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EN-63AB FABRICATION AND COMPARISON OF RO-LIKE AND NF-LIKE FORWARD OSMOSIS MEMBRANES

Chen Jian Hong Eugene

SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
COLLEGE OF ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY

AY 2011/12
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Submitted by
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AY 2011/12
Abstract

Forward Osmosis (FO) technology is becoming popular due to its potential applications in many important fields and its numerous advantages. As such, there is a demand for high-performance FO membranes (i.e. high water permeability, A and low salt permeability, B). A few RO-like and NF-like membranes have been developed in literature and demonstrated good FO performance. Complicated influences of membrane properties on FO performance, depending on operational conditions were discussed in this study. To meet future FO applications, systematic comparison is necessary.

Thin film composite (TFC) membranes with tailored rejection layer were fabricated in the current study. Two types of high-performance FO membranes were prepared, by two steps. The resultant RO-like and NF-like FO membranes were tested and investigated on its performance and effect of separation properties on FO performance. The relationship of FO water flux between both the membrane water permeability and its salt rejection was demonstrated in the current study. While both membranes displayed good rejection with divalent ion solution, NF-like FO membrane had poor monovalent NaCl salt retention. Analysis from FO tests results also highlights NF-like FO membrane excellent FO performance with divalent ion draw solution. This study suggests that membrane optimization would allow better and efficient performance with different FO applications.
Acknowledgements

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List of Symbols

A  Water permeability, L/m².h.bar

Aₘ  Effective membrane area, m²

B  Salt permeability, m/s

Cᶠ  Bulk feed water concentration, kg/m³

D  Diffusion coefficient of solute, m²/s

Jₛ  Solute Flux, g/m².h

Jᵥ  Pure water flux, L/m².h

K  Solute resistivity, s/m

R  Salt rejection, %

s  Structural parameter, mm

t  Membrane thickness, m

Δπ  Osmotic pressure difference, bar

ε  Porosity, %

εₘᵢₜ  Effective porosity, %

σ  Reflection coefficient

τ  Tortuosity
Chapter 1: Introduction

1.1 Background

With increasing demand for new potable water supplies worldwide, membrane technologies have emerged as a cost-effective and a viable solution for various water treatments [1]. Membrane filtration was considered as an important separation property since last century [2]. The availability, efficiency and reliability of membrane systems have therefore significantly increased.

A membrane is a selective barrier [2] that allows the separation between two phases in a mixture. One of the phases will be allowed to pass through while the other is being rejected.

Various membrane structures (symmetric, asymmetric or composite) can be constructed with different formation methods. On the principle of mass transfer through the membranes, there are two categories of membranes, namely porous and non-porous. The mode of mass transfer (i.e. the water flux and the salt flux) in porous membranes is through convection. Particles or molecules greater in size than the pore size of the membrane will be sieve out and retain during filtration process [3]. Microfiltration (MF) and Ultrafiltration (UF) membranes are typical examples of porous membranes.

The solution- diffusion model controls the mass transfer through non-porous membranes. Transport is done firstly by the dissolution of the component to be transported, follow by diffusion through the membrane [3]. These non-porous membranes consist of nanofiltration (NF) and reverse osmosis (RO) membranes.

MF, UF, NF and RO are pressure-driven processes which uses hydraulic pressure to force water molecules through the membranes. While impurities are retained and concentrate in the feed water, the water that passes through the membrane is recovered as permeate or product. Both NF and RO non-porous membranes requires a much higher pressure to effect the water transport due to the much smaller membrane pore size. Due to small pore size, NF and RO membranes are capable of having better rejection with small molecules and ions. The table below summarises the properties of pressure-driven membranes.
Over the past century, these pressure-driven membrane processes have been studied and developed intensively. There is a growing significance of using membranes for the separation of solutes from solution in the water treatment process. Such membrane technologies are thus vital in the field of water treatment and recovery such as filtration and desalination [8]. In the recent years, forward osmosis (FO) has received increasing attention from researchers and has been seen as a great opportunity in various fields of water treatment.

Reverse osmosis (RO) is a process whereby an external pressure greater than the osmotic pressure is applied to the solution with higher solute concentration. The movement of the pure solvent is hence reverse; flowing from the region of higher solute concentration to an area of low solute concentration [4]. The typical RO membranes used can effectively reject solutes with dissolved ions.

More commonly, RO processes are used in water treatment processes such as seawater desalination and wastewater reclamation [7]. However, high amount of external hydraulic pressure is required to overcome the osmotic pressure of an aqueous feed solution. This results in a high operating cost [5]. Another disadvantage of RO is that the amount of clean water recovered from the process during seawater desalination is relatively low [6].

Similar to RO, FO uses a semi-permeable membrane to allow separation of water from dissolved solutes. FO, on the other hand, is an osmotically driven membrane process in which water diffuses through the semi-permeable membrane under an osmotic pressure difference across the membrane [8]. Little or no hydraulic pressure is required for the induction of water movement in the FO processes. The driving force is the difference in osmotic pressure between

Table 1. Typical properties of pressure-driven membranes [2].

<table>
<thead>
<tr>
<th></th>
<th>Microfiltration</th>
<th>Ultrafiltration</th>
<th>Nanofiltration</th>
<th>Reverse osmosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size (nm)</td>
<td>50–10 000</td>
<td>1–100</td>
<td>~2</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Water permeability (l/m²h·bar⁻¹)</td>
<td>&gt; 500</td>
<td>20–500</td>
<td>5–50</td>
<td>0.5–10</td>
</tr>
<tr>
<td>Operating pressure (bar)</td>
<td>0.1–2.0</td>
<td>1.0–5.0</td>
<td>2.0–10</td>
<td>10–100</td>
</tr>
<tr>
<td>MWCO (Da)</td>
<td>Not applicable</td>
<td>1000–300 000</td>
<td>&gt; 100</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>Targeted contaminants in water</td>
<td>Bacteria, algae, suspended solids, turbidity</td>
<td>Bacteria, virus, colloids, macromolecules</td>
<td>Di- and multivalent ions, natural organic matter, small organic molecules</td>
<td>Dissolved ions, small molecules</td>
</tr>
<tr>
<td>Membrane materials</td>
<td>Polymeric, inorganic</td>
<td>Polymeric, some inorganic</td>
<td>Thin-film composite polyamide, cellulose acetate, other materials (Schafer et al., 2005)</td>
<td>Thin-film composite polyamide, cellulose acetate</td>
</tr>
</tbody>
</table>
the feed and draw solution. Draw solution is the solution on the permeate side of the membrane which has a higher osmotic pressure than the feed solution [8].

Due to the osmotically-driven principles, the use of FO has exhibited much advantages compared with the pressure-driven membrane process - FO applications have a low energy advantage [9]. Moreover, FO processes show high rejection for a wide range of contaminants [13, 14], possess lower fouling propensity, better fouling removal [10-12] and higher water recovery [15, 16].

1.2 Problem statement

Although FO processes have been widely suggested and integrated in many applications, the viability of FO technology still faces a number of critical challenges. There is still a lack of high performance FO membrane with respect to concentration polarization phenomenon, membrane fouling, reverse solute diffusion, as well as improving the membrane development and formulating better draw solutions that can generate large osmotic pressures [17].

Recently, high performance FO membranes have been reported [18-22]. These membranes are developed in a two-step synthesis [22] which will be covered later in chapter 3: Methodology and Experiments. Thin-film composite (TFC) membranes allow individual membrane optimization of the substrate and the rejection layer [22, 24]. According to [22, 24], the fabricated TFC membranes achieved high salt rejection and water permeability.

Both RO-like and NF-like FO membranes are revealed in literatures [23-27]. Investigation on the effect of TFC polyamide layer fabrication conditions on FO performance was carried out [25]. By changing the monomers concentration used in interfacial polarization, the resultant polyamide rejection layer can be optimized to create better FO performance with different draw solution. From a review conducted by Peterson [24], TFC FO membranes with RO-like layer are able to completely reject the solutes/ions similar to RO membrane. It is understood that a strong trade-off exists between TFC-based membranes separation properties (i.e. water permeability and salt rejection). On the contrary, TFC FO membranes with NF-like layer showed a good performance due to high water permeability in multivalent ions rejection such as MgCl₂. Therefore, this type of membrane has good potential for water treatment like water softening, or removal of industrial waste water containing heavy metals using FO process [26, 27].
The motivation behind this project is to help users to select the most suitable membranes for a given FO application by altering the synthesis and optimization of TFC FO membranes.

1.3 Objectives

The objectives of the project were to developed high-performance FO membranes with NF-like or RO-like rejection layer, which have different water permeability and salt rejection. Investigation on the FO performance of these two types will be carried out under different operating conditions; Guidance for membrane selection and optimization.

1.4 Scope of Work

This study will cover basic theory of water and solute transfer process in forward osmosis and discuss some critical FO challenges which are important to determine membrane selection and optimization. BY running the RO tests, a series of characterization was obtained to determine the NF-like and RO-like FO membranes’ solute rejection and pure water permeability. The FO water and reverse solute flux of the both NF-like and RO-like FO membranes will also be determined under active-layer facing draw solution and active-layer facing feed solution configuration over a range of draw solution concentration.
Chapter 2: Literature Review

2.1 Forward Osmosis

2.1.1 Working principle of Forward Osmosis

FO is an osmotically driven membrane process using semi-permeable membrane to separate water from dissolved solutes [8]. In the FO process, the membrane active layer can be placed facing either the feed or the draw solution. Rather than using hydraulic pressure differential (as in RO) for the transportation of water, FO uses the osmotic pressure differential ($\Delta\pi$) across the semi permeable membrane as the effective osmotic driving force [28]. No external pressure is applied across the membrane of the two solutions with different $\pi$. Osmosis equilibrium is reached when a final hydrostatic pressure difference is reached. This pressure difference is known as the osmosis pressure ($\Delta\pi$). This FO process results in the dilution of the originally concentrated draw solution and the concentration of the originally diluted feed solution [8]. According to Cath et al. [8], the equation that illustrates the general water transport in RO and FO is given as follows:

$$J_v = A(\sigma\Delta\pi - \Delta P)$$  \hspace{1cm} \text{Equation 1}

Where $J_v$ is the water flux across the membrane, $A$ is the water permeability coefficient of the membrane, $\sigma$ is the reflection coefficient, $\Delta P$ is the applied hydraulic pressure. The difference ($\sigma\Delta\pi - \Delta P$) represents the effective driving force [17]. As discussed earlier, FO process uses only osmotic pressure difference (between the draw and feed solution) to drive water across the membrane, thus, $\Delta P = \text{zero}$ (Figure 1). In FO, water flux can be expressed by:

$$J_v = A(\pi_{\text{draw}} - \pi_{\text{feed}})$$  \hspace{1cm} \text{Equation 2}

Where $\pi_{\text{draw}}$ and $\pi_{\text{feed}}$ are the osmotic pressure of the draw and feed solutions, respectively.
Concentration Polarization

ECP and ICP were studied systematically by this paper: Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis [5].

In both pressure driven and osmotically driven membrane processes, concentration polarization (CP) is a common and inevitable phenomenon [5, 8, 30-32]. As illustrated in Figure 2, CP in FO processes is caused by the concentration gradient from bulk solution to surface of membrane, as a result of accumulation of solute [17].

Two types of CP, namely external concentration polarization (ECP) and internal concentration polarization (ICP) [8] can take place in FO processes. Generally, ECP exists at the surface of the membrane active layer and ICP occurs within the porous support layer of the membrane.
2.2.1 External Concentration Polarization

When membrane porous support layer is facing the draw solution and feed solution flows on the active layer, there will be a build-up of solutes at the membrane active layer. This increases the concentration at the membrane surface and eventually, the osmotic pressure. As a result, the permeate flow of the osmosis process decreases. This is known as concentrative ECP phenomenon.

On the other hand, dilution of the draw solution arises when the draw solution flows on to the permeate side. Dilution by the permeate water reduces the concentration. Dilutive ECP happens when convective water flow drags the dissolved draw solute away from the membrane surface at the permeate side [5].

Figure 2. Illustration of both internal concentration polarization (ICP) and external concentration polarization (ECP) through an asymmetric FO membrane. ECP exist at the membrane surface while ICP occurs within the porous support. Figure adapted from [5].

(a) Active layer against the draw solution (AL-DS); the profile illustrates concentrative ICP and dilutive ECP.
(b) Porous support layer against the draw solution (AL-FS); the profile illustrates dilutive ICP and concentrative ECP.

(\(\pi_{D,b}\): bulk draw osmotic pressure, \(\pi_{D,m}\): membrane surface osmotic pressure on the permeate side, \(\pi_{F,b}\): bulk feed osmotic pressure, \(\pi_{F,m}\): membrane surface osmotic pressure on the feed side, \(\pi_{F,i}\): effective osmotic pressure of the feed in AL-DS orientation, \(\pi_{D,i}\): effective osmotic pressure of the draw solution in AL-FS orientation)
The effect of concentrative ECP is a reduced net driving force due to increased osmotic pressure at the membrane active layer interface on the feed side of the membrane. With dilutive ECP, osmotic pressure decreases at the membrane active layer surface on the draw solution side [17]. To minimize the accumulation of the rejected solutes on membrane surface, the cross-flow velocity or turbulence or velocity can be increased. Similarly, optimizing the water flux can mitigate the adverse effect of ECP [2, 8]. As such, ECP has lesser impact on FO performance than ICP.

2.2.2 Internal Concentration Polarization

Internal concentration polarization (ICP) is a significant problem in FO, being the main cause for the reduced flux [5, 33]. Figure 3 shows two types of ICP occurring in the FO process under different membrane orientation.

Concentrative ICP happens when the active layer of the membrane faces the draw solution (AL-DS) [7]. In the AL-DS orientation, shown in Figure 3(a), solutes in the feed solution enter the porous support layer and transport to the active layer. Due to the dense active layer, solutes are unable to penetrate through, leading to a build-up of the solutes. The phenomena occur within the porous layer. In comparison to the bulk feed water concentration, $C_f$, a much higher concentration on the membrane wall, $C_3$, is formed. The profile in Figure 3(a) illustrates the effects of the accumulation; a lower effective osmotic pressure difference $\Delta \pi_{\text{eff}}$ across the active layer as compared to the apparent osmotic pressure difference $\Delta \pi_{\text{app}}$, causing a reduced flux.
In the active layer facing feed water (AL-FW) orientation; dilutive ICP occurs within the membrane support layer as water penetrates through the active layer and dilutes the draw solution [5]. As illustrated in Figure 3(b), a decline in solute concentration happens from C5 to C4. This concentration decrease result in a reduced effective osmotic pressure difference, $\Delta \pi_{\text{eff}}$, and thus yielding a lower-than-expected water flux.

As ICP effects occur within the asymmetric membrane’s porous support layer, it makes much difficult to control and minimize as it cannot be overcome by changing the hydraulics flow in the membrane unlike ECP [33]. Since altering the hydrodynamic conditions cannot eliminate ICP, membranes need to be redesigned to suit the operation of FO system.

### 2.2.3 Modelling of ICP

According to classical solution-diffusion theory [4, 36, 37], effect of respective ICP on the water flux ($J_w$) can be expressed [37] by:

Concentrative ICP (AL–DS):

$$J_w = \frac{1}{K} \left[ \ln \frac{A\pi_{\text{draw}} - J_w + B}{A\pi_{\text{feed}} + B} \right]$$

Equation 3

Dilutive ICP (AL–FS):

$$J_w = \frac{1}{K} \left[ \ln \frac{A\pi_{\text{draw}} + B}{A\pi_{\text{feed}} + J_w + B} \right]$$

Equation 4

Where B is the solute permeability coefficient of the membrane, and K is the solute resistivity. K is a measure of solute transport into or out of the membrane support layer and it can reflect the degree of ICP in the support layer. Larger K values mean greater extent of ICP, leading to $J_w$ decline. K is expressed [7, 19] as:

$$K = \frac{\tau \varepsilon}{D}$$

Equation 5

Where t is the membrane thickness, $\tau$ is the tortuosity, $\varepsilon$ is porosity, $s$ is the structural parameter and $D$ being the diffusion coefficient of the draw solution. From equation 5, it is understood that both the membrane properties (the term $\frac{\tau \varepsilon}{D}$ or $s$) and characteristics of the draw solution ($D$) is an important intrinsic parameter of a membrane where it influences the ICP in the membrane support [5, 60].
To reduce the dominance of ICP, the only way is to limit flux or lower the solute resistivity, $K$ [5]. According to Elimelech’s group [5], diffusion coefficient of the draw solution need to be raised in order to lower the $K$ value. This can be done externally by increasing temperature or changing the draw solute. In addition, tailored membrane with a more porous support layer or a smaller thickness can help lower $K$ value.

2.3 Membrane fouling

Membrane fouling is another critical and inevitable phenomenon in FO processes. Early studies on membrane fouling, by Cath et al., reported that FO processes are less prone to membrane fouling [35]. However, in long term operations, fouling become obvious in FO [9]. Effects of such long term fouling will increase the resistance of membrane and thus causing an overall decline in membrane permeability. The FO fouling problem, was however, not considered in this study.

2.4 Reverse diffusion of solute

An ideal FO membrane would only allow water transfer while preventing leakage of dissolved draw solute into the feed solution. No matter how good the membrane barrier is, there will still be permeation of small quantities of dissolved solute across the membrane [41].

Due to the concentration difference in feed and draw solution, reverse diffusion of the draw solute through the membrane to the feed solution happens. Diffusion of draw solute first occurs through the support layer, opposing the convective flow of solvent. Upon entering into the interface between the porous and rejection layer, the draw solute partitions into the rejection layer and thereafter into the feed solution [41]. Reverse diffusion of solute (i.e. large $J_s$ value) is an important factor which can hinder FO performance [8, 38].

The specific reverse solute flux is introduced as a consideration for the evaluation of FO performance. It is defined as the ratio of the reverse solute flux to the forward water flux ($J_s/J_v$), a measure of membrane selectivity [38]. A higher ratio indicates a decrease in membrane selectivity and a reduced FO efficiency. A high ratio is due to the influence of severe draw solute leakage into the feed solution. A low water flux contributing from poor substrate structure (i.e. high $s$ value) as well as poor membrane separation properties (i.e. small $A$ value) would also bring about an undesirable high $J_s/J_v$ ratio [22, 58, 59]. Beside the promotion of
severe ICP, the effective osmotic pressure difference across the membrane would also be reduced as a result of increased solute reverse diffusion [62].

Studies from Lay et al. and Lee et al. have proven that reverse diffusion of the draw solute can aggravate FO fouling which leads to flux reduction, an important problem [39, 40]. Therefore, in some FO applications where high rejection is desired, multivalent ion solutions with lower diffusion coefficients is preferred [8]. Nonetheless, it is also critical to increase membrane selectivity of the active layer to minimize effects of solute reverse diffusion [62].

A review finding suggested that high selectivity of the membrane active layer can minimize the reverse solute diffusion, and thus improve FO performance [41]. Using a multivalent ion solution as the draw solution can also help minimize the reverse solute diffusion [38]. However, multivalent ion solutions may lead to a resultant higher ICP due to larger ion sizes and lower solution diffusion coefficients [34].

This problem is very important for this study, the comparison of NF-like and RO-like membranes. As such, reverse solute diffusion should be carefully considered. Greater efforts in the developments and selection of both FO membranes and draw solutes would be needed.

### 2.5 Draw solution development

The ideal draw solutes for osmosis-driven processes should have criteria such as: (1) having a relatively high osmotic pressure [8], (2) having an easy and economical recovery of the diluted draw solution [8, 42], (3) the draw solute should exhibit minimized ICP, (4) zero toxicity.

Many research efforts have been attempted to develop the ideal draw solutions. Very often, due to its high solubility, non-toxicity, and the ease of re-concentration, NaCl is used as draw solution [10, 15, 63]. According to Elimelech and co-workers [9, 28, 64], a draw solution of a water-soluble mixture of NH₃ and CO₂ containing ammonium bicarbonate (NH₄HCO₃) can promote high driving force thus leading to high water flux. A variety of both inorganic chemicals and organic compounds were also investigated as draw solutes in the studies [42, 60].

Recent attempts to develop draw solution to minimize reverse solute diffusion were carried using hydrophilic nanoparticles [65-67]. The problem is reduced as these nanoparticles solute cannot cross the membrane active layer. However, low osmotic pressures have been exhibited by the nanoparticle-based draw solutions for applications involving seawater desalination.
To reduce the effects of ICP, a draw solution with greater diffusion coefficients, lower viscosities and smaller ion sizes is generally preferred [34]. Better permeate fluxes can thus be expected. From the past investigations [9, 43-45], it is reviewed that the selection criteria of draw solution is critical to FO performance.

From the research by Achilli and team [60], it is understood that an increasing draw solution osmotic pressure will lead to greater water flux while reverse solute diffusion decreases with decreasing draw solution concentration due to decreasing driving force. In addition, the research also shown that draw solutions containing larger-sized hydrated anions, will have a lower reverse solute diffusion. This behavior will be important in the current study where various draw solutes have been used.

### 2.6 Development of FO membrane

An ideal FO membrane calls for high water permeability, A and low solute permeability, B as well as a support layer with high chemical and mechanical stability [8]. In addition, a membrane support layer with low resistance to mass transfer (represented by a structural parameter, s) and a high selective active layer are desired [17]. A highly porous and hydrophilic support with low tortuosity, lowers ICP, resulting higher water flux. A highly selective active layer improves the salt rejection and minimizes reverse solute diffusion.

<table>
<thead>
<tr>
<th>Year</th>
<th>Membranes</th>
<th>Materials</th>
<th>Preparation methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>Capsule wall membrane</td>
<td>Cellulose acetate or ethyl cellulose</td>
<td>Dip-coating, phase inversion</td>
</tr>
<tr>
<td>2007</td>
<td>Hollow fiber NF</td>
<td>Polyanhydridarate (PBA)</td>
<td>Dry-jet wet phase inversion</td>
</tr>
<tr>
<td>2008</td>
<td>Flat sheet cellulose acetate</td>
<td>Cellulose acetate</td>
<td>Phase inversion and then annealing at 80-95°C</td>
</tr>
<tr>
<td>2009</td>
<td>Dual-layer hollow fiber NF</td>
<td>PBI-PES/PVP</td>
<td>Dry-jet wet phase inversion (i.e. coextrusion technology)</td>
</tr>
<tr>
<td>2010</td>
<td>Hollow fiber</td>
<td>PES substrates, polyamide active layer</td>
<td>Dry-jet wet spinning and interfacial polymerization (IP)</td>
</tr>
<tr>
<td>2010</td>
<td>Hollow fiber NF</td>
<td>Cellulose acetate</td>
<td>Dry-jet wet spinning</td>
</tr>
<tr>
<td>2010</td>
<td>Flat sheet double-skinned</td>
<td>Cellulose acetate</td>
<td>Phase inversion, and then annealing at 85°C</td>
</tr>
<tr>
<td>2010</td>
<td>Flat sheet TFC membrane</td>
<td>Polysulfone (PSF) support, Polyamide active layer</td>
<td>Phase inversion and IP</td>
</tr>
<tr>
<td>2010</td>
<td>Double dense-layer membrane</td>
<td>Cellulose acetate</td>
<td>Phase inversion</td>
</tr>
<tr>
<td>2011</td>
<td>Modified RO</td>
<td>PSF support modified by polydopamine</td>
<td>Chemical coating</td>
</tr>
<tr>
<td>2011</td>
<td>Flat sheet composite</td>
<td>Cellulose acetate cast on a nylon fabric</td>
<td>Phase inversion</td>
</tr>
<tr>
<td>2011</td>
<td>Flat sheet composite</td>
<td>PDA/PAN supports, multiple PAA/PSS polyelectrolyte layers</td>
<td>Layer-by-layer assembly</td>
</tr>
<tr>
<td>2011</td>
<td>Positively charged hollow fiber</td>
<td>PAN substrate treated by PEI</td>
<td>Chemical modification</td>
</tr>
<tr>
<td>2011</td>
<td>Positively charged flat sheet</td>
<td>PAN substrate treated by PEI</td>
<td>Chemical modification</td>
</tr>
<tr>
<td>2011</td>
<td>Flat sheet TFC polyamide</td>
<td>PES/PSF substrate, Polyamide active layer</td>
<td>Phase inversion and IP</td>
</tr>
<tr>
<td>2011</td>
<td>Flat sheet TFC polyamide</td>
<td>PES/sulfonated polymer substrate, Polyamide active layer</td>
<td>Phase inversion and IP</td>
</tr>
<tr>
<td>2011</td>
<td>Flat sheet TFC polyamide</td>
<td>PSF support, polyamide active layer</td>
<td>Phase inversion and IP</td>
</tr>
<tr>
<td>2011</td>
<td>Nanoporous PES</td>
<td>PES cast on PET fabric</td>
<td>Phase inversion</td>
</tr>
<tr>
<td>2011</td>
<td>Cellulose ester membrane</td>
<td>Cellulose ester</td>
<td>Phase inversion</td>
</tr>
<tr>
<td>2011</td>
<td>Flat sheet TFC polyamide</td>
<td>PES nanofiber support, polyamide active layer</td>
<td>Electrospinning and IP</td>
</tr>
<tr>
<td>2011</td>
<td>Flat sheet TFC polyamide</td>
<td>PSF nanofiber support, polyamide active layer</td>
<td>Electrospinning and IP</td>
</tr>
</tbody>
</table>

Table 2. Recent developments of FO membrane [17].
In the past decade, there has been much advancement in membrane development. Table 2 shows an overview of these developments [17]. Currently, the only available commercial FO membranes are based on cellulose triacetate (CTA) developed by Hydration Technology Inc. (HTI, Albany, OR) [5, 36]

From the various advantages of cellulose and its derivatives, there is no doubt that it has been widely use to prepare RO and FO membranes via phase inversion. Cellulose acetate (CA) has a relatively high hydrophilicity that favors high water flux and low fouling propensity. Moreover, it possesses good mechanical strength and more resistance to chlorine degradation [46-48] when compared with TFC polyamide RO membranes.

Recently, Chung and co-workers have developed several cellulose ester-based membranes for FO applications, including both hollow fiber and flat sheet modules [48-51]. From his research, it is observed that, during the phase inversion, the interaction between the polymer and the casting substrate played an important role in the membrane structure formation [48, 51].

Nevertheless, cellulosic membranes still lack of high water permeability and salt rejection. FO membranes developed have poor resistance to thermal, chemical and biological degradation [46, 47, 52, 53].

To develop high performance FO membranes with high water flux and low salt passage, extensive efforts have been made. The use TFC membrane has been seen as a better approach towards high performance FO membranes [22]. There are much more flexibility in the optimization of the substrate and the rejection layer. Furthermore, better water permeability and solute rejection is expected from the polyamide rejection layer formed by interfacial polymerization [23, 24].

Wang’s group [18, 19] have developed thin film composite (TFC) FO hollow fibers with a RO-like selective layer. It was observed that sponge-like layer in the thin and highly porous FO substrate structure gave good FO performance [19]. Further, they also synthesized and characterized flat sheet TFC FO membranes with unique structures like straight finger-like pores under a thin sponge-like layer layer using PSf as the substrate [22]. They concluded that substrate structure played an important role in FO performance. More critically, the straight finger-like pore structure was preferred over the spongy pore structure due to the minimized ICP of the former [22].
More recently, Setiawan et al. fabricated a type of hollow fiber FO membrane with a positively charged NF-like selective layer by polyelectrolyte post treatment of a polyamide-imide (PAI) microporous substrate using polyethyleneimine (PEI) [26]. The chemically modified membrane showed reduced ICP and improved water flux in FO tests.

It is understood that FO performance on A and B values is non-linearly dependent [25]. It is however, dependent on the dominance mechanism; either fraction-loss-mechanism or back-diffusion enhanced internal concentration polarization (Js-enhanced-ICP) mechanism [25]. Generally, A value will be a critical constraint when fraction-loss mechanism dominates, e.g. membrane with low A value is used or system operates at low water flux level, etc. On the other hand, B value will be critical when Js-enhanced-ICP mechanism dominates, for instance, system operates at high water flux level or the membrane has high A value but very low B value, or is exposed to high concentration draw solution. There is always a trade-off of A and B values for the TFC FO membranes.

![Diagram of FO membrane and its properties](image)

Figure 4. Relationship between ICP, reverse solute diffusion, membrane fouling, the membrane characteristics and the draw solute properties in FO. Figure taken from [17].
From the discussion above, we can relate the relationship between the five key challenges in FO (Figure 4). The literature review highlights that a highly porous membrane support layer is desired to reduce ICP, and that the membrane active layer should be highly selective (i.e. high A and low B) to lower effects of reverse solute diffusion. Additionally, using a draw solution capable of generating large osmotic pressure can maximize the water flux. Together with a minimized reverse solute diffusion, a more effective and efficient FO process can be achieved.

The criteria for favorable draw solutes are more critical as small ion size can bring about a lower ICP [34] but a greater reverse solute diffusion. Generally, high reverse solute diffusion can cause severe membrane fouling, and vice versa [39, 40]. Moreover, ICP and membrane fouling may result in coupled adverse effects on water flux in FO [36]. At the same time, ICP, reverse solute diffusion and membrane fouling are fundamentally determined by both the membrane characteristics and the draw solute properties [17].

In this current study, we will compare the results of both RO-like and NF-like membranes’ water and salt fluxes in relation to their membrane selectivity and draw solutes of different osmotic pressures, concentrations as well as the ion sizes of dissolved salts.
Chapter 3: Methodology and Experiments

3.1 Chemicals for membrane characterizations

Unless otherwise specified, all reagents and chemicals used in the study were of analytical grade with purity over 99% and were used as received. Ultrapure water, supplied from a Milli-Q ultrapure water system (Millipore Singapore Pte Ltd) with a resistivity of 18.2 MΩcm, was used throughout the study. High grade salts (Merck KGaA) were used to make the draw solutions. These draw solutions include NaCl, Na₂SO₄, Na₂SO₅, Na₂SO₆, Na₂SO₇. For each draw solution tested, several osmotic pressures were evaluated.

3.2 Chemicals for preparing substrate

Polysulfone beads (PSf, molecular weight Mₗ ≈ 75000-81000 Da, SOLVAY Advanced Polymers) were used the membrane substrates preparation. N-methyl-2-pyrrolidone (NMP, Merck Schuchardt OHG) was used as the solvent for the casting solution. Polyethylene glycol (PEG, Samchun Pure Chemical Co. Ltd.) and lithium chloride (LiCl, Merck Schuchardt OHG) were used as additives in the casting solution.

3.3 Chemicals for preparing active rejection layer

Interfacial polymerization (IP) is done to synthesis the ultrathin active rejection layer of TFC FO membranes. For the interfacial polymerization step, chemicals used included m-phenylenediamine (MPD, Sigma-Aldrich), piperazine (Sigma-Aldrich), trimesoyl chloride (TMC, Sigma-Aldrich), and n-hexane (Merck KGaA).

3.4 Synthesis of flat- sheet TFC FO membrane

The flat sheet TFC FO membrane was prepared through a two-step process. Firstly, the membrane substrate was formed by phase inversion method. Next, interfacial polymerization step is carried out to form the active rejection layer on top of the substrate.
3.4.1 Fabrication of FO substrates

The preparation of the casting solution, dope, requires the dissolution of certain amount of PSf, PEG and LiCl in NMP. To ensure complete dissolution, solution was continuous stirred by magnetic stirrer, at 70°C until it was homogenous and transparent. After cooling down to room temperature (23°C), the dope would be degassed, in an air tight bottle overnight [22].

An Elcometer 4340 Motorised Film Applicator (Elcometer Asia Pte Ltd) was used to spread the dope onto a clean glass plate. Desired thickness of the film was set at 150 μm. The plate with the uniform film was then quickly and smoothly immersed into a coagulant bath containing tap water at room temperature (23 ± 1°C). This process induces phase separation. Residual solvent will be washed away, after the resultant PSf substrate was transferred from the coagulant bath to flowing tap water. The FO substrate was then stored in ultrapure water before use.

3.5 Formation of active rejection layer

The rejection layer of the TFC flat-sheet FO membrane is formed by interfacial polymerization. The synthesis of RO-like layer and NF-like layer employed interfacial polymerization of TMC with MPD and piperazine (PIP) respectively, as shown in Table 3. Both membranes were synthesized using the same PSf substrate.

Before the interfacial polymerization step, pre-casted PSf substrates were first heated in a hot Milli-Q water bath at 70°C for two minutes and cooled down to room temperature using cold water bath. This help to form a more compact and stable pore structure [25]. Large water droplets on substrate surface were removed with compressed nitrogen before soaking in aqueous MPD solution (RO-like layer) or PIP solution (NF-like layer) for two minute. Substrate surface was blown with compressed nitrogen to remove excessive MPD or PIP solution. It was followed with an interaction of n-hexane TMC solution for 1 minute to form the polyamide rejection layer. Subsequently, the excess TMC were drained off and after membrane surface is dry, resultant membrane was rinsed with tap water. After removing the residual reactants on the membrane, it would be stored in Milli-Q water before use.
Table 3. Synthesis conditions for RO-like and NF-like FO membranes.

<table>
<thead>
<tr>
<th>Rejection layer via interfacial polymerization</th>
<th>MPD (wt.%)</th>
<th>PIP (wt.%)</th>
<th>Water (wt.%)</th>
<th>TMC in n-hexane (wt./v%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO-like layer</td>
<td>1.5</td>
<td>-</td>
<td>98.5</td>
<td>0.1</td>
</tr>
<tr>
<td>NF-like layer</td>
<td>-</td>
<td>1.0</td>
<td>99.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 4. Structure and molecular weight of piperazine (PIP), m-phenylenediamine (MPD), trimesoyl chloride (TMC). Table adapted from [54].

3.6 Membrane characterization

Characterisations were performed to determine these membrane properties: membrane structure, porosity, contact angle, membrane intrinsic separation properties and FO performance.

3.6.1 Membrane structure and morphology

The structure and morphology of the FO membranes were observed using a Zeiss EVO 50 scanning electron microscope (SEM, Carl Zeiss Pte Ltd) according to Ref. [22]. The membrane samples were vacuum dried at 23°C for 24 hours, followed by fracturing in liquid nitrogen. Samples were uniformly coated with a thin layer of gold using an EMITECH SC7620 sputter coater (Quorum Technologies Ltd, UK) before SEM imaging of the membrane surface and the cross sections. Thicknesses of membranes were measured from the SEM cross-sectional images and verified with a micrometer measurement.
3.6.2 Membrane porosity

The membrane porosity, $\varepsilon$ is defined as the volume of the pores divided by the total volume of the membrane. Measurement of the dry and wet mass of the membrane samples was taken to determine $\varepsilon$. Membrane porosity can be obtained using the equation [19, 22]:

$$\varepsilon = \frac{(m_{\text{wet}} - m_{\text{dry}})/\rho_w}{\frac{m_{\text{wet}} - m_{\text{dry}}}{\rho_w} + \frac{m_{\text{dry}}}{\rho_m}} \times 100\%$$  \hspace{1cm} \text{Equation 6}

Where $m_{\text{wet}}$ and $m_{\text{dry}}$ are the wet and dry mass of membrane respectively, $\rho_w$ and $\rho_m$ are the density of the ultra-pure water and polymer respectively.

3.6.3 Measurement of contact angle

Measurements of the membranes’ contact angles were obtained with the sessile drop method, using an OCA contact angle system (DataPhysics Instruments GmbH). The membrane samples were vacuum dried at room temperature before measurement. Profiles of the small water droplets, on the membrane surface, were captured to determine the contact angles. With the contact angles, hydrophilicity of the membrane can be determined.

![Contact angle classification of membranes.](image)

Figure 5. Contact angle classification of membranes.

3.6.4 Measurement of intrinsic separation properties of FO membranes

RO tests were performed to evaluate the intrinsic separation properties namely the water permeability, $A$, and the salt permeability $B$, of the FO membrane using a cross-flow RO filtration setup in accordance to Ref. [36]. The feed solution was pumped from the feed tank to the feed inlet. From the inlet, the feed solution flowed through the cross-flow membrane module,
tangentially across the membrane surface. Portion of the solution that permeates through the membrane was collected in a manifold and flowed out the permeate outlet. Solutes rejected by the membrane then flowed out as the concentrate. The concentrate was recycled back into the feed tank.

Figure 6. Schematic diagram of cross-flow RO filtration setup. Diagram adapted from [55].

All RO tests were performed under a constant temperature of 23°C. With an applied pressure 5 bar, the water permeability, $A$ can be evaluated using ultra-pure water as the feed solution. Before any measurement, the membrane may require of compaction to reach steady water flux. Based on the gravimetric measurement of permeate water flux, water permeability, $A$ of the membrane can be determined with the equation:

$$A = \frac{J}{\Delta p}$$  \hspace{1cm} \text{Equation 7}

Where $\Delta p$ is the trans-membrane pressure and $J$ is the permeate water flux.

For solute rejection measurements, two tests were run using feed solution of a 10mM of NaCl or a 10mM of Na$_2$SO$_4$ solution. The setup configuration and experimental conditions for solute permeability test remain unchanged from the water permeability test.
Based on the conductivities of both the feed solution \( C_f \) and the permeate \( C_p \) (Ultrameter IITM 4P, Myron L Company, Carlsbad, CA), solute rejection, \( R \) can be calculated.

\[
R = 1 - \frac{C_p}{C_f}
\]

Equation 8

At least three repeats of the RO test were carried out. An average of the rejection values were obtained and used to calculate the salt permeability coefficients, \( B \) for both \( \text{NaCl} \) and \( \text{Na}_2\text{SO}_4 \).

\[
B = J \left( \frac{1}{R} - 1 \right)
\]

Equation 9

### 3.6.5 Measurement of FO performance

FO performance of membrane was evaluated with a cross-flow FO setup at room temperature. An effective membrane area, \( A_m \) of 60 cm\(^2\) from both the NF-like and RO-like membrane, was used in each test. The membrane samples were positioned, in the cross-flow cell, with diamond-patterned spacers on both side of the membrane. This can help create turbulence to reduce ECP in both the feed and draw solution.

Briefly, the feed solution and the draw solution were pumped into the setup using two variable-speed peristaltic pumps. Condition of the pump speed was set at 500 ml/min to circulate the solutions at a fixed cross rate. The water flux of the FO membranes was determined by measuring the weight changes of the feed solution. The weight of the feed solution was recorded by a digital mass balance. Water flux, \( J_w \), can thus be determined.

\[
J_w = \frac{\Delta V_{\text{feed}}}{A_m \times \Delta t} = \frac{\Delta m_{\text{feed}}}{A_m \times \Delta t} \rho_{\text{feed}}
\]

Equation 10

Where \( \Delta V_{\text{feed}} \) and \( \Delta m_{\text{feed}} \) represents the volume and weight changes of feed solution respectively. \( \rho_{\text{feed}} \) is the density of the feed solution. \( \Delta t \) is the measured time interval.

0.5 M and 10 mM of \( \text{NaCl} \) solutions were used as the feed solution. A various concentrated draw solutions were tested upon which can be found in Appendix A1. Conductivity of the feed solution was measured constantly. FO solute flux, \( J_s \), was determined by monitoring the change of salt content in the feed solution.
\[ J_s = \frac{V_tC_t - V_0C_0}{A_m\Delta t} \]  

Equation 11

Where \( V_0 \) and \( V_t \) represents the initial and final volume of feed solutions respectively; \( C_0 \) and \( C_t \) is the initial and final salt concentration in the feed solution respectively.

Both AL-DS and AL-FS membrane orientations were tested. A schematic diagram of the bench-scale FO setup is shown in Figure 7 below.

![Figure 7. Schematic diagram of FO test setup. Adapted from [8].](image)

### 3.6.6 Membrane structural parameter

The structural parameter, \( s \) is an important property for FO membranes. It can be determined experimentally by the water flux equation 3 and equation 4 substituted with \( K = \frac{s}{D} \). Values of rejection layer water permeability \( A \) and solute permeability \( B \) will be obtained from cross-flow RO system (Section 3.6.4).

Concentrative ICP (AL–DS):  
\[ J_v = \frac{D}{s} \left[ \ln \frac{A\pi_{\text{draw}} - J_{w+}B}{A\pi_{\text{feed}} + J_{w+}B} \right] \]  

Equation 12

Dilutive ICP (AL–FS):  
\[ J_v = \frac{D}{s} \left[ \ln \frac{A\pi_{\text{draw}} + B}{A\pi_{\text{feed}} + J_{w+}B} \right] \]  

Equation 13
Chapter 4: Results and Discussions

4.1 TFC FO Membrane Properties

4.1.1 Structure and morphology

Two TFC FO membranes with different rejection layer were been fabricated in this project (Table 3), RO-like layer and NF-like layer, respectively. The following figures show the SEM micrographs of substrate’s cross-section and surfaces of the 2 different active rejection layers.

Formation of both RO-like and NF-like FO membrane employed the use of a similar PSf substrate. From the SEM micrograph, the substrate had a thickness approximately 75µm (Figure 8). The cross-section morphology of the substrate showed a tightly straight long finger-like structures without forming large spherical macro-voids. (Figure 8). According to earlier studies [22], the straight needle-like pores are preferred for FO membranes as they provides a smaller structural parameter, $s$. Together, the relatively low structural parameter and contact angle help reduce the ICP [22, 56]. The detailed characteristic parameters were presented in Table 5.

Table 5. Properties of PSf substrates.

<table>
<thead>
<tr>
<th>Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (µm)</td>
<td>74.64 ± 0.81</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>77.04 ± 0.63</td>
</tr>
<tr>
<td>S value (mm)</td>
<td>0.87 ± 0.18</td>
</tr>
<tr>
<td>Contact angle (°)</td>
<td>78.1 ± 0.9</td>
</tr>
</tbody>
</table>
The interfacial polymerization was carried out using amine solutions (MPD for RO-like layer and PIP for NF-like layer) and acid chloride solutions (TMC in n-hexane). From the SEM images (Figure 9), RO-like layer possesses a rough surface and valley-ridge morphology as typical to that of a fully aromatic polyamide layer. The NF-like rejection layer is semi-aromatic poly (piperazine-amide), thus it has a smoother (grainy) surface. The contact angle of the FO membranes were measured and shown below:

- Contact angle: $39.2 \pm 5.2^\circ$ (RO-like layer)
- $25.7 \pm 3.9^\circ$ (NF-like layer)
It was reported by McCutcheon and Elimelech [56] that water flux decreases with a reduced substrate hydrophilicity as a result of a lesser substrate wetting. Compared to the commercial HTI FO membranes (contact angle ~ 70° [22]), the composite membrane significantly possess a much smaller contact angle. As mentioned (Section 3.6.3), a lower contact angle indicates better substrate hydrophilicity. Thus, a better FO water flux is expected.

Further, comparing the two composite membranes with different rejection layer, NF-like layer showed a smaller contact angle than that of RO-like layer. Being more hydrophilic, NF-like layer had lesser tendency towards fouling problem, and this aids in achieving a considerable high water flux.

### 4.1.2 Intrinsic separation properties

Both NF-like and RO-like membrane intrinsic membrane separation properties, the water permeability A, NaCl permeability and Na₂SO₄ permeability were determined in a cross flow RO setup at 23°C.

Table 6. Intrinsic separation properties of synthesized TFC FO membranes.

<table>
<thead>
<tr>
<th>Feed</th>
<th>Pressure (bar)</th>
<th>RO-like FO membranes</th>
<th>NF-like FO membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A (L/m².h.bar)</td>
<td>Rejection %</td>
<td>B (10⁻⁸ m/s)</td>
</tr>
<tr>
<td>Milli-Q</td>
<td>5</td>
<td>3.46</td>
<td></td>
</tr>
<tr>
<td>10mM NaCl</td>
<td>5</td>
<td>97.50</td>
<td>11.00</td>
</tr>
<tr>
<td>10mM Na₂SO₄</td>
<td>5</td>
<td>99.61</td>
<td>1.66</td>
</tr>
</tbody>
</table>

*Results are average of at least three repeats.

Water permeability of the membranes was tested with Milli-Q ultrapure water under a 5 bar pressure. It can be seen from the data given in Table 6 that the two composite membranes displayed different intrinsic separation properties. Between the two membranes, the NF-like FO membrane had a significantly higher water permeability value of 5.01 L/m².h.bar. In comparison, the RO-like membrane had A value of only 3.46 L/m².h.bar.

Additionally, NF-like membrane had the highest NaCl and Na₂SO₄ permeability, 1453 x10⁻⁸ m/s and 7.81x10⁻⁸ m/s respectively. While RO-like membrane displayed insignificant B values when compared to NF-like membrane, suggesting that this membrane had a much better retention against NaCl and Na₂SO₄. In contrast, NF-like membrane was the most water permeable but the least salt selective.
As demonstrated, it can be seen that there is a distinct trade-off between water and salt permeability of the membrane, which is in good agreement with the literature [23]. While the higher water permeability of a “looser” membrane tends to improve FO water flux due to reduced membrane resistance [22], the “looser” membrane also brings about a higher salt permeability. Simultaneously, a more severe ICP will be caused by the poorer salt rejection due to the solute reverse diffusion. This has an opposite effect to reduce the FO water flux [57].

When tested with 10mM of NaCl feed solution, RO-like layer showed a good rejection of 97.5% at hydraulic pressure of 5 bar. On the other hand, the NF-like layer displayed a low rejection of 33.3% under the same pressure. This great contrast in the membrane rejection simply attribute to the difference in membrane rejection layer.

With regards to Na₂SO₄ rejection, both RO-like and NF-like FO membranes exhibited outstanding rejection of over 99% and 98%, respectively. These results identified NF-like layer as an excellent rejection layer for divalent ions.

4.2 FO performance

4.2.1 Water and Salt Fluxes

To study different operational conditions, FO water flux and salt flux of the synthesized TFC membranes were evaluated using NaCl feed solution of 10mM (for usual conditions) and 0.5M (for FO desalination) in both AL-DS and AL-FS membrane orientations A total of three series of different concentration and various feed and draw solutions, were tested upon on both the NF-like and RO-like membrane.

Results show that water flux and NaCl salt flux increase with increasing draw solution concentration. Clearly, the concentration of feed solutions used, was much lower than the draw solutions. With increased draw solution concentration, a higher concentration difference and osmotic pressure differential would be promoted. Therefore, resulting to a greater driving force to drive the water through the membrane; increase in water flux.
As observed when tested with 10mM NaCl feed (Table 7 & 8), the RO-like membrane had a significantly high water flux of 17 to 33 L/m² h and low reverse salt flux of 3.21 to 7.12 g/m² h compared to NF-like membrane. The flux values confirm that RO-like membrane is more selective and permeable compared to NF-like membrane. The favourable low $J_v/J_s$ ratio (Figure 11) of the RO-like FO membrane was an effect of the high salt rejection [25].

<table>
<thead>
<tr>
<th>Draw concentration (M)</th>
<th>AL-DS orientation</th>
<th>AL-FS orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J_v$ (L/m².h)</td>
<td>$J_s$ (g/m².h)</td>
</tr>
<tr>
<td>0.375</td>
<td>17.47</td>
<td>3.21</td>
</tr>
<tr>
<td>0.75</td>
<td>24.55</td>
<td>4.80</td>
</tr>
<tr>
<td>1.125</td>
<td>29.44</td>
<td>7.02</td>
</tr>
<tr>
<td>1.5</td>
<td>33.19</td>
<td>7.12</td>
</tr>
</tbody>
</table>

* Draw solution: NaCl solution (various concentrations); Feed solution: 10mM NaCl solution.

* Results are average of at least three repeats.

<table>
<thead>
<tr>
<th>Draw concentration (M)</th>
<th>AL-DS orientation</th>
<th>AL-FS orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J_v$ (L/m².h)</td>
<td>$J_s$ (g/m².h)</td>
</tr>
<tr>
<td>0.375</td>
<td>2.05</td>
<td>49.71</td>
</tr>
<tr>
<td>0.75</td>
<td>2.98</td>
<td>87.14</td>
</tr>
<tr>
<td>1.125</td>
<td>3.80</td>
<td>119.50</td>
</tr>
<tr>
<td>1.5</td>
<td>4.69</td>
<td>143.62</td>
</tr>
</tbody>
</table>

* Draw solution: NaCl solution (various concentrations); Feed solution: 10mM NaCl solution.

* Results are average of at least three repeats.
Figure 10. Water flux of synthesized TFC FO membranes tested with 10mM NaCl as feed solution in AL-DS orientation.

Figure 11. Water flux of synthesized TFC FO membranes tested with 10mM NaCl as feed solution in AL-FS orientation.
A second set of experiments was conducted with 0.5M NaCl feed and higher draw concentration. The concentrations were adjusted to have high osmotic pressure difference to effect the driving force. Water flux as a function of the bulk draw solution concentration is shown in Figure 12. Similarly, the results indicated a more permeable RO-like membrane over the NF-like membrane. Water flux through RO-like membrane is much higher than through NF-like membrane. FO membrane with RO-like rejection layer would thus be more efficient in FO desalination.
4.2.2 Reverse salt diffusion in FO process

Despite the superior water permeability ($A=5.01$ $\text{L/m}^2\text{h}$) over the RO-like FO membrane, the NF-like FO membrane displayed poor FO water flux (Figure 14). This can be explained by the reverse diffusion of the solute from the draw solution to the feed solution through the membrane. While higher water permeability tends to enhance FO water flux due to the smaller loss in membrane resistance, its poor solute retention has the tendency to promote a more severe ICP,
reducing water flux [25]. Based on the results (Table 9), the NF-like membrane suffered from severe ICP. Meanwhile, the \( J_s/J_v \) ratio of the NF-like FO membrane, an important FO performance parameter [58-60], was excessively large. In this current study, the average specific reverse salt flux (\( J_s/J_v \)) for RO-like and NF-like membrane is 0.21 g/L and 28.91 g/L, respectively. The direct relation between the \( J_s/J_v \) ratio to the membrane selectively had been demonstrated in previous studies [22, 36, 41, 57, 58, 59].

Table 9. Performance of synthesized TFC FO membrane.\(^{ab}\)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>( J_v ) (L/m(^2).h)</th>
<th>( J_s ) (g/m(^2).h)</th>
<th>( J_s/J_v ) (g/L)</th>
<th>( J_v ) (L/m(^2).h)</th>
<th>( J_s ) (g/m(^2).h)</th>
<th>( J_s/J_v ) (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO-like layer</td>
<td>33.19</td>
<td>7.12</td>
<td>0.21</td>
<td>16.96</td>
<td>4.04</td>
<td>0.24</td>
</tr>
<tr>
<td>NF-like layer</td>
<td>4.69</td>
<td>143.62</td>
<td>30.65</td>
<td>7.02</td>
<td>98.14</td>
<td>13.99</td>
</tr>
</tbody>
</table>

\(^a\) Draw solution: 1.5 M NaCl solution; Feed solution: 10mM NaCl solution.

\(^b\) Results are average of at least three repeats.

Consistent with the poor rejection of monovalent ion, high salt transportation occurs in the NF-like layer. The large ratio (i.e. lower selectivity) led to severe solute accumulation on the feed side arising from solute reverse diffusion [58]. Subsequently, it increased risk of membrane fouling [59], and reduce rejection.

The much lowered FO water flux observed in both orientations also confirmed that \( J_s \)-enhanced-ICP mechanism dominates when system was exposed to high concentration draw solution. In contrast, a higher membrane rejection may be more important under conditions where solute reverse diffusion may cause enhanced ICP of the back-diffused draw solutes [25]. Water flux of RO-like FO membrane still surpassed that of NF-like FO membrane (Table 7 & 8).

4.2.3 Effect of membrane orientation

Compared to the AL-DS orientation, the AL-FS orientation displayed lower water flux for the 10mM NaCl solute. Both RO-like and NF-like FO membrane showed similar trend in the AL-FS orientation using the same testing conditions. Similarly, the non-linear flux behaviour with increasing draw solution concentrations was due to the influence of dilutive ICP. As shown in Table 7 & 8, the water flux rate in the AL-FS orientation is significantly lower as compared to AL-DS orientation. This indicates that dilutive ICP is more severe than the concentrative ICP in
the AL-DS orientation in the FO process. The water will greatly dilute the concentration of the draw solution within the membrane porous structure, thereby causing a reduced effective osmotic gradient, hence lower flux was obtained. Thus, lower $J_v/J_i$ ratio can be observed. The RO-like FO membrane was observed to have greater effect from dilutive ICP with close to 50% decline in water flux in AL-FS orientation.

On the other hand, it was observed that both membranes had comparable water flux with 0.5M NaCl solute in both AL-DS and AL-FS orientation (Table 10 & 11). It is suggested that the AL-FS orientation may be better suited for feed solutions with high concentration [68]. Therefore, in FO applications, selection of membrane orientation is mainly determined by the water flux performance [69].

### Table 10. Performance of RO-like FO membrane$^{ab}$

<table>
<thead>
<tr>
<th>Draw concentration (M)</th>
<th>AL-DS orientation</th>
<th>AL-FS orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J_v$ (L/m².h)</td>
<td>$J_v$ (L/m².h)</td>
</tr>
<tr>
<td>0.75</td>
<td>2.51</td>
<td>2.36</td>
</tr>
<tr>
<td>1.125</td>
<td>4.65</td>
<td>4.56</td>
</tr>
<tr>
<td>1.5</td>
<td>6.39</td>
<td>6.14</td>
</tr>
<tr>
<td>2.25</td>
<td>8.98</td>
<td>8.74</td>
</tr>
<tr>
<td>3.0</td>
<td>11.09</td>
<td>10.07</td>
</tr>
</tbody>
</table>

* Draw solution: NaCl solution (various concentrations); Feed solution: 0.5 M NaCl solution.

b Results are average of at least three repeats.

### Table 11. Performance of NF-like FO membrane$^{ab}$

<table>
<thead>
<tr>
<th>Draw concentration (M)</th>
<th>AL-DS orientation</th>
<th>AL-FS orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J_v$ (L/m².h)</td>
<td>$J_v$ (L/m².h)</td>
</tr>
<tr>
<td>0.75</td>
<td>0.77</td>
<td>0.67</td>
</tr>
<tr>
<td>1.125</td>
<td>1.26</td>
<td>1.26</td>
</tr>
<tr>
<td>1.5</td>
<td>1.70</td>
<td>1.78</td>
</tr>
<tr>
<td>2.25</td>
<td>2.37</td>
<td>2.53</td>
</tr>
<tr>
<td>3.0</td>
<td>3.06</td>
<td>3.15</td>
</tr>
</tbody>
</table>

* Draw solution: NaCl solution (various concentrations); Feed solution: 0.5 M NaCl solution.

b Results are average of at least three repeats.
4.2.4 Effect of different rejection layer on water flux

The last series of test were carried using varied concentration of divalent ion solution as the draw solution. Figure 16 and 17 presents the FO water flux with 10mM NaCl feed solution in both AL-DS and AL-FS orientation. An increasing water flux trend was observed for both orientations with higher draw concentration. Similarly, this was because of the large the concentration difference which means greater the osmotic pressure differential. As a result of the greater driving force, FO water flux increases.

![Graph](image1)

**Figure 16.** Water flux of synthesized TFC FO membranes tested with 10mM NaCl as feed solution and varied concentration of divalent ion solution in AL-DS orientation.

![Graph](image2)

**Figure 17.** Water flux of synthesized TFC FO membranes tested with 10mM NaCl as feed solution and varied concentration of divalent ion solution in AL-FS orientation.
Consistent with the high membrane solute rejection, both membranes showed high water flux. Both membranes had high rejection against divalent ions as discussed in section 4.1.2. It was observed that the NF-like membrane exhibit a comparable or better FO water flux than RO-like membrane in the AL-DS orientation (Table 12). It could be due to the higher water permeability of the “looser” NF-like membrane. With a reduced membrane resistance, FO water flux can be enhanced [22, 57]. As such, it will be more efficient to apply NF-like FO membrane to applications dealing with divalent ions draw solution.

Table 12. FO results with divalent ion solution.

<table>
<thead>
<tr>
<th>Draw concentration</th>
<th>RO-like layer</th>
<th>NF-like layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AL-DS orientation</td>
<td>AL-FS orientation</td>
</tr>
<tr>
<td></td>
<td>(J_v) (L/m(^2).h)</td>
<td>(J_v) (L/m(^2).h)</td>
</tr>
<tr>
<td>(0.25\text{M Na}_2\text{SO}_4)</td>
<td>16.29</td>
<td>7.42</td>
</tr>
<tr>
<td>(0.5\text{M Na}_2\text{SO}_4)</td>
<td>23.63</td>
<td>9.31</td>
</tr>
<tr>
<td>(0.75\text{M Na}_2\text{SO}_4)</td>
<td>28.81</td>
<td>10.39</td>
</tr>
<tr>
<td>(1.0\text{M Na}_2\text{SO}_4)</td>
<td>32.46</td>
<td>11.36</td>
</tr>
</tbody>
</table>

\(^a\) Draw solution: Divalent ion solution (various concentrations); Feed solution: 10mM NaCl solution.

\(^b\) Results are average of at least three repeats.

According to the literature [38], employing a multivalent ion solution as the draw solution may minimize the reverse solute diffusion. This can be explained in the first and last FO test performed. With NaCl as the draw solution, the low FO water flux of NF-like membrane was likely due to the dominance of the Js-induced-ICP mechanism. A severe solute reverse diffusion effect was thus experienced with the NF-like membrane.

On the other hand, with divalent ions like \(\text{Na}_2\text{SO}_4\) as draw solution, the FO water flux had a significantly increase in flux (of about 10 times) with 0.75 M of monovalent NaCl draw solution in the AL-DS orientation (Table 8 & 12). Therefore, divalent ion solutions with lower diffusion coefficients and the use of NF-like FO membrane may be preferable in applications requiring high rejection.

It was also worthwhile to note that multivalent ion solutions may also introduce more severe ICP due to their larger ion sizes and lower solution diffusion coefficients [34]. As a result, the risk of membrane fouling was increased with higher ICP [38]. Careful consideration would be needed to design of both FO membranes and draw solutes.
Chapter 5: Conclusions

In this study, the influence of membrane selectivity on the draw solutes and the resultant TFC FO membrane separation properties on FO performance was investigated. The FO membranes fabricated in this study demonstrated that the RO-like and NF-like layer can be obtained by simply changing the monomers used in interfacial polarization. It can be concluded that a RO-like FO membrane is suitable to remove both monovalent and divalent ions. However, a NF-like FO membrane would be a better choice to remove divalent ions as it exhibit better water permeability.

From both RO and FO tests, it can be confirmed that there is a direct relationship between FO solute reverse diffusion and the membrane rejection. A higher solute rejection tends to reduce the \( J_w / J_v \) ratio. Eventually, a decreased risk of reverse-diffusion-induced membrane fouling can be expected. Both the membrane water permeability and salt rejection were influenced by the FO water flux. By increasing the water permeability of the membrane in conditions where frictional-loss mechanism dominates (e.g. membrane with low A value is used or system operates at low water flux level, etc), a better FO water flux can be achieved. While in conditions where solute reverse diffusion may cause back-diffusion enhanced ICP, a higher membrane rejection may become significant.

Under varied conditions of the feed and draw solution, the two synthesized FO membrane displayed different FO performance. The RO-like FO membrane was preferred with monovalent ion draw solution such as NaCl. Furthermore, NF-like FO membrane exhibited excellent FO water flux with divalent ion draw solutions. In view of FO test results obtained, TFC FO membranes should be optimized in accordance to the application requirement.
A1. Experimental results. Results are average of at least three repeats. Highlighted data is the standard deviation.

### Intrinsic separation properties of FO membranes

<table>
<thead>
<tr>
<th>Feed</th>
<th>Pressure (bar)</th>
<th>RO-like FO membranes</th>
<th>NF-like FO membranes</th>
<th>Rejection A</th>
<th>m/s</th>
<th>Rejection B</th>
<th>m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>Rejection</td>
<td>B</td>
<td>A</td>
<td>Rejection</td>
<td>B</td>
</tr>
<tr>
<td>Milli-Q</td>
<td>5</td>
<td>5.46</td>
<td>0.34</td>
<td>5.01</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 mM NaCl</td>
<td>5</td>
<td>97.50</td>
<td>0.17</td>
<td>1.10E-07</td>
<td>1.58E-06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 mM Na_2SO_4</td>
<td>5</td>
<td>99.81</td>
<td>0.09</td>
<td>1.94E-08</td>
<td>4.19E-09</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### FO water and salt flux of FO membranes

<table>
<thead>
<tr>
<th>Membrane orientation</th>
<th>Feed</th>
<th>Draw</th>
<th>Draw of draw</th>
<th>RO-like FO membranes</th>
<th>NF-like FO membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>m/s</td>
<td>Jv (L/m².h)</td>
<td>Js (g/m².h)</td>
</tr>
<tr>
<td>10 mM NaCl</td>
<td>0.46</td>
<td>0.275 M NaCl</td>
<td>17</td>
<td>9.99</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.75 M NaCl</td>
<td>34.6</td>
<td>24.55</td>
<td>3.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.25 M NaCl</td>
<td>53.1</td>
<td>29.44</td>
<td>3.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5 M NaCl</td>
<td>72.6</td>
<td>33.19</td>
<td>4.51</td>
</tr>
<tr>
<td>0.5 M NaCl</td>
<td>22.8</td>
<td>0.25M Na_2SO_4</td>
<td>12.6</td>
<td>16.29</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5M Na_2SO_4</td>
<td>23.8</td>
<td>23.63</td>
<td>2.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.7M Na_2SO_4</td>
<td>34.8</td>
<td>28.81</td>
<td>2.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1M Na_2SO_4</td>
<td>46</td>
<td>22.46</td>
<td>1.91</td>
</tr>
<tr>
<td>10 mM NaCl</td>
<td>0.46</td>
<td>0.275 M NaCl</td>
<td>17</td>
<td>9.99</td>
<td>1.33</td>
</tr>
<tr>
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<td>16.29</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
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<td>46</td>
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<td>0.75 M NaCl</td>
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<td>2.19</td>
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<tr>
<td></td>
<td></td>
<td>1M Na_2SO_4</td>
<td>46</td>
<td>22.46</td>
<td>1.91</td>
</tr>
</tbody>
</table>
A2. Salt flux of synthesized TFC FO membranes tested with 10mM NaCl as feed solution in AL-FS orientation.

A3. Salt flux of synthesized TFC FO membranes tested with 10mM NaCl as feed solution in AL-DS orientation.
References


