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Forward Osmosis Membranes – A Review: Part II

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Abstract

Forward osmosis (FO) is a technical term describing the natural phenomenon of osmosis: the transport of water molecules across a semipermeable membrane by osmotic pressure from a feed solution (FS) to a draw solution (DS). The diluted DS is then reconcentrated to recycle the draw solutes as well as to produce purified water. As the driving force is only the osmotic pressure difference between two solutions, meaning that there is no need to apply an external energy, this results in low fouling propensity of membrane and minimization of irreversible cake forming, which are the main problems controverted by membrane applications, especially in biological treatment systems (e.g., FO membrane bioreactor (FO-MBR)). The purpose of the book chapter is to bring an overview on the FO membrane manufacturing, characterizing and application area at laboratory or full scales. This book chapter is published in two parts. In the second part, which appears here, characterization of mass transport in FO membranes, fouling mechanisms and foulants on FO membranes in naturally asymmetric structure and application areas of FO membranes in the literature are mentioned. Cutting-edge technologies on FO studies are comprehensively reviewed and following major and minor titles are stated truly on the new technologies.

Keywords: forward osmosis, characterization, structural parameter, membrane fouling, concentration polarization, water/wastewater treatment, desalination, hybrid processes, membrane bioreactor

1. Introduction

FO membranes are preferred over the last few years due to the high rejection of a wide range of contaminants and the lack of hydraulic pressure, resulting in less irreversible fouling on

the membrane surface compared to pressure-driven membranes. However, due to the asymmetric structure of the FO membrane, concentration polarization (CP) becomes more important, which motivates many researchers to focus on the selection and/or development of new membrane materials for both active and support layers to decrease CP.

In this second part of the chapter, characterization of FO membranes, such as determining rejection capabilities of membrane layers by analytical approaches and experimental procedures, is thoroughly stated by considering both review and research articles in the available literature. In the following section, fouling phenomena in FO membranes are referred by considering membrane orientation, and before Conclusion, application areas of FO process are presented. Since the permeate (diluting DS) of the FO membrane is not actually a product water, this filtrate (diluted DS) needs to be treated again. For this reason, the FO process needs an additional process to recover the water from the diluted draw solution. In this context, hybrid FO processes are also included in this section. Finally, the general summary of the research is evaluated and the future prospects for FO membranes and applications are introduced.

2. Characterization of FO membranes

Although the model development on characterization for FO membranes is described in some literature [1], more general information from some is given here. The membrane in separation process using osmotic pressure as driving force must be capable of rejecting both the FS and the DS. When there is no solute retention in membrane, the FS and DS are easily diffused from the membrane, and osmosis does not occur. All existing membranes that can be used for this purpose are asymmetric. Many of the problems in the FO process resulted from this asymmetric structure. As with all membrane processes, mass transfer boundary layers form near the selective interface. On the FO membrane, these boundary layers occur on both sides of the selective layer interface. However, in an asymmetric membrane, one of these interfaces is embedded in the support layer. Therefore, the support layer significantly reduces the mixing and prevents the mass transfer [2]. The support layers in the TFC RO membranes are relatively thick on the FO membranes and have 25–45% porosity [3]. Solutes must be transported by support layer to reach to the selective layer on which diffusion or rejection is performed. If the mass transfer in these layers is weak, the situation called ICP occurs. Similar to conventional CP, ICP reduces the osmotic driving force. In an FO membrane where there is an asymmetric support layer in which no mixing occurs, the osmotic driving forces can be severely reduced, resulting in no water flux from the membrane [4]. The severity of ICP is greatly influenced by the support layer. This structure is often referred to a metric known as the structural parameter, S

$$S = \frac{t\tau}{\varepsilon} \quad (1)$$

where t is the thickness, τ is the tortuosity, and ε is the porosity of the support layer. In the FO process, membranes with lower S values are preferred to reduce ICP severity. To this end, a

number of studies have been conducted on the production and modification of new FO membranes with low S values since 1990. Tiraferri et al. [5] conducted studies on the effects of solvent quality, dope polymer concentration, backing layer wetting, and casting blade gate on support layer production on one of the first TFC membranes designed for the FO membrane. The pore morphology of the support layer was characterized with the aid of cross-sectional SEM images and reported that the optimum FO membrane must be formed from a mixed structured backing layer and that the upper part of the thin sponge-like layer should be placed on high porosity macrovoids. Shi [6] investigated UF-type phase inversion cast supports for hollow fiber FO membranes and reported that substrates with 300 kDa (molecular weight cut-off (MWCO)) should be preferred to obtain a “good” semipermeable skin.

It has also been claimed that, considering the suitability of the substrate for IP, taking into account the MWCO parameter is more appropriate than the mean pore size. It is estimated that membrane thickness is more important than porosity and tortuosity in recent studies with nanofiber membranes [7]. Moreover, the support layer pore diameter, which is thought to be very effective only in the formation of the selective layer, has also been shown to influence ICP [8]. The influence of the support layer structure on transport is typically expressed using the structural parameter concept. To calculate S , the membrane thickness (can be measured by SEM and relatively easily), porosity, and tortuosity should be measured independently. However, it is quite difficult to measure these last two, especially tortuosity, accurately and reliably. The reason for this is that the characterization of the pore structure of soft materials is an area where work is still developing and there is no standardization for the comprehensive and accurate characterization of 3D structures. Hence, researchers on FO use and develop numerical models more commonly than calculating S parameters with Eq. (1).

Experimental measurements are used when the S parameter is calculated, and therefore, the experimental conditions as a factor are emerging from the structural properties of the membrane. This means that changes in experimental conditions will directly affect the estimated S value. Therefore, no significant comparison can be made between these support layers unless the same experimental conditions are used to test different membranes. In a study by Cath et al., this limitation of the semiempirical method is clearly emphasized [9]. In this study, researchers from 7 different laboratory groups tested 2 different membranes from the same production line under the same experimental conditions but on different systems. One was an HTI-CTA membrane commercially available from HTI, and the other was a TFC membrane from Oasys Water. Significant deviations could be observed between the effective S values obtained by different groups as shown in **Figure 1**. Therefore, researchers report that the experimental conditions are the main factors in the calculation of the effective S parameter in semiempirical calculation method [1].

More recently, a simple characterization method based on a combination of a single FO test and a statistical approach has been developed to avoid pressure RO testing, which can damage the FO membrane or misread membrane properties in the characterization of FO membranes [10]. In this single test, the membrane is operated in AL-FS mode to measure water and reverse salt flux using deionized water (DI) as feed and NaCl as the DS. The statistical approach uses

Figure 1. Structural parameters of TFC and asymmetric FO membranes [9].

both ICP and external concentration polarization (ECP) models to predict J_w and J_s on the tested membrane and finds the most appropriate water and salt permeability (A and B) and salt diffusion resistance in the support layer. Verifications using various experimental results in this study and other literature have shown that this new FO membrane characterization method sets parameters (A, B, and KICP) more reliably than the conventional characterization method based on the pressure-RO experiment to estimate the experimental J_w and J_s . The consideration of ECP helps to determine more accurate FO membrane parameters (especially KICP), but it is difficult to accurately model the ECP for the FO membrane channel tested.

The evaluation of porosity and tortuosity has been carried out with traditional characterization techniques such as SEM and porosimetry as well as newer tools such as x-ray computed tomography (XCT). While none of these techniques comply with all of the difficulties listed above, some are more suitable than others according to the type of the membrane material being tested. Imaging approaches provide good visuals for evaluating the qualities of porous membranes. However, expensive and time-consuming techniques are required to obtain this information from images. It also requires usage expertise. But all of these, as well as resolution and field-of-view (FOV) limitations, are disadvantages that reduce the quantitative value of these images.

Membrane pore structure analysis can also be done without relying on the images. There are a number of analytical techniques that can examine the pore structure by means of probing. While these approaches do not reintroduce visual presentation of membranes, they can provide critical characterization information about FO membrane, including porosity and tortuosity, by using basic models.

Compared with imaging techniques, analytical techniques allow for greater comparisons between different FO membrane structures by easily analyzing a larger sample volume. However, the

Figure 2. Direct measurement techniques of intrinsic structural parameters (adapted from [1]).

assumptions used to derive the models calculating the porosity and tortuosity must be carefully considered before adapting to the sample being analyzed. Similarly, when analyzing data from them, the biases of different analytical techniques should be considered [1]. Direct measurement techniques of intrinsic structural parameters are presented together in **Figure 2**.

Designers of membranes for osmotic processes need to be able to better calculate the mass transfer resistance of the membrane to overcome the difficulties in nature of osmotic systems. Unless major structural parameters such as porosity and tortuosity are known, wrong areas of designs may be focused on. In order to overcome these difficulties, the above-mentioned methods for membrane characterization need to be further developed [1].

3. Fouling in FO membranes

Today, the greatest challenges of FO technology can be summarized into three main classes: the difficulty of developing a correct and an effective FO membrane, the lack of recyclable and economical DS, and the limited availability of information on membrane fouling [11]. Although fouling of FO membranes is more reversible than RO membranes, removal of contaminants may become more difficult when the feed stream in the FO membrane contacts the support layer [12, 13].

She et al. [14] investigated the membrane fouling in osmotically driven membrane processes and concluded that fouling in pressure-driven membranes can occur at different locations of the membrane [15, 16]. As shown in **Figure 3(a)**, the foulants in the FS are transported to the active layer surface of the membrane in the AL-FS mode, resulting in a cake layer similar to fouling of the RO membranes. This type of pollution is called external pollution. Fouling occurring in the FO membrane in AL-DS mode is more complicated. **Figure 3(b)** shows possible fouling scenarios in AL-DS orientation. If the contaminant has a relatively small size and is able to enter the porous support layer by convection of the FS, it will either be adsorbed through the walls of the pores of the support layer or eventually be retained by the active layer and accumulate on the back surface of the active layer. Subsequently, the foulants entering the porous support layer will adhere to the contaminants that are adsorbed on the walls of the support layer pores or to the accumulated contaminants on the back surface of the active layer, thus leading to “pore clogging.” This form of pollution is called internal fouling (scenario (1) in **Figure 3(b)**). In severe fouling conditions, contaminants will continue to accumulate on the outer surface of the porous support layer, as well as internal pore clogging. This type of membrane fouling is referred to as combined internal and external fouling (scheme (2) in **Figure 3(b)**). If the foulants have relatively large sizes and cannot enter the porous support layer, they may only accumulate on the outer surface of the porous support layer. In this case, only external fouling occurs (scenario (3) in **Figure 3(b)**). If contaminants are present in the feedwater in different sizes, both external fouling and internal fouling may occur (scenarios (4) and (5) in **Figure 3(b)**).

According to She et al. [15], compared to internal fouling, it is easier to remove the external fouling from the membrane surface by optimizing the hydrodynamic conditions of the feed stream (such as by increasing the cross-flow rate, applying pulsed flow [17] and employing air scouring [18]). For this reason, most researchers suggest AL-FS orientation in the FO process to prevent undesired internal fouling, even though the ICP in AL-FS is more severe than in AL-DS mode [13, 19]. However, external fouling is more reversible in FO membranes, as there is no such matter as compaction of pollution due to hydraulic pressure in the RO membrane [20]. On the other hand, the internal fouling within the porous support layer functions as an unmixed layer. Internal pollution is less reversible than external pollution, as it is more difficult to control the optimization of hydrodynamic conditions [21]. Internal fouling usually occurs in PRO membranes operating in AL-DS mode [22]. Although the osmotic backwash method has been developed to clean contaminants in the support layer [21], the development

Figure 3. Fouling types in FO membranes (a) FO mode, (b) PRO mode (adapted from [14]).

of more effective strategies for internal pollution control will still be an important research topic in the future.

Classification and interaction of foulants in osmotic pressure-driven membrane processes [22] can be grouped into four main classes: (i) colloidal fouling by accumulation of colloidal particles on the membrane, (ii) organic fouling by deposition and adsorption of the macromolecular organic compounds on the membrane surface, (iii) inorganic scaling by precipitation or crystallization of inorganic compounds that are poorly soluble on the membrane surface, and (iv) biofouling by adhesion and accumulation of the microorganisms to the membrane surface and eventually biofilm development. The specific pollutants in the different groups are closely related to the characteristics of the feedwater. Contaminants specifically present in raw and treated wastewaters are particles, colloids, and organic macromolecules such as polysaccharides, humic substances, and proteins [23]. In addition, these substances are also commonly found in natural waters such as rivers, seawater, and ground waters [13]. Zhou et al. [23] used gas chromatography-mass spectrometry (GC-MS) to identify soluble microbial products (SMPs) containing a large portion of polysaccharides, proteins and humic substances in raw and wastewater. Recently, organic carbon detection-organic nitrogen detection (LC-OCD-OND) has become increasingly popular for the identification of these pollutants [24]. Organic contaminants deposited on the membrane can be identified by Fourier transform infrared (FTIR) spectroscopy, solid-state ^{13}C -nuclear magnetic resonance (NMR) spectroscopy, and high performance size exclusion chromatography (HP-SEC) [25]. Total organic carbon (TOC) measurement and UV analysis were also performed to determine the density of organic foulant deposition on the membrane [26]. Transparent exopolymer particles (TEPs) are another important organic pollutant typically found in natural waters. TEP in the feedwater is determined by two methods: microscopic counting and colorimetric detection [27].

Silica is a major inorganic foulant and is usually present in dissolved form or as colloidal particles in sea water, brackish water, and wastewater [24]. In addition, other inorganic contaminants are dissolved salts such as calcium carbonate, calcium sulfate, and calcium phosphate [28]. These inorganic contaminants deposited on the membrane surface can be extensively characterized by scanning electron microscopy-energy dispersive X-ray diffraction (SEM-EDX) [28] and X-ray diffraction (XRD) [29]. Microorganisms are mainly found in activated sludge in membrane bioreactors (MBR) as biofoulants [28]. These microorganisms can also be found in natural waters and cause biofouling in seawater and brackish water desalination [24]. Microbial populations within the biofilm can be characterized by analysis of DNA extracted from living cells using microbiological methods such as polymerase chain reaction denaturing gradient gel electrophoresis (PCR-DGGE) and fluorescent in situ hybridization (FISH) [23].

She et al. [15] indicated that membranes in osmotic pressure-driven membrane processes are contaminated by natural or industrial waters and wastewaters, and membrane fouling involves the combination of the four fouling categories above [24]. The understanding of mixed pollution mechanisms is difficult because of the various and numerous pollutants. Many studies to understand these fouling mechanisms are generally based on the consideration of a single foulant and the use of a synthetic FS [13, 19]. Meanwhile, the number of studies on fouling of FO membranes is also increasing. In particular, osmotic MBR studies have the

potential to conduct research with more complex wastewaters [28, 30]. Working with a single model of foulant is more advantageous in terms of easier control of the selected foulant and understanding of the foulant-foulant or foulant-membrane interactions. The physicochemical properties are also important factors affecting the stability of contaminants in the FS, as well as information on the tendency to contaminate the membrane [31]. With the understanding of the fouling mechanisms in a single foulant system, future studies may focus on the study of the fouling mechanisms for mixed foulant systems, which may lead to a better understanding of the membrane fouling mechanisms.

Colloidal and organic fouling with highly complex mechanisms in FO membranes is affected by a number of physical and chemical factors, and in general, these factors can be divided into five groups: (i) operating conditions such as initial water flow, cross-flow rate, spacer features, ventilation, and temperature; (ii) feedwater characteristics such as foulant type, concentration, pH, temperature, ionic strength, and ionic composition; (iii) DS properties such as solute type and concentration; (iv) Membrane properties such as structural and surface characteristics; (iv) membrane orientation as AL-FS and AL-DS [31].

The composition of the FS is one of the most important factors affecting membrane fouling. The effect of the feedwater composition on FO membrane fouling is similar to that of pressure-based membrane processes, and recently some investigations have been conducted on this topic [13, 32]. Generally, the degree and rate of fouling are strongly dependent on the properties and concentration of pollutants in the feedwater. In addition, since the FS chemistry significantly affects the physico-chemical properties of the contaminant [22, 33], it will also play a role in foulant-foulant and foulant-membrane interactions and determine the membrane's fouling behavior.

The composition and concentration of the DS, the main source of osmotic pressure in the FO process, not only affects water and salt flux but also plays a role on the membrane fouling. In general, as the DS concentration increases, the initial water flux increases and exacerbates membrane fouling. Studies in the literature have reported membrane fouling increases with increasing DS concentration [13, 19, 34]. The high hydraulic drag force caused by the high flux also leads to the accumulation of foulant on the surface of the membrane. In this context, the change in DS concentration leads mainly to changes in hydrodynamic conditions. For this reason, pollution behavior due to DS concentration can be well explained by the flux-dependent fouling mechanism in which hydrodynamic conditions play a dominant role.

Membrane material and properties may also affect membrane fouling behavior. Membranes used in osmotic processes are generally originated from a nonporous active layer formed on a porous support layer [35–37]. The intrinsic separation properties of the active layer and the structural properties of the support layer govern the transport of water and solutes, which may affect membrane fouling behavior. Membranes with superior separation properties and structural properties (i.e., more water permeability, high selectivity, and membranes with smaller structural parameters) can provide higher water flux. However, the increased hydrodynamic drag force due to increased water flow will also increase the membrane fouling potential. On the other hand, membranes with low separation and selectivity properties may increase the risk of membrane fouling as there may be more solute transfer between DS and

FS. When designing or selecting membranes for FO applications in the future, the separation and structural properties of the membranes should be considered not only in terms of water flow performance but also in terms of the fouling behavior [15].

Membrane fouling and CP behave differently in different orientations of membrane (AL-FS or AL-DS) in osmotic pressure-driven membranes (**Figure 4**). Therefore, fouling and CP are defined as cake-enhanced external concentration polarization (CE-ECP) in the AL-FS mode [38], while in the AL-DS mode, it is defined as pore clogging-enhanced internal concentration polarization (PCE-ICP) [19]. It is reported that the main factor that dominates water flux in osmotic pressure-driven membranes is ICP and PCE-ICP presumably plays a leading role in the flux declining. Furthermore, while CE-ECP is very effective in AL-FS mode membrane fouling, a strong ICP effect can moderate flux decline rate. On the other hand, PCE-ICP can cause much more severe flux declines. However, systematic studies are still needed to explore the effects of CE-ECP and PCE-ICP on membrane clogging in osmotic pressure-driven membranes.

As shown in **Figure 5**, membrane fouling, CP (both ICP and ECP), and RSD are closely interrelated and can be modeled using the osmotic-resistance filtration model. Factors and mechanisms affecting FO membrane fouling such as hydrodynamic conditions, feedwater composition, membrane properties, and cake-enhanced concentration polarization (CE-CP) are also applicable for NF/RO processes. Osmotic pressure is the indispensable parameter for osmotically driven membrane processes. The composition and concentration of this solution may also affect other factors by means of membrane fouling. This is the point where osmotically driven

Figure 4. Schematic illustration of concentration profile across the membrane due to fouling-enhanced concentration polarization (a) fouling-enhanced ECP in AL-FS orientation. (b) Fouling-enhanced ICP in AL-DS orientation (adapted from [14]).

Figure 5. The intrinsic interrelationship among membrane fouling; CP (concentration polarization) and RSD (reverse salt diffusion) (adapted from [14]).

membranes are separated mainly from hydraulic pressure-driven membranes in terms of the fouling mechanism. Membrane orientation (AL-FS/AL-DS or FO/PRO) is another factor affecting membrane fouling, and FO mode is more preferred as it is less prone to fouling and provides a more stable water flux. However, PRO mode can also be preferred for strong membrane stability under high pressure and fewer ICPs. However, this mode has a tendency for internal fouling, which is less reversible. Both the size exclusion mechanism and CE-CP can affect membrane fouling, which can increase or decrease the rejection of contaminants. Modification of the membrane may be a strategy to reduce the fouling of the membrane and to increase reversibility of membrane fouling, which facilitates membrane cleaning [14].

4. Application areas of forward osmosis membranes

FO can be applied for the treatment of various kind of wastewaters including strong industrial effluents, i.e., from textile processes, oil and gas well fracturing waste streams, landfill leachates, nutrient-rich liquids, activated sludge, municipal wastewater, and even nuclear-origin wastewaters have been mentioned [39]. The applications of FO process can be classified as in **Figure 6**. The FO membrane rejects particles, pathogens, and emerging substances with an average porosity of 0.25–0.37 nm [40]. FO is also able to reject high levels of salt that cannot be achieved by normal treatment systems, and the total dissolved solids (TDS) from complex water can effectively be removed [41]. FO is no required for pretreatment of feedwaters (wastewaters) with complex contents. Conversely, RO and NF processes are more susceptible to fouling. Pretreatment is required to increase membrane lifetime and reduce costs [42]. FO can also be used for dewatering applications [43], useful for an efficient anaerobic digestion of wastewater, and is simpler and more environmentally friendly than classical dewatering processes [11]. High saline currents can be processed by the FO, not by the RO [44].

Figure 6. Forward osmosis applications (adapted from [45]).

4.1. Water/wastewater treatment

According to FO literature in the last 10 years, about 7% of the studies have used complex water. However, the number of studies on wastewater is also increasing. The advantages of FO observed in these studies encourage they prefer FO instead of current technologies in future studies [45].

In municipal wastewater treatment processes, integrated FO-membrane distillation (MD) system is applied for sewer mining. In a continuous operating period, a stable water flux has been achieved at a recovery rate of up to 80% [46]. FO rejects most organic pollutants at a moderate level, whereas MD rejects almost the entire residue. Recovery of clean water from secondary wastewater was performed by FO electro dialysis (FOeED)-integrated system powered by photovoltaic energy source. This process removed total organic carbon from wastewater and produced fresh water [47]. Utilizing natural energies (osmotic pressure and solar energy), this hybrid system is a convenient process for potable water supply in isolated areas, remote areas, and islands.

MBR, which contains both activated sludge process and membrane filtration, has become one of the most widely applied technologies in wastewater treatment. The integration of the biological system with the FO membrane (FO-MBR or OMBR) can reduce energy consumption in conventional MBR. In recent years, studies on FO-MBR have been increasing [48–50]. This process not only reduces the cost of MBRs used by UF or MF but also provides fouling control through air cleaning in conventional MBR; at the same time, a more stable flux is obtained. Thus, with the help of the FO membrane in the MBR, more efficient removal efficiency is obtained with less fouling tendency without the need for hydraulic pressure [45].

FO was tested for dewatering of the nutrient-rich anaerobic digester concentration [51] in which organic compounds are rejected by FO membrane, and an RO membrane can be used to recover fresh water from a clean and diluted DS. The FO membrane was also used for activated sludge dewatering [52]. The EDTA sodium salt has been tested as DS for dewatering of activated sludge with high nutrient content. The nutrients in the sludge were successfully removed by means of FO membrane. The macromolecular DS can be posttreated with an NF process for the recovery of freshwater. Alternatively, the concentration of the RO membrane

was used as DS in Zhu's investigation and an effective sludge thickening was obtained. Thus, RO concentration is also osmotically diluted and safe disposal is possible while the volume of sludge is reduced by that study.

Another important source of pollution for wastewater treatment plants is industrial wastewater. In the US, a company has installed a pilot FO plant for the recycling of dye containing wastewater from textile and carpet mill processes [53]. In another study, the FO process was used to recover heavy metals from industrial wastewaters [54]. The effects of hydrodynamic conditions, organic pollution, temperature, and FS and DS properties on the separation efficiency were investigated. It has been reported that almost all metals such as Pb, Zn, Cu, and Cd have been removed in the study and that the FO process has the potential to be an effective and economical process for the treatment of industrial wastewater.

Linares et al. [45] expressed that, today, most FO applications for industrial wastewater treatment are devoted to the treatment and recovery of wastewater from the oil and gas (O&G) industry. In these applications, capacity for the treatment of emulsifier oil waters with FO has been stated [55]. Fresh water was recovered from wastewater by FO membrane containing up to 200,000 ppm of oil and a reasonable water flux value about 12 LMH was obtained. Many studies at the laboratory or commercial scale have been directly applied to the real wastewater of the O&G industry. Combined with RO in a closed loop, FO was used for drilling wastewater treatment from the gas exploration process [56]. The wastewater recovery capacity of the plant is 242,000 gallons of water per day, reducing the need for additional fresh water. Similar studies and applications have been performed by different companies and research groups using different membrane materials, modules, DS, and process configurations [57–59]. In these studies, it was reported that the volume of wastewater was greatly reduced, the need for fresh water was reduced, and a well-designed FO process could be a much more advantageous option than RO [60].

4.2. Desalination

Conventional desalination technologies include membrane-based separation processes such as RO, NF, and electrodialysis and thermal desalination technologies such as multieffect distillation (MED), multistage flash (MSF), and mechanical vapor compression (MVC). Pretreatment of feedwater has critical precaution to prevent the physical equipment of conventional processes from being damaged by wastewater components and to facilitate their performance by maintaining the consistent quality of the pretreated feedwater. Today, pretreatment technologies for desalination are designed to reduce the potential for contamination of feedwater by removing natural organic matter and suspended solids. However, pretreatment technologies are typically not designed to remove dissolved solids [61]. Inorganic scaling in membrane and thermal desalination processes caused by low solubility dissolved salts in food water limits operating conditions and system performance. In MED and MSF, scaling reduces heat transfer efficiency and system recovery rates and limits operating temperatures [62–65].

Shaffer et al. [65] notified that to prevent the harmful effects of the scaling, the FO pretreatment can act to remove dissolved organic material and dissolved inorganic scalants in addition to suspended solids from the FS. When the FO process is used for pretreatment, the traditional desalination process used for recovery of the DS is only affected by NaCl solution

or an ammonia-carbon dioxide solution with negligible fouling and scaling potential of these engineered DS. The reversibility of the FO fouling shows that it can maintain the flow and performance of the FO membranes when they come in contact with raw feedwater with high fouling potential, under proper hydrodynamic conditions. A schematic view of the FO process applied for pretreatment prior to a classical membrane or thermal desalination process is presented in **Figure 7**.

The use of the FO process as pretreatment can improve the performance of conventional desalination processes by removing the small amounts of scalants present in the feedwater. The combined desalination processes can be operated at higher pressures or temperatures without the risk of scaling, resulting in higher system recovery. Testing the process modeling of an FO-RO system [66] and testing both bench-scale FO-RO [67] and FO-NF [68] systems proved the feasibility of pretreatment of the FO process. Furthermore, when FO is used instead of processes such as ion exchange and NF in the pretreatment, there is also the advantage that not only specific cations or anions but also all ions in the feedwater can be removed, in addition to the low membrane fouling tendency [45].

Linares et al. [45] notified that the direct use of FO for desalination is similar to the use of RO and NF processes conventionally used to obtain fresh water from sea water directly. This process uses seawater as FS, while nonvolatile NaCl or volatile ammonia-carbon dioxide is used as the DS [69]. However, in this process, an additional operation is required to recover the DS

Figure 7. Schematic of FO pretreatment for a conventional membrane desalination process [65].

from the diluted DS solution to obtain fresh water [70]. One of the most common desalination studies is the use of ammonia-carbon dioxide solution as a DS and recovering fresh water with a thermal process and regenerating the osmotic agent [2, 71]. In another study, it was reported that the total equivalent work requirement of this process was less than the conventional desalination process, such as RO, and achieved energy savings of up to 85% when expressed in terms of energy [72]. Researchers have investigated the CP in the direct desalination FO process in which ammonium bicarbonate is used as a DS and have concluded that recovery of fresh water from saline water by FO is a fairly feasible method [73]. There are also different and new DS solution searches to perform an easier and more sustainable DS regeneration in direct FO desalination studies. Generally, an ideal DS should be easy to recover and reusable with high osmotic pressure and high resolution, not toxic, easily available, and inexpensive [70]. In a study where hydrophilic nanoparticles were used as FS for DS and synthetic seawater, about 93% of salt recovery was obtained with flux and UF at around 6 LMH [74]. In a study where divalent salts such as Na_2SO_4 were used as DS and brackish water as FS, 98% of the DS was rejected using NF, while 8–10 LMH flux was obtained [68]. Most DSs investigated for direct FO desalination were not commercially viable due to their high cost, limited maximum water flux they could produce, or low recovery of DS efficiencies. The world's only commercial FO facility for direct sea water treatment, was established in Al Najdah, Oman. This plant is still in operation and has reduced chemical consumption and provides longer membrane life and lower carbon footprint [75] compared to competing technologies such as traditional high-pressure RO membrane systems, saving significant operational and capital costs. These advantages have been associated with the reduction of RO membrane fouling due to the use of FO as a pretreatment step. In the direct FO desalination, similar to the RO desalination, a pretreatment process may be required. Currently, there are very few studies using natural seawater in direct FO desalination. For this reason, the fouling tendency of the FO membrane in these conditions has not been adequately investigated. However, Li et al. [24] reported that a foulant matrix containing natural organic matter and polymerized silica was formed on the membrane when natural seawater was used as feedwater.

In the indirect FO desalination, there is a degraded matrix, such as wastewater or urban stormwater runoff, on the FS side, while DS is using high salinity solution [54, 76]. Potential DS in indirect FO desalination is seawater and brackish water. In addition to being free of charge DS, the main attraction is fresh water recovery through free osmotic energy from the FS, and then a partial dewatered water (diluted DS) that can be desalinated by a low-pressure RO [77]. Thus, the cost of the entire desalination process is also reduced. These studies show that FO desalination integrates fresh water treatment operations from wastewater treatment and seawater, providing a water-energy nexus for coastal cities and a promising process [54, 76].

These studies, in particular the use of primary wastewater as FS for FO, have introduced a concept of the feasibility of FO membrane, which can avoid high-cost treatment of wastewater by conventional treatment processes. For example, an anaerobic process that can be used to treat concentrated primary wastewater (concentrated FS) will provide both biogas production and reduced wastewater treatment costs [78]. Indirect desalination experiments have demonstrated the ability of FO membranes to reject waste water nutrients, especially COD and phosphate and moderately nitrogen. In addition, Linares et al. [76] could adapt the system

to the primary clarifier tank using a submerged membrane module, in partial desalination of seawater. This study also showed that FO membranes could reject up to 98% of heavy metals in wastewater. Direct and indirect layouts of desalination systems employing FO membrane are shown in **Figure 8**.

According to a fractional organic carbon analysis carried out in the fouling layer of the FO membrane, it has been reported that this fouling is mainly composed of biopolymers and protein-like substances. A similar result was observed in the FO membrane in the osmotic MBR that was used for municipal wastewater treatment [28]. When the FO system is combined with a low-pressure RO system, this hybrid process has been found to function as a double barrier against selected microcontaminants including pharmaceutically active compounds, hormones, and other organic micropollutants [79]. In practice, most of the micropollutants are rejected by FO membrane using secondary municipal wastewater as FS and sea water as DS, and removal rates were 44–95% for hydrophilic neutral compounds, 48–92% for hydrophilic neutral contaminants, and 96–99% for hydrophilic ionic microcontaminants.

In the FO process coupled with low-pressure RO, the removal of low molecular weight hydrophilic neutral micropollutants was effective (>89%) and the removal of the remaining compounds was over 99% [80]. A membrane cleaning protocol was investigated in the FO application in which municipal secondary wastewater was used as FS and sea water was employed as DS for removing of NOM-fouling through the active layer and removing of transparent exopolymeric particles from the support layer by reporting many cleaning procedures. Osmotic backwashing did not seem to help the recovery of water flux. However, when air was scoured in concentrated wastewater for 15 minutes as a cleaning technique, 89.5% flux recovery was achieved. Cleaning of the active layer with Alconox and EDTA chemistry slightly increased pollution reversibility (93.6%). The chemical cleaning of the support layer removed the reversible pollution of SL up to 94.5%. The irreversible pollution rate in these experiments was 5.5% and it was attributed to biopolymers and trace TEP that cannot be removed from the

Figure 8. Layout of the two FO processes for desalination (a) direct, (b) indirect (adapted from [45]).

membrane surface [18]. It has been reported that the source of irreversible contaminants on the membrane surface after chemical cleaning and at negligible level is the minimal compaction and of the nature of the FO membrane [45, 79].

In some FO applications, the saline water is used as a major DS rather than the FS. The simplest of these applications is FO, which is used as a pretreatment for RO. In this case, seawater is used as a DS and freshwater is used as an FS for more favorable RO conditions by pressurizing and diluting sea water. Thanks to this pretreatment, the energy required for desalination of the water is greatly reduced. A similar process is pretreatment of RO water using wastewater as FS. The benefit of using such water is that the RO feedwater is diluted to more favorable operating conditions; thus, concentrated feedwater is more appropriate for effective handling. Similarly, a new procedure using ocean water to dewater an algae/nutrient solution for the production of algae biofuels is being investigated [45, 81].

In a recent analysis, McGovern and Lienhard [82] compared the specific energy consumption of a two-pass RO system with FO for desalination of seawater. At 50% recovery, for desalination of seawater containing 35,000 mg/L TDS, the two-pass RO energy consumption has been 3.0 kWh/m³ including UF (for pretreatment), first- and second- pass RO. The energy consumption for the FO process with the dilution and regeneration process of DS consuming 0.10 and 3.48 kWh/m³, respectively, for the same conditions was calculated as 3.58 kWh/m³. Therefore, in order for the FO to be able to compete with the RO in terms of energy consumption, the regeneration process must be significantly more efficient than RO. However, the FO process has the advantage of having less tendency to membrane fouling compared to RO due to the lack of a hydraulic driving pressure. The FO process is also suitable for niche applications where the salinity levels of the water to be treated are higher than the salinity that can be treated by RO process [83].

4.3. Novel/hybrid processes

In their review on emerging desalination technologies, Subramani and Jacangelo [83] reported that the combination of the two technologies (hybrid) has shown that a hybrid technology is more effective than single use. Different hybrid configurations are being evaluated for the treatment of the hard waste waters of various industrial sources. All these industrial sectors require drinking water for various operations and applications. Emerging desalination technologies not only purify these complex wastewaters but also provide water recovery with low operating and maintenance costs and reduce the cost of electricity consumption and membrane cleaning chemicals.

Two hybrid configurations that can be used for the purification of various industrial wastewaters are shown in **Figure 9**. An FO system in **Figure 9a** is combined with an RO system for the treatment of highly contaminated wastewaters [59, 83]. Since hydraulic pressure is not present in FO, the accumulation of contaminants in the membrane is lower and the pretreatment need is eliminated. Again due to the lack of applied pressure, osmotic cleaning using a low salinity solution on the DS side will cause water transport from the DS to the FS [11]. This transport will remove loose deposits of foulants from the membrane surface and lead to more effective cleaning. The concentration of the DS is carried out using a known RO system. Because of the maximum feed pressure limit in RO, the hybrid configuration of FO and RO

Figure 9. Two hybrid FO applications for wastewater treatment (a) FO-RO, (b) FO-MD [83].

can only be used for the treatment of feedwater streams with low salinity. For feedwater streams with a TDS > 40,000 mg/L, DS recovery can be achieved using a gaseous NH_3/CO_2 mixture. In this case, additional energy requirements must be taken into account in order to recover the DS using heat or other thermal methods. This configuration is particularly suitable for the refining of reflux water in the petroleum and gas industry when reuse of the water is desired. Purified water can be reused as feedwater for boilers or irrigation [83].

In **Figure 9b**, an FO system is combined with an MD system. The MD system is used for the concentration of the DS [46]. Depending on the salinity of the feed water, various DSs can be used. Since salinity is not a limiting factor for the performance of the MD system, this hybrid configuration can be used to treat wastewater with high salinity. A typical application involves flowback or processing of produced water in the oil and gas industry [84]. This hybrid configuration guarantees a minimum energy requirement when a waste heat source is available to heat the drawing solution and to reconcentrate it using MD [83].

Holloway et al. [51] suggested a hybrid FO-RO system for anaerobic digester concentration. The high energy consumption of the RO ($\sim 4 \text{ kWh/m}^3$) has been a major limiting factor for the process, although water recovery has been achieved up to 75% with a high concentration of DS (70 g/L NaCl). In a further study [85], seawater was used as a DS solution in a two-stage FO process for sludge concentration to be used as fertilizer. However, high reverse salt flux and membrane fouling due to cake layer formation have been reported as serious problems of the system. Hau et al. [52] suggested a hybrid FO-NF system for a sludge dewatering application. The results showed that the FO performance was better in terms of water flux and reverse salt flux when EDTA was used as DS instead of conventional NaCl or sea water. In addition, FO has successfully rejected more than 90% of the nutrients released from the feed sludge. They also indicated that the NF recovery of EDTA sodium salts exhibiting high charged compounds performed well and had a high salt rejection of 93%. While the water flux was constant during the first hours of operation, the FO membrane was then rapidly reduced due to the increased buildup of the sludge cake layer in the concentrated feed and diluted DS.

Oasys Water Inc. has operated a pilot scale thermal-based hybrid FO system for water with high salinity (>70,000 ppm TDS), which is a product of shale gas industry [41, 60]. The results

Figure 10. Summary of the benefits of current hybrid FO systems and direction for future research (adapted from [86]).

show that this hybrid system can exhibit feedwater recovery performance (60%) similar to evaporative saline concentration technologies and that the final product water meets surface water discharge criteria in terms of TDS, chlorides, barium, and strontium. However, although the RO required less specific energy when desalinating waters with lower salinity, it was found that this study was not sufficient to purify the challenging feedwater. The hybrid FO distillation system can be integrated to provide a zero-liquid discharge (ZLD) facility designed as a membrane brine concentrator (MBC). The MBC system is ideal for the oil and gas industry and provides up to 85% water recovery while discharging brine with salt concentration up to 25%. A summary of the benefits of current hybrid FO systems and direction of future research are schematized in **Figure 10** [86].

5. Conclusions

FO process has a big potential to be an alternative solution for water/wastewater treatment and desalination purposes over conventional membrane processes. To benefit from this potential at maximum, ICP and low flux challenges should be completely solved or minimized by changing operational parameters. Changing membrane orientation (to increase water flux), utilizing various DSs (to increase osmotic pressure), and changing sludge retention time (i.e., to hinder salt accumulation in FO-MBR) are some of the basic procedures used since former FO studies.

The use of hybrid systems such as FO-RO and FO-MD even with seawater desalination and optimization energy consumption could be more feasible and better alternative than the performance exhibited by the FO process alone for wastewater recovery. However, the indispensable factor affecting the process performance is FO membrane. According to the current studies, utilizing novel nanomaterials, substrates, and layer-by-layer assumptions in manufacturing of FO membrane undoubtedly enhance the water flux and rejection of the pollutants and minimize the membrane fouling but using synthetic wastewater-generally, containing one model foulant or DI water as feed solution makes it difficult to predict how FO membranes will act in real wastewaters or harsh environmental conditions. Therefore, working with complex foulants and real wastewaters to better understand membrane behaviors and using modeling tools for fouling prediction and new cleaning strategies are essential to mitigate intrinsic challenges of the FO membranes.

In ongoing researches, the developed new support layers appear to continue increasing water flux slightly; however, lower water flux remains as a main challenge of the process when compared to the conventional membrane systems. It is also a fact that the diffusion provided by draw solution in the process is not effective alone to increase product water volume; therefore, some promotive factors such as rehabilitated hydrodynamic behaviors or simultaneous filtration could be provided together with diffusion phenomena in further researches.

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References

- [1] Manickam SS, McCutcheon JR. Understanding mass transfer through asymmetric membranes during forward osmosis: A historical perspective and critical review on measuring structural parameter with semi-empirical models and characterization approaches. *Desalination*. 2017;**421**:110-126. DOI: 10.1016/j.desal.2016.12.016

- [2] Cath TY, Childress AE, Elimelech M. Forward osmosis: Principles, applications, and recent developments. *Journal of Membrane Science*. 2006;**281**:70-87. DOI: 10.1016/j.memsci.2006.05.048
- [3] Manickam S, McCutcheon JR. Characterization of polymeric nonwovens using porosimetry, porometry and X-ray computed tomography. *Journal of Membrane Science*. 2012;**407**:108-115. DOI: 10.1016/j.memsci.2012.03.022
- [4] McCutcheon JR, McGinnis RL, Elimelech M. A novel ammonia-carbon dioxide forward (direct) osmosis desalination process. *Desalination*. 2005;**174**(1):1-11. DOI: 10.1016/j.desal.2004.11.002
- [5] Tiraferri A, Yip NY, Phillip WA, Schiffman JD, Elimelech M. Relating performance of thin-film composite forward osmosis membranes to support layer formation and structure. *Journal of Membrane Science*. 2011;**367**:340-352. DOI: 10.1016/j.memsci.2010.11.014
- [6] Shi L, Chou SR, Wang R, Fang WX, Tang CY, Fane AG. Effect of substrate structure on the performance of thin-film composite forward osmosis hollow fiber membranes. *Journal of Membrane Science*. 2011;**382**(1):116-123. DOI: 10.1016/j.memsci.2011.07.045
- [7] Bui NN. Engineered osmosis for sustainable water and energy: Novel nanofiber supported thin-film composite membrane design & updated flux model proposal [thesis]. Storrs: University of Connecticut; 2013
- [8] Huang L, McCutcheon JR. Impact of support layer pore size on performance of thin film composite membranes for forward osmosis. *Journal of Membrane Science*. 2015;**483**:25-33. DOI: 10.1016/j.memsci.2015.01.025
- [9] Cath TY, Elimelech M, McCutcheon JR, McGinnis RL, Achilli A, Anastasio D, Brady AR, Childress AE, Farr IV, Hancock NT. Standard methodology for evaluating membrane performance in osmotically driven membrane processes. *Desalination* 2012;**312**:31-38. DOI: 10.1016/j.desal.2012.07.005
- [10] Lee J, Choi JY, Choi JS, Chu KH, Yoon Y, Kim S. A statistics-based forward osmosis membrane characterization method without pressurized reverse osmosis experiment. *Desalination*. 2017;**403**:36-45. DOI: 10.1016/j.desal.2016.04.023
- [11] Chung TS, Zhang S, Wang KY, Su J, Ling MM. Forward osmosis processes: Yesterday, today and tomorrow. *Desalination*. 2012;**287**:78-81. DOI: 10.1016/j.desal.2010.12.019
- [12] Chung TS, Li X, Ong RC, Ge QC, Wang HL, Han G. Emerging forward osmosis (FO) technologies and challenges ahead for clean water and clean energy applications. *Current Opinion in Chemical Engineering*. 2012;**1**:246-257. DOI: 10.1016/j.coche.2012.07.004
- [13] Mi B, Elimelech M. Chemical and physical aspects of organic fouling of forward osmosis membranes. *Journal of Membrane Science*. 2008;**320**:292-302. DOI: 10.1016/j.memsci.2008.04.036
- [14] She Q, Wang R, Fane AG, Tang CY. Membrane fouling in osmotically driven membrane processes: A review. *Journal of Membrane Science*. 2016;**499**:201-233. DOI: 10.1016/j.memsci.2015.10.040

- [15] Zhang M, Hou D, She Q, Tang CY. Gypsum scaling in pressure retarded osmosis: Experiments, mechanisms and implications. *Water Research*. 2014;**48**:387-395. DOI: 10.1016/j.watres.2013.09.051
- [16] Yip NY, Elimelech M. Influence of natural organic matter fouling and osmotic back-wash on pressure retarded osmosis energy production from natural salinity gradients. *Environmental Science and Technology*. 2013;**47**:12607-12616. DOI: 10.1021/es403207m
- [17] Boo C, Elimelech M, Hong S. Fouling control in a forward osmosis process integrating seawater desalination and wastewater reclamation. *Journal of Membrane Science*. 2013;**444**:148-156. DOI: 10.1016/j.memsci.2013.05.004
- [18] Valladares-Linares R, Li Z, Yangali-Quintanilla V, Li Q, Amy G. Cleaning protocol for a FO membrane fouled in wastewater reuse. *Desalination and Water Treatment*. 2013; **51**:4821-4824. DOI: 10.1080/19443994.2013.795345
- [19] Tang CY, She Q, Lay WCL, Wang R, Fane AG. Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration. *Journal of Membrane Science*. 2010;**354**:123-133. DOI: 10.1016/j.memsci.2010.02.059
- [20] Mi B, Elimelech M. Organic fouling of forward osmosis membranes: Fouling reversibility and cleaning without chemical reagents. *Journal of Membrane Science*. 2010;**348**:337-345
- [21] Arkhangelsky E, Wicaksana F, Chou S, Al-Rabiah AA, Al-Zahrani SM, Wang R. Effects of scaling and cleaning on the performance of forward osmosis hollow fiber membranes. *Journal of Membrane Science*. 2012;**415-416**:101-108. DOI: 10.1016/j.memsci.2012.04.041
- [22] Fritzmann C, Löwenberg J, Wintgens T, Melin T. State-of-the-art of reverse osmosis desalination. *Desalination*. 2007;**216**:1-76. DOI: 10.1016/j.desal.2006.12.009
- [23] Zhou W, Wu B, She Q, Chi L, Zhang Z. Investigation of soluble microbial products in a full-scale UASB reactor running at low organic loading rate. *Bioresource Technology*. 2009;**100**:3471-3476. DOI: 10.1016/j.biortech.2009.03.006
- [24] Li ZY, Yangali-Quintanilla V, Valladares-Linares R, Li Q, Zhan T, Amy G. Flux patterns and membrane fouling propensity during desalination of seawater by forward osmosis. *Water Research*. 2012;**46**:195-204. DOI: 10.1016/j.watres.2011.10.051
- [25] Meng F, Chae SR, Drews A, Kraume M, Shin HS, Yang F. Recent advances in membrane bioreactors (MBRs): Membrane fouling and membrane material. *Water Research*. 2009; **43**:1489-1512. DOI: 10.1016/j.watres.2008.12.044
- [26] Wang YN, Tang CY. Fouling of nanofiltration, reverse osmosis, and ultrafiltration membranes by protein mixtures: The role of inter-foulant-species interaction. *Environmental Science and Technology*. 2011;**45**:6373-6379. DOI: 10.1021/es2013177
- [27] Berman T, Mizrahi R, Dosoretz CG. Transparent exopolymer particles (TEP): A critical factor in aquatic biofilm initiation and fouling on filtration membranes. *Desalination*. 2011;**276**:184-190. DOI: 10.1016/j.desal.2011.03.046

- [28] Zhang J, Loong WLC, Chou S, Tang C, Wang R, Fane AG. Membrane biofouling and scaling in forward osmosis membrane bioreactor. *Journal of Membrane Science*. 2012;**403-404**:8-14. DOI: 10.1016/j.memsci.2012.01.032
- [29] Kang NW, Lee S, Kim D, Hong S, Kweon JH. Analyses of calcium carbonate scale deposition on four RO membranes under a seawater desalination condition. *Water Science and Technology*. 2011;**64**:1573-1580. DOI: 10.2166/wst.20U.671
- [30] Zhang H, Ma Y, Jiang T, Zhang G, Yang F. Influence of activated sludge properties on flux behavior in osmosis membrane bioreactor (OMBR). *Journal of Membrane Science*. 2012;**390-391**:270-276. DOI: 10.1016/j.memsci.2011.11.048
- [31] Tang CY, Chong TH, Fane AG. Colloidal interactions and fouling of NF and RO membranes: A review. *Advances in Colloid and Interface Science*. 2011;**164**:126-143. DOI: 10.1016/j.cis.2010.10.007
- [32] Kim Y, Elimelech M, Shon HK, Hong S. Combined organic and colloidal fouling in forward osmosis: Fouling reversibility and the role of applied pressure. *Journal of Membrane Science*. 2014;**460**:206-212. DOI: 10.1016/j.memsci.2014.02.038
- [33] Palecek SP, Zydney AL. Intermolecular electrostatic interactions and their effect on flux and protein deposition during protein filtration. *Biotechnology Progress*. 1994;**10**:207-213. DOI: 10.1021/bp00026a010
- [34] Zou S, Wang YN, Wicaksana F, Aung T, Wong PCY, Fane AG, Tang CY. Direct microscopic observation of forward osmosis membrane fouling by microalgae: Critical flux and the role of operational conditions. *Journal of Membrane Science*. 2013;**436**:174-185. DOI: 10.1016/j.memsci.2013.02.030
- [35] Song X, Liu Z, Sun DD. Nano gives the answer: Breaking the bottleneck of internal concentration polarization with a nanofiber composite forward osmosis membrane for a high water production rate. *Advanced Materials*. 2011;**23**:3256-3260. DOI: 10.1002/adma.201100510
- [36] Chou S, Wang R, Shi L, She Q, Tang C, Fane AG. Thin-film composite hollow fiber membranes for pressure retarded osmosis (PRO) process with high power density. *Journal of Membrane Science*. 2012;**389**:25-33. DOI: 10.1016/j.memsci.2011.10.002
- [37] Han G, Chung TS. Robust and high performance pressure retarded osmosis hollow fiber membranes for osmotic power generation. *AIChE Journal*. 2014;**60**:1107-1119. DOI: 10.1002/aic.14342
- [38] Boo C, Lee S, Elimelech M, Meng Z, Hong S. Colloidal fouling in forward osmosis: Role of reverse salt diffusion. *Journal of Membrane Science*. 2012;**390-391**:277-284. DOI: 10.1016/j.memsci.2011.12.001
- [39] Lutchmiah K, Verliefde ARD, Roest K, Rietveld LC, Cornelissen ER. Forward osmosis for application in wastewater treatment: A review. *Water Research*. 2014;**58**:179-197. DOI: 10.1016/j.watres.2014.03.045

- [40] Fang Y, Bian L, Bi Q, Li Q, Wang X. Evaluation of the pore size distribution of a forward osmosis membrane in three different ways. *Journal of Membrane Science*. 2014; **454**(0):390-397. DOI: 10.1016/j.memsci.2013.12.046
- [41] Coday BD, Xu P, Beaudry EG, Herron J, Lampi K, Hancock NT, Cath TY. The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams. *Desalination*. 2014;**333**(1):23-35. DOI: 10.1016/j.desal.2013.11.014
- [42] Kim ES, Liu Y, El-Din MG. The effects of pretreatment on nanofiltration and reverse osmosis membrane filtration for desalination of oil sands process-affected water. *Separation and Purification Technology*. 2011;**81**(3):418-428. DOI: 10.1016/j.seppur.2011.08.016
- [43] Zhu H, Zhang L, Wen X, Huang X. Feasibility of applying forward osmosis to the simultaneous thickening, digestion, and direct dewatering of waste activated sludge. *Bioresource Technology*. 2012;**113**(0):207-213. DOI: 10.1016/j.biortech.2011.12.064
- [44] Hydranautics. Element Spec Sheets. Hydranautics a Nitto Group Company. 2014. Available from: http://membranes.com/index.php?pagename=spec_sheets [Accessed: August 11, 2017]
- [45] Linares RV, Li Z, Sarp S, Bucs S, Amy G, Vrouwenvelder JS. Forward osmosis niches in seawater desalination and wastewater reuse. *Water Research*. 2014;**66**:122-139. DOI: 10.1016/j.watres.2014.08.021
- [46] Xie M, Nghiem LD, Price WE, Elimelech M. A forward osmosis membrane distillation hybrid process for direct sewer mining: System performance and limitations. *Environmental Science and Technology*. 2013;**47**(23):13486-13493. DOI: 10.1021/es404056e
- [47] Zhang Y, Pinoy L, Meesschaert B, Van der Bruggen B. A natural driven membrane process for brackish and wastewater treatment: Photovoltaic powered ED and FO hybrid system. *Environmental Science and Technology*. 2013;**47**(18):10548-10555. DOI: 10.1021/es402534m
- [48] Li ZY, Valladares-Linares R, Yangali-Quintanilla V, Amy G. A sequential batch reactor forward osmosis system for water reuse. In: *Proceedings of American Membrane Technology Association Membrane Technology Conference and Exhibition*. Phoenix: AWWA/AMTA Publishing; February 27–March 1, 2012
- [49] Qiu G, Zhang S, Raghavan DSSS, Das S, Ting YP. The potential of hybrid forward osmosis membrane bioreactor (FOMBR) processes in achieving high throughput treatment of municipal wastewater with enhanced phosphorus recovery. *Water Research*. 2016;**105**:370-382. DOI: 10.1016/j.watres.2016.09.017
- [50] Zhang S, Liu P, Chen Y, Jin J, Hu L, Jian X. Preparation of thermally stable composite forward osmosis hollow fiber membranes based on copoly(phthalazinone biphenyl ether sulfone) substrates. *Chemical Engineering Science*. 2017;**166**:91-100. DOI: 10.1016/j.ces.2017.03.026

- [51] Holloway RW, Childress AE, Dennett KE, Cath TY. Forward osmosis for concentration of anaerobic digester centrate. *Water Research*. 2007;**41**(17):4005-4014. DOI: 10.1016/j.watres.2007.05.054
- [52] Hau NT, Chen SS, Nguyen NC, Huang KZ, Ngo HH, Guo W. Exploration of EDTA sodium salt as novel draw solution in forward osmosis process for dewatering of high nutrient sludge. *Journal of Membrane Science*. 2014;**455**:305-311. DOI: 10.1016/j.memsci.2013.12.068
- [53] Catalyx. Forward osmosis for recycling dye wastewater. *Filtration and Separation*. 2009;**46**(3):14. DOI: 10.1016/S0015-1882(09)70120-X
- [54] Li Z, Valladares Linares R, Abu-Ghdaib M, Zhan T, Yangali- Quintanilla V, Amy G. Osmotically driven membrane process for the management of urban runoff in coastal regions. *Water Research*. 2004;**48**:200-209. DOI: 10.1016/j.watres.2013.09.028
- [55] Duong PHH, Chung TS. Application of thin film composite membranes with forward osmosis technology for the separation of emulsified oil-water. *Journal of Membrane Science*. 2014;**452**:117-126. DOI: 10.1016/j.memsci.2013.10.030
- [56] HTI. Oil Wastewater Treatment & Gas Wastewater Treatment: Lead Story [Internet]. 2011. Available from: http://www.htiwater.com/divisions/oil-gas/lead_story.html [Accessed: Sep 11, 2017]
- [57] Nelson CE, Ghosh AK. Oil & Natural Gas Technology-Membrane Technology for Produced Water in Lea County. Lea County Government and New Mexico Institute of Mining and Technology [Internet]. 2011. Available from: <https://www.netl.doe.gov/File%20Library/Research/Oil-Gas/nt0005227-final-report.pdf> [Accessed: Sep 15, 2017]
- [58] Abousnina RM. Oily wastewater treatment: Removal of dissolved organic components by forward osmosis [thesis]. University of Wollongong; 2012
- [59] Hickenbottom KL, Hancock NT, Hutchings NR, Appleton EW, Beaudry EG, Xu P, Cath TY. Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations. *Desalination*. 2013;**312**:60-66. DOI: 10.1016/j.desal.2012.05.037
- [60] McGinnis RL, Hancock NT, Nowosielski-Slepowron MS, McGurgan GD. Pilot demonstration of the NH_3/CO_2 forward osmosis desalination process on high salinity brines. *Desalination*. 2013;**312**:67-74. DOI: 10.1016/j.desal.2012.11.032
- [61] Greenlee LF, Lawler DF, Freeman BD, Marrot B, Moulin P. Reverse osmosis desalination: Water sources, technology, and today's challenges. *Water Research*. 2009;**43**:2317-2348. DOI: 10.1016/j.watres.2009.03.010
- [62] El-Dessouky HT, Ettouney HM. Fundamentals of Salt Water Desalination. 1st ed. Amsterdam: Elsevier Science Ltd; 2002. p. 690. DOI: 10.1016/B978-0-444-50810-2.50018-X
- [63] Van der Bruggen B, Vandecasteele C. Distillation vs. membrane filtration: Overview of process evolutions in seawater desalination. *Desalination*. 2002;**143**:207-218. DOI: 10.1016/S0011-9164(02)00259-X

- [64] Kim HI, Kim SS. Plasma treatment of polypropylene and polysulfone supports for thin film composite reverse osmosis membrane. *Journal of Membrane Science*. 2006;**286**:193-201. DOI: 10.1016/j.memsci.2006.09.037
- [65] Shaffer DL, Werber JR, Jaramillo H, Lin S, Elimelech M. Forward osmosis: Where are we now? *Desalination*. 2015;**356**:271-284. DOI: 10.1016/j.desal.2014.10.031
- [66] Zaviska F, Zou L. Using modelling approach to validate a bench scale forward osmosis pre-treatment process for desalination. *Desalination*. 2014;**350**:1-13. DOI: 10.1016/j.desal.2014.07.005
- [67] Bamaga OA, Yokochi A, Beaudry EG. Application of forward osmosis in pretreatment of seawater for small reverse osmosis desalination units. *Desalination and Water Treatment*. 2009;**5**:183-191. DOI: 10.5004/dwt.2009.574
- [68] Zhao S, Zou L, Mulcahy D. Brackishwater desalination by a hybrid forward osmosis–nanofiltration system using divalent draw solute. *Desalination*. 2012;**284**:175-181. DOI: 10.1016/j.desal.2011.08.053
- [69] Chekli L, Phuntsho S, Shon HK, Vigneswaran S, Kandasamy J, Chanan A. A review of draw solutes in forward osmosis process and their use in modern applications. *Desalination and Water Treatment*. 2012;**43**(1-3):167-184. DOI: 10.1080/19443994.2012.672168
- [70] Li D, Zhang X, Simon GP, Wang H. Forward osmosis desalination using polymer hydrogels as a draw agent: Influence of draw agent, feed solution and membrane on process performance. *Water Research*. 2013;**47**(1):209-215. DOI: 10.1016/j.watres.2012.09.049
- [71] Gray GT, McCutcheon JR, Elimelech M. Internal concentration polarization in forward osmosis: Role of membrane orientation. *Desalination*. 2006;**197**(1-3):1-8. DOI: 10.1016/j.desal.2006.02.003
- [72] McGinnis RL, Elimelech M. Energy requirements of ammonia-carbon dioxide forward osmosis desalination. *Desalination*. 2007;**207**(1-3):370-382. DOI: 10.1016/j.desal.2006.08.012
- [73] Chanukya BS, Patil S, Rastogi NK. Influence of concentration polarization on flux behavior in forward osmosis during desalination using ammonium bicarbonate. *Desalination*. 2013;**312**:39-44. DOI: 10.1016/j.desal.2012.05.018
- [74] Ling MM, Chung TS. Desalination process using super hydrophilic nanoparticles via forward osmosis integrated with ultrafiltration regeneration. *Desalination*. 2011;**278**(1-3):194-202. DOI: 10.1016/j.desal.2011.05.019
- [75] Modern Water. Membrane Processes Forward Osmosis: Desalination [Internet]. 2013. Available from: https://www.modernwater.com/pdf/MW_Factsheet_Membrane_HIGHRES.pdf [Accessed: Sep 14, 2017]
- [76] Valladares Linares R, Li Z, Abu-Ghdaib M, Wei CH, Amy G, Vrouwenvelder JS. Water harvesting from municipal wastewater via osmotic gradient: An evaluation of process performance. *Journal of Membrane Science*. 2013;**447**:50-56. DOI: 10.1016/j.memsci.2013.07.018

- [77] Cath TY, Hancock NT, Lundin CD, Hoppe-Jones C, Drewes JE. A multi-barrier osmotic dilution process for simultaneous desalination and purification of impaired water. *Journal of Membrane Science*. 2010;**362**(1-2):417-426. DOI: 10.1016/j.memsci.2010.06.056
- [78] McCarty PL, Bae J, Kim J. Domestic wastewater treatment as a net energy producer – Can this be achieved? *Environmental Science and Technology*. 2011;**45**(17):7100-7106. DOI: 10.1021/es2014264
- [79] Cath TY, Drewes JE, Lundin CD. A novel hybrid forward osmosis process for drinking water augmentation using impaired water and Saline water sources. In: *Proceedings of the 24th Annual WaterReuse Symposium*. Seattle: Water Research Foundation; Sep 13-16, 2009. Available from: http://inside.mines.edu/~tcath/research/projects/Cath_WRS_2009_AwwaRF4150.pdf [Accessed: October 23, 2017]
- [80] Valladares Linares R, Yangali-Quintanilla V, Li Z, Amy G. Rejection of micropollutants by clean and fouled forward osmosis membrane. *Water Research*. 2011;**45**(20):6737-6744. DOI: 10.1016/j.watres.2011.10.037
- [81] Hoover LA, Phillip WA, Tiraferri A, Yip NY, Elimelech M. Forward with osmosis: Emerging applications for greater sustainability. *Environmental Science and Technology*. 2011;**45**(23):9824-9830. DOI: 10.1021/es202576h
- [82] McGovern RK, Lienhard V. On the potential of forward osmosis to energetically outperform reverse osmosis desalination. *Journal of Membrane Science*. 2014;**469**:245-250. DOI: 10.1016/j.memsci.2014.05.061
- [83] Subramani A, Jacangelo JG. Emerging desalination technologies for water treatment: A critical review. *Water Research*. 2015;**75**:164-187. DOI: 10.1016/j.watres.2015.02.032
- [84] Department of Energy (USDOE). Advanced, Energy-efficient Hybrid Membrane System for Industrial Water Reuse [Internet]. Available from: https://energy.gov/sites/prod/files/2016/12/f34/0877-Hybrid%20Membrane%20System-090716_compliant.pdf, [Accessed: Sep 10, 2017]
- [85] Nguyen NC, Chen SS, Yang HY, Hau NT. Application of forward osmosis on dewatering of high nutrient sludge. *Bioresource Technology*. 2013;**132**:224-229. DOI: 10.1016/j.biortech.2013.01.028
- [86] Tsai JH, Macedonio F, Drioli E, Giorno L, Chou CY, Hu FC, Li CL, Chuang CJ, Tung KL. Membrane-based zero liquid discharge: Myth or reality? *Journal of the Taiwan Institute of Chemical Engineers*. 2017;**80**:192-202. DOI: 10.1016/j.jtice.2017.06.050