

# *A Review: Desalination by Forward Osmosis*

G.P. Syed Ibrahim<sup>1</sup>, Arun M. Isloor<sup>1</sup> and Erna Yuliwati<sup>2</sup>

<sup>1</sup>Membrane Technology Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Mangalore, Karnataka, India <sup>2</sup>Faculty of Chemical Engineering, Universitas Muhammadiyah Palembang, Palembang, Indonesia

## **1 Introduction**

Incessant population growth has elevated substantial anxieties on the sustainability of drinking water [1–4]. In the total global water distribution, only 2.5% is available as freshwater. Whereas the remaining 97.5% is present as saline water. Further, by 2025 around 1.2 billion people will reside in the water-stressed countries [5]. The drinking of unhygienic water will cause a variety of diarrheal diseases. Thus, production of drinking water with low energy consumption is one of the challenging tasks in this recent scenario, as it affects the nations' growth and economy. To produce clean water, thermal or membrane-based desalination technology can be adopted. However, the former technology is highly energy intensive, which requires 7–14 kWh/m<sup>3</sup> for seawater desalination whereas the membrane-based technology requires only 2–6 kWh/m<sup>3</sup> [6–8]. In recent days, reverse osmosis (RO) membranes have gained remarkable attention toward the production of drinking water from saline water [9]. The increased efficiency and easy access to the production of clean water has made RO indispensable in membrane science and technology. Nevertheless, there are some drawbacks such as membrane fouling and higher operating pressure (above 25 bar) with less freshwater recovery making the RO membranes less productive [10,11].

Forward osmosis (FO) is evolving as a pretreatment process for RO membrane desalination in terms of less energy consumption and is also used for some other applications such as controlled drug release [12], power generation [13], and food processing [14,15]. FO opens up the venue for the improvement of high water recovery, which will reduce the volume of desalination brine ultimately. Moreover, the reduced fouling, high water flux, and removal of various contaminants enhanced the FO membrane practical applicability [16,17]. A model FO membrane would have the qualities such as high water flux and salt rejection, chemical stability, high fouling resistance, and mechanical strength [18]. The schematic

representation of FO desalination process is represented in Fig. 1. Fig. 2 depicts the growing interest in FO desalination from 1965 to 2018 (by February) and also the application of FO in a different field. The increased number of publications indicate the potential use of FO membranes for desalination.

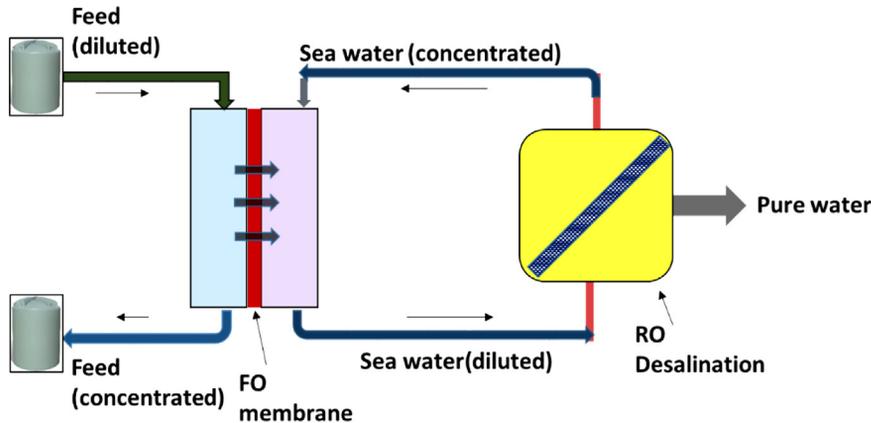


Fig. 1  
Schematic representation of FO desalination process.

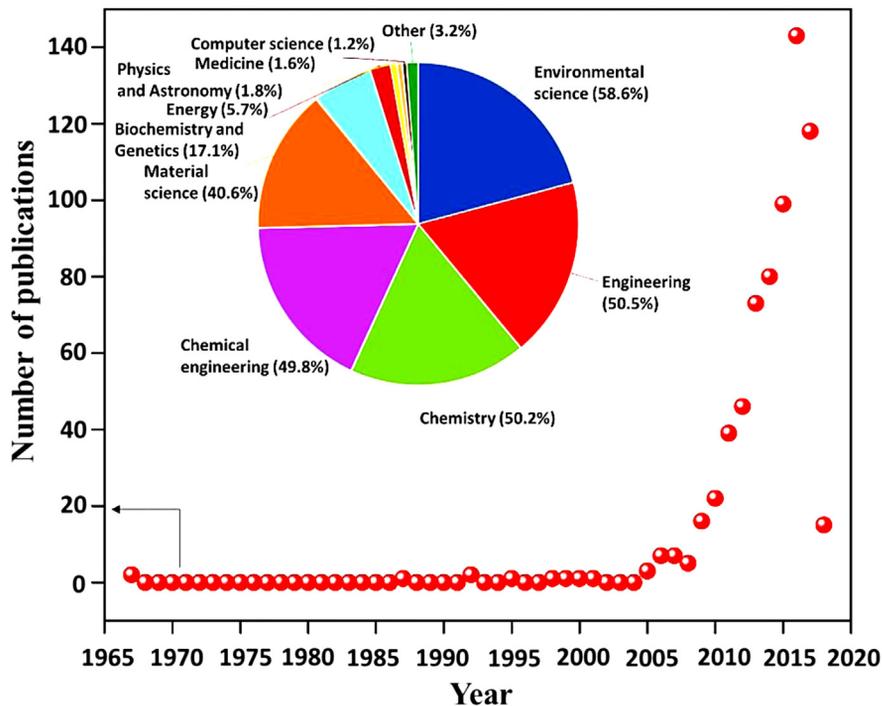


Fig. 2

The number of publications based on the key phase “desalination by forward osmosis” and the application of FO in different fields (inset) from the Scopus database as on February 18, 2018.

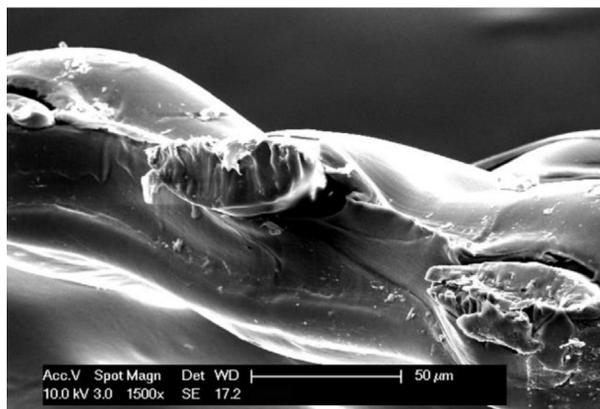
In this chapter, efforts have been taken to discuss the usage of different types of membranes for FO desalination application and their performance enhancement by suitable modification. In each section, the modifications or developments and challenges have been highlighted.

## **2 Forward Osmosis Membranes**

The correct choice of the membrane for FO still remains a major challenge for all researchers. Before the development of RO membranes by Loeb and Sourirajan in the 1960s, several types of membrane materials such as pig's bladder, porcelain, rubber, and collodion (nitrocellulose) had been employed. However, since the 1960s, RO membranes had been explored for FO applications [19]. Based on the preparation method and nature, the FO membranes can be classified as cellulosic membranes, thin-film composite (TFC), thin-film nanocomposite (TFN), and mixed matrix membranes.

### **2.1 Cellulosic Membranes**

The green polymer cellulose acetate (CA) was used by Loeb and Sourirajan for the preparation of asymmetric RO membranes [20,21]. CA derives from the acetylation of cellulose and as membrane material has many advantages such as comparative hydrophilicity, which is necessary to improve the water flux and reduce the fouling tendency, widespread availability, low cost, and mechanical strength. The commercial cellulose triacetate (CTA) FO membrane, which was developed by Hydration Technologies Inc. (HTI) exhibited higher water flux than commercial RO membranes. Still, Elimelech et al. (2006) reported that the water flux was around 80% less than that expected using HTI membrane [22]. The reason for the reduced water flux was attributed to the internal and external concentration polarization. The double-skinned CA flat sheet FO membranes with water flux of 48.2 L/m<sup>2</sup> h was reported by Wang et al. [23]. Nonetheless, the reverse solute flux was high, which holds back its practical applicability. In addition, the degree of acetylation and pH of the solution affect the CA membrane performances. For instance, the increase in the degree of acetylation decreases the water flux with increased solute rejection [24]. Further, at low or higher pH, it undergoes hydrolysis, which increases the pore size and porosity [25]. Thus the optimum operation pH of this kind of membrane was 4–6 [26]. As a result, the membrane performance in salt rejection was severely affected. Therefore, there are many reports in the literature for the improvement both of water flux and reduced reverse solute flux of cellulosic membranes. Nguyen et al. [27] prepared CA/CTA blend FO membranes, which exhibited higher water flux of 10.39 L/m<sup>2</sup> h and reverse solute flux of 0.084 mol NaCl/m<sup>2</sup> h [27]. On the other hand, the current market is predominantly dominated by the polyamide (PA) membranes over cellulosic membranes. Many efforts have been put forward to improve the PA membrane performances.



**Fig. 3**

SEM cross-sectional image of HTI FO membrane [28].

## 2.2 Polyamide Membranes

The typical TFC FO membrane comprises of top selective PA layer and porous sublayer. The TFC FO membranes exhibited high rejection to inorganic salt. At the same time, these membranes were distressed from reduced water flux due to severe internal concentration polarization (ICP) and increased reverse solute flux. The FO TFC membrane from HTI comprises of three parts with a whole membrane thickness of around 50 μm. The middle layer was sandwiched between the thin selective layer and loose supporting layer. The SEM cross-sectional image is shown in Fig. 3. Although this membrane demonstrated higher rejection of salt, the water flux was less. In another way, the TFC membranes are prepared using an amine and acid chloride via interfacial polymerization (IP) process, which was developed by Cadotte [29]. The first flat sheet TFC FO membranes were prepared by Elimelech's group using *m*-phenylenediamine and trimesoyl chloride on polysulfone (PSF) substrate via IP [30]. It was indicated that the perfect choice of solvent mixture and polymer composition led to the formation of mixed finger-like and sponge-like morphologies of the substrate. The properties of top PA layer and substrate are proven to affect the FO performances. The reverse solute flux and salt rejection are mainly controlled by the TFC top PA layer. Correspondingly, the substrate layer enhances the water permeability and affects the ICP. Thus, in recent times there is much research that has been carried out in terms of the effect of substrate and PA layer modification to improve the TFC FO membrane performances.

### 2.2.1 Effect of substrate

The representative PA-TFC FO membrane substrate should have the following characteristics, such as highly porous, thin, hydrophilicity, low tortuosity, and chemical and mechanical stability. The most commonly used polymeric materials for preparing PA-TFC RO substrate are PSF and polyethersulfone (PES) due to their pore size formed during the

phase inversion falls in the range of ultrafiltration (UF) to nanofiltration (NF) [31]. However, in case of PA-TFC FO membranes, PSF and PES as substrate are not tremendously used because these are thick, dense, and less hydrophilic in nature. Thus, it could intensify the ICP and decrease the osmotic driving force. As a result, the water flux will be less [32]. Therefore, the selection and modification of substrate becomes a vital part, since it affects the PA-TFC FO membrane performances. Considering the importance of PA-TFC FO membrane substrate, tailor-made PA-TFC membranes can be prepared.

Recently, electrospun nanofibrous membranes as the substrate are emerging owing to the fact that they have excellent mechanical strength and large surface-to-volume ratio. The usage of PSF/polyacrylonitrile (PAN) nanofibers as a substrate for preparing nanofiber-TFC (NTFC) FO membranes was demonstrated (Fig. 4; [33]). The main advantage of using nanofibers as substrate was due to their higher porosity, which reduced the contact angle

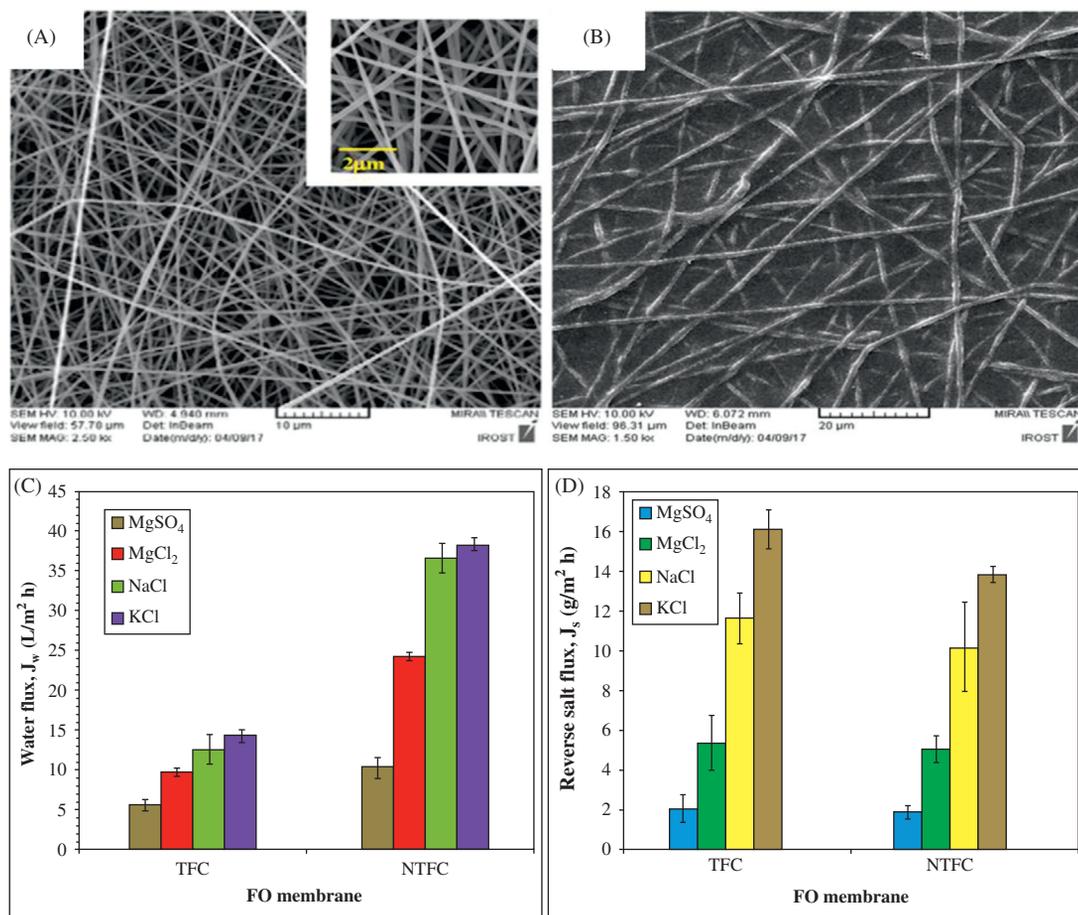


Fig. 4

SEM top surface of the (A) PSF/PAN nanofibrous substrate (inset-higher magnification), (B) NTFC membrane, (C) water flux, and (D) reverse solute flux of TFC and NTFC membrane [33].

(59.7 degrees) as well. It was understood that the solvent ratio played an important role in the optimization of substrate morphology. The solvents such as DMF, which has a higher vapor pressure of 513.28 Pa at 25°C, will evaporate fast during the course of electrospinning. Consequently, the obtained nanofibers were dry with weak adhesion between the fibers, which led to the disintegration of fibers from the spinning drum surface. Thus, NMP (vapor pressure 66.7 Pa at 25°C) was mixed with DMF to diminish the solvent evaporation. The optimum solvent ratio reported in this work was 50/50 NMP/DMF, which exhibited higher water flux of 37 L/m<sup>2</sup> h and reduced reverse solute flux of 0.32 L/m<sup>2</sup> h with nanofiber average diameter of 250–500 nm. In addition, the FO membrane exhibited reduced ICP, which was attributed to the higher porosity and reduced tortuosity of the nanofiber substrate.

The surface modification of the substrate is one of the feasible techniques to improve the PA-TFC FO membrane performances, as the hydrophilic substrates are not commercially available and very expensive. In the course of IP, the formation of meniscus shape between the organic and aqueous phase is controlled by the substrate layer hydrophilicity, which influences the PA-TFC membrane performances [34]. Further, the hydrophilic substrate is encouraged to use for FO process. This improved substrate hydrophilicity on the surface and inside the pores can efficiently suppress the ICP [35]. Han et al. modified the PSF substrate using bioinspired polydopamine (PDA) for preparing PA-TFC FO membranes (Fig. 5; [36]). The surface hydrophilicity was increased with increasing the PDA coating

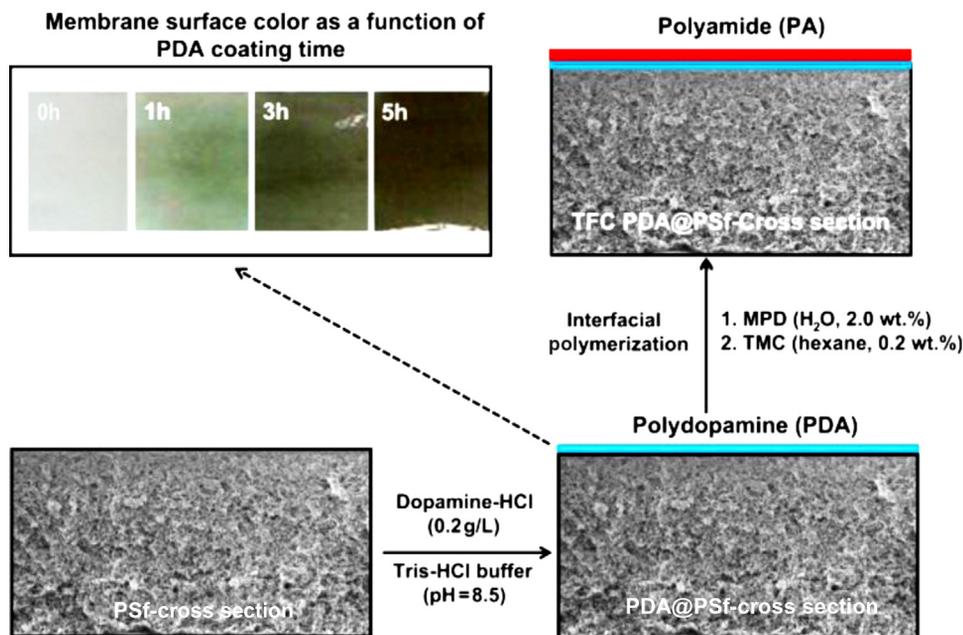


Fig. 5

Fabrication of PA-TFC FO membrane using PDA coated PSF substrate [36].

time. The lowest contact angle of 54 degrees was observed after 5 h of the coating. The increased surface hydrophilicity was ascribed to the penetration of dopamine (DA) molecules on the pore walls and deposits via self-polymerization. At the same time, the pore size of the substrate was reduced with an increased contact time of PDA, which affected the pure water permeability (PWP) of the substrate. Precisely, up to 1 h of PDA coating, the PWP was increased and started decreasing for the substrates coated for 3 and 5 hours. Besides, the surface roughness was also decreased with increasing PDA contact time due to the reduced pore size. The surface modified PA-TFC FO membrane revealed the reduced reverse solute flux. However, the increased time of PDA coating did not improve the water flux to a greater extent.

The incorporation of nanomaterials in the substrate is another approach to tailor the PA-TFC FO membrane properties. Tian et al. incorporated silica nanoparticles into polyetherimide nanofibrous substrate mainly to alleviate the ICP [37]. The as-prepared TFN FO membrane revealed the water flux of 42 L/m<sup>2</sup> h in FO mode and 72 L/m<sup>2</sup> h in PRO mode. The enhanced water flux was ascribed to the presence of silica nanoparticles, as there was an enhancement in the porosity and pore size of the substrate. The added silica nanoparticles improved the heat-press resistance of the nanofibrous substrate, which circumvented the porosity reduction and substrate compaction during heat-press. Addition of TiO<sub>2</sub> nanoparticles in the PSF substrate to fabricate TFN FO membrane was reported from the Ismail group [38]. The best-performed membrane exhibited the water flux of 18.81 L/m<sup>2</sup> h using DI water as feed and 0.5 M NaCl as draw solution (DS) in FO mode. In addition, the water flux of TFN membrane was reported as 8.1 L/m<sup>2</sup> h in FO mode and 13.8 L/m<sup>2</sup> h while using seawater as feed and 2 M NaCl as DS. The higher water flux was attributed to the reduced S value (0.39 mm). However, with 0.9 wt% of TiO<sub>2</sub> nanoparticles, the reverse solute flux started increasing. Layered double hydroxide nanoparticles were used as a nanofiller in the PSF substrate to fabricate the TFN FO membrane (Fig. 6; [39]). The TFN FO membrane demonstrated the highest water flux of 26.9 L/m<sup>2</sup> h as compared with the pristine membrane. The nanoparticles bestowed the higher surface hydrophilicity and porosity to the PSF substrate. Further, it mitigated the ICP by decreasing the substrate layer tortuosity through facilitating the formation of finger-like macrovoids. In another report, reduction of ICP using CaCO<sub>3</sub> nanoparticles as an additive to PSF substrate for the fabrication of TFN FO membrane [40]. As reported, the water flux and reverse solute flux were increased with the increase of nanoparticle concentration in PSF substrate in both FO and pressure retarded osmosis (PRO) mode. However, the structural parameter (S) was decreased to the minimum level of 525 μm, which is believed to decrease the ICP of TFN FO membrane. The TFN membrane, which was composed of 10 wt.% of CaCO<sub>3</sub> nanoparticles in substrate revealed the water flux of 25.4 L/m<sup>2</sup> h in FO mode using DI water as feed and 2 M NaCl as DS. Li et al. [41] addressed the ICP issue in FO by using the porous PES substrate [18]. The porous

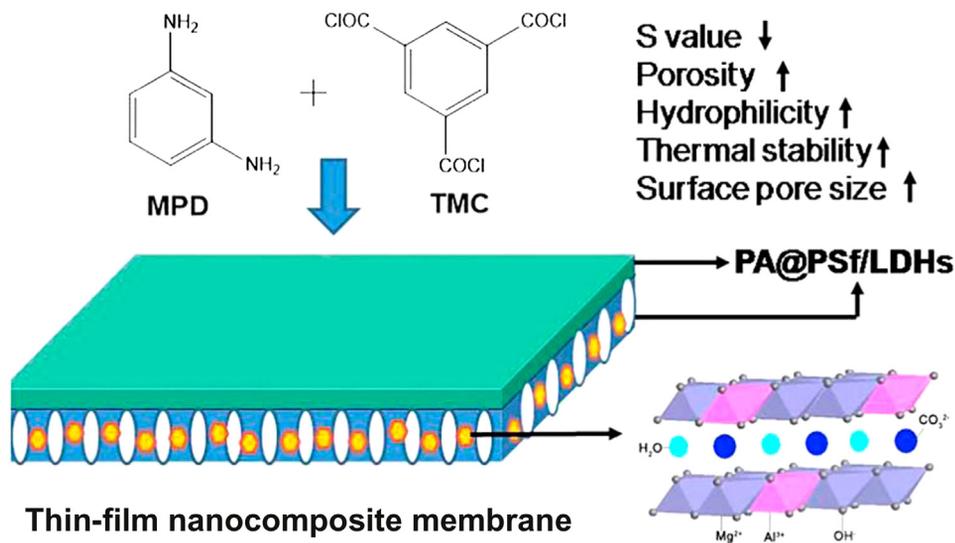


Fig. 6

TFN membrane with layered double hydroxide nanoparticles in the PSf substrate [39].

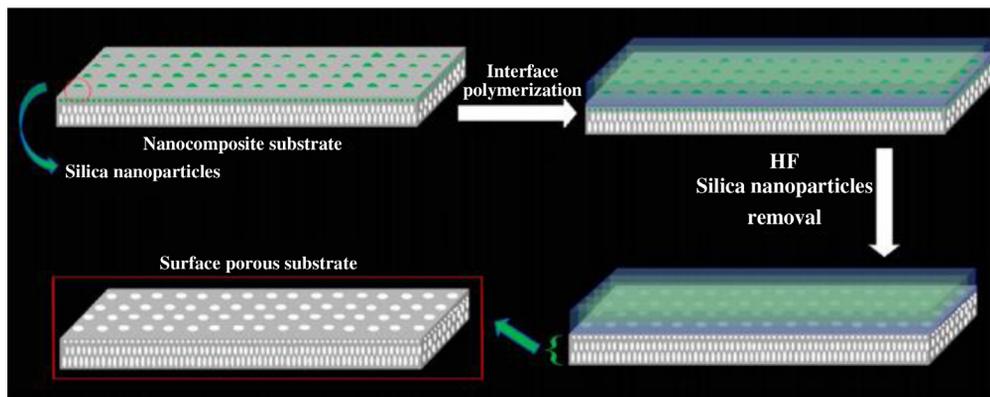


Fig. 7

Preparation of silica-templated TFC FO membrane [18].

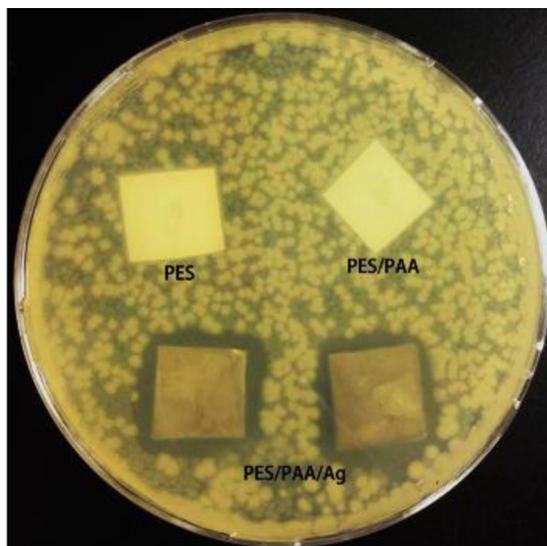
substrate was prepared by etching the encapsulated silica nanoparticles using hydrofluoric acid (HF). The water flux was improved after HF etching due to the formation of the porous and interconnected pore structure of the substrate, which favored the salt back diffusion in the substrate, and the S value was also decreased after etching. The schematic representation of silica-templated TFC FO membrane preparation is presented in Fig. 7.

### 2.2.2 Effect of polyamide layer modification

The PA layer in TFC or TFN FO membrane plays an important role in the determination of salt rejection and fouling resistance. Addition of metal–organic framework (MOF) encompassing silver (I) and 1, 3, 5-benzene tricarboxylic acid nanocrystals in PA layer to develop the structural properties and desalination performance of TFN FO membranes was proposed [42]. The surface hydrophilicity of the TFN membrane increased with the increase of nanocrystals loading. However, there was no significant change in the surface roughness, which emphasizes the good compatibility between the added nanocrystals and PA layer. The highest water permeability of  $7.1 \text{ L/m}^2 \text{ h bar}$  was observed with 0.08 wt.% MOF loading, which was 238% higher than the TFC membrane. The increased water permeability was owing to the influence of nanocrystals in the formation of disturbed polymer chain packing during IP process. The flux decline during the seawater desalination was only about 7% for the TFN FO membrane with higher flux recovery of 58%, whereas the TFC FO membrane exhibited the flux decline of 18% and flux recovery of only 43%.

Addition of  $\text{TiO}_2$  by Emadzadeh et al. [43] increased the water flux of  $26.41 \text{ L/m}^2 \text{ h}$  in FO mode using 10 mM and 0.5 M NaCl as feed and DS [43]. The increase in water flux was ascribed to the formation of “leaf-like” and “ridge and valley” structure on the addition of the nanoparticles. Nevertheless, a higher concentration of  $\text{TiO}_2$  decreased the salt rejection in RO mode due to the agglomeration of nanoparticles. The TFN FO membrane revealed the reverse solute flux of  $0.085 \text{ mol/m}^2 \text{ h}$  in FO mode and  $0.106 \text{ mol/m}^2 \text{ h}$  in PRO mode. It was also indicated that as-prepared TFN FO membrane demonstrated the increased antifouling property against organic foulant in the course of FO process with highest water flux recovery by a simple water wash. The enhanced surface hydrophilicity and negatively charged membrane surface were helped in increasing the antifouling property of the TFN membrane.

The two main factors, that is, ICP and microbial fouling in FO, were effectively alleviated using Ag/AgCl nanocomposite coating [44]. The nanocomposite membrane exhibited the improved water flux, which was owing to the presence of silver nanoparticles and AgCl. The nanocomposite formed hydrogen bond with water molecules and  $\text{Cl}^-$  and the ionic bond between the  $\text{Ag}^+$  and water molecules. As a result, the membrane contact angle was reduced, which contributed to the increased surface hydrophilicity. As the improved membrane hydrophilicity reduced the water transport resistance across the membrane, ICP of the FO membrane was decreased to result in the higher water flux. Further, the specific reverse water flux ( $J_s/J_w$ ) of nanocomposite membrane was less when compared with the pristine membrane. The antibiofilm ability of nanocomposite membrane was evaluated using *Escherichia coli* cells. The formation of biofilms on the membrane surface will lead to pore blockage and even membrane digestion. The results indicated that the pristine membrane was fully covered with *E. coli* cells, whereas only a few colonies of the *E. coli*



**Fig. 8**

Antimicrobial property of nanocomposite FO membrane [44].

cells were patterned on the membrane surface, which clearly indicated the antibiofilm nature of the membrane (Fig. 8).

### 3 Desalination

Seawater desalination using FO membrane has been recommended since 1965. The typical FO desalination process consists of osmotic dilution of DS and freshwater production from the diluted DS. Although several patents have been granted for desalination using FO [45–50], most of them are not feasible to implement in commercial scale. However, in recent times, as the commercial FO membranes are available, the desalination of seawater or brackish water using FO membranes has been invigorated. Recently, FO membrane performance towards the desalination was improved by modifying both the DS and FO membranes [51–54].

The FO membrane performance mainly depends on the property of the DS. The ideal DS should have the following characteristics: Provide high osmotic pressure (higher than the feed osmotic pressure), be inexpensive and nontoxic, provide easy recovery of the solute, be stable, and reduce ICP. The osmotic pressure of various DS as a function of concentration had presented by Cath et al. [19]. Therefore, appropriate selection of DS is a crucial part of the FO process. In literature various DS such as organic solutes, hybrid organic and inorganic nanoparticles, inorganic solutes, gas and volatile compounds are found.

In 1965, the usage of a volatile solute such as sulfur dioxide (SO<sub>2</sub>) in FO was described [48]. SO<sub>2</sub> was mixed to sea or freshwater to prepare the DS with high osmotic pressure. After the FO separation, the draw solute was removed by heating. Nonetheless, the data regarding the recovery of solute was not provided. Subsequently, McGinnis demonstrated the usage of SO<sub>2</sub> in combination with KNO<sub>3</sub> as draw solute for seawater desalination [55]. The SO<sub>2</sub> was recycled by distillation. However, the distillation of SO<sub>2</sub> is dangerous, as it is corrosive, volatile, and highly reactive with both oxidizing and reducing agents.

Later, the major breakthrough was achieved by using two highly soluble gases, such as ammonia (NH<sub>3</sub>) and carbon dioxide (CO<sub>2</sub>) as DS [5,22,56,57]. In the typical process, the DS was prepared by dissolving an appropriate quantity of NH<sub>3</sub> and CO<sub>2</sub> in water, which forms ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>). The as-formed NH<sub>4</sub>HCO<sub>3</sub> salt was a highly soluble and small molecule, and it could generate high osmotic pressure. It was stated that the higher average water recovery rate of 64% and low energy consumption of 0.25 kWh/m<sup>3</sup> were obtained by using this DS. Moreover, the recovery of these two gases was achieved by simple heating to around 60°C, where the NH<sub>4</sub>HCO<sub>3</sub> salt decomposes to NH<sub>3</sub> and CO<sub>2</sub> gases, which further separated from the water. On the other hand, the complete removal of NH<sub>3</sub> from the water still remains a serious concern. Thus, it may fail to fulfill the World Health Organization standards of drinking water, typically 1.5 mg/L [58].

To mitigate the above-said problem, usage of switchable polarity solvents (SPS) was established [59]. In the proposed strategy, the water miscibility and immiscibility of SPS were altered with CO<sub>2</sub>. According to Eq. (1) [59], the tertiary amine such as N,N-dimethylcyclohexylamine was immiscible in water. Conversely, in the presence of CO<sub>2</sub>, it becomes miscible by the protonation of a tertiary amine. The 7.6 mol/kg DS exhibited the osmotic pressure of 325 atm.



The maximum amount of FO studies had been carried out using inorganic solutes as DS, as these are nontoxic, low cost, and provide high osmotic pressure and water solubility [60]. The most studied inorganic salts are NaCl, KNO<sub>3</sub>, and NH<sub>4</sub>Cl as they exhibited higher water flux. Still, the usage of such inorganic materials led to severe reverse solute flux and finally, they should be removed by RO after the dilution of DS, which was highly energy intensive. To get rid of these difficulties, many types of novel DS have been proposed in the recent literature. A hybrid FO-NF in closed loop system with Na<sub>2</sub>SO<sub>4</sub> as DS was suggested by Kim et al. [61] for impaired water treatment. This hybrid system revealed the lowest operating cost, which was attributed to the lower DS loss and reasonably low cost of Na<sub>2</sub>SO<sub>4</sub>. Moreover, as Na<sub>2</sub>SO<sub>4</sub> can be easily removed from the water by NF, the process was highly energy efficient. DS containing the mixture of Triton X-100 and Na<sub>3</sub>PO<sub>4</sub> for mitigating the reverse solute flux during FO was investigated [62]. The results indicated

that the reverse solute flux of  $0.13 \text{ g/m}^2 \text{ h}$  was observed for the DS, which contains  $0.5 \text{ mM}$  Triton X-100 and  $0.55 \text{ M}$   $\text{Na}_3\text{PO}_4$ . The interaction of a tail hydrophobic group of Triton X-100 with FO membrane was ascribed to the decreased salt leakage. Further, the solute recovery was carried out using the two-stage UF-NF system and 98% of solute recovery was obtained.

A series of organic phosphonate salts (OPSs) used as novel DS in FO for oil–water separation [63]. The highest water flux of  $47\text{--}54 \text{ L/m}^2 \text{ h}$  was achieved with the negligible amount of reverse solute flux in PRO mode. Amongst the OPSs, tetraethylenepentamine heptakis(methylphosphonic) sodium salt demonstrated the higher flux at the concentration of  $0.5 \text{ mol/kg}$ . Finally, the solute recovery was attained above 92% via NF. In another approach, organic salts such as sodium acetate and sodium formate were screened as DS for FO performances [64]. The DS provided improved water flux and osmotic pressure. Yet, the water flux and osmotic pressure were improved while using NaCl as an additive to form the ternary DS mixture. However, the reverse solute flux was increased with increasing the concentration of NaCl.

Graphene oxide (GO) incorporated PA-TFN membrane was synthesized using PSF as substrate [65]. It was identified that the surface hydrophilicity was increased with the addition of GO in the PA layer, which was due to the presence of hydrophilic functional group such  $-\text{OH}$  and  $-\text{COOH}$  on the GO nanosheet. Further, while using the DI water as feed and  $1 \text{ M}$  NaCl as DS, the TFN membrane exhibited the water flux of  $34.7 \text{ L/m}^2 \text{ h}$  in PRO mode and  $14.5 \text{ L/m}^2 \text{ h}$  in the FO mode with  $0.1 \text{ wt.}\%$  of GO loading. The reverse solute flux was reduced up to 39%. Thus, the present TFN membrane is more suitable for FO applications in PRO mode. More detailed studies on the effect of FO membrane for improving the desalination performances have been discussed in Sections 2.1 and 2.2.

#### **4 Conclusions and Future Trends**

FO membranes have exhibited their versatility in many fields of science and technology. Especially in the field of wastewater treatment and seawater desalination, FO membranes play a vital role as an effective alternative to the conventional methods such as NF and RO. The effective FO membrane should have high water permeability, reduced ICP, stability, more selectivity, and high mechanical strength. Moreover, the DS must be nontoxic and able to bestow high osmotic pressure, energy efficient draw solute recovery, and decreased ICP. In this chapter, we have discussed briefly the several recent advancements in the FO membrane development and its application for desalination. Nevertheless, there is an urgent need for the development of both DS and FO membrane to overcome the difficulties in the moving from laboratory research to the practical applications. Overall, as the FO process is simple and cost-effective, FO technology will persist to play a vital role in wastewater and seawater desalination in the future.

## List of Acronyms

<b>CA</b>	cellulose acetate
<b>CTA</b>	cellulose triacetate
<b>DS</b>	draw solution
<b>DMF</b>	dimethylformamide
<b>ECP</b>	external concentration polarization
<b>FO</b>	forward osmosis
<b>IP</b>	interfacial polymerization
<b>ICP</b>	internal concentration polarization
<b>MPD</b>	m-Phenylenediamine
<b>MMM</b>	mixed matrix membrane
<b>MOF</b>	metal–organic framework
<b>NMP</b>	N-methyl-2-pyrrolidone
<b>PA</b>	polyamide
<b>PDA</b>	polydopamine
<b>PEI</b>	polyetherimide
<b>PRO</b>	pressure retarded osmosis
<b>PES</b>	polyethersulfone
<b>PAN</b>	polyacrylonitrile
<b>PSF</b>	polysulfone
<b>RO</b>	reverse osmosis
<b>TFC</b>	thin-film composite
<b>TFN</b>	thin-film nanocomposite
<b>TMC</b>	trimesoyl chloride

## References

- [1] T.-S. Chung, S. Zhang, K.Y. Wang, J. Su, M.M. Ling, Forward osmosis processes: yesterday, today and tomorrow, *Desalination* 287 (2012) 78–81.
- [2] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, *Science* 333 (6043) (2011) 712–717.
- [3] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Mariñas, A.M. Mayes, Science and technology for water purification in the coming decades, *Nature* 452 (7185) (2008) 301–310.
- [4] S. Zhao, L. Zou, C.Y. Tang, D. Mulcahy, Recent developments in forward osmosis: opportunities and challenges, *J. Membr. Sci.* 396 (2012) 1–21.
- [5] M. Elimelech, The global challenge for adequate and safe water, *J. Water Supply: Res. Technol. --AQUA* 55 (1) (2006) 3–10.
- [6] M.A. Anderson, A.L. Cudero, J. Palma, Capacitive deionization as an electrochemical means of saving energy and delivering clean water. Comparison to present desalination practices: will it compete? *Electrochim. Acta* 55 (12) (2010) 3845–3856.
- [7] R. Semiat, Energy issues in desalination processes, *Environ. Sci. Technol* 42 (22) (2008) 8193–8201.
- [8] S. Veerapaneni, B. Jordan, G. Leitner, S. Freeman, J. Madhavan, Optimization of RO desalination process energy consumption. International Paper Presented at the Desalination Association. World Congress, Singapore, 2005.
- [9] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination—development to date and future potential, *J. Membr. Sci.* 370 (1-2) (2011) 1–22.
- [10] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: water sources, technology, and today’s challenges, *Water Res.* 43 (9) (2009) 2317–2348.

- [11] B. Van der Bruggen, L. Lejon, C. Vandecasteele, Reuse, treatment, and discharge of the concentrate of pressure-driven membrane processes, *Environ. Sci. Technol.* 37 (17) (2003) 3733–3738.
- [12] F. Theeuwes, S. Yum, Principles of the design and operation of generic osmotic pumps for the delivery of semisolid or liquid drug formulations, *Ann. Biomed. Eng.* 4 (4) (1976) 343–353.
- [13] R.L. McGinnis, M. Elimelech, Global challenges in energy and water supply: the promise of engineered osmosis, *Environ. Sci. Technol.* 42 (23) (2008) 8625–8629. Available from: <https://doi.org/10.1021/es800812m>.
- [14] E.M. Garcia-Castello, J.R. McCutcheon, M. Elimelech, Performance evaluation of sucrose concentration using forward osmosis, *J. Membr. Sci.* 338 (1-2) (2009) 61–66.
- [15] K.B. Petrotos, H.N. Lazarides, Osmotic concentration of liquid foods, *J. Food Eng.* 49 (2-3) (2001) 201–206.
- [16] A. Achilli, T.Y. Cath, E.A. Marchand, A.E. Childress, The forward osmosis membrane bioreactor: a low fouling alternative to MBR processes, *Desalination* 239 (1-3) (2009) 10–21.
- [17] T.Y. Cath, N.T. Hancock, C.D. Lundin, C. Hoppe-Jones, J.E. Drewes, A multi-barrier osmotic dilution process for simultaneous desalination and purification of impaired water, *J. Membr. Sci.* 362 (1-2) (2010) 417–426.
- [18] J. Li, Q. Liu, X. Li, Y. Liu, J. Xie, Template-assisted fabrication of thin-film composite forward-osmosis membrane with controllable internal concentration polarization, *Ind. Eng. Chem. Res.* 55 (18) (2016) 5327–5334.
- [19] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: principles, applications, and recent developments, *J. Membr. Sci.* 281 (1-2) (2006) 70–87.
- [20] S. Loeb, S. Sourirajan, Sea water demineralization by means of an osmotic membrane, *Saline Water Conversion—II*, vol. 38, American Chemical Society, 1963, pp. 117–132.
- [21] (a) S. Sourirajan, T. Matsuura, *Reverse Osmosis & Ultrafiltration, Process Principles*, National Research Council Canada, Ottawa, 1985.  
(b) W.S.W. Ho, K.K. Sirkar, *Membrane Handbook*, Chapman & Hall, New York, 1992.
- [22] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, Desalination by ammonia–carbon dioxide forward osmosis: influence of draw and feed solution concentrations on process performance, *J. Membr. Sci.* 278 (1-2) (2006) 114–123.
- [23] K.Y. Wang, R.C. Ong, T.-S. Chung, Double-skinned forward osmosis membranes for reducing internal concentration polarization within the porous sublayer, *Ind. Eng. Chem. Res.* 49 (10) (2010) 4824–4831.
- [24] H. Lonsdale, U. Merten, R. Riley, Transport properties of cellulose acetate osmotic membranes, *J. Appl. Polym. Sci.* 9 (4) (1965) 1341–1362.
- [25] J.-H. Choi, K. Fukushi, K. Yamamoto, A submerged nanofiltration membrane bioreactor for domestic wastewater treatment: the performance of cellulose acetate nanofiltration membranes for long-term operation, *Sep. Purif. Technol.* 52 (3) (2007) 470–477. Available from: <https://doi.org/10.1016/j.seppur.2006.05.027>.
- [26] K.D. Vos, F.O. Burris, R.L. Riley, Kinetic study of the hydrolysis of cellulose acetate in the pH range of 2–10, *J. Appl. Polym. Sci.* 10 (5) (1966) 825–832.
- [27] T.P.N. Nguyen, E.-T. Yun, I.-C. Kim, Y.-N. Kwon, Preparation of cellulose triacetate/cellulose acetate (CTA/CA)-based membranes for forward osmosis, *J. Membr. Sci.* 433 (2013) 49–59.
- [28] S. Zhao, L. Zou, Effects of working temperature on separation performance, membrane scaling and cleaning in forward osmosis desalination, *Desalination* 278 (1-3) (2011) 157–164.
- [29] J.E. Cadotte, Interfacially synthesized reverse osmosis membrane: U.S. Patent 4, 277, 344, 1981.
- [30] N.Y. Yip, A. Tiraferri, W.A. Phillip, J.D. Schiffman, M. Elimelech, High performance thin-film composite forward osmosis membrane, *Environ. Sci. Technol.* 44 (10) (2010) 3812–3818. Available from: <https://doi.org/10.1021/es1002555>.
- [31] K. Boussu, C. Vandecasteele, B. Van der Bruggen, Study of the characteristics and the performance of self-made nanoporous polyethersulfone membranes, *Polymer (Guildf)*. 47 (10) (2006) 3464–3476.

- [32] J.R. McCutcheon, M. Elimelech, Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis, *J. Membr. Sci.* 284 (1-2) (2006) 237–247.
- [33] S. Shokrollahzadeh, S. Tajik, Fabrication of thin film composite forward osmosis membrane using electrospun polysulfone/polyacrylonitrile blend nanofibers as porous substrate, *Desalination* 425 (2018) 68–76.
- [34] A.K. Ghosh, E.M. Hoek, Impacts of support membrane structure and chemistry on polyamide–polysulfone interfacial composite membranes, *J. Membr. Sci.* 336 (1-2) (2009) 140–148.
- [35] N. Widjojo, T.-S. Chung, M. Weber, C. Maletzko, V. Warzelhan, A sulfonated polyphenylenesulfone (sPPSU) as the supporting substrate in thin film composite (TFC) membranes with enhanced performance for forward osmosis (FO), *Chem. Eng. J.* 220 (2013) 15–23.
- [36] G. Han, S. Zhang, X. Li, N. Widjojo, T.-S. Chung, Thin film composite forward osmosis membranes based on polydopamine modified polysulfone substrates with enhancements in both water flux and salt rejection, *Chem. Eng. Sci.* 80 (2012) 219–231. Available from: <https://doi.org/10.1016/j.ces.2012.05.033>.
- [37] M. Tian, Y.-N. Wang, R. Wang, A.G. Fane, Synthesis and characterization of thin film nanocomposite forward osmosis membranes supported by silica nanoparticle incorporated nanofibrous substrate, *Desalination* 401 (2017) 142–150.
- [38] D. Emadzadeh, W.J. Lau, T. Matsuura, A.F. Ismail, M. Rahbari-Sisakht, Synthesis and characterization of thin film nanocomposite forward osmosis membrane with hydrophilic nanocomposite support to reduce internal concentration polarization, *J. Membr. Sci.* 449 (2014) 74–85. Available from: <https://doi.org/10.1016/j.memsci.2013.08.014>.
- [39] P. Lu, S. Liang, L. Qiu, Y. Gao, Q. Wang, Thin film nanocomposite forward osmosis membranes based on layered double hydroxide nanoparticles blended substrates, *J. Membr. Sci.* 504 (2016) 196–205. Available from: <https://doi.org/10.1016/j.memsci.2015.12.066>.
- [40] W. kuang, Z. Liu, H. Yu, G. Kang, X. Jie, Y. Jin, et al., Investigation of internal concentration polarization reduction in forward osmosis membrane using nano-CaCO<sub>3</sub> particles as sacrificial component, *J. Membr. Sci.* 497 (2016) 485–493. Available from: <https://doi.org/10.1016/j.memsci.2015.06.052>.
- [41] D. Li, Y. Yan, H. Wang, Recent advances in polymer and polymer composite membranes for reverse and forward osmosis processes, *Prog. Polym. Sci.* 61 (2016) 104–155.
- [42] A. Zirehpour, A. Rahimpour, M. Ulbricht, Nano-sized metal organic framework to improve the structural properties and desalination performance of thin film composite forward osmosis membrane, *J. Membr. Sci.* 531 (2017) 59–67.
- [43] D. Emadzadeh, M. Ghanbari, W. Lau, M. Rahbari-Sisakht, T. Matsuura, A. Ismail, et al., Solvothermal synthesis of nanoporous TiO<sub>2</sub>: the impact on thin-film composite membranes for engineered osmosis application, *Nanotechnology.* 27 (34) (2016) 345702.
- [44] Q. Liu, J. Li, Z. Zhou, G. Qiu, J. Xie, J.Y. Lee, Dual-functional coating of forward osmosis membranes for hydrophilization and antimicrobial resistance, *Adv. Mater. Interfaces.* 3 (12) (2016).
- [45] B.S. Frank, Desalination of sea water: US 3,670,897, 1972.
- [46] D.N. Glew, Process for liquid recovery and solution concentration: U.S. Patent 3,216,930, 1965.
- [47] K. Lampi, E. Beaudry, J. Herron, Forward osmosis pressurized device and process for generating potable water: US 6,849,184, 2005.
- [48] G.W. Batchelder, Process for the demineralization of water: U.S. Patent 3,171,799, 1965.
- [49] K. Stache, Apparatus for transforming sea water, brackish water, polluted water or the like into a nutritious drink by means of osmosis: U.S. Patent 4,879,030, 1989.
- [50] J. Yaeli, Method and apparatus for processing liquid solutions of suspensions particularly useful in the desalination of saline water: U.S. Patent 5,098,575, 1992.
- [51] D.J. Johnson, W.A. Suwaileh, A.W. Mohammed, N. Hilal, Osmotic’s potential: an overview of draw solutes for forward osmosis. [Review], *Desalination* 434 (2018) 100–120. Available from: <https://doi.org/10.1016/j.desal.2017.09.017>.

- [52] S.S. Ray, S.S. Chen, N.C. Nguyen, H.T. Nguyen, N.P. Dan, B.X. Thanh, et al., Exploration of polyelectrolyte incorporated with Triton-X 114 surfactant based osmotic agent for forward osmosis desalination. [Article], *J. Environ. Manage.* 209 (2018) 346–353. Available from: <https://doi.org/10.1016/j.jenvman.2017.12.086>.
- [53] N. Song, X. Gao, Z. Ma, X. Wang, Y. Wei, C. Gao, A review of graphene-based separation membrane: materials, characteristics, preparation and applications. [Review], *Desalination* 437 (2018) 59–72. Available from: <https://doi.org/10.1016/j.desal.2018.02.024>.
- [54] W. Cheng, X. Lu, Y. Yang, J. Jiang, J. Ma, Influence of composition and concentration of saline water on cation exchange behavior in forward osmosis desalination. [Article], *Water Res.* 137 (2018) 9–17. Available from: <https://doi.org/10.1016/j.watres.2018.02.048>.
- [55] R.L. McGinnis, Osmotic desalination process: U.S. Patent 6,391,205, 2002.
- [56] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, A novel ammonia—carbon dioxide forward (direct) osmosis desalination process, *Desalination* 174 (1) (2005) 1–11.
- [57] R.L. McGinnis, M. Elimelech, Energy requirements of ammonia—carbon dioxide forward osmosis desalination, *Desalination* 207 (1-3) (2007) 370–382.
- [58] R. Ou, Y. Wang, H. Wang, T. Xu, Thermo-sensitive polyelectrolytes as draw solutions in forward osmosis process, *Desalination* 318 (2013) 48–55.
- [59] M.L. Stone, C. Rae, F.F. Stewart, A.D. Wilson, Switchable polarity solvents as draw solutes for forward osmosis, *Desalination* 312 (2013) 124–129.
- [60] L. Chekli, S. Phuntsho, H.K. Shon, S. Vigneswaran, J. Kandasamy, A. Chanan, A review of draw solutes in forward osmosis process and their use in modern applications, *Desalin. Water Treat.* 43 (1-3) (2012) 167–184.
- [61] J.E. Kim, S. Phuntsho, L. Chekli, J.Y. Choi, H.K. Shon, Environmental and economic assessment of hybrid FO-RO/NF system with selected inorganic draw solutes for the treatment of mine impaired water, *Desalination* 429 (2018) 96–104. Available from: <https://doi.org/10.1016/j.desal.2017.12.016>.
- [62] H.T. Nguyen, S.-S. Chen, N.C. Nguyen, H.H. Ngo, W. Guo, C.-W. Li, Exploring an innovative surfactant and phosphate-based draw solution for forward osmosis desalination, *J. Membr. Sci.* 489 (2015) 212–219. Available from: <https://doi.org/10.1016/j.memsci.2015.03.085>.
- [63] Q. Long, L. Shen, R. Chen, J. Huang, S. Xiong, Y. Wang, Synthesis and application of organic phosphonate salts as draw solutes in forward osmosis for oil-water separation. [Article], *Environ. Sci. Technol.* 50 (21) (2016) 12022–12029. Available from: <https://doi.org/10.1021/acs.est.6b02953>.
- [64] J.Y. Law, A.W. Mohammad, Multiple-solute salts as draw solution for osmotic concentration of succinate feed by forward osmosis. [Article], *J. Ind. Eng. Chem.* 51 (2017) 264–270. Available from: <https://doi.org/10.1016/j.jiec.2017.03.011>.
- [65] S. Shokrgozar Eslah, S. Shokrollahzadeh, O. Moini Jazani, A. Samimi, Forward osmosis water desalination: fabrication of graphene oxide-polyamide/polysulfone thin-film nanocomposite membrane with high water flux and low reverse salt diffusion, *Sep. Sci. Technol.* 53 (3) (2018) 573–583. Available from: <https://doi.org/10.1080/01496395.2017.1398261>.