Advanced Membrane Technologies for Saline Wastewater Treatment

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Abstract. Since releasing saline wastewater into the environment without first treating it can seriously harm the ecosystem by contaminating soil, surface water, and groundwater, it has become one of the main problems in many nations. This paper highlights forward osmosis membrane and forward osmosis membrane bioreactor, electrodialysis, and electrodialysis metathesis techniques for saline water and wastewater treatment. Besides, the fouling issues of membranes and mitigation methods are discussed. Among them, the prospects and challenges faced by membrane technology include membrane pollution, the lack of pilot-scale research, and problems related to economic aspects. Additionally, the methods that have obvious effects on alleviating membrane pollution are presentment before the main membrane device, physical or chemical cleaning, and membrane modification.

Keywords: Membrane Technologies, Forward Osmosis Membrane, Electro-dialysis, Electro-dialysis Metathesis Techniques, Membrane Contamination.

1. Introduction

Freshwater scarcity has become one of the greatest global challenges facing humanity in the 21st century. With the growth of population, urbanization, and the increase of agricultural irrigation areas, the demand of human civilization to obtain clean water and freshwater continues to increase, and the sustainability of fresh resources has become a problem that has to be faced [1-2]. At the same time, many daily activities and different industries have produced a large amount of wastewater containing salt, which poses a great threat to the environment. Improper use of wastewater containing salt will lead to secondary salinization and damage to the ecosystem [3].

Numerous physical, chemical, and biological methods for treating saline wastewater have been developed over the last few decades. Physico-chemical treatment method mainly includes thermal techniques, coagulation-flocculation, ion exchange, electrochemical process, and membrane [4]. Biological treatments contain different activated sludge processes and different bioreactors.

This review focuses on the membrane technologies dealing with saline water and wastewater, and the main objective is to discuss the development, principle, characteristics, applications, and future view of two membrane technologies. Also, the review will cover the discussion about the fouling issues of membranes used in the treatment process.

2. Forward Osmosis Membrane Bioreactor Technology and Forward Osmosis Membranes

The concept of the forward osmosis membrane bioreactors was originally proposed by Dutch academic Cornelissen et al. in 2008. The working process of the forward osmosis membrane is shown in Figure 1. After a decade of development, this new technology has been widely used for wastewater treatment. Compared to conventional membrane bioreactors, the innovation of the forward osmosis

membrane bioreactor is that it replaces the micro-filtration and ultra-filtration membranes used in conventional bioreactors with the forward osmosis membranes to achieve complete separation of water and solid residues in wastewater treatment. A comprehensive overview of the osmosis membrane will be provided below.

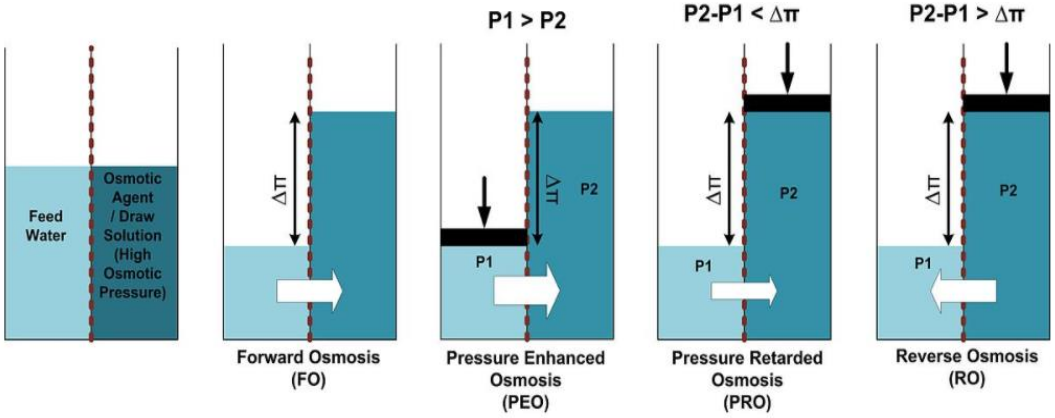


Figure 1. Osmotic Processes Diagram [5]

2.1. Principal of the forward osmotic process

A forward-osmosis membrane bioreactor is a system that uses forward-osmosis membranes to treat wastewater. A typical forward osmosis membrane bioreactor consists of three components: the bioreactor, the membrane master key, and the liquid withdrawal system. The membrane master key component in this reactor refers to the Forward Osmosis membrane separation unit. Forward osmosis (FO) membranes are the antithesis of reverse osmosis membranes and are a mutually inverse approach. Forward Osmosis could be a new membrane separation technology that uses the distinction in pressure level between the two facets of the membrane to maneuver water molecules from the facet with the upper chemical potential to the side with the lower chemical potential.

2.2. Benefits of positive osmosis membranes

The positive osmosis membranes have the advantages of low energy consumption, low membrane contamination, and high contamination retention. This is because the entire treatment process is not driven by a water pressure differential but by a permeate pressure differential. In addition, the energy consumption of the filtration method is correspondingly lower because of the various driving forces. The plates also tend to be less pressure driven than the pressure-driven-typed membrane. As a result, water quality produced using forward osmosis membrane bioreactors is better than conventional membrane biotechnology.

2.3. Disadvantages of forward osmosis membranes

The FO structure has a very thick deep layer, which results in an operating flux of only 10 LMH for the forward osmosis membrane, compared to about 30 LMH-50 LMH with a conventional membrane bioreactor (MBR). It is clear from the data that the operating flux of a forward osmosis membrane bioreactor is very low, only one-fifth or one-third of the conventional flux. The membrane flux here is the amount of water that can pass through a specific membrane area in a defined period of time. This formula can be used to calculate the membrane flux. In this equation $J=A/V\times T$. J is the membrane flux ($L/m^2\times h$), V is the sampling volume (L), A represents the effective membrane area (m^2), and T means the time sampling time (s).

2.4. Application and future perspectives

Forward osmosis membrane bioreactor technology and forward osmosis membranes are considered to be one of the better-developed technologies in the field of membrane technology. As a result, this technology is used in many water treatment aspects. Examples include desalination of

seawater, treatment of wastewater and waste leachate, re-concentration of concentrated brine, treatment of recycled wastewater, etc. The use of positive osmosis membranes is particularly prominent in wastewater treatment. For example, in the treatment of industrial wastewater, positive osmosis membranes can concentrate and purify industrial wastewater, and positive osmosis membranes can form strong permeation isolation of metal ions to achieve treatment effects [6]. The FO structure has a very thick deep layer, which results in an operating flux of only 10 LMH for the forward osmosis membrane, compared to about 30 LMH-50 LMH with a conventional MBR. It is clear from the data that the operating flux of a forward osmosis membrane bioreactor is very low, only one-fifth or one-third of the conventional flux. The membrane flux here is the amount of water that can pass through a specific membrane area in a defined period. This formula can be used to calculate the membrane flux. In this equation, $J=A/(V\times T)$. J is the membrane flux ($L/(m^2\times h)$), V is the sampling volume (L), A represents the effective membrane area (m^2), and T means the time sampling time (s).

Despite the relative maturity of the technology, it still exhibits some types of problems in use, such as those mentioned by the authors in section 2.3 regarding the accumulation of low fluxes and high salinities. Therefore, in the future, researchers could pay more attention to aspects such as forward osmosis membrane bioreactor technology and how forward osmosis membranes can control high salinity and improve membrane flux in FO to refine this technology.

3. Electro-Dialysis (ED) and Electro-Dialysis Metathesis (EDM)

As early as 1890, the Germans E. Maigrot and J. Sabates introduced electric fields into the dialysis process. Over a hundred years, electrodialysis has advanced into a membrane-based technology in a fluid that employs an electric field for efficient ion separation. The technology is cost-efficient in desalinization because it is appropriate for a range of applications together with briny water treatment, brine treatment, and, therefore the production of added chemicals. Additionally, it is additional energy economical than traditional bio-membrane technologies, like those exploitation natural action resins.

Electrodialysis metathesis (EDM) is a technology that evolved from electrodialysis. It has a unique property of recombination and concentration of ions because of its unique structure, occurring reaction by recombination of ions. This unique characteristic has great advantages in desalination technology

3.1. Background of ED and EDM

Table.1. Properties of membranes process

Membrane process	Mechanism	A solute capable of separation		
		Pathogenic bacteria	Organic	Inorganic
Electrodialysis	C	NO	NO	ALL
Reverse osmosis	S,D	C,B,V	DBPs, SOCs	ALL
Nanofiltration	S	C,B,V	DBPs, SOCs	ALL
Microfiltration	S	C,B	NO	NO
Ultrafiltration	S	C,B,V	NO	NO

1. In the mechanism C=charged S=sieving D=diffusion
2. In the pathogenic bacteria C=giardia cells B=bacteria V=virus
3. In the organics, DBPs=disinfection by-products SOCs=synthetic organics

To summarize Table 1 above, when dealing with saltwater containing a large number of inorganic substances such as sodium chloride, ED, and reverse osmosis (RO) are preferred among the major technology [7].

3.2. Principle of ED and EDM

Electrodialysis's principle is also a desalting technology, ED is similar to RO; they both use external energy to cause particles in the water to migrate through the membrane to achieve separation. But the charged particles migrate during the ED process, and the hydron migrates during the RO.

Selectively permeable membranes are alternately placed parallel between the positive and negative electrodes. These membranes will form four compartments, and these four compartments will be filled with an aqueous solution containing particles. When applying an electric field at both ends, positively charged cations in solution move toward the cathode. On the contrary, the negatively charged anion moves toward the anode. Because the membrane has selective permeability, the anion in the dilute chamber enters the concentrated water chamber through the membrane, but the anions in the concentrate cannot migrate out because of the membrane. Thus ion decrease in the dilute and achieves the effect of desalination. Ion increases the concentration and achieves the effect of enrichment.

Electrodialysis metathesis's principle is different from ordinary electrodialysis technology. Electrodialysis metathesis technology has an extra two compartments. There is a new concentration chamber and a new dilute chamber, respectively. This unique design allows low-solubility salts to be converted into high-solubility salts. It divides concentrate into two streams of extremely soluble salts, one containing Na with anions and the other containing chlorides with cations [8].

The ion exchange membrane principle means that the opposite charge attracts under the influence of an electric field. The cation is attracted to the positive membrane and through the membrane into other compartments. But the anion is repelled. Conversely, the anion is attracted to the anion membrane and through the membrane into other compartments. But the cation is repelled. This is the ion-selective permeability of the membrane. The function of ion exchange membranes is ion selection rather than ion exchange.

3.3. Advantages and disadvantages

Table.2. Advantages and Disadvantages of ED [9]

Name	Advantages	Disadvantages	Salinity limit(g/L)	Energy requirement	recovery
ED	High salt removal rate and less susceptible	High capital cost	150-200	10-25(seawater) 0.4-4(brackish water)	85-90%
	Reverse polarity reduces membrane fouling	Membrane fouling			
	No osmotic pressure limitation	1. Microorganisms and organic impurities not removed from water 2. High energy consumption 3. Low restricting current thickness requires a tall layer range			
	No regeneration chemicals required				
	High operating temperature up to 50℃				

According to the table above, there are still many advantages of electrodialysis exists. Despite the high construction cost, the high desalting rate is satisfying. In addition, compared to reverse osmosis technology, ED has its unique advantages in terms of flexibility. For example, ED does not need pressure, and lower salinity limits are required. Besides, ED does not need chemicals to react with water; it also leads to the fact that it does not pollute the environment. Such loose conditions also greatly increase the service life of the membrane and the electrode.

However, due to the immaturity of the technology, ED still needs improvement in many ways. For instance, ED consumes much energy in the desalination of seawater. Compared with other biofilm technologies such as RO, this is a pyrrhic gain. Furtherly, the microorganism in the water can cause pollution to the membrane. Before electrodialysis can be carried out, other means are needed to remove microorganisms from the water.

In brief, electrodialysis has no problem dealing with desalting brackish water, but in desalting seawater, traditional membrane technology represented by RO has more advantages.

3.4. Application of ED

There is a case of ED for desalting groundwater in Barcelona. This is the Abrera Drinking Water Treatment Plant. In Barcelona, the water network provides water to 3.1 million people. Barcelona has two main sources of tap water, the Besos River and the Llobregat River. Llobregat River is the main source of drinking water in Barcelona. But the river has been polluted by industrial, agricultural and municipal sewage for years. And it regularly suffers from floods and droughts. This leads to a decrease in the river's ability to dilute. The phenomenon of high salinity is common. In the tests of various desalination technologies, reverse osmosis technology was phased out because of its instability. After 28 months of testing, the tester discovers that the ED technology is very suitable for desalination treatment of Llobregat River water [10].

An ordinary water treatment handles pre-oxidation with potassium permanganate, coagulation, flocculation, oxidation with chlorine dioxide, sand filtration, GAC filtration and last chlorination utilizing chlorine gas been embraced in desalination treatment. A bromides reduction rate of 60%-80%, a conductivity reduction rate of 60%-80% and an overall water recovery rate of over 90% were achieved by using the EDR method.

4. Membrane fouling issue

One of the main problems in treating saline wastewater involving membrane technologies still is the pollution of fouling. In theory, the fouling issue is caused by depositing harmful substances (the foulants) on the membrane surface, reducing the flux. In certain circumstances, membrane holes would also be blocked by the fouls, leading to inner damage. The consistency of inorganic ions in water outnumbers the counterpart in a saturated situation, which usually leads to fouling. Consequently, these circumstances can be attributed to inorganic ions entering the nucleation step, which can lead to crystal growth and deposition on the film surface or micro holes [11]. The fouling would be affected by some elements, such as the function of the membrane, the component of feed water, and operating factors, including pH and temperature. There may be various fouling in saline water, which would cause the formation of complex dirt. The salinity of wastewater usually exacerbates the biofouling associated with microbial adhesion to membrane surfaces. The salt environment can induce endogenous respiration of bacteria and the polymerization of cells and engender more aggregation from the extra of the cell by the secretion of cell [12]. Wastewater will become even more viscous due to the large extracellular polymer content, which will cause an impossible-to-remove cake layer to form on the membrane surface.

4.1. Preliminary treatment process

The installation of recent therapeutic systems before the only most significant membrane unit could also be an economical pretreatment to get rid of the preponderance of contaminants from feed water before it reaches the membrane unit. The pretreatment procedures may be allotted mistreatment membranes or different pretreatment ways that are deemed acceptable for the actual waste because they will eliminate larger suspended materials that may severely back up the tighter membrane, like nanofiltration (NF) and RO, microfiltration (MF) and ultrafiltration (UF) area units often used in membrane pretreatment [13].

Other non-membrane technologies also can be used as pretreatment once membrane processes might not be appropriate. Utilizing neutralizing colloidal charges, for instance, those suspended solids could be removed within the solidification process. Two coagulation processes can be used as pretreatment units: chemical coagulation and electric coagulation.

In addition to coagulation treatment, using the activated carbon in the pretreatment has also been applied to treat brine wastewater. Although dissolved organic carbon could be eliminated by activated carbon in the shape of powder and granular, microorganisms and particles cannot be removed via this pretreatment method. Therefore, to reduce pollution effects, including biological pollution, the activated carbon and UF need to be combined as a pretreatment step.

4.2. Physical/chemical cleaning

In order to minimize contamination, it is crucial to clean the membranes often during the wastewater treatment procedures. Physical and chemical cleaning are the two general categories of membrane cleaning techniques. A common physical cleaning technique used in membrane applications is water flushing.

Chemical cleaning is necessary to eliminate irreversible fouling, as opposed to the physical cleaning frequently used to eliminate reversible fouling. Acid, base, chelating agents, and surfactants are only a few of the chemical agents that have been utilized to clean membranes during the treatment of actual saline wastewater.

4.3. Membrane modification

The hydrophilicity and smoothness of the membrane surface may influence the fouling phenomena. The fouling propensity of membranes with hydrophobic and rough surfaces is more noticeable. Therefore, methods for surface modification have been suggested to improve the smoothness and hydrophilicity of membranes. A polyamide film combination film was created by Chen et al. in Fo to remediate the backwater left over from fracking for shale gas. At a susceptibility of 3.5lmh/bar, the membrane can resist 95 percent of sodium chloride. However, substantial pollution can still be seen with flux decreases of up to 70 percent [14]. Therefore, the poly (ethylene glycol) (PEG) grafting method is used for surface modification to reduce the pre-pollution density in the process of fo operation. The results showed that polyethylene glycol grafting successfully reduced the pollution by increasing the membrane's smoothness and reducing the adhesion of membrane fouling.

5. Challenges and prospects for the future

5.1. Membrane fouling

It has been claimed that different membrane modification techniques, such as coating, grafting, and the insertion of inorganic particles, can effectively control or postpone the fouling phenomena. Nevertheless, a brief test was frequently used to gauge these tactics' effectiveness. The interaction between the foulants is a lot of crucial in influencing the membrane performance over an extended amount, no matter the sort of membrane. In addition to membrane alteration, a membrane cleaning method can also help to prevent fouling. However, its impact on the entire treatment cost is still unclear. Installing a pretreatment procedure is helpful when using an MBR to handle saline wastewater because it prevents microorganisms from being shocked by salinity, but doing so will eventually raise the cost of the entire treatment process.

5.2. Lack of pilot-scale research

It ought to be noted that the many proportions of the membrane performance within the interconnected brine treating waste were evaluated through victimization lab-scale tests. Thanks to the restricted information supported pilot-scale integrated membrane treatment that's currently obtainable, the implementation of those membrane processes within the industrial saline waste

material treatment business has been delayed as yet. Notwithstanding the latest reports on a pilot survey of a number of saline treating wastewater showing promising outcomes in seawater desalination, estimating the total cost of water treatment is inconceivable.

5.3. Economic dimension

The promotion of the zero liquid discharge (ZLD) technique has increased the capacity and scale of saline wastewater treatment. To improve water sustainability and achieve the subjective ZLD target, a number of membrane treatments, such as pre and post-treatment steps, must be integrated. This is a result of saline sewer water being so complex. If the integrated membrane method includes a FO unit, the value of putting in the DS regeneration unit should even be considered. According to one report, during generated water treatment, the FO unit with the thermal regeneration stage may require 25-150 kWh/m^3, which is more energy than the RO process (which uses 4-16 kWh/m^3 of energy) [15]. Although the inclusion complex membrane method for the treatment and management of various high salinity sewage sources appears to be effective, cost analyses are rarely provided.

Future research must solve the aforementioned problems to make membrane technology for treating saline wastewater commercially viable. Given the complexity of saline wastewater, it is critical to assess how well fouling mitigation strategies affect membrane fluidity over an extended length of time. To fully realize the potential of membrane technology, research on new materials for making membranes with high penetration capacity and smudge resistance qualities is still required. Applying halophilic (salt-tolerant) microorganisms in MBR is an alternative to inserting a preconditioning device sometimes needed to forestall the shocking of high saline matters in MBR. The MBR salt tolerance higher limit may be raised to one hundred fifty g/L by utilizing the matter that is less complicated to create in a high concentration salt setting. To additional investigate its potential in MBR development, extra analysis from the microbiological perspective, like the metabolic shift of the halophilic species following salinity amendment, is also conducted. In terms of money, it is attainable to use waste heat to cut back the worth of saline sewer water treatment operations. For instance, it was found that the integrated FO-MD system's desalinization value for treating farm sewer water reduced from \$17.33/m^3 to \$11.25/m^3 once waste heat was accustomed to power the MD [16]. In addition, the operation value may be shriveled if DS, not regeneration, is used within the FO unit. In order to further persuade the industry to use membrane technology in its brine sewage treatment facility, more pilot studies on membrane performance are required in future work.

6. Conclusion

To summarize, this study focuses on the characteristics and applications of two different membrane technologies in the treatment of saline wastewater. Compared with traditional methods, there are still many challenges (e.g. membrane fouling, lack of pilot scale studies, economic aspects) to developing membrane technologies in this field. Among them, the problem of membrane pollution is particularly serious in the process of using membrane technology to treat salty wastewater. In the case of forwarding biofilm treatment technology, the membrane contamination is low, which is an advantage of forwarding osmosis membranes. However, it also has a very low membrane flux, and there is salt accumulation on the membrane. In electrodialysis, during separation, especially of oxygen and salt, some of the inorganic salts precipitate and organic matter is adsorbed on the surface of the ion membrane. As a result, the flux of ion membrane particles is reduced. But effective pretreatment operations can be carried out before the main membrane device. At the same time, the membrane can also be cleaned regularly by using physical methods and chemical agents in the process of treating wastewater. Secondly, the membrane can be modified by improving the smoothness and hydrophilicity of the membrane (that is, reducing the hydrophobicity and surface roughness of the membrane), To reduce the degree of membrane pollution. Therefore, even though membrane technology as an emerging technology has many challenges, it does not affect that membrane technology can be considered a functional technology that can achieve the desired outcome.

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