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ELECTRODIALYSIS (ED): A REVIEW ON THE FUNDAMENTAL CONCEPT, ADVANTAGES, LIMITATIONS AND FUTURE TREND

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ABSTRACT

The membrane-based method is one of the most widely applied and commercially proven desalination technologies in recent years. Electrodialysis (ED) is one of the common membrane technologies used for water desalination. This review paper aims to provide the fundamental concept of electrodialysis and its application in water desalination. The advantages, limitations, challenges, and future trends of electrodialysis have been discussed and delineated.

Keywords: electrodialysis, reversal, fouling, membranes

INTRODUCTION

Freshwater is a basic human need. However, there is only 2.5% of the freshwater available for daily usage [1]. The world's population continues to soar, causing the demand for water to increase dramatically throughout the years [2]. This issue has led to a catastrophic water shortage in water-stressed region countries such as Singapore and the United Arab Emirates [3]. Therefore, desalination technology becomes significant in providing human beings with new access options to freshwater [4].

Since the 1950s, electrodialysis (ED) technology has been used for water desalination [5]. In the 1960s, electrodialysis reversal (EDR) was introduced in order to avoid the problems caused by the organic fouling [6]. Within 30 years, this technology has dominated as a desalting process that exceeding other membrane technologies in terms of total plant capacity in European countries [7]. Electrodialysis with ion-exchange membranes is an electrochemical process that utilises the charged membranes (anode and cathode membrane) to separate the ions [8]. The ions are separated from one solution to another through the driving force of the potential difference. It is one of the most significant membrane methods used to produce drinking water from brine water, seawater and brackish water [9]. The most extensive single application of electrodialysis is converting brackish water to drinkable water. Globally, there are more than capacity of the electrodialysis plants installed to desalt the brackish water [10].

Fundamentals of Electrodialysis in Water Desalination

Anion exchange and cation exchange membranes are the two membranes used in electrodialysis [11]. These two different membranes are arranged alternately in a membrane stack [9], [12]. The installation of the membranes is started with anode membranes and is followed by cathode membranes. Thus, the first compartment is equipped with the anode exchange membrane at the right while the cathode exchange membrane at the left [13]. The electrode is installed at both ends of the membrane stack to provide a difference in electrical potential [14]. During the process, the water is pumped into the compartment, and each compartment is separated by the ion exchange membrane.

When a potential difference is applied, cathode which is negatively charged attracts the cations in the water. Thus, the cations migrate to cathode and allow them to pass through the cation exchange membrane. The ions are not able to pass through the second membrane as it is the anion exchange membrane. The same concept applied to the anions in water [15], which is clearly shown in Figure 1. In short, the cation exchange membranes permeate cations and block anions, and the anion exchange membranes permeate anions and block cations. At the end of the process, the concentration of the ions increases in the alternate compartments while depletes in others' compartment. The depleted solution, generally known as diluate, while the concentrated solution is known as concentrate or brine [9].

For the industrial application of electrodialysis, approximately 100 - 200 cell pairs of the electrodialysis stack are arranged between the electrodes. Different types of the stack, as well as the spacer, are being used [16]. Figure 2 shows the arrangement of the sheet flow stack [16].

There are two types of ion-exchange membranes, i.e., cation exchange membranes and anion exchange membranes. Both membranes are different in ionic groups attached to the membrane matrix. For instance, negatively charged groups such as $-PO_3H^-$, $-C_6H_4O^-$ are present in the cation exchange membrane while positive groups such as $-NR_2H^-$, $-NR_3$ presents in the anion exchange membrane [17]. Furthermore, ion exchange membranes are classified as homogenous or heterogeneous membranes, depend on how the charge groups connect to their chemical structure. Homogenous membranes are mainly made from ion exchange resin which is mixed with a binding polymer solution (PVC, rubber, styrene/divinylbenzene copolymer, etc.) after granulating into small size. Ionisable functional groups are also added to the polymeric film to synthesise the homogenous membrane [15], [18]. Mechanical strength and electrical resistance are greatly affected by the ratio between binding polymer and resin grains. The mechanical strength of the homogenous membrane is increased when more binding grains are added, and at the same time, it increases the electrical resistance [19]. However, heterogeneous membranes generally carry a characteristic with high electrical resistance and limited mechanical strength. Thus, the most common practical ion exchange membranes used in the electrodialysis process are homogenous membranes [17].

General properties required for a membrane are a) high transport number of counterions, b) high mechanical strength, c) low cost, d) high chemical stability and durability, e) low electrical resistance, and f) low diffusion coefficient of salt [20]. In order to enhance the effectiveness of the desalination process, various efforts have been made. Profiled membranes, a membrane with a specific surface geometry have been introduced recently [21]. The surface of the membrane is the main difference between the conventional and the profiled membrane. The conventional membrane has a flat surface, while the profiled membrane has a profiled or corrugated surface [16]. The advantages

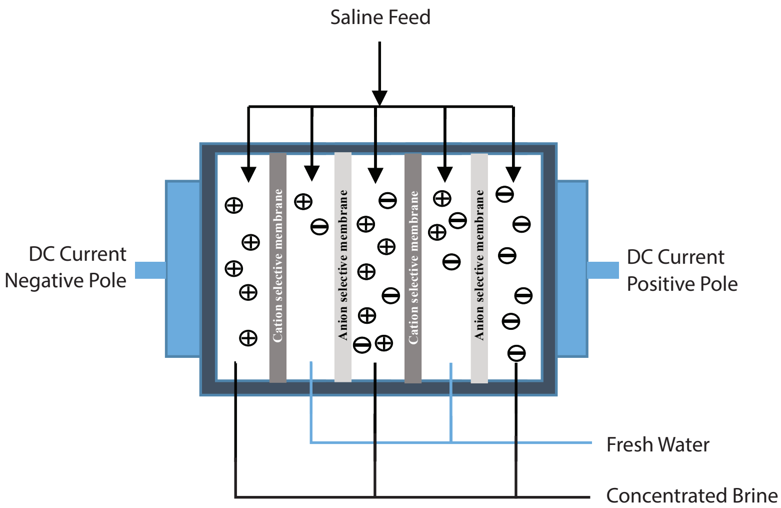

Figure 1 Desalination process through electrodialysis process

of using profiled membranes in electrodialysis stack compared to the conventional flat membranes are as follows,

1. A stack with profiled membranes required lower energy as it has a lower stack resistance.
2. The profiled membrane's effective surface area is increased by 40% as the membrane's surface is trapeze-shaped instead of a flat surface.
3. The profiled membrane surface is able to provide adequate mixing of the solution without the spacer.
4. The membrane area required for the electrodialysis system is lower as profiled membranes have higher limiting current densities [16].

On the other hand, different manufacturers of ion exchange membranes offer membranes for specific applications and offer different properties of membranes involving size, thickness, area resistance and composition [18]. The main manufacturers are DuPont Co. (USA), FuMA-Tech GmbH (Germany), a few to name as summarise in Table 1.

Table 1 Main manufacturers of ion exchange membranes

Manufacturer	Origin Country	Commercial brand
DuPont Co.	USA	Nafion
FuMA-Tech GmbH	Germany	Fumasep
Tianwei Membrane Co.Ltd.	China	TWAED
MEGA a.s.	Czech Republic	Ralex
PCA GmbH	Germany	PC

Spacers

Spacers are the spaces located between the membranes that represent the flow paths of the diluate and concentrated streams, known as diluate and concentrate water flow spacer. Polypropylene or low-density polyethylene is the main material used. To ensure each stream is manifolded together, independent flow paths are created through the alternate arrangement of the spacers between the membranes in the stack [18], [22]. Apart from functioning as the separator for the membranes, it helps to mix the solution in the cell as well. There are two types of spacer designs, a spacer with a tortuous path or with sheet flow. For sheet flow design, there is an open frame with a plastic screen which function as a separator for the membranes.

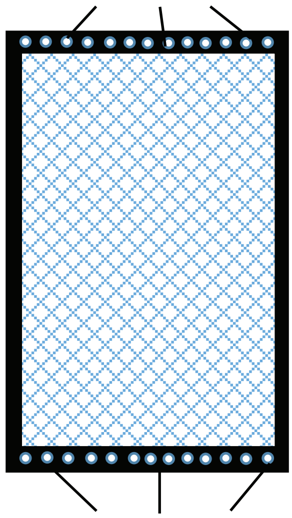

Figure 2 The design of a sheet flow spacer

The main differences between both designs are the arrangement of the membrane and the spacer and the process path. Spacer with tortuous path stack design is generally arranged horizontally, but spacer with sheet flow design arranged vertically [16], as shown in Figure 2. Additionally, the path for the liquid to flow in the tortuous path is much longer as compared to sheet flow.

In order to achieve a specific rate of desalting, both types of spacers are running at lower flow velocities. The feed velocity in sheet flow is between 2 and 4 cm/s, and there is the only low-pressure loss in the stack, around 0.2 and 0.4 bars. The feed velocity of the tortuous flow is relatively high, around 6 to 12 cm/s, which increase the limiting current densities and reduce the concentration polarisation. However, there is a high-pressure loss in the feed flow channels, around 1 to 2 bars [18]. Spacers increase the required power for the desalination process as it increases the electrical resistance. The material of the spacer should choose wisely as it affects the slip/no-slip condition of the flow channel and fluid dynamics in terms of pressure drops [23].

Electrodes

Direct current for the system is supplied into the stack through the metal electrodes at both ends of the membranes stack. There are few elements present in the electrode compartments which include the electrode, heavy cation or anion membrane, and an electrode water-flow spacer. The electrode spacer is designed to be thicker than the normal spacer in order to increase the water velocity, and thus scaling can be prevented [18]. Titanium is the most common material used in electrode production to overcome the corrosion issue at the anode compartment [24]-[25]. The amount of amperage supplied to the electrode and ionic composition of the source water is the main factor that affects the life span of the electrode. The electrode life becomes shorter when high amperages are supplied, and a large amount of chlorides are found in the source water. Additionally, the electrode that is used in electrodialysis reversal (ERD) which involves the polarity reversal has a shorter life span than the non-reversing system [18].

Advantages and Limitations of Electrodialysis in Water Desalination

There are advantages of electrodialysis technology which will be delineated in this section.

a. Less membrane fouling or scaling due to electrodialysis reversal
Electrodialysis reversal (EDR) is a variation on the electrodialysis process. The unique difference between EDR and ED is that the polarity of the DC power in ERD is reversed. Normally, the polarity for EDR is reversed two to four times per hour [26]. EDR is able to help in reducing the fouling rate of the membranes. When the polarity of the DC power reversed, it leads to a change in driving force for the colloidal, and hence the colloidal will be removed from the membrane[5]. With reverse polarity, an electrodialysis reversal system (EDR) operates with a continuous free chlorine residual that up to 1 ppm. Therefore, the potential for the formation of biological fouling will significantly reduce [27].

b. High water recovery rates even for raw water that contains high sulfate content
Generally, reverse osmosis has a lower recovery rate compared to ERD, which is only around 65-75%. However, the electrodialysis reversal system achieves up to 80-90% of the recovery rate when dealing with brackish water. The main reason behind the different recovering rate is the sensitivity to fouling and scaling [12], [28]. Since EDR is less sensitive to fouling and scaling, less resistance will be created in the membrane, and thus high recovering rate can be achieved. With the high recovery rate, the system's feedwater usage and the cost for wastewater discharge reduced [18], [27].

c. The longer life span of membranes due to higher chemical and mechanical stability
The electrodialysis reversal is equipped with a thick membrane that provides 7 to 10 years of life span to the membranes. Nevertheless, the reverse osmosis membranes are only designed for 5-7 years as the membranes are sensitive to various operating factors [12]. For instance, RO membranes are more likely to dry up especially in the countries with hot weather, but EDR membranes are not. Additionally, no special storage solution is needed for ERD membranes storage as they can prevent the attack from bacteria and capable of withstanding high temperatures. Special storage solution and controlled storage temperature are needed for RO system [20]. With all the factors mentioned above, it can be concluded that the EDR system is equipped with coarse, very resistant, and composite membranes that have a longer life span compared to RO membranes.

d. Required less raw water pre-treatment and the process can easily be adjusted to different feed water quality; therefore, the cost will reduce
The EDR system treats various types of feedwater quality and has lower sensitivity toward the pre-treatment problem compare to the RO system [29]. Silt density index (SDI) is a measurement of the fouling potential. Higher SDI indicates higher fouling potential of the suspended solids. Generally, the EDR system is capable of functioning with an average SDI of 12. However, the capability of the RO system is relatively low as it only functions with an average SDI of 3 [27]. Recently, water pre-treatment for RO on a bigger scale has become more complicated, reaching up to 8 stages. The water pre-treatment for electrodialysis is relatively simple.

e. Possible to clean manually without damaging the membrane properties
With the plate and frame configuration in the electrodialysis system, the membranes are easy

to remove from the system for manual cleaning purposes. However, the reverse osmosis system is equipped with spiral wound configuration; thus, it is impossible to clean manually and must be replaced with the new membrane [9].

Despite all the advantages, ED has few limitations in the desalination area, which caused ED to be a less attractive choice in recent years. Consequently, most of the ED desalination processes have been replaced by RO. One of the limitations of the ED process is limited application. ED process is generally only suitable for brackish water that carries a characteristic of salinity lower than 12,000 mg/L TDS. Since the salinity of water to be treated is directly proportional to power consumption, the cost of the ED desalination process will be much higher compared to RO when the salinity of water exceeds 12,000 ppm TDS [18]. In addition, neutral toxic components such as viruses or bacteria are not removed from a feed stream [10]. In what follows, post-treatment is required for the product water. Table 2 summarises the difference between ED and RO technology in water treatment.

CURRENT APPLICATIONS AND CASE STUDIES

Various applications of EDR technology can be found around the world. The smallest application of the EDR technology has only one stack, while there are 576 stacks for the biggest application. The main application of EDR is still the desalination due to its performance and cost-effectiveness in this area [18]. A typical example is the desalination of the concentrated brine that came from the RO plant. The main purpose of this treatment is to protect the marine ecosystems from the harmful brine water [20]. Apart from desalination, electrodialysis technology also has been applied in industrial wastewater as electrodialysis is feasible in terms of the separation of monovalent and divalent ions. The energy required for the process is generally between 6 to 11 kW h/m^3 of feed stream [15].

At the early stage, limited suppliers are available, but various suppliers can be found recently. General Electric water is the biggest supplier of the ERD technology used in the desalination process to provide drinking water [18].

Case study 1: The Abrera drinking water treatment plant

More than 4.5 million drinking water is supplied from the Llobregat and Ter River to Barcelona residential area. Raw water from the Llobregat River is directly flowing to the drinking water treatment plant [18]. There are a few problems associated with the raw water from the Llobregat river. Those problems present in the river are, a) low and irregular flow, b) high salinity contains Na^+, K^+, Cl^-, and Br^- that caused by natural and anthropogenic processes [30], and c) high level of microbiological and micropollutant that caused by sewage from urban and industrial. All these problems interrupt the desalination process for a few hours. Consequently, a high concentration of trihalomethane (THMs) is produced from the combination of bromide, temperature and natural organic matter after chlorination.

Table 2 Summary of the comparison between ED and RO system. [3], [18], [27]

	Subject	Electrodialysis	Reverse Osmosis
1	Power consumption at 2g/L TDS, kW/m^3	1.1-1.35	1.5-1.85
2	Water recovery rate (%)	80-90	65-75
3	Membranes life span (years)	1-3	7-10
4	Pre-treatment system	Single-stage	Multi-stage, cartridge
5	Membranes stability		
	Attack by bacteria	Not affected	Affected
	Affect by high temperature	Not affected	Affected and thus storage temperature should control
6	Manually clean without damaging membranes properties	Possible	Not possible
7	Cost in brackish water desalination (USD)	0.022	0.13

To reduce the THMs problem, Aigües Ter Llobregat (ATLL), a public company of the Autonomous Government of Catalonia, carried out some trials using RO pilot plant for six months. Unfortunately, RO technology does not perform well as it has a low recovery and certain instability. Furthermore, the poor quality of raw water, for instance, high turbidity, high fouling potential and chemical pollution also caused the process to experience frequent shutdowns.

Therefore, electrodialysis reversal (EDR) has been introduced by ATLL to replace reverse osmosis technology. Surprisingly, the EDR system performs well as the chemical and aesthetic quality of the drinking water have been improved to the desired quality. The level of the THMs has been reduced to meet the standard level, which is 100 ug/L. Generally, 4 m^3/s of the water can be processed by Abrera DWTP with conventional treatments. The Abrera DWTP is the world's largest desalination plant using EDR technology, and it produces up to 2.2 m^3/s of water.

The conventional treatments are pre-oxidation with potassium permanganate, coagulation, flocculation, oxidation with chlorine dioxide, sand filtration, granular activated carbon (GAC) filtration, electrodialysis reversal (ERD) and final chlorination using NaClO.

Case study 2: The Depurbaix wastewater treatment plant

The Depurbaix wastewater treatment plant located in Sant Boi de Llobregat, near Barcelona, is used to desalinate the brackish water for agricultural purposes. By using electrodialysis technology, the Depurbaix WWTP produces more than 57000 m^3 of water per day. This WWTP can be known as one of the worlds' biggest plants that use to treat wastewater through EDR technology. The EDR technology is supplied by MEGA a.s., and the work is carried out by Spanish temporary consortium BEFESA-ACSA [18].

CHALLENGES OF ELECTRODIALYSIS TECHNOLOGY

Membrane Fouling

There are several challenges in ED technology. One of the main challenges faced by electrodialysis is the fouling problem [12], [28], [31]. The membrane fouling problem increases the resistance of the membrane as the foulants are accumulating on the membrane. As a result, it reduces the system's efficiency and increases the energy consumption of the system. Therefore, during the design of an ED system, some corrective actions should be carried out in order to meet a specific objective. Colloidal material and organic compounds are two sources that caused the fouling problem in ED membranes [5].

Colloidal Fouling

Colloidal particles are ubiquitous in natural water as well as wastewater. Colloids have various sizes, from a few nanometres to a few micrometres. Colloidal silica, iron and calcium carbonate precipitates are examples of the colloids [32]-[33]. Colloidal particles tend to form deposits on the surface membrane of EDR systems. This situation is known as colloidal fouling. Colloidal fouling occurs in most of the EDR plant. Around 30 years ago, the first EDR operating on municipal wastewater was installed in the Middle East. The ERD system is free from organics and bio growth fouling. However, half of the plants are facing a colloidal fouling problem. There are few corrective actions that can be implemented to reduce the potential of colloidal fouling.

Organic Fouling

EDR membranes are made up from resins which pose a potential of internal resin fouling by organic matters in the water. Organic fouling is caused by the substances that dissolved in the feed solution and accumulated at the surface of the EDR membrane due to adsorption. Oil, proteins, macromolecules, whey, polyelectrolytes are the foulants that contribute to an organic gel layer located on top of the membrane or even in the pores [32],[34]. Allison [5] experimented using both cationic and anionic dyes to foul ion exchange membranes. The experimental results proved that only the organics with molecular weights ranging from 250 to 700 penetrate into the membrane structure and contribute to internal resin fouling.

Furthermore, the result shows that organic fouling only occurs in anion exchange resins in natural water. Lee et al. [35] claimed that most organic foulants in many effluent streams are negatively charged. This proved that the fouling organics are anionic.

Environmental and health aspects

With the advances of desalination technologies, the environmental footprint of desalination has been reduced. However, there are still some environmental impacts, such as the discharge of the brine from the ED desalination plant. The brine discharge will definitely pollute the aquatic life as it is a concentrated salt solution containing various chemicals [36]. The emission of the greenhouse effect is another significant impact that brings to the environment from the desalination process. Large quantities of energy are required for a desalination process, and generally, the energy used is produced from fossil fuels. Thus, there will be large quantities of CO_2 and SO_2 emissions [18]. Interestingly, recent studies showed that energy could be harvested by using the potential between electrodes [37]. Further, power-free ED is introduced [38].

CONCLUSION

Despite the fact that most of the ED water desalination process has been replaced by RO technology, it is undeniable that electrodialysis is still the best technology for brackish water desalination. High chemical and mechanical strength of ED membranes and high-water recovery rates have shown that ED is still a high potential and useful technology for water desalination. The next generation of electrodialysis technology is aimed to equip with characteristics such as high-water recovery rate, low fouling potential, the least environmental impact and low energy consumption.

Recently, the application of electrodialysis has been significantly replaced by reverse osmosis in the desalination area. Therefore, all the challenges of electrodialysis such as fouling, environmental impact and high cost have to be overcome to survive in the desalination area. The renewable energy source (RES) is the new trend solution to cover the fundamental needs of power and reduce the environmental impact caused by the ED process [21]. Several renewable energy sources such as photovoltaics, wind and wave energy have started to apply in ED water desalination [39]. Additionally, the combination of RES and battery energy storage (BES) concept have been introduced lately. Energy accumulation, storage and supply are the key components of the BES system which improve process performance along with better resource economics and the least environmental impact [40].

A new method to desalinate water has been proposed, known as shock electrodialysis. It is a technique that purifies water through the exploits of deionisation shock waves in porous media. Schlumpberger et al. [41] noted that the prototype of the shock electrodialysis could remove more than 99% of salt from various electrolytes over a range of concentrations. The water recovery rate can also be enhanced to 79 % with the increasing current. These results showed that it is possible to use shock electrodialysis for practical water desalination. The main advantage of shock electrodialysis is that the process efficiency would not affect fouling as the water flows across those membranes, not through them [41]. Therefore, more studies can be focused on shock electrodialysis to overcome fouling challenges, and it might be the future trend of electrodialysis in the desalination area.

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