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Andréa Moura Bernardes Marco Antônio Siqueira Rodrigues Jane Zoppas Ferreira *Editors* 

# Electrodialysis and Water Reuse

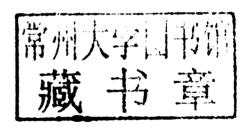
**Novel Approaches** 



Andréa Moura Bernardes Marco Antônio Siqueira Rodrigues Jane Zoppas Ferreira Editors

### Electrodialysis and Water Reuse

Novel Approaches





Editors

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### **Topics in Mining, Metallurgy and Materials Engineering**

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To Prof. Dr. Adão Mautone, who planted the ideas that led to this book

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### **Preface**

The electrodialysis process principles are well known for over 70 years, but the large-scale industrial applications were only possible after the development of the multi-cell stack design and the production of efficient and stable ion-exchange membranes. Although the largest application of electrodialysis, the desalination of brackish water, has been around the world before reverse osmosis, the other applications like the treatment of certain industrial wastewaters have only recently been explored.

This book is an integrated presentation of electrodialysis with the first chapters covering in a very comprehensive manner the transport principles, the control parameters and membrane materials and characterization, and the last six chapters covering applications of treatment of wastewaters in industries that are water intensive users like oil refineries, leather, and metallurgy.

The book is an outstanding contribution to the advancement of the application of electrodialysis as a large-scale technology for the treatment of industrial waste waters.

Lisbon, Portugal, 22 June 2013

Maria Norberta de Pinho Chemical Engineering Department Instituto Superior Técnico

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### Chapter 1 Introduction

Jane Zoppas Ferreira

Water is known to be an essential resource for Humanity. People around the world are convinced about the need of providing new and improved means of maintaining a healthy environment. Despite its abundance on the planet, water tends to become scarce because of disordered consumption, which contaminates our reserves and make them unsuitable for use, either for human consumption, or for industrial use. The most varied industrial processes use lots of water directly. This water must be adequate for use. Countries without major natural resources treat seawater, in so-called demineralization processes, to produce drinking water for the population. All this water that is used for either domestic or industrial ends, must be returned to reservoirs as clean as possible because its contamination will make its reuse impossible. Industries are having difficulties in obtaining proper water because of the growing water scarcity caused by pollution. As a consequence, treatment costs are increasing, which limits productivity.

In the last few years, several wastewater treatment processes have been proposed that would enable water reuse, with special emphasis on waste minimization (e.g. process modification, material recovery) and hazardous waste treatment (e.g. from surface finishing industries, destruction of organic solvents).

One of these processes employs electrochemistry. This science is concerned with the way that electricity produces chemical changes and how chemical changes result in the production of electricity. Although there are many established applications, modern research has led to a great expansion in the possible uses of electrochemistry with exciting future developments. In the environmental area, electrochemistry has the potential to monitor or remove various polluting substances that affect the environment.

It is in this context that electrodialysis offers an electrochemical technique that removes ionic pollutants from an aqueous solution, producing two new solutions:

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one concentrate of ions and another consisting of almost pure water. The first solution can be reintroduced to the industrial process and the water can be reused. Associated to another field of research, such as membrane technology, this technique can be powerful in the treatment of industrial effluents.

The use of electrodialysis is particularly significant because it approaches membrane technology as an advanced environmental technology that enables the development of clean treatment sequences for the recovery of water in industrial processes. The promotion of the use of the electrodialysis process, and the synthesis and characterization of membranes, will require a multidisciplinary effort in different fields, such as materials science, physics, chemistry, and sanitary engineering. Water reuse is a subject of great interest that involves the scientific and business communities, the government and society at large.

Based on the results obtained by our research group in the past decade, this book presents novel techniques to evaluate electrodialysis processes, to synthesize ionic membranes and characterize their properties, and to show the potential use of this membrane process in the treatment of effluents generated by many industrial sectors, such as refineries, leather industries, and electroplating processes. This book is aimed at students, researchers and engineers who are interested in membrane technologies for the rational utilization and reuse of water.

## Chapter 2 General Aspects of Membrane Separation Processes

Andréa Moura Bernardes

**Abstract** This chapter focuses on the current challenges of water and wastewater treatment aiming reuse. Membrane separation processes are presented and electrodialysis is compared to pressure driven membrane processes, especially reverse osmosis.

#### 2.1 Water and Wastewater Treatment for Reuse

The increasing demographic and industrial expansion observed in recent decades has resulted in a rising commitment of the rivers, lakes and reservoirs. Water use, treatment and reuse are still a worldwide challenge. The management of water resources should always address the multiple uses of water and the most efficient water management system is the one that applies a water treatment process that is compatible with the subsequent use of water. Appropriate quality parameters should be set for each specific use of water. The quality of water used for public supply is often not compatible with the characteristics required for industrial use. Furthermore, drinking water quality parameters may not be the most suitable for the use in processes that require demineralized water.

Water and wastewater treatment processes are chosen mainly based on the initial quality of the water, on the parameters established by regulations and on the proposed use. Nowadays, water for public supply and domestic or industrial wastewater are usually treated by physicochemical or biological processes, as presented in Fig. 2.1.

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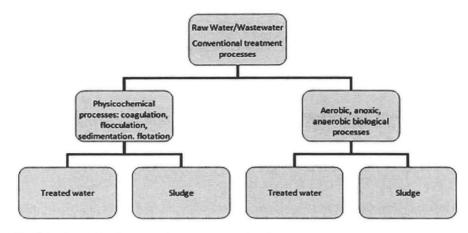


Fig. 2.1 Conventional water and wastewater treatment processes

These conventional treatment processes are not always suitable for potable uses, especially if the raw water contains nitrates, phosphates or other contaminants in small concentrations, which are not going to be removed by physicochemical or biological processes.

Considering the possibilities for the reuse of treated wastewater, the treated water generated after these processes can be reused, depending on the final characteristics, for such purposes as the irrigation of crops or landscapes, for the refill of aquifers and for non-potable urban uses, such as firefighting, flushing toilets, the washing of vehicles, streets and bus stops, etc... However, for industrial applications, such as cooling, boiler feed or processing water, as well as for drinking purposes, conventional treatment processes do not produce water that is of a high enough quality for reuse.

The growing demand for water has made the planned reuse of water a current topic of great importance. From this perspective, the treated effluents play a key role in the planning and sustainable management of water resources as a substitute for the use of water for industrial purposes, among others, contributing to the conservation of resources and adding an economic dimension to the planning of water resources. Reuse reduces the pressure on water sources because of the replacement of drinking water with lower quality water.

The membrane separation processes applied to water and wastewater treatment provide the use/reuse of these resources. These processes, however, have different properties and specific applicability. The ideal process would recover all the water, leaving behind only the salt. All current technologies produce a concentrate stream that must be discharged into the environment, or must undergo additional treatment to reduce the volume and remove the dissolved solids.

### 2.2 Membrane Separation Processes

The membrane technology has played an important role in developing more efficient and selective production with a reduced consumption of raw materials, energy and water and the minimization of wastewater and solid waste. Membrane processes have been introduced in industrial operations in order to treat the water, recycle process water and for the potential reuse and recovery of byproducts.

Different membrane separation processes are used in the treatment of water, sewer and industrial wastewater. Commercial membrane processes present different characteristics, as can be seen in Table 2.1.

Among the membrane processes presented in Table 2.1, pressure driven membranes (MF, UF, NF and RO) as well as electrodialysis (ED) are the ones applied to water and wastewater treatment.

In membrane separation processes driven by pressure, a pressure difference is applied across a membrane that can be of a Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO) nature. The membrane acts as a semi-permeable barrier and may have different selectivities for different compounds.

Microfiltration is typically used for the removal of suspended solids or bacteria, using membranes with pore diameters ranging between 0.1 and 10  $\mu$ , and the transport mechanism is stereochemical exclusion, where molecules with a radius greater than the radius of the membrane pore are rejected.

Ultrafiltration is usually associated with the separation and concentration of macromolecules, using membranes with micropores of the order of 1–100 nm. The transport mechanisms that are generally employed in these kinds of membranes are molecular exclusion and diffusion. However, in many cases these mechanisms are associated to other phenomena, and the nature of the feed stream is very important, since the presence of colloidal material or the propensity to adsorb to the membrane leads to clogging and adsorption phenomena that alter the prevalent mechanisms of this type of operation (MF and UF). In certain cases, the productivity of membranes with quite different hydraulic permeabilities and selectivities can be shown to be similar, due to the clogging phenomena [1].

MF and UF technologies are typically used to treat water with high turbidity, to ensure the removal of viruses and bacteria from drinking water, or as a pretreatment in reverse osmosis systems [18].

Reverse osmosis is used to separate salts and small organic molecules from liquid streams, using membranes with dense active layers, where the preferred transport mechanisms are often attributed to solution/diffusion. Due to the high density of the active layer, operating pressures have to be much higher than those used in microfiltration and ultrafiltration.

The nanofiltration process is an intermediate separation process between reverse osmosis and ultrafiltration, commonly used in the separation of organic solutes with low molecular weight (200–1000 Da) and in the partial demineralization (essentially polyvalent salts) of liquid streams. The transport mechanisms that operate in these types of membranes are diffusion (as in reverse osmosis) and

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Table 2.1 Membr	ane separanon	able 2.1 Memorane separation process characteristics [1, 3, 1/]		
Process	Driving force	Typical separation mechanism	Retentate	Permeate
Microfiltration (MF)	ΔP (0.5–2 bar)	Sieve	Suspended solids, bacteria MW > 500000 Da (0.01 µm)	Water and dissolved solids
Ultrafiltration (UF)	ΔP (1–7 bar)	Sieve	Colloids, macromolecules MW > 2000 Da	Water, salts and compounds of low molecular weight
Nanofiltration (NF)	ΔP (5–25 bar)	Sieve + solution/ diffusion + exclusion	Molecules 500 Da < MW < 2000 Da	Water, salts and compounds of low molecular weight
Reverse osmosis (RO)	ΔP (15–80 bar)	solution/diffusion -80 bar) + exclusion	All soluble or suspended material	Water, solvent
Dialysis (D)	ΔC	Difusion	Molecules MW > 5000 Da	Ions and organic compounds of low molecular weight
Electrodialysis (ED)	ΔE	Ion exchange	Macromolecules and non ionic compounds	lons
AP - Pressure difference	Prence			

AP = Pressure difference ΔC = Concentration difference ΔE = Potential difference MW = Molecular weight

molecular exclusion (as in ultrafiltration), but electrostatic interactions are also detected, which lead to selective removal of polyvalent ions [1].

Electrodialysis is a membrane separation process in which ions are transported through ion selective membranes from one solution to another under the influence of an electric field [2, 3, 20]. This transport generates two new solutions: one that is more diluted and one that is more concentrated than the original [4, 19].

### 2.3 Electrodialysis as an Alternative for Reverse Osmosis

Two membrane methods of water desalination, reverse osmosis (RO) and electrodialysis (ED) compete for a dominant position in a very large market, a competition that is continuously intensified by the increased shortage of water resources. Historically, electrodialysis had been developing faster than RO. In the 1960s, only electrodialysis was used in the industry. There were no RO units at all. The development of organic synthesis technologies has changed this situation, resulting in the manufacture of acetate and polyamide membranes, followed by free fiber high efficiency membranes. This development made RO began to dominate among the membrane methods. The construction simplicity of the units and the availability of membranes enabled even small companies to assemble the units and this promoted their entry in the market. In its two decades of operational experience, RO has demonstrated its strong properties, but the euphoria that accompanied its initial success has ebbed away and, today, the time has come for a matter-of-fact attitude towards both methods in order to choose the most optimal concept of membrane desalination [5]. Three factors need to be considered in evaluating the implementation of the two methods: the pre-treatment required for the feed water, in addition to the consumption of chemicals; the lifetime of membranes; and power consumption.

Membrane fouling is one of the most important factors that limit greater use of desalination membranes. Fouling occurs due to particulate matter, organic matter, microorganisms forming biofilms, and inorganic scaling [6]. Bacterial contamination problems have been reported as one of the main causes of membrane fouling in osmosis. This is caused by the characteristic of the membrane that serves as a barrier between the feed water and the product, which not only removes dissolved solids, but also bacteria, viruses, and insoluble substances.

ED only removes ions. Therefore, any bacteria, colloidal material, or silica present in the feed water stream will remain in the product stream. To minimize fouling and thus the need for the addition of chemical products, the polarity of the system can be reversed with electrodialysis reversal (EDR). By reversing the polarity (and the solution's flow direction) several times per hour, ions move in the opposite direction through the membranes, minimizing buildup. It is important to note that the EDR process does not directly filter the treatment stream through the membranes; contaminants are transferred out of the treatment stream and trapped by the membranes. This generally minimizes membrane fouling, decreasing pretreatment requirements in comparison to RO [7].

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In general, electrodialysis reversal (EDR) is more attractive for the desalination of brackish water and in cases where the removal of organic matter and microbial control are not important. EDR is also of interest in treating brackish waters where silica is an important limitation [6].

With respect to energy consumption, the literature indicates that the electrodialysis reversal process consumes less power when applied to waters with a total concentration of dissolved solids below 2,000 ppm. On the other hand, reverse osmosis is most advantageous when applied to waters with salinity greater than 4,000 ppm [8]. Other authors indicate that electrodialysis is more economical than osmosis in concentrations greater than 8,000 ppm when maintenance costs are taken into account [21].

Several studies comparing desalination technologies with electrodialysis were performed on groundwater, surface water and effluents [9-15]. The main advantage of electrodialysis compared to reverse osmosis is that very little feed pretreatment is required, since membrane fouling and scaling is reduced to a minimum due to the reverse polarity operation. In addition, a much higher brine concentration can be achieved in electrodialysis when compared to reverse osmosis, since there are no osmotic pressure limitations. The chemical and mechanical stability of the ion-exchange membranes guarantees a long use life even in feed waters with aggressive and oxidizing components. Electrodialysis, however, has several severe technical and economic limitations. A major disadvantage, especially for the production of potable water, is the fact that only ions are removed, while uncharged components such as microorganisms or organic contaminants are not eliminated. Another disadvantage of electrodialysis is the relatively high energy consumption when solutions with high salt concentrations have to be processed. Likewise, the investment costs are prohibitively high when very low salt concentrations must be achieved in the diluate because of the low limiting current density, which requires a large membrane area. Thus, electrodialysis can only be applied cost effectively in water desalination for a certain range of salt concentrations of the feed water and quality of the product water. Outside this range of feed water composition and required product water quality, electrodialysis is not competitive when compared to other desalination processes [16].

Although water reclamation and reuse is practiced in many countries around the world, current levels of reuse constitute a small fraction of the total volume of municipal and industrial effluent generated [6]. Electrodialysis can be part of the solution in different applications, and this is going to be discussed in more detail in the following chapters.

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