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Abstract

Forward osmosis (FO) is a technical term describing the natural phenomenon of osmosis: the transport of water molecules across a semi-permeable membrane. The osmotic pressure difference is the driving force of water transport, as opposed to pressure-driven membrane processes. A concentrated draw solution (DS) with osmotic pressure draws water molecules from the feed solution (FS) through a semi-permeable membrane to the DS. The diluted DS is then reconcentrated to recycle the draw solutes as well as to produce purified water. As a major disadvantage, nature of FO membranes (asymmetric structure) causes internal concentration polarization (ICP) which promotes the decrease in water flux. Therefore, the number of studies related to improving both active and support layers of FO membranes is increasing in the applications. The purpose of the chapter is to bring an overview on the FO membrane manufacturing, characterizing and application area at laboratory or full scales. This chapter is published in two parts. In the first part, which appears here, the overview of membrane technologies and the definition of forward osmosis process are stated. The manufacturing methods of support and active layers forming FO membranes are described with common and/or new modification procedures.

Keywords: forward osmosis, water flux, reverse salt flux, active layer, support layer, thin film composite, structural parameter, porosity, internal concentration polarization

1. Introduction

Membrane separation processes have been widely applied for many years in environmental, industrial applications, and domestic use such as water/wastewater treatment, desalination, specific industrial purposes and energy recovery. Among the concentration-driven processes, FO
has recently attained many attractions due to its advantages such as less energy requirement, lower fouling tendency or easier fouling removal and higher water recovery. However, all drawbacks of FO process such as; (i) membrane fouling originated from ICP, (ii) lower flux, and (iii) reverse salt diffusion (RSD) limit the performance of the FO applications in environmental studies. Moreover, “necessity of concentrate management” and “meeting of discharge standards with high amounts of product water” oblige the developing new processes, membrane materials or modifications and finding new DS. In recent studies, developing new FO membranes by optimization of thickness, porosity, tortuosity of active/support layer of FO membrane to increase water flux and decrease ICP are mainly focused.

FO is a technical term describing the natural phenomenon of osmosis: the transport of water molecules across a semi-permeable membrane. The osmotic pressure difference is the driving force of water transport, as opposed to pressure-driven membrane processes A concentrated DS with osmotic pressure draws water molecules from the FS through a semi-permeable membrane to the DS. The diluted DS is then reconcentrated to recycle the draw solutes as well as to produce purified water. As the driving force is only the osmotic pressure difference between two solutions which means that there is no need to apply an external energy, this results in low fouling propensity of membrane and minimization of irreversible cake forming which are the main problems controverted by membrane applications-especially- in biological treatment systems (e.g. FO-MBR). However, nature of FO membranes (asymmetrical structure) causes ICP which promotes the decrease in water flux. Therefore, the number of studies related to improving both active and support layers of FO membranes is increasing in the applications.

In this first part of chapter, advantages of FO over conventional membrane processes and main drawbacks originated from the nature of FO membranes are thoroughly stated by considering both review and research articles in the available literature. The book chapter consists of three main titles firstly including introduction section, the second of which states a literature survey on early definitions of diaphragm, membrane and selectivity phenomenon by considering about last two centuries. Basic principles of FO phenomenon is also expressed in this part. However, the special aspects of FO process are discussed in the third part in view of FO membrane properties. The water flow is mainly determined by the support layer, while the selectivity is by the active layer of FO membrane. Therefore, both support and active layer designing are overemphasized by addressing new materials, manufacturing methods and modification steps to overcome the main challenges of FO processes such as low water flux and concentration polarization phenomena causing the membrane fouling.

2. General aspects of membrane processes

2.1. Membrane technology

Systematic studies of the membrane phenomenon can be traced to the eighteenth century philosopher scientists. For example, Abb’e Nolet prepared an ‘osmosis’ word in 1748 to describe
water permeability through a diaphragm. Through the nineteenth century and beginning of the twentieth century, membranes were not used for industrial or commercial purposes, but they were used as laboratory tools to develop physical/chemical theories. For example, the measurement of solution osmotic pressure by membranes by Traube and Pfeffer was used by van’t Hoff in 1887 to improve the limit law, which describes the behavior of ideal diluted solutions; this work led directly to the van’t Hoff equation. At the same time, Maxwell and others used a perfectly selective semipermeable membrane concept in the development of the kinetic theory of gases [1].

Early membrane researchers have experimented with all sorts of diaphragms available for themselves, such as pigs, cattle or fish and sausage covers made of animal guts. Later, nitrocellulose membranes were preferred because they could be reproducibly produced. In 1907, Bechhold developed a technique for preparing nitrocellulose membranes of a graded pore size determined by the bubble test [2]. Other early workers, the technique of Bechhold and were introduced into the market of microporous nitrocellulose membranes at the beginning of the 1930s [3–5]. In the following 20 years, this early microfiltration (MF) membrane technology has expanded to other polymers, especially cellulose acetate. Membranes found their first important practice in drinking water testing at the end of the Second World War. Drinking water sources serving large communities in Germany and elsewhere in Europe were destroyed and filters were urgently needed to test water safety. The research effort to develop these filters, backed by the US Army, was later exploited by Millipore Corporation, the first and largest producer of US MF membranes. By 1960, elements of modern membrane science were developed, but membranes were used only in a few laboratories and small, specialized industrial applications. An effective membrane industry was not available and the total annual sales of the membranes for all industrial applications probably did not exceed US $ 20 million in 2003. There were four problems that prevented membranes from being widely used as a separation process: they were too unreliable, too slow, too unselective and too expensive. Solutions for each of these problems have been developed over the past 30 years and membrane separation systems have become more common [1].

The first discovery of the conversion of membrane separation into an industrial process from a laboratory appeared with defect-free, high-flux anisotropic reverse osmosis (RO) membranes produced by the Loeb-Sourirajan process at the beginning of the 1960s [6]. These membranes consisted of an ultra-thin, selective surface on a much thicker but more permeable microporous support providing mechanical strength. The flux of the first Loeb-Sourirajan RO membrane was 10 times higher than that of any available membrane, and this performance made the RO potentially a practical method for desalinating water. Loeb and Sourirajan’s work and large-scale research and development by the US Department of Interior Office of Saline Water (OSW) have been a pioneer in the commercialization of RO and this has been a major factor in the development of MF and ultrafiltration (UF) membranes. In addition, the development of electrodialysis was supported by OSW funding. With the development of these industrial applications of membranes, the development of
especially artificial kidneys, has been provided for medical separation procedures. Kolff et al. [7] demonstrated the first successful artificial kidney in Holland in 1945. It took about 20 years for technology to be applied to large-scale works, but these developments were completed in the early 1960s. Since then, the use of membranes in artificial organs has become an important life-saving procedure [1].

Currently, more than 800,000 people are protected with artificial kidneys and about 1 million of people who have undergone open heart surgery every year through a possible procedure by developing a membrane blood oxygenator. The sales of these devices easily exceed the total industrial membrane separation market. Another important medical application of membranes is for controlled drug delivery systems. An important figure in this area was Alex Zaffaroni, who founded Alza, a company dedicated to developing these products in 1966. Membrane techniques developed by Alza and his competitors are widely used in the pharmaceutical industry to improve efficacy and safety of drug delivery. Significant stages were recorded in the membrane technology of 1960–1980 period. Using the original Loeb-Sourirajan technique, other membrane production methods including interface polymerization and multilayer composite casting and coating were developed to produce high performance membranes. Membranes produced using these methods and containing thin layers of 0.1 μm or less are now produced by many companies. Along with the membrane type, membrane modules have been developed by working on the packing volume and the number of studies for increasing the membrane stability has increased. In the 1980s, large-scale installations involving MF, UF, RO and electrodialysis began to become widespread all over the world [1].

2.2. Conventional membrane processes

RO is primarily used to remove salts from brackish water or seawater while it can reject synthetic organic compounds. One of the latest developed membrane process, nanofiltration (NF), is used to soften fresh water and clear disinfection by-products (DBP) precursors. Electrodialysis is used to demineralize brackish and sea water and to soften fresh water. UF and MF are used to remove turbidity, pathogens and particles in fresh water. In the broadest sense, a membrane, a common element of all of these processes, can be defined as any barrier to the flow of suspended, colloidal or dissolved species in any solvent. Applicable size ranges for membrane processes are shown in Figure 1. Generally, the cost of membrane processing increases when the size of the solute is reduced. The ionic range in Figure 1 includes potable water solubles such as sodium, chloride, total hardness, maximum dissolved solids, and smaller DBP precursors. Macromolecular range includes large and small colloids, bacteria, viruses, and colors. The fine particle range includes particles that produce larger turbidity, most suspended solids, cysts, and larger bacteria. Membrane processes normally used in the ionic range can remove macromolecules and fine particles, but are not as cost effective as larger pore membranes due to some operational problems [9]. The comparison of the membrane properties with each other is given in Table 1.

RO is the tightest membrane process in liquid/liquid separation. In principle, water is the only substance passing through the membrane; essentially all dissolved and suspended material is rejected. The RO membranes with much larger pores are sometimes confused with
NF membranes. True NF rejects ions with more than one negative charge, such as only sulfate or phosphate, while passing single charged ions. NF also rejects uncharged, dissolved materials and positively charged ions according to the molecular size and shape. Finally, the sodium chloride (NaCl) rejection varies from 0 to 50%, depending on NF and the rejected feed concentration. In contrast, “loose RO” is an RO membrane with reduced salt rejection. Such membranes are highly effective for a range of applications where moderate desalination is acceptable and, therefore, the operating pressure and power consumption are significantly reduced. Therefore, the costs are reduced in cases where complete desalination is not required.

UF is a process in which all low molecular weights compounds (LMWC) are freely permeable, while the high molecular weights compounds (HMWC), such as proteins, and suspended solids are rejected. Therefore, none of the mono- and di-saccharides, salts, amino acids, organics, inorganic acids or sodium hydroxide are rejected. Microfiltration (MF) is ideally a process where only suspended solids are rejected, and even proteins pass free through the membrane.

A wide range of products using membranes, but water desalination uses more than 80% of all membranes having ever been sold. The remaining 20% is used for mostly milk processing, while the rest is sold for use with many different liquids. Some liquids are waste products and some of which are very expensive pharmaceutical products. Table 2 lists some typical applications and as seen in the table the permeate as well as the concentrate can be the desired product [10].
van’t Hoff’s semipermeable membrane, which he assumed to promote the dilution of aqueous solution theory, is a permeable barrier to water (solvent), which is completely impermeable to dissolved solutes. For this reason, removal of the solvents results in a model barrier for all membrane filtration processes where the solutions are retained (concentrated). Like all joining properties, osmotic effects are limited to liquid solutions. Since we know nature is a watery system, the following solvent is water. When pure water and a random aqueous solution come in contact with the environment through a semi-permeable membrane, pure water is “drawn” into the solution, as if to dilute it: Osmosis. As is well known, osmosis is extremely important for the functioning of life when understood as a transport phenomenon at the molecular level. Live cell walls are osmotic barriers with improved selectivity towards inorganic and organic solutes (“biological membranes”). The direction of osmotic water transport, irrespective of the nature of the solution, indicates that the solution has a lower free energy (potential) than pure water. Specifically, the effectiveness of the solvent must be reduced by the effect of the solute, since the model barrier is assumed to communicate only through solvent [11].

Forward osmosis, an evolving separation/desalination process, has received increased interest in both academic research and industrial development in the past decade [12]. In FO, a semi-permeable membrane is placed between two solutions of different concentrations: a concentrated DS and a more dilute FS. Using the osmotic pressure differential to provide water permeation through the membrane, FO may respond to some of the deficiencies of hydraulic pressure driven membrane processes such as RO [13].

<table>
<thead>
<tr>
<th>Membrane process</th>
<th>Reverse osmosis</th>
<th>Nanofiltration</th>
<th>Ultrafiltration</th>
<th>Microfiltration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Asymmetrical</td>
<td>Asymmetrical</td>
<td>Asymmetrical</td>
<td>Symmetrical</td>
</tr>
<tr>
<td>Thickness</td>
<td>150 μm</td>
<td>150 μm</td>
<td>150–250 μm</td>
<td>10–150 μm</td>
</tr>
<tr>
<td>Thin film</td>
<td>1 μm</td>
<td>1 μm</td>
<td>1 μm</td>
<td>1 μm</td>
</tr>
<tr>
<td>Pore size</td>
<td>&lt;0.002 μm</td>
<td>&lt;0.002 μm</td>
<td>0.2–0.02 μm</td>
<td>4–0.02 μm</td>
</tr>
<tr>
<td>Rejection of</td>
<td>HMWC, LMWC</td>
<td>HMWC</td>
<td>Macromolecules,</td>
<td>Particles</td>
</tr>
<tr>
<td>Glucose</td>
<td>Mono-, di- and</td>
<td>Polyvalent neg.</td>
<td>Clay</td>
<td>Bacteria</td>
</tr>
<tr>
<td>Amino acids</td>
<td>oligosaccharides</td>
<td>ions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane material(s)</td>
<td>CA</td>
<td>CA</td>
<td>Ceramic</td>
<td>Ceramic</td>
</tr>
<tr>
<td>Thin film</td>
<td>Thin film</td>
<td>PSO, PVDF, CA</td>
<td>PP, PSO, PVDF</td>
<td></td>
</tr>
<tr>
<td>Membrane module</td>
<td>Tubular,</td>
<td>Tubular,</td>
<td>Tubular,</td>
<td></td>
</tr>
<tr>
<td>Spiral wound,</td>
<td>Spiral wound,</td>
<td>Hollow fiber</td>
<td>Spiral wound,</td>
<td></td>
</tr>
<tr>
<td>Plate-and-frame</td>
<td>Plate-and-frame</td>
<td></td>
<td>Plate-and-frame</td>
<td></td>
</tr>
<tr>
<td>Operating pressure</td>
<td>15–150 bar</td>
<td>5–35 bar</td>
<td>1–10 bar</td>
<td>&lt;2 bar</td>
</tr>
</tbody>
</table>

Table 1. Comparing membrane processes [10].

### 2.3. Forward osmosis process
<table>
<thead>
<tr>
<th></th>
<th>Permeate</th>
<th>Concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO</td>
<td>Dyeing effluent</td>
<td>Clean water, BOD, salt, chemicals, waste products</td>
</tr>
<tr>
<td>Water</td>
<td>Low salinity water</td>
<td>Salty water</td>
</tr>
<tr>
<td>Whey</td>
<td>Low BOD permeate</td>
<td>Whey concentrate</td>
</tr>
<tr>
<td>Antibiotics</td>
<td>Salty waste product</td>
<td>Desalted, concentrated antibiotics</td>
</tr>
<tr>
<td>NF</td>
<td>Dyeing effluent</td>
<td>Clean, salty water BOD/COD, color</td>
</tr>
<tr>
<td>water</td>
<td>softened water</td>
<td>Waste product</td>
</tr>
<tr>
<td>Whey</td>
<td>Salty waste water</td>
<td>Desalted whey concentrate</td>
</tr>
<tr>
<td>Antibiotics</td>
<td>Clarified fermentation broth</td>
<td>Waste product</td>
</tr>
<tr>
<td>Bio-gas waste</td>
<td>Clarified liquid for discharge</td>
<td>Microbes to be recycled</td>
</tr>
<tr>
<td>Carrageenan</td>
<td>Waste product</td>
<td>Concentrated carrageenan</td>
</tr>
<tr>
<td>Enzymes</td>
<td>Waste product</td>
<td>High value product</td>
</tr>
<tr>
<td>Milk</td>
<td>Lactose solution</td>
<td>Protein concentrate for cheese production</td>
</tr>
<tr>
<td>UF</td>
<td>Oil emulsion</td>
<td>Oil free water (&lt;10 ppm) Highly concentrated oil emulsion</td>
</tr>
<tr>
<td>Washing effluent</td>
<td>Clarified water</td>
<td>Dirty water (waste product)</td>
</tr>
<tr>
<td>Water</td>
<td>Clarified water</td>
<td>Waste product</td>
</tr>
<tr>
<td>Whey</td>
<td>Lactose solution</td>
<td>Whey protein concentrate</td>
</tr>
<tr>
<td>Xantan</td>
<td>Waste product</td>
<td>Concentrated xantan</td>
</tr>
</tbody>
</table>

Table 2. Type of membrane process for several products (the shaded area representing the main product) [10].

Figure 2. Illustration of comparison between FO and RO processes [16].
The transport of water molecules from a semipermeable membrane to the concentrate/saline solution on the other side of the membrane is referred to a technical term as forward osmosis. Contrary to conventional pressure-driven membrane processes, no pressure is applied to the side of water or concentrated solution. The difference in osmotic pressure between the aqueous medium on both sides of the membrane serves as the driving force to transport the water. [14]. Concentrated solution (DS), which pulls water molecules, is diluted during the process. The diluted DS is then re-concentrated in order to separate the water from the DS with a suitable further process. Where appropriate, the re-concentrated solution can be used again as DS. [15]. The FO process is shown in Figure 2. The main advantages of FO are it is not operated

![Figure 3](image_url)

**Figure 3.** Annual number of publications on FO since 2006 until fourth quarter of 2017 (retrieved from science direct database search) (updated and adapted from Eyvaz et al. [16]).

![Figure 4](image_url)

**Figure 4.** The number of publication about FO studies different research topics since 2006 until fourth quarter of 2017 (retrieved from science direct database search) (updated and adapted from Eyvaz et al. [16]).
under any hydraulic pressure, that a wide range of pollutants can be rejected at a high level and have lower irreversible pollution than pressure-based membrane processes [17].

As a method for water desalination, FO has been investigated for about four decades [18] and many researchers have found that (i) the selection or development of (new) membrane materials [19, 20], (ii) determining the suitable DS [21] The understanding of the mechanism of pollution [22], (iv) the characterization of concentration polarization (CP) [23]. In these pure academic publications, the FO survey and the increasing tendency of various special topics have been shown in Figures 3 and 4 for the last 10 years. As seen in Figure 3, the number of researchers has been steadily increasing, and recent research has focused heavily on membrane properties and development [16].

3. Manufacturing of forward osmosis membranes

Currently used membranes are mostly asymmetric porous membranes [24, 25]. In asymmetric porous membranes, the structure and transport properties change across the membrane thickness. An asymmetric membrane normally consists of a dense layer of 0.1–1 μm thick and supported by a highly porous, 100–200 μm thick support layer [24]. The dense layer provides most of the selectivity for the membrane. The separation properties are determined by the chemical structure, the size of the pores (0.4–1 nm) and the thickness of the skin layer. It is believed that the porous substrate provides mechanical support for the thin and fragile selective layer and has little effect on the separation performance of the membrane. However, recently the effects of the chemical properties of the support layer (e.g., hydrophilicity/hydrophobicity) and pore structure (e.g., pore size and porosity) on composite membrane transport have been reevaluated [26–28].

In thin film composite (TFC) membranes, the porous support layer is generally an integrally skinned membrane formed by a non-solvent induced phase separation (NIPS) process. The skin layer is typically formed by either interfacial polymerization (IP) or dip coating followed by crosslinking [24]. The most common thin film chemistry for RO membranes is based on a completely aromatic polyamide (PA) formed by the IP of meta-phenylenediamine (MDP) and trimesoyl chloride (TMC). In contrast, the popular PA NF membranes are formed by IP of piperazine and TMC [29]. It is assumed that the dense selective layer formed by the IP is heterogeneous (20–200 nm) throughout the thickness and is highly cross-linked. The surface properties of a PA film are different from those of the PA dense layer because the polymer density is not uniformly distributed [30]. The PA dense layer is extremely negatively charged because acyl chloride groups are not completely converted to amide during the formation process; however, recent direct titration experiments have demonstrated the presence of both positive and negative fixed charges in the dense layer of composite PA NF membranes [31]. According to [28], Freger and Srebnik suggested that the fixed charge is not uniform and that the film is actually a “sandwich” with two oppositely charged layers [32].

The dense coating layer has been treated as a non-porous film in the past. More advanced identification techniques such as atomic force microscopy, scanning electron microscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy, electron spin resonance, nuclear magnetic resonance (NMR), small angle X-ray scattering, and molecular
dynamics simulations have been used to state the structure of the dense layer. In the literature [28], a highly cross-linked PA skin layer structure with sub-nanoscale pores (0.2–1 nm) and low porosity has been reported [33, 34].

Wang et al. [28] stated that mixed matrix membranes contain both organic and inorganic phases. The first mixed matrix membranes were produced to enhance the performance of the gas separation membranes by providing interconnected flow paths of materials with a high diffusion rate [35]. In aqueous separations, mixed matrix membranes are typically formed of a polymer matrix in which inorganic fillers are dispersed. Classically, micron-scale inorganic fillers (e.g., zeolites and silicalite) have been added to polymer membranes to create preferential flow paths for rapid transport of certain molecules [36]. When nanomaterials (e.g., metal and zeolites nanoparticles) are used as the inorganic filler, these membranes are called nanocomposite membranes [37].

Inorganic particles may be present throughout the thickness of a symmetric or integrally-skinned membrane or exclusively in the coating film of a composite membrane. Theoretically, mixed matrices add an additional degree of freedom to membrane production because the advantages of a particular filler material can be imbued into a bulk membrane material [35]. Mixed matrices have been used to enhance the mechanical and chemical stability of organic membranes and to add specific functionality to the interface of polymer membranes, such as desired degradation, reduced fouling or increased selectivity [38, 39]. Organic and inorganic hybrid membranes are very interested in using it as a new generation of membrane materials for water treatment. According to Wang et al. [28], scientists have begun to use nanoparticles TiO$_2$ [40], carbon nanotubes [41], zeolites [42], clay [43], nonporous amorphous silica [44] and such as, to increase the water flux.

In another study [45] a new nanocomposite FO membrane is designed to perform oil/water separation and desalination at the same time. This nanocomposite FO membrane consists of an oil-repelling and salt-rejecting hydrogel selective layer on the top surface of graphene oxide (GO) nanosheets grafted into a polymeric support layer (Figure 5). This selective layer demonstrates strong underwater oleophobicity, which leads to superior anti-fouling properties under various oil/water emulsions and ICP can be decreased by and can be significantly reduced by GO in view of membrane structural parameter (S) decrease by about 20%. Compared to the commercial FO membrane, this new FO membrane has a markedly low membrane fouling tendency, having higher removal rates for oils and salts (>99.9% in oil and >99.7% in multivalent ions) for treatment of simulated shale gas wastewater (Figure 6). These combined advantages will endorse this new FO membrane in the treatment of highly saline and oily wastewater.

Xu et al. [46] reported that the availability of suitable FO membranes is crucial for the development of FO technology. Problems such as high RSD, high concentration polarization (CP) and poor mechanical strength are frequently encountered in FO processes. Meanwhile, although FO tends to exhibit a lower membrane fouling than pressure driven membrane processes, fouling is still the most serious problem that adversely affects FO performance. To overcome these problems, many new FO membranes have been fabricated or ready-made membranes have been modified by means of surface chemistry in recent years [47].

Chung et al. [48] stated that a few comprehensive reviews on FO membrane development are available in the literature [12, 18, 49]. Basically, most FO membranes are fabricated with conventional phase inversion [49] and TFC by IP processes [50]. Each layer of FO membranes have
been investigated, but reverse solute diffusions (RSD) tend to be high [51]. Employing hydrophilic materials as substrates in FO membranes is crucial to increase water flux [52]. Recently, TFC-FO-membranes synthesized on nanofiber [53, 54] and multi-bore [20] surfaces with good mechanical properties have also been reported. Future R & D should focus on innovative membranes with low fouling and ICP. Until recently, double-skinned FO membranes with dense RO skin and a loose RO skin, have been promised reduced membrane fouling and ICP [55].

Xu et al. [46] declared that the FO membrane serves as a selective barrier to control the water transport and solute retention to maintain the separation efficiency. The initial attempt to use the RO membrane in the FO process faced with some operational limitations; such as low flux, due to the thick sponge-like substrate and compact support of the RO membrane hindering mass transfer and causing severe ICP within the support layer [28–30]. Hydration Technologies, Inc. (HTI) developed the first commercial FO membranes [56], one of which has a characteristic structure embedding a thin polyester mesh support in cellulose triacetate (CTA) (Figure 7). These membranes provide significantly better separation performance than commercially available RO membranes. In addition to the commercial CTA FO membranes, HTI has then introduced the TFC FO membrane to the market; The flux of the spiral element was twice that of existing CTA membranes. This is thought to be a new criterion in future studies on FO membranes [58]. However, FO membranes with superior water permeability and salt rejection are still subjects to be developed for commercialization of FO technology. SEM images of the other some commercial FO membranes are presented in Figure 8.

According to the research in literature, it is shown that the adjustment of the sub-layers is of great potential in tailoring PA-TFC membranes. In addition, the flexibility of PA-TFC membrane
Figure 6. The study of simultaneously deoiling and desalting shale gas wastewaters [45].

Figure 7. Cross-sectional SEM images of hydration technologies CA (the bar in each SEM image is 100 μm) (adapted from McCutcheon and Elimelech [57]).
structures has a positive effect on the improvement of the sub-layers, since each of the surface active and support layers can be individually constituted for a particular purpose (Figure 9) [59].

3.1. Support layer properties and manufacturing techniques

Li et al. [60] have recently reviewed recent researches on polymer and polymer composite membranes for RO and FO processes comprehensively. In one of these studies, a TFC FO flat membrane has a thin selective layer on top of a flat porous polymeric support that is produced by phase inversion with/without a thin nonwoven layer [50]. More recently, nanofiber mats with high porosity have been proposed as a support layer to reduce the ICP to a minimum [53, 54, 61]. Bucky-papers made from CNTs are also being tested as support layer candidates due to their flexibility, strength and high porosity, it is also recommended to investigate other low cost and high porosity materials such as metal oxide nanotubes [62]. Parallel to the studies with TFC flat plate modules, the number of research related to hollow fiber configuration is also increasing due to its advantages such as high packing density and enhanced flow

Figure 8. Cross-sectional SEM images for the (a) Osmonics CE, (b) Filmtec SW30 XLE and (c) Filmtec SW30 XLE, (d) Osmonics CE membrane with the fabric layer removed (the bar in each SEM image is 100 μm) (adapted from McCutcheon and Elimelech [58]).
pattern and self-supporting structure [20, 63]. Under the same drive force effect, higher fluxes were obtained with hollow fiber membranes than with flat sheet membranes [64].

Similar to the characteristics of the support layers required to produce high performance PA TFC RO membranes, it is desirable that the support layers of the TFC FO membranes have high hydrophilicity, stability and mechanical strength, [65]. In addition, resistance to chemicals, temperature and oxidation, as well as low fouling tendencies, increase the potential use of FO membranes in harsh industrial environmental conditions. [66]. However, the thin support layer, high porosity, and low tortuosity will help reduce ICP [67]. For this reason, some of the research related to FO membranes have focused on support layer fabrication and modification. In these studies, fabrication parameters such as optimization of polymer concentration, solvent composition and functional additives have been considered in the synthesis of the support layer [68]. For example, a simultaneous casting of two polymer solutions with a co-casting technique, a synthesized support layer has played an important role in reducing ICP, improving water flux and reducing reverse salt flux [69]. Furthermore, even the selection of non-woven fabrics underneath the polymeric support layer significantly affects the adhesion of the support layer polymer to this non-woven sheet. For example, selecting a fabric with high tortuosity, large thickness, and low porosity leads to an undesirable decrease in the water flux of the FO membrane. Moreover, the addition of foreign components to the substrate casting solution can help improve the substrate properties. For example, when lignin content is incorporated into the polysulfone (PSf) substrate, the bulk porosity enhanced, shorter diffusion pathway is provided and TFC membrane performance is improved [70]. By using diethylene glycol as a pore forming agent in the PSf/sulfonated poly (ether ketone)/N-methylpyrrolidone (NMP) casting solution, greater porosity and wider pore size distribution were obtained which reduced the resistance of the support layer to the solution and the reverse salt flux was also relatively controlled [65]. Addition of PEG to the preparation of the CAP substrate increased the connectivity
of the pores and prevented macrovoids, as well as positively interacted with the cast glass blade. The resulting support is suitable for high performance TFC FO membrane fabrication since it has a high porosity bottom and a tight top surface [52]. The result is that the TFC membrane with macrovoids (or finger-like structure) support facilitates mass transport and reduces ICP in FO [67]. However, these porous structures may become mechanically weak points in the membrane structure and may, in practice, worsen membrane separation under continuous water flow or backwash conditions [71]. The highly porous support can also increase the difficulty in forming an excellent active selective layer with the necessary mass transport properties [67]. However, the sponge-like structure of small pores surrounded by dense walls may be convenient to form an integral thin active layer and may exhibit better mechanical stability on the finger-like property; however, it increases resistance to mass transfer [64]. Experimental studies suggest that the ideal support with a sponge-like film on a finger-like substrate is very important in the fabrication of high-performance TFC FO membranes [50].

Recently, nanofiber support layers with scaffold-like and interconnected porous structures have been seen as promising alternatives to overcoming the disadvantages of sponge-like structures. The nanofiber supported PA TFC membranes exhibited much lower S (~80 μm) than a commercial HTI FO membrane (S = 620 μm) and thus with a low molarity (0.5 M NaCl) DS and a DI water as the FS, it has been observed that the water flux has increased by five times [72]. An FO membrane with tubular nanofiber support was manufactured for the first time in the study of Arslan et al. [53]. In the first stage of the manufacturing, the support layer (polyacrylonitrile (PAN) nanofiber) was coated on the hollow braided rope (backing layer) by electrospinning method. In the second step, the active layer called the TFC layer was coated on the formed nanofiber by the IP process. Schematic illustration of FO membrane manufacturing is shown in Figure 10 and SEM images are presented in Figure 11. The TFC layer is the main selective barrier that prevents the transfer of the salt to the diluted side and allows the water molecules to diffusion into the DS side.

According to aforementioned review [60], Han et al. [65] pointed out that the hydrophilicity and support layer thickness are critical parameters in controlling of water transport. It is reported that the TFC membrane with support layer which is completely sponge-like and has a hydrophilic upper surface, provides a higher water flux than a TFC membrane with support layer which is completely hydrophobic and has finger-like structure. In order to prepare or modify the support layer, hydrophilic materials such as sulfonated polysulfone (sPSf), sulfonated copolymer made of polyethersulfone (PES) and polyphenylsulfone (PESU-co-sPPSU), sulfonated poly(ether ketone), poly-dopamine (PDA) or poly(vinyl alcohol) (PVA) have been explored [73–75]. Emadzadeh et al. improved the mass transfer and reduced ICP by applying TFC on the PSF support layer containing TiO$_2$ thus increasing the water flow of the FO membrane [76].

Liang et al. [77] for the first time in the production of TFC-FO membranes, it has been proposed to use vertical porous substrates as a support layer. The addition of acetone in aqueous phase promotes IP on vertical porous substrates. Positron annihilation lifetime analyses indicated that new FO membranes in the study have thicker and dense selective layers than conventional FO membranes with asymmetric substrates. These new FO membranes have a low structural parameter, indicating a greatly reduced ICP effect.
The selective layer exhibits an unprecedented water flux up to 93.6 L/m².h (LMH) (Figure 12) when driven by a 2 M NaCl as DS. This performance is evidenced by the FO membranes reported in the literature and commercially available. The authors suggested according to the results that substrates with vertically oriented porous structure are ideal supports for
developing FO membranes with lower ICP and ultra-high water flux. Proposed lower ICP in vertically oriented porous layer compared with a tortuous sponge-like structure in FO membranes by means of salt concentration profile are illustrated in Figure 13 [77].

In a more recent study, Kwon et al. [78] produced a highly permeable and mechanically resistant TFC-FO membrane with a new support layer which has been already commercialized porous polyethylene (PE) membrane as the lithium ion battery separator. The very open and interconnected pore structure of the PE support, when combined with the thickness (~8 μm), is useful for alleviating the ICP, thus increasing the FO water flux. The use of a suitable plasma treatment and a surfactant in the PE support resulted in a stable formation of a PA permselective layer on the support by IP process. The prepared PE supported TFC (PE-TFC) membrane exhibited high water flux and low reverse salt flux performance due to its significantly low structural parameter. The performance values obtained in this study are also compared with other flux values in the literature (Table 3). The PE-TFC membrane has superior mechanical properties compared

Figure 12. (a) Water flux and (b) reverse salt flux of the FO membranes in a process mode of the selective layer facing the FS (VOPS: vertically oriented porous substrates) [77].

Figure 13. The salt concentration profiles of (a) VOPS-TFC and (b) PI-TFC FO membranes. \( \pi_D \) and \( \pi_F \) denote the osmotic pressure of draw solution and FS, respectively. \( \Delta \pi_{\text{ideal}} \) indicates the osmotic pressure difference between the bulk feed and the bulk draw solution. \( \Delta \pi_{\text{eff}} \) means the effective osmotic pressure driving force due to the presence of ICP effect [77].
to the much thicker commercial FO membrane due to the exceptionally high mechanical integrity of the PE support. The proposed strategy offers a new material platform for FO membranes with strong commercial potential and excellent performance and durability.

In another recent study on the support layer, Zhang et al. [90] manufactured hollow fiber FO membranes with improved thermal stability using IP process on the lumen side of the co-poly(phthalazinone biphenyl ether sulfone) (PPBES) substrate. The increase in water flow in the PPBES substrate also increased the flow in the FO membrane. IP preparation parameters such as solvent, monomer concentrations, reaction time and curing conditions have been shown to seriously affect the development of composite FO membrane properties. The water flux of composite FO membranes increased from 24.0 to 66.5 LMH without a significant change in salt flux/water flux ($J_s/J_w$) ratio when the draw solution temperature was raised from 23 to 85°C (Figure 14).

3.2. Active layer properties and manufacturing techniques

Li et al. [60] in their comprehensive review stated some recent applications on manufacturing or modifying active layer of FO membranes. Accordingly, the preparation of PA TF FO membranes is also similar to the preparation of TFC RO membranes. It is necessary to optimize the parameters such as the reaction time and the air drying duration and compositions of the monomers. Klaysom et al. [91] noted that both the surfactant additive and the drying of excess amine solution prior to the reaction are two critical parameters in PAN support preparation to control membrane properties. The addition of SDS increases polymerization and helps to form

<table>
<thead>
<tr>
<th>Membranes</th>
<th>S (μm)</th>
<th>$J_w$(LMH)</th>
<th>$J_s/J_w$ (g/L)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-TFC</td>
<td>161</td>
<td>41.9/45.1</td>
<td>0.50/0.49</td>
<td>[78]</td>
</tr>
<tr>
<td>PES hollow fiber-TFC</td>
<td>219</td>
<td>26.5/37.6</td>
<td>0.17/0.14</td>
<td>[64]</td>
</tr>
<tr>
<td>PAN flat sheet-TFC</td>
<td>350</td>
<td>28.8/36.3</td>
<td>0.10/0.13</td>
<td>[79]</td>
</tr>
<tr>
<td>Cellulose ester flat sheet-TFC</td>
<td>32</td>
<td>56.9/89.5</td>
<td>0.14/0.12</td>
<td>[52]</td>
</tr>
<tr>
<td>PESU-co+PPSU flat sheet-TFC</td>
<td>324</td>
<td>20.0/25.0</td>
<td>0.12/0.13</td>
<td>[80]</td>
</tr>
<tr>
<td>PTA-co-POD flat sheet-TFC</td>
<td>236</td>
<td>37.5/78.4</td>
<td>0.15/0.15</td>
<td>[81]</td>
</tr>
<tr>
<td>PSi/SiPO (50 wt% SPEK) flat sheet-TFC</td>
<td>381</td>
<td>16.0/32.0</td>
<td>0.28/0.19</td>
<td>[82]</td>
</tr>
<tr>
<td>PSU/SPEK (50 wt% SPEK) flat sheet-TFC</td>
<td>107</td>
<td>23.0/34.0</td>
<td>0.18/0.20</td>
<td>[65]</td>
</tr>
<tr>
<td>PES/SpES (50 wt% SpES) flat sheet-TFC</td>
<td>245</td>
<td>25.2/33.7</td>
<td>0.28/0.26</td>
<td>[83]</td>
</tr>
<tr>
<td>Polydopamine-coated PAI flat sheet-TFC</td>
<td>456</td>
<td>14.0/48.0</td>
<td>0.44/0.17</td>
<td>[84]</td>
</tr>
<tr>
<td>PSi-silica NPs flat sheet-TFC</td>
<td>216</td>
<td>31.0/60.5</td>
<td>0.24/0.26</td>
<td>[85]</td>
</tr>
<tr>
<td>PS-zéolite flat sheet-TFC</td>
<td>340</td>
<td>33.0/65</td>
<td>0.55/0.47</td>
<td>[86]</td>
</tr>
<tr>
<td>PS-LDH flat sheet-TFC</td>
<td>148</td>
<td>18.1/34.6</td>
<td>0.45/0.36</td>
<td>[87]</td>
</tr>
<tr>
<td>PES nanofiber-TFC</td>
<td>106</td>
<td>46.0/50.0</td>
<td>—</td>
<td>[72]</td>
</tr>
<tr>
<td>Nylon 6,6 nanofiber-TFC</td>
<td>—</td>
<td>21.0/27.0</td>
<td>0.24/0.44</td>
<td>[88]</td>
</tr>
<tr>
<td>PVDF nanofiber-TFC</td>
<td>193</td>
<td>22.0/31.0</td>
<td>0.17/0.43</td>
<td>[89]</td>
</tr>
</tbody>
</table>

Table 3. Comparison of the FO performance of RO-grade membranes (FS: DI water, DS: 1.0 M NaCl) [78].
a uniform and highly cross-linked PA film. Thus, the rate of salt uptake in this study increased from 57% to over 95%, and the decrease in permeability did not occur. On the other hand, the removal of the excess amine solution before interacting with TMC resulted in the formation of a less rough membrane with improved salt rejection [91]. Due to the ionic interaction between cetyltrimethylammonium chloride (CTAC) and m-phenylenediamine (MPD) in the aqueous solution, CTAC may alter the reaction of the monomers of the presence and polymer molecular aggregation. Increasing the CTAC content improves the formation of the linear PA structure and microcrystalline structure of the active layer, but consequently the water flux of the PA TFC hollow fiber membrane with PES support layer is reduced, despite the high reverse salt selectivity [92]. Thermal annealing after SDS/glycerol treatment on TFC FO membranes facilitates the removal of residual unreacted monomers from the surface of the active layer, increasing the free volume size/fractional free volume ratio and reducing the total membrane thickness; so that the water flux can be improved without losing the rejection performance of the membrane [52]. Another major problem encountered in FO processes is membrane fouling, although it is less severe and reversible compared to RO processes. The structures of the support layers also significantly affect the active layer properties and hence the fouling characteristics of the TFC FO membranes. Surfaces with high roughness and large leaf-like structures are more prone to foulant accumulation and exhibit a dramatic decline in flux through these membranes, making it more difficult to improve the flux by physical cleaning of the membrane [93]. When the TFC FO membrane surface is modified, for example by covalent attachment of PEG, the tendency of surface contamination is significantly reduced due to surface barriers that adsorb pollutants [74]. On the other hand, attachment of the functionalized silica on TFC membrane via covalent amide bonds between amine groups of functionalized nanoparticles and the carboxyl groups of the TFC surface improve the fouling resistance and reduce the BSA or alginate adhesion. This is explained by the presence of the tightly bound hydration layer and the reduction of the charged carboxyl groups on the TFC membrane surface [94].

A more recent research in the literature has produced nanoporous thin-film inorganic (TFI) FO membranes with a tetraethylorthosilicate-driven sol-gel process (Figure 15(a)). The produced
membrane was used for the removal of four typical ionic divalent heavy metals. In laboratory scale FO process, 69 LMH flux was obtained by using four heavy metal containing FS at pH 4.5 and 2 M NaCl as DS (Figure 15(b)). An average of 94% metal removal from the 200 mg/L FS solution was obtained. Since the hydrated ion diameters of the metals are smaller than the membrane pore size, the charge-interaction should be responsible for heavy metal rejection. Based on the classical Debye-Hückel theory and the Gouy-Chapman model, You et al. [95] have shown the importance of double-layer overlap in the membrane pore induced by electrostatic interaction between heavy metal ions and silica-made pore walls. Thus, the selectivity of the TFI membrane depends primarily on the function of the membrane pore size, the surface potential of the membrane pore wall, and Debye length (Figure 16). This study not only confirms the feasibility of the TFI membrane in the treatment of acidic heavy metal wastewater without pH adjustment, but it also suggests a simple theoretical scheme for better understanding and design of the charged membrane for FO applications.

Figure 15. (a) Schematic diagram of TFI membrane formation (SSM: Stainless steel mesh, TEOS: Tetraethylorthosilicate), (b) FO water flux obtained under AL-FS and AL-DS mode at initial heavy metal concentration of 200 mg/L and pH 4.5 ± 0.5 for TFI membrane (adapted from You et al. [95]).

Figure 16. Schematic illustration of proposed mechanisms for rejection of heavy metal ions in FO process based on charge exclusion effect within the pores of TFI membrane [95].
Salehi et al. [96] in their work, fabricated a new and highly efficient FO membrane by using electrostatic interaction on a porous support layer employing layer-by-layer (LbL) assembly of positive chitosan (CS) and negative GO nanosheets. The support layer was prepared by mixing the hydrophilic sulfonated polyethersulfone (sPES) and PES using the wet phase inversion process (Figure 17).

Various characterization techniques have been used to confirm that the LbL membrane has been successfully fabricated. The number of layers formed in the SPES-PES support layer was easily adjusted by repeating the CS and GO deposition cycles. A TFC membrane with the same SPES-PES support layer and PA active layer was also prepared to compare membrane performances. Water permeability and salt rejection of the fabricated membranes were obtained with two types of DS (including Na$_2$SO$_4$ and sucrose) for two different membrane orientations. The results showed that the membrane coated by a CS/GO double layer had a flow rate of 2–4 orders of magnitude as much as the TFC. By increasing the number of CS/GO double layers, the selectivity of the LbL membrane was improved. The newly fabricated LbL membrane showed better fouling resistance than the TFC in the FS containing 200 ppm sodium alginate as the foulant model (Figure 18).

Xu et al. [60] reported that generally, the flux obtained in the active layer facing draw solution (AL-DS) (PRO) configuration is higher than in the active layer facing feed solution (AL-FS) (FO) mode, but more fouling may occur in the PRO mode if the FS containing scalants/foulants is easily transported to the porous support layer. Two active layered hollow fiber membranes, one at the top of the high porosity support layer and one at the bottom, have been proposed by Wang’s group [97] so that scaling or fouling can be controlled without reducing water flux in the AL-DS mode. The hollow fiber membranes with RO and NF-like scales fabricated on a PAI support were subjected to high water flux and reverse salt flux values (41.3 and 5.2 LMH) using 2 M NaCl DS and DI as FS in AL-DS mode after IP reaction and polyethyleneimine (PEI) modification. In addition, the presence of the NF-like layer on the support layer can greatly increase the resistance to scaling in the AL-DS mode. A double-skinned hollow fiber membrane with CaHPO$_4$ scaling with a 2-hour backwash recovers 96% of the water flux while a hollow fiber membrane with a single RO selective layer has a recovery of 78% [97]. Recent studies have used polyelectrolyte LbL to form an NF-like skin in the support layer studies conducted without chemical modification, while PA-RO-like layers have also been formed. Since the resulting NF-like skin does not directly contact

![Figure 17. Schematic illustration of CS/GO LbL assembly procedure [96].](image-url)
the FS and support layer, it prevents the transport of pollutants such as humic acid, dextran and lysozyme and thus the pore clogging. As a result, for a double-skinned hollow fiber membrane, the decrease in water flux was less than 30% during 4 hours operation, whereas for RO layer hollow fiber membranes, this reduction was 30–40% when 200 ppm foulant was used [98].

4. Conclusions

The active layer of an ideal FO membrane must be very thin and dense to achieve high salt retention. In order for the membrane to be able to be operated for a long time and the internal concentration polarization to be low, the support layer should be thin, hydrophilic, porous and exhibit mechanical strength as possible. The hydrophilicity must be high so that high flux and low fouling can be achieved. According to the current studies, utilizing novel nanomaterials, substrates and layer-by-layer assumptions in manufacturing of FO membrane undoubtedly enhance the water flux, rejection of the pollutants and minimize the membrane fouling but using synthetic wastewater -generally- containing one model foulant or DI water as feed solution makes it difficult to predict how FO membranes will act in real wastewaters or harsh environmental conditions. Therefore working with complex foulants and real wastewaters to better understanding of membrane behaviors, using modeling tools for fouling prediction and new cleaning strategies are essential to mitigate intrinsic challenges of the FO membranes.

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

This work was supported by the Scientific and Technological Research Council of Turkey (TUBITAK), grant number: CAYDAG-113Y340.

Author details

Murat Eyvaz*, Serkan Arslan1, Derya İmer2, Ebubekir Yüksel1 and İsmail Koyuncu2

*Address all correspondence to: meyvaz@gtu.edu.tr

1 Environmental Engineering Department, Gebze Technical University, Gebze-Kocaeli, Turkey

2 Environmental Engineering Department, İstanbul Technical University, Maslak-İstanbul, Turkey

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