.30}$$

where ΔG^o, is the free energy of a reaction, kcal/gmol; n, the number of electrons exchanged during the reaction per gmol; F, the Faraday constant, 23062 kcal/volt-equiv.; E^o, the standard electrode potential (volts), R, the gas constant, $1.98 \cdot 10^{-3}$ kcal/gmol·K; and, T, temperature, K.

E^o may be determined from tabulated half reactions (see for example, LaGrega et al. 1994). The Nernst equation allows determining E at conditions other than standard:

$$E = E^{o} - (RT / \ln F) \ln Q \tag{2.31}$$

$$Q = \frac{\Pi(products)^{x}}{\Pi(reac \tan ts)_{y}} \tag{2.32}$$

where x,y represent the coefficients of the products and reactants in the original equation and Q is termed the reaction quotient. At equilibrium, $Q = K$.

The most common applications of redox processes are the cyanide and organic matter oxidation, and the reductive treatments for the removal of chromium.

4.4.1. *Cyanide Treatment*

Cyanide can be oxidized to the cyanate form under alkaline conditions both by chlorine and permanganate, according to the following reactions:

$$CN^{-} + Cl_2^{0} + H_2O \rightarrow 2HCl + CNO^{-}$$

In this reaction 2.75 mg/L chlorine is required for each milligram per liter of CN^{-}.

$$3CN^{-} + 2MnO_4^{-} + H_2O \rightarrow 2MnO_2 + 3CNO^{-} + 2OH^{-}$$

In this reaction 4.1 mg/L $KMnO_4$ is required for each milligram per liter of CN^{-}. Both of these reactions are carried out at a pH greater than 10. In the case of chlorine, it is important to maintain this pH to avoid formation of toxic cyanogens chloride. Although the cyanate is much less toxic than cyanide, complete destruction is often necessary, requiring further oxidation of the cyanate with chlorine or hypochlorite:

$$3CNO^{-} + 3OCl^{-} + H_2O \rightarrow N_2 + 3Cl^{-} + 2HCO_3^{-}$$

Combined with the above reaction, complete destruction of CN^{-} to N_2 requires 6.9 mg/L Cl_2 per milligram per liter of CN^{-}. The optimum pH for the second stage of this reaction is approximately 8.5. As in other oxidation reactions, time is an important factor to be studied; the cyanide reactions generally require over 10 min and an excess of oxidizing agent in order to provide complete destruction.

4.4.2. *Removal of Organic Matter*

Oxygen and air are seldom used directly for oxidation of organic material, but they are of course used in biologically mediated oxidation systems, such as in the activated sludge process. At high temperatures (about 150°C and above) and high pressures, air or oxygen injected into a reaction vessel will oxidize appreciable organic matter (the so-called Zimmerman process). Likewise, other oxidizing agents are also used.

Ozone is a blue gas at normal temperature and pressure that is used as a disinfectant in water. The primary advantage of ozone as an oxidizing agent is that it has a very high free energy, which indicates that the oxidation reaction may proceed to completion. However, kinetics indicates that the reaction rates for ozone oxidation are not always high. A disadvantage of ozone is its rapid dissociation to oxygen in the atmosphere. This dissociation can compete with any chemical oxidation reactions during waste treatment, and therefore, ozone must be generated and immediately applied at the treatment location. The transformation of compounds in aqueous solutions by ozone via its decomposition in water is due to a chain reaction involving the OH (hydroxyl) radical.

Chlorine and chlorine compounds such as chlorine dioxide are frequently utilized as chemical oxidizing agents in waste treatment applications. For aqueous waste treatment applications, chlorine is evaporated to a gas and mixed with water to provide a hypochlorous acid (HOCl) solution:

$$Cl_2(aq) + H_2O \rightarrow HOCl + H^+ + Cl^-$$

Hypochlorous acid ionizes as:

$$HOCl \rightarrow H^+ + OCl^-$$

This is a very pH dependent reaction, with the dissociation constant of hypochlorous acid being approximately 7.6 at ambient temperatures. The oxidizing power of chlorine tends to increase with pH. At pH values higher than 7.5, OCl^- is the predominant species.

4.4.3. *Reduction of Hexavalent Chromium*

Hexavalent chromium is reduced to trivalent chromium to further chromium hydroxide precipitation. The reduction is carried out in acid medium, by sulfur dioxide, sodium bisulphite or iron sulphate:

$$2CrO_3 + 3SO_2 + 3H_2O \rightarrow Cr_2(SO_4)_3 + 3H_2O$$
$$2CrO_3 + 3NaHSO_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3NaHSO_4 + 3H_2O$$
$$2CrO_3 + 6FeSO_4 + 6H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 6H_2O$$

The two first reactions occur simultaneously at pH lower than 2.5, decreasing its kinetics with the pH; critical pH value is 3.5. Reduction by the third reaction should proceed at pH lower than 6. This last reaction is less commonly used since a huge volume of sludge is obtained in this process.

Chemical oxidation/reduction is typically conducted in complete mixed tanks or plug flow reactors. The contaminated water is introduced at one side of the tank and the treated water exits at the other side. The reactive is either injected into the contaminated water just before in enters the tank or is dosed directly into the tank. Complete mixing of the water with the oxidizing agent must be provided, either by mechanical agitation, pressure drop, or bubbling into the tank. Complete mixing, which prevents short-circuiting in the tank, is necessary to ensure contact of the contaminant with the oxidizing agent for a minimum period of time, and, thus, reduce the chemical dosage required to obtain a specific effluent concentration.

In assessing the effectiveness of the design and operation of a chemical oxidation and reduction system, the following parameters are of great interest (Noyes 1994):

- *Residence time*. For a batch system, the residence time is controlled by adjusting the treatment time in the reaction tank. For a continuous system, the waste feed rate is controlled to make sure that the system is operated at the appropriate design residence time
- *Amount and type of oxidizing/reducing agent*. The amount of oxidizing/ reducing agent required to treat a given amount of constituent(s) will vary with the agent chosen. Theoretically, the amount of agent to be added can be computed from oxidation/reduction reaction stoichiometry; in practice, an excess of oxidant should be used.
- *Degree of mixing*. Process tanks must be equipped with mixers to ensure maximum contact between the agent and the waste solution. Proper mixing also limits the production of any solid precipitates from side reactions that may resist oxidation. The quantifiable degree of mixing is a complex assessment that includes, among other factors, the amount of energy supplied, the length of time the material is mixed, and the related turbulence effects of the specific size and shape of the tank.

- *pH*. Operation at the optimal pH maximizes the chemical reactions and May – for oxidations and depending on the oxidizing agent used – limit the formation of undesirable reaction by-products or the escape of cyanide from solution as HCN, CNCl, or C_2N_2 gas. For reduction, the reaction speed is usually significantly reduced at higher pH values (typically above 4.0). It is worth noting that some reduction reactions may proceed better under alkaline conditions, in which case pH must be properly controlled to the appropriate alkaline range. The pH is controlled by the addition of caustic, lime, or acid to the solution.
- *Temperature*. Temperature affects the rate of reaction and the solubility of the reactants in the waste. As the temperature is increased, the solubility of the reactants, in most instances, is increased and the required residence time, in most cases, is reduced.

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METALS REMOVAL FROM INDUSTRIAL EFFLUENTS

DJAMAL-EDDINE AKRETCHE*
Laboratory of Hydrometallurgy and Inorganic Molecular Chemistry, U.S.T.H.B., Algiers (ALGERIA)

Abstract. We summarize a review of the various techniques used for removal metals from industrial effluents. From the classical methods to innovative of them, we describe the processes showing both their advantages and inconvenient. On the other hand, we talk about some hybrid processes which are tested at laboratory scale and which would be an alternative for some treatments. It has been shown that the choice of the metals removal technique is highly dependent of the nature of the stream.

1. Introduction

Wastewaters containing heavy metals are discharged to the environment by variety of industries, such as galvanic, metallurgical, electronic, etc. The removal of heavy metals from wastewaters is of critical importance due to their high toxicity and tendency to accumulate in living organisms. Moreover, heavy metals cannot be degraded or destroyed. Various heavy metal cationic wastewater treatment methods have been developed in recent years. Use of effective wastewater treatment technologies allows the industrial facilities to create water recycling systems, saving discharge fees and freshwater supply payment. Industrial effluents contain generally heavy metals which give rise to environmental problems. Their treatment is always a looking for a compromise between the metal valorization and the water reuse. The scarcity of water resources increases the pertinence of the application of a process where metals are removed if they cannot be recovered. Generally, industrial effluents contain a variable quantity of metals. The most of them are designed as heavy metals with an atomic

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* E-mail: dakretche@usthb.dz

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number greater than about 50. Heavy metals that are typically encountered in waters include copper, zinc, cadmium and chromium.

The metal removal and recovery processes include the following techniques:

- Precipitation.
- Adsorption and biosorption.
- Coagulation and flocculation.
- Electrowinning.
- Cementation.
- Solvent extraction and ion exchange.
- Membrane processes.

According to the treated case, each process shows advantage or inconvenient. There is not a typical treatment for removing metals from effluents.

2. Precipitation

Precipitation and co-precipitation are the most used and studied methods for metal removal from industrial waste waters (Blais et al. 1999). Solubility equilibrium is any type of chemical equilibrium relationship between solid and dissolved states of a compound at saturation. K_{sp} stands for "solubility product" or "solubility equilibrium". It is the equilibrium constant for the reaction in which a solid salt dissolves to give its constituent ions in solution.

The equilibrium of solubility is given by the equation:

$$A_{(s)} \leftrightarrow xB^{p+}{}_{(aq)} + yC^{q-}{}_{(aq)} \tag{3.1}$$

The solubility and solubility product are tied with the equation:

$$\sqrt[n]{\frac{K_{sp}}{x^x y^y}} = \frac{C}{M_M} \tag{3.2}$$

Where:

n is the total number of moles on the right hand side, i.e., $x + y$, dimensionless.

x is the number of moles of the cation, dimensionless.

y is the number of moles of the anion, dimensionless.
K_{sp} is the solubility product, $(\text{mol/kg})^n$
C is the solubility of A expressed as a mass fraction of the solute A in the solvent (kg of A per kg of solvent).
M_M is the molecular mass of the compound A, kg/mol.

The method of precipitation, which is often used, consists of precipitating the metals as hydroxides. Wastewater treatment systems for metals are pretty well defined for precipitation systems. The incoming solution is pH adjusted to the optimum range for precipitating the metal as a hydroxide (Aziz and smith, 1992). In difficult situations, a sulfide is added to increase the recovery. The treated water is run through a clarifier to settle the solids. The effluent water is pH adjusted, if needed, to meet city limits and the hydroxide sludge is filter pressed to a cake for recycling. Wastewater precipitation systems operate on the principal that give enough time and a low enough flow, a solid will settle out of a liquid. The standard heavy metal wastewater treatment methodology for metals removal has been hydroxide precipitation with or without the addition of a sulfide. The sulfide results in a lower solubility than hydroxide precipitation alone. In some cases, neither seems to be able to consistently obtain satisfactory results. We have found in most cases, this was cause by either and undersized system (flow too high for the settling area) or incompatible constituents resulting in a carryover of the flock. The two solutions are obvious, size the system correctly in the first place or add a polishing filter to the end of the system.

The usual procedure involves the addition of chemicals such as lime (CaO or $Ca(OH)_2$), $Mg(OH)_2$, $NaHCO_3$, Na_2CO_3, $(NH_{4,})_2CO_3$, $NaOH$, NH_4OH or KOH. Certain heavy metal hydroxides, such as the hydroxides of zinc, copper, lead, cadmium and chromium, are amphoteric compounds which exhibit minimum solubility in the pH range of about 8–12. They become soluble if the pH increases over 12 or decreases under 8. The precipitation of metals by carbonates or sulphides is also an effective alternative to hydroxides precipitation. The use of carbonates allows the precipitation of metals to occur at pH values lower then those necessary for the hydroxides (Patterson et al. 1977). Moreover, the precipitates formed are denser and are easily separated from liquid. Precipitation by sulphides is normally carried out with reagents such as Na_2S, $NaHS$, H_2S or FeS. In acidic media, the lower solubility of metal sulphides makes it possible to reach concentrations lower than those obtained through hydroxides as it is shown on the Tables 3.1 and 3.2.

TABLE 3.1. Solubility products of some hydroxides (http://www.csudh.edu/oliver/chemdata/data-ksp.htm, 2007).

Product	**Solubility product K_{sp}**
$Al(OH)_3$	5×10^{-33}
$Cr(OH)_3$	4×10^{-38}
$Fe(OH)_2$	1×10^{-15}
$Fe(OH)_3$	5×10^{-38}
$Mg(OH)_2$	1×10^{-11}
$Zn(OH)_2$	5×10^{-17}

TABLE 3.2. Solubility products of some sulphides (http://www.csudh.edu/oliver/chemdata/data-ksp.htm, 2007).

Product	**Solubility product K_{sp}**
Ag_2S	1×10^{-49}
CdS	1×10^{-26}
CoS	1×10^{-20}
CuS	1×10^{-35}
FeS	1×10^{-17}
HgS	1×10^{-52}
MnS	1×10^{-15}
NiS	1×10^{-19}
PbS	1×10^{-27}
ZnS	1×10^{-20}

Another major problem with this technology is with chelates. Chelates are organic compounds that hold metals in solutions at high pH. Hydroxide precipitation depends on the insoluble metal hydroxide forming and the chelating agent prevents this. Some sulfides and strong reducing agents can break weak chelates but EDTA is more difficult. The other possibility of breaking chelates is to do a substitution. A non hazardous metal is added that the chelate prefers over the target metal. For EDTA at high pH, Calcium, Magnesium, and Iron are all preferred over the hazardous divalent metals such as Copper, Nickel, and Zinc. Adding any one of these would increase the precipitation of the divalent metals.

Metals precipitated are stored as sludges and this fact is a convenient for both the space and the environment (Baltpurvins et al. 1997). Moreover, these conventional systems were used for years when the limits were 5 ppm heavy metals. Additives keep these systems alive but the cost of sulfiding and reducing agents make them very expensive to operate. They are characterized by:

- Lowest capital cost
- High sludge volume
- May require final filter
- May require chelate breaker
- Continuously surveillance required
- Single pipe system is possible with chelate breaking additives
- Very large floor space required

3. Adsorption and Biosorption

Adsorption is a surface phenomenon by which molecules of pollutants (adsorbates) are attracted to the surface of adsorbent by intermolecular forces of attraction. It takes place when atoms of surface functional groups of adsorbent (activated carbon per example) donate electrons to the adsorbate molecules (usually organic pollutants). The position of the functional groups (which are generated during activation process) of the adsorbent determines the type of adsorbent–adsorbate bond, and thus the type of adsorption. The physical adsorption is mainly caused by van der Waals' and electrostatic bonds between the adsorbate molecules and the atoms of the functional groups. The process is reversible, and thus desorption of the adsorbed solute can occur. The physical adsorption takes place at lower temperature (in the neighborhood of room temperature), and it is not site-specific. The adsorption can occur over the entire surface of the adsorbent at multilayers. On the other hand, the chemical adsorption involves ionic or covalent bond formation between the adsorbate molecules and the atoms of the functional groups of the adsorbent. The chemical adsorption is irreversible, and the heat of adsorption is typically high. The chemical adsorption process is site-specific and it occurs only at certain sites of the adsorbent at only one layer (monolayer). Because the wastewater contains a large amount of organic and inorganic substances, it is possible that both physical and chemical adsorption takes place when it comes into contact with an adsorbent (usually activated carbon). However, for simplicity, only the physical adsorption process is discussed, as most of the adsorption-separation processes depend on physical adsorption.

The adsorption process with wastewater is competitive in nature. The extent of competition depends on the strength of adsorption of the competing molecules, the concentrations of these molecules, and the characteristics of the adsorbent (activated carbon). In a competitive adsorption environment, desorption of a compound may takes place by displacement by other compounds, as the adsorption process is reversible in nature. It sometimes results in an effluent concentration of an adsorbate greater than the influent concentration.

Basically, an adsorbate passes through four steps to get adsorbed onto the porous adsorbent. First, the adsorbate must be transported from bulk solution to the boundary layer of the wastewater surrounding the adsorbent (bulk solution transport). The transport occurs by diffusion if the adsorbent is in a quiescent state. In the fixed-bed or in the turbulent mixing batch reactors, the bulk solution transport occurs by turbulent mixing. Second, the adsorbate must be transported by molecular diffusion through the boundary layer surrounding the adsorbent particles (film diffusion transport). Third, after passing through the boundary layer, the adsorbate must be transported through the pores of the adsorbent to the available adsorption sites (pore transport). The intraparticle transport may occur by molecular diffusion through the wastewater solution in the pores (pore diffusion) of by diffusion along the surface of the adsorbent (surface diffusion). Finally, when the adsorbate reaches the adsorption site, the adsorption bond is formed between the adsorbate and the adsorbent. This step is very rapid for physical adsorption. Thus, it is either the bulk solution transport or film diffusion transport or pore transport that controls the rate of species removal from the wastewater. In turbulent mixing condition (in fixed-bed or in batch reactor), it is most likely that a combination of film diffusion and pore diffusion controls the rate of adsorption of organics. At the initial stage, the film diffusion may control the adsorption rate but after the accumulation of adsorbates within the pore of the adsorbent, it is possible that the adsorption rate is controlled by the pore transport.

Adsorption methods are also widely applied and examined for the metal removal, however, in the most cases, the use of adsorbents requires an effluent neutralization step. Indeed, the neutralization of acid effluents must take place to allow their disposal in sewerage systems.

A wide variety of adsorbents can be employed (Al-Asheh and Duvnjak 1998, Ho and McKay et al. 1999): both organic and inorganic as aluminium or iron oxides, sand, activated carbon, mixtures of coal and pyrite, iron particles, gravel and crushed bricks, cement, etc. Studies have demonstrated that the possibility of eliminating metals can occur by adsorption on vegetables matters: peat moss, sawdust, wood bark, etc. Chitin and chitosan, two natural polymers that are abundant in the cell walls of funghi and shellfish, have also excellent properties of metal fixation. Agricultural by-products such peanuts skins, onion skins, coffee powder, etc., have been also proposed for the metal adsorption. Effectively, any material which presents an interesting specific surface can be tested for adsorption. It should be verify by the Freundlich law and shows a high adsorption rate. However, generally, the desorption do not find a practical solution and the discontinuity of the process gives rise to another convenient.

The adsorption processes used in practice are either batch mode or fixed bed mode depending on the characteristics of the adsorbent. In the batch mode, adsorbent is added to the tank containing wastewater. The pollutants such as heavy metals are adsorbed onto the adsorbent surface and are subsequently removed by sedimentation–filtration processes. In fixed–bed mode, adsorbents are packed in a column, and the wastewater is passed through the column either from the top or from the bottom (fluidized mode). The pollutants are adsorbed on the adsorbent surface and thus the effluent of better quality is achieved. Activated carbons, both granular activated carbon (GAC) and powdered activated carbon (PAC), are the oldest and most widely used adsorbents commercially as well as in the laboratory. They can be used in wastewater effluent treatment, potable water treatment, solvent recovery, air treatment, decolorizing, and many more other applications. The GAC is used as a fixed filter bed whereas the PAC is used directly in the aeration tank.

3.1. BATCH ADSORPTION SYSTEM

The batch adsorption system is usually used for the treatment of small volumes of wastewater. In the batch adsorption system, the adsorbent is mixed with the wastewater to be treated in an agitated contacting tank for a period of time. The slurry is then filtered to separate the adsorbent from wastewater. It can be performed in the single-stage or multistage system depending on the characteristics of adsorbate and adsorbent.

3.2. FIXED-BED ADSORPTION SYSTEM

Depending on the characteristics of the wastewater and the adsorbent, the fixed-bed adsorption column can be operated in single or multiple units. The operation can be upflow or downflow. In the downflow operation, the filtration process is more effective. However, it suffers more pressure drop compared to the upflow operation. When a highly purified effluent is required, the fixed-bed adsorption columns are operated in series.

3.3. PULSED-BED ADSORPTION SYSTEM

In the pulsed-bed adsorption system, the adsorbent is removed at regular intervals from the bottom of the column and replaced by the fresh adsorbent from the top. The column is normally packed full of adsorbent so that there is no freeboard for bed expansion during operation.

3.4. FLUIDIZED-BED ADSORPTION SYSTEM

In upflow operation, the adsorption bed is completely fluidized and hence expanded. When the adsorbent particle size is small, it is advantageous to use the fluidized-bed adsorption system. It reduces the excessive head due to the fixed bed clogging with particulate matter often experienced in downflow adsorption system.

3.5. POWDERED ACTIVATED CARBON TREATMENT (PACT)

The performance of the aerobic or anaerobic biological treatment process can be improved by adding powdered activated carbon (PAC) to the process. The PAC particles help in reducing the problems of bulking of sludge or foaming associated with the activated-sludge process. The PAC particles enhance the biological assimilation of organics. During the process, the adsorption capacity of the PAC is also partially renewed by concurrent microbial degradation of adsorbed organic substances. The primary advantages of using PAC are the fixed bed adsorption columns in parallel operational mode. Low capital investment cost with the possibility of changing the PAC dose as the water quality changes. The main disadvantages of use of PAC are the high operating cost if high PAC dose is required and the low TOC removal combined to the inability to regenerate. There is also a difficulty of sludge disposal. However, the use of PAC can enhance the performance of the existing biological treatment system by removing dissolved substances, forming settleable flocs, and stabilizing the system against toxicity and shock loadings.

3.6. BIOSORPTION

Biosorption can be also an interesting alternative of metals removing from dilute industrial waste water (Al-Asheh and Duvnjak 1996). It implies the use of live or dead biomass and their derivatives. Many studies have been carried out for the capacities of adsorption of metals on various types of biomass (bacteria, yeasts, fungi, freshwater algae). The microorganisms used for the metal adsorption step should be immobilized in a matrix or in an easily recoverable support. The immobilizing agents or matrices most usually employed are alginate, polyacrylamine, polysulphone, silica-gel and cellulose.

4. Coagulation and Flocculation

Coagulants and flocculants enhance dissolved metal removal and reduce sludge volume during conventional acidic drainage and high-density sludge treatment. Coagulants and flocculants are chemicals that can be added during acidic drainage treatment. Although some chemicals can be considered both coagulants and flocculants (iron and aluminum salts), coagulation and flocculation are two distinct processes. Coagulation describes the consolidation of smaller metal precipitate particles into larger metal precipitate particles (flocs). Coagulants reduce the net electrical repulsive force at the surface of the metal precipitate particles. The purpose of adding coagulants to acidic drainage waters is to increase the number of flocs present in the treatment water. As floc density increases, interparticle contact increases due to Brownian motion, promoting agglomeration of colloidal particles into larger flocs for enhanced settling (Qasim et al. 2000).

Coagulants are widely used in water treatment systems and but are not commonly used at conventional acidic drainage treatment operations. The most common coagulants are aluminum and iron salts. Aluminum and iron coagulants react with bicarbonate alkalinity (HCO_3^-) in acid drainage creating aluminum, ferric or ferrous hydroxide flocs which attract metals in solution through co-precipitation.

Flocculation involves the combination of small particles by bridging the space between particles with chemicals (Skousen et al. 1996). Essentially, coagulants aid in the formation of metal precipitate flocs, and flocculants enhance the floc by making it heavier and more stable. For this reason, flocculants are sometimes referred to as coagulant aids at water treatment operations (Tillman 1996, Faust and Aly 1999).

Two main groups of flocculants exist: mineral which includes activated silica, clays, and metal hydroxides and synthetic which include anionic, cationic, and nonionic compounds (Skousen et al. 1996). Activated silica has been used as a flocculant since the 1930s to strengthen flocs and reduce the potential of deterioration. It is usually produced on-site by reacting sodium silicate with an acid to form a gel. When using activated silica, the resultant floc is larger, denser, more chemically stable, and settles faster than iron and aluminum flocs.

5. Electrowinning

Electrowinning, also called electroextraction, is the electrodeposition of metals from their ores that have been put in solution or liquefied. Electrorefining uses a similar process to remove impurities from a metal. Both processes use electroplating on a large scale and are important techniques for the economical and straightforward purification of non-ferrous. The resulting metals are said to be *electrowon*.

Electrowinning can be also employed to remove metallic ions from concentrated rinse water, spent process solutions, and ion exchange regenerant (Dutra et al. 2000). An advantage of electrowinning is that the metal removed from the effluent is plated out as a solid metal. However, the metal concentration should be sufficient for allowing the current transport. Sometimes to enable automated system operation, electrowinner is equipped with an on-line metal sensor to provide real-time monitoring of the concentration of the metal to be removed. To monitor the efficiency of the electrowinning process other parameters monitored are current, voltage and temperature. In electrowinning, a current is passed from an inert anode through a leaching solution containing the metals which are to be recovered. Thus, the metal is extracted as it is deposited in an electroplating process onto the cathode. In electrorefining, the anodes consist of unrefined impure metal, and as the current passes through the acidic electrolyte the anodes are corroded into the solution so that the electroplating process deposits refined pure metal onto the cathodes.

The most common electrowon metals are lead, copper, gold, silver, zinc, aluminium, chromium, cobalt, manganese, and the rare-earth and alkali metals. For aluminium, this is the only production process employed. Several industrially important active metals (which react strongly with water) are produced commercially by electrolysis of their pyrochemical molten salts. Experiments using electrorefining to process spent nuclear fuel have been carried out. Electrorefining may be able to separate heavy metals such as plutonium, caesium, and strontium from the less-toxic bulk of uranium. Many electroextraction systems are also available to remove toxic (and sometimes valuable) metals from industrial waste streams.

Most metals occur in nature in their oxidized form (ores) and thus must be reduced to their metallic forms. The ore is dissolved following some preprocessing in an aqueous electrolyte or in a molten salt and the resulting solution is electrolyzed. The metal is deposited on the cathode (either in solid or in liquid form), while the anodic reaction is usually oxygen evolution. Several metals are naturally present as metal sulfides; these include copper, lead, molybdenum, cadmium, nickel, silver, cobalt and zinc. In addition, gold and platinum group metals are associated with sulfidic base metal ores. Most metal sulfides or their salts are electrically conductive and this allows electrochemical redox reactions to efficiently occur in the molten state or in aqueous solutions.

Concerning the electrowinning components, they are composed by:

- A process tank in polypropylene or lined steel.
- Cathodes and anodes. Cathode materials are stainless steel, metal coated foam or carbon fibers. Anode materials are titanium, niobium; coated with precious metal or metal oxides.
- Transfer pump.
- Rectifier.
- Electrolyte.
- System controls.

The electrowinning process parameters are:

- Metal ion concentration, which is defined as it follows:

  - High: 1000–20000 mg/L
  - Medium: 100–1000 mg/L
  - Low: <100 mg/L (use HSA, HMT cathodes)

- Surface area and type of cathode
- Current density (CD) which is ranged between 10 and 5000 ampères/ft^2
- Electrolyte agitation
- Species of metal ion
- Temperature

Additives, such as chloride, thiourea, glue and Avitone, are used extensively in electrorefining as grain refiners and leveling agents for deposition (Safizadeh et al. 2010). They allow the production of smooth dense cathodes which will not encapsulate impurities either in the electrolyte or secondary phases. While additives have been used for many decades, the monitoring of these has only recently been employed

6. Cementation

Cementation is a type of precipitation method implying an electrochemical mechanism according to the reaction:

$$mN^{n+} + nM_s \rightarrow nM^{m+} + mN_s \tag{3.3}$$

In this process, a metal having a lower redox potential passes into solution. For example, the oxidation of metallic iron to ferrous ion Fe (II) allows to replace as a solid a metal of higher redox potential. Copper is the metal that is frequently separated by cementation. However, the noble metals (Au, Pt, Pd, Ir, …) as well as Cd and Ga can also be recovered by this manner. Cementation allows to recover metals as solids, however, it is generally efficient in acidic media ($pH < 2$) (Hayes 1985). The agitation rate should be also optimized. The kinetic and the efficiency are also dependent of the redox potential difference between the two metals (Brooks 1991).

7. Solvent Extraction and Ion Exchange

Solvent extraction was used for many years for a broad range of separations in hydrometallurgy (Marcus and Kertes 1969). This technique is employed today for some cases of removal of soluble metals (Cd, Cr, Co, Cu, Ni, …) from wastewater.

Separation is carried out in contact with immiscible organic phase to form salts or complex compounds which give a favorable solubility distribution between the aqueous and organic phases.

Various types are used such carboxylic acids and aromatic amines as extractants of the metals. The non selective removal of metallic ions can take place with a whole range of organic reagents. However, to improve the selectivity, new reagents are proposed more and more through recent studies. Other parameters should be optimized such pH, nature of solvent, ratio of extractant and solvent, temperature.

Metals can be also removed by cation exchange on resins which are insoluble substances having in their molecular structure an acidic group (i.e. $SO_3^- H^+$) able to exchange, without change of their physical structure, the positive ion fixed at these groups. The selectivity of these exchangers is improved by the fixation of specific chelate and the process takes place through either a fixed or a moving bed. The technology is easy; however, it is limited by the discontinuity of the process. The fixation of metals should be stopped when the resin is saturated and elution (regeneration) takes place.

Ion exchange is a simple process where an organic molecule has been substituted with acid or base exchange sites. As a solution with exchangeable ions passes through the resin, the ions are captured and exchanged for the ions on the resin. For example, some weak acid ion exchange resins can use the carboxylic acid radical, in the sodium form, R–COO–Na as the exchange site. As solutions of metal ions such as Magnesium (Mg), Calcium (Ca), or Copper (Cu) pass through the resin, they are exchanged for the Na (Sodium) at that site. The molecule would now appear like this R–COO–Ca, for a calcium exchange.

$$\mathrm{R-COO-Na+Ca^{2+}\rightarrow R-COO-Ca+2Na^{+}} \tag{3.4}$$

These resins are used in water softeners where the alkaline earth metals such as calcium and magnesium are exchanged for sodium. In a water softener sodium chloride (salt, NaCl), is used to “regenerate” the resin. The salt solution is passed through the resin in very high concentrations and the sodium displaces the metals attached to the active sites. When the concentration of sodium is low, the sites prefer the alkaline metals again and the resin can be used to “soften” water again.

The same principles apply in industrial ion exchangers except that usually a strong acid or base is used to regenerate the resins (except in industrial water softeners). To remove a metal from your waste stream at a low pH using ion exchange, the most cost effective method is to use a weak acid chelating resin. An iminodiacetic acid resin is useful to remove a metal when a chelate such as ammonia or EDTA is present. The pH is adjusted to the correct range remove the metal, but kept under 6 to prevent the formation and precipitation of hydroxides and oxides of metals.

This resin has a hierarchy of preferences, i.e., it prefers copper more than zinc. This requires their use mainly in compatible metal systems. If only one metal is being passed through the column, there is no competition for sites and the progress of the system is easier to monitor. Reclaiming the metal is also easier as multiple metal systems are difficult to plate.

The ion exchange resin used in most metal recovery systems is what is called a “weak acid” resin. This system allows low chemical usage, usually about 1.25 times the theoretical amount to regenerate the column. This resin is used in the sodium form. This allows us to regenerate with an acid and recover the metals in a useful form. The resin is then conditioned so that the pH does not drop to low when we start up the column. The basic chemistry of this system is as follows:

1. The solution is adjusted to a pH which is optimum for the resin but low enough to prevent hydroxides from forming and high enough to ensure the capture of the metals.

2. The solution is passed through a media filter to remove any solids and then through the lead/lag columns where a metal is exchanged for sodium ions. The capacity of the columns is about 1.8 pounds of metal per cubic foot of resin depending on the competing ions passing through with the metal.

8. Membrane Processes

Membrane technology is considered as one of the most effective processes for water and wastewater treatment. It is a compact system, economically feasible and has high rejection level of pollutants. Membrane technology has been given special focus in water treatment processes because of its capability in removing physical and chemical matters at a higher-degree of purification. Membrane technologies are various and are considered as proper methods. They rarely need an adding of chemical. Membrane technology is presently an established of several industrial processes and is a relatively new technology, which can be found in all industrial areas. A membrane is a thin barrier capable of perm-selective mass transport. Advantages of membrane filtration among others are low energy consumption. The membrane process can be carried out continuously, up-scaling is relatively simple and membrane technology can be used for almost any kind of separation. There are many categories of membrane techniques and their classification is based on particle's size range; which can be rejecting and driving force. Functional available membrane processes for liquid separation includes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and dialysis (D). The membrane techniques that are often used for metals removal are electrodialysis (electric driving force), ultrafiltration and nanofiltration (pressure driving force). Sometimes, Donnan dialysis (concentration gradient) is proposed.

Electrodialysis can be considered as a conventional technique for metals removal; however, it becomes uneconomical when solutions containing components in concentration lower than 5×10^{-3} M are treated. It is limited by some current density and a polarization concentration takes place.

In an electrodialysis stack, Figure 3.1, the diluate (D) feed stream, brine or concentrate (C) stream, and electrode (E) stream are allowed to flow through the appropriate cell compartments formed by the ion exchange membranes. Under the influence of an electrical potential difference, the negatively charged ions (e.g., chloride) in the diluate stream migrate toward the positively charged anode. These ions pass through the positively charged

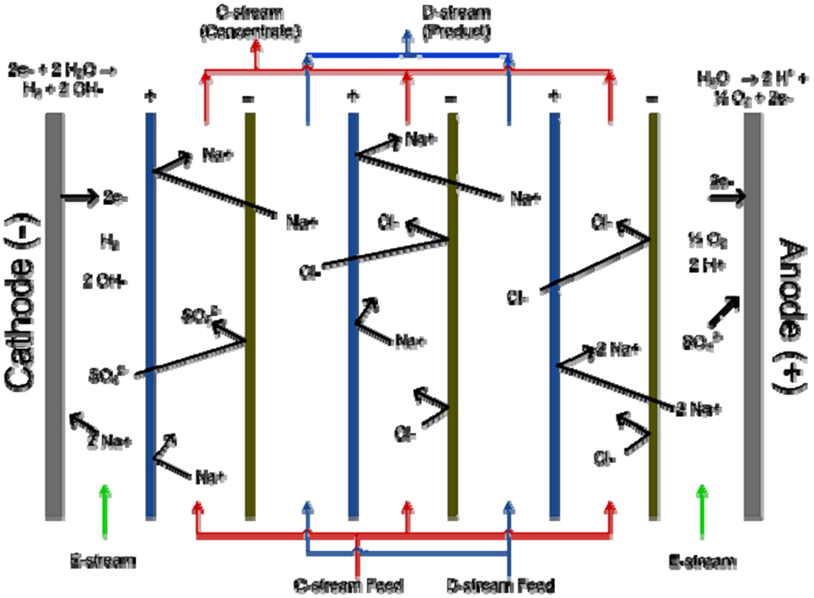

Figure 3.1. Principle of_electrodialysis (Chérif 1989).

anion exchange membrane, but are prevented from further migration toward the anode by the negatively charged cation exchange membrane and therefore stay in the C stream, which becomes concentrated with the anions. The positively charged species (e.g., heavy metal) in the D stream migrate toward the negatively charged cathode and pass through the negatively charged cation exchange membrane. These cations also stay in the C stream, prevented from further migration toward the cathode by the positively charged anion exchange membrane. As a result of the anion and cation migration, electric current flows between the cathode and anode. Only an equal number of anion and cation charge equivalent are transferred from the D stream into the C stream and so the charge balance is maintained in each stream. The overall result of the electrodialysis process is an ion concentration increase in the concentrate stream with a depletion of ions in the diluate solution feed stream. The E stream is the electrode stream that flows past each electrode in the stack. This stream may consist of the same composition as the feed stream (e.g., sodium chloride) or may be a separate solution containing a different species (e.g., sodium sulfate). Depending on the stack configuration, anions and cations from the electrode stream may be transported into the C stream, or anions and cations from the D stream may be transported into the E stream. In each case, this transport is necessary to carry current across the stack and maintain electrically neutral stack solutions.

Electrodialysis gives rise to reactions at each electrode. At the cathode, we get:

$$2e^- + 2H_2O \rightarrow H_{2(g)} + 2OH^- \tag{3.5}$$

while at the anode, water oxidation takes place as:

$$H_2O \rightarrow 2H^+ + \tfrac{1}{2}O_{2(g)} + 2e^- \quad \text{or} \quad 2Cl^- \rightarrow Cl_{2(g)} + 2e^- \tag{3.6}$$

Small amounts of hydrogen gas are generated at the cathode and small amounts of either oxygen or chlorine gas (depending on composition of the E stream and end ion exchange membrane arrangement) at the anode. These gases are typically subsequently dissipated as the E stream effluent from each electrode compartment is combined to maintain a neutral pH and discharged or re-circulated to a separate E tank. However, the collection of hydrogen gas can be used in energy production.

In application, electrodialysis systems can be operated as continuous production or batch production processes. In a continuous process, feed is passed through a sufficient number of stacks placed in series to produce the final desired product quality. In batch processes, the diluate and/or concentrate streams are re-circulated through the electrodialysis systems until the final product or concentrate quality is achieved.

Electrodialysis has inherent limitations, working best at removing low molecular weight ionic components from a feed stream. Non-charged, higher molecular weight, and less mobile ionic species will not typically be significantly removed. Also, in contrast to RO, electrodialysis becomes less economical when extremely low salt concentrations in the product are required and with sparingly conductive feeds: current density becomes limited and current utilization efficiency typically decreases as the feed salt concentration becomes lower, and with fewer ions in solution to carry current, both ion transport and energy efficiently greatly declines. Consequently, comparatively large membrane areas are required to satisfy capacity requirements for low concentration (and sparingly conductive) feed solutions. Innovative systems overcoming the inherent limitations of electrodialysis (and RO) are available; these integrated systems work synergistically, with each sub-system operating in its optimal range, providing the least overall operating and capital costs for a particular application.

As with RO, electrodialysis systems require feed pretreatment to remove species that coat, precipitate onto, or otherwise give rise to fouling the surface of the ion exchange membranes. This fouling decreases the efficiency of the electrodialysis system. Species of concern include calcium and magnesium hardness, suspended solids, silica, and organic compounds. Water softening can be used to remove hardness, and micrometre or multimedia filtration can be used to remove suspended solids. Hardness in particular is a concern since scaling can build up on the membranes. Various chemicals are also available to help prevent scaling. Also, electrodialysis reverse systems seek to minimize scaling by periodically reversing the flows of diluate and concentrate and polarity of the electrodes.

Donnan dialysis can be the appropriate ion exchange membrane process to recover metals from dilute solutions. Donnan dialysis is an ion exchange process that can be used for the purification and concentration of diluted solutions (Akretche and Kerdjoudj 2000). It is generally applied in analytical fields where the preconcentration of various cations and anions is necessary. The process is often studied by means of cation exchange with the H^+ ion as the driving ion, and is based on a chemical potential difference between two compartments separated by an ion-exchange membrane. However, Donnan dialysis is not applied in industry mainly because of its slow kinetics, in spite of its having some advantages such as economic and energy saving.It is based on an electrochemical potential difference established between two compartments separated by an ion exchange membrane. Donnan Dialysis is:

- Economical
- Energy saving
- Technologically simple

However, Donnan dialysis has also some disadvantages:

- A low kinetic
- Osmosis phenomenon (water flux)

Ultrafiltration and nanofiltration performances are estimated through the measurement of the rejection yields given by the relation:

$$R = 1 - \left(\frac{C_p}{C_0} \right) \tag{3.7}$$

Where C_P is the metal concentration in the permeate and C_0 the initial concentration.

The pore sizes of UF and NF membranes (1–100 nm) imply a need of adding chemicals to allow the metal retention. This occurs by adding soluble polymers or micelles to obtain hybrid systems such PEUF or MEUF (Barakat 2008).

Uncharged dissolved materials, and some positively charged ions, will be rejected if they are of sufficient size. Nanofiltration membranes have a molecular weight cut off of approximately 150–250 Da. Therefore, species such as glucose and fructose (MW 180 Da) are being rejected. Large, positively charged ions such as heavy metals are rejected, at least partly, based on molecular weight.

Surfactants due to their high selectivity properties can also be used in enhancing membrane filtration for the removal of metal ions in aqueous solutions. Natural surfactants are preferred to synthetic surfactants because the synthetic surfactants have the disadvantage of introducing secondary pollutants into the filtrate. In addition, the natural surfactants are non-toxic, biodegradable and abundant. These processes are limited by the membrane fouling and they give rise to a polymer recycling operation.

Low Pressure Reverse Osmosis Membrane (LPROM) has been introduced to water and wastewater industries in the past few years due to the high cost of operational and maintenance of conventional high-pressure RO membrane system (Pawlak et al. 2006, Myzairah 2007). LPROM may remove more than 90% of heavy metals depending on the operating conditions of the system. LPROM with operating pressure less than 100 psi is commercially available to make treatment system more affordable and cost effective.

Thus, hybrid processes have been proposed for removing metals, but many of them were carried out only at a laboratory scale. Per example, as a perspective, electrodeionization can be used for wastewater treatment although it is a technique which allows to product ultrapure water where a value of less than 1 μS conductivity can be obtained (Souilah et al. 2004). By this fact, many works have been performed concerning the unconventional water supply by means of recycling industrial effluents or brackish water. As it was described above, electrodialysis is known as an usual electro-membrane process in this field, however, both of the polarization phenomenon and the concentration of solutions limit it. The high global conductivity of the system needed is incompatible with the deionization of the dilute compartment. Then, the avoiding of this phenomenon can be obtained by replacing the aqueous solution by an ion exchanger resin inside the central compartment. Electrodeionization can be decomposed in two operations: electropermutation when the ions contained in the feed solution are fixed on the ion exchanger resin and electroregeneration in which the ions fixed are removed from the resin. Application to a surface treatment industrial effluent has been studied through both the transfer mechanism and the flux of the preponderant metal which is the zinc.

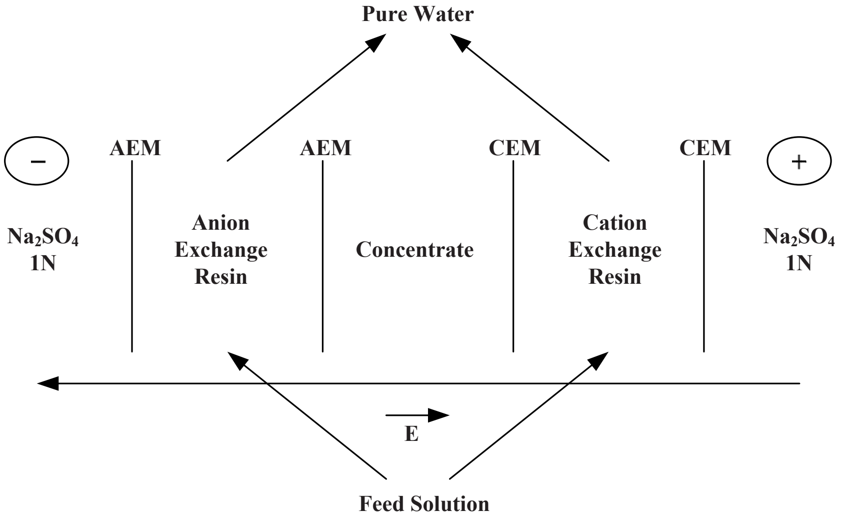

Figure 3.2. Scheme of the electrodeionization cell.

In an example of application, electrodeionization experiments have been performed using a five compartment KelF cell with a working membrane area of 16 cm^2. The two extreme compartments were composed of metallic electrodes (platinum–coated titanium sheets) immersed in a rinsing solution of 1M Na_2SO_4. The central compartment contains water and it receives the salt ions from the treated solution. On both sides of this compartment two circuits of 250 mL are located through two separated beds of resins (one of cation exchange while the other is of anion exchange) inserted between ion exchange membranes. They receive the industrial stream to extract metals ions. The cell scheme of this electrodeionization system is represented on the Figure 3.2.

The treated effluent contains some metallic ions whose concentrations are represented on Table 3.3.

TABLE 3.3. Average composition of a treated effluent

Element	Amount (mg/L)
Zn	40
Cu	6
Cd	4
Mg	850
Fe	<0.2
Pb	<0.4
Mn	<0.2
Sulphates	3840

The treatment of the above effluent by electrodeionization allows to obtain the results represented on the Figures 3.3 and 3.4. The treatment by electrodeionization of this effluent allows to get a pure water with a conductivity of around 40µS and concentration factors of metals bigger than 100. On the other hand, a continuous circuit during more than 1400 hours is obtained.

Ion exchange resins can also be combinated to both ultrafiltration and nanofiltration. The combination of ultrafiltration with ion exchange resins is examined (Helis 2009). A simulated effluent is used where the behavior of copper and nickel is studied.

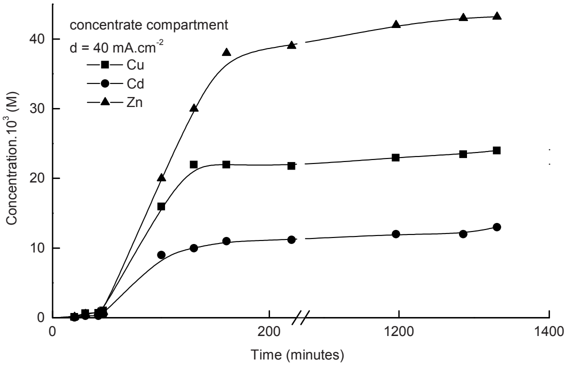

Figure 3.3. Concentration of metals in the concentrate versus time.

Ultrafiltration of various solutions was performed using a laboratory tangential ultrafiltration cell with a mineral membrane (alumina) of 50 nm porosity (250 cm^2 of area). Ion exchange resins are inserted as it is shown on the Figure 3.5. This system occurs without adding chemicals. Thus, metals removal by ultrafiltration can take place without adding polymers or micelles as it is usually done.

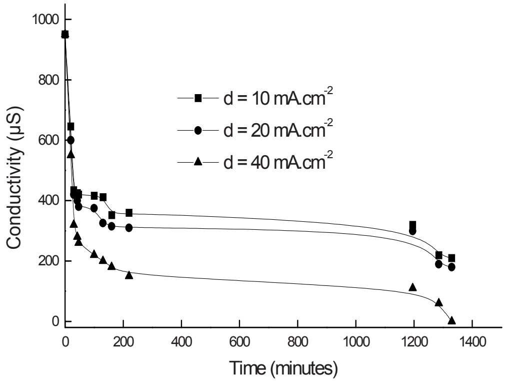

Figure 3.4. Conductivity of purified water as a function of the current density.

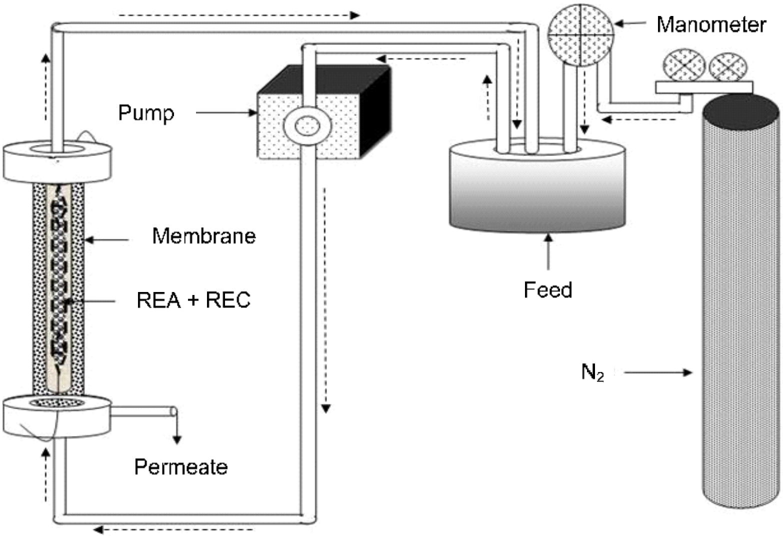

Figure 3.5. Coupled resin – UF Cell.

Ion exchange textiles (or fiber ion exchange) can replace the ion exchange resins in these two processes (Berdous and Akretche 2002). This fact can improve the technology performances of the hybrid systems proposed. In effect the ion exchange textile is easily manipulated and it consists in a compact material which can be inserted in any system. Whatever the case, the use of these hybrid processes gives rise to a pure water which can be reused and a concentration of metals which can be reinserted in the electrolysis circuit. Both economy and zero rejection are obtained.

9. Conclusions

Removal of metals from industrial effluents is a versatile operation. The choice of the method is dependent of the nature and the composition of the stream. The cost value of the metal recovered is also an important parameter which can favors a specific and selective method that cannot be recommended to another case. Hybrid processes can give synergetic solutions to the various problems due to the metal rejection.

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THE ION-EXCHANGE MEMBRANE BIOREACTOR: DEVELOPMENTS AND PERSPECTIVES IN DRINKING WATER TREATMENT

SVETLOZAR VELIZAROV, MARIA A. REIS,
JOÃO G. CRESPO*
Requimte / CQFB, Department of Chemistry
FCT/Universidade Nova de Lisboa, Campus da Caparica,
Caparica (PORTUGAL)

Abstract. Until recently, membranes in bioreactors were essentially regarded as micro/ultra porous barriers to promote high cell concentrations for process intensification and to avoid contamination of the treated water with the biocatalyst. This chapter will discuss in particular the use of membrane bioreactors for treatment of water supplies contaminated with micro-polluting ions. The contamination of drinking water sources with inorganic compounds is a matter of concern, because of their harmful effect on human health. Some of these compounds are highly soluble in water and dissociate completely, resulting in ions that are chemically stable under normal water conditions. Examples of polluting ions include nitrate, nitrite, perchlorate, bromate, arsenate and ionic mercury, for which the proposed guideline values for drinking water quality are quite low (in the range of μg/L to a few mg/L) owing to their carcinogenic effects or other risk factors to public health.

1. Background and Motivation

The contamination of drinking water sources with inorganic compounds is a matter of concern because of their potential negative impact on human health. Some of these compounds are highly soluble in water and dissociate completely, resulting in ions, which are chemically stable under normal water conditions. Examples of polluting ions are nitrate, nitrite, perchlorate,

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* E-mail: jgc@dq.fct.unl.pt

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bromate, arsenate and ionic mercury, for which the proposed guideline values for drinking water quality are in the range of μg L^{-1} (ppb) to few mg L^{-1} (ppm), due to their carcinogenic effects or other risk factors to public health (Richardson 2003, Petrović et al. 2003, Smith et al. 2002, Carraro et al. 2000). Some of these ions may also be present simultaneously in contaminated water in different range of concentrations, ranging from μg L^{-1} to mg L^{-1}.

Technologies available for the treatment of water contaminated with inorganic ionic compounds are based on physical, chemical and biological processes (Van der Bruggen and Vandecasteele 2003, Centi and Perathoner 2003, Kapoor and Viraraghavan 1997, Min et al. 2004, Coates and Anderson 2000). Within the first group, ion exchange (Gu et al. 2003) as well as membrane processes such as electrodialysis (Roquebert et al. 2000) and nanofiltration or reverse osmosis (Amy et al. 2003) are commonly used. In this type of processes, ions are concentrated rather than destroyed – a brine stream, containing high concentrations of ions is generated, which, in many cases, has to be treated before disposal.

Biological processes show potential for the effective and economical removal of inorganic ionic compounds from water. Several bacteria use ions as electron acceptors and organic or inorganic compounds as electron donors (e.g. ethanol, acetate, hydrogen gas). Most of the contaminated water streams are carbon limited, thus requiring addition of an electron donor, which concentration has to be carefully controlled. Indeed, in the presence of chemical oxidants, some organic electron donors can serve as precursors to the generation of novel contaminants (e.g. disinfection by-products), which have been recognized as potential carcinogens (Richardson 2003, Carraro et al. 2000). Furthermore, overdosing with organic electron donors that are readily biodegradable, can promote microbial growth in water distribution systems, thus requiring post-treatment to produce safe and biologically stable water. In addition, in most common biological process configurations, microbial cells come into direct contact with the water stream containing the pollutant. Therefore, the elimination of polluting ions by technologies that rely only on biological processes may induce secondary contamination of the treated water by cells, residual carbon source and/or metabolic byproducts.

In order to avoid secondary contamination, dosage of electron donors must be carefully controlled in response to fluctuations in ion concentration in the contaminated water, and this represents one disadvantage of the biological processes. In order to prevent the chemical contamination of water, hydrogen has been used as electron donor for the removal of ions form drinking water streams. However, its use requires special hydrogen supply devices due to safety reasons (Fang et al. 2002).

In this chapter, a new concept combining transport of ionic pollu tants through a dense ion exchange membrane with their simultaneous biodegradation avoiding secondary contamination of treated water, is presented.

2. The Ion-Exchange Membrane Bioreactor concept

The Ion-Exchange Membrane Bioreactor (IEMB) concept was firstly patented (Crespo et al. 1999, Crespo and Reis 2003) and published in the scientific literature (Fonseca et al. 2000) a decade ago. This concept integrates the transport of target ionic pollutants from an aqueous stream, through a dense ion-exchange membrane, to a receiving compartment where these ionic compounds are biologically reduced to harmless products (see Figure 4.1).

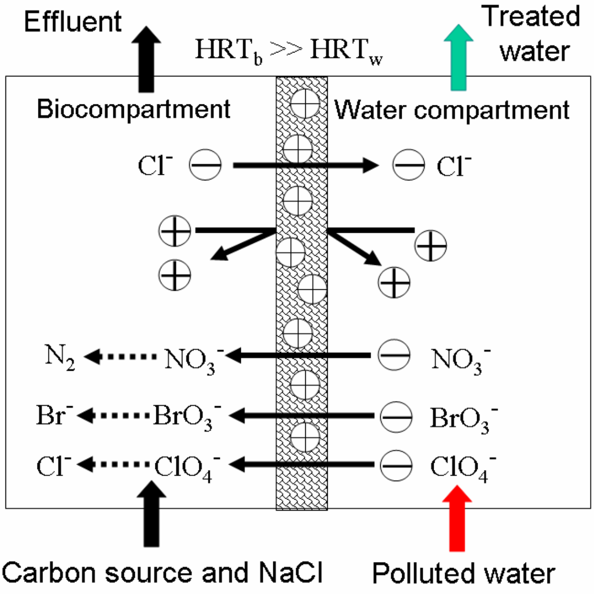

Figure 4.1. Schematic diagram of the ion transport mechanism in the ion-exchange membrane bioreactor (IEMB) for the case of target anionic pollutants.

In order to enhance the transport of the target ionic pollutants, an appropriate counter ion is added to the receiving compartment at sufficiently high concentration. This procedure makes possible to transport the target pollutant, even against its own concentration gradient. Once the ionic pollutant reaches the receiving compartment, it is converted by an appropriate microbial culture, which is able to reduce it under anoxic conditions. A non-charged and non-fermenting carbon source (used as electron donor) is fed to the receiving biological compartment in enough amounts, in order to assure that the complete biological reduction of the transported ionic solutes.

This concept is rather simple but it presents a series of extremely interesting features, which answer to most problems previously encountered in physical/chemical and biological treatment of charged pollutants:

1– The microbial culture able to reduce the target pollutant(s) is physically separated from the water stream by a dense, non-porous membrane, thus assuring that the treated water is never in contact with the microorganisms responsible for the bioconversion.
2– As the membrane selected is charged (fixed charge opposite to the charge of the solutes aimed to be transported) and non-porous, it is possible to assure that transport of metabolic by-products is extremely reduced, or even avoided if they present a charge identical to that of the membrane fixed functional sites.
3– If a non-charged carbon source is used to feed the biological compartment its transport to the water stream can be extremely reduced (as it will be discussed later).
4– It has been observed that, naturally, a biofilm develops on the membrane surface contacting the biological compartment. This biofilm acts as an active reaction zone, where most of the aimed reaction process takes place, also providing an additional barrier to the transport of excess carbon source. These four features assure that secondary contamination of treated water by microorganisms, metabolic by-products and excess carbon source can be avoided if an appropriate membrane and operating conditions are selected. Also, strict control of the rate of addition of carbon source, aiming to avoid a situation of excess or deprivation, is not necessary.
5– As the microbial culture can be defined by using appropriate selective pressure conditions, only target ionic pollutants are converted. As a consequence, the driving force for transport of ionic compounds from the water stream is only kept high for compounds that are biologically converted. This feature assures that the water stream is not unspecifically depleted from ions which may be important to maintain an adequate

water composition balance (as it happens in some physical water treatment processes, such as reverse osmosis).

6– As anoxic conditions are used in the biological compartment, the yield (and rate) of cell mass production is much lower than the one typical for aerobic membrane bioreactors, where biofilm development represents a significant problem in terms of resistance to mass transfer and membrane clogging and fouling. In the IEMB system, the biofilms that develop naturally at the membrane surface are rather thin, having a positive impact as an active reaction zone and barrier to carbon source loss through the membrane. Also, as the membrane is non-porous, clogging problems are not an issue. The IEMB system proved that it can be operated during long periods of time without flux decline and need for membrane cleaning.

7– The concentration of driving counter-ion (e.g., Cl^-) may be adjusted in order to assure a high transport rate of the target polluting ion (see Eq. (4.3)), even against its own concentration gradient. This feature is also particularly interesting if (e.g., due to some operating problem) the target ion accumulates in the biocompartment.

8– As the target ionic pollutants are converted to harmless products (e.g., N_2, Cl^-) and not just transferred and concentrated in a receiving compartment/stream, as happens in physical processes for water treatment, brine solutions are not produced, thus avoiding the need of their treatment and/or disposal.

9– The hydraulic residence time (HRT) can be adjusted independently in both water and biological compartments. Typically, very large residence times may be used in the biological compartment (remember that the biological reaction takes mostly place within the biofilm at the surface of the membrane), originating a waste stream with an extremely reduced volume when compared with the volume of treated water.

10–Finally, if the use of genetically modified microbial cultures is required, the IEMB offers a fully containment solution, avoiding their release to the environment.

3. Mathematical Modelling of Transport in the Ion-Exchange Membrane Bioreactor

With the goal of describing, predicting and optimizing the IEMB process performance, a mathematical model of the flux of target charged pollutant(s) from the water to the biocompartment is highly desirable. The ionic transport through charged membranes has been so far described in the literature by various approaches. They range from purely empirical (e.g. considering a formal analogy of the dependence of the flux of a target counter-ion, *i*, on its concentration $J_i = f(C_i)$ to a Langmuir-type function with two empirical parameters (Zheleznov et al. 1998) to complete descriptions of the transport process, considering possible kinetic coupling between different fluxes and friction between individual components as in the Maxwell-Stefan formalism (Wesselingh et al. 1995, Heintz et al. 1997).

Depending on the selected theoretical approach, knowledge of different parameters is needed, e.g. thermodynamic (dielectric constant, ion selectivity coefficients, concentration of fixed charges in the membrane), kinetic (diffusion coefficients for counter- and co-ions both in the two solutions and across the membrane) or structural. The latter approach has motivated the development of structure-kinetic models such as the charged capillary model (Cwirko and Carbonell 1990, Yang and Pintauro 2000) and the micro-heterogeneous model, in which the membrane is considered a medium comprising two homogenous phases – a gel phase and an electro-neutral solution phase (Zabolotsky and Nikonenko 1993). The obvious advantage of the structural models is that they are more physically realistic, while their main limitation stems from the necessity of using an increased number of parameters. Therefore a rigorous modelling has been demonstrated so far only for simple ion exchange membrane systems, in which all components and parameters can be well-defined and quantified. Moreover, when dealing with ionic separations in real complex multi-ionic solutions, a rigorous identification of all components and parameters to describe the transport process, besides being an extremely difficult task, often becomes also unnecessary from a practical point of view.

For dense ion exchange membranes, which are those used in the IEMB process, and dilute electrolyte solutions (usually a quite reasonable assumption at least for the polluted drinking water side), in which the individual ion activities ($a_i = \gamma C_i$) could be approximated by the respective molar concentrations C_i, since the ionic activity coefficients ($\gamma_{i\,i}$) are close to unity, inter-diffusion of counter-ions through the membrane has been most frequently described by the Nernst-Planck equation (Eq. (4.1)) without inclusion of a convection term (Sato et al. 1990, Ktari et al. 1993, Pourcelly et al. 1993, Jan et al. 1994, Picincu and Pletcher 1998), in which the symbols used have their usual meanings:

$$J_i = -D\left(gradC_i + z_i C_i \frac{F}{RT} grad\phi \right) \tag{4.1}$$

The value of the inter-diffusion coefficient, D, thus obtained is usually not constant, but depending more strongly of the transported ion of lower concentration (Helfferich 1962). Therefore D should be regarded as an "effective" or apparent parameter one since the membrane is considered as a homogenous phase, while in reality it is not. The membrane contains polar and non-polar micro-domains, which tend to cluster. The polar domains attract water and form a porous-like structure, which become permeable.

Further simplifications to Fick´s law (Eq. (4.2)) could be introduced for cases of self-diffusion, isotopic diffusion and trace counter-ion inter-diffusion (Helfferich 1962, Blaedel et al. 1969), in which the flux equation can be reduced to:

$$J_i = -D_i gradC_i \tag{4.2}$$

Since the effective diffusivity in inter-diffusion of a trace counter-ion against a counter-ion of much higher concentration is dominated by the diffusivity of the trace counter-ion (Helfferich 1962), the value of the inter-diffusion coefficient, D, approaches the value of the individual diffusion coefficient, D_i, of the trace counter-ion, i, for both the membrane and the two adjacent liquid boundary layers. Due to these fundamental reasons, building up on the general formalism for transport of trace counter-ions through ion exchange membranes proposed by Blaedel et al. (1969), a resistances-in-series steady-state transport model (Eq. (4.3)) considering a inter-diffusion of a trace polluting counter-ion (present in the water compartment) against an excess of a major bulk "driving" counter-ion (added to the biocompartment) was previously elaborated (Velizarov et al. 2000/2001, 2003).

$$J_i = \frac{\dfrac{C_{i,1}}{C_{a,1}{}^z} - \dfrac{C_{i,2}}{C_{a,2}{}^z}}{\dfrac{L}{P_{i,m} \times \left(\dfrac{Q}{a}\right)^z} + \dfrac{\delta_1}{D_{i,w} \times C_{a,1}{}^z} + \dfrac{\delta_2}{D_{i,w} \times C_{a,2}{}^z}} \tag{4.3}$$

where $C_{i,1}$ and $C_{i,2}$ are the molar concentrations of a target trace counter-ion i in the water and in the receiving IEMB compartment (bio-compartment), respectively noted as 1 and 2; $C_{a,1}$ and $C_{a,2}$ are the molar concentrations of the major (usually referred to as "driving") bulk counter-

ion in each compartment. Chloride is most commonly, but not always necessarily, the preferred driving counter-ion in case of transport of trace anionic counter-ion(s) because it is abundant, cheep and generally non-toxic in the mg/L to g/L concentration range; z represents the ratio between the valence of the target counter-ion (i) and the valence of the major bulk counter-ion (a); δ_1, and δ_2 are the thickness of the corresponding boundary layers next to the membrane surfaces at the water and bio-medium sides, respectively; L is the membrane thickness; $P_{i,m}$ is the membrane permeability to the target counter-ion; Q is the volumetric ion exchange capacity of the membrane and $D_{i,w}$ is the diffusion coefficient of the target counter-ion i in water at the IEMB process working temperature.

The development of Eq. (4.3) was based on various assumptions (described in detail in Velizarov et al. 2003), the most important of which is the assumption of a negligible osmotic water flux through the membrane and considering that the counter-ion transport rate is not limited either by ion exchange or any (bio)reaction phenomena. The second ratio in the driving force term (in the numerator of Eq. (4.3)) can usually be neglected because the concentration ($C_{i,2}$) of the target counter-ion in the IEMB biocompartment is decreased to a very low level due to its biological conversion, while the major counter-ion is kept at a relatively higher concentration ($C_{a,2}$) in this compartment.

For situations in which 1:1 electrolytes are the major compounds in the two compartments (e.g. NaCl in the biocompartment versus $NaNO_3$ in the water compartment) and assuming a perfect Donnan exclusion (no electrolyte "leakage" through the membrane) of the co-ions (Na^+), the model could be further simplified through approximating the bulk counter-ion (Cl^-) concentrations in the two compartments to the corresponding co-ion (Na^+) concentrations due to the charge balance restrictions in each compartment and negligible contributions of the trace counter-ion to these balances.

All parameters (except for the membrane permeability parameter, $P_{i,m}$) in Eq. (4.3) can either be independently measured or calculated through existing correlations, which makes the model use rather easy and straightforward if a "calibration" experiment is performed. The procedure consists of plotting experimentally obtained Donnan dialysis flux values against the driving force (the nominator of Eq. (4.1)) and determining the membrane permeability towards a target counter-ion from the slope of the resulting straight line under a set of given operating conditions. The membrane permeability parameter may be therefore viewed as a lumped parameter, since it accounts also for any possible effects on the transport of the target counter-ion, which are not explicitly recognized by the model. Since for all situations tested so far, the rate of the IEMB process has been found to be diffusion rather than reaction limited, the permeability parameter can be obtained through simple and rapid Donnan dialysis tests with identical water and receiving solution ionic compositions and not in actual IEMB operations, which is convenient from a practical point of view. After determining the P_m value, it has been demonstrated that the model can be successfully applied for predicting the flux of different target counter-ions in a number of IEMB process operations (Velizarov et al. 2000/2001, Matos et al. 2006, 2008a, 2009). Typical P_m values obtained for some oxy-anions in experiments with selected anion exchange membranes, performed under similar hydrodynamic conditions, are listed in Table 4.1.

TABLE 4.1. Typical experimentally determined membrane permeability values, P_m, for target anions through selected anion exchange membranes (adapted from Matos et al. 2008a)

Anion	**Permeability parameter, P_m ($cm^2\ s^{-1}$)**	
	Excellion I-200 (SnowPure, USA)	**Neosepta ACS (Tokuyama Soda, Japan)**
ClO_4^-	$9.7 \cdot 10^{-8}$	$3.6 \cdot 10^{-8}$
NO_3^-	$6.1 \cdot 10^{-8}$	$3.4 \cdot 10^{-8}$
BrO_3^-	$4.3 \cdot 10^{-8}$	$3.4 \cdot 10^{-8}$
SO_4^{2-}	$2.2 \cdot 10^{-10}$	$1.8 \cdot 10^{-12}$

As can be seen from Table 4.1, the permeability values determined correspond well to the properties of the two membranes. As expected, the ACS membrane presents a SO_4^{2-} permeability, which is two orders of magnitude lower than the value determined for the Excellion membrane. The ACS membrane is a mono-anion permselective membrane due to the presence of a thin, highly cross-linked surface modified layer with some negative charges, which causes higher rejection for multi-valent than for mono-valent anions, due to both steric (main effect) and electrostatic repulsion phenomena (Sata 1986, Saracco and Zanetti 1994).

It is interesting to compare the value obtained for nitrate permeability through Neosepta–ACS in these experiments ($3.4 \cdot 10^{-8}$ $cm^2\ s^{-1}$) in which the treated water stream had a very low salinity, typical for drinking water, to the value of $0.74 \cdot 10^{-8}$ $cm^2\ s^{-1}$ obtained for high salinity multi-ionic water used in a public oceanarium (Matos et al. 2009). The reduction of the apparent permeability of the membrane to nitrate in the second case might have occurred due to various effects, influencing both the driving force and the membrane properties under such high salinity conditions.

However, in each situation the model was able to correctly predict the real IEMB operation fluxes, if the corresponding pre-determined P_m values are used.

4. Removal of Nitrate, Perchlorate and Bromate for Drinking Water Production

Nitrate is often found in drinking water resources also contaminated with perchlorate (Logan and LaPoint 2002); however, while perchlorate is usually present at low concentrations (up to 100 ppb), nitrate is often found in much higher concentrations (in the ppm range). Nitrate can be biologically reduced to nitrogen gas ($NO_3^- – NO_2^- – NO – N_2O – N_2$), while perchlorate can be reduced to chloride ($ClO_4^- – ClO_3^- – ClO_2^- – Cl^-$).

The capacity of IEMB to remove these two ions at different range of concentrations was evaluated by feeding a polluted water stream containing 100 ppb of ClO_4^- and 60 ppm of NO_3^- at hydraulic retention times in the water compartment ranging from 1.4 to 8.3 h. Concentrations of both ions in the treated stream were reduced below the recommended levels of 4 ppb for ClO_4^- and 25 ppm for NO_3^- (Table 4.2). In these experiments, ethanol was used as electron donor in a diverse range of concentrations. The results showed that, when IEMB was operated under ethanol limitation, no increase of perchlorate and nitrate concentrations in the treated water was observed for up to 6 days, because the transport of these ions from the water compartment to the biocompartment was always favored by the higher concentration of Cl^- in the biocompartment. Therefore, if an unexpected disturbance in the ethanol supply occurs it does not affect the water quality for a reasonably long period of time, which is likely to be sufficient for the detection and correction of that operational problem. On the other hand, when an excess of ethanol in the biocompartment as high as 200 mg L^{-1} was used, ethanol concentration in the treated water stream was always below the quantification limit of 50 mg L^{-1} (Matos et al. 2008a). This behavior can be explained by the development of a biofilm on the surface of the membrane in contact with the biocompartment, which acts as an additional reactive barrier against ethanol transport. Therefore, using the IEMB it is possible to prevent secondary contamination of the treated water by excess of carbon source and, even more important, no strict control of electron donor is required.

The results presented in Table 4.2 were obtained at a water flow rate per membrane area (F/A) ratio of 3.1 L $m^{-2}h^{-1}$. Experiments were also performed to evaluate the IEMB process efficiency to treat higher amounts of polluted water per membrane area using model water contaminated with 100 ppb of ClO_4^- and 60 ppm of NO_3^-, but operated at different F/A ratios of 3.1, 7.7, 15.4 and 18.5 L m^{-2} h^{-1}. The results are presented in Figure 4.2. As expected, the concentrations of NO_3^- and ClO_4^- in the treated water were dependent from the F/A ratio and increased when increasing the water flow rate. In this specific case, the amount of water that can be treated, with the same membrane area, depends on the quality desired in terms of ClO_4^-, because NO_3^- was always removed from the water to a level much lower than the recommended values (e.g., 25 ppm by the EU).

TABLE 4.2. Concentrations of NO_3^-, ClO_4^- and BrO_3^- in the treated water and in the biocompartment of the IEMB fed with different contaminated drinking water streams at a flow rate per membrane area (F/A) ratio of 3.1 L m^{-2} h^{-1}

Contaminant	**Polluted water**	**Treated water**	**Biocom-partment**	**Anion flux, mg m^{-2} h^{-1}**	**Reference**
NO_3^- (mg L^{-1})	60	0.3	2.4	200	Matos et al. 2006
ClO_4^- (µg L^{-1})	100	3.6	<10*	0.3	
NO_3^- (mg L^{-1})	60	0.6	<0.1*	184	Matos et al. 2008b
BrO_3^- (µg L^{-1})	200	17.8	<10*	0.56	
NO_3^- (mg L^{-1})	60	0.3	<0.3	200	Velizarov et al. 2008
ClO_4^- (µg L^{-1})	100	3.6	<10*	0.3	
BrO_3^- (µg L^{-1})	200	18	<10*	0.6	

*Detection limit

Bromate is a disinfection by-product with carcinogenic properties that has to be removed from drinking water to concentrations below 10 or 25 µg L^{-1} (World Health Organization 1996). Bromate can be biologically reduced to bromide (BrO_3^-…Br^-) (Hijnen et al. 1999).

The IEMB process was tested for the treatment of a polluted water stream containing 200 µg L^{-1} of BrO_3^--and 60 mg L^{-1} of NO_3^- at a F/A ratio of 3.1 L $m^{-2}h^{-1}$ (Matos et al. 2008b) The concentrations of the two target anions, in the treated water stream, were reduced to 17.8 µg L^{-1} of bromate and 0.6 mg L^{-1} of nitrate in a short period of time after the start-up of the IEMB, and these values remained stable for more than 16 days (Table 4.2). In the biocompartment, nitrate and bromate were both reduced by an enriched microbial culture to values below their detection limits (10 µg L^{-1} for bromate and 0.1 mg L^{-1} for nitrate). Furthermore, nitrite was neither detected in the treated water nor in the biocompartment.

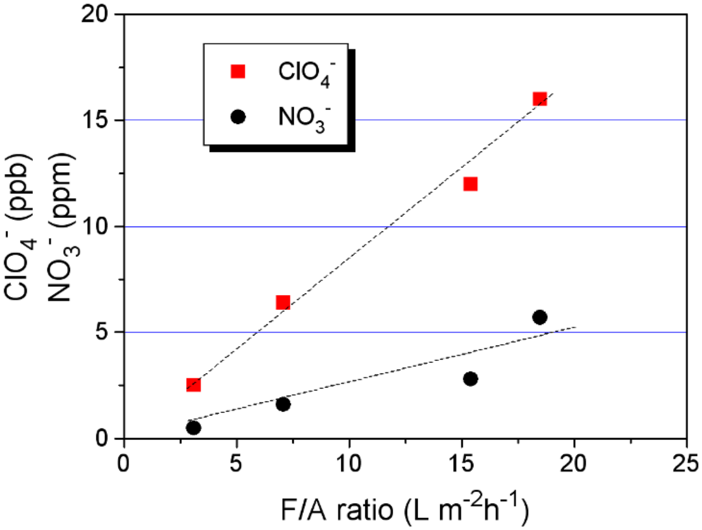

Figure 4.2. Concentrations of ClO_4^- and NO_3^- in model water contaminated with 100 ppb of perchlorate and 60 ppm of nitrate and treated by the IEMB at different water treatment rate (F) per unit area of membrane (A) ratios.

The enriched culture was used in batch tests with the same concentrations of bromate and nitrate as in the IEMB. The results showed that the biological reduction of bromate was much slower than that of nitrate (maximum specific reduction rates of 36.68 mg NO_3^- g^{-1} cell dry weight h^{-1} and 0.027 mg BrO_3^- g^{-1} cell dry weight h^{-1}, respectively) and only occurring after the complete reduction of nitrate. Since in the IEMB bromate and nitrate were not detected in the biocompartment, those two pollutants were likely removed in the biofilm formed on the membrane surface contacting the biocompartment. It was proposed (Matos et al. 2008b) that the reactive zone in the biofilm is probably composed by two contiguous regions: the region closer to the membrane surface associated with the nitrate/nitrite reduction; a second adjacent region, where bromate reduction would occur in the absence of the competing electron acceptor (nitrate).

Furthermore, operation of the IEMB for prolonged periods of ethanol limitation did not cause accumulation of nitrate and bromate in the treated water, showing that, as it was observed for the water contaminated with perchlorate and nitrate, the process could support fluctuations in the carbon supply without affecting the quality of the treated water.

Finally, the IEMB capacity to remove bromate, perchlorate and nitrate simultaneously present in polluted water was evaluated. Water contaminated with 100 ppb of ClO_4^-, 200 ppb of BrO_3^- and 60 ppm of NO_3^- was fed to the IEMB using a F/A ratio of 3.1 L m^{-2} h^{-1}. The three pollutants were simultaneously transported through the membrane from the water compartment to the biocompartment with fluxes controlled by their concentrations in the polluted water. In the biocompartment, a mixed microbial culture was able to biodegrade nitrate, perchlorate and bromate efficiently to nitrogen, chloride and bromide, respectively, in spite of the much higher availability of nitrate as an electron acceptor for the carbon source (ethanol in this case) oxidation. The concentrations of the three target anions, in the treated water stream, were reduced below the recommended levels (Table 4.2).

5. Extension of the Ion-Exchange Membrane Bioreactor Concept

5.1. REMOVAL OF NITRATE FROM SALINE WATER

The potential of the IEMB process for removal of target polluting anions from water with high salinity was tested for the case of nitrate, accumulated in water of oceanic aquariums. This water is of high salinity since it has to provide conditions that mimic as much as possible the real oceanic water composition. On the other hand, elimination of toxic nitrogenous metabolites such as nitrate is essential for maintenance of marine life and, therefore, this is an important concern of aquaria designs.

The removal of nitrate (or other anionic pollutants) from high salinity water streams through the IEMB concept represented two main challenges compared to the case of treating polluted drinking water streams. Firstly, in order to enhance the transport of nitrate through the membrane and prevent possible co-transport of other anions (which could be important for the ionic water balance required by fish) from the treated water, the concentrations of chloride and other anions in the receiving compartment (biocompartment) should be as high as their concentrations in the water compartment. However, as can be seen from Eq. (4.3), lower driving forces than those achievable in drinking water applications should be expected, because of the higher chloride concentration and correspondingly lower numerical values of the first term in the numerator. Secondly, the high salinity environment in the biocompartment might have had a negative impact on the nitrate-reducing activity of the microbial culture – an assumption that needed confrontation with experimental data in order to be accepted or rejected.

The performance of the IEMB process was investigated and compared to that of a Donnan dialysis system, in which the biocompartment was operating only as a receiving compartment (i.e. without adding microbial culture and ethanol to it). The results obtained are presented in Table 4.3. As it can be seen, if a sufficiently low HRT of the stripping solution in the receiving compartment is maintained, we may minimize the concentration of nitrate transported to this compartment through nitrate "wash-out", so a situation close to that obtained with nitrate bioreduction (or nitrate removed by reaction) could be imitated. These conditions were provided in experiment 3, in which the HRT in the receiving compartment was reduced to 1 h. As expected, this led to a significant reduction of nitrate accumulated in the receiving compartment and a corresponding increase in both flux ($J_{NO3}-$) and nitrate removal degree (η) was obtained.

The IEMB process clearly performed better in terms of waste effluent production from the boiocompartment, which was not only 15 times (HRT = 120) lower than in a Donnan dialysis process (HRT = 8, see experiment 2) allowing for the same degree of nitrate removal but, even more important, the biocompartment effluent was practically free of nitrate (~1 mg L^{-1}) due to its effective biodegradation in the biocompartment (experiment 4, Table 4.3). Thus, the IEMB is undoubtedly a more sustainable alternative to Donnan dialysis in terms of their environmental impact. The results showed that the higher salinity in the biocompartment did not affect negatively the nitrate-reducing capacity of the mixed microbial culture, most probably due its autoselection under these conditions. The IEMB process was also two times more productive in terms of the amount of water treated per membrane area, 8 L m^{-2} h^{-1} compared to 4 L m^{-2} h^{-1} due to the lower HRT = 4 h (experiment 4) versus HRT = 8 h in Donnan dialysis (experiment 2). The higher IEMB productivity is due to an increased driving force for nitrate transport in the IEMB process (nitrate is consumed on its arrival into the biocompartment) compared to Donnan dialysis, in which nitrate is accumulated in the receiving compartment.

It is interesting to mention that the same aquarium water may be used as receiving solution (compare the results of experiments 1 and 2) which reduces the complexity of the process and the need to prepare dedicated stripping solutions.

It was recently demonstrated (Matos et al. 2009) that the IEMB process was able to remove naturally accumulated nitrate with a concentration of 251 mg L^{-1} to about 27 mg L^{-1} (experiment 5 in Table 4.3) from water taken from the Lisbon public oceanarium, which is Europe's largest oceanarium. Such a high degree of nitrate removal was obtained by increasing the HRT in the water compartment to 28 hours. Therefore, the corresponding water treatment rate (0.9 L m^{-2} h^{-1}) was also lower than those set in experiments 1, 2 and 3 (8 L m^{-2} h^{-1}) and in experiment 4 (4 L m^{-2} h^{-1}), respectively.

TABLE 4.3. Donnan dialysis (experiments 1 to 3) and IEMB (experiments 4 and 5) treatment of aquarium water from the Oceanarium of Lisbon. The membrane used was Neosepta ACS. The feed water (FW) was water after fish cultivation with an average nitrate concentration of 327 mg L^{-1} (for experiments 1 to 4) and 251 mg L^{-1} (experiment 5)

Exp. No.	**Stripping solution (ss)**	**HRT rw h**	**HRT ss h**	**Feed outlet mg NO_3^- L^{-1}**	**Receiver outlet mg NO_3^- L^{-1}**	**η %**	**$J_{NO_3^-}$ g m^{-2} h^{-1}**
1	0.5 M NaCl	8	8	193 ± 12	119 ± 15	41	0.52 ± 0.04
2	Fresh Oceanarium water	8	8	203 ± 9	119 ± 12	38	0.48 ± 0.03
3	0.5 M NaCl	8	1	119 ± 7	~12	64	0.80 ± 0.02
4	Used Oceanarium water + microbial culture + ethanol	4	120	222 ± 28	5 ± 2	32	0.81 ± 0.05
5	Fresh Oceanarium water + microbial culture + ethanol	28	120	27 ± 4	2.2 ± 0.3	89	0.19

Overall, the IEMB proved to be a selective technology for nitrate removal, while preserving the original composition of the water with respect to other ions. This is an advantage of the IEMB concept, since it allows for reutilization of the treated water by the aquarium, thus decreasing the need for water renewal and the frequency of wastewater discharge. The results obtained are promising since they suggest that target trace pollutants could be efficiently removed from both low and high salinity multi-ionic water streams, which substantially increases the range of the IEMB concept applications.

5.2. REMOVAL OF IONIC MERCURY FROM WATER STREAMS

One of the most severe water contamination problems, relevant for both drinking water resources and industrial and/or domestic liquid waste streams are associated with their high eco-toxicity if heavy metal pollutants are present. Amongst them, mercury is the heavy metal with the highest toxicity. It has been found in potentially harmful concentrations in numerous water systems due to natural or industrial pollution sources, usually in the cationic form (Hg^{2+}). Therefore the maximum possible contaminant level set by the WHO for mercury in drinking water is 1 ppb.

Heavy metals are commonly removed from drinking water supplies via membrane separation, ion exchange or adsorption processes, where the disposal of the associated concentrate solution produced from either the retentate, or from adsorbent regeneration, is one of the primary drawbacks. One possible way of overcoming these problems is through the IEMB concept, using in this case a cation exchange membrane and hydrogen or sodium cations as the driving counter-ions for ionic mercury counter-transport to the biocompartment as schematically illustrated in Figure 4.3.

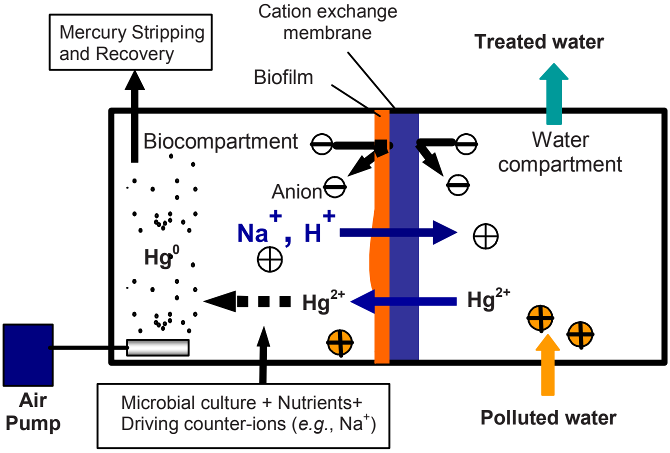

Figure 4.3. Ion exchange membrane bioreactor concept for treatment of water contaminated with ionic mercury.

The IEMB potential for the removal of $Hg^{2+}$was investigated. It was found that the key parameters for achieving Hg^{2+} removal involve the choice of an appropriate cation exchange membrane (Oehmen et al. 2006, Velizarov et al., 2008) and the enrichment of a suitable microbial culture for Hg^{2+} biological reduction to elemental mercury (Oehmen et al. 2009). The transport of Hg^{2+} was evaluated for a number of commercial cation exchange membranes in a series of batch and continuous-flow tests. The Fumatech FKE membrane exhibited a reasonably high ionic mercury flux and, at the same time, it is relatively inexpensive when compared to Nafion-type membranes and was therefore selected for application in the integrated system.

Before the IEMB operation, optimization of the biological conditions were performed through experiments with pure and mixed cultures of microorganisms, which were tested with different carbon sources in order to select a suitable microbial culture. A mixed culture enriched with glucose as the carbon source displayed a high rate of Hg^{2+} removal, which was comparable to that achieved by pure cultures, with the advantage that a simpler enrichment procedure can be employed (not requiring aseptic conditions). Following the culture and carbon source selection, the IEMB was set up. The process performance was evaluated for a time period of 35 days at two different water treatment rates, changing from a high (15 L m^{-2} h^{-1} during the first 12 days) to a ten times lower one (1.5 L m^{-2} h^{-1}) until the end of the experiment. The results of this test are presented in Figure 4.4.

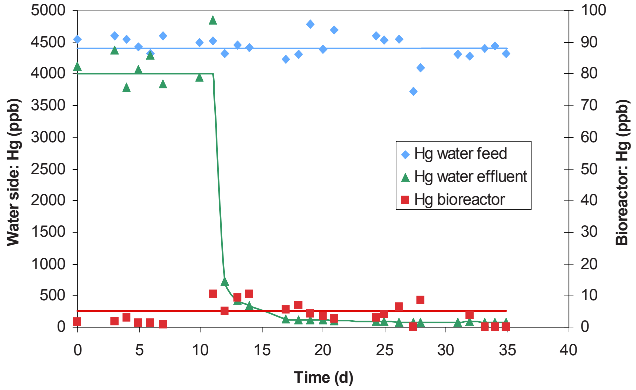

Figure 4.4. IEMB process performance for removal of ionic mercury from a contaminated water stream. Initial ionic mercury concentration = 4.5 ppm; Membrane used: Fumatech FKE. After 12 days of continuous operation, the water flow rate per square meter of membrane was decreased from 15 L m^{-2} h^{-1} to 1.5 L m^{-2} h^{-1} until the end of the experiment.

As can be seen in Figure 4.4, removal of Hg^{2+} from water was high (>98%) for the lower treatment rate, while the Hg^{2+} level in the biocompartment was kept below 10 ppb due to reductive biotransformation of mercuric ions to elemental mercury and its subsequent stripping to the gas phase through aeration (major effect) and partial adsorption to the biomass. It was also found out that if the concentration of ionic mercury in the treated water is low (<100 ppb), the membrane initially serves as a sink of mercury before its appearance in the biocompartment. This is most probably due to the high complex-formation tendency of mercury and, therefore, its strong interaction with the ion exchange functional sites of the membrane. Thus, after the process start-up there is an ionic mercury concentration-dependent period, during which its removal is due to adsorption in the membrane rather than due to its biological reduction to elemental mercury. Although not affecting the overall ionic mercury removal efficiency from the treated water, it is worth considering this observation since it might affect the process design (e.g., in terms of inoculating and starting the biocompartment operation only after the ionic mercury break-through into this compartment.

In conclusion, there is a potential for extending the IEMB process concept for a wide range of other cationic heavy metals, in addition to Hg, through suitable optimization of the biocompartment conditions. In any case, it has to be kept in mind that since the toxicity of a heavy metal is due to the element itself rather than the ionic form, in which it is present in water, the strategies that have to be followed are different from the case of nitrate, perchlorate and bromate, for which the bioreduction products are non-toxic. When dealing with heavy metals, their removal from the biocompartment has to be done by other means such as, for example, air stripping (in case of Hg) or precipitation and or adsorption in case of treating non-volatile heavy metals (e.g., Cr and Ni).

5.3. REMOVAL OF ARSENATE FROM WATER STREAMS

Arsenic is generally present in polluted drinking water sources as negatively charged arsenate ($H_2AsO_4^-$) or arsenite ($H_2AsO_3^-$). However, contrary to the cases of nitrate, perchlorate and bromate neither the biologically catalyzed reduction of arsenate to arsenite nor the oxidation of arsenite to arsenate are feasible since they do not result in the formation of innocuous products. The arsenic-related toxicity is due to the metal itself and not due to the oxy-anionic form in which it is present. Therefore a new integrated process was developed (Velizarov et al. 2008) replacing the usual application of a mixed microbial culture in the receiving compartment by co-precipitation with iron or aluminium as a way of achieving arsenic removal in the receiving compartment solution (Figure 4.5). Obviously, this process cannot be any longer referred to as an IEMB but, perhaps, more correctly as an ion exchange membrane reactor (IEMR).

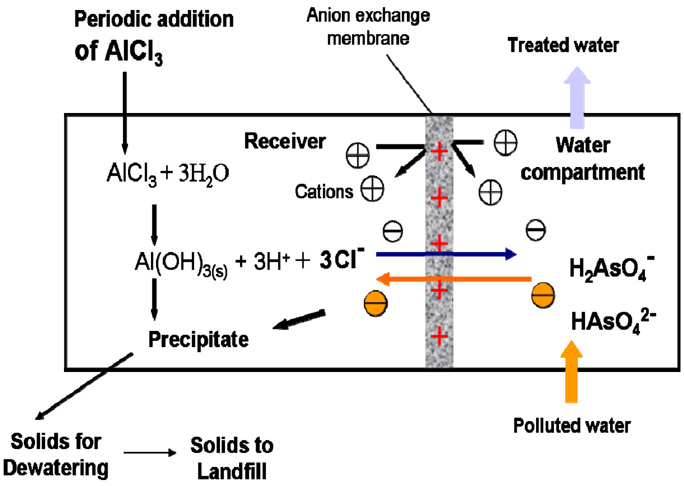

Figure 4.5. Integrated anion exchange membrane / coagulation process for the removal of negatively charged arsenic-containing species from a polluted drinking water stream.

The arsenic co-precipitation process with $FeCl_3$ or $AlCl_3$ is usually considered as one of the most feasible and economically adequate since these chemicals are easily available and relatively cheap (Lakshmanan et al. 2008). The disadvantages of this process are mainly related to the need for direct coagulant addition to the polluted water stream, thus leading to possible secondary contamination of the treated water with residual levels of iron or aluminium. The EU-Council (1998) recommends a limit of 200 ppb for both Fe and Al in drinking water. The coagulation process is also rather sensitive to pH and requires its adjustment in many cases. Therefore its integration with an anion exchange membrane transport of the pollutant could solve these problems.

The main advantage of the integrated process is in avoiding secondary contamination of the treated water by isolation of the drinking water stream by an anion exchange membrane barrier, through which arsenic (in the form of arsenate and/or arsenite) diffuses to a receiving compartment, to which the coagulant and, if necessary, pH-controlling reagents can be periodically added to guarantee the most appropriate conditions for arsenic precipitation.

Moreover, the coagulant is completely utilized as a chemical precipitant (e.g., Al^{3+}) and as a source of counter-ions for arsenate transport (i.e. Cl^-), simultaneously achieving both purposes with the addition of only one chemical (Figure 4.5). The driving force for arsenic transport is maintained at its maximum possible level due to arsenic precipitation by the coagulant added to the receiving compartment. Other potential advantages of this process are a significantly reduced volume of the arsenic-containing brine solution and increased time duration before its discharge, due to the use of a closed-circuit receiving compartment.

The results obtained so far showed that this integrated process can remove efficiently arsenate present in drinking water supplies, even at a water treatment rate per square meter of membrane as high as 40 L m^{-2} h^{-1}. The treated water thus obtained can be further blended with water from an arsenic-free source in order to conform with the current EU limit of 10 ppb of arsenic in drinking water (EU-Council 1998). If this option is not possible due to lack of arsenic-free water or other reasons, the flow rate through the water compartment of the anion exchange membrane module can be reduced in order to obtain arsenic levels below the 10 ppb limit. In this case, however, a lower water treatment rate per square meter of membrane is achievable (2–5 L m^{-2} h^{-1}).

A long-term operational stability test was also performed. For this test a water treatment rate of 2.4 L m^{-2} h^{-1} was set and $AlCl_3$ was used as the coagulant in the stripping compartment. The results are presented in Figure 4.6.

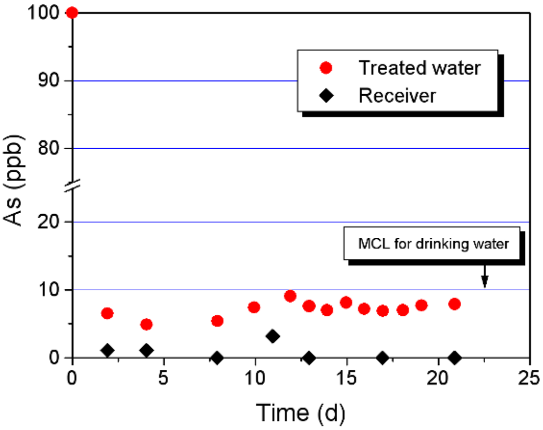

Figure 4.6. Soluble arsenic concentration in the receiver compartment and effluent of the water compartment with daily addition of $AlCl_3$ to the receiver compartment over a 3 weeks operational stability test (Initial As concentration in polluted water = 100 ppb). Drinking water Maximum Contaminant Level (MCL) = 10 ppb. Membrane used: Ionics AR204-UZRA. The water treatment rate per square meter of membrane was 2.4 L m^{-2} h^{-1}.

As can be seen from Figure 4.6, very good performance of the system was observed for more than 20 days of continuous operation. During all this period, the arsenic concentration in the treated water was always below the 10 ppb limit. It is even more notorious that, the system was operating for the last 2 weeks of the experiment without a necessity for $AlCl_3$ addition, most probably, due to presence of still sufficient amounts (added in the beginning of the process) for arsenic precipitation. This can be viewed as a strong advantage of this new process, especially, if operated in remote areas, in which the operator presence and the need of interventions could be reduced significantly.

6. New Approaches for Integrated Modelling of the Ion-Exchange Membrane Bioreactor

The main merit of the mechanistic model developed (Eq. (4.3)) is its simplicity and straightforward rationalization and interpretation of the data obtained. This is due to the correct identification of the main driving force for transport of a target counter-ion, which is the deviation from its Donnan equilibrium condition between the two IEMB compartments. The model also allows for an easy evaluation and comparison of the contributions of the three main possible resistances to the transport of a target counter-ion from the treated water to the biocompartment. On the other hand, an inherent disadvantage of the model is its limited range of validity. Therefore it can be applied only for a system operating under conditions, for which the model assumptions are satisfied. Any extensions to other, even similar systems, may lead to serious deviations from the model predictions.

For situations, in which the building assumptions used in developing the mechanistic transport model are not satisfied (particularly if the biological reactions kinetics are influencing the IEMB process rate), extensions to the model through introducing additional terms (e.g., a reaction term) are required. Another possibility in such cases is to use different approaches, such as purely statistical or hybrid modelling in order to obtain relations between input and output data sets which describe the IEMB process behavior.

Hybrid models combine mechanistic models with statistically based models in a single arrangement. This approach could be rather useful to obtain a more general IEMB process model since prior knowledge about the system can be incorporated. The statistically based (non-parametric) fraction may account for effects not included explicitly in the mechanistic model. Moreover, the parametric model could control the extrapolation of the hybrid model to regions which lack in calibration data. Hybrid models have been classified as parallel or serial (Thompson and Kramer 1994). For the case of the IEMB process, a hybrid parallel configuration appears to be a better choice. A non-parametric Projection to Latent Structures (PLS) type of modelling has been selected in order to cover the information that need to be added to the mechanistic model. PLS is a common technique used to reveal linear relations between the data, by maximizing the covariance between the X matrix (inputs) and a Y (output). It is often described as the major regression method, since it is a robust technique that can handle with correlated and multiple variables (Wold et al. 2001).

For the IEMB process, the use of the PLS approach translates into identifying relations between experimentally determined fluxes of target counter-ion(s) and a large set of different process operating conditions such as pH, temperature, concentrations of pollutants and other compounds, hydrodynamic conditions, etc. The PLS thus trained with IEMB process data may estimate the mechanistic model residuals. Therefore, hybrid model structures could combine the prediction of the mechanistic model and the PLS model in a single output.

This approach has the advantage of requiring less data than purely statistical models. Our preliminary results are rather encouraging demonstrating that the hybrid model is able to predict the system performance in simultaneous removal of perchlorate and nitrate from polluted drinking water streams over a broad range of operating conditions, including biological reaction-limited situations, and can therefore be used for further optimizing the IEMB process performance (Ricardo et al. 2009).

7. Up-Scaling Challenges and Process Economics

The practical implementation of the IEMB process has been constrained so far by the limited market offer of ion-exchange membranes suitable for this type of application. There are a number of manufacturers that supply ion-exchange membranes, typically used industrially for electrodialysis processes, but their properties and performance have not been specifically optimized for meeting the IEMB process operating conditions which require a low membrane resistance to the transport of target charged compounds (as in electrodialysis), and also a relatively high membrane resistance to transport of the carbon source from the biological to the water compartment (a unique feature of the IEMB process). Moreover, the cost per unit area is largely above the cost of membranes for competing processes, such as nanofiltration (NF) and reverse osmosis (RO). The cost of ion-exchange membranes is in the range of 3–5 times the cost of NF and RO membranes, which represents at this stage a serious problem for the full scale implementation of IEMB systems.

Under the actual circumstances, the cost for membrane equipment represents between 50% and 60% of the total capital costs of an IEMB plant, while membrane replacement represents between 60% and 70% of the total operating and maintenance (O&M) costs. A simple sensitivity analysis of the cost structure of this process makes clear that the IEMB system will become competitive once the associated membrane costs drop by a factor of 2 (half of the actual cost). It should be noticed that this analysis is rather conservative because, some of the costs strongly associated with other competing technologies, namely the costs for brine disposal and energy, are expected to increase significantly in the next decade, which will position the IEMB process in a favorable situation.

At this moment, the high cost of ion-exchange membranes is not the only significant limitation. The fact that these membranes are industrially produced only with a flat geometry (for electrodialysis processes), limits the compactness of the membrane reactor and the control of the fluid dynamic conditions in the water compartment (remember that the controlling boundary layer is most frequently at the membrane/water interface). Therefore, the development of ion-exchange membranes with hollow fibre geometry would make possible the design of IEMB systems extremely compact and also with an excellent control of the water fluid dynamics, by circulating this stream inside the lumen of the fibres.

In the absence of suitable hollow fibre ion-exchange membranes, plate-and-frame configurations have to be used (similar with available equipments for electrodialysis), designed and optimized for full scale operation. The most significant aspect that has to be taken into consideration is the design of the flowing channels in both the biological and water stream sides, in order to avoid clogging in the biological channel and provide adequate fluid dynamic conditions in the water channel. The design of dedicated and appropriate spacers to be introduced in the water channel, assuring reduced mass transfer resistance, a low pressure drop and reduced energy input, is of major importance.

Nevertheless, it should be kept in mind that up-scaling of this process for the case of treating oxyanions (such as nitrate, perchlorate and bromate) is rather simple and straightforward because the reactor operates under anoxic conditions. Therefore, usual issues associated with the up-scaling of aeration conditions are not required in this case. The only major issue that has to be taken into consideration, when up-scaling the process, is the control of the fluid dynamic conditions in the water compartment and the corresponding pressure drop.

8. IEMB Development and Market Prospectives

The cost of treatment of drinking water supplies using the IEMB process has been discussed and it seems clear that the success of this technology will strongly depend on the possibility of using high performing low-cost ion-exchange membranes with a hollow fibre geometry. The analysis of the actual costs trend suggests that a technology that avoids the formation of brine solutions and associated disposal issues and requires a reduced input of energy, when compared with the technological alternatives available, has certainly a high potential for implementation in the near future.

Additionally, the water quality that the IEMB process may assure – no direct contact with the microbial culture involved, decreased risk of secondary contamination of the treated water, well-balanced water in terms of its ionic composition without depletion of desirable ions – may not translate at this moment with the actual legislation into a tangible value. However, it is sure that the concern for water with high quality, which assures the best requisites in terms of public health, will become of major concern for consumers and public opinion and, ultimately, to legislators. The IEMB process, due to its characteristics and features, is certainly among the water treatment technologies that can respond effectively to this concern.

Finally, it should be referred that the IEMB and the extensions of this concept, have been applied so far to the treatment of drinking water supplies (and high salinity water media). However, this concept may be easily extended to other domains of application where the selective removal (or recovery) of a target ion is required, without affecting or deteriorating the chemical balance of the original matrix. Potential applications in the food industry are obvious (e.g., removal of nitrate in the production of purées for infants) as well as in the pharmaceutical industry (e.g., for selective desalination of media).

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TREATMENT OF COMPLEX SYSTEMS – ADVANCED OXIDATION PROCESSES

THOMAS W. CHAPMAN*
University of Wisconsin-Madison (U.S.A.) and Centro de Investigación y Desarrollo Tecnológico en Electroquímica, Querétaro (MÉXICO)

Abstract. Many water streams, both wastewater effluents and drinking-water sources, contain pollutants that cannot be removed or destroyed by conventional physical or biological treatment processes. In such cases it is necessary to seek alternatives. One approach is to destroy the pollutant by application of a strong oxidizing agent. Chlorine is one candidate reagent, but it can produce undesirable reaction products, and residual chlorine can be toxic to aquatic life. Ozone is also used, but it is expensive, and its low solubility in water limits process efficiency. Another category of oxidation processes has been developed in recent years based on the oxidizing strength of hydroxyl radicals. Other processes that involve electrochemical treatment or ultraviolet radiation have received attention. This chapter describes some of these processes, particularly those using peroxide and catalyzed by iron ions in the so-called Fenton reaction (Fenton 1894). Modifications and enhancements of the Fenton process include combinations with UV radiation, semiconductor catalysts, and electrolysis. It has been found that such combinations are necessary and appropriate in order to achieve satisfactory water purification.

1. Introduction

Because of the global expansion of industrial activity as well as population growth pristine sources of drinking water have become more and more rare. For most consumers their water supply involves use of recycled or reclaimed water, either from underground sources or surface streams.

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* E-mail: chapman_tom@yahoo.com

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Unfortunately, most of those sources are contaminated, more or less, with a great variety of organic and sometimes inorganic pollutants that can be dangerous to public health. For example, many chemicals that have found their way into the water cycle are known or suspected to be carcinogenic or contributing to other medical problems such as endocrine disruption. Thus, it is imperative to remove or destroy those trace contaminants.

Although conventional physical processes, such as adsorption or precipitation, can remove the bulk of pollutants from water, and biological treatment is sometimes effective, low levels of many chemicals can persist. Thus, it is necessary to consider more extensive chemical treatment of wastewater discharges and drinking-water supplies. The most common strategy for chemical destruction of trace pollutants in water is to apply chemical oxidation, which can also be effective in destroying biological contaminants. In particular, aeration and chlorine or chlorine-based oxidants are often used. Unfortunately, these processes are not effective for destroying persistent organic chemicals present in low concentrations. For that reason researchers and engineers have been actively seeking more efficient water-treatment processes that can remove dangerous chemicals from water, and many such processes may be classified as *advanced oxidation processes* (AOPs). This chapter describes some of the AOPs that have received the most attention. An excellent source of more detailed information is the monograph, *Advanced Oxidation Processes for Water and Wastewater Treatment*, edited by Simon Parsons and published by IWA Publishing in 2004 (Parsons 2004). This monograph presents not only technical descriptions of the candidate processes but also the results of large-scale testing with cost estimates.

2. Oxidation and Candidate Oxidants

The ideal objective of oxidation is the complete destruction of trace organic pollutants, or *mineralization*. That is, all of the organic molecules would be converted to carbon dioxide and water by the oxidation process. Achieving such a goal is nearly impossible in most cases because of equilibrium and rate limitations, not to mention economics. The first oxidant to consider would be oxygen in the air, used in an *aeration* process. Although aeration is effective in promoting biological treatment, the slow reaction kinetics of molecular oxygen limits its efficiency for treating organic pollutants. The next most common oxidant in use is chlorine, either in it elemental form or as hypochlorite, chlorine dioxide, or other related forms. Chlorine is of course effective in destroying bacteria in the water and provides protection during storage and distribution of drinking water, but with other chemicals mineralization is not achieved. In fact, it has been found that products of chlorination, e.g., chlorinated hydrocarbons, may be more dangerous that the original pollutants. Also, the fate of other elements, such as nitrogen, phosphorus, sulfur, etc., needs to be considered in analyzing the chemistry of a treatment process. Thus, we are forced to seek other candidate oxidants and to study their detailed behavior in any specific application.

The word “oxidation” has at least two meanings. First, it can simply imply reaction with oxygen, producing oxides. In the more fundamental and general chemical sense, it is used to denote the removal of electrons from a target, often causing the molecule to decompose. Thus, good oxidizing agents are strong attractants for electrons. One way to identify theoretical oxidizing strength is to look at the oxidation potential associated with particular half-cell reactions, i.e., reactions that involve the electron as a reactant. Many of these can be measured in electrochemical experiments, and others can be calculated indirectly from related thermodynamic data. Table 5.1 gives a list of candidate oxidants with their standard half-cell potentials, which are reported relative to the standard hydrogen electrode. More positive potential is indicative of a stronger tendency to attract electrons.

In Table 5.1 one can see that, from equilibrium thermodynamic considerations, chlorine is a bit stronger than oxygen as an oxidizing agent, but hypochlorite and chlorine dioxide are less strong. These latter two have come into favor in common water-treatment practice because of ease of handling and other advantages. A significant problem with the use of chlorine is that it often forms chlorinated hydrocarbons rather than yielding complete mineralization. Furthermore, those reaction products may be more toxic and hazardous than the original pollutant.

Oxygen is less favored than chlorine for water purification because it reacts much more slowly that the chlorine chemicals. Also, aeration does not offer much residual protection aside from being necessary for aquatic life. The effectiveness of oxygen, specifically from air, is enhanced by raising the temperature and pressure in the treatment process, in so-called *wet-air oxidation* (Mishra et al. 1995). Although that reagent is essentially free (except for energy costs of compression and heating) and those conditions speed the reaction rates, the major negative is accelerated corrosion of pumps and contacting equipment. A more popular and common alternative is to use hydrogen peroxide, which is relatively inexpensive, available, and easy to handle. Also, its effectiveness can be enhanced by combination with a catalyst.

TABLE 5.1. Electrode potentials of candidate oxidizing agents. More positive potential indicates a stronger tendency to extract electrons. (Extensive tables of such reaction potentials are available in standard references, such as the *CRC Handbook of Chemistry and Physics* (Lide 2010))

Oxidant	**Reduction reaction**	**Potential (V@25°C)**
Peroxide (alk.)	$H_2O_2 + 2e^- \rightarrow 2OH^-$	0.87
Hypochlorite (alk.)	$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	0.90
Chlorine dioxide	$ClO_2 + e^- \rightarrow ClO_2^-$	1.15
Oxygen (acid)	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
Chlorine	$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.39
Hypochlorite (acid)	$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O$	1.49
Permanganate	$MnO_4^{-2} + 4H^+ + 2e^- \rightarrow MnO_2 + 2\ H_2O$	1.68
Peroxide (acid)	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.76
Ferrate (acid)	$FeO_4^{-2} + 8H^+ + 3e^- \rightarrow Fe^{+3} + 4\ H_2O$	2.20
Hydroxyl radical	$2OH\bullet + 2H^+ + 2e^- \rightarrow 2H_2O$	2.80
Ozone	$O_3 + 2H_2O + 4e^- \rightarrow 4OH^-$	2.87
Electrons	Extracted at an anode	+++

Table 5.1 indicates other candidate oxidants that are in principle much stronger than oxygen or chlorine. Aside from permanganate and ferrate, we find ozone and hydroxyl radical. Those two will be discussed in later sections of this chapter. The problems with permanganate are that it is rather expensive and somewhat more difficult to apply than the fluid reactants. Its iron analog ferrate is intriguing, but it suffers from the same drawbacks, and it is more difficult to synthesize (Lee et al. 2009). The other "reactant" listed at the bottom of Table 5.1, electrons extracted by a positive anode, will also be considered below. In principle, an anode in an electrochemical cell can absorb electrons at an arbitrarily high potential. In practice, however, other reactions from the aqueous phase, such as massive evolution of oxygen, will occur and depolarize or block the anode surface, limiting the effective anodic potential and preventing a desired oxidation from proceeding.

In considering a process for oxidizing a target organic pollutant one must recognize that the driving force for the overall reaction depends also on the half-cell potential for oxidation of the target because it is the difference between that potential and the half-cell potential of the oxidant that constitutes the driving force for reaction. That difference is proportional to the free-energy change for the overall reaction, and thus it indicates the thermodynamic tendency for the reaction to proceed. Table 5.2 gives a list of potentials for simple representative organic oxidations. It is seen that all of those shown are more negative than the potentials for any of the oxidants given in Table 5.1. Thus, all of these organics should be susceptible to oxidation by any of the oxidants in Table 5.1. Unfortunately, half-cell potentials are not available for most of the more complex target substances appearing in water, and the reactions of those substances must go through many successive steps. One must remember also that the potentials shown in Tables 5.1 and 5.2 are for standard-state conditions, i.e., a unit activity (molality) and 25°C. The driving force as well as the kinetics of any particular oxidation reaction will be diminished at lower concentrations of the reactants.

TABLE 5.2. Electrode potentials of some representative oxidation reactions (Lide 2010)

Simple organics	**Oxidation reaction**	**Potential (V@25°C)**
Methane	$CH_4 + H_2O \rightarrow CH_3OH + 2H^+ + 2e^-$	0.59
Oxalate	$C_2O_4^{-2} + 2H_2O \rightarrow 2CO_3^{-2} + 4H^+ + 4e^-$	0.48
Methanol	$CH_3OH \rightarrow HCHO + 2H^+ + 2e^-$	0.23
Formaldehyde	$HCHO + 2H_2O \rightarrow H_2CO_3 + 4H^+ + 4e^-$	−0.05
Formic acid	$HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$	−0.20

Beyond the thermodynamic considerations indicated by the half-cell potentials, which determine the tendency for a reaction to occur, other practical factors must also be weighed. Those involve rates of reaction under actual operating conditions as well as by-product identification and economics. All of these are impacted by factors such as oxidant solubility, reactor design, mixing conditions, mass-transport rates, reaction kinetics, and reaction selectivity. Thus, any particular water-treatment process involves all of the considerations that arise in the design and control of industrial chemical processing but under more challenging conditions because of low concentrations, varying feed conditions, and stringent cost limitations.

3. Ozone Oxidation of Trace Organics in Water

It can be seen in Table 5.1 that one of the stronger candidate oxidizing agents is ozone, and accordingly it has been used in water treatment and other applications, primarily for disinfection because it is effective in killing bacteria. Because of its high oxidation potential one would expect it to be similarly effective in destroying toxic organics. It is instructive to review the quantitative engineering factors that impact its ultimate utility.

Ozone, a highly reactive gas, cannot be stored for any significant time. Thus, it has to be produced on-site just as it is to be applied. Its synthesis involves passing air or oxygen through a high-voltage electric discharge. This process produces only a low concentration in the gas phase, up to 8% in pure oxygen but only 3% in air. Furthermore, the solubility of ozone in water is rather limited so delivery to an aqueous target molecule can be a challenge. Therefore, design of an ozone process for water treatment requires careful engineering analysis.

To serve as a guide to such engineering analysis and design, Yeung developed a computer model of gas-liquid reactors that involve absorption of a reactant from the gas phase, such as ozone, into a liquid where it reacts with a non-volatile solute, the target pollutant (Yeung 1981, Yeung and Chapman 1986). The model, which describes countercurrent contactors as well as stirred reactors and bubble columns, accounts for the gas-phase mass-transfer resistance as well as the diffusion and reaction of the oxidant with the target in the liquid-phase boundary layer and in the bulk liquid. The model predicts the absorption efficiency of the gaseous reactant as well as the conversion of the substance in the liquid phase. This requires identification of numerous parameters, including physical mass-transfer coefficients, solubility, and the homogenous reaction-rate constant as well as the operating conditions and geometrical factors. Two of the dimensionless combinations of the parameters that determine reactor performance are:

$$K_1 \equiv \frac{k_L aSH}{L} \tag{5.1}$$

and

$$K_2 \equiv \frac{k_2 C_{B,in} D_A}{k_L^2} \tag{5.2}$$

where k_L is the liquid-film mass-transfer coefficient, α is the interfacial area per unit volume, S is column cross-section, H is column height, and L is the volumetric flowrate of liquid. The parameter k_2 is the second-order rate constant for reaction between oxidant A and liquid-phase substrate B, D_A is the liquid-phase diffusion coefficient of A, and $C_{B,in}$ is the inlet concentration of B. The K_1 parameter is called the number of transfer units based on the liquid phase in traditional mass-transfer literature (Treybal

1980). K_2 is the nominal ratio of reaction rate to absorption rate. For a stirred tank or a mixed-liquid bubble column, (*SH*) is reactor volume.

Figures 5.1 and 5.2 present typical results of the reactor simulation for a countercurrent column with the aqueous solution introduced at the top and an oxidant-bearing gas stream introduced at the bottom. These graphs were calculated with other parameters selected to represent a typical ozone-based water treatment process. Figure 5.1 shows the relative depletion of the oxidant in the gas-phase exit stream as a function of K_1 and K_2. It is seen that with little or no reaction ($K_2 \rightarrow 0$), only about 50% of the reactant A (e.g. ozone) is absorbed into the water in a reactor of reasonable size ($K_1 = 2$). For faster reaction rates, as K_2 gets larger, the absorption efficiency increases such that nearly all of the ozone fed to the reactor is absorbed in a column with $K_1 = 1$. Unless the reaction is relatively fast, the low solubility of ozone would limit its uptake, and much of the costly reagent (ozone) would be wasted.

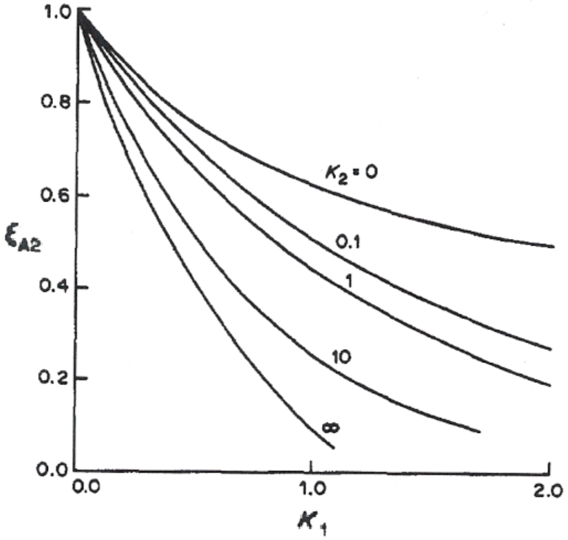

Figure 5.1. The efficiency of absorption of a gas-phase reactant, such as ozone, in a countercurrent gas-liquid contactor as a function of parameters K_1, the number of transfer units, and K_2, the relative reaction rate. The ordinate is the fractional concentration of A remaining in the exit gas stream. Other parameters were chosen to correspond to conditions in a typical ozonation process.

Figure 5.2 shows the fractional conversion of the target substrate B in the liquid phase under the same conditions. For a very slow reaction ($K_2 = 0.1$) hardly any of the B is destroyed in a column of size such that $K_1 = 1.6$. On the other hand, as the reaction rate approaches infinity, an instantaneous reactions that would occur at a plane in the liquid-phase diffusion layer, more than 90% of B would be destroyed in a contactor with K_1 = 1.2. These calculations could be extended to accommodate more complex reaction mechanisms and multiple simultaneous and successive reactions in the liquid phase. In any case the strong effect of the reaction rate parameter K_2 indicates that it is critical to know with some confidence the reaction kinetics of ozone oxidation with a target substrate or substrates (and its own decomposition rate) in order to design an efficient treatment process with confidence.

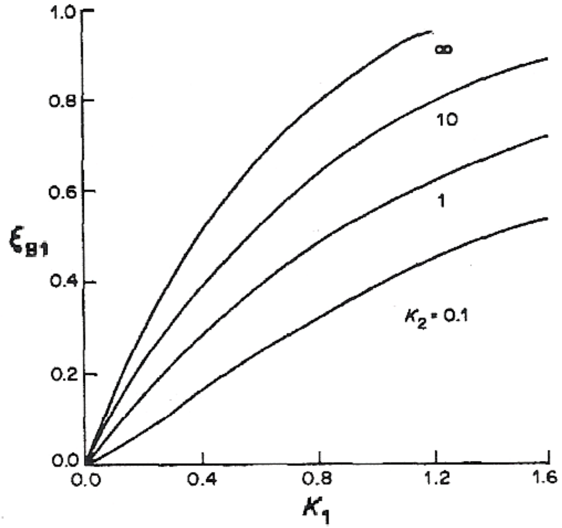

Figure 5.2. The fractional conversion of the liquid-phase reactant in the exit stream under the same conditions as Figure 5.1.

A number of workers have reported studies of the kinetics of various ozonation reactions in water. Full-scale implementation of ozone-based water-treatment processes have been reported, particularly for removal of color, cyanide, or phenols (Bollyky et al. 1976, Chu and Ma 2000, Rosen 1980). It appears that the reactions of the latter two targets are exceptions to the general case in the sense that their reaction rates with ozone are relative fast. Most other organics have been found to be more refractory to ozone oxidation, and in many cases the reactions yield a wide variety of products from the incomplete oxidation (Gould and Weber 1976). More detailed study is needed to identify the best opportunities for economical and effective use of ozone.

Keller has developed an experimental technique for measuring the absorption-reaction kinetics of ozone with aqueous solutes (Keller 1981). A stagnation-point flow cell (SPFC), based on work of Bauer (Bauer 1974, Bauer and Chapman 1975), provides well-characterized flow and mass-transfer conditions. Keller demonstrated the utility of the method by reacting gas-phase ozone with aqueous iodide. As the ozone absorbs it rapidly oxidizes the iodide ion to iodine (or triiodide). That reaction is so fast that it sets up a reaction plane in the mass-transfer boundary layer where the ozone and iodide annihilate one another. An interesting aspect of this system is that the iodine formed reacts more slowly with dissolved ozone near the gas-liquid interface to form iodate. By measuring the rates of accumulation of iodide and iodate, Keller could confirm the validity of the theoretical model and the potential for measuring ozone oxidation kinetics and reaction selectivity.

Subsequently, Keller measured the rate of ozone oxidation of methanol to formaldehyde in his SPFC (Keller 1981). His results compared favorably with conversion rates predicted by the transport-reaction model based on a kinetics model of Kuo and Wen (1977). Although he did not analyze the solution to determine the extent of further reaction of formaldehyde to formic acid, his results indicated that the primary reaction of methanol is sufficiently fast to occur primarily in the liquid-phase boundary layer and to enhance the physical absorption rate of ozone by a factor of 2 or 3, depending on the methanol concentration. These results confirm the ability of SPFC experiments to characterize the reaction kinetics of other ozonation reactions.

4. Electrochemical Oxidation of Trace Pollutants

Table 5.1 suggests that a high anodic electrode potential could be effective in oxidizing trace organics in water. Indeed, electrochemical oxidation is the process used to make almost all of the stronger chemical oxidants, and chlorine is sometimes produced on site by an electrolytic process. There are, however, two serious challenges to the direct application of electrochemical oxidation. First, not all electrode reactions are fast, and a proper catalytic surface or an excessively high potential (overpotential) may be required to drive a desired reaction at an acceptable rate. Second, because anodic oxidation is necessarily a heterogeneous process, sufficient electrode area is needed, and efficient transport of a dilute reactant to the electrode may be difficult to achieve. These requirements increase the process costs, both through capital investment and energy costs.

An example of an electrochemical oxidation process is the work of Hofseth on destruction of dilute aqueous cyanide (Hofseth 1993, Hofseth and Chapman 1992, 1999). Cyanide ion in alkaline solution can be oxidized to less toxic cyanate according to the reaction

$$CN^- + 2OH^- \rightarrow CNO^- + H_2O + 2e^- \tag{5.3}$$

Unfortunately, Reaction (5.3) does not proceed readily on most electrode materials and requires a potential considerably in excess of the theoretical equilibrium potential. When the potential is increased sufficiently, even on a material such as platinum, another competing reaction occurs:

$$4\,OH^- \rightarrow H_2O + 4e^- \tag{5.4}$$

Such a competing reaction reduces current efficiency and increases the net energy cost. On the other hand, if the concentration of hydroxide ion at the electrode surface can be limited, Reactions (5.3) and (5.4) cannot proceed as written. Indeed, the cyanide-oxidation Reaction (5.3) changes to:

$$CN^- \rightarrow \frac{1}{2}C_2N_2 + e^- \tag{5.5}$$

forming cyanogen rather than cyanate. The cyanogen thus formed is readily converted to cyanate when it encounters a higher-pH region in the bulk solution:

$$C_2N_2 + 2OH^- \rightarrow CN^- + CNO^- + H_2O \tag{5.6}$$

Thus, efficient destruction of cyanide by anodic oxidation requires (1) that the cyanide be transported to the electrode surface, (2) that the oxidation Reaction (5.5) (or 5.3) be catalyzed to proceed at a sufficiently fast rate, (3) that the hydroxide concentration at the electrode be limited to near zero, and (4) that the pH of the bulk solution remain alkaline, not only to drive Reaction (5.6) but also to prevent formation and liberation of toxic HCN.

Hofseth was able to satisfy all of these conditions. First, he discovered that trace amounts of copper in solution can be deposited as an oxide on a carbon anode and serve to catalyze cyanide oxidation. Further, he used a porous flow-through reticulated vitreous carbon electrode (FTPE) to provide high electrode surface area and to promote mass transfer of the dilute cyanide to the carbon surface. Diagrams of his experimental equipment are shown in Figures 5.3 and 5.4.

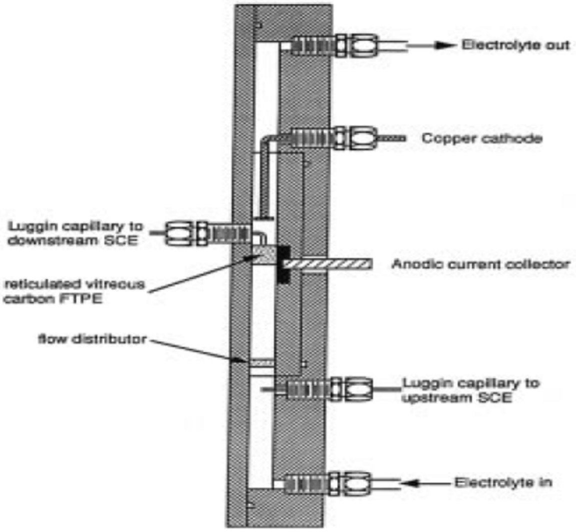

Figure 5.3. Cross-sectional diagram of the electrochemical cell for cyanide oxidation. The cell contains a porous flow-through reticulated-carbon anode and a copper cathode (Hofseth and Chapman 1999).

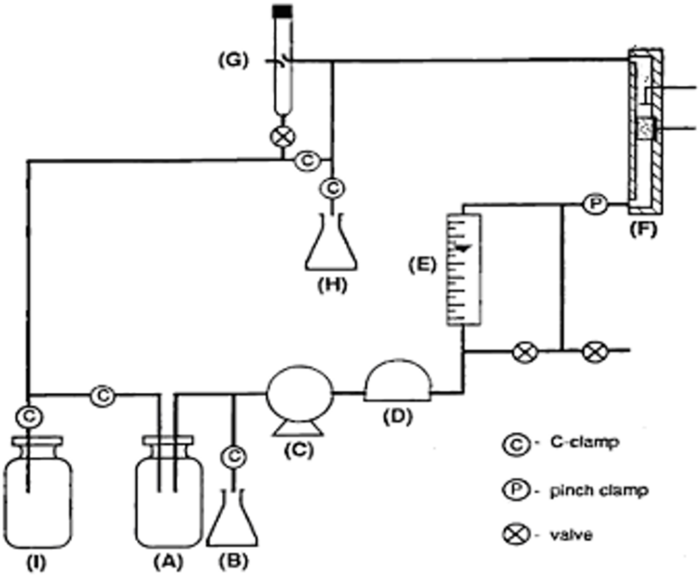

Figure 5.4. Bench-scale apparatus to test electrochemical destruction of dilute cyanide in a wastewater solution. The electrochemical cell (F) is that shown in more detail in Figure 5.3.

Some of the results obtained from semi-batch experiments conducted in the apparatus shown in Figure 5.4 are given in Figure 5.5. Figure 5.5 shows the effects of adding a catalytic amount of copper(II) ion to the feed solution. For the same applied cell potential, the initial current shown in Figure 5.5a is much greater when copper is present at 40 micromolar concentration than in the absence of copper, indicating that the trace amount of copper is indeed catalytic for the anodic oxidation of cyanide. Figure 5.5b shows the corresponding concentrations of cyanide in the solution exiting from the electrochemical cell, with and without copper in the feed. Note that the concentration scale in Figure 5.5b is logarithmic and that the cyanide concentration is decreased by two orders of magnitude, from 5.0 mM to 0.05 mM in 3 hours, when copper is present. Destruction of cyanide is much slower and less effective without the added copper.

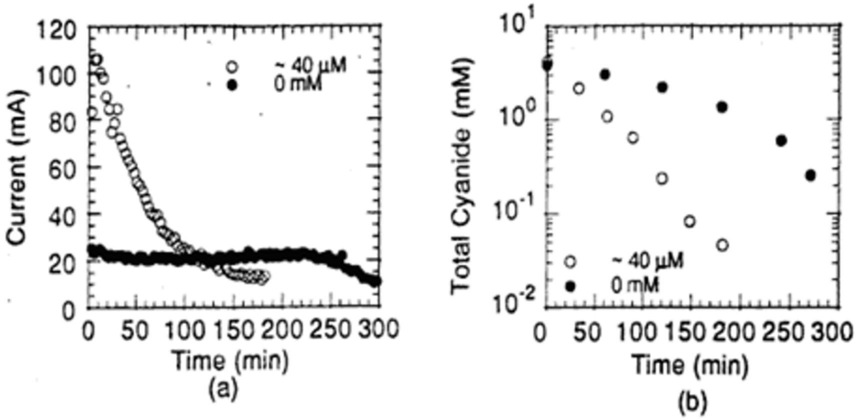

Figure 5.5. Currents and cyanide concentrations measured during operation of the electrochemical system shown in Figures 5.3 and 5.4. Feed solution was pumped from flask A through the electrochemical cell and then recycled to the same feed reservoir. The measurements shown compare the results with and without copper added to the feed.

Hofseth developed a mass transfer-reaction model of this system taking into account the specific chemistry of the cyanide solution (Hofseth and Chapman 1999). Depending on the pH of the feed to the cell, or more precisely the ratio of OH− to CN−, the anodic reaction can occur through one of three regimes: at high pH Reactions (5.3) and (5.4) both occur on the carbon surface. As a test proceeds, and as the solution flows through the electrode, hydroxide is consumed, and the pH in the solution drops to the point where the interface becomes neutral. When there is no hydroxide available to react at the anode, Reaction (5.5) occurs forming cyanogen. Cyanogen produced at the interface diffuses out and reacts rapidly with hydroxide in the bulk solution where it is readily converted to cyanate by Reaction (5.6). At intermediate OH^- levels, that reaction can occur in the diffusion layer near the electrode. If sufficient hydroxide is consumed by the reactions in the cell, the conversion of cyanogen to cyanate occurs in the mixed feed tank upon its recycle.

Figure 5.6 compares experimental measurements with the predictions of Hofseth's model for a representative test case. The solid lines are computed with the model, and points are experimental data. Figure 5.6a shows the decrease in cyanide concentration in the effluent from the cell. Figure 5.6b gives differential and overall current efficiencies for cyanide destruction. Figures 5.6c and 5.6d present the changes in copper concentration and pH during the course of the process. The ability of the mathematical model to simulate the performance of the bench-scale tests provides evidence that an electrochemical oxidation process such as this, involving rather complex chemistry, can be designed and scaled up with some confidence.

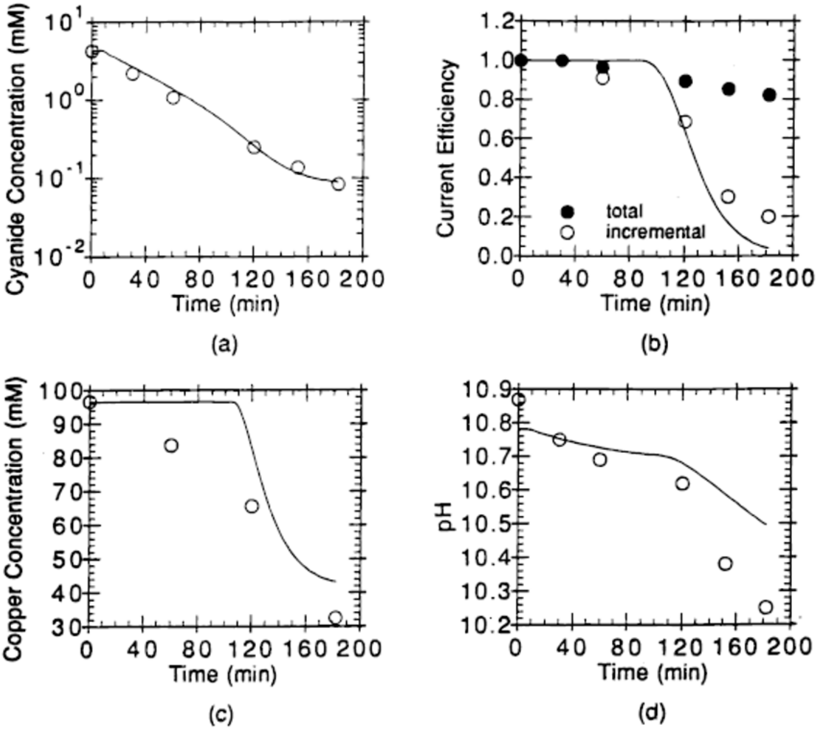

Figure 5.6. Comparisons of experimental measurements (points) with model predictions (lines) for a test of the process represented by Figures 5.3 and 5.4. Concentrations were measured in the cell effluent prior to recycling to the feed flask A. Details are given by Hofseth (Hofseth and Chapman 1999).

5. Removal of Organic Solutes by UV Photolysis

Another approach to destruction of harmful organics in water is by application of UV radiation. Such radiation is found to be effective in disinfection by killing harmful bacteria. As a result large-scale commercial equipment has been developed for applications such as sterilization in food processing. The availability of such equipment provides an opportunity for application in water treatment (Parsons 2004 Ch. 3). Although UV radiation itself may not act as an oxidizing agent, it does promote the decomposition of some organic solutes, particularly chromophores that are not susceptible to other treatment methods.

Many molecular bonds absorb radiation in the UV region of the spectrum, and this absorption energizes the molecule to an activated state. This makes the molecule more susceptible to oxidative attack or even causes it to decompose. Generally the radiation must come at a wavelength shorter than 400 nm to be effective. Mercury-vapor lamps produce radiation in this, the UV region, and hence they are mostly the source of choice. Low-pressure Hg lamps are monochromatic at 254 nm, whereas high-pressure lamps are polychromatic.

The effectiveness of UV radiation in promoting photolysis depends on a number of factors. First, one must consider the power and wavelength of the radiation source. Then there is the geometry of the illumination optics. As the radiation passes through an aqueous solution absorption decreases its local intensity. Finally, the photolysis rate depends on the efficiency of absorption by the target molecule and the specific extent of reaction. For a batch experiment the kinetics of photolysis may be expressed by an equation such as

$$\left(\frac{dC_R}{dt}\right)_{\lambda} = -\Phi_{R,\lambda}\frac{\varepsilon_{R,\lambda}C_R}{\alpha_{\lambda}+\varepsilon_{R,\lambda}C_R}I^{o}_{\lambda}\left(1-10^{-\alpha_{\lambda}l}\right) \tag{5.7}$$

where C_R is the concentration of the reactant. In this equation, which is written for illumination at a single specific wavelength λ, I^{o}_{λ} is the intensity of the incident radiation, and l is the total path length in the solution. The factor α_{λ} is the attenuation coefficient of the solution resulting from the optical absorption of the solvent matrix. The factor $\varepsilon_{R,\lambda}$ is the molar absorption coefficient of the solute R, and $\Phi_{R,\lambda}$ is the reaction quantum yield, defined as the number of moles converted per mole of photons absorbed by R at wavelength λ, a chemical property of the reactant.

For a source providing polychromatic radiation, this expression would have to be integrated over the spectrum to obtain the total conversion rate.

The form of Eq. (5.7) indicates that the global photolysis rate for a given wavelength increases with $\Phi_{R,\lambda}$, $\varepsilon_{R,\lambda}$, and I_λ^o but is diminished for larger values of α_λ and l. All of the parameters appearing in Eq. (5.7) are in principle accessible to experimental measurement, and values are available for many substances, at least at the most common wavelengths in use, such as 254 nm, or at the wavelength where their absorption coefficient reaches its maximum value. Typical values for solutes of interest are tabulated in Parsons (Parsons 2004 Ch. 3). The molar absorption coefficient for various solutes at any particular wavelength can take on almost any value, ranging from perhaps 10 to 40000 $M^{-1}cm^{-1}$. Also, the values of $\Phi_{R,\lambda}$ cover a wide range, from a few percent to as high as 0.9.

In addition to the direct absorption of UV light by organic solutes, water can also absorb radiation at wavelengths shorter than 190 nm to form hydroxyl radicals:

$$H_2O + h\nu \rightarrow H\bullet + OH\bullet \tag{5.8}$$

where $h\nu$ is a quantum of radiant energy, which has the value of $(1.2 \times 10^5)/\lambda$ kJ/mol where $\lambda = c/\nu$, ν is frequency, and c is the speed of light. As indicated by the potential shown in Table 5.1, the hydroxyl radical produced by this process can serve as a very powerful oxidizing agent. Unfortunately most commercial lamps do not produce radiation at sufficiently short wavelengths to drive Reaction (5.8). Hydrogen peroxide, which is also a source of the hydroxyl radical, has been used in many advanced oxidation processes. Exposed to UV radiation it exhibits a high quantum yield for hydroxyl production, near 1.0. Unfortunately, it presents like water a relatively low value of $\varepsilon_{R,\lambda}$, only 20 $M^{-1}cm^{-1}$ at 254 nm compared to 3300 $M^{-1}cm^{-1}$ for ozone. The peroxide concentration must be optimized. A relatively high concentration is needed because of its low efficiency of absorption, but an excessively high concentration is detrimental because the peroxide also scavenges the hydroxyl radicals that are produced.

Thus, we see that the potential for UV radiation in treating a particular aqueous system depends on a number of factors: Does the target molecule absorb the incident radiation efficiently? Does it decompose with high efficiency? Does the matrix obscure the radiation by competing absorbance or reflection? Do the lamps become fouled during operation? Are the products of decomposition or oxidation more or less benign than the original target? Can the process be enhanced by combining it with additional treatments, such as filtering, or by addition of a catalyst? And finally, there is always the question of cost.

6. Combination of Effects in Advanced Oxidation Processes

Because the simple use of the most obvious oxidizing agents may not be effective in any particular application or presents drawbacks, such as undesired reaction products, lamp fouling, or reactor corrosion, a number of advanced oxidation processes that combine several effects have been investigated. These include the combinations of ozone with hydrogen peroxide, of ozone or peroxide with ultraviolet radiation, of ozone or peroxide with homogeneous or heterogeneous catalysts including semiconductors, or of any of these with electrochemistry (Gogate and Pandit 2004, Parsons 2004). These processes might be used for polishing a water stream after it has been exposed to primary and secondary treatment and perhaps a membrane separation.

Probably the most studied of the catalytic processes is the so-called Fenton reaction (Parsons 2004 Ch. 5). The Fenton reaction is the process that occurs when ferrous iron is added to a peroxide solution, presumably forming free hydroxyl radicals that serve as the active oxidant. Parsons describes several large-scale tests of combined processes for destruction of pesticides, phenolics, dioxane and other persistent hydrocarbons (Parsons 2004). Two particular targets have been N-nitrosodimethylamine (NDMA) and MTBE, which appear in certain groundwaters.

7. Fenton Processes

One primary attraction of the Fenton reaction is that the reagents, hydrogen peroxide and ferrous iron, are available and relatively inexpensive. Furthermore, it appears that the catalyzed reaction is effective in oxidizing many important targets in water treatment. It is believed that the mixture of the two reagents produces hydroxyl radicals that perform the observed oxidation. The mechanism of hydroxyl formation is not known definitely, but it is believed to proceed through a scheme something like the following:

$$\begin{aligned}&Fe(II) + H_2O_2 \rightarrow Fe(III) + OH\bullet + OH^- \\ &Fe(III) + H_2O_2 \Leftrightarrow \left(Fe\cdots O_2H\right)^{+2} + H^+ \\ &\left(Fe\cdots O_2H\right)^{+2} \rightarrow Fe(II) + HO_2^- \\ &\text{etc.}\end{aligned} \tag{5.9}$$

It is still not clear exactly what species exist in solution or how the subsequent oxidation reactions proceed. One generally observes only the overall disappearance of the target substances.

One example of a fairly rigorous study of a Fenton process is that of Sanz et al. (2003) who observed the destruction of phenol in dilute aqueous solution (Peralta-Hernández et al. 2006). Figure 5.7 shows the effect of iron concentration in the destruction of the phenol, with the level of phenol remaining after 14 minutes dropping linearly with increasing iron concentration. Figure 5.8 shows the effect of pH in the same system. It is interesting to see that the fastest reaction occurs at a pH of 3, whereas the reaction is slower at higher pH but hardly goes at all at a pH of 2.4. This effect is interpreted to indicate that the active ferric iron species to allow regeneration of Fe(II) in the catalytic mechanism is $FeOH^{+2}$, as that species becomes dominant in a narrow range of pH around 3.0.

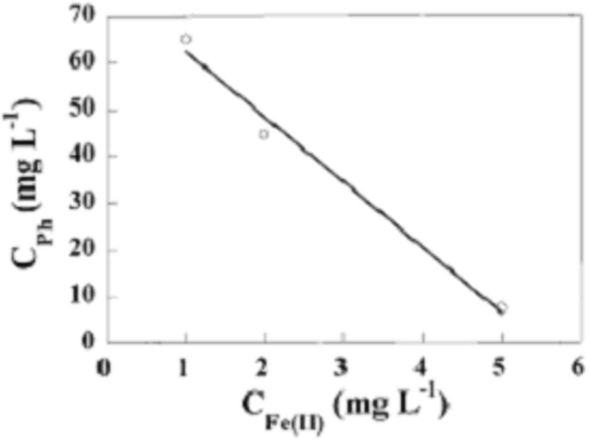

Figure 5.7. Effect of iron concentration on the degree of phenol destruction by the Fenton reaction. Initial peroxide:phenol ratio = 4; contact time = 14 minutes (Sanz et al. 2003).

Studies such as that of Sanz et al. (2003) provide a number of design guidelines for Fenton processes. First, it is noted that addition of hydrogen peroxide and ferrous sulfate to water is relatively simple to do. The fairly complex kinetics provides a challenge in reactor design however. Within limits, addition of extra peroxide or iron does not speed the overall reaction. On the other hand, it appears that the pH needs to be controlled; the reaction might be quenched at excessively low pH, but ferric iron may precipitate if the pH rises too much. A series of stirred tanks with successive addition of peroxide might be advantageous to facilitate pH control. Because of the complicated chemistry of these solutions extensive pilot experiments with the real water to be treated should be conducted to determine the system behavior. One complication might be complexation of iron by extraneous species in the water, and such effects need to be identified and dealt with.

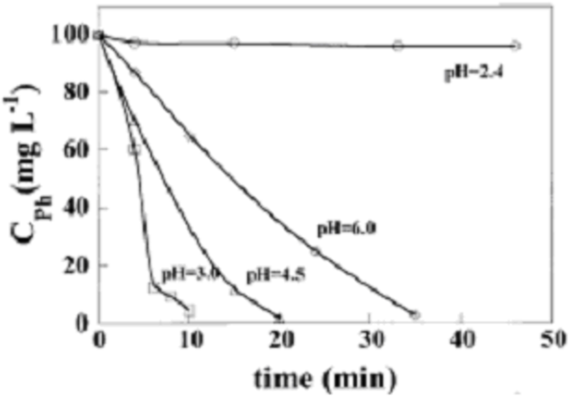

Figure 5.8. Effect of pH on the destruction of phenol by the Fenton reaction. Initial peroxide:phenol ratio = 8 (Sanz et al. 2003).

A number of variations have been developed based on the Fenton chemistry. For example, the hydrogen peroxide can be produced *in situ* by cathodic reduction of dissolved oxygen:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{5.10}$$

The peroxide thus formed can in the presence of ferrous iron ions generate the hydroxyl radical by the overall Fenton reaction:

$$H_2O_2 + Fe^{+2} \rightarrow Fe(OH)^{+2} + OH\bullet \tag{5.11}$$

Furthermore, upon exposure to UV radiation, the hyroxy-ferric complex can also produce hydroxyl radicals by photolysis:

$$Fe(OH)^{+2} + h\nu \rightarrow Fe^{+2} + OH\bullet \tag{5.12}$$

Application of this latter reaction for water treatment is called the *photo-Fenton process*. Direct photolysis of hydrogen peroxide also produces hydroxyl radicals. The availability of these various routes to hydroxyl obviously suggests various combinations of effects to accomplish an advanced oxidation process.

Peralta-Hernández compared various processes, i.e. photo-Fenton, electro-Fenton, and photoelectro-Fenton schemes, to destroy the color of dilute orange dye II (OG-II) in water (Peralta-Hernández et al. 2006, 2008). A diagram of their experimental apparatus is shown in Figure 5.9. Concentric carbon-cloth electrodes were installed in a cylindrical cell around a tubular UV lamp, and the oxygenated solution was pumped through the cell. The intensity of color of the solution was monitored with time under several conditions. Total organic carbon (TOC) was also monitored. Typical results are shown in Figure 5.10.

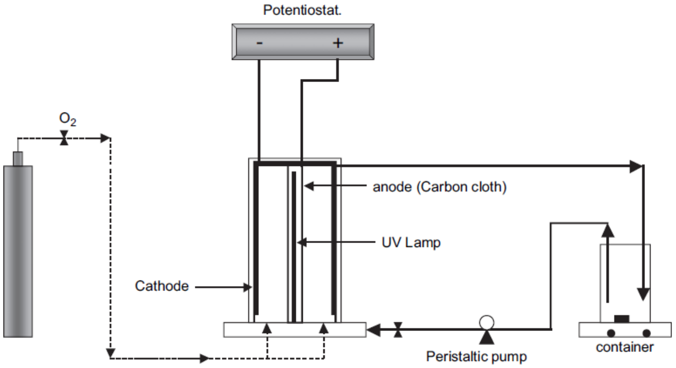

Figure 5.9. Diagram of experimental apparatus to study decolorization of orange dye II solution by various modes of the Fenton reaction (Peralta-Hernández et al. 2008).

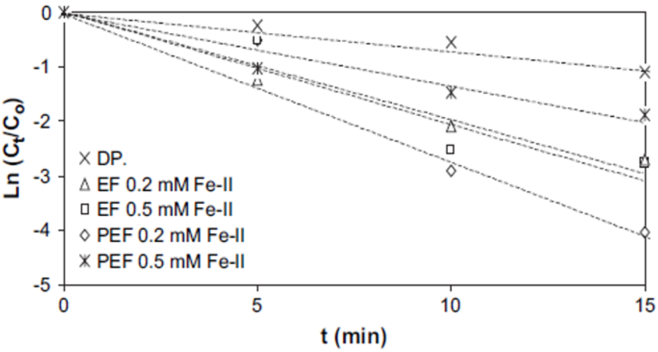

Figure 5.10. Variation of the color intensity of orange dye II under various modes of operation the cell shown in Figure 5.9 (Peralta-Hernández et al. 2008).

It is seen in Figure 5.10 that the color of the dye was destroyed by all modes of operation. The slowest reaction was observed with only direct photolysis (DP) of the dissolved oxygen, without iron ions or the application of electrical current. The fastest decolorization occurred with the photoelectro-Fenton (PEF) operation with a ferrous concentration of 0.2 mM. Electro-Fenton operation, without UV radiation, provided an intermediate rate. It is surprising to see that the photoelectro-Fenton (PEF) process, in which both electrical current and UV radiation were applied, was less efficient with a higher concentration of iron present. Nevertheless, it is seen that the color intensity of the dye was diminished by several orders of magnitude within 15 minutes. Furthermore, the photoelectro-Fenton process with 0.2 mM Fe(II) removed 80% of total organic carbon in 1 hour, but only 60% of TOC was removed with 0.5 mM Fe(II) added.

As a further enhancement of advanced Fenton processes, one may use a semiconductor catalyst, such as TiO_2, to enhance the efficiency of hydroxyl generation (Parsons 2004 Ch. 7). The mechanistic scheme of a Fenton process employing TiO_2 in contact with a carbon electron conductor is shown in Figure 5.11 (Peralta-Hernández et al. 2007). When the semiconductor is illuminated with the proper wavelength of radiation, an electron is promoted to a higher energy state, leaving behind a positive hole. If the electron is extracted into an adjacent carbon phase before falling back to its initial energy state, the semiconductor hole can oxidize water to produce hydroxyl radicals. At the same time the electron in the carbon phase can reduce dissolved oxygen to peroxide, which can in turn participate in a Fenton reaction.

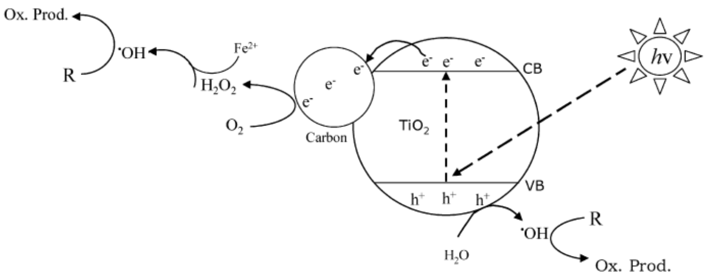

Figure 5.11. Schematic diagram of the reaction scheme involving semiconducting TiO_2 in contact with carbon and an aqueous solution containing dissolved oxygen, ferrous ions, and a target molecule to be oxidized (Peralta-Hernández et al. 2007).

Peralta-Hernández and co-workers have explored the possibility of implementing such a scheme to accomplish more efficient oxidative treatment of water (Peralta-Hernández et al. 2007). They developed an electrophoretic process for depositing nanoparticulate TiO_2 on a carbon electrode and tested the material in a cell similar to that shown in Figure 5.9, the difference being that the inner electrode was coated with a porous film of TiO_2. It was found that, with UV illumination, a composite of carbon and TiO_2 nanoparticles was more effective in oxidizing orange dye II than was a film of TiO_2 on conducting glass. Furthermore, in treating a dilute solution of DY-52 dye, the best results for removal of both color and total organic carbon were obtained in the photoelectro-Fenton mode with 0.25 mM Fe(II) present.

8. Conclusion

This chapter has provided a summary of various approaches to destruction of harmful pollutants in water and wastewater. In any particular case, especially those involving persistent or refractory substances such as pesticides or pharmaceuticals, it is likely that a combination of processes will be required to achieve satisfactory purification. For example, groundwater containing such chemicals might be processed first by filtration and conventional secondary treatments, such as precipitation or aeration, but then subjected to one of the advanced oxidation processes, such as those based on the Fenton reaction, for final purification.

The engineer faced with a particular water problem must analyze the situation systematically. First, one must do thorough chemical analysis to identify the target pollutants as well as other parameters of water quality. What are the concentrations and flow rates of the stream to be treated, and what are the government water-quality requirements for use or discharge? Having the answers to those questions, one can proceed to consider the technical options, the available processes such as those mentioned here. It is likely that bench-scale laboratory tests will be required to evaluate candidate processes and to compare alternatives. It is important that such tests be done with the actual water to be treated. An important question that should not be overlooked is what new chemicals might be produced by a given process. Could they be more harmful that the original target? Finally, complete engineering design must be done, and that design should predict the process effectiveness reliably and reveal the ultimate cost of the process.

In addition to the processes outlined here, a number of other options are being examined. For example, ultrasound is reported to generate free radicals in water, and those free radicals can lead to oxidation or decomposition of pollutants. Electron-beam radiation is another way of producing free radicals. An active oxidant appearing in Table 5.1 but not currently in use because of the difficulty in its synthesis is the ferrate form of iron, Fe(VI) as $FeO_4^{=}$, an analog of permanganate. Nanoscale particles of silver are effective in disinfection. Modification of catalyst surfaces, electrodes, or membranes can improve chemical and electrochemical process effectiveness. Advanced work is being done in all of these areas, and thus it is likely that the list of process alternatives will continue to grow.

Although a number of processes and combinations of effects have been examined, and in some cases processing costs have been reported (Parsons 2004), many situations involve unique solution chemistry, especially as new threats to health and environment are indentified. Thus, experimental testing and careful engineering are required to ensure safe and economical process implementation. The examples given here indicate that there is still a wide opportunity for development of new, more effective water-treatment processes.

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WATER SAVING IN INDUSTRY BY CLEANER PRODUCTION

JURGIS K. STANIŠKIS[*]
Institute of Environmental Engineering, Kaunas University of Technology, Kaunas (LITHUANIA)

Abstract. According to Cleaner Production (CP) strategy, industrial companies have a number of options for exploring improvements of the water resource management and reducing pollution generation, e.g. input substitution, product/production process modification, optimization of technological processes, improvement of process control, technology substitution. The value of simple good-housekeeping measures should not be underestimated too. This chapter deals with water saving, reuse and recycling in Lithuanian industrial companies by Cleaner Production strategy, which is achieved by applying know-how, by improving technology and/or by changing attitudes. Cleaner Production strategy included the following prevention methods: good housekeeping, input substitution, better process control, equipment modification, technology change, product modification and on-site recovery/reuse. In Lithuania, CP strategy was introduced in 1993. Since then 12 Cleaner Production programmes have been implemented in different economic sectors (three CP programmes were integrated with implementation of environmental management systems). To facilitate implementation of CP innovations that require investments, a special revolving facility to finance CP investments was created in the Nordic Finance Corporation (NEFCO) in 1998. The main objective of the facility is to provide soft loans for the implementation of high-priority CP investments with rapid payback that yield environmental and economical benefits. The results of innovations on water saving and reuse by applying CP methods from 69 companies, representing 12 branches of industry is presented.

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[*] E-mail: Jurgis.Staniskis@ktu.lt

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1. Introduction

Natural resources include both the raw materials necessary for most human activities and the different environmental media, such as air, water and soil, which sustain life on our planet. Therefore, careful management of the use of these resources is a basis for sustainable development. In contrast with raw material it is their declining quality that causes concern. It is not question of how much there is, but what state they are in.

Resource efficiency or resource productivity can be defined as the efficiency with which we use energy and materials throughout the economy, i.e. the value added per unit of resource input. An example of resource productivity calculation on a national level is total material (water) use divided by the total economic activity by the country, expressed in GDP.

Sustainable development calls for processes with a closed loop philosophy and in recycling becomes thus a normal, rather than exceptional solution. Water reuse and recycling in industry is one of the most important ways enabling absolute and relative decoupling of environmental impact from economic growth. There are more and more corporations focusing development efforts on Cleaner Production (CP) methods, i.e. systematic approach to using resource more efficiently, and avoiding the use of hazardous substances where substitutes are available.

Cleaner Production is a focused development and implementation of preventive innovations to maximize the efficient use of raw materials, energy and water, and minimize the output of waste and harmful materials. The key idea is to remove the reasons of problems rather than their symptoms. CP is applied to production processes and products, using the methodology which includes the following basic steps: planning, analysis of pollution causes, development of CP options, feasibility study, implementation of feasible measures, and assessment of innovation performance.

More specifically, Cleaner Production aims to reduce the consumption of natural resources per unit of production, the amount of pollutants generated, and their environmental impact, while making alternative products and processes financially and politically more attractive. As the European Environment Agency states, “Cleaner Production is about the creation of a truly sustainable economy”. Cleaner Production brings economic benefits via increased resource efficiency, innovation and reduction of pollution control costs. The most important ways for achieving Cleaner Production are:

- Changing attitudes – finding a new approach to the relationship between industry and the environment and re-thinking processes or products in view of prevention approach.
- Applying know-how – improving efficiency, adopting better management techniques, changing housekeeping practices, revising policies, procedures and institutions as necessary.
- Improving technology – i.e., redesigning products, changing manufacturing technologies.

Partnership among all actors and sectors is crucial for effective adoption of Cleaner Production. All actors in society gain from application of Cleaner Production as a win-win strategy, and all actors have important roles to play in adopting Cleaner Production, including government, industry, civil society, educational facilities and non-governmental organizations.

Cleaner Production recognizes the fundamental need for businesses to incorporate not just environmental concerns, but economic performance in the improvement process. This is something that previous approaches have often failed to do. CP fosters the change process to help businesses cater to customer requirements for more environmentally sound products. At the same time there is a need to ensure a healthy and safe work environment and a solid bottom line.

2. The Concept of Cleaner Production: Theory

The concept of cleaner production was introduced by UNEP in 1989 as a response to the question of how industry could work towards sustainable development.

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 reduction of risks to humans and the environment (see Figure 6.1) (Staniskis and Strahl 1997):

1. *For 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.
2. *For products*, CP focuses on reducing impacts along the entire lifecycle of the product, from raw material extraction to the ultimate disposal of the product.

3. *For services*, using a preventive approach involves design issues, housekeeping improvement, and a better selection of material inputs (in the form of products).

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. Additionally, CP strategy includes a clearly defined CP management system, which ensures continuous improvement of environmental and economic performance (European Environment Agency 1998, Profiting from Cleaner Production 2001).

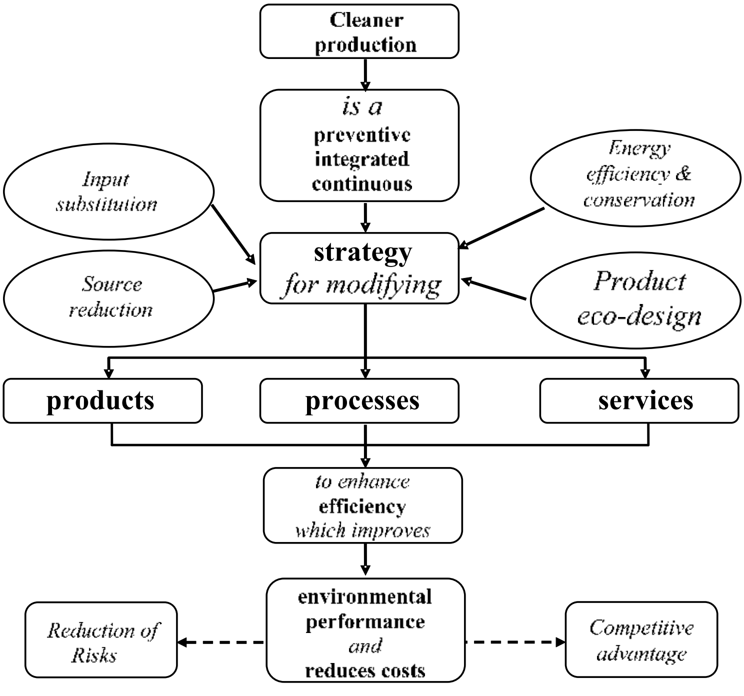


Figure 6.1. Cleaner production concept.

CP should not be considered only as an environmental strategy, because it also relates to economic considerations. In this context, waste is considered as a “product” with negative economic value. Each action to reduce consumption of raw materials and energy, and prevent or reduce generation of waste, increases productivity and brings financial benefits to the enterprise.

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 is also a sign of inefficient production processes or management. In practice, cleaner production means the following (Kemp and Andersen 2004):

1. Avoiding or reducing the amount of waste produced
2. Using energy and resources/water efficiently
3. Producing environmentally sounder products and services
4. Generating less waste, reducing costs and increasing profits

2.1. CLEANER PRODUCTION PRINCIPLES AND TECHNIQUES

The precaution principle. Precaution is not simply a matter of avoiding to being "of law", it is also ensures that workers are protected from irreversible ill-health and that the plant is protected from irreversible damage. The precautionary principle calls for the reduction of 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 extensive throughput of materials.

The preventive principle. Prevention is equally important, especially in cases where a product or process is known to cause harm. The preventive principle is to look to changes upstream in the causal network of the system of production and consumption. The preventive nature of cleaner production calls for the new approach to reconsider product design, consumer demand, patterns of material consumption, and indeed the entire material basis of economic activity.

The integration principle. Integration involves adopting a holistic view of the production cycle, and one method for introducing the idea is through life-cycle analysis. One of the difficulties in the preventive approach is the integration of environmental protection measures across system boundaries. The 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 (World Business Council for Sustainable Development 1996, Zwetsloot and Geyer 1996).

Cleaner production is achieved by applying know-how, by improving technology, and/or by changing attitudes. Cleaner production strategy includes the following prevention practices (Staniskis et al. 2005):

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 in order to minimize waste and emission generation during production.
6. *Product modification*: modification of the product characteristics in order to minimize the environmental impacts of the product during or after its use (disposal) or to minimize the environmental impacts of its production.
7. *Using energy efficiently*: energy is a very significant source of environmental impact. Energy use may result in effects on land, water, air, and biodiversity, as well as in the production of large quantities of solid wastes. The environmental impacts resulting from energy use can be decreased by improved energy efficiency as well as by using energy from renewable sources, such as the sun and wind.
8. *On-site recovery/reuse*: reuse of waste materials/water in the same process or for another useful application within the company.

2.2. CLEANER PRODUCTION PROCEDURES

The below described logical steps of CP assessment are embedded in an organized procedure. This procedure is instrumental in organizing the CP efforts, informing the necessary stakeholders within the company and bringing together those persons that can develop, evaluate and implement CP opportunities. CP assessment is most often divided in five phases (see Figure 6.2) (Van Berkel and Walstra 1997, Staniskis et al. 2001):

1. *Planning and Organization.* This phase starts once one or a few persons in the company become interested in Cleaner Production. In the course of this phase, "promoters" convince key persons in the company of the necessity to adopt Cleaner Production and establish a proper project organization for the smooth execution of the Cleaner Production assessment;
2. *Pre-assessment*. The prime objective of the pre-assessment phase is the selection of one or a few assessment focuses. In the next phases, these assessment focuses are evaluated in detail in order to identify, evaluate and – as far as these are feasible – implement CP options. The selection of these assessment focuses requires a preliminary identification and evaluation of the CP potential at the plant level. While doing so, a first inventory of obvious options is made as well as a preliminary estimate of the waste generation costs;
3. *Assessment.* This phase consists of the in-depth evaluation of the selected assessment focus(es) in order to develop a comprehensive set of alternative CP options. This requires a quantification of the volume and composition of the various waste streams and emissions as well as a detailed understanding of the causes of these waste streams and emissions;
4. *Feasibility studies*. These studies have to prove whether each of the options 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 option, since options may vary from simple operational improvements, use of alternative materials to installation of advanced equipment. A preliminary evaluation is therefore useful to determine which detailed evaluations have to take place for each of the options.
5. *Implementation and Continuation.* the feasible prevention measures are implemented and provisions taken to assure the ongoing application of CP. The development of such an ongoing program requires monitoring and evaluation of the results achieved by the 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 the implementation of the feasible options; and (iii) initiation of ongoing Cleaner Production activities.

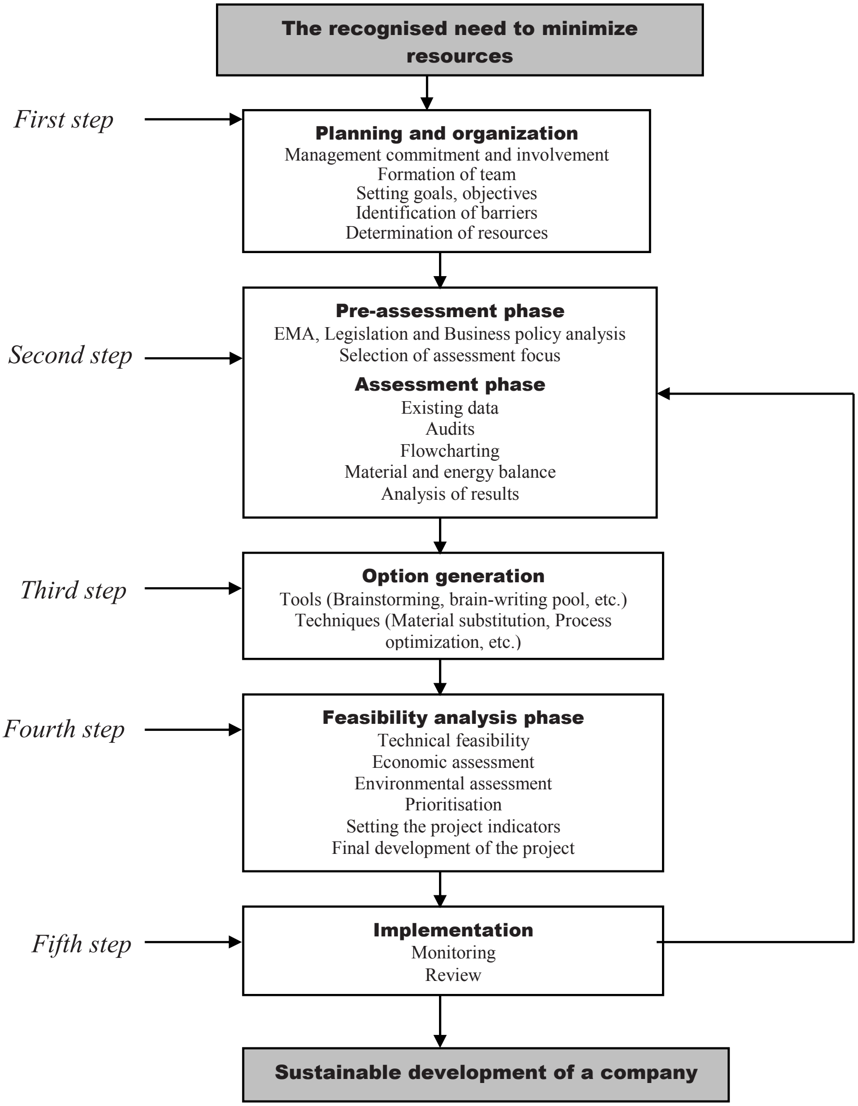


Figure 6.2. Cleaner production procedures.

The actual investments in Cleaner Production take place in the last phase of the assessment procedure. However, difficulties encountered while preparing and implementing CP investments may have been caused in earlier stages of CP assessment (due to e.g. insufficient depth of the diagnosis of the process waste generation sources and causes, lack of quantification of the final benefits from low and no costs options implemented in earlier stages).

2.2.1. *Planning and Organization*

Planning and organization starts once one or a few persons in the company become interested in CP. The following four separate, but interrelated tasks need to be executed in case of a CP assessment for a company:

1. *Obtain management commitment.* Generally, management commitment can only be generated by highlighting the possible economic benefits (through resource conservation and waste minimization), encouraging "responsible care" and pro-active action and illustration of the possible environmental advantages of CP over end-of-pipe approaches. While it might be difficult to generate management commitment in the first place, it is of at least equal importance to safeguard management involvement over the course of the CP assessment. Therefore, it is advisable to involve at least a management representative in the project team (preferably the production manager). In addition, management should be informed frequently about the achievements and the tangible benefits (for instance in terms of expected monetary savings). Finally, the enthusiasm and commitment of the promoters in the company is usually of vital importance for keeping the management involved.
2. *Identify barriers and solutions.* Like many other changes, CP will face a number of barriers. In order to anticipate and prepare solutions, the project team takes some time to discuss which barriers might exist; for instance people's concepts and attitudes, the company's organization and management system, technology, economics and/or availability of information and knowledge. A proper analysis of these barriers may reveal that these are based on misunderstandings rather than facts, which calls for information dissemination within the company. In addition, perceived economic barriers can often be eliminated with a simple calculation of the monetary losses caused by the raw material, intermediate product and/or product-content losses in the largest waste streams of the company.
3. *Set plant-wide goals*. Plant-wide CP goals set the stage for the assessment and should challenge the project team. The tendency of companies to

underestimate the CP potential in the first place is often reflected in comparatively low goals, which in turn are not a favorable condition for developing innovative prevention options. A comparative evaluation of internal productivity standards, (international) developments in environmental standards and legislation, technology bench-marks and historic trends in production data might result in more challenging, but still fairly realistic, short and long term CP goals.

4. *Organize a project team.* The project team initiates, co-ordinates and supervises the assessment activities. In order to be effective, the project team should have enough process knowledge to analyze and review the present production practices, enough creativity to develop and evaluate changes for the current production practices and enough authority to implement and maintain the proposed changes in the production practices.

CP planning is a systematic, comprehensive method for identifying options to reduce or avoid the generation of waste. The Cleaner Production planning process itself also has its own results and benefits:

- A careful planning process ensures the selection and implementation of the most cost-effective cleaner production options.
- Systematic planning ensures that cleaner production objectives and activities are consistent with the objectives and activities identified in the organization's broader planning process.
- Effective CP planning facilitates broader business planning investment analysis and decision making (such as capital budgeting and purchasing).
- A documented cleaner production plan may be a condition for receiving financing or insurance at more attractive rates.

2.2.2. *Assessment procedure*

CP focuses on the production process that causes the waste stream 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".

1. For the *source identification*, an inventory is made of the material flows, entering and leaving the company with the associated costs. This results in a process flow diagram, allowing for the identification of all sources of waste and emission generation.
2. Next is the *cause diagnosis*: an investigation of the factors that influence the volume and composition of the waste and emissions generated. A

checklist of possible waste generation causes is used to assess all possible factors influencing the volume and/or composition of the waste stream or emissions. A material and energy balance is needed for the evaluation of the relative importance of each of the possible waste generation causes.

3. The purpose of the next logical step (*option generation*) is to create a vision on how to eliminate or control each of the causes of waste and emission generation. The generic prevention practices specified before are used to develop appropriate CP options. After CP options have been identified, they are evaluated following the same procedure used for evaluation of other investments or technical innovation options.

2.2.2.1. *Source Identification*

The source identification starts with drafting a list of unit operations with their associated material inputs and outputs as wells as material transformations. Production generally comprises a number of such unit operations. These can be defined as an area of the process or a piece of equipment where materials are input, a function occurs and materials are output, possibly in a different form, state or composition.

It is important to choose the right level of detail during division of the production process into unit operations. It might be wise to start with a general list with the main unit operations and go into details in a later stage only for those unit operations that cause serious waste generation. By connecting the individual unit operations in the form of a block diagram the process flow diagram can be created.

An essential step is checking the process flow diagram. What goes in, must come out somewhere. So, all inputs should have related outputs, as product or waste, and all outputs have to be traced back to inputs. All unit operations can be the source of various waste streams. Therefore, the completed process flow diagram is used to check all unit operations for waste generation, and helps to compile the list of all waste sources.

2.2.2.2. *Material and Energy Balance*

Material and energy balance is very important source of information in data collecting. It helps to identify *where*, *why* and *how much* of raw materials and other input mass are converted to final products and how much of the input mass is transformed to waste, and how much energy is lost. Mass and energy balance should answer the following important questions:

- Where are pollutants generated?
- Where do energy losses occur?
- What are the causes of pollution and energy losses?

The information is needed to determine inputs and outputs and to quantify them. It is not easy to create and verify mass and energy balances, but they are usually considered as an essential part of a structured approach to dealing with an assessment. The actual balance need not be completely “closed”, but each stream does need to be noted and the derivation of the figures given – with an indication of the errors and credibility of the data (Figure 6.3).

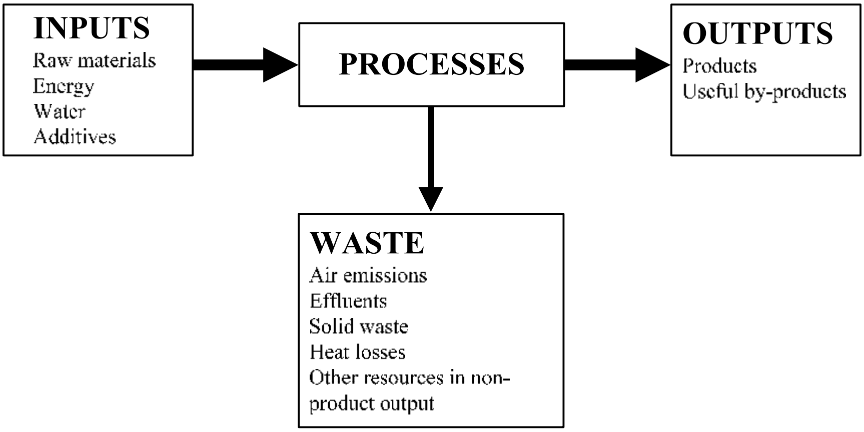


Figure 6.3. Important data gathering areas for mass balances.

For many operations it will not be possible to achieve a perfect mass or energy balance. Data will be inadequate and it will not approach closure (i.e. what goes in does not equal what comes out). The importance of this step is to indicate the type of information that is missing and alert the assessors to poor data quality and ensure they concentrate on priority issues.

Data gathering is an essential part of this process. Therefore there is a need to know what data is required, how it will be gathered, how it will be measured, timing, place and the relevant accuracy parameters involved.

Inputs to a process or a unit operation may include raw materials, chemicals, water, air and energy. Outputs include primary product, by-products, rejects, wastewaters, gaseous wastes, liquid and solid wastes that need to be stored and/or sent off-site for disposal or reuse. Material and energy balances are closely aligned. Balance carried out exclusively to understand energy flows is called an Energy Balance (Karlsson 2001, Staniskis and Stasiskiene 2002).

TABLE 6.1. Steps for material balance formation

Determine Inputs	Include raw materials, chemicals, water, energy, etc. to the process/operation for which material balance is being assessed. Measurements should be taken for an appropriate length of time to ensure that the results are representative. Averages should be taken wherever necessary and appropriate. Existing levels of material recycling should not be missed. They should be incorporated while balancing.
Quantify Outputs	Outputs consist of products, by-products and wastes. Attention should be paid to any off-spec products and reprocessing sequences.
Selection of Compounds	Suitable and representative compounds should be selected for preparing the material balance.
Prepare a Preliminary	Based on the inputs and outputs, a preliminary balance should be constructed. Discrepancies should be calculated and wherever in doubt, measurements or analysis should be repeated to refine the material balance.
Refine Material	The preliminary material balance should be improved by balance verifying the collected data during site inspections and by brainstorming.

The basic principle of a material balance is easy to understand (Table 6.1). In its simplest form, a material balance for any production system is drawn up according to the following principle:

$$\text{Material and Energy Inputs} = \text{Products} + \text{Waste}$$

Material inputs include: raw material, chemicals, energy, etc.
Energy includes: fuel, electricity, etc.
Products include: final products from the factory as well as by-products.
Waste includes: effluents, air emissions, solid wastes, waste heat, etc.

When discrepancies appear, the process can be traced backwards to identify problems and then the root cause(s) will be addressed.

Before commencing measurements in a material balance, the information should be checked with the operators and staff on standard operating procedures, frequencies and amounts of material inputs. In addition to water, chemicals, etc., energy is an important tie compound particularly for energy intensive and process sectors such as iron and steel, textile, pulp and paper, etc.

An energy balance may be defined as a quantitative account of the input and output forms of energy in a production process. Similar to a material balance investigation, the first step in an energy balance requires to develop a process flow diagram for the plant. Quantities of various forms of energy inputs for the plant or operating unit would then need to be measured and recorded. Energy inputs to a process or an operating unit may be in the form of steam, hot water, electricity, etc. as shown in Figure 6.4. Include the fuel sources needed to generate the heat in the inputs. The output is to be quantified in terms of the enthalpy (the heat content of the process) of the products, wastewater (process, condensate and cooling) and any energy losses such as steam leakage, etc. Doing an energy balance is very similar to a material balance.

Energy and material balances can be carried out for the various equipment and utilities that enable production, it can include maintenance and cleaning, in addition to the main process (see Figure 6.4).

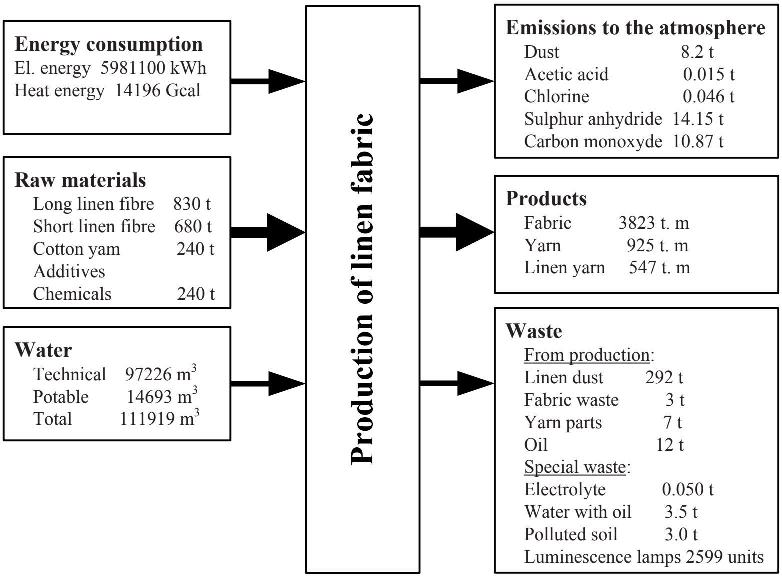


Figure 6.4. Material and energy balance.

3. Application of Cleaner Production Approach for Water Saving in Industry

In Lithuania Cleaner production measures have mainly been used to reduce energy and water consumption. In terms of innovation type, most of investments have been used for process optimization and technology change.

Some key learning points concerning cleaner production are as follows (Jorgensen 2000, Kemp and Andersen 2004, Staniskis and Arbaciauskas 2004):

- CP approach reduces pollutant generation at every stage of the production process and thus minimizes or eliminates wastes that need to be treated at the end of the process.
- CP is not a one-time event, it is a continuous process.
- CP can be achieved through good operating practices, process modification, technology changes, raw material substitution, and redesign and/or reformulation of product.
- 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.
- The economic advantages of CP are that it is more cost-effective than pollution control. The systematic avoidance of waste and pollutants increases process efficiency and improves product quality. Through pollution prevention at the source, the cost of final treatment and disposal is minimized.
- The environmental advantage of CP is that it solves the waste problem at its source. Conventional end-of-pipe treatment often only moves the pollutants from one environmental medium to another.
- The barriers to CP are mostly related to human rather than technical factors. The end-of-pipe approach is well known and accepted by industry and engineers. Existing government policies and regulations often favor end-of-pipe solutions. There is a lack of communication between those in charge of production processes and those who manage the wastes that are generated. Managers and workers, who know that the factory is inefficient and wasteful, are not rewarded for suggesting improvements.
- Considering that CP addresses the problem at several levels at the same time, introduction of an industry/plant level programme requires the commitment of top management and a systematic approach to cleaner production in all aspects of the production process.

In spite of the results presented below, industry very rarely considers cleaner production initiatives as an option for improving productivity in parallel to a reduction of the impact on the environment. End-of-pipe solutions are still commonly applied if environmental demands are to be met.

Experience from CP projects implemented in Lithuania has shown that it is difficult to ensure the follow-up of CP activities on a company level after the project end. Therefore, a decision has been made to integrate CP and environmental management systems (EMS) and to start the implementation of preventive environmental management systems (Staniskis and Arbaciauskas 2004):

- Firstly, cleaner production is not a continual and normal practice for industry.
- Secondly, EMS does not guarantee that CP will be applied or even that an environmental performance above regulatory requirements will be obtained, i.e. EMS focuses on the quality and strengths of procedures and not the actual outcome of these procedures regarding pollution abatement and improved resource productivity.

Investments in CP can have attractive economic benefits due to reduction of input costs for materials, energy and water, and reduced expenditures related to waste treatment and disposal. Several international organizations, banks and donors have initiated and implemented projects to facilitate introduction of CP investments. However, these domestic and international efforts to strengthen environmental financing still face a number of serious obstacles, many of them being related to profound economic, political and social problems. The obstacles to financing CP investments could be described under two major groups:

- On the demand side, enterprises have insufficient experience in preparing a real CP project systematically evaluated from the environmental, economic and technical points of view and to prepare motivated applications for the project financing. The lack of knowledge in CP auditing and assessment, evaluating the financial aspects of the project efficiency and investments often blocks implementation of CP projects. Even when capital is available, CP is one among a range of investment options.
- On the supply side, there are obstacles in capital markets, since environmental expertise is lacking and loan rates unattractive to enterprises. Also, 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. Generally, experience in the implementation of economically viable CP projects is little.

Furthermore, an effective financing system requires environmental strategies with clear goals and priorities. There is a need for training and education in environmental management and financing, especially at the local level. In many countries, capacities for preparing financially and environmentally sound projects should be increased (Bennett et al. 2003, Staniskis and Stasiskiene 2003b).

In 1998, under APINI initiative the Nordic Environment Finance Corporation (NEFCO) established a special Revolving Facility for Baltic States and North West Russia. NEFCO is a risk capital institution financing environmental projects in Central and Eastern Europe. It was established in 1990 by the five Nordic countries (Denmark, Finland, Iceland, Norway and Sweden). The environmental, technical, institutional, economical and financial feasibility of the project should be demonstrated through an adequate feasibility study. NEFCO requires projects to meet reasonable profitability criteria but, this having been established, focuses more on the environmental effects. In this NEFCO represents a green equity concept, unlike commercial investment funds.

The Revolving Facility addresses the needs to enhance the financing of the CP projects that otherwise would not have been implemented with a high leverage for donors and an effective use of scarce resources. The Facility enables the financing of smaller investment projects in the target countries. It constitutes a follow-up of various CP programmes and projects supported by donors in Central and Eastern European countries.

Priority is given to projects that have environmental effects for the Nordic region, i.e. to projects leading to reduction of pollution in the Baltic Sea and the Barents Sea regions or reduction of transboundary and global air pollution.

The Facility's conditions are very attractive for Lithuanian companies (Staniskis and Stasiskiene 2003c, Staniskis et al. 2008):

- Max loan amount 350000 EUR (until 2004 the amount was 200000 EUR).
- Interest rate 2.5% (until 2004 the rate was 3%).
- The loan should be repaid during the CP project payback period (max 4 years).
- The collateral is 150% of loan amount and should be a movable property.

In terms of CP investment financing, the APINI experts play a crucial role in CP project identification, evaluation, implementation and reporting, because they:

- Prepare a loan application on behalf of the applicant, including assistance in calculation of costs savings and environmental benefits.
- Assist the financing institution in communication with the applicant and preparation of loan documentation, project description and reporting requirements.
- Prepare the project progress and completion reports to be presented as part of the borrower’s disbursement request.
- Assist in the project monitoring and supervision, including the supervision of procurement and project implementation progress as compared to the budgets and implementation plan as well as the project objectives (Staniskis and Stasiskiene 2003a, Staniskis et al. 2005).

The facility has considerable catalytic effects in Lithuania by demonstrating to other financiers and enterprises that the financing of priority cleaner production investments yields environmental and economic benefits. The main objective of the facility is to finance, on favorable terms, implementation of high-priority CP innovations with a rapid payback, which yield environmental and economic benefits (“win-win projects”). The innovations should be commercially viable with an identifiable and secure stream of earnings to be used to repay the loan. The basis for providing a loan is a cash flow of CP investment and ability of the enterprise to repay the loan over the agreed period (see Table 6.2).

TABLE 6.2. Implementation of CP in Lithuanian industry

Industry sector	**Number of enterprises**	**Number CP options analyzed**	**Number implemented CP measures**	**CP investments, EUR (×1000)**	**Savings from implemented CP measures, EUR/year (×1000)**
Textile industry	14	42	39	2734	2474
Food industry	13	27	25	2027	1365
Chemical industry	6	15	14	435	493
Machinery production	5	5	5	1033	389
Production radio, TV, telecommunication	2	6	6	1478	613
Furniture production	6	10	10	1030	421
Wood industry	3	6	6	1431	1067

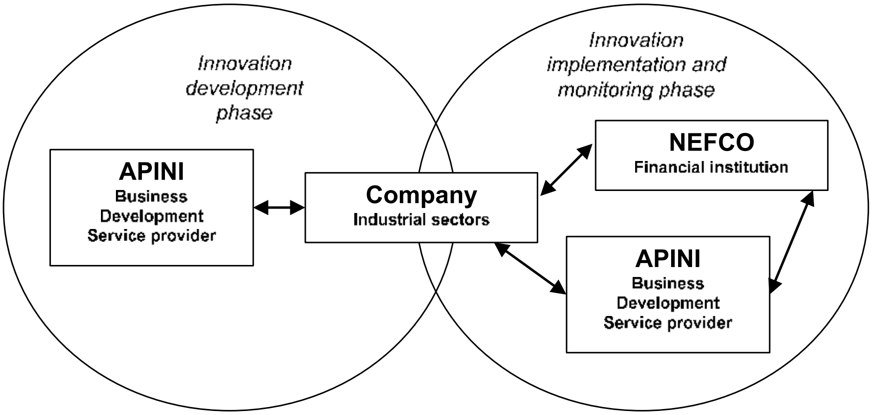


Figure 6.5. APINI SPIN system for CP innovation development and implementation in industry.

According to the APINI–NEFCO methodology (Figure 6.5), environmental issues in the CP investment project development focus on the following:

- Location of the project with respect to population centres, sensitive local land uses, and the existing levels and sources of pollution.
- Pollution category (air, surface water, ground water, hazardous waste, etc.).
- The scale of the pollution impact.
- The effect associated with the pollution, including possible toxicity to human health, possible impact on climate change, and damage to the natural ecosystems and habitat.

Most of the Lithuanian companies provided with NEFCO soft loans for CP project implementation graduated from the Lithuanian–Norwegian CP training programme. Therefore, a full CP assessment was performed in the companies. CP assessment is one of the basic grounds for CP investment project development according to the APINI–NEFCO methodology, which covers (Staniskis and Kliopova 2006):

- CP pre-assessment: CP audit preparation; division of processes into unit operations; construction of process flow diagrams linking the unit operations.
- Material balance: determination of process inputs and outputs; derivation of a material balance (gathering the input and output information, deriving a preliminary material balance, evaluating and refining the material balance).
- Synthesis: identification of CP options; environmental, technical and economic evaluation of CP options; design of CP action plan.

- The company's "economic health" analysis.
- Development of a CP investment project.

The database was created with the aid of Microsoft Assess 2000 program in 2002 and is periodically renewed. Currently, this database presents the technical, environmental, economical and financial information on 175 implemented CP innovations in 80 companies from different Lithuanian sectors of economy since 1993. These CP projects were implemented and evaluated during various CP, CP financing, EMS, IPPC programmes organized by the Institute of Environmental Engineering (APINI) in Lithuania.

The results of water savings by Cleaner Production methods and investments and savings are summarized in Tables 6.3–6.5.

TABLE 6.3. Water savings by CP methods

Applied CP methods	**Reduction of potable water consumption,** ***1000 m^3/year***	**Reduction of technical water consumption,** ***1000 m^3/year***	**Minimization of waste water volume,** ***1000 m^3/year***
Input substitution	9.96	5.6	11.83
Technology modification	44.30	34.1	57.50
Process optimization	249.05	376.2	629.85
Waste recycling	26.6	25.4	52.1
Good housekeeping	2.7	27.7	27.7
Total	332.61	469	778.98

TABLE 6.4. Investments in water recycle innovations (×1000 EUR)

Industry	**Wastewater recycle**	**Condensate recycle**	**Cooling water recycle**
Textile	94.5		103
Metal products		5.55	
Machinery and equipment	95.5		284.7
Food products	102	0.35	909
Transport and communication	55		
Tanneries	16		13.3
Total	363	5.9	1310

TABLE 6.5. Yearly savings from water recycle innovations (×1000 EUR)

Industry	**Wastewater recycle**	**Condensate recycle**	**Cooling water recycle**
Textile	93.3		373.3
Metal products		5.3	
Machinery and equipment	30.5		124
Food products	124.4	3	351.8
Transport and communication	21		
Tanneries	48.8		38.7
Total	318	8.3	887.8

4. Water Saving by CP Cases

4.1. RECYCLING OF WATER AND OIL IN THE WET SPINNING PROCESS

This innovation enables to reuse water and oil from the spinning process after additional cleaning. The innovation has been developed and implemented in Lithuanian textile company.

The essence of this innovation is recycling of water and oil in the wet spinning process, i.e. installation of oil cleaning filter and water treatment equipment. After treatment, water is used for equipment cleaning (see Figure 6.6).

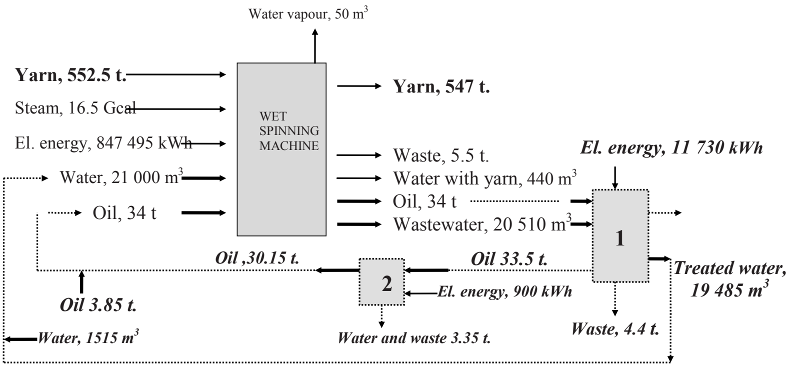
Recycling of oil and water in the wet spinning process has clear economic and environmental benefits. This technology has been practically tested. Implementation of this system is relatively simple.

Environmental aspects:

- Reduction of water consumption (~20000 m^3/year in a given case).
- Reduction of oil consumption (~30 t/year).

Economic aspects:

- Total investment is approximately 28000 USD. Payback period for implementation of this innovation was only 9 months. In addition to savings associated with reduced water and oil consumption, environmental taxes have been reduced.



1-equipment for water treatment ;
2 –oil treatment (IHDC4003 filter).

Figure 6.6. Water and energy balance for wet spinning process.

4.2. WATER RECYCLE IN TEXTILE INDUSTRY

4.2.1. *Recycling of Cooling Water in the Bleaching Process*

- CP measure – Process optimization.
- Reduction of water consumption: 17.3 × 1000 m^3/year
- Reduction of wastewater volume: 17.3 × 1000 m^3/year
- The process uses 5 m^3/h of cold water. Before implementation of this project, cooling water was going to the sewage system (see Figure 6.7).

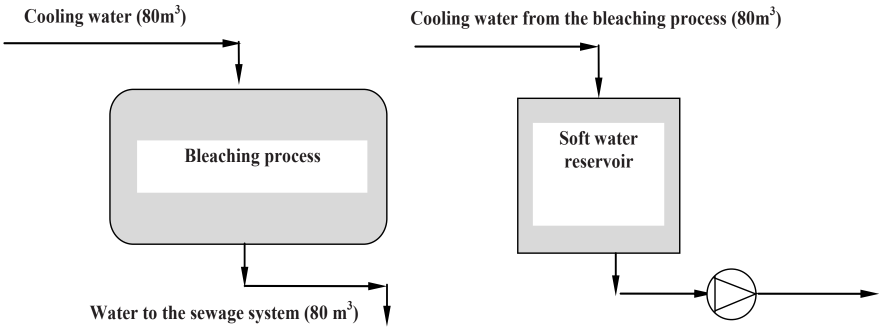


Figure 6.7. Recycling of cooling water in the bleaching process.

4.2.2. *Reconstruction of Air-Conditioning Systems in the Production Premises*

- CP measure – Process optimization.
- Reduction of water consumption: 7.1 × 1000 m^3/year

- Removal of a compressor that required 7080 m^3 cooling water yearly (see Figure 6.8).

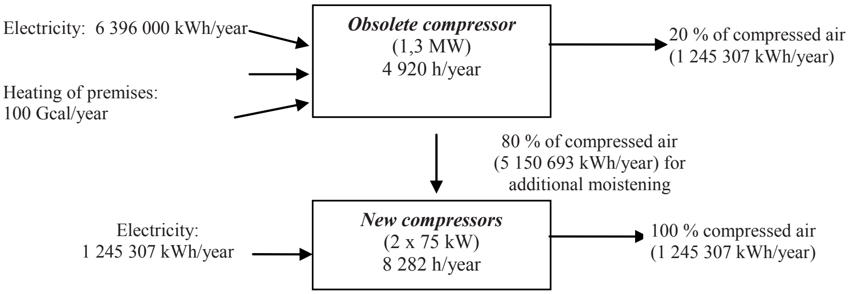


Figure 6.8. Reconstruction of air-conditioning systems in the production premises.

4.2.3. *Water Recycling in Textile using Membrane Filtration*

In order to get the best rubbing and wash fastness the goods are usually washed too long and too intensely.

Therefore, a large amount of water is consumed and accordingly wastewater generated.

To solve the problem the membrane filtration was applied (see Figures 6.9 and 6.10).

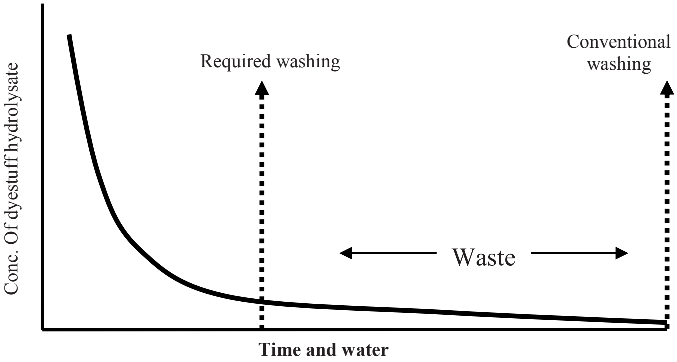


Figure 6.9. Water recycling in textile.

Benefits:

After implementation of closed water cycle savings are:

- 86% overall water resources of the company.
- From 35 m^3/t to 5.1 m^3/t.

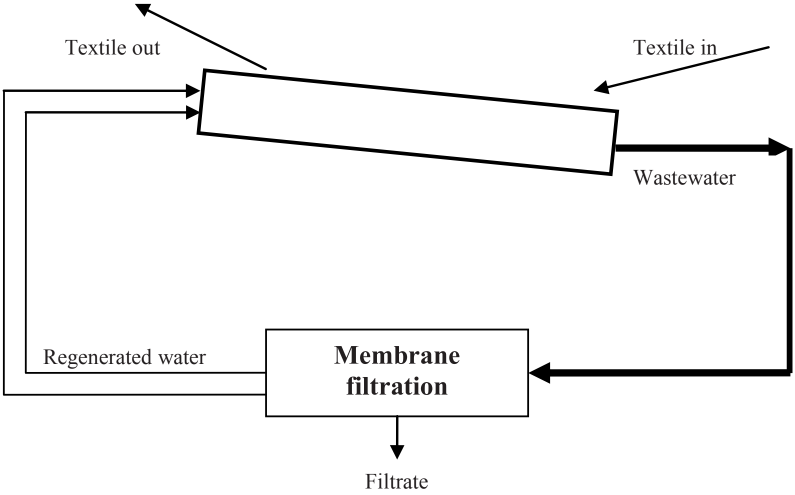


Figure 6.10 Direct wastewater reuse using membrane filtration.

4.3. MODERNIZATION OF OXIDATION-PHOSPHATATION PROCESS IN THE GALVANIZATION DEPARTMENT

Lithuanian company producing electric appliances and metal products modernized oxidation-phosphatation process that enabled to reduce consumption of water, chemicals, generation of galvanic sludge and air emissions as well as fuel consumption due to introduction of water recycling and electric heating instead of heat energy produced in the boiler house.

This innovation comprises of several preventive measures, i.e. recycling of water and chemicals, introduction of electric heating, introduction of conductivity controller for better process control. Structural scheme of the process after modernization is presented in the Figure 6.11.

Modernization of oxidation-phosphatation process in the galvanization department focused on water recycling has clear economic and environmental benefits. The technology is practically tested.

Environmental aspects:

- Reduction of water consumption – more than 1000 m^3/year
- Reduction of chemicals' consumption – 2.8 t
- Reduction of galvanic sludge – 1.35 t/year
- Reduction of air emissions from the boiler house – 7.6 t/year

Total investment is approximately 78000 EUR. Total profit from the project implementation in a given case was almost 30000 EUR/year (payback period – 2.8 years).

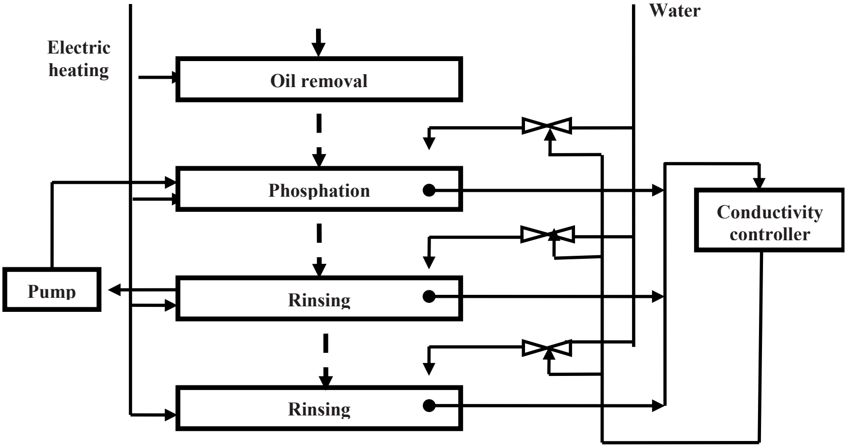


Figure 6.11. Efficient use of water resources in of oxidation-phosphatation process.

4.4. WASTE WATER RECIRCULATION AT A SHEEP SKINS TANNERY

The processing of hides comprises the following steps: beamhouse operations, tanning and finishing. The cleaner technology proposal deals with the beamhouse operations.

Currently, all water used in beamhouse operations is fresh water supplied directly from the river, Nemunas. All waste water from the beamhouse (653 m^3/day) becomes sewage. This waste water contains detergents and other chemicals (formalin, sodium carbonate). The working temperature is about 350°C. The temperature of the river water is 50°C in winter time and 150°C in summer time. Great losses of water, steam energy and chemicals occur because of inefficient technology and operations.

4.4.1. *Taken Measures*

In order to minimize the water and chemicals consumption, it was proposed to rearrange several processes and to use wastewater from one process in another as the raw water. The following is a description of different steps made in the tannery (see Figure 6.12):

- Step 1: The wastewater from the degreasing & rinsing (60 m^3) operations would be used in the soaking operation.
- Step 2: The wastewater from the squeezing operations after first and second washing (140 m^3) would be used for squeezing after soaking.
- Step 3: The wastewater from degreasing & rinsing operations (70 m^3) would be used for squeezing after the first washing.
- Step 4: The wastewater from the second washing (53 m^3) would be used for the first washing. The wastewater from the degreasing operation (17 m^3) would be used for the first washing.
- Step 5: The wastewater from the degreasing & rinsing operations (53 m^3) would be used for the second washing.

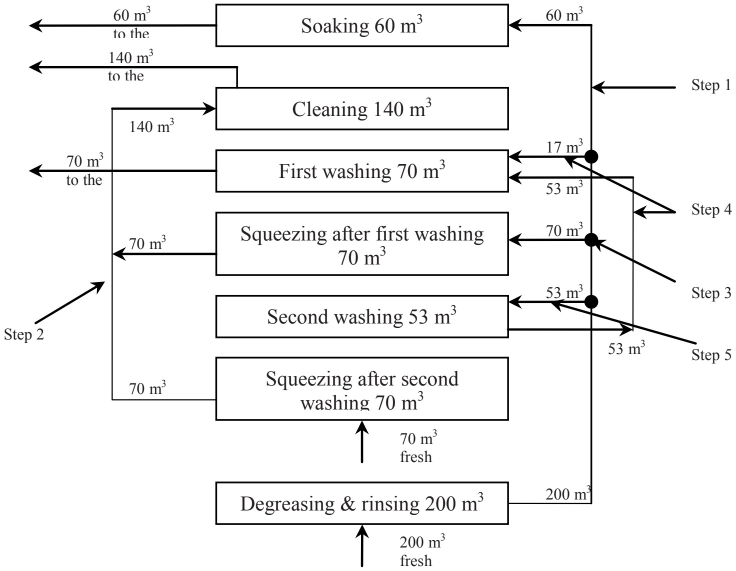


Figure 6.12. Water recycling in beamhouse operations.

4.4.1.1. *Environmental Advantages*

Less water used in the processes.
Savings of chemicals.
Savings of energy.
Decreased pollution load to the wastewater.

4.4.1.2. *Economic Benefits*

Investment in the changed production processes (reuse of waste water) cost USD 50000. Because of reduced costs for chemicals and more efficient use of water the yearly savings at his facility amount to USD 100000. This yields a simple return on investment in 6 months.

5. Discussion and Consideration

Protection and sustainable management of the natural resource/water within the carrying capacity of ecosystems, the control of emissions and reduced use of hazardous substances should be the underlying principles behind industrial development in all countries. The development and application of sound environmental and resource-efficient technology complemented by integrated management systems, which create synergies between quality, environmental, social and organizational management aspects, and environmentally sound products and services lead towards economic, social and environmental sustainability.

CP innovations developed in accordance to the methodology developed by the Institute of Environmental Engineering (APINI) (Lithuania) have mainly been used to reduce energy and ***water consumption*** and to minimize pollution. In terms of innovation type, most of investments have been used for process optimization and technology change (see Table 6.6) (Staniskis and Kliopova 2006).

TABLE 6.6. Results on implemented preventive innovations in Lithuania (1997–2009)

Number of companies	69
Number of implemented preventive innovations	141
Environmental results (yearly):	
El. energy consumption reduced	30,365 MWh
Heat energy consumption reduced	60,510 MWh
Waste amount reduced	86,700 t
Chemicals consumption reduced	850 t
Air emission reduced	79,500 t
Drinking water consumption reduced	297,500 m^3
Diesel consumption reduced	387,000 L
Natural gas consumption reduced	5,883,000 m^3
Petroleum consumption reduced	656,800 t
Wastewater amount reduced	622,500 m^3
Industrial water consumption reduced	468,900 m^3
Economic benefit:	
Total investment in preventive innovations	16,529,000 EUR
Yearly savings from preventive innovations	9,605,000 EUR

Some key learning points concerning cleaner production concept application:

1. CP approach reduces pollutant generation at every stage of the production process in order to minimize or eliminate wastes that need to be treated at the end of the process.
2. CP is not a one-time event, it is a continuous process.
3. CP can be achieved through good operating practices, process modification, technology changes, raw material substitution, and redesign and/or reformulation of the product.
4. 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.
5. The economic advantages of CP are that it is more cost effective than pollution control. The systematic avoidance of waste and pollutants increases process efficiency and improves product quality. Through pollution prevention at the source, the cost of final treatment and disposal is minimized.
6. The environmental advantage of CP is that it solves the waste problem at its source. The conventional end-of-pipe treatment often only moves the pollutants from one environmental medium to another.
7. The barriers to CP are mostly related to human rather than technical factors. The end-of-pipe approach is well known and accepted by industry and engineers. Existing government policies and regulations often favor end-of-pipe solutions. There is a lack of communication between those in charge of production processes and those who manage the wastes that are generated. Managers and workers who know that the factory is inefficient and wasteful are not rewarded for suggesting improvements.
8. Considering that CP addresses the problem at several levels at the same time, introduction of an industry/plant level programme requires the commitment of top management and a systematic approach to cleaner production in all aspects of the production process.

Therefore it can be stressed that CP is promoted because it minimises the use of resources/water and reduces the wastes discharged to the environment. In many cases the implementation of CP improvements can reduce or even eliminate the need for end-of-pipe investments and therefore can have both environmental and economic benefits. As a rough guide, 20–30% reductions in pollution can often be achieved with no capital investment required and a further 20% or more reduction can be obtained with investments, with a payback time of only months (see Figures 6.13 and 6.14).

CP is also attractive because of concerns about the lack of effectiveness of end-of-pipe solutions: there are numerous examples of a poor operation and maintenance of treatment plants with the resulting failure of the system to achieve its objectives.

CP and related approaches will have an increasing importance in environmental management in the future as resource prices and disposal costs continue to rise and new opportunities arise for pollution prevention and reductions in treatment costs.

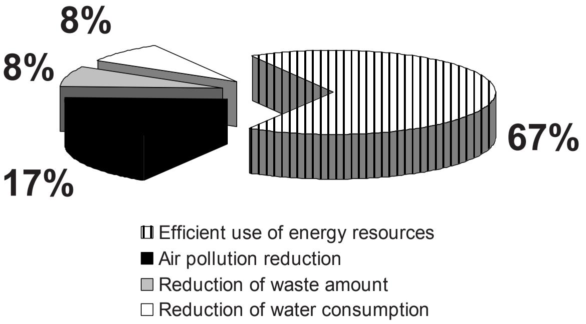


Figure 6.13. Implementation of preventive innovations by environmental areas.

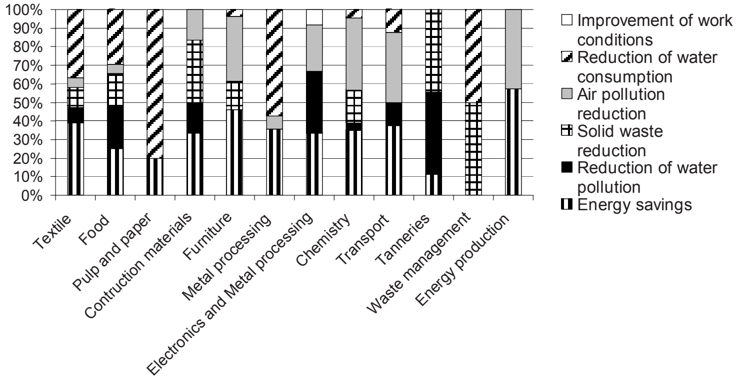


Figure 6.14. Preventive innovation areas in different industries

Properly implemented CP (Staniskis et al. 2008):

Always:
- Reduces long-term liabilities which companies can face many years after pollution has been generated or disposed at a given site.

Usually:
- Increases profitability, lowers production costs and enhances productivity by avoiding or reducing pollution control and waste treatment/disposal costs.
- Provides a rapid return on any capital or operating investments required.
- Leads to a more efficient use of energy and raw materials.
- Increases product yield, as waste generation along the production chain is minimized.
- Results in improved product quality.
- Increases staff motivation through reduced worker risks and relies on active worker participation in idea generation and implementation.
- Reduces consumer risks associated with products containing hazardous substances.
- Reduces the risk of environmental accidents.
- Is supported by employees, local communities, customers and the public.

Often:
- Avoids regulatory compliance costs.
- Leads to insurance savings.
- Provides enhanced access to capital from financial institutions and lenders.
- Is fast and easy to implement.
- Requires little capital investment.

Considering the commitments in the Johannesburg Plan of Implementation related to strengthening of the contribution of industrial development to poverty eradication and sustainable natural resource management the following activities should be supported according to Plan of Implementation of the World Summit on Sustainable Development (Staniskis and Stasiskiene 2002, 2005):

- Enhancing industrial productivity and competitiveness – including environmentally sound technology transfer.
- Assistance in the creation of income generating employment opportunities, especially promotion of the development of micro and SM enterprises.

- Support for safe low cost preventive innovations.
- Support for sustainable management of natural resources.

Industrial development is closely linked to changing unsustainable consumption and production patterns as well as trade and these must also be taken into account. This means achieving progress in:

- De-linking economic growth and environmental degradation through improving efficiency and sustainability in the use of resources and production processes and reducing resource degradation, pollution and waste.
- Increasing investment in cleaner production and other preventive innovations.
- Integrating the issue of production and consumption patterns into sustainable development programmes, policies and strategies.
- Enhancing corporate environmental and social responsibility and accountability, based inter alia on the Rio principles.
- Encouraging relevant authorities at all levels to take sustainable development considerations into account in decision-making, including business development.
- Preventing and minimizing waste and maximize reuse, recycling and use of environmentally friendly alternative materials.

To reach all mentioned goals the following means should be applied:

- *Cleaner Production*, which is continuous application of an integrated preventive environmental strategy to processes, products, and services to increase overall efficiency, and reduce risks to humans and the environment. Cleaner Production can be applied to the processes used in any industry, to products themselves and to various services provided in society.
- *Environmental Management Accounting (EMA)*, which is simply better and more comprehensive approach to management accounting, with a particular focus on costs related to wasted raw materials and other environmental issues.
- *Eco-design*, an approach to design a product with special consideration for the environmental impacts of the product during its whole life-cycle, i.e. procurement, manufacture, use and disposal.
- *Preventive Environmental Management* – the management of man's interaction with and impact upon the environment based on preventive

measures and covering politics (networking), programs (projects), and resources (i.e. money, facilities, etc.). The environment also involves the relationships of the human environment, such as the social, cultural and economic environment with the bio-physical environment.
- *Sustainability reporting* – developed by company report where companies on a voluntary basis present integrated social and environmental concerns of their business operations and interactions with their stakeholders.

Environmental sustainability implies avoiding degradation of biomass and bio-productivity – major components of our "natural capital". Economic sustainability is a concept with clear quantitative implications; it can only be realized if one spends less than the interest on one's accumulated capital. Sustainability can also be achieved by spending all the interest, but this allows for no growth, and the most prudent course in the long run is to delay consumption and invest as much as possible to increase future income. If one discounts the interests of future generations, one can spend more than the interest and deplete the capital, but this is unsustainable, and the wealth will steadily vanish. Sustainable development means that renewable resources can be managed in the same way as money, thereby preventing a decrease of resources, and preferably an increase for future generations.

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SOLID DISPOSAL FROM EFFLUENTS TREATMENT

MIGUEL A. SUÁREZ, JOSÉ COCA*
Department of Chemical Engineering and Environmental Technology, University of Oviedo, Oviedo (SPAIN)

Abstract. In most wastewater treatment processes large quantities of solids and sludge (refuse) are produced that must be disposed of. Such refuse is a complex mixture of substances, both physically and chemically. The properties of solid waste streams generated during the treatment of municipal and industrial wastewaters are summarized, and alternatives for their treatment and final disposal are reviewed. The main alternatives currently used for the management of these wastes, such as conditioning, thickening (sedimentation and flotation), and dewatering (evaporation and centrifugation) are described along with relevant process-performance parameters.

Final disposal alternatives using landfill and incineration methods are considered in detail. These include methods such as land disposal, composting or anaerobic treatment, and the co-treatment of sludge with other waste streams, such as municipal solid wastes (MSW). The performance of MSW incineration for the disposal of MSW-stabilized sludge is presented, and rules are identified for selection of appropriate MSW/sludge ratios leading to efficient treatment of these blends.

1. Introduction

Municipal and industrial wastewaters are effluents of a different nature. Industrial wastewaters may be chemically simpler than sewage. Each plant within a factory complex may produce a different effluent. Solid wastes are the final product that ultimately must be disposed of in any treatment process.

In conventional wastewater treatment, Figure 7.1, particulate solids or insoluble liquids are removed in the primary treatment. Biological treatment is used to degrade dissolved organic compounds. Tertiary treatment removes

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* E-mail: jcp@uniovi.es

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dissolved ions rendering the wastewater appropriate for recycle or safe disposal.

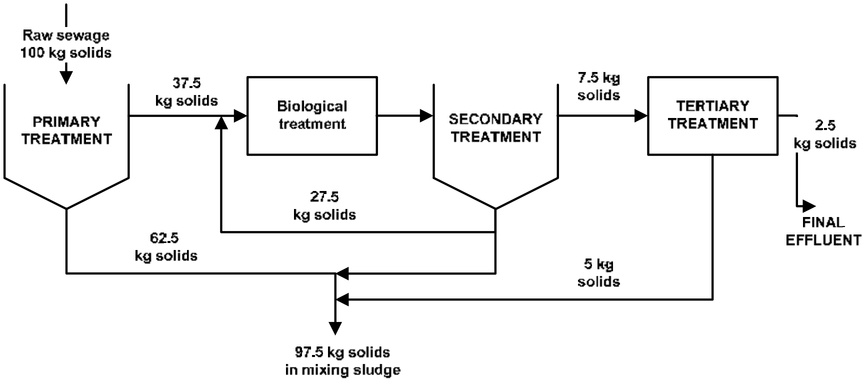

Figure 7.1. Flow diagram of typical urban waste water treatment and solids content.

A liquid stream and a suspended solids stream are generated in every treatment step. The solid streams are called sludge or sewage sludge if they come from urban wastewaters.

1.1. PRIMARY TREATMENT

Settleable solids are removed in the primary treatment by the process of settling or sedimentation. Solids removal by sedimentation is typically 65%, depending upon the strength and character of the sewage and the residence time. Removed solids represent 4% of total feed. The remaining clarified water, around 96%, passes forward for secondary treatment.

1.2. SECONDARY TREATMENT

The organic matter left in the sewage after settling is oxidized by the bacteria and organisms present in the sewage, along with other microorganisms maintained in the biological process. The two main methods are biological trickling filters and activated sludge. After the biological treatment, a settling tank separates the activated sludge. This is partially pumped back to the biological treatment tank with a proportion drawn off containing around 30% of the solids in the raw sewage.

1.3. TERTIARY TREATMENT

A tertiary treatment stage is necessary if higher effluent standards are required. This typically involves the removal of the remaining suspended matter. A variety of clarifiers and filtering methods are used for this purpose. Membrane technology works well and yields good water quality. It is estimated that 5% of the solids in the raw sewage are recovered by means of tertiary treatment.

The sludge from the wastewater treatment plant is a complex mixture of substances, both physically and chemically, that contain about 95–97% water (*primary sludge*) and as much as 99.0–99.5% water (*secondary sludge*). Processes such as gravity thickening and flotation are used to reduce the volume of sludge, before subsequent conditioning and dewatering process stages.

The final treated sludge may be spread on agricultural land, discharged into landfills or it can also be thermally treated by incineration or gasification. Other methods such as wet air oxidation, composting or valorization for brick production are also possible.

2. Sludge Characteristics

The choice of the sludge final disposal is influenced by several factors. Sludge characteristics are the key factor to determine the three treatment stages: conditioning, dewatering, and disposal. The most important are the following:

- *Solids concentration.* The amount of solid matter contained in the sludge which remains after evaporation. It influences the sludge volume and is related to the organic matter content (range between 45 and 85% dry solids). Sludge may behave as a liquid or as a solid depending on the solids-water ratio. This affects sludge handling. Sludge is generally dewatered by mechanical methods that increase solids concentration up to 30–45%.
- *Volatile solids content (VSC).* Sludge conditioning may be carried out by heat treatment in the range of 175–200°C. Volatile compounds vaporize and, depending on the oxygen concentration, combustion of some organic matter may occur. The difference between total dry solids and the remaining residue after thermal treatment is expressed as volatile solids content (VSC), which is related to combustible organic matter content. Sludge disposal might prove difficult if VSC is high.

- *Chemical composition.* Chemical analysis of the sludge is a key parameter regarding applications where availability of nitrogen, phosphorus and potassium is important. Heavy metal content must be determined if the sludge is to be used for agricultural purposes or composting (*e.g.* Cd 0–1000 mg/L). All heavy metals are treated and removed by the flue gas cleaning methods if the sludge is incinerated.
- *Heating value.* It is the energy generated by total combustion of a material, and is a key parameter if sludge is incinerated. High moisture content produces steam along with the steam generated by the combustion reaction. This leads to two kinds of heating values:

  - *Higher heating value (HHV)*
  - *Lower or net heating value (LHV or NHV)*

  In HHV, steam condensation is not considered. Its value is higher than LHV, where condensation is taken into account. Heating value is expressed in units of energy by unit mass. However, it may be referred to different basis that have to be taken into account in mass and energy balances calculations:

  - *Wet basis (wb)*. It corresponds to the whole waste weight, including its moisture content.
  - *Dry basis (db)*. It corresponds to the dry fraction of the waste
  - *Ash and moisture free basis (awf)*. It corresponds to the combustible fraction of the waste (excluding the ash).

Relationships between HHV and LHV are as follows:

$$LHV_{bas} = HHV_{bas} - \lambda(9H_{bas}) \tag{7.1}$$

$$LHV_{wb} = LHV_{db}(1 - v_m) - \lambda v_m = LHV_{awf} v_{comb} - \lambda v_m \tag{7.2}$$

where:

λ = heat of vaporization of water (2445 kJ/kg)
H_{bas} = hydrogen content (wt% on the same basis as HHV and LHV)
y_m = moisture weight fraction
y_{comb} = combustible weight fraction

Sludge heating value is highly influenced by pretreatment processes, especially those involving water removal and biological digestion, which influences the combustible matter content. Different treatments lead to different LHV values as shown in Table 7.1.

TABLE 7.1. Range for reference LHV values for sewage sludge

Reference	LHV (MJ/kg, dry basis)
Fytili and Zabaniotou (2008)	9–13
Stasta et al. (2006)	8–12
Niessen (1995)	12.75
Corbitt (1998)	12.80
BREF (2006) (raw)	14.12–17.34
BREF (2006) (digested)	9.34–12.14

Sewage sludge HHV (in kcal/kg) can be estimated by a modification of the Dulong equation, as proposed by Niessen (1995):

$$HHV = 55.47\mathrm{C} + 182.87\mathrm{H} - 17.2\mathrm{O} + 10\mathrm{N} + 16.67\mathrm{S} + 6.27\mathrm{Cl} \tag{7.3}$$

where C, H, O, N, S and Cl are concentrations (in wt%) of carbon, hydrogen, oxygen, nitrogen, sulphur and chlorine, respectively. Concentrations and HHV values are given on ash and moisture free basis. An example of an anaerobically digested sewage sludge composition is shown in Table 7.2.

TABLE 7.2. Sewage sludge composition, wt% (Niessen 1995)

Element	Dry basis	Ash and free moisture
C	31.4	54.7
H	3.91	6.82
O	15.2	26.5
N	4.52	7.89
S	1.54	2.68
Cl	0.80	1.40

HHV can be easily transformed into LHV by Eq. (7.1). Eq. (7.3) gives somewhat lower values (Channiwala and Parikh 2002), and consequently is useful for conservative estimations.

- *Rheological characteristics.* Sewage sludge handling also depends on its rheological characteristics. It can be considered as a pseudoplastic fluid. Viscosity decreases with increasing shear rate, or that it is a shear-thinning fluid. It may become a plastic fluid as solid concentration increases, which means that a minimum yield stress is needed to behave as a fluid.

3. Processes for Sludge Treatment and Disposal

Sludge may be treated by a number of processes, including thickening, conditioning and disposal, as shown in Figure 7.2.

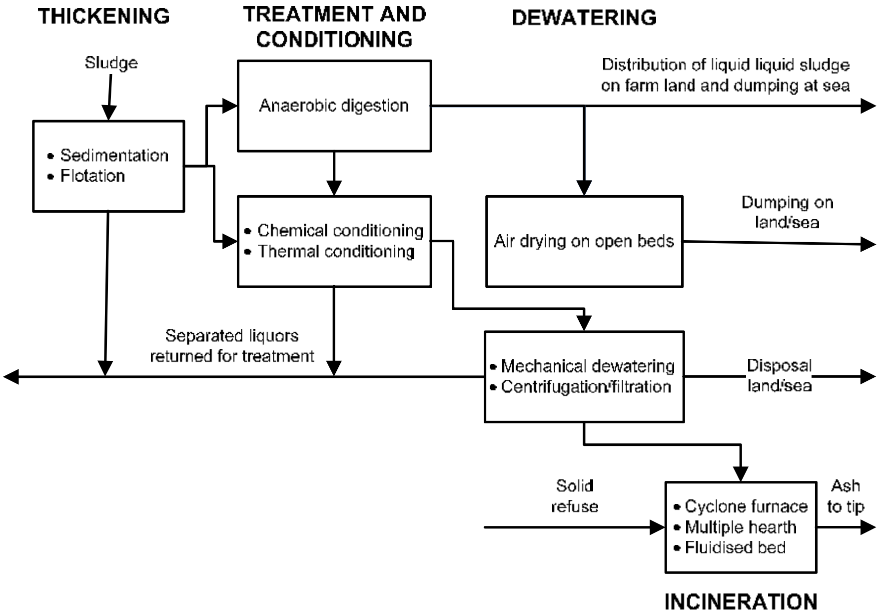

Figure 7.2. Flow diagram of sludge treatment (from IChemE 1974).

Water reduction may be achieved by different processes according to the type of water in the sludge, as shown in Table 7.3.

TABLE 7.3. Water distribution in sewage sludge and treatment methods for its removal

Kind of water	Treatment method for removal	Solids content after removal
Free water	Thickening	4–8%
Capillary water	Mechanical dewatering	20%
Adsorbed water	Mechanical dewatering + polymer conditioning	22–35%
Intracellular water	Thermal drying	92–98%

3.1. THICKENING

Free water removal is the first and easiest step for sludge treatment as sludge volume can be decreased by 80% (Oleszkiewicz and Mavinic 2002). Thickening can be achieved by different methods such as gravity, flotation, and centrifugation, as well as gravity belt thickeners and rotary drums.

3.2. TREATMENT AND CONDITIONING

Biological and chemical reactions take place in raw sludge, making of it an unstable waste that must be treated before disposal to avoid environmental and health impacts.

Sludge stabilization includes processes that lead to volatile solids reduction and a decrease in sludge putrescibility. Aerobic and anaerobic digestions are the most common processes. Another method is chemical conditioning by lime stabilization, adding $Ca(OH)_2$ or CaO. A pH of 11 is reached within 1–14 days.

3.2.1. *Aerobic Digestion*

Aerobic digestion is carried out by aeration in an open tank. The process requires long residence times. Total degradation is generally not reached and dewatering becomes more difficult. Heat released by bacteria during the oxidation keeps the reaction (autothermal) going, a thermophillic process. Generally this takes place in a cascade of at least two reactors, the first reactor at a temperature of 50–55°C and the second at 55–70°C (Oleszkiewicz and Mavinic 2002).

3.2.2. *Anaerobic Digestion*

Sludge is stored for several weeks in close heated tanks, as shown in Figure 7.3. Bacteria decompose organic matter into volatile organic acids as a result of biochemical transformations. New bacteria use volatile organic acids to reproduce and transform them into a gas mixture of methane and carbon dioxide, leaving a stabilized product.

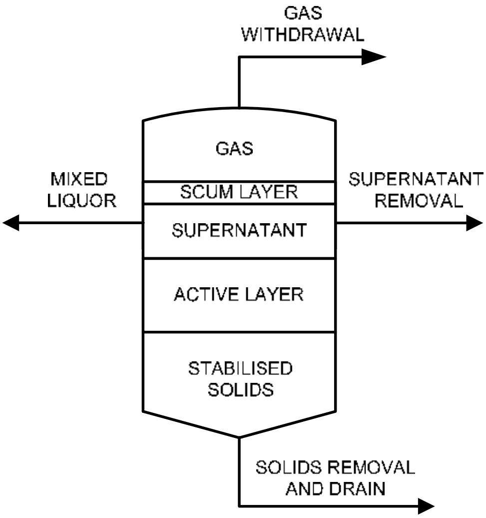

Figure 7.3. Anaerobic digestion of sludge.

Anaerobic digestion can be classified as mesophilic or thermophillic. Mesophillic process temperature is in the range 36–38°C, but pathogens are not efficiently killed under these conditions. Thermophillic processes take place at temperatures of 48–57°C and most of the pathogens are destroyed (Oleszkiewicz and Mavinic 2002).

The anaerobic digestion bioreactor, Figure 7.3, has several layers depending on the materials present. There is an active layer where anaerobic biological reactions take place. Below it stabilized solids can be removed at the bottom, and there is a supernatant layer on the active layer which is also removed. The biogas is collected at the top of the bioreactor. Its throughput is estimated as 0.6 m^3 gas/kg volatile solids.

Anaerobic digestion can be followed by aerobic digestion or composting to oxidise reduced compounds produced under anaerobic reactions (Oleszkiewicz and Mavinic 2002).

3.2.3. *Composting*

Composting is another kind of aerobic treatment that takes place in solid phase. It is an autothermal process and involves biodegradation and polymerization of organic matter. Bulking agents must be added to increase solids concentration up to 40–50% (Oleszkiewicz and Mavinic 2002) as sludge solid content is low for composting. Bulking agents can be wood

chips, but also the organic fraction of municipal solid waste. Decomposition reactions take place at temperatures in the range of 60–70°C (IChemE 1974).

Composting may take place in windrows or in bioreactors. However, odor problems have been reported, especially for open-air windrows.

3.2.4. *Chemical and Thermal Conditioning*

Sludge and stabilized solids from digestion processes have a dry solids content in the range of 3–5%. This requires a liquid-solid separation for water removal. Addition of flocculants and coagulants improves performance with an increase in dry solids content to 15–20%. Higher values can be reached by heat conditioning or low pressure oxidation.

3.3. DEWATERING

Sludge dewatering is the final process of sludge volume reduction to make it suitable for final disposal. It is seldom used unless sludge is to be incinerated. Some of the most common dewatering techniques are presented in this section.

3.3.1. *Sand Bed Drying*

This system consists of a 25 cm layer of sand over a gravel bed. Sludge is poured into the bed to a depth of 20–30 cm and water drainage takes place. Efficiency of the process can be improved by chemical conditioning, as the amount of filtrate increases.

3.3.2. *Plate and Frame Filtration*

Filter pressing is one of the oldest mechanical sludge dewatering methods. Sludge is pumped into the unit (1.8 atm) and a solid cake is formed in the filter press chamber. The main advantage of the method is the high degree of solids separation and the low moisture content of the filtered sludge. However, the filter must be cleaned after every dewatering cycle, which lasts approximately 2 hours.

3.3.3. *Belt Filtration*

In the belt press two continuous porous belts are mounted with the space between them tapered at the lower end. Sludge is previously pretreated by polyelectrolyte solution addition. Then sludge is sandwiched between the belts, as shown in Figure 7.4. Water is released in different zones (gravity drainage, compression, and shear zones) along the belts and is recovered as filtrate. The filter cake is expelled at the opposite end of the belt.

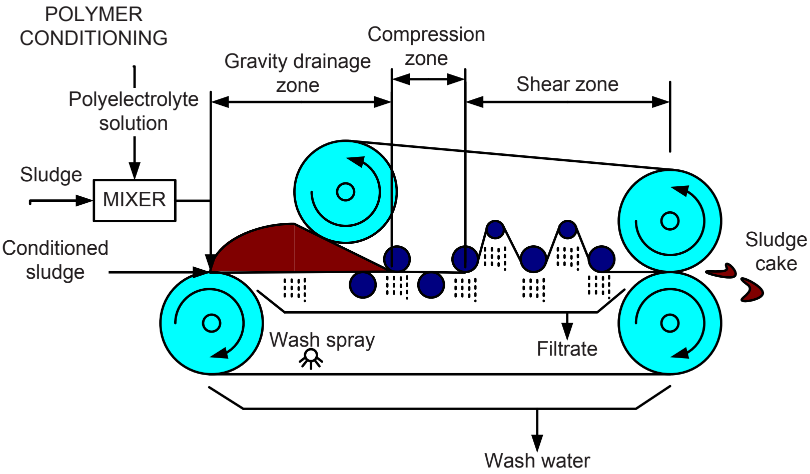

Figure 7.4. Diagram of a belt filter.

3.3.4. *Centrifugation*

The use of new polyelectrolytes combined with new developments in centrifuge design has increased the performance of these units for sludge dewatering. They consist of a rotating bowl and an inner screw conveyor, as shown in Figure 7.5. Sludge is fed into the centrifuge and the rotating device separates by means of centrifugal forces from 3500 to 6000 *g*. This process allows 60–70% solids recovery from unconditioned sludges.

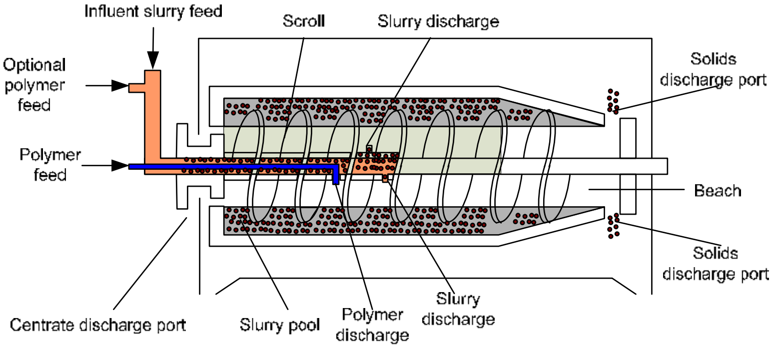

Figure 7.5. Diagram of a continuous bowl centrifuge.

The key is to obtain a good floc formation rather than the use of high *g* forces to achieve solid capture above 95%.

3.3.5. *Screw Pressing*

Screw pressing, shown in Figure 7.6, increases total solids content up to 50–55%. Conditioned sludge is fed into a chamber, where an endless screw is installed. This screw rotates and pushes the sludge against the walls. Drainage occurs and water is recovered as filtrate. Sludge cake is expelled at the end of the chamber. The compression ratio is set according to the treated material. Screw pressing is more effective for primary sludge treatment.

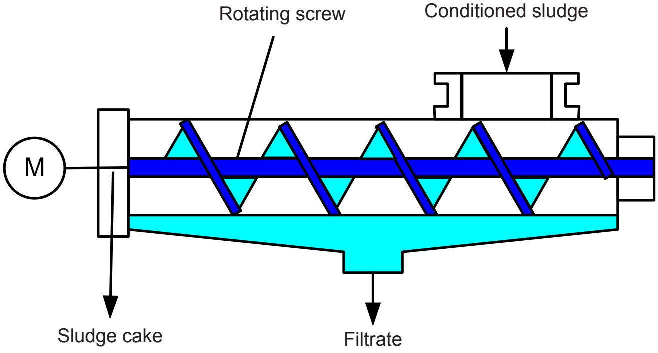

Figure 7.6. Diagram of a screw press.

3.3.6. *Thermal Drying*

Very high water removal can be only achieved by using a heating agent, such as steam or hot air. There are several drier designs, such as disk driers, rotary drum driers or fluid beds. Heat or steam for drying can be produced at an incineration plant, improving energy efficiency. A fluid bed drier is shown in Figure 7.7, where sludge is fed into the sand fluid bed and it is contacted with hot air. Dry sludge is removed and further dry sludge is recovered in a cyclone, previous to gas treatment.

Thermal drying can be classified as partial drying (60–80% dry solids) and complete drying (80–90% dry solids) according to the final solids content.

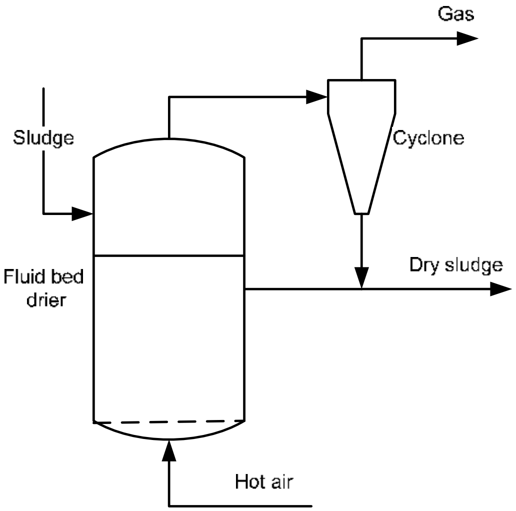

Figure 7.7. Diagram of a fluid bed drier.

4. Sludge Disposal

Several methods have been used for sludge disposal. Some of the most common are: land application, landfill and incineration. Only the last method will be treated in more detail.

- *Land application*. Treated sludge can be used as fertilizer or soil conditioner. There are several geographic factors which may influence its performance, such as the soil type, geology and climate. Successful applications in silviculture operations have been reported. Sludge contaminated with toxic materials from industrial wastes should not be disposed on agricultural land.
- *Landfill*. Although land application implies sludge recycling, the most common method for sludge and solid waste disposal is still landfill. There are many critical elements involved in landfill disposal, such as leachate collection and transmission system, bottom liner, cover and natural hydrogeological setting. Decreasing sludge moisture content is positive because water that ends as leachate is removed.

5. Sludge Incineration

Dewatered sludge combustion in incineration plants is becoming the primary disposal practice where disposal by other methods is problematical.

Sludge organic matter reacts with oxygen to form carbon dioxide and steam with the following reaction:

$$C_aH_bO_cN_dS_eCl_f + [a+e+0.25(b-f)-0.5c]O_2 \rightarrow aCO_2 + 0.5(b-f)H_2O + 0.5dN_2 + eSO_2 + fHCl$$

The air-waste ratio should be higher than the stoichiometric ratio in order to ensure correct combustion. Excess air depends on the incineration technology and nature of the sludge. Gasification takes place if the ratio is lower than the stoichiometric one.

5.1. SLUDGE INCINERATION TECHNOLOGIES

There are different furnace technologies for sewage sludge incineration (*i.e.* fluid beds and multiple hearth furnaces). These differ from those used for municipal solid waste (MSW) incineration (grate furnaces), but in some cases sewage sludge is co-combusted in MSW incineration plants.

In a fluidized bed system, Figure 7.8, dewatered sludge is introduced to a fluidized sand bed with a specific particle size and heated to approximately 800°C. Combustion air is fed from the bottom and causes fluidization of the bed particles. Sludge contacts air and particles. Moisture evaporation and combustion takes place with good heat transfer rates. Auxiliary fuel is required to start combustion. Combustion products are scrubbed and entrained solids removed, *e.g.* by a cyclone.

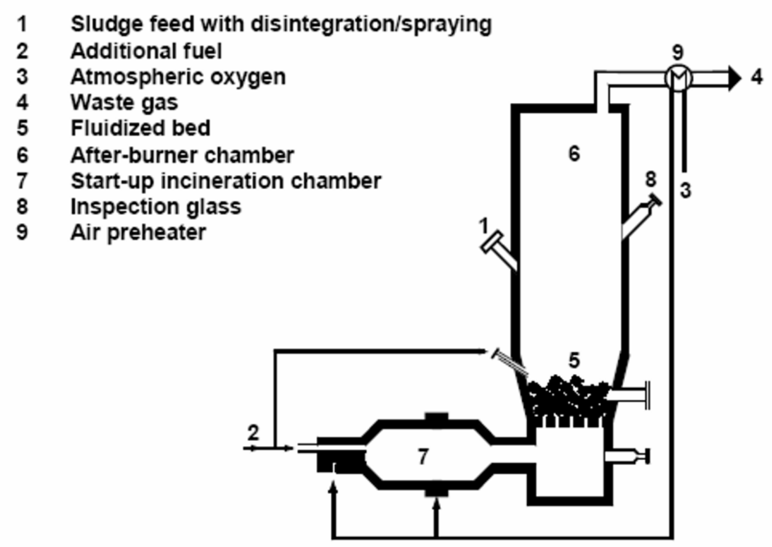

Figure 7.8. Diagram of a fluidized bed furnace for sewage sludge incineration (BREF 2006).

A multiple hearth furnace is also very common for sludge incineration, but not for other kinds of wastes (*i.e.* MSW). It consists of a column with several hearths, as shown in Figure 7.9. Combustion air is fed by a central tube onto all them, providing suitable incineration conditions. Sludge is fed from the top and falls from one hearth to another. Ashes are finally collected from the bottom. Air is fed in different parts of the furnace and there is an auxiliary burner. The temperature is maintained at 750°C and the exhaust gases are scrubbed for the control of air pollution to avoid odor production.

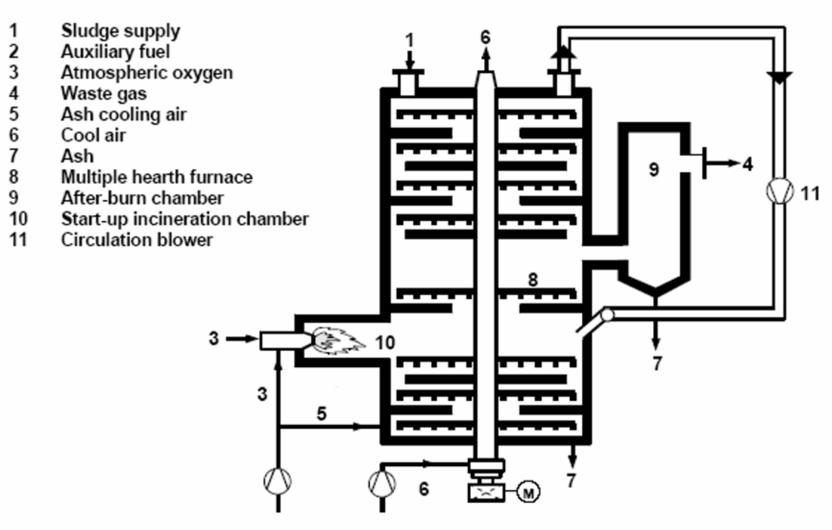

Figure 7.9. Multiple hearth furnace for sewage sludge incineration (BREF 2006).

Other technologies used for sewage sludge incineration are:

- *Multiple hearth fluid bed furnaces*. These are a combination of the aforementioned furnace technologies. A sand fluidized bed is located under a multiple hearth furnace. Sludge from the hearths falls onto the fluidized bed.
- *Cycloid chamber furnaces*. These furnaces can be used only with very dry sewage sludge. They consist of a chamber with a hopper shape. Sludge is fed at the bottom through radial chutes and air is injected at the bottom, and tangentially at different levels.

5.2. SLUDGE INCINERATION PERFORMANCE

- *Theoretical combustion temperature (TCT). TCT* is the temperature reached by flue gases if all the energy produced during combustion were spent on heating the flue gas. It is calculated from mass and energy balances applied to the gas phase in the furnace. These balances take into account air feed, gases produced during combustion and flue gases, and also the heat released during combustion. The EU Waste Incineration Directive (2000/76/CE) establishes a minimum combustion temperature of 850°C for any waste incineration, to ensure proper and safe combustion leading to destruction of dioxin and other toxic materials.
- *Auto-thermal incineration.* Incineration is auto-thermal if the sludge heating value is high enough to maintain the combustion. This occurs when the LHV is at least 3.5 MJ/kg (wet basis). However, typical LHV between 4.8 and 6.5 MJ/kg (wet basis) have been reported (BREF 2006). Sludge moisture is a key parameter for auto-thermal incineration. Pretreatments are required in order to increase heating value. Generally, dry solids content of 35% is enough for auto-thermal combustion, but this condition depends strongly on the heating value (BREF 2006).
- *Auxiliary fuel.* An auxiliary fuel, such as natural gas is required to provide enough heat to evaporate the moisture so that combustion takes place when auto-thermal incineration is not possible. Auxiliary fuel is also required when combustion temperature does not reach the legal minimum of 850°C.
- *Flue gas treatment.* Sewage sludge incineration must comply with strict gas emissions legislation (European Directive 2000/76/EC). Several pollutants are produced in the furnace and flue gas cleaning systems must be implemented to reach the low emission limits established by legislation. These systems typically include dust removal equipment (fabric filter, electrostatic precipitator), wet or dry scrubbers for acid gases absorption, and activated carbon adsorption for organic pollutants.

Several mostly interrelated parameters must be taken into account for sewage sludge incineration, as shown in Figure 7.10. The kind of waste incinerated (only sludge or together with other wastes) determines moisture and combustible matter content, as well as the most suitable incineration technology (fluidized bed, multiple hearth, grate). These parameters determine the heating value, which is the key factor. Sludge pretreatment has an important influence on combustible matter (*i.e.* digestion) and moisture content (dewatering). However, the incineration technology chosen also determines the most suitable dewatering method.

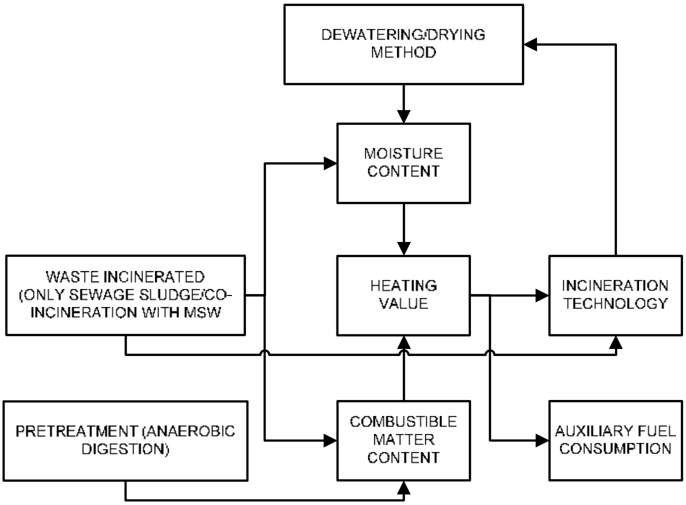

Figure 7.10. Key parameters in sludge incineration.

5.3. CO-INCINERATION OF SLUDGE AND MSW

Sewage sludge can be incinerated together with other wastes or fuels. For example, it can be combusted with coal in power plants or cement kilns as a substitute fuel. Furthermore, sewage sludge can also be incinerated with municipal solid wastes in grate or in fluidized bed furnaces. However, co-incineration with MSW might effect operation as sewage sludge moisture content may decrease combustion temperature. It has been reported (BREF 2006) that the MSW-sludge (20–30% dry solids) ratio should be lower than 9:1. Otherwise additional drying may be required.

Three techniques are available for feeding sewage sludge together with MSW in grate furnaces:

- *Dust blowing*. Sludge can be directly blown into the grate furnace when sewage sludge dry solids content is very high (>90%), typically after thermal drying.
- *Previous mixing*. Sludge is mixed with MSW before incineration, typically in a waste bunker, and then fed together into the furnace. This is done when sewage sludge dry solids content is in the range of 50–60%.

- *Separate sludge spraying*. In this case, sewage sludge with 20–30% dry solids is sprinkled separately into the furnace and distributed on the grate so that they get mixed with movements.

TCT estimation has been made for a hypothetical co-incineration with MSW. Heating values for MSW and sewage sludge were 9.42 MJ/kg (wet basis) and 8.68 MJ/kg (dry basis), respectively, and for a MSW-sewage sludge ratio of 9:1 (24% sludge dry solids). Air preheating to 100°C was assumed. The effect of sewage sludge moisture content on TCT was determined by an energy balance. Results are plotted in Figure 7.11.

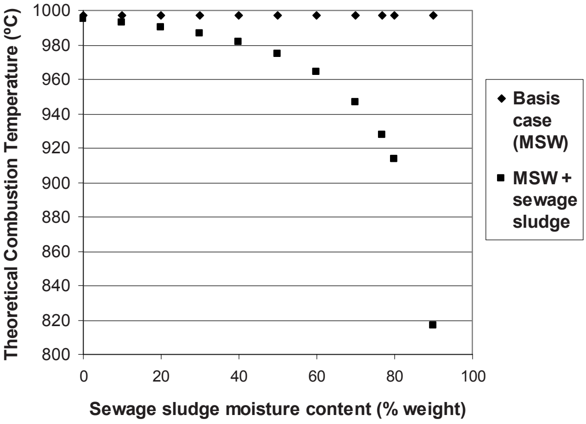

Figure 7.11. Effect of sewage sludge moisture content on TCT.

Results show that TCT in MSW-sewage sludge co-incineration decreases drastically with increasing sewage sludge moisture content, for the same dry solids content. Despite this decrease, the combustion temperature of 850°C is ensured for typical mechanically dewatered sludge (75% moisture content). Some problems might arise if MSW heating value is decreased. This can happen if high calorific MSW fractions (*i.e.* plastics, paper) concentration decreases (Suárez et al. 2008).

6. Conclusions

The primary objectives in sludge treatment and disposal are stabilization by organic matter decomposition into relatively stable compounds, pathogen control and destruction in order to provide safe sludge management and disposal. Sewage sludge volume reduction by dewatering from an initial low solid content of 4.5% is necessary, to make further treatments, recycling and disposal easier. Operation costs can be reduced using process by-products, such as calcium chloride which allows material valorization and reduces the amount of waste to be treated or disposed. Finally, the most important objective is sludge removal from the water works to the environment, without danger to health or nuisance to humans, animals or plants.

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LIST OF PARTICIPANTS

Abdessemed, Djamal, University of Science and Technology Houari Boumedien (USTHB), (Algeria)

Allende, David, University of Oviedo (Spain)

Atyaoui, Atef, Centre of Water Researches and Technologies (Tunisia)

Bach, Altai, Israel Institute of Technology (Israel)

Ben Amar, Raja, Faculty of Science of Sfax (Tunisia)

Bozkurt, Hande, Middle East Technical University (Turkey)

Daghari, Lassaad, National research institute for rural engineering, water and forestry (Tunisia)

Doudou, Khalid, Al Akhawayn University (Morocco)

Ejekki, Fatima, Al Akhawayn University (Morocco)

El Mansour El Jastimi, Massoud, Abdelmalek Essaidi Univesity (Morocco)

Farnosova, Elena, Moscow State University (Russia)

Gemza, Natalia, Mendeleyev University of Chemical Technology (Poland)

Gutierrez, Gemma, University of Oviedo (Spain)

Hakopian, Christina, Yerena State University (Armenia)

Harea, Diana, Academy of Science of Moldova (Moldova)

Jaworska, Agnieszka, Centre of radiochemistry and nuclear technology (Poland)

Kamel, Daoud, University of Science and Technology Houari Boumedien (USTHB) (Algeria)

Karabacak, Asli, Middle East Technical University (Turkey)

Kocaoba, Sevgi, Middle East Technical University (Turkey)

Matos, María, University of Oviedo (Spain)

Mitryaeva, Olga, Mendeleyev University of Chemical Technology (Russia)

Mohamed Wahib, Naceur, University of Saad Dahlab de Blida (Algeria)

Muñoz, Emilio, University of Oviedo (Spain)

Nadjib, Drouiche, University of Science and Technology Houari Boumedien (USTHB), (Algeria)

Shamrukh, Mohamed, Minia University (Egypt)

Sheiko, Nataliia, Kyiv Taras Shevchenko National University (Ukraine)

Sutzkover-Gutman, Iris, Israel Institute of Technology (Israel)

Tarik, Ouslimane, University of Science and Technology Houari Boumedien (USTHB), (Algeria)

Telegeev, Igor, Chuiko Institute of Surface Chemistry of National Academy of Science (Ukraine)

Ünsul Erdemli, Burcu, Middle East Technology University (Turkey)

Yüzügüllü, Onur, Middle East Technical University (Turkey)

Zeyniyev, Sabit, Scientific and Research Institute of Erosion and Irrigation (Azerbaijan)

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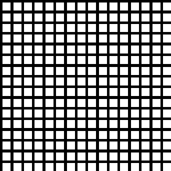
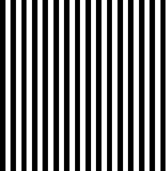
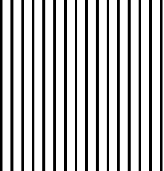
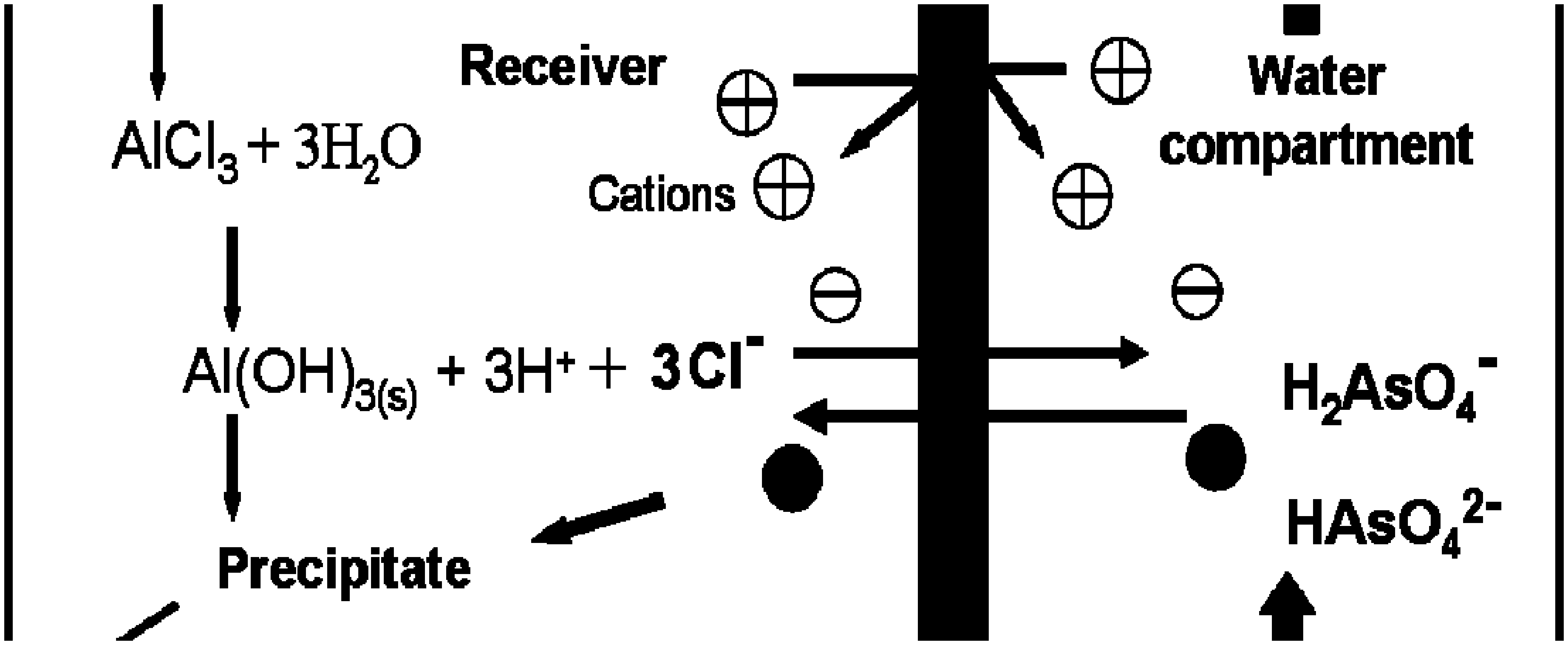
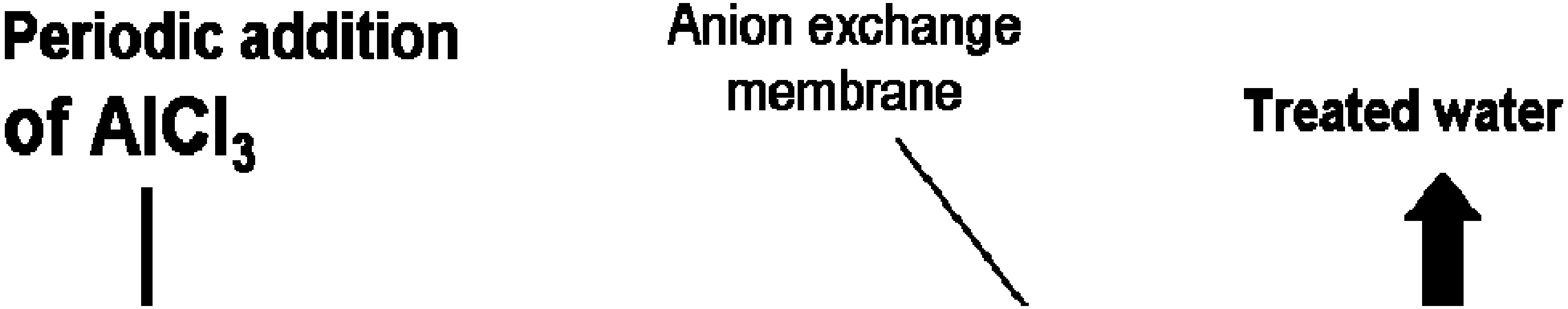


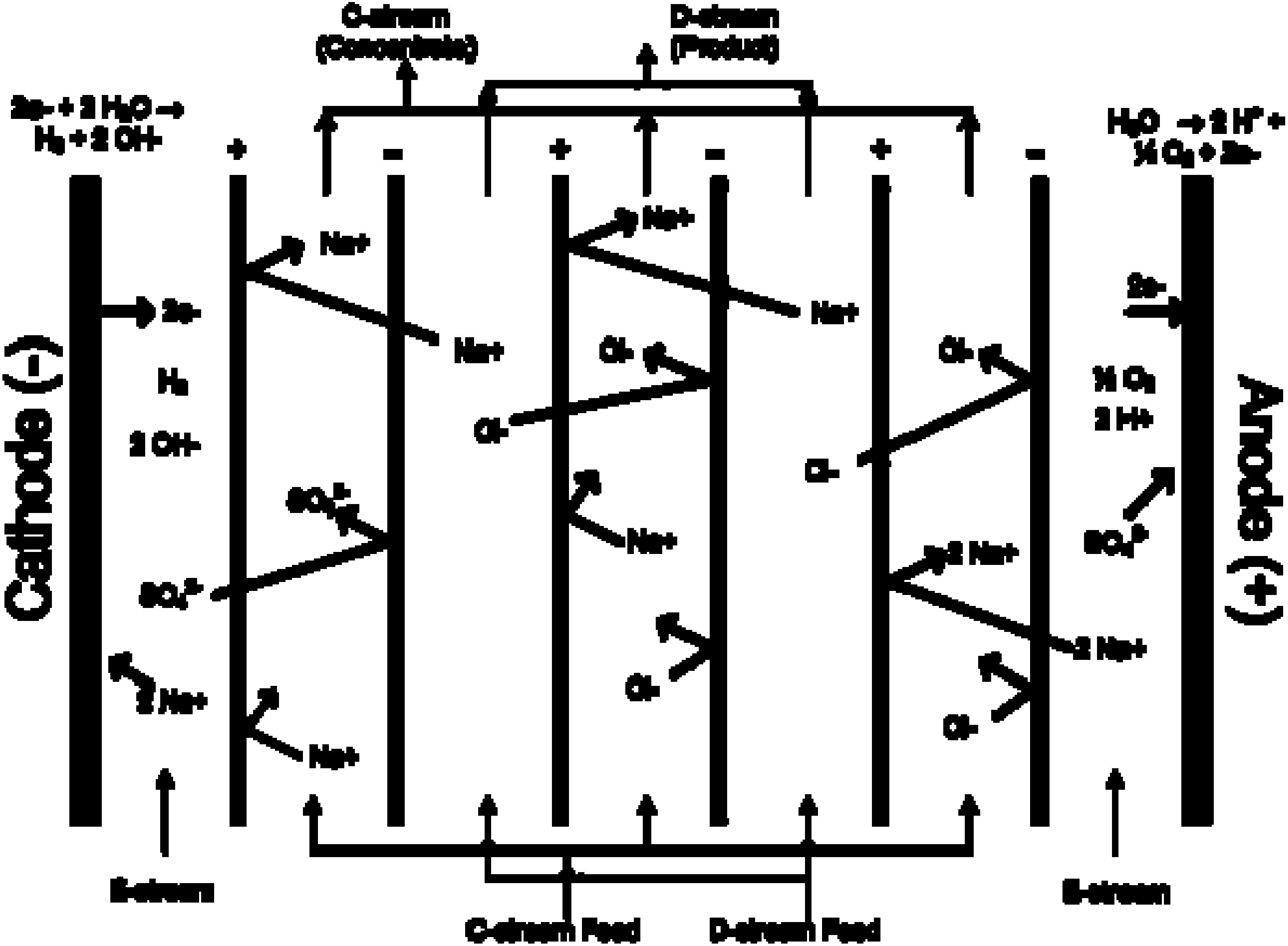





Solids for Dewatering
Solids to Landfill
Polluted water


Receiver
$AlCl_3 + 3H_2O$
Cations
$Al(OH)_{3(s)} + 3H^+ + 3Cl^-$
Precipitate
Water
compartment
$H_2AsO_4^-$
$HAsO_4^{2-}$


Periodic addition of $AlCl_3$
Anion exchange membrane
Treated water


C-stream (Concentrate)
D-stream (Product)
2e- + 2 H2O → H2 + 2 OH-
H2O → 2 H+ + ½ O2 + 2e-
+
-
+
-
+
-
Na+
Na+
2 Na+
Na+
Cl-
Cl-
Cl-
Cl-
2e-
2e-
H2
2 OH-
½ O2
2 H+
SO4 2-
SO4 2-
SO4 2-
Na+
2 Na+
2 Na+
Cl-
Cl-
2 Na+
Na+
Cathode (-)
Anode (+)
E-stream
E-stream
C-stream Feed
D-stream Feed