



Recent advancements in forward osmosis desalination: A review



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HIGHLIGHTS

- The stage reached in forward osmosis (FO) have been reviewed.
- Publications from 2009 up to date were examined to discuss current developments.
- Major challenges, limitations and hindrances of FO activities have been presented.
- Improvements in FO membrane permeability and regenerative draw solutes.

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ABSTRACT

Forward osmosis (FO) is one of the evolving membrane technologies in desalination with recent expanded new interest as a low energy process. The most significant parts of FO process are the membrane and draw solution since both play a substantial role in its performance. Hence, the selection of an appropriate membrane and draw solution is crucial for the process efficiency. Improvements in the development of membranes and draw solutes have been recorded recently. However, limitations such as fouling of FO membranes, reverse solute flux, concentration polarization, and low permeate flux in standalone FO systems. This work targets the review of recent progress in FO, aiming on the prospects and challenges. It starts with addressing the advantages of the FO process. The crucial part of this review is a thorough discussion of hybrid FO systems, different FO membranes, and draw solutes available coupled with their effects on FO performance. Finally, the future of FO for sustainable desalination is also discussed.

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1. Introduction

The world population has continued to grow exponentially in recent times, and this growth places huge burden on the available water and energy resources. The nexus between water and energy is inextricable; getting freshwater requires energy and in most situations, huge quantity of water is needed for producing power. Oftentimes, this water is not available and has to be created via means like the desalination of seawater or brackish water. Unlike reverse osmosis (RO) that needs external pressure to function, forward osmosis (FO) is driven by osmotic pressure difference across a semipermeable membrane. FO as a new membrane separation technology has gained wider attention in many applications such as desalination, power generation, food processing and wastewater treatment [1]. For seawater desalination, the energy requirement

of a standalone FO process is much higher than that of RO [5]. However, FO hybrid systems can be used for the desalination of high-salinity waters, which is not possible using standalone RO process. FO hybrid systems using thermolytic draw solutions consume less total energy for desalting high-salinity waters, and can be economically more feasible than other desalination technologies [2]. As a general definition, FO involves two major steps: the osmotic dilution of the draw solution and the generation of fresh water from the diluted draw solution. As described by [3], when salty feed water and highly concentrated solute (draw solute) are separated by a semipermeable membrane, there is movement of water from the salty water to the draw solution due to osmotic gradient, while retaining solute on both sides of the membrane. The reason for the call for widespread applications of FO is due to its advantages over RO such as low energy consumption, minimal fouling problems, and considerably high water recovery. These advantages are not without some accompanied challenges such as limited choices of draw solutes. An ideal draw solute should be characterized by the ability to ensure high osmotic gradient, substantial water flux, and efficient recovery at minimal

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energy consumption [3]. For osmosis-driven desalination, an ideal draw solute should have zero toxicity and low cost as some of its characteristics [4]. Researches have been conducted for creating suitable draw solutes for desalination processes. Chung et al. [4] gave a comprehensive account of the history and the development of draw solutions and how they have evolved over the years in desalination. Their paper addressed the technical feasibility of integration of FO (for desalination) and RO (for draw solute recovery) but industrial impracticability was cited as the major barrier for the deployment of this technology. In recent years, highly hydrophilic nano-sized magnetic particles, functionalized by polyacrylic acid have been discovered to be crucial in the application of draw solutes in FO desalination as this engineering can yield high osmotic pressure and high water flux [5]. Magnetic separators can be used to recycle the magnetic particles; however, agglomeration of these particle constitutes a major barrier which can be effectively reduced by ultrasonication [4]. FO-ultrafiltration (FO-UF) system for desalination and water reuse has also been shown as an integrated sustainable system with the aid of super hydrophilic nanoparticles as draw solutes that use FO membrane as the semipermeable membrane for salts rejection, super hydrophilic nanoparticles as draw solutes for water induction across FO membrane, and UF membrane for the regeneration of the draw solutes without increasing nanoparticles size or reducing osmotic functionality [6]. It has been suggested that more research should be focused on integrated FO-UF system as this could be the future for FO desalination and recovery of draw solute [4].

Recently in desalination technology; hydrogels have been proposed as draw agents for FO. Hydrogels have the ability to absorb water across FO membrane as a result of their swelling pressure. Their insoluble cross-linked network enables dewatering under the influence of stimuli (thermal or mechanical) [7,8]. However, several drawbacks of hydrogels, such as energy-intensive dewatering process, low water flux and minimal recovery hinder their practicability as draw agents [9]. Zeng et al. reported that polymer-graphene composite hydrogels resulted in increased water flux and found the water recovery rate to be twice as fast than that for pure hydrogels [10]. Meanwhile, Zhao has reported that the swelling pressure is not the same as the osmotic pressure of a traditional solution [11]. Zhao concluded that it is unreasonable to use “forward osmosis” in hydrogel absorbing water because the chemical residues present in hydrogels are responsible for their water-absorption properties and not osmotic pressure. However, Wang et al. argued that hydrogels are essentially draw agents for FO because the network structure of a polymer hydrogel is an osmotic membrane from a thermodynamics perspective [12]. One of the challenges that still remain in desalination technology is related to separation and recovery of the draw solution from the desalinated water. The success of FO desalination in the future will heavily rely on the ease and efficiency of draw solute recovery from the desalinated water. Several innovative regeneration approaches such as RO, UF, membrane distillation (MD), heating, application of magnetic field, and hydrogel swelling have been explored to obtain fresh water and recover the draw solution. The recovery method is primarily determined by the choice of the draw solute [13].

Another important aspect of FO desalination is the quality and efficiency of its membranes. In early stages of FO applications, animal bladders, nitrocellulose, rubbers and porcelains were tested as membranes [1]. Recently however, membrane development has been categorized into three classifications according to their fabrication methods, which include; cellulosic, thin-film composite (TFC), and chemically-reformed membranes [14]. Uneven cellulosic osmotic driven membranes designed through phase inversion have been used for osmotic drug delivery before being applied lately for the treatment of water. Cellulose acetate is the matrix

polymer and the conventional phase inversion is the preparation method for most of these membranes [15,16]. There are currently two types of commercially available (TFC) membrane and they are composed of multiple layers. These membranes have been used extensively in various FO studies. A nanofiber TFC = FO membrane has been developed recently via electrospinning followed by interfacial polymerization (ES-IP) [17]. A significant reduction in the structural parameter of the nanocomposite membrane leading to improved FO performance was obtained, as a result of the membrane's high porosity and low tortuosity. Another class of FO membranes involves membranes prepared by chemical modification methods. Polydopamine (PDA) has been used as a novel bio-inspired hydrophilic polymer to modify the support layers of commercial TFC membranes for engineered osmosis applications [18].

In this work, we set out to review recent and current publications on FO seawater desalination applications, the most-recently proven advantages of FO over the conventional pressure-driven desalination techniques, and different characteristics that define the performance of FO desalination application. The challenges still being faced and opportunities for the future have also been discussed.

2. Advantages and potential uses of FO

FO desalination processes have an array of prospective benefits if they are deployed in large scale. The low hydraulic pressure needed during osmotically-driven FO process is responsible for most of these benefits. FO is beneficial for achieving low energy consumption, thereby ensuring process costs reduction, if the draw solution recovery step is economically and technically viable. This could be one of the most striking points of FO, particularly under the pressure of the world energy crisis. Unlike commonly applied membrane processes such as RO, FO requires minimal energy input to achieve separation since according to thermodynamic principles, the process occurs spontaneously [19]. However, the “low energy and low cost” feature of FO remains debatable because significant amount of energy may still be required to regenerate the draw solution. The integration of FO and RO for water purification have been proposed to further minimize the overall energy requirement of FO [20–24]. A hybrid system used renewable draw solution with high osmotic pressure such as seawater to draw water from a feed solution with lower osmotic potential such as treated wastewater or brackish water [20]. Therefore, the first step is a draw dilution process followed by a regeneration step in which the diluted draw is treated using RO [20]. Different system configurations were proposed. For example, a once through system in which there is no regeneration of FO draw solution, a closed loop system in which the draw solution is regenerated in the form of brine from RO, and a closed loop with recovery of osmotic potential between the draw and feed solution using a turbine.

Limited studies, however, looked into the economic and energetic feasibility of FO–RO systems. FO–RO can potentially reduce the overall cost and energy compared to standalone RO by driving the seawater salinity down in the FO dilution step [20,22,23]. Quintanilla et al. estimated that approximately 1.3–1.5 kWh/m³ is needed for an FO–RO system that dilutes seawater by drawing water from secondary wastewater effluent. This is lower than standalone single pass RO which has an average energy consumption of around 2.5 kWh/m³ [25]. The economic feasibility using a pilot system was also investigated by Cath et al. [20] by assuming that the majority of the FO cost is associated with membrane area. Therefore, the study assumed that incremental increase in FO membrane area would result in incremental increase in seawater dilution which is favorable for RO treatment. However, beyond

an FO recovery of 63%, it was found that the attainable energy and cost savings from RO would be exceeded by increasing FO membrane area and at that point, the FO–RO system loses its attractiveness [20]. Shaffer et al. attempted to model the energy savings associated with replacing a two pass RO process and its associated pretreatment step with an integrated FO–RO process [24]. They showed that the integrated system resulted in lower specific energy – 3 kWh/m³, compared to that of a two pass RO operating at 50%, 4 kWh/m³ (Fig. 1a) [24]. Some studies, however, argued that the results depend largely on a number of factors influencing the FO process. Such factors include FO transmembrane flux, draw solution concentration, and recovery rate [26–28]. A recent study obtained the energy required for standalone RO and FO–RO by assuming certain efficiency rates for both configurations (Fig. 1b) [28]. The energy balance of the FO–RO system still exceeds that of the standalone RO process because of the energy penalty associated with the regeneration process. The study also argued that increasing the efficiency of the FO dilution step by at least 23% is pivotal for the economic operation of the integrated FO–RO [28]. In terms of cost, FO membranes at their current state, i.e., low packing density and low performance, will continue to drive up the capital cost of FO–RO system installation [29]. It has been established that FO–RO integration may prove to be favorable in a market where per unit cost of RO permeate is high (exceeds \$0.1/m³). The integration of FO with RO can be justified as long as the flux in the dilution step is also sufficiently high (exceeds 30 LMH) (Fig. 1c). Thus, this demonstrates the major gap in FO implementation and need for research that can overcome two main obstacles: (1) low permeate flux and (2) high membrane cost.

The optimal conditions required for integrating FO and RO processes while maintaining high performance has also been carried out via modeling and verified using bench scale experiments [30]. In the modeling approach, the following parameters were investigated: FO water recovery, water flux, FO dilution time and draw solution concentration, and how such parameters influence the RO energy consumption. A combination of ideal conditions were then deduced including water recovery time of 179 min at a recovery rate of 30% and flow rate of 450 mL/minute using water flux of 14 LMH which resulted in RO energy consumption of 2.67 kWh/m³. Additionally, harvesting of energy can be achieved by mixing fresh and saline water in pressure and pressure-retarded osmosis [24]. Another attempt has been made to integrate FO with MD [31]. This study involves the use of an integrated FO–MD system for higher recovery of water from oily water sources. The idea involves a system that combines both MD and FO for treatment of complex feed water such as wastewater, especially for the production of potable water. Such a system is designed so as to overcome the drawbacks of each process individually [31]. In this system, water is recovered from oily effluents using RO brine as feed. The diluted brine solution can then be regenerated for reuse as draw and for generation of potable water using MD [31]. The process achieved up to 90% water recovery with only trace levels of organics. Pure water has also been separated from 200,000 ppm concentration of oil in oil–water emulsion. Water flux of 11.8 ± 1.6 LMH and 99.88% oil rejection were obtained by using a TFC membrane (PAN-TFC) and 1 M NaCl as the draw solution [32]. A recent study also focused on the optimization of key operational parameters to enhance the energy efficiency of FO process [33]. Based on efficiency calculations, Tow et al. deduced that potential energy savings can be ensured by improving the performance of the FO exchanger (i.e. draw dilution step) and draw regeneration system which are also linked to the system flow rate [33]. By optimizing the mass flow rate of recirculating fluids, the FO process efficiency can be increased by 3–21%.

In recent years, it has been demonstrated by some studies that FO membrane fouling is moderately [25], more reversible [26,27]

and can be decreased through the optimization of the system's hydrodynamics [28]. Furthermore, a range of pollutants can be successfully removed through the FO process [29]. FO also has the prospect to help attain reasonable water flux and water recovery when high osmotic pressure gradient is maintained across the membrane. Thus, a reduction in the quantity of rejected brine would result from high water reclamation and reduce the environmental burden of brine disposal being faced by many desalination plants currently. This high water reclamation could help reduce the amount of rejected brine, which is a major environmental issue for current desalination plants, particularly for offshore desalination. An FO pretreatment scheme for multi-effect distillation (MED) to enhance the removal of divalent scaling ions such as calcium, magnesium and sulfate has been proposed [34]. Scaling was not only prevented through the reduction of scaling ion concentrations for MED feed but also the distillate flow rate was increased in the subsequent thermal process. FO has also been used for organics and nitrate removal from low-strength wastewater. The integration of FO and anaerobic membrane bioreactor (OsMBR) is a novel technique that has been investigated for the production of high-quality effluent from the integrated MBR system [35]. Unlike conventional MBR, the integrated OsMBR has the potential of excluding organics and nitrate thus producing higher quality permeate. However, Chen et al. [35] observed some challenges after experimenting with a pilot scale system over a 22-day period when the flux not only declined, but also, salt reversal was experienced and the salinity in the anaerobic tanks increased. This increase in salinity could compromise the activity of microbial populations in the anaerobic tank. A niche FO application which considers rainwater for the replenishment of cooling water used as the draw solution has been developed [36]. Cooling water is needed in thermal distillation approaches for seawater desalination and the quality of cooling water could have significant effect on the cost of water production. However, the low water flux obtained, 0.65 LMH, suggests the need for more studies to optimize this novel technique for rainwater treatment and cooling water dilution and reuse.

An effort has also been made to couple microbial desalination cells (MDCs) for desalination of saline water whereby the anode effluent from the MDC was used as FO feed [37]. When compared to a standalone MDC, the MDC–FO system reduced the saline water conductivity by half. The draw solution was 100-mL NaCl solution (35 g/L) recirculated at the same velocity (Fig. 2). The findings showed that MDC–FO system is promising for brackish water treatment or for pre-desalination of high-salinity water, while simultaneously treating wastewater.

A hybrid electrodialysis (ED) – FO system powered by solar energy and known as ED–FO Renewable energy Desalination (EDFORD) has been proposed for potable water production from brackish water (Fig. 3) [38]. Organic and inorganic substances were rejected by the FO membrane and the diluted draw solution was desalted in the ED unit powered by solar energy, where high-quality water was produced. Low concentration of total organic carbon (TOC), carbonate, and cations, and low conductivity were reported for the potable water. However, the cost of water production was high around 3.32–4.92 EUR/m³, when compared with conventional commercial processes.

An FO–MD hybrid system for removal of trace organic contaminants (TrOCs) from raw sewage at water recovery up to 80%, with removal rates ranging from 91–98%, has also been developed. It was reported that the accumulation of contaminants in the draw solution can be prevented using adsorption via granular activation carbon and ultraviolet radiation leading to >99.5% rejection of TrOCs [39]. A critical review of TrOC rejection by FO has been carried out by Coday et al. and the influence of FO membrane, scale of experiment, feed and draw solution characteristics, and temperature on

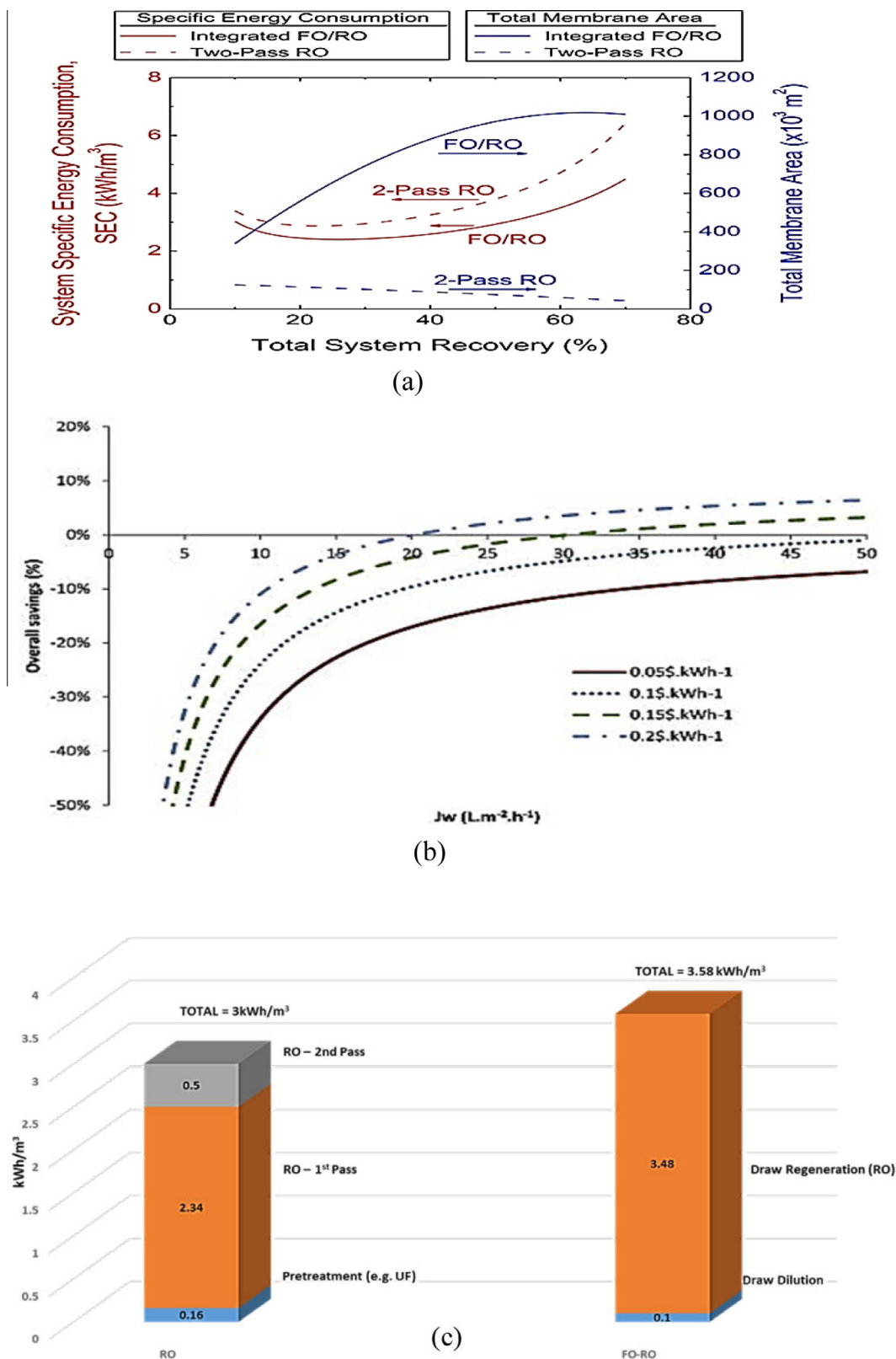


Fig. 1. Findings comparing FO-RO to standalone RO demonstrate the current divide with regards to the economics and energetics of the system (a) FO/RO outcompetes a standalone two pass RO [24] (b) FO-RO is energetically higher than RO when considering low efficiency of FO process [28] (c) Overall energy savings using FO-RO would only be observed at flux greater than 30 LMH and in markets where actual cost of standalone RO is already high [29].

process performance were examined [40]. Specifically, membranes made using different solvents (dimethylformamide, DMF and N-methyl-2-pyrrolidinone, NMP) but similar methods were

compared. The feed contained a model organic foulant and the NMP-TFC membrane recorded lower flux decline when compared to the DMF-TFC membrane i.e. $7.47 \pm 0.15\%$ and $12.70 \pm 2.62\%$,

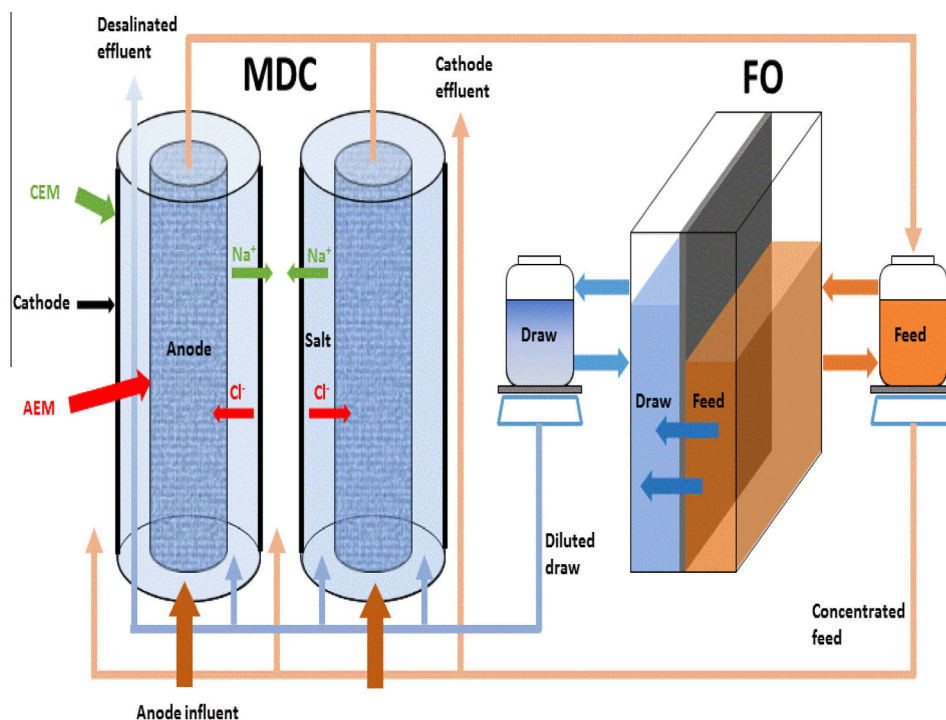


Fig. 2. MDC-FO system (CEM represents cation exchange membrane and AEM-represents anion exchange membrane) [37].

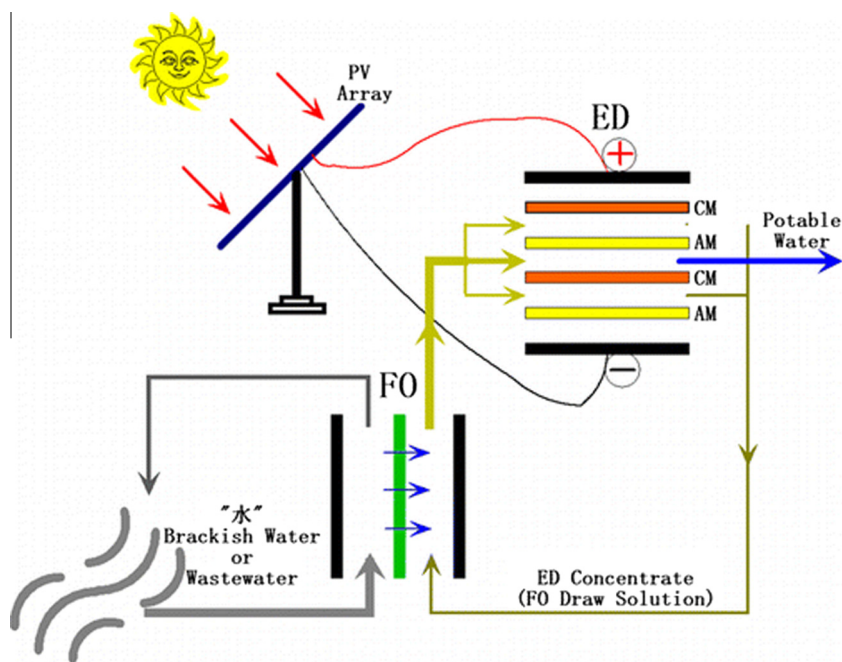


Fig. 3. The EDFORD system [38].

respectively. However, for the NMP-TFC membrane, physical cleaning was more suitable for achieving water flux recovery [41].

Talaei et al. used FO in a fully automatic system to pretreat environmental water samples to be passed through a cell culture [42]. FO has also been tested for metal ions removal through the use of a TFC membrane made from interfacial polymerization on a macrovoid-free polyimide support and hydroacid complex $\text{Na}_4[\text{Co}(\text{C}_6\text{H}_4\text{O}_7)_2] \cdot 2\text{H}_2\text{O}$ (Na-Co-CA) as the draw solute to curtail

reverse solute flux. More than 99.5% heavy metals rejections were removed from 2000 ppm heavy metal solutions ($\text{Na}_2\text{Cr}_2\text{O}_7$, Na_2HASO_4 , $\text{Pb}(\text{NO}_3)_2$, CdCl_2 , CuSO_4 , $\text{Hg}(\text{NO}_3)_2$) using 1 M Na-Co-CA draw solution at room temperature [43]. Boron transport through polyamide-based TFC FO membranes using model seawater as feed has also been investigated [44]. The boron rejection rate, water and solute fluxes obtained under different NaCl feed concentrations are provided in Fig. 4.

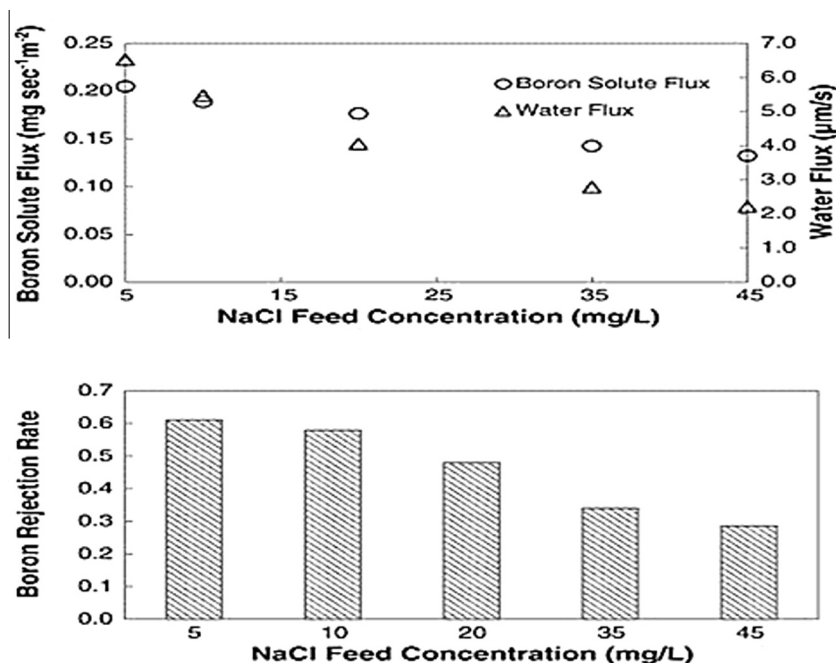


Fig. 4. Boron removal using FO under different NaCl feed concentrations [44].

Due to its array of potential benefits and usefulness, FO has been recommended for use and investigated in a number of applications.

3. Major problems associated with FO

FO does not operate with hydraulic pressure but with osmotic pressure difference; thereby requires lower energy and is less susceptible to membrane fouling compared to traditional pressure-driven membrane processes like RO. Additionally, FO mostly allows fouling removal by physical cleaning without the need of chemicals [45], higher removal of extensive range of ion contaminants [16], and higher water recovery [46] over pressure-driven membrane processes. Despite FO possessing these favorable characteristics, there are several challenges faced by FO that limit its application in large scale processes. Some of these limiting factors include concentration polarization, membrane fouling, and reverse solute diffusion, which are governed by factors like membrane orientation [1], inadequate membrane design [47], concentration and nature of draw and/or feed solution and operating conditions (temperature of feed/draw solute) [48].

3.1. Concentration polarization

Concentration polarization (CP) is a phenomenon arising in all kinds of membrane separation processes, whether the process is pressure driven or osmotically driven. CP develops due to occurrence of concentration difference at the membrane-solution interface arising from selective transfer of species through a semi-permeable membrane [49]. In membrane processes that are osmotically driven such as FO and PRO, CP arises due to concentration gradient between draw and feed solutions through an asymmetric FO membrane. CP arising in FO process can be further classified as internal concentration polarization (ICP), which occurs within the membrane support layer, and external concentration polarization (ECP), which exists at the membrane active layer surface. In FO, the transmembrane osmotic pressure is chiefly responsible for controlling the water flux and recovery. Based on the

extensive research conducted on CP, it was found that the occurrence of CP on both sides of FO membrane greatly reduces the effective transmembrane osmotic pressure; therefore, it is one of the major factors that contributes to declining water flux and recovery across the semi-permeable membranes [50].

3.1.1. External concentration polarization

ECP is a phenomenon that is common to both FO and RO. ECP occurs at the surface of the active layer of the membrane due to difference in the concentration of the solution at the membrane surface from that of the bulk solution. Unlike pressure-driven membrane process where only concentrative ECP can occur, both concentrative and dilutive ECP can take place in membrane processes driven by osmotic pressure in accordance with membrane orientation. The modeling results of FO desalination by Sagiv et al. through the coupling of hydrodynamics and mass transfer equations suggest that counter-current FO or allowing the membrane skin to face draw solution provides water flux improvements and decreased the cross transfer of solutes [51]. Concentrative ECP takes place when the dense active faces the feed (FO mode) whereas, dilutive ECP occurs when the dense active layer faces the draw solution (PRO mode) due to diffusion of water from the side of the feed to that of the draw solution [52]. The adverse effect of dilutive ECP can become the limiting effect when water flux is high [53].

ECP plays a substantial role in decreasing the osmotic gradient; hence, inhibiting the flux of water across the membrane. However, the extent of ECP is considerably smaller than ICP during FO. ECP is extensively researched and modeled for RO and FO, and studies show that the effects of ECP on permeate flux can be alleviated by controlling the water flux and increasing the turbulence and shear rate of flow across the membrane [54]. The effects of ECP are insignificant when permeate water fluxes are reasonably low [55]. In addition, the occurrence of ECP depends on the choice of draw solution. A recent study has shown that ECP does not have a significant effect in micellar draw solutions just above the critical micelle concentration (CMC). Gadelha et al. concluded that the use of micelles or aggregates of the monomers in surfactant solutions

as draw solutes generated more stable flux compared to other inorganic draw solutes at concentrations slightly above the CMC [56]. Both deionized water and saline solutions were used as the feed solution. Between 3 and 300 times less reverse transport was shown by all surfactants (sodium dodecyl sulfate, 1-octane sulfonic acid sodium salt, meristyltrimethyl ammonium bromide, trimethyloctylammonium bromide, and tetraethyl ammonium bromide) compared to NaCl at similar concentrations. Also, FO has been used to recover water from pre-treatment sludge of seawater RO process through the use of two draw solutions (MgCl_2 and NaCl) [57]. The effect of cross flow velocity through FO membrane on flux was also studied. The water flux achieved by MgCl_2 was slightly higher than that of NaCl, when similar conditions of feed and draw solutions were applied. Although marginal increase in flux was obtained as cross flow velocity was increased from 0.25 to 1.0 m/s due to ECP, the highest fluxes were obtained at 1.0 m/s for both draw solutions.

3.1.2. Internal concentration polarization

It is evident from experimental studies that the diminution of water flux in FO is mainly caused by ICP. ICP refers to the occurrence of CP layer within the porous layer of the membrane due to the inability of the solute to penetrate the dense selective layer of the membrane easily [58]. Despite the lower fouling propensity observed in FO compared to other membrane processes, FO faces major drawbacks in maintaining a sufficiently high transmembrane flux and this has inhibited its commercialization. The discovery of phase inverted asymmetric membranes comprising of a dense active layer fabricated at the top of a porous support layer such as polyethersulfone (PES) or polysulfone (PSf) revolutionized the membrane separation sector. However, it can be found from the very first studies that ICP could decrease the water flux by over 80% [52,59]. Recently, several experiments have been performed to allow better understanding of ICP and the various ways in which effects of ICP could be mitigated to boost FO performance.

Depending on the orientation of asymmetric membranes, two types of ICP can occur: concentrative ICP and dilutive ICP. Concentrative ICP prevails for saline feed solution with low water flux [60]. Concentrative ICP occurs when operating in PRO mode, where the feed faces the porous membrane support layer. In PRO mode, permeation of solute through the active layer causes the feed solution to concentrate, resulting in the formation of an immobile zone in the porous support layer where the

transportation of solute arises merely due to hindered diffusion; thereby further reducing the effective osmotic driving force (Fig. 5a) [33].

The dotted and solid lines represent profiles of concentration for water and salt solution, respectively. (a) PRO mode (mode I): feed solution against the support layer; (b) FO mode (mode II): feed solution against the active layer. $\Delta\pi_w$ and $\Delta\pi_{S1}$ in mode I denote the effective driving forces for water and sodium chloride respectively being used as feed, whereas $\Delta\pi_{S2}$ is the effective driving force for sodium chloride being used as feed in mode II. The bulk concentrations on the feed and draw side are represented by C_5 and C_1 , respectively. The concentrations at the boundary layer on the feed and draw side are denoted by C_4 and C_2 , respectively. When salt solution and water was used as feed, the concentrations at support and active layer intersection are denoted by C_3 and C_3 , respectively. The vertical dotted lines stand for the lines of the boundary near the support and active layers.

McCutcheon et al. [49] used ammonium bicarbonate draw solution for FO desalination process, and observed low water fluxes due to occurrence of excessive ICP in the fabric layers and porous support of the RO membrane. Similarly, Chanukya et al. [39] used ammonium bicarbonate draw solution to study the effect of CP on water flux behavior during FO desalination. FO mode was compared to PRO mode and a lower water flux was reported for the FO mode due to intensive CP on the draw solution side and negligible ICP and ECP on the feed side. Hence, operating at PRO mode is considered to be more desirable than FO mode in order to have higher water flux during desalination [55]. The water flux (J_w), in PRO mode can be expressed using Eq. (1) [61]:

$$J_w = \frac{\frac{1}{K} \ln(A\pi_{\text{draw}} + B - J_w)}{A\pi_{\text{feed}} + B} \quad (1)$$

where K is the solute resistivity, A is the membrane's pure water permeability coefficient, π_{draw} and π_{feed} are the osmotic pressure of the draw and feed solutions, respectively and B is the permeability coefficient of the solute. The solute resistivity (K) is a measure of salt transport in the support layer of the membrane, reflecting the extent of ICP in the support layer. Smaller K value is associated with lesser ICP, resulting in higher water flux. K is defined using Eq. (2) [62]:

$$K = \frac{t_s \tau}{D\varepsilon} = \frac{S}{D} \quad (2)$$

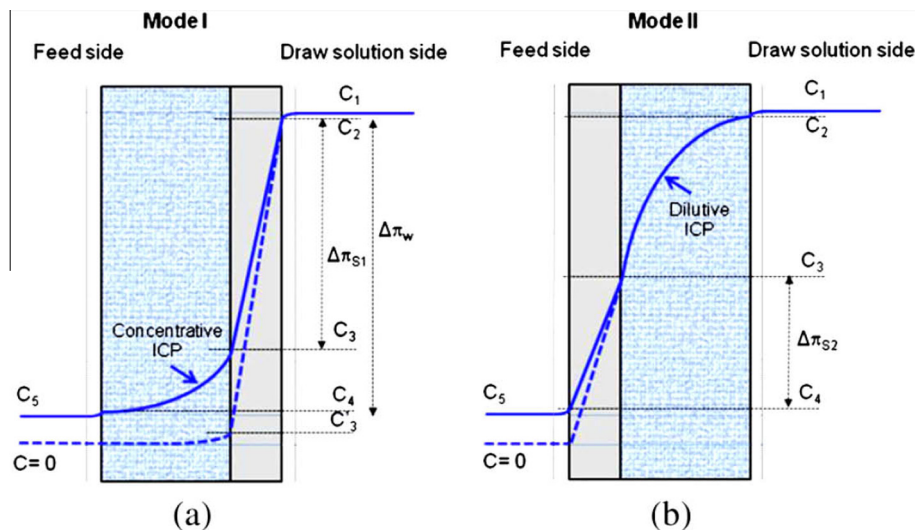


Fig. 5. Transport through asymmetric FO membrane [55].

where t_s is the thickness of the support layer, τ is tortuosity of the membrane, D is the draw solute's diffusion coefficient, ε is the porosity of the membrane and S is the structural parameter. It can be observed from Eq. (2) that to obtain a smaller K and an efficient membrane, the support layer should be as porous and thin as possible. The draw solute must also have a high diffusivity in the porous support layer. Additionally, the structural parameter (S) is an essential inherent membrane parameter as it determines the ICP within the membrane support via porosity, membrane thickness, and tortuosity. Consequently, for a newly synthesized membrane, it is important to characterize the membrane structural parameter [63]. Conversely, dilutive ICP occurs when operating in FO mode, where the feed solution is facing the membrane active layer. In FO mode, water permeates through the membrane from the feed solution to the draw solution and the draw solution is diluted in the interior of the porous support layer [64]. Due to the concentration gradient, more draw solute diffuses into the porous support layer until the rate of diffusion becomes zero. However, within the active layer, the concentration is significantly lesser than that in the bulk of the draw solution (Fig. 5b). As a result, the collective effect of water diffusion through the active layer and the draw solute diffusion into the porous support layer results in dilutive ICP [55]. The water flux (J_w), in FO mode can be expressed using Eq. (3) [61] as:

$$J_w = \frac{\frac{1}{K} \ln(A\pi_{draw} + B)}{A\pi_{feed} + B + J_w} \quad (3)$$

Certain components in FO feed can also contribute to dilutive ICP. Shu et al. studied the influence of the concentration of multiple cations in feed solution on FO performance [65]. The concentration of the draw solution was kept at either 2.0 M NaCl or CaCl_2 but the feed consisted of different mixtures of NaCl and CaCl_2 so that the flux obtained from the mixtures can be compared with the flux obtained when only NaCl was present in the feed stream. They demonstrated that less flux was obtained when there were more components in the feed. A worse dilutive ICP was obtained when CaCl_2 was increased in the feed. Unlike ECP, which takes place outside the membrane, both dilutive and concentrative ICP occurs inside the porous support layer; hence, cannot be mitigated by hydrodynamics like increasing the water flow rate or turbulence. ICP, therefore, significantly decreases osmotic driving force and thus the permeate flux [58].

3.2. Membrane fouling

Membrane fouling is significantly associated with all membrane processes and can adversely affect the performance of membranes and decrease the water flux across the membrane. However, membrane fouling is less prominent in osmotically driven membrane processes compared to pressure-driven processes because the former processes operate with low or no hydraulic pressure [66]. Hence, FO or PRO can be attractive choices over other pressure-driven processes because lower fouling membranes require less cleaning and maintenance, have a longer membrane life, and can produce more product water over time; hence lowering the operational and capital costs. FO has been used to treat domestic wastewater and activated sludge due to low consumption of energy and low fouling propensity of FO membranes. Unlike fouling in RO membranes, most FO membranes can be easily cleaned by osmotic backwashing for organic and inorganic fouling and may reduce or completely eliminate the need for any chemical reagents for cleaning. Also, electric field has been applied for fouling removal in FO [67]. The FO membrane was a conductive membrane prepared with chitosan (CHS), polyvinyl alcohol (PVA), and graphene (Gr) [CHS/PVA/Gr]. The feed was either lake or

distilled water whereas the draw agent was 4 M NaCl solution. The application of electrical current for cleaning the FO set-up resulted in the restoration of water flux to its original value for both feeds. Nevertheless, if membranes are not cleaned periodically, fouling can become a serious problem in the long term. In contrast to organic and inorganic fouling, it is difficult to physically clean and control biofouling because of the strong bacterial adhesion onto the membrane surface and the formation of sticky extracellular polymeric substance matrix. Hence, physical cleaning cannot recover the declined flux caused by biofouling and will need to be controlled by chemical cleaning using chlorine [68]. Recently, biofouling has been controlled by innovative membrane design. Perreault et al. fabricated TFC polyamide membranes with antimicrobial properties by surface functionalization with graphene oxide to prevent biofouling. Their results showed that direct microbial contact with the functionalized graphene oxide caused inactivation of bacteria (*E. coli*) at the surface of the membrane by 65% after the contact time of 1 h [69]. Ag/TiO₂-coated membranes have also been tested in PRO mode in FO process. The bacterial growth on the Ag/TiO₂-coated membrane was found to be almost 11 times less, compared to the uncoated membrane as a result of the antibacterial effects of the silver nanoparticles [70]. An overview of the recent studies on FO membrane fouling is presented in Table 1.

CP and membrane fouling are serious and unavoidable occurrences in FO as they cause an increase the resistance of membrane and reduction in the overall membrane permeability. More understanding of the mechanisms of CP and fouling are required to enhance FO efficiency.

3.3. Reverse solute flux

Reverse solute flux across the membrane from the draw to the feed solution seems to be unavoidable in FO due to the concentration gradient. According to Cath et al., it is important to carefully account for the draw solute's reverse flux as it might harm the process [82]. Recently, many researches have been conducted to study the effect of reverse diffusion of the draw solute on membrane fouling. It has been shown by Lee et al. and Lay et al. that draw solute's reverse flux can worsen membrane fouling by heightening the CEOP effect [66,83]. Hence, solutions containing multivalent ions with lower diffusion coefficients may be desirable in situations where considerable salt rejection is desired [84]. However, after reverse solute diffusion, some multivalent ions like calcium and magnesium ions may intensify membrane fouling by interfering with the fouling agents in the feed [85]. Additionally, more severe ICP can be caused due to the lower solution diffusion coefficients and larger ion sizes of multivalent ion solutions [86].

Hancock and Cath have presented the specific reverse solute flux or the fraction of the reverse flux of draw solute to the forward flux of water, as a measure of the selectivity of FO membrane [82]. Apart from permeate flux and salt rejection, specific reverse solute flux is the third evaluation parameter for the FO performance. A higher ratio indicates a lower FO efficiency and a reduction in membrane selectivity. Phillip et al. has demonstrated that specific reverse solute flux is dependent on the membrane selectivity but is unaffected by the membrane support layer structure and the draw solution concentration [87]. This outcome also implies the importance for the development of a new FO membrane with a highly selective membrane active layer so that the reverse solute diffusion can be minimized to aid FO performance. Moreover, it has also been proposed that the use of draw solution consisting of multivalent ions might reduce reverse solute flux [82], which will in turn lessen membrane fouling [66] but the resulting higher ICP [86] can increase the potential risk of fouling [85].

Table 1
Recent studies on FO membrane fouling.

Fouling type	Mitigation measure	Findings
Organic fouling [71]	Physical cleaning (hydrodynamics control strategies)	Minor fouling of support layer resulting from impact of organic and particulate matter with seawater/brine as draw solution and DI water as feed; formation of less compact fouling layer on the surface of the membrane; the use of spacer in the feed channel and pulsed flow easily eradicated the foulants from the membrane surface
Organic fouling (Alginate) [72]	Hydraulic cleaning	Alginate fouling was reversible, up to 98%, through a short-time physical cleaning
Inorganic fouling (Gypsum scaling) [73]	Hydraulic cleaning	Water flux recovery of 90% and 75% was obtained for CA and PA membranes, respectively, by rinsing membranes in water; PA membrane requires chemical cleaning to almost recover initial water flux
Organic fouling [74]	Hydraulic cleaning	Removal of natural organic matter including biopolymers; organic fouling was removed by 98% using water flushing
Combined organic and colloidal fouling (alginate, humic acid, and bovine serum albumin as organic model foulants; silica colloids as inorganic model foulants) [66]	Physical cleaning (hydrodynamics control strategies)	Reverse draw solute flux into the feed solution influenced both colloidal and organic fouling causing accelerated cake-enhanced osmotic pressure (CEOP); reverse diffusion of dextrose was insignificant compared to sodium chloride due to much bigger hydrated radius of dextrose compared to sodium chloride
Inorganic fouling (scaling) [75,76]	Physical cleaning	Reverse diffusion of diammonium phosphate (DAP) from the draw solution to the feed solution caused significant scaling; main contributors to membrane scaling were phosphates of magnesium, magnesium ammonium, and calcium; physical cleaning was effective for permeate flux recovery
Combined organic and inorganic fouling (Alginate and gypsum as model foulants) [77]	Physical cleaning (rinsing the membrane surface with pure water and continuously introducing air bubbles)	Synergistic effect between gypsum scaling and alginate fouling resulted in faster water flux reduction; scaling mechanism changed from bulk crystallization to heterogeneous/surface crystallization in the presence of alginate; recovery of initial water flux after combined fouling would still require chemical cleaning
Combined organic–colloidal fouling (Alginate, silica colloids, and their mixture as model foulants) [78]	Physical cleaning (hydrodynamics control strategies)	Combined fouling resulted in a faster flux decline than the individual foulants because of the synergistic effect of alginate and silica colloids; applied hydraulic pressure on the feed side resulted in higher fouling propensity and lower fouling reversibility of combined organic–colloidal fouling; single foulants were removed easily under all conditions
Organic fouling (sodium alginate as a model foulant for extracellular polymeric substances (EPS) that exist in seawater and wastewater) [79]	Physical cleaning (osmotic backwash using salt solution and ultrapure water)	Permeate flux decline was caused mainly by the formation of calcium–alginate complexes, especially at high calcium concentrations; initial adhesion of alginate particles on the membrane surface was caused by the chemical interactions between the alginate and membrane; permeate flux recovery of greater than 80% was achieved
Biofouling [80]	Spacer thickness	The impact of biofouling on membrane flux was diminished by thicker spacers; biofilm spatial distribution changed with feed spacer thickness
Inorganic fouling (scaling) [81]	Physical cleaning (change in working temperature)	Higher operating temperature significantly enhanced initial permeate fluxes and water recoveries but caused more serious water flux decline and membrane scaling in brackish water desalination; foulants crystallization on the membrane surfaces became more compact as the temperature was increased from 25 to 45 °C
Biofouling [69]	Graphene oxide surface functionalization	Inactivation of bacteria (<i>E. coli</i>) by 65% after the contact time of 1 h
Biofouling [70]	Ag/TiO ₂ -coating	The bacterial growth on the Ag/TiO ₂ -coated membrane was found to be almost 11 times less, compared to the uncoated membrane

In principle, ICP can be minimized by hindering the diffusion and accumulation of molecules in the porous support layer. This can be achieved either through the development of support layer that limits its diffusion of solute molecules or by increasing their back diffusion into bulk solution or by using draw solutes of suitable size and diffusion rates [78]. Previous work has shown that the extent and severity of ICP is dependent partly on the orientation of the support layer toward either the draw or feed side [86,88]. The diffusion of draw solutes into the porous membrane layer combined with the dilution effect of the permeate water can lead to substantial reduction in the flux. Therefore, it has been concluded that draw solute selection is pivotal for reducing this phenomenon [89]. For example, reverse

draw solute permeation has been coupled with experimental and theoretical (via solution-diffusion model) FO rejection for both AL-FW (active layer facing the feed water) and AL-DS (active layer facing the draw solution) orientations. Synthetic feed water consisting of 10 mmol/L background NaCl solution and 200 µg/L of each of nine haloacetic acids was used, and the draw solution contained 0.1–3 mol/L NaCl [90]. Lower reverse draw solute flux was obtained for the AL-FW orientation when compared with AL-DS orientation. When the draw solution concentration was increased, the measured reverse draw solute flux also increased for both orientations. It was also reported that reverse draw solute permeation can be predicted from the combination of solution-diffusion model with CP [90].

Double-blade casted substrate membranes which kept the active layer ideal and intact for FO salt rejection and ensured reduced reverse solute diffusion have also been developed [91].

For NaCl draw solutes, reverse solute diffusion can be worsened when the concentration of NaCl is increased [90]. This statement is supported by [92]. Kim et al. [92] reported that when NaCl concentration in the draw solution increased, stronger driving forces for both water permeation and reverse solute diffusion caused permeate water and reverse draw solute fluxes to increase. Shibuya et al. reported that the reverse diffusion of permeate water and salt leakage leads to ICP in the porous support layer of commercial membranes [93]. They also evaluated three types of cellulose triacetate (CTA) hollow fiber forward osmosis membranes with diameters of less than 200 μm under various operating conditions i.e. draw solution concentration, cross flow velocity, membrane orientation, and temperature. High water flux-to-reverse salt flux ratios, more than 800 L/mol and higher than those of commercial membranes, were obtained for the CTA HF membranes [93]. In general, reverse solute diffusion is one of the major challenges in FO and it should be fully taken into consideration and should be reduced during the future development of draw solutes and FO membranes.

3.4. Draw solutes/solutions advancement

In FO seawater desalination, saline feed water that contains lower solute concentration is sent to a semi-permeable membrane (separating agent). The driving force in this process is naturally created by the difference in osmotic gradient between the feed seawater and the draw solution. The tendency of the solvent to move across the membrane due to this osmotic gradient is what has given FO process an advantage over the conventional RO desalination. The benefits of using FO over RO are largely due to the lower energy cost for external pressure that is needed for RO and lower membrane fouling potential. This is why research in FO should be directed toward the building of highly efficient FO membrane and the development of high-performing draw solutions. Three major requirements should be met by an acceptable FO draw solution: high flux of water, simple recovery with low energy requirement, and minimal reverse solute diffusion [9]. In addition, the draw solution must be non-toxic, inexpensive, membrane-friendly, and non-responsive to pH changes.

3.4.1. Draw solution characteristics affecting FO performance

The osmotic agent, otherwise known as draw solution, has several factors that can readily affect FO performance. These factors mainly comprise of osmotic pressure of draw and feed solution [78], solubility of draw solute, temperature, draw solution concentration, molecular weight and particle size of draw solute. Recently, the number of research publications on FO have increased, greater efforts have been directed toward the development of new membranes and process performance, but little on the development and improvement of draw solution [3]. The driving force, osmotic gradient is the lifeline of FO desalination and the performance of this factor plays an important role in the FO process efficiency. A high osmotic pressure of the draw solution and minimal osmotic pressure of the feed induces high water fluxes across the membrane. An ideal solution's osmotic pressure, as given by Van't Hoff equation and provided in the work of [3], is shown in Eq. (4):

$$\Pi = n \left(\frac{c}{MW} \right) RT \quad (4)$$

n represents the number of mole of species formed by the dissociation of solutes in the solution, c is the solute concentration in g/L of solution, MW is the molecular weight of the solute, R represents

the gas constant and T stands for the absolute temperature of the solution in Kelvin. As given by [94], the above equation is limited to extremely diluted solutions and it is generally used for the determination of large molecular weight. A general form of the equation is found in the work of [95] and it is shown in Eq. (5):

$$\Pi/cRT = 1 + Bc + Cc^2 + Dd^2 \quad (5)$$

B , C and D are the osmotic coefficients that can be determined experimentally by fitting experimental osmotic pressure data. As given in Eq. (4), it is clear that, the osmotic pressure depends on solute concentration, the number of species formed by dissociation in the solution, solute's molecular weight and the solution temperature. This means that high solubility of draw solute induces high osmotic pressure and therefore, can achieve high water flux and high recovery rates. A solute with small molecular weight combined with high water solubility can generate higher osmotic pressure (on equal mass basis) and therefore can lead to higher water fluxes [96]. Small molecular weight solutes produce higher osmotic pressure than larger molecular weight for equal mass of draw solute, but induce higher reverse draw solute flux than the larger molecular weight draw solute. Additionally, draw solution with a low viscosity combined with high diffusivity and smaller ion/ molecule sizes will result in high water fluxes, which can make a draw solution more effective during desalination [3,86]. It was also found that higher temperature would not only allow greater initial fluxes and more water passage but would also induce more hostile effects on the scaling of FO membrane. For – temperature-driven FO desalination as reported by [7], thermally responsive semi interpenetrating (semi-IPN) hydrogels have been employed as draw agents whereby cyclic heating and cooling ensured quasi-continuous desalination within a moderate change in temperature. Moreover, concentration of draw solution is crucial for maintaining the desired water flux across the membrane. At higher draw solution concentration, increase in water flux has been observed [97]. At higher draw solution concentration, dilutive concentration polarization drastically increases resulting in less effective water flux improvement. Achilli et al. reported that ICP has been significantly influenced by the draw solution's diffusion coefficient [97].

Furthermore, a new class of draw solution can display some unique properties. Such properties can be particle sizes or particle agglomeration due to special magnetic properties when using magnetic nanoparticles (MNPs). Some draw solutions can also act as precursor to scaling and membrane fouling during reverse diffusion when draw solution containing SO_4^{2-} and Mg^{2+} are used respectively.

3.4.2. Types and classifications of draw solution

It was found that the type of draw solute is more important than the osmotic pressure of draw solution, as osmotic pressure of draw solution does not play a significant role at higher osmotic pressure [77]. Hence, initial draw solution concentration should be chosen so that the feed recovery is not very high that can speed up membrane scaling. There are different types of draw solutes that are categorized into organic-based draw solutes, inorganic-based draw solutes, and other compounds including emerging draw solutions such as magnetic nanoparticles (MNPs) and RO brines. These classifications can be sub-classified into ionic (electrolyte) and non-ionic (non-electrolyte) solutions based on whether the solution is made up of charged ions or if it is completely neutrally charged solutes. Some new draw solutions have been suggested recently [99]. Ge and co-researchers have studied the use of sodium polyacrylate (PAA-Na) polyelectrolytes as FO draw solutes [98]. Although this class of draw solutes is characterized with comparatively high molecular mass, they can reduce reverse flux. MD and UF are capable of recovering draw solutions made from

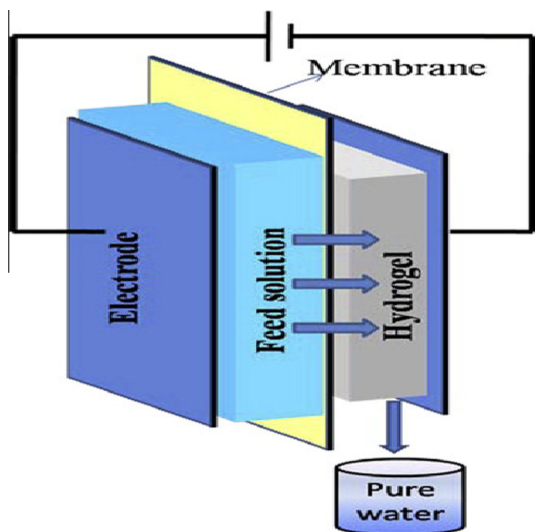


Fig. 6. FO desalination using polymer hydrogel as the draw agent [101].

polyelectrolytes. Surfactant/micellar solution containing organic and amphiphilic molecules can be aggregated above a certain critical concentration and used as draw solution [56]. Compared to inorganic salts, micellar solutes generated a more stable flux and resulted in significantly less reverse solute flux while also achieving high levels of regeneration via UF. Recently, interesting polymer hydrogels comprising of three-dimensional networks of polymer chains were investigated because of the presence of ionic species in the polymer that can create a high internal osmotic potential, swell, absorb water, and most importantly, dewater under the influence of stimuli such as sunlight, heat or an electric field [100–102]. An example is of the application of electric-responsive hyaluronic acid/polyvinyl alcohol (HA/PVA) polymer hydrogel is shown in Fig. 6.

Li et al. added 1 g of the hydrogel polymer to the active side of FO membrane. Water was allowed to permeate and the structure swelled after which it was dewatered [102]. However, similar to nanoparticles, polymer based draw solutes are incapable of generating an appreciably high osmotic potential that can induce high flux [102]. Also, the dewatering process using thermal stimuli require an estimated 10 kWh/m^3 which is lower than the energy required by thermal desalination process but three times higher compared to conventional membrane processes [100]. Polyelectrolytes such as polyacrylic acid-sodium have high solubility in water, provide high osmotic pressures, and can be recycled via UF. However, argument holds that the regeneration step using UF is still energetically demanding, which suggests that the use of polyelectrolytes would not be any different from using inorganic salts with an RO recovery step [2]. Very recently, discovery of the use of switchable polarity solutes and trimethylamine (TMA)-carbon dioxide revealed that solutions with very high osmotic strengths that are high enough to draw water from feeds as saline as seawater and brine can be obtained [103]. The miscibility of this type of draw solutes can be manipulated via the addition or removal of carbon dioxide from the solution, thereby making recovery a potentially simple step through the addition or removal of CO_2 [103]. However, the economic and energetic opportunity of this system still needs to be assessed to determine its feasibility for FO desalination [2]. For efficient recovery of product water in FO, a draw solution consisting of MgSO_4 with the concentration of 240,000 ppm and a commercial cellulose acetate membrane have been used for the desalination of highly saline feed including brackish water and seawater [104]. Mean water fluxes of 0.60 and $4.06 \text{ L/m}^2 \text{ h}$ were reached, respectively, for seawater and brackish water feed. From the diluted MgSO_4 draw solution, product water with 350 ppm salinity was obtained through barium hydroxide treatment and the soluble draw solute was precipitated as precipitates of barium sulfate and magnesium hydroxide. Also, it has been shown that the blending of draw solutes with ammonium bicarbonate could improve water flux [105]. Liu et al. studied the

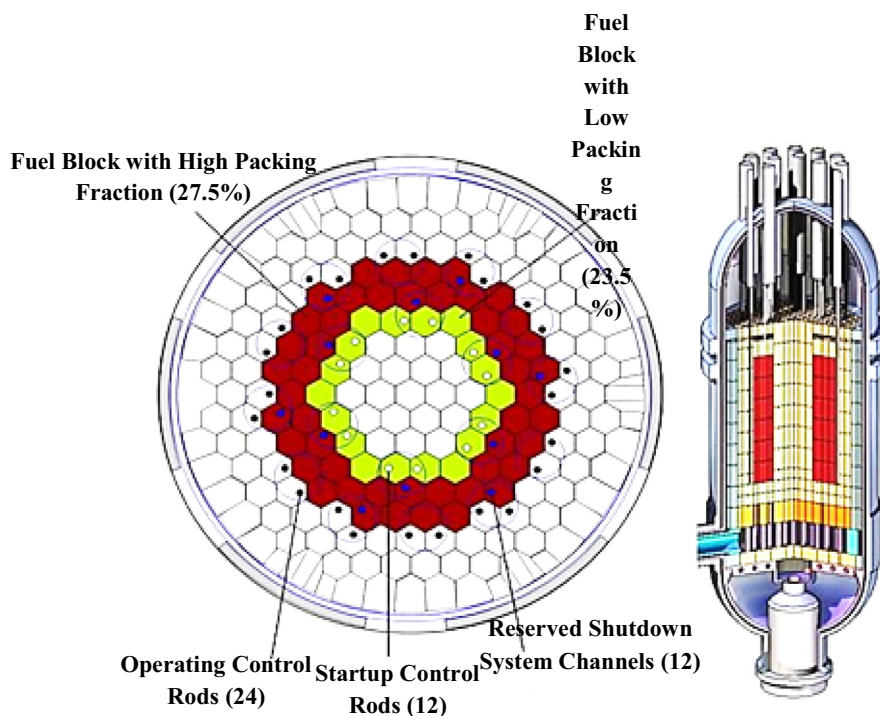


Fig. 7. The core of a very high temperature reactor (VHTR) for VHTR-FO desalination [106].

Table 2

Recently developed draw solutes, reported fluxes and testing conditions.

Type of draw agent	Flux/LMG (mode)	Testing conditions
Sodium chloride [107]	30 LMH (PRO), 50 LMH (FO)	Standard Protocol: TFC membrane; Cross flow rate: 0.25 m/s; Draw solution: 1 M NaCl; Feed solution: Deionized water; Temperature: 20 °C
Ammonium bicarbonate [108]	36 LMH (PRO)	Cross flow rate: 30 cm/s; Osmotic pressure difference: 236.2 atm; Temperature: 50 °C
Magnetic nanoparticles (polyacrylic acid) [5]	7.7–10 LMH (PRO)	Cross flow rate: 6.4 cm/s; Draw solution concentration: 0.15 mol/L; Feed: Deionized water; Temperature: 22 ± 0.5 °C
Polymer hydrogels-poly (sodium acrylate) [102]	1.06–0.49 LMH (PRO)	Draw agent amount: 1 g; Hydrogel density: 1 g/cm ³ ; Draw agent size: 100 to 200 µm; Feed: 2000 ppm NaCl
Hydroacid complex Na ₄ [Co(C ₆ H ₄ O ₇) ₂]·2H ₂ O (Na–Co–CA) [43]	11–16 LMH (FO)	Cross flow rate: 0.2 L/min; Draw solution concentration: 1 M; Feed: 2000 ppm heavy metal solution; Temperature: 23–60 °C
Hydrophilic nanoparticles [6]	18 LMH (PRO)	Cross flow rate: 6.4 cm/s; Draw solution concentration: 0.08 mol/L (70 atm); Feed: DI, Temperature: 22 ± 0.5 °C
Polyelectrolytes (polyacrylic acid sodium salts-PAA-NA) [98]	12 LMH (PRO), 7 LMH (FO)	Cross flow rate: 6.4 cm/s; PAA-NA molecular weight: 1800 Dalton; Draw solution concentration: 0.08 mol/L (70 atm); Osmotic pressure difference: 20 atm; Feed: Deionized water; Temperature: 25 ± 0.5 °C
Polymer hydrogels [7]	0.24 LMH (PRO)	Feed: 2000 ppm NaCl
EDTA sodium salt [109]	FPRO: 7.12 LMH (PRO)	Cross flow rate: 384 cm/s; Draw solution: 0.1–1 M EDTA sodium salt; Feed: Deionized water; pH: 8, 25–28 °C
Polymer hydrogels [100]	0.325–0.125 LMH	Cross flow rate: 384 cm/s; Draw solution: 0.12 g of hydrogel; Feed: 2000 ppm NaCl; pH: 8; Temperature: 25–28 °C
Switchable polarity solvents - dimethylcyclohexylammonium hydrogen carbonate [103]	FO: 35 LMH	Cross flow rate: 0.4 L/min; Draw osmotic pressure: 325 atm; Draw amount: 7.6 mol/kg [HN(Me) ₂ Cy HCO ₃]; Feed: 0–5 mol/kg NaCl; Temperature: 30 °C; Carbon dioxide (30 mL/min)
Zwitterions [110]	5 LMH	Cross flow rate: 375 L/h; Feed: Deionized water; Draw solution osmotic pressure: ~25 atm
Trimethylamine–carbon dioxide [111]	33.4 LMH (PRO), 14.5 LMH (FO)	Cross flow: 17.1 cm/s; Draw solution concentration: 1 M TMA–CO ₂ ; Draw osmotic pressure: 48.8 atm; Feed: Deionized water, 25 ± 0.5 °C
Electro-responsive polymer hydrogels [101]	1.7 LMH (FO)	Cross flow rate: 22.22 cm/s; Draw hydrogel: 0.6 g; Feed: 2000 ppm NaCl; Applied voltage: 6–9 V; DI feed
Polyelectrolytes (polyacrylamide) [112]	PRO: 5–8 LMH, FO: 3–5 LMH	Cross flow rate: 10 cm/s; Feed: Dyeing wastewater (0.05 g/L dye); Draw agent: 20 g/L–40; Draw osmotic pressure: 366–824 mOsm/kg H ₂ O; Temperature: 35 ± 0.5; pH: 6.37

water flux behavior of draw solutions formed by ammonium bicarbonate (NH₄HCO₃) and eight soluble inorganic salts (K₂SO₄, NaCl, KCl, KNO₃, NH₄Cl, NH₄NO₃, urea and (NH₄)₂HPO₄), respectively, by using a laboratory-scale plate-and-frame FO setup with TFC FO membrane. The water flux behavior of all salt solutions was enhanced after blending with NH₄HCO₃. When deionized or simulated brackish water was used as feed solution, the highest water flux behavior was exhibited by the mixture of NH₄Cl and NH₄HCO₃ and the lowest flux was obtained from urea and NH₄HCO₃ mixture. An improved and novel regeneration process using waste heat as source for dissociating ammonium bicarbonate has been investigated [106]. 60% of heat from nuclear reactors is removed in the form of waste heat; however, the use of nuclear waste heat for regenerating ammonium bicarbonate has been identified as a promising area of integration. The core of the nuclear reactor or very high temperature reactor (VHTR) used for the VHTR-FO desalination is shown in Fig. 7.

Table 2 gives a general overview of recently developed draw solutes, reported fluxes and testing conditions. The reported fluxes in Table 2 have been plotted in Fig. 8 in order to show the dependence of FO performance on draw agents and applied operating conditions.

3.4.2.1. Inorganic-based draw solutions. Inorganic-based draw solutions have been extensively studied. They are majorly composed of electrolyte solutions, and there are few that are non-electrolytes [3]. From analysis of performance, the high-ranking draw solutions are calcium chloride (CaCl₂), potassium hydrogen carbonate (KHCO₃), magnesium chloride (MgCl₂), and sodium hydrogen carbonate (NaHCO₃), whereas from analysis of replenishment cost, the high-performing draw solutions are KHCO₃, magnesium sulfate (MgSO₄), sodium chloride (NaCl), NaHCO₃, and sodium sulfate

(Na₂SO₄) [97]. For both analyses, NaHCO₃, KHCO₃, and MgSO₄ were rated high and can be considered for FO process when the type of membrane that will be considered is also taken as a factor. However, for feed solutions with scale precursor ions such as barium, calcium, magnesium, sulfate and carbonate, likely occurrence of mineral scaling would result when the concentration of the feed solution goes beyond the limits of solubility of minerals that are sparingly soluble in water such as barium sulfate (BaSO₄), calcium carbonate (CaCO₃), calcium sulfate (CaSO₄), and magnesium hydroxide (Mg(OH)₂). However, the formation of magnesium hydroxide at pH more than 9 can occur [97]. Therefore, draw solutions such as MgSO₄, Na₂SO₄, NaHCO₃, and KHCO₃ which might pose scaling threats are constrained to applications involving pure feeds such as food concentration. Most especially, KHCO₃ and NaHCO₃ are desired because they can ensure low reverse salt diffusion and high water flux. Because of the complex ion matrix of the feed solutions, draw solutes with scale precursors are not suggested for water treatment. For most water treatment applications, MgCl₂ is desired as a draw solute because it reduces scaling threat. Table 3 shows the solubility, and other relevant characteristics of the studied inorganic-based draw solutions that have effects on the performance of FO processes especially in seawater desalination.

Several studies have used NaCl in wide range of applications. It has been applied in food production and wastewater treatment [45]. The reason for the wide use of NaCl as draw solute for many FO processes is mainly because saline water is abundant on earth, making seawater a natural and cheap source of draw solution. Not only this, NaCl is often utilized because it is relatively straightforward to re-concentrate with RO process without the risk of scaling, and it has high water solubility and exhibit high osmotic pressure - the characteristics that have positive effects on the performance of FO processes.

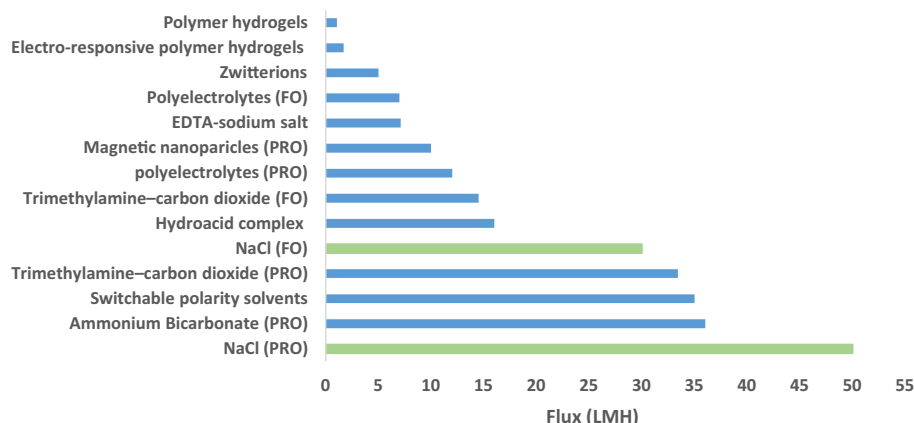


Fig. 8. Water flux by draw solute compared to NaCl tested under standard testing conditions (from Table 2).

Table 3

Properties and experimental water fluxes of inorganic compounds tested as experimental draw solutions (modified from [3]).

Experimental draw solute	Osmotic Pressure at 2.0 M (atm)	pH at 2.0 M	Max. solubility (M)	Scale precursor ions	Reverse salt diffusion (g/m ² h)	Experimental water flux (μm/s)	References
CaCl ₂	217.6	6.29	7.4	Yes (Ca ²⁺)	7.9	2.64	[97]
KBr	89.7	6.92	4.5	No	22	2.84	[97]
KHCO ₃	79.3	7.84	2	Yes (CO ₃ ²⁻)	1.4	2.25	[97]
K ₂ SO ₄	32.4	7.33	0.6	Yes	3.7	2.52	[97]
MgCl ₂	256.5	5.64	4.9	Yes	4.8	2.33	[97,113]
MgSO ₄	54.8	6.7	2.8	Yes	1.2	1.54	[97,113]
NaCl	100.4	6.98	5.4	NO	7.2	2.68	[97,113]
NaHCO ₃	46.7	7.74	1.2	Yes	1.7	2.47	[97]
Na ₂ SO ₄	95.2	7.44	1.8	Yes	2.7	2.14	[97,113]
NH ₄ HCO ₃	66.4	7.69	2.9	Yes	18.2	2.04	[97]
NH ₄ NO ₃	64.9	4.87	84	Yes	227.9	4.177	[75]
(NH ₄) ₂ SO ₄	92.1	5.46	5.7	Yes	2.6	5.391	[75]
NH ₄ Cl	87.7	4.76	7.4	No	64.1	5.348	[75]
Ca(NO ₃) ₂ ·4H ₂ O	108.5	4.68	7.9	Yes	7.7	5.022	[75]
NaNO ₃	81.1	5.98	10.5	No	84.9	5.706	[75]
KCl	89.3	6.8	4.6	No	59.6	6.337	[75]
NH ₄ H ₂ PO ₄	86.3	3.93	3.7	No	28.7	4.349	[75]
(NH ₄) ₂ HPO ₄	95	8.12	6.5	No	4.6	3.892	[75]
KNO ₃	64.9	5.99	3.3	No	176.7	4.429	[75]

Table 4

Physicochemical properties and experimental water fluxes of some organic-based draw solutions.

Draw solution tested	Osmotic Pressure at 2.0 M (atm)	pH at 2.0 M	Max. solubility (M)	Experimental water flux (LMH)	References
Ethanol	43.93	7	Miscible	N/A	[114]
Sucrose	56.81	6.18	6.1	0.35	[115]
Glucose	55.03	7.01	800	0.24	[117]
Fructose	55.02	7.01	22.4	7.5	[117]

Note: LMH is L/m² h.

3.4.2.2. Organic-based draw solution. In the last ten years, glucose and fructose have been tested severally as draw solutions for sea-water desalination [3]. These compounds and many other organic-based draw solutions are usually non-electrolytes; they however have the potential to generate high osmotic pressure as they generally exhibit high solubility that can be attributed to hydrogen bonding. Ethanol has also been tested as draw solution in FO desalination [114]. Table 4 shows other works that made use of organic-based draw solutions for FO desalination processes. Other organic-based draw solutions include polyethylene glycol 400 (PEG) to concentrate tomato juice [115], ethanol from recovery of water from highly impaired sources [114] and 2-methylimidazole-based compounds [116] among others.

3.4.2.3. Magnetic nanoparticles draw solution. Studies conducted recently have focused on hydrophilic magnetic nanoparticles (MNPs) [118]. Three different types of MNPs have been investigated as potential draw solution for FO desalination. These include polyacrylic acid magnetic nanoparticles (PAA MPNs), the 2-pyrrolidone-magnetic nanoparticles (2-pyrrol MNPs) and the triethyleneglycol magnetic nanoparticles (TREG MNPs). Although they are non-electrolytes, their major benefit is their huge surface-to-volume ratio and large sizes compared to organic and inorganic molecules that facilitate recovery using magnetic fields and membrane processes such as microfiltration or nanofiltration (NF) [5]. In addition, they are capable of producing very high osmotic pressure of about 70 atm which is far higher than the seawater

Table 5
Recent FO membrane fabrication.

Year	Membranes	Materials	Preparation methods	References
2005	Capsule wall	Cellulose acetate (CA) or ethyl cellulose	Dip-coating, phase inversion	[120]
2007	Hollow fiber NF	Polybenzimidazole (PBI)	Dry-jet wet phase inversion	[120]
2008	Flat sheet cellulose acetate	Cellulose acetate	Phase inversion and then annealing at 80–95 °C	[121]
2009	Dual-layer hollow fiber NF	PBI–PES/PVP	Dry-jet wet phase inversion (i.e. coextrusion technology)	[122]
2010	Hollow fiber	PES substrates, polyamide (PA) active layer	Dry-jet wet spinning and interfacial polymerization (IP)	[123]
2010	Hollow fiber NF	Cellulose acetate	Dry-jet wet spinning	[124]
2010	Flat sheet double-skinned	Cellulose acetate	Phase inversion, and then annealing at 85 °C	[125]
2010	Flat sheet TFC	Polysulfone (PSf) support, PA active layer	Phase inversion and IP	[62,126]
2010	Double dense-layer	Cellulose acetate	Phase inversion	[16]
2011	Modified RO	PSf support modified by polydopamine	Chemical coating	[18]
2011	Flat sheet composite	CA cast on a nylon fabric	Phase inversion	[127]
2011	Flat sheet composite	PAN substrate, multiple PAH/PSS polyelectrolyte Layers	Layer-by-layer assembly	[14]
2011	Positively charged hollow fiber	PAI substrate treated by PEI	Chemical modification	[128]
2011	Positively charged flat sheet	PAI substrate treated by PEI	Chemical modification	[129]
2011	Flat sheet TFC PA	PES/SPSf substrate, PA active layer	Phase inversion and IP	[53]
2011	Flat sheet TFC PA	PES/sulfonated polymer substrate, PA active layer	Phase inversion and IP	[130]
2011	Flat sheet TFC PA	PSf support, PA active layer	Phase inversion and IP	[131]
2011	Nanoporous PES	PES cast on PET fabric	Phase inversion	[132]
2011	Cellulose ester	Cellulose ester	Phase inversion	[133]
2011	Flat sheet TFC PA	PES nanofiber support, PA active layer	Electro-spinning and IP	[17]
2011	Flat sheet TFC PA	PSf nanofiber support, PA active layer	Electro-spinning and IP	[134]
2012	Polymeric nanofiber incorporated TFC PA	Polyethylene terephthalate (PET) nanofibers, PSf microporous support, PA active layer	Electro-spinning, phase separation and IP	[135]
2012	TFC PA	Super porous CNT non-woven Bucky-paper (BP) support, PA active layer	Plasma treatment of CNT BPs support and IP	[136]
2012	Dual layer hollow fiber NF	PES inner support layer and PAI active layer post-treated by PEI	Dry-jet wet spinning, one-step coextrusion, multi-layer polyelectrolyte depositions	[137]
2013	Thin-film inorganic (TFI)	Stainless steel mesh (SSM) substrate, micro-porous silica xerogels active layer	Dip-coating and calcining for 4 h at 500 °C in nitrogen followed by cooling to 25 °C	[118]
2014	Thin-film nanocomposite (TFN)	PSf-titanium dioxide(TiO ₂) nanocomposite substrate, PA active layer	IP	[138]
2014	Tri-bore hollow fiber TFC	Matrimid® 5218 polymer substrate, PA active layer	Dry-jet wet spinning and IP	[139]

osmotic pressure of 26 atm which make them very attractive for desalination processes [6].

3.4.2.4. RO Brines as draw solution. The discarding of concentrated brines from a RO desalination plant is an important and critical environmental issues [3]. RO concentrate consists of waste flow with extremely concentrated organic and inorganic compounds. Hence, there is a need to sustainably manage the RO concentrate in order to avoid any adversarial effects on the receiving environment. However, there have been recent developments on the potential use of RO brines as draw solution in order to solve RO concentrate issues [119]. Bamaga et al. [21] designed a hybrid FO/RO process whereby the RO feed is pretreated using the first FO process to minimize scaling risk during the desalination process. RO brine is used as draw solution for the second FO process to concentrate impaired water and minimize its volume for further treatment. Therefore, in this application, the FO process combining with RO brines as draw solution is used to lower energy requirement for desalination.

3.5. Membrane advancement

Since the 1960s, most studies on FO were carried out using RO membranes [84]. However, studies on development of membranes explicitly for FO applications were initiated before 2000. An overview of the recent advancements in FO membrane is presented in Table 5. These newly developed membranes can be categorized into three types based on the fabrication methods: cellulosic, TFC, and chemically modified membranes.

The first of phase inversion membranes explicitly used for FO applications were developed by Wang et al. [120]. Wang et al. fabricated a type of asymmetric polybenzimidazole (PBI) NF hollow

fiber membrane via dry-jet wet phase inversion. It was found that this membrane could be effectively used for FO as it possessed distinctive NF properties and excellent mechanical strength. It is also chemically stable. This membrane showed high divalent ions rejection and considerable water flux desirable water permeation flux and high rejection to divalent ions, thus having great prospective to be applied in the FO process [120]. The asymmetric PBI NF hollow fiber membrane was then improved to obtain a higher permeate flux and salt rejection by using p-xylene dichloride for cross-linking [140].

FO membranes have been prepared extensively using cellulose acetate (CA) through phase inversion due to its favorable properties like good mechanical strength, wide availability, relatively high hydrophilicity which allows low fouling tendency and good water flux, and good resistance to chlorine and other oxidants degradation [16,141]. Recently, a number of cellulose ester-based membranes, including both hollow fiber and flat sheet modules, have been fabricated for FO applications [16,124,125,133]. The derived membranes were found to possess two skin layers, which have the ability to decrease ICP [125]. Zhang et al. also reported two-skin layers with selective layer at membrane polymer's bottom interface that could minimize ICP in FO processes [16]. Zhang et al. found that the casting substrate and the polymer interact to play a significant role in the membrane structure formation during phase inversion [16,133]. Tang et al. have modeled a similar double-skinned FO membrane and have observed that the best double-skinned FO membrane should maintain a mass transfer coefficient that is high for the porous support, have a brackish water RO type draw skin, a feed skin with low rejection NF [142]. Su et al. have also fabricated double-skinned CA hollow fibers consisting of an inner or outer selective layer by employing different phase inversion rates and extent of thermal annealing at

both layers. The comparatively dense outer skin of the fibers formed via phase inversion considerably reduced the impact of CP occurring in the porous sublayer. It was observed that the dense outer layer significantly helped in increasing the water flux and the CA hollow fibers annealed on the shell side showed better FO performance compared to those annealed at the lumen side [143]. Similarly, Sairam et al. developed flat sheet FO membranes CA using zinc chloride, maleic acid, and lactic acid to form pores at different annealing temperatures. It was observed that the membrane fabricated using zinc chloride as the pore-forming agent gave comparatively a high permeate flux and salt (sodium chloride) rejection [127].

Despite the favorable characteristics of CA membranes, the drawbacks of CA must be considered before it is used for the development of FO membranes. Although, CA membranes are more resistant to chlorine degradation and are more hydrophilic than the TFC PA RO membranes, they show poor inhibition to biological attachment and hydrolysis. Therefore, it is important to maintain the feed and draw solutions at pH 4–6 or temperature below 35 °C so that the hydrolysis of CA membranes can be abated [1,141]. Similar to RO, a different class of composite membranes has also been considered for FO applications. Presently, commercially available FO membranes from HTI™ are TFC- membranes with multiple layers. The overall thickness of the first type of HTI™ TFC membrane FO-1 is very thin i.e. approximately 50 µm; whereas, the second one indicated as FO-2, has a thickness greater than 100 µm. Both membranes are asymmetric and CTA based membranes [1,84,144]. Mostly FO-1 type membranes have been used for FO studies because they give greater water flux relative to the FO-2 type. On one side of FO-1 membrane, a thin selective layer exists, and there is a support layer on the other side. There is a polyester mesh between the layers to support the membrane mechanically. Similarly, according to the HTI patent, the structure of the FO-2 membrane consists of three layers: a polymeric skin layer (8–18 µm), a porous scaffold layer and a support fabric [144]. FO-2 membrane provides a higher salt rejection but lower water flux than the FO-1 type.

The fabrication method for flat sheet and hollow fiber TFC PA FO membranes are mostly similar to those for fabricating TFC PA RO membranes. The fabrication involves the development of a porous substrate via phase inversion and a thin PA active layer by interfacial polymerization [17,53,60,126,130,131]. Tiraferri et al. prepared flat sheet TFC FO membrane by interfacial polymerization of *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC) on porous polysulfone (PSf) substrates, which were then cast on polyester nonwoven fabrics. From the experimental results, it was confirmed that a mixed-structure support layer was necessary for an optimal FO membrane. It was concluded that fabrication of high performance FO membrane requires optimization of the structural properties of the support layer and transport features of the active layer [126]. Later, a similar method was used to synthesize hollow fiber FO membranes, i.e., interfacial polymerization of TMC and MPD on the inner or outer surface of a porous PES substrate [122,145]. Using PSf as substrate, TFC membranes with thin sponge-like skin layer and structures containing distinctive straight finger-like pores [131]. The prepared TFC FO membranes was then compared with commercial FO and RO membranes and it was observed that the substrate structure was of critical importance in determining performance of FO. The substrate with straight finger-like pore structure was desired over spongy pore structure to minimize ICP. Similarly, Widjojo et al. synthesized TFC FO membranes using sulfonated material for the substrate as it plays an important role in the creation of macrovoid-free structure and induces hydrophilic properties with improved water fluxes and reduced ICP [130].

A study conducted by Wei et al. examined the response of the separation and performance characteristics of FO membrane to

effect of monomer concentrations (MPD and TMC). Between salt rejection and water permeability, a significant trade-off was observed. Higher permeability but lower salt rejection resulted from increasing the TMC or decreasing the MPD concentration. Increasing the TMC concentration or decreasing the MPD concentration caused higher membrane permeability but lower salt rejection [60]. However, the study concluded that FO membrane optimization will largely be influenced by the operating conditions during explicit application (for example draw solute concentration and membrane orientation). Due to higher non-linear reliance of FO on the conditions of operation or characteristics of FO membrane, an optimized membrane for one explicit application does not inevitably promise a good performance under other operating conditions. Moreover, the hydrophilicity of the membrane support layer was found to play a critical role in FO water flux. A support layer with high hydrophilicity could improve water flux across the membrane [130,146]. Wang et al. fabricated TFC FO membranes via interfacial polymerization of *p*-Phenylenediamine and 1,3,5-trimesoylchloride monomers on the surface of polyethersulfone (PES)/sulfonated polysulfone (SPSf)-alloyed porous substrates with improved hydrophilicity [53]. Yu et al. also used phase inversion only (without interfacial polymerization) to synthesize a high-performance nonporous PES FO membrane. At the top of support layer consisting of polyester fabrics, the activate layer of the PES membrane was formed. The membrane contained nanopores and a loose finger-like structure – the properties that contributed to high water flux. Additionally, the support layer thickness and the backing resulted in low reverse solute flux. It was also concluded that increasing the membrane surface hydrophilicity is better than reducing the membrane thickness as it allows selective increase in the water flux without increasing the reverse solute flux [132].

Song et al. reported that electrospinning-formed support layers made of scaffold-like nanofiber and fabricated with interlinked pore structure was better than the conventional phase-inversion support layers because of its high porosity and low tortuosity, which considerably helped to reduce the structural parameter of the membrane. Consequently, the water flux of the ES-IP-formed FO membranes were three times higher than the membranes formed by phase inversion followed by interfacial polymerization [17]. Bui et al. also confirmed the enhanced performance of FO nanofiber supported-PA composite membranes resulted in five times higher water flux and 100 times lower salt flux compared to a standard commercial FO membrane [134]. It can be observed from the above discussion that majority of the approaches used for synthesis of both asymmetric CA and TFC FO membranes are similar to the conventional techniques for fabrication of RO membranes. Generally, the active layer of an appropriate TFC FO membrane should be very selective so that salt rejection can be increased and reverse solute diffusion can be minimized. In addition, the support layer should be highly porous and hydrophilic so that ICP can be minimized. Hence, in the future, it is important to emphasize on the modification of the structural properties of membrane support layer for FO membranes as it can significantly improve water flux and minimize ICP [78].

In addition to phase inversion membranes and TFC membranes, few chemical modification methods have also been used recently for synthesis of novel FO membranes. For example, synthesizing support layers using novel material such as incorporation of titanium dioxide nanoparticles [138], carbon nanotubes [148] or zeolites [149] into themembrane have been shown to improve support layer structural features. A bio-inspired hydrophilic polymer (polydopamine or PDA) has been used by Arena et al. to coat and chemically modify the support layers of two commercially available TFC RO membranes to improve their hydrophilicity. The resultant modified membrane reduced ICP and increased hydrophilicity, which

enhanced the membrane water flux in FO tests. Improvements in water flux by eight to fifteen times was shown by the modified membranes [18,150]. As a result, the modification method will allow the existing TFC membranes to be used for all engineered osmosis applications.

In another study, Setiawan et al. used microporous hollow fibers with polyamide-imide substrate and polyethyleneimine polyelectrolyte post-treatment to make a FO membrane with a positively charged selective layer. Unlike neutral membranes, these positively charged FO membranes limit salt transport through the membrane in FO mode by providing double electric repulsions to the salt transport, whereas in PRO mode configuration, the positive charges enable salt transportation [128]. Later, a flat sheet membrane was similarly fabricated using a positively charged selective layer and substrate embedded on a woven fabric. By embedding the PAI membrane on a woven fabric, the thickness of the substrate was reduced to 55 μm and the mechanical strength of the membrane was enhanced. [129]. In addition to the above FO membrane fabrication methods, novel FO membranes using the layer-by-layer (LbL) assembly method were first synthesized and characterized by Saren et al. [14]. Other authors have seen the need for further investigations into the performance of these FO membranes. Saren et al. and Qui et al. prepared polyacrylonitrile (PAN) substrate through phase inversion. Post-treatment was carried out using sodium hydroxide to improve the hydrophilicity and density of negative charge at the surface. The polyanion and polycation were poly (sodium 4-styrene-sulfonate) and poly (allylamine hydrochloride) (PAH), respectively [14,151]. Saren et al. observed that an increase in polyelectrolyte layers enhanced the LbL membranes selectivity but decreased their water permeability and reverse salt flux. The membrane water permeability and reverse solute transport were found to strongly affect the membrane water flux. Qui et al. observed relatively high water permeability and high water fluxes for both cross-linked (LbL series) and non-cross-linked (xLbL series) membranes, where ICP was minimized in the support layer with the help of a thin substrate with finger-like pores [151]. However, the cross-linked xLbL membranes showed relatively low reverse salt flux. Cui et al. [152] also used PSS and PAH as the polyanion and polycation, respectively, and concluded that the use of 3-bilayer membranes improved water flux. Cui et al. observed non-linear growth in membrane thickness and concluded that this growth becomes insignificant after 6-bilayer depositions. In future, more membranes may be fabricated using LbL assembly, and more studies may be conducted to explore recently developed practices such as polyelectrolyte dip-coating (currently used for NF membranes) [153,154] and UV-photographing [155–157] to synthesize highly efficient membranes.

3.6. Assessment of membrane performance

Commonly, FO membranes that show low salt rejection also exhibit high water permeability. Hence, a better parameter for FO performance evaluation may be specific reverse solute flux, or solute flux in the reverse direction per unit of water flux in the forward direction [129]. FO performance assessment using the osmotic water and specific reverse solute fluxes will be more practical in the presence of ICP and membrane fouling. The three most important challenges to FO membrane performance are ICP, reverse solute diffusion and membrane fouling. Hence it is important to consider these factors when developing new FO membranes. Until now, not much research has been conducted to account for anti-ICP and antifouling requirements during membrane fabrication. It can be seen from Eqs. (1)–(3) that water flux through FO membrane is dependent on the membrane water and solute permeability, and structural parameter. Hence, evaluation of both K

and S is required besides A and B for synthesis of a new FO membrane. Here, ICP is reflected by the solute resistivity (K), which considerably affects the FO water flux. Nevertheless, the effect of ICP in FO is found to very low or even negligible at low solution concentration [86].

Some studies have recognized the effect of structural parameter on FO performance; however, not much focus has been directed toward the occurrence of ICP during membrane fabrication [17,62,131]. Research has also been carried out on the improvement of support layers as a means for overcoming ICP through reduction of the support layer's tortuosity and increasing porosity [138,158,159]. For example, addition of electro-spun polyvinyl alcohol nanofibres into PSf support layer resulted in improved support layer features that allowed an enhancement in flux by up to 8 times compared to commercial FO membranes [52]. Support layers have been synthesized using different materials. For example, titanium oxide nanoparticles [138], sulfonated poly(phenyl oxide) [58], sulfonated polyphenylenesulfone [147], and zeolites [149] have been incorporated into support layers. Modifications such as polyelectrolyte layers have been introduced to form a double skinned membrane [160] and the membrane fabrication process has been optimized to fabricate ultra-thin FO membranes in order to reduce ICP [16]. Although, such manipulations enhanced flux, tradeoffs in terms of salt rejection were observed in some of those studies [161]. Sun et al. attempted to increase water flux and minimize ICP through manipulating the PSf to PES ratio in the membrane formation process. Their study showed that a ratio of 2:3 in the blend introduced a large open bottom section in the support layer and increased surface roughness which minimized ICP. However, the support layer enhanced water flux but came at the cost of also increasing solute reverse flux [162].

A modeling study has been used to examine the dependence of ICP on porous support structure [163]. Using a blockage probability function P_b , a statistical correlation between the FO membrane performance and distinct network substructures was identified, indicating that the macroscopic structural parameters (porosity and the tortuosity) were significantly influenced by the dispersive solute transport through the membrane. The simulation results also established that there is considerable reliance of ICP on the substructures. The effect of structural parameters on ICP has also been observed by studying the impact of an ultra-thin selective layer at the bottom interface of polymer and casting substrate (with 95 nm thickness) during phase inversion of cellulose acetate (CA) FO membrane [16]. Substrates with different hydrophilicity (glass and Teflon plates) were tested. A double dense-layer structure was formed when glass plate was used as the casting substrate and water as the coagulant. Low salt leakage due to reduced ICP was reported and modeled structural parameter (S_s) of the membrane was significantly lower than reported values in previous studies. Prior immersion into a solvent/water mixed bath before complete water immersion would result into membranes with single dense layer and much smaller S_s value [16]. The incorporation of zeolite nanoparticles into membrane substrate would also lead to the reduction of structural parameter and mitigation of ICP [149]. Polysulfone-nanocomposite (PSfN) substrates were prepared through the integration of zeolite nanoparticles with polysulfone by phase inversion. Improved surface porosity and hydrophilicity was shown by the resulting PSfN0.5 membrane (with 0.5 wt% zeolite loading) substrate. Also, water permeability of the TFC-PSfN0.5 membrane obtained was more than twice higher than that of conventional polysulfone TFC membrane. The nanocomposite substrate had influenced the reduction of substrate structural parameter ($S = 0.34 \text{ mm}$ for PSfN0.5-TFC compared to 0.96 mm for TFC) and ICP [149]. Furthermore, an implementation of hydrophilic sulfonated polyphenylenesulfone (sPPSU) materials containing various portions of sulfonated units i.e. 2.5 and 5 mol%

3,3'-di-sodiumdisulfate-4,4'-dichlorodiphenyl sulfone (sDCDPS) monomer as supporting layers of TFC FO membranes has improved water transport across the membrane and induced formation of fully sponge-like structures which reduced ICP [147]. An increase in the contents of the sulfonated materials in membrane substrates would lead to significant reduction in ICP.

It is clear from aforementioned examples that water and reverse salt flux, salt rejection, anti-fouling characteristics, anti-CP tendencies and membrane structural parameter should be taken into consideration during the characterization of a newly fabricated membrane. Moreover, several repetitions of FO membrane fabrication and thorough testing for evaluation of FO performance will be required before the membrane goes to commercialization.

4. Sustainability in seawater desalination

The current most energy efficient seawater desalination technology that is widely in use is RO. However, energy costs are responsible for up to 75% of the total operating costs in RO plants [21]. Energy usage in RO desalination plants varies between 0.5–3 kWh/m³ for brackish water and 3–7 kWh/m³ for seawater. Brackish water plants often require more energy because they are able to achieve higher water recovery [164]. As compared to undiluted seawater with higher salinity, lower amount of energy would be needed for desalting diluted seawater because the required osmotic pressure becomes reduced when the seawater is diluted [20,21]. Sources such as wastewater effluent or other impaired water can be used to dilute seawater before it is fed to RO [20,21]. It is noteworthy that the direct mixing of such streams with seawater would be counterproductive because more pollutants can be introduced into the feed stream, thereby further limiting the effective processing of the seawater and impaired water. Thus, the use of FO can ensure that the seawater is efficiently diluted by the impaired water without direct mixing and this will have a significant energy reduction in the entire plant since less energy is needed to desalinate diluted seawater when compared with full strength seawater. There is no one-size-fits-all approach for lowering the energy requirements of FO desalination. The method to be used would depend on the nature of feed and draw solute, the type of FO membrane, and the scale of production. Efficient draw solution recovery is a key step and a sustainable application of FO for future desalination would most likely be achieved by the integration of FO with other desalination technologies. There are prospects of reduced energy requirements when the diluted saline draw of FO are used as feed in RO, MD, ED, MDC, and thermal distillation. Enhanced cost savings can be achieved in the future if diluted seawater from FO with lower osmotic potential is fed into full-scale RO plants.

In addition, water recovery from oily water sources via FO–MD process holds promising benefits for FO process cost in the future. More research and development of FO–MED to remove scaling ions could reduce cost of membrane replacement in the future. Other hybrid systems such as Multi-stage flash-FO (MSF-FO), ED-FO, MDC-FO, and MBR-FO hold great promise for removal of salinity and organics from water through FO. Improvements of draw solution to guarantee higher permeate flux and recovery rate through newly-developed draw solutions and membranes would also open a vista of new opportunities for future FO development. As against NaCl draw solute, the use of hydroacids complexes that can restrict reverse solute diffusion, CP-inhibiting micellar solutions, polymer hydrogels, simple-regenerative switchable polarity solvents, poly-electrolytes, and hydrophilic nanoparticles has ensured the attainment of impressive water fluxes (Fig. 8). Although these recently developed draw solutions could minimize CP and reverse salt transfer associated with NaCl, efforts to improve the lower flux and high regeneration energy required by them would be a significant boost

for future FO applications. Progress in recent efforts on the use of FO membranes to remove heavy metals and hazardous substances from water feeds such as boron would lead to the production of high-quality product water and ensure sustainable health. FO membrane replacement costs could be diminished through the reduction of membrane structural parameter by developing membrane support layers that would protect the active layer and overcome ICP. Recent efforts on the incorporation of nanomaterials and hydrophilic sulfonated polymers into TFC, and development of double skinned membranes hold promising alternatives for FO.

The use of FO as pretreatment for RO process would also reduce RO membrane fouling, which will further reduce the operation and maintenance cost of RO process because the energy needed for water transfer through FO membrane is almost negligible [165]. When compared with pressure-driven processes, the process constraints posed by membrane fouling to FO is less [72]. FO creates fewer problems with membrane cleaning, thus further reducing maintenance and operating cost. Like RO membranes, pathogens and large-sized particles are rejected by FO membranes. Therefore the combination of FO with RO ensures safe processing of the impaired water. However, biofouling could be a difficult problem. Nonetheless, the use of electrified membranes and results obtained from recent efforts aimed at the incorporation of functionalized nanoparticles with FO membrane are promising for bio-fouling control. FO does not leave carbon footprint like other pressure-driven desalination processes. In order to reduce the environmental impacts of FO desalination and prevent carbon emissions from the use of fossil-fuel energy in FO hybrid systems, the application of sustainable energy to desalinate and recover the dilute draw solution is a sustainable approach. Recent FO studies such as EDFORD, VHTR-FO, and use of concentrated solar energy to dewater polymer hydrogels [100] would have substantial impacts on greenhouse gas emission reduction and environmental preservation (since convectional petroleum fuels have not been used) if they are developed for large scale applications. The coupling of other renewable energy sources such as hydro, wind, and bioenergy with FO systems would be an attractive venture for future sustainable FO advancements if low process costs would be achieved. Therefore, FO has the potential to produce clean water more sustainably, when the right operating conditions are used.

Also, the creation of different pilot plants to test the available research data on FO would be necessary to optimize the FO process for commercial desalination processes. The first commercial FO plant for direct seawater desalination has been set up by Modern Water in 2012 and is located in Al Najdah, Oman. The plant is currently under operation and has demonstrated significant savings in operating and capital expenditure, robust fouling resistant membranes, reduced consumption of chemicals and a lower carbon footprint than competing technologies such as multi-stage flash (MSF) distillation and conventional high pressure RO membrane systems [166]. In addition, domestic commercial-scale seawater FO desalination test facility is currently being built by California-based Trevi Systems in collaboration with Masdar Company for the production of 1500 m³ per day of potable water powered by solar energy in the United Arab Emirates (UAE). The project had shown that it can desalinate water at below 1 kWh/m³ and the water produced can meet the needs of around 500 homes. The pilot test plant will be located 90 km northwest of the capital city, Abu Dhabi – close to seawater and utilities from a nearby decommissioned desalination plant would be used [167,168].

5. Conclusions

This review has been conducted to evaluate the current trend in FO desalination processes and also the challenges that inhibit the large scale deployment of FO technology in desalination.

Publications from 2009 up to date are examined except in some cases where older studies are necessary in order to know how current developments have been influenced by past efforts and challenges in the characteristics that make FO a preferred desalination process. Thorough research and publications on FO for desalination, whether as a full-fledged process or in hybridization with other desalination technologies, have been carried out, but to advance from experimental studies to actual commercial and economically-viable implementations, the development of new and durable high-performing draw solutes and membranes is pivotal to attain sustainable FO applications. FO membranes that are chemically and mechanically stable, with features that can ensure minimal ICP, high water flux and negligible reverse solute flux are desired for the optimization of FO desalination process efficiency. The draw solutes for future FO desalination applications would be those that can be easily regenerated using minimum energy. For increased productivity, the ability of draw solutes to induce significantly high osmotic pressure, higher than that of traditional draw solutes, would be a critical factor. A highly porous membrane support layer will also be required to minimize ICP, and a highly selective membrane active layer will be required to curtail reverse solute diffusion. Reduction in FO membrane fouling would be enhanced when membrane support layers that can restrict the reverse flux of draw solutes considerably are developed. ICP can also be minimized using draw solute with small molecule/ion size; however, it can cause an increase in reverse salt diffusion. Therefore, a very important area that can open wide-ranging opportunities for FO desalination in the future is the minimization of reverse mobility of draw solute, while maintaining high water flux in the forward direction. Simultaneously, both draw solute properties and membrane characteristics essentially determine ICP, membrane fouling and reverse solute diffusion. Finally, the advancement of hybridized FO systems and incorporation of renewable energy into FO desalination for draw solution recovery and water production would enhance the sustainable applications of FO.

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