Development of thin-film composite membrane for forward osmosis process

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**DEVELOPMENT OF THIN-FILM COMPOSITE
MEMBRANE FOR FORWARD OSMOSIS PROCESS**

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Interdisciplinary Graduate School
Nanyang Environment and Water Research Institute
Singapore Membrane Technology Centre

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MEMBRANE FOR FORWARD OSMOSIS PROCESS**

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Nanyang Environment and Water Research Institute
Singapore Membrane Technology Centre**

A thesis submitted to the Nanyang Technological University in
partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Daniel Ng Yee Fan

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Date

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Prof. Wang Rong

Authorship Attribution Statement

This thesis contains material from two papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 4 is published as D. Y. F. Ng, B. Wu, Y. Chen, Z. Dong, R. Wang, A novel thin film composite hollow fiber osmotic membrane with one-step prepared dual-layer substrate for sludge thickening. *Journal of Membrane Science*, Volume 575, 2019, Pages 98-108. DOI: 10.1016/j.memsci.2019.01.007.

The contributions of the co-authors are as follows:

- Prof Rong Wang and Assoc Prof. Zhili Dong provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by A/Prof Bing Wu and Dr Yunfeng Chen.
- I co-designed the study with Prof. Rong Wang and A/Prof Bing Wu and performed all the laboratory work at Singapore Membrane Technology Centre. I also analyzed the data.
- Dr Yunfeng Chen assisted in the preparation of materials for TFC membrane fabrication.
- The sample preparation for scanning electron microscopy was conducted by me in Singapore Membrane Technology Centre.
- Dr Yunfeng Chen assisted in the collection of the scanning electron microscopy data.

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The contributions of the co-authors are as follows:

- Prof Rong Wang and Assoc Prof Zhili Dong suggested the materials area and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript was revised together with Dr Yunfeng Chen and Prof Rong Wang.
- I performed membrane fabrication, membrane performance evaluation, scanning electron microscopy, transmission electron microscopy and atomic force microscopy.
- Dr Yunfeng Chen assisted in the preparation of materials for TFC membrane fabrication and assisted in the collection of the scanning electron microscopy data.

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Date

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Daniel Ng Yee Fan

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LIST OF PUBLICATIONS

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LIST OF SYMBOLS

Letters

A	Pure water permeability coefficient, L/m ² /h/bar (LMH/bar)
A_m	Effective membrane area, m ²
B	Solute permeability coefficient, L/m ² /h (LMH)
C	Concentration of solute, M or mM
C_d	Concentration of draw solute in draw solution, M or mM
$C_{d,b}$	Concentration of draw solute in bulk draw solution, M or mM
$C_{d,m}$	Concentration of draw solute at membrane surface facing draw solution, M or mM
C_f	Concentration of draw solute in feed solution, M or mM
$C_{f,b}$	Concentration of draw solute in bulk feed solution, M or mM
$C_{f,m}$	Concentration of draw solute at membrane surface facing feed solution, M or mM
$C_{s/s}$	Concentration of draw solute at support layer-selective layer interface, M or mM
d_h	Hydraulic diameter, m
D	Solute diffusivity, m ² /s
D_s	Effective solute diffusivity within microporous substrate, m ² /s
i	van' Hoff coefficient
ID	Inner diameter of hollow fiber membrane, μ m
J_w	Water flux, L/m ² /h (LMH)
J_s	Solute flux, g/m ² /h (gMH)
J_s/J_w	Specific reverse solute flux, g/L

k_d	Mass transfer coefficient at membrane surface facing the draw solution, m/s
k_f	Mass transfer coefficient at membrane surface facing the feed solution, m/s
K	Mass transfer resistance of the membrane support layer, L/m ² /h (LMH) or m/s
l	Length of the membrane
L	Length of flow channel
OD	inner diameter of the hollow fiber membrane, μm
ΔP	Transmembrane pressure, bar
R	Hydraulic resistance, m ⁻¹
$R(a)$	Retention coefficient of dextran with molecular weight of “a” g/mol
Re	Reynolds number
R_g	Universal gas constant, 8.3145 Pa·m ³ /K/mol
R_s	Salt rejection, %
S	Structure parameter of the membrane substrate, μm
Sc	Schmidt number
Sh	Sherwood number
t	Thickness of the membrane, μm
T	Temperature,
Δt	Time interval, h
ΔV	Volume change, L

Greeks

δ_d	Boundary layer thickness at the draw solution side of membrane
------------	--

δ_f	Boundary layer thickness at the feed solution side of membrane
ε	Porosity of the membrane substrate, %
η	Viscosity, Pa·s
π	Osmotic pressure, bar
ρ_w	Density of water, kg/m ³
σ	Reflection coefficient
τ	Tortuosity of the membrane substrate

Summary

Forward osmosis (FO) is a membrane process that occurs when solutions of different osmotic pressures are separated by a membrane which is selectively permeable to water. It is a process that drives water permeation across the membrane spontaneously even in the absence of hydraulic pressure difference across the membrane. FO has attracted lots of attention over the last decade and has been explored as a potential alternative to desalination, wastewater treatment and liquid food processing. Significant progress has been made in the development of high-performance FO membranes with high water flux and low reverse solute flux, particularly cellulosic membranes, thin-film composite (TFC) membranes and polyelectrolyte-based membranes. Yet, a few major challenges continue to hamper the widespread implementation of the process in the industry, mainly internal concentration polarization, reverse solute diffusion, membrane fouling, mechanical durability and draw solution regeneration. Most of these challenges are associated with membrane characteristics, which has significantly limited the efficiency of the FO process.

To address these challenges, firstly, hollow fiber ultrafiltration membranes were fabricated from polyethersulfone (PES) via a non-solvent induced phase separation (NIPS) process and were used as substrates to prepare inner-selective TFC hollow fiber membranes via an interfacial polymerization (IP) process. The effect of the hollow fiber substrate fabrication conditions on the properties of the substrate and TFC membranes were briefly investigated. The FO performance of the TFC membranes were characterized by using 0.5 M NaCl and DI water as the draw and feed solutions. when the membrane was operated in the active layer-facing-feed solution (AL-FS) and active layer-facing-draw solution (AL-DS) configurations, water flux as high as 41.2 L/m²/h and 74.9 L/m²/h were achieved, while specific reverse solute flux were 0.11 g/L and 0.10 g/L, respectively.

Subsequently, a novel double-skinned hollow fiber TFC FO membrane has been successfully fabricated. The FO membrane consisted of a one-step dual-layer substrate and a thin inner selective layer formed via the IP process. The

substrate comprises a dense ultrafiltration (UF) outer layer and a relatively porous UF inner layer, both of which were constructed from PES by using a dual-layer co-extrusion technique. The fouling resistance of the double-skinned hollow fiber membrane was evaluated under various testing conditions to verify the viability of double-skinned hollow fiber membranes as a solution to membrane fouling in the FO process. Compared to the commercial and reported double-skinned FO membranes, the FO membrane developed in this thesis exhibited a higher permeate flux with humic acid solution as a feed solution. Furthermore, the double-skinned FO membrane was applied in concentrating activated sludge using 0.5 M NaCl as a draw solution. A permeate flux at 5.4 L/m²/h was achieved after 5-hour operation, which was higher than, or comparable to, those of the reported FO membranes. Membrane autopsies and foulant analysis suggested that the dense UF skin layer helped to reject larger-sized organic foulants (> 300 Da), which shed light on the importance of fabrication features and promising application of the double-skinned hollow fiber TFC FO membrane in sludge concentration.

On the other hand, a series of characterization revealed that TFC hollow fiber membranes may experience significant compaction during the FO process despite the lack of applied pressure. Three TFC hollow fiber membranes were fabricated with varied water permeability to study the effect of the osmotic pressure on the TFC membranes. The TFC membranes were continuously tested in FO experiments for 24 h using DI water as feed and varied concentration of NaCl solutions as draw solutions, and their performances were evaluated again using fresh feed solutions. At the end of the FO experiments, all TFC membranes experienced water and salt flux decline to different extents. Visible changes in the cross-sectional morphology and surface topography of the TFC membranes were observed. These observations suggested that the occurrence of membrane compaction is strongly associated with the characteristics of the hollow fiber substrates that were used to prepare the TFC membranes and may be attributed to “negative pressure” build-up within the support layer of the TFC membranes.

Chapter 1 Introduction

1.1. Background

1.1.1. Motivation

The water-energy-food nexus is central to human's sustainability. Yet, the demand for all three resources has been constantly growing due to population growth, rapid urbanization and climate changes [1, 2].

Among the domains, freshwater resource is crucial to the production of both energy and food. It is estimated that the global water demand would increase by 55% by 2050, mainly because of growing demands from the manufacturing sector (400% increase) [3]. Nonetheless, water scarcity remains a persistent problem that continues to plague many parts of the world today [4]. The problem may be caused by either physical unavailability or economic unaffordability [5]. Physical water scarcity refers to situations where the existing water resources fail to meet the demand, whereas economic water scarcity represents situations where the water resources in the region are not effectively accessible due to unaffordability. Many of the water-scarce regions have access to brackish groundwater and seawater, which means that these regions could be relieved of water scarcity by the deployment of desalination facilities [6]. Water reuse and reclamation may also be considered as a viable solution to tackle water shortage problems. However, there remains a gap in current technologies to deliver an efficient and affordable solution to ensure sustainable water security in these regions.

On the other hand, global energy demand is projected to increase by 48% from year 2012 to 2040 [7]. Fossil fuels have been well exploited over the last century and they remain a major source of energy today. However, the excessive dependence on fossil fuels has brought about major environmental issues due to emission problem, and there are rising concerns regarding the depletion of these limited resources [8]. Therefore, it is necessary to develop more efficient and sustainable solutions for energy generation from renewable resources.

Nevertheless, there are other concerns associated with the implementation of renewable energy, which are typically related to the intermittency of the source of power (such as wind energy and solar energy) and their environmental impact. The ocean may be considered as a huge source of energy with great potential. Other than harvesting energy from waves and tidal forces, the salinity of seawater may also be used to generate power if properly harnessed [9]. This energy, known as the blue energy, is released during the mixing of solutions with different salinities, but it is challenging to control and scale-up the mixing process. [10].

Osmotically driven membrane processes are deemed compelling solutions to close the technology gap and unlock the promise of blue energy. Specifically, the forward osmosis (FO) and pressure retarded osmosis (PRO) processes show great promise for water treatment and power generation. Membrane is one of the key components of these processes and yet the membranes to date still suffer from a lack of optimization and several materials-related limitations, which will be addressed in this thesis.

1.1.2. Overview on osmotically driven membrane processes

Osmosis is a physical phenomenon that describes the preferential movement of water across a semipermeable barrier, which selectively impedes the movement of solutes. The observation of osmosis was first documented by Jean-Antoine Nollet in 1748 [11], Historically, this phenomenon has been exploited by mankind as a method for desiccation and preservation of food stuffs.

The concept of utilizing osmosis as the driving force in membrane separation process was brought up by Batchelder [12], who mentioned the use of volatile solutes like sulfur dioxide to create solution that extracts water from seawater across a semipermeable cellulosic membrane. Similar ideas have also been proposed by Glew [13] and Frank [14], where different gases or liquids that are miscible with water (aliphatic alcohols), or precipitable salts (aluminum sulfate) were used instead to create solutions with sufficiently high osmotic pressure to drive desalination of seawater. Kravath et al. [15] reported the use of glucose to produce potable solution from seawater by osmosis across cellulose acetate

membrane, and suggested that the process could be useful in the event of water shortages such as emergency ration on sea. This idea was also applied in a patent disclosed by Stache [16], where fructose was used as a solute to generate high osmotic pressure. After Elimelech and coworkers reported the use of ammonium-bicarbonate as draw solute for desalination by the FO process [17], there was a surge in the numbers of publications on FO and other osmotically driven membrane processes (ODMP) [18].

On the other hand, it is also possible to convert osmotic pressure gradient into hydrostatic pressure gradient by using semipermeable membranes. Such a concept was first brought up by Loeb [19], who proposed to apply the process in energy harvesting from mixing natural water bodies with different salinity for power generation. This process was coined PRO by Loeb later on [20]. In the PRO process, water spontaneously permeate through the membrane into the solution with higher osmotic pressure against the applied pressure in the solution. The volumetric expansion of solution produces work which can be harvested to generate electricity, or to assist other pressure-driven processes by using pressure exchanger and other energy recovery devices. It has drawn significant amount of attention over the last decade, particularly due to its potential as a renewable energy alternative.

Osmotically driven membrane process has gained increasing attention over the last few decades, and large number of investigations have been carried out to assess the potential of osmotically driven membrane processes in various applications [21-25]. The key features of the osmotically driven membrane processes were listed in Table 1.1. Particularly, FO has demonstrated great potential in desalination, liquid food processing, water reuse and reclamation and wastewater treatment processes. Some of the desirable characteristics of FO includes ambient temperature and low-pressure operation, as well as the high selectivity of FO membrane made it an attractive alternative process to conventionally applied technologies.

Table 1.1. An overview on osmotically driven membrane processes.

Type of ODMP	Forward osmosis (FO)	Pressure retarded osmosis (PRO)
Key features	<p>A low-pressure membrane separation process which is solely driven by osmotic pressure difference between solutions.</p> <p>Potential applications:</p> <ul style="list-style-type: none"> Desalination [17, 23, 26-29] Liquid food processing (food and beverage concentration) [25, 30-34] Water and wastewater treatment processes (municipal and industrial wastewater, mining, oil and gas, landfill leachate) [21, 35-39] 	<p>A membrane process that utilize osmotic pressure difference between solutions to produce useful work.</p> <p>Potential applications:</p> <ul style="list-style-type: none"> Power generation [9, 10, 40, 41] Energy recovery in desalination process [41-43] Osmotic heat engine [41, 44, 45]
Advantages	<ul style="list-style-type: none"> Operates under ambient temperature Low pressure process High membrane selectivity enables the rejection a variety of contaminants Could achieve high water flux and recovery with high osmotic pressure gradient Membrane fouling is more reversible. May be applied to concentrate feed streams with high salinity. 	<ul style="list-style-type: none"> Operates under ambient temperature May be applied for power generation from sustainable resources
Disadvantages	<ul style="list-style-type: none"> An additional process is required for the regeneration of draw solute and extraction of water from diluted draw solution, which may significantly increase the overall energy consumption [29, 46-49] It is not a standalone process; adequate feed pre-treatment may be necessary to sustain membrane performance [50] Feed could be contaminated by draw solute due to reverse solute diffusion 	<ul style="list-style-type: none"> Energy recovery efficiency may be greatly limited if osmotic pressure gradient between draw and feed streams is low [41]. Membrane is susceptible to fouling and deformation. [41, 42, 51-53] Feed could be contaminated by draw solute due to reverse solute diffusion High capital cost associated with membrane and installations [54]

Since FO process is purely driven by the osmotic pressure difference between the solution on two sides of the membrane, the energy consumption associated with pumping of feed streams is greatly reduced. Yet, aside from concentrated feed stream, a separate stream of diluted solution (draw) is simultaneously produced as well. For some applications, the separation and recovery of draw solute from the diluted stream may be necessary, which is often achieved via a separate pressure driven membrane process or thermal process [29, 46-49]. Depending on the requirement of the application and the type of draw solute

recovery process involved, the total energy consumption associated with the operation of FO process may vary substantially [55]. The draw solute may have to be replenished periodically, which contributes to the operating cost as well. As such, aside from the cost associated with the installation, operation and maintenance of membranes and pumping facilities in FO process, the cost of draw solute recovery process needs to be carefully evaluated as well in order to assess the economic feasibility of adopting FO process in different applications.

Currently, there are a few challenges that hampered the widespread adoption of FO process, such as concentration polarization, reverse solution diffusion, and membrane fouling. Most of them are associated with the characteristics of the membrane, and could substantially diminish the efficiency of FO process, shorten the service lifetime of membrane, and/or lead to degradation of product quality. As such, there is a need for more investigations to elucidate the influence of membrane characteristics on these undesirable phenomena and subsequently develop effective yet scalable solutions to mitigate their impact on FO process.

1.2. Objectives

The overall objective of this dissertation is to investigate the potential challenges associated with the use of hollow fiber membranes when they are employed in the FO process. The focus of the investigation was placed on fabricating and characterizing the hollow fiber membranes, and subsequently, evaluate their performances in the FO process under operating conditions realistic of potential applications. The common goal of these investigations is to understand the nature of membrane degradation under different operating conditions. Subsequently, the influence of mass transfer mechanism and membranes properties on membrane degradation shall be investigated. Finally, it is intended to devise viable strategies from membrane fabrication and process operation perspectives to reduce and potentially mitigate membrane degradation and achieve sustainable performance in the long term. An overview on the focus of studies presented in this dissertation is illustrated in **Figure 1.1**.

Chapter 2: Review and summarize the fundamental concepts, potential applications, main challenges, and progress in membrane development relevant to FO process.

Chapter 3: Fabricate hollow fiber substrates and TFC membranes by non-solvent induced phase separation and interfacial polymerization technique, and subsequently evaluate the influence of substrate fabrication parameters on the performance of TFC membrane in FO process.

Chapter 4: Fabricate double-skinned hollow fiber TFC membrane and evaluate the FO performance and fouling resistance of the membrane in sludge thickening process.

Chapter 5: Investigate the relationship between substrate properties, operating conditions and the degradation of membrane performance associated with membrane compaction phenomenon in FO process.

Figure 1.1. A summary on the focus of studies in this dissertation.

The specific objectives include:

1. Design and fabricate inner-selective thin-film composite (TFC) hollow fiber membranes with water high permeability, high selectivity and low structural parameter for FO process.
2. Investigate the influence of fabrication parameters on the pore size distribution of the hollow fiber substrates as well as the permeability and selectivity of the TFC membranes.
3. Fabricate TFC hollow fiber membranes by incorporate innovative membrane fabrication strategies and evaluate its influence on the characteristics of the hollow fiber membranes.
4. Evaluate the performance of TFC hollow fiber membranes in FO process when handling feed stream of extremely high fouling potential and identify the major drawbacks associated with existing hollow fiber membranes and the mass transfer mechanism.
5. Evaluate the performance of TFC hollow fiber membranes in FO process under different operating conditions to explore other drawbacks associated with the characteristics of the support layer of the hollow fiber membranes.

1.3. Scope of the thesis

This thesis comprises six chapters. Chapter 1 introduces the background and overall objectives of this dissertation.

Chapter 2 reviews the fundamental concepts, potential applications and the challenges associated with FO process. The desirable characteristics of FO membranes, as well as the recent development on membranes fabrication for FO process are summarized as well.

Chapter 3 presents the fabrication of inner-selective TFC hollow fiber membranes and the evaluation of the FO performance of the membranes. The TFC hollow fiber membranes were fabricated by phase inversion and interfacial polymerization (IP) technique. Four different hollow fiber membranes were fabricated by varying the fabrication conditions to investigate the characteristics of the substrate that were associated with the FO performance of the TFC hollow fiber membranes.

Chapter 4 presents the fabrication of a double-skinned hollow fiber membrane and the evaluation of its performance in sludge-thickening process by FO. The fouling behavior of the double-skinned membrane was compared with a conventional hollow fiber TFC membrane and a commercial FO membrane when operated under the same experimental conditions. The main causes of membrane fouling in sludge-thickening process were investigated and the advantages of double-skinned membranes were presented.

Chapter 5 presents the findings on the occurrence of compaction in TFC membranes during the FO process. The fabrication and characterization of three inner-selective hollow fiber TFC membranes were described, and their FO performances in the active layer-facing-draw solution (AL-DS) orientation were evaluated. Irreversible decline in FO performance was observed within 24 hours of operation in FO tests. Based on the changes in the performance of the three TFC membranes under different testing conditions, the causes of performance decline and the mechanism involved were proposed.

Chapter 6 summarizes the findings from all the studies carried out in this dissertation and concluded on the major obstacles in the development of suitable membranes for the FO process.

Chapter 2 Literature review

2.1. Fundamental concepts

2.1.1. Definitions

Osmosis is a physical process which describes the net movement of water across a semipermeable membrane that separates two solutions of different water chemical potential [37]. In the situation where a solution is separated from the pure water by a semi-permeable membrane, the amount of external pressure which has to be applied to the solution to stop the movement of water across the membrane is defined as the osmotic pressure (π) of the solution. Osmotic pressure is a colligative property of the solution, which means it is proportional to the concentration of solutes. More specifically, the colligative property refer to a few properties of the solution which is affected by the ratio of the number of solute particles to the number of water particles in the solution [56]. Other colligative properties of the solution include reduction of vapor pressure, elevation of boiling point and depression of freezing point as the concentration of solute increases. Osmosis involves the spontaneous movement of water from the solution that has low osmotic pressure (also known as the feed solution) into the solution that has high osmotic pressure (also known as the draw solution) [37]. As osmosis commences, the draw solution becomes increasingly diluted, while the feed solution gets more concentrated. As a result, the osmotic pressure difference across the membrane decreases over time, and osmosis would eventually cease when the osmotic pressure of two solutions becomes equal.

A solution's osmotic pressure can be estimated by the van't Hoff equation [57-59],

$$\pi = i \cdot C \cdot R_g \cdot T \quad (Eq. 2.1)$$

where i is the van't Hoff coefficient, C is the solute concentration (M), R_g is the universal gas constant ($8.3145 \text{ Pa} \cdot \text{m}^3 \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), and T is the temperature of the solution.

2.1.2. Water and solute transport across membrane

The magnitude and direction of the net water flux across the membrane may vary with the hydraulic pressure difference across the membrane, which is schematically depicted in **Figure 2.1**. When there is no hydraulic pressure difference across the membrane, the movement of water is purely driven by the osmotic pressure difference across the membrane, and this process is known as forward osmosis (FO, also known as direct osmosis or DO). If the hydraulic pressure of the solution with lower osmotic pressure is higher, the net driving force is the sum of osmotic pressure difference and hydraulic pressure difference. Therefore, the net water flux is higher as compared to FO, and this process is known as pressure-assisted osmosis (PAO, also known as pressure-enhanced osmosis or PEO).

If the hydraulic pressure of the solution with higher osmotic pressure is higher, the net water movement due to osmosis will be suppressed. If the hydraulic pressure difference is smaller than the osmotic pressure difference, the process is known as PRO. The direction of net water movement in PRO remains unchanged as compared to FO and PAO, but the net driving force is equal to the difference between the osmotic pressure differential and the hydraulic pressure differential. Since the rate of net water movement in FO, PAO and PRO is proportional to the osmotic pressure gradient across the membrane, they are all considered as ODMP.

As the hydraulic pressure of the solution with higher osmotic pressure increases, the net water flux in PRO decreases, which would eventually cease when the hydraulic pressure difference is equal to the osmotic pressure difference. This is known as the flux reversal point, and a further increase in hydraulic pressure difference beyond this point would result in a change in the direction of the net water flux across the membrane. When the hydraulic pressure of the solution of higher osmotic pressure is significantly higher such that the hydraulic pressure difference is greater than the osmotic pressure difference, there is a net movement of water away from the solution of higher osmotic pressure, and the process is known as reverse osmosis (RO).

Figure 2.1 Classifications of the different types of osmotic processes.

In ODMP, the water flux (J_w) across the membrane is proportional to the osmotic pressure difference ($\Delta\pi$) across the membrane, which is generally described by the expression [37],

$$J_w = A \cdot (\sigma \cdot \Delta\pi - \Delta P) \quad (\text{Eq 2.2})$$

where A is the water permeability coefficient, σ is the reflection coefficient, and ΔP is the hydraulic pressure difference across the membrane. The reflection coefficient accounts for the deviation of the effective osmotic pressure difference due to the imperfections in the membrane.

Ideally, a perfectly selective permeable membrane allows only the water to move freely across it, while rejects all the solutes and retains them on one side of the membrane. However, most of the membrane developed today is still slightly permeable to solutes, despite that the solutes permeability of the

membranes is usually very much lower as compared to water permeability. Therefore, there exists a net solute flux in the opposite direction to the water flux in ODMP, which is defined as the reverse solute flux (J_s). The reverse solute flux is proportional to the concentration difference of the solute (ΔC) across the membrane, as described by the expression [60],

$$J_s = B \cdot \Delta C \quad (\text{Eq 2.3})$$

where B is the solute permeability coefficient of the membrane. The ratio of reverse solute flux to water flux is known as the specific reverse solute flux (J_s/J_w). The specific reverse solute flux is related to the selectivity of the membrane by the following expression [58, 61],

$$\frac{J_s}{J_w} = \frac{B}{A \cdot i \cdot R_g \cdot T} \cdot \left(1 + \frac{A \cdot \Delta P}{J_w} \right) \quad (\text{Eq 2.4})$$

While reverse solute flux is independent of the hydraulic pressure difference across the membrane, the specific reverse solute flux in ODMP increases with hydraulic pressure on the draw solution side of the membrane. When the hydraulic pressure difference across the membrane is sufficiently high such that the direction of water flux is reversed (that is, when moving into the RO region in **Figure 2.1**), the direction of specific reverse solute flux is reversed as well. Further increase in the hydraulic pressure difference results in reducing specific reverse solute flux instead.

2.2. Potential applications of FO process

FO process has been proposed as a potential solution, either on its own or integrated with other membrane separation process, for desalination [24, 62-65], wastewater treatment and resource reclamation [24, 66, 67], landfill leachate treatment [68], direct fertigation [69] as well as enrichment processes of liquid food or other high value-added feed streams [70-72]. The advantages associated with FO process are mainly due to the low hydraulic pressure required in this osmotically driven process [73]. As FO process can be operated in the absence of high hydraulic pressure, there is less constraint on the

mechanical strength of the membranes [74]. It is therefore possible to achieve low energy consumption with FO, provided that suitable draw solutes and regeneration methods can be economically developed. The potential applications of FO are briefly described in the following sections.

2.2.1. Desalination

Desalination is an important process that enables the extraction of freshwater from seawater and brackish water. It is widely adopted in many regions with limited freshwater resources. Currently, RO is considered the most energy efficient technology in seawater desalination process [75]. The energy consumption of seawater desalination by RO process can be as low as 3 kWh/m³ [76], which is close to the theoretical minimum energy requirement of 1 kWh/m³ [77]. However, the energy consumption of the desalination process is still much higher than the treatment of local surface water resources [78], as it is necessary to exert high hydraulic pressure to overcome the osmotic pressure of seawater. In order to reduce the energy requirement of desalination process, it was proposed to apply FO as an alternative desalination method by utilizing the inorganic salts of ammonia and carbon dioxide gases as the draw solute [17, 26, 27]. Osmotic pressure that is much higher than that of seawater can be generated with the draw solute, which drives high water flux across the membrane and enables high water recovery without applying high hydraulic pressure. Subsequently, product water is yielded after recovery of the draw solute from the diluted draw solution, which is based on thermal decomposition of the salts at 60 °C [27]. The energy requirement of the FO desalination process was estimated to be 0.84 kWh/m³, which is significantly lower than other desalination technologies.

FO can be combined with RO to reduce the energy consumption in desalination process [23, 28, 29]. When low salinity impaired water is available, it can be used as a feed for FO process, which dilute seawater before it is fed to the RO process. As diluted seawater has a lower osmotic pressure, the hybrid process could reduce energy consumption of the desalination process. Incorporation of FO could also increase the capacity of desalination process to handle feed water with high concentration of contaminants [29]. Alternatively, PRO process may

be incorporated to recover energy from the osmotic pressure gradient between the brine stream and the low salinity stream. It was estimated that the combination of FO-RO-PRO processes could reduce the energy consumption of seawater desalination by half [79].

Evaluation of FO membranes for desalination were mostly carried out by using sodium chloride (NaCl) solutions as a model seawater feed [80, 81]. McCutcheon et al. investigated the use of ammonia and carbon dioxide as a draw solute for desalination of NaCl solutions by the FO process [80]. By using FO membrane from Hydration Technologies Inc. (HTI), water flux of 3.6-36.0 L/m²/h was achieved and NaCl rejections were found to be 95-99% when using 0.05-2.0 M NaCl as feed. Sukipaneenit et al. tested the desalination performance of their tailor-made TFC hollow fiber membranes with 3.5 wt% NaCl as feed and 2 M NaCl as draw solution, which achieved water flux of 15-18 L/m²/h when testing in the PRO mode [81]. Han et al. tested TFC FO membranes fabricated from polysulfone substrates blended with sulfonated poly(ether ketone) in the PRO mode with 2 M NaCl as draw solution and 3.5 wt% NaCl as feed, which obtained water flux of 22 L/m²/h [82].

2.2.2. Concentration and dewatering of food products

Liquid concentration is one of the important steps in liquid food processing industry [25, 83]. By concentrating liquid food, the mass and volume of food products can be reduced, which lowers the cost of packing, transport, handling and storage [83]. The removal of excess water from food product is also necessary to improve product stability and prepare the product for complete drying treatment [83]. Conventionally, concentration of liquid food is achieved by using thermal processes such as evaporation and freeze concentration process [83]. One major drawback of thermal evaporative process is the loss of volatile compounds from the product due to heating [83, 84]. The aromatic compounds can be partially recovered by vapour distillation, but it may substantially increase the cost of production [83]. Thermal evaporative process may also degrade the flavour and colour of food products and alter their original tastes [25]. RO process has also been developed as a concentration technique which has low thermal effect, high aromatic retention, lower equipment cost and

lower energy consumption [25, 83]. Nevertheless, the degree of concentration of food products by RO process is limited by the final osmotic pressure of the final product, and further increase in concentration results in severe membrane fouling and reduction in permeate flux [25, 84].

Some alternative low-pressure membrane processes for liquid concentration included FO, membrane distillation and osmotic distillation [83]. The lower cost of FO membranes and their longer life cycle are some of the advantages of the FO process over other potential solutions [84]. Liquid concentration by FO is also known as direct osmosis concentration (DOC) process and has been proposed as an efficient alternative to thermal evaporation for concentrating food products [25]. Food products that have been investigated in DOC process included grape juice [30], raspberry juice [31], tomato juice [32, 33] and grapefruit juice [34]. The process usually employs draw solutes that are non-toxic and inert towards the flavour, odour and colour of the food product (such as sodium chloride, sucrose or glycerol, cane molasses or corn syrup) [25]. This quality of the concentrate is improved as the food product is not exposed to high temperature during the FO process, although evaporation process is still required to regenerate the diluted draw solution generated from the DOC process.

2.2.3. Wastewater treatment

FO process may be applied in wastewater treatment processes with a few advantages over conventional technologies. Particularly, FO membranes exhibit relatively high selectivity, such that all particulates, pathogens and most dissolved solids can be retained [21, 37, 85]. A comprehensive review on the application of FO in wastewater treatment was published in 2014 [22].

Conventional municipal wastewater treatment facilities produce stabilized biomass known as sludge after degrading the organic constituents in wastewater. The sludge is typically dewatered prior to land applications or disposal. Holloway et al. investigated the feasibility of applying FO in concentrating nutrient-rich centrate generated from sludge dewatering process and using it as a pretreatment for RO. They demonstrated that sustainable

performance could be achieved for an extended period of time [86]. Other than sludge treatment, FO can be used to reclaim water directly from wastewater. Achilli et al. developed an osmotic membrane bioreactor (OsMBR) by incorporating a submerged cellulose triacetate flat sheet FO module into a bioreactor [35]. In addition to sustainable water flux and low draw solute leakage into the mixed liquor, the OsMBR process achieved 99% organic carbon removal and 98% ammonium-nitrogen removal. A long-term pilot tests has been conducted to determine the sustainability and permeate quality of a coupled FO-RO system fed with raw wastewater. Serious membrane fouling was found after four months of operation [36]. Besides that, salinity in the bioreactor increased steadily due to reverse salt flux from draw solution through the FO membrane, which suppressed the biological activity in the activated sludge.

FO is also applied to concentrate landfill leachate, a liquid waste that originates from the decomposition of waste and rainwater that seeped through solid waste [21]. A pilot study on FO process was conducted to treat landfill leachate, which operated at 94-96% water recovery and effectively reject contaminants without significant membrane fouling [37]. A full-scale FO system was also constructed to concentrate landfill leachate and treat diluted draw solution with RO to produce high quality permeate that meets discharge standards [87]. The process achieved more than 99% rejection of cadmium, chromium, copper, lead, zinc and ammonia, and the effluent has biological oxygen demand (BOD) of less than 5 mg/L.

In addition, FO is also used in the field of oil and gas exploration, which generates huge quantities of grid-laden wastewater containing high concentrations of chemical oxygen demand (COD) and total dissolved solids (TDS) from well drilling operations [21]. By using a mobile system known as the Green Machine, it was shown that the wastewater can be concentrated by more than 3.5 times using 26 wt% NaCl as draw solution (which is subsequently diluted to 7 wt% NaCl) [21]. Exploration of unconventional oil and gas by hydraulic fracturing also produces large amount of wastewater that is several times the volume of oil and gas recovered [88]. These waste streams contain varying TDS concentration, free and emulsified hydrocarbons, silt and clay leached from the formation [38]. Hutchings et al. employed FO for the treatment

of oil and gas fracturing waste streams [39]. They were able to reduce the wastewater volume for disposal and minimize freshwater demand through the reuse of water recovered from the waste, which lowered the trucking demand and resulted in a reduction of carbon footprint.

2.3. Challenges in FO process

2.3.1. Concentration polarization

Osmotically driven water flux across a selectively permeable membrane could translate to convective movement of solutions, which disturbs the local concentration of solutes near the membrane. This phenomenon is known as concentration polarization (CP), which is schematically illustrated in **Figure 2.2**. As osmotic pressure is proportional to the solute concentration, the occurrence of CP may significantly reduce the osmotic pressure difference across the membrane [37]. This could be translated to a lower water flux across the membrane due to diminished osmotic driving force.

2.3.1.1. External concentration polarization (ECP)

On the feed side of the membrane, solutes are carried along with the feed solution which is constantly moving towards the membrane to replenish the water drawn into the draw solution. As the solutes are rejected by the membrane, they are accumulated near the surface of the membrane. Meanwhile, the solute concentration gradient that results from the build-up of local solute concentration due to convection drives the diffusion of solutes away from the membrane surface. The solute flux across membrane surface can therefore be described as the sum of the convective and diffusive components,

$$J_s = C(x) \cdot J_w - D \cdot \frac{dC(x)}{dx} \quad (\text{Eq 2.5})$$

Figure 2.2 Concentration polarization in asymmetric membrane operating with (a) active layer-facing-draw solution (AL-DS) configuration and (b) active layer-facing-feed solution (AL-FS) configuration.

where $C(x)$ is the solute concentration at any point of distance x from the membrane. At steady state, the net solute flux at membrane surface would be equal to the solute flux across the selective layer. When there is no net solute flux across the membrane, a closed form solution could be obtained by the film theory approach [89], and the solute concentration at the surface of the membrane can be expressed as:

$$\text{Boundary conditions: } C(x) = \begin{cases} C_{f,b}, & x = -\delta_f \\ C_{f,m}, & x = 0 \end{cases}$$

$$C_{f,m} = C_{f,b} \cdot \exp\left(\delta_f \cdot \frac{J_w}{D}\right) \quad (\text{Eq 2.6})$$

where $C_{f,m}$ is the solute concentration at membrane surface facing the feed solution, $C_{f,b}$ is the solute concentration in bulk feed solution, and D is the

diffusivity of the solute. δ_f is the thickness of the boundary layer on the feed side surface of the membrane, beyond which the concentration of solutes is the same as the bulk feed solution. This phenomenon is known as concentrative external concentration polarization (CECP).

On the other hand, CP also occurs on the side of the membrane facing the draw solution, but the effect is the opposite to the CP happening on the feed side. The water permeated from feed side constantly dilutes the draw solution and carries the solutes in the draw solution away from membrane surface. As the result, the local concentration of solutes on the draw side surface of the membrane is lower than the bulk draw solution. A closed form solution can be derived in a similar way as equation 2.6, and the steady-state concentration of solutes on membrane surface is described by the expression:

$$\text{Boundary conditions: } C(x) = \begin{cases} C_{d,m}, & x = 0 \\ C_{d,b}, & x = \delta_d \end{cases}$$

$$C_{d,m} = C_{d,b} \cdot \exp\left(-\delta_d \cdot \frac{J_w}{D}\right) \quad (\text{Eq 2.7})$$

where $C_{f,m}$ is the solute concentration at membrane surface facing the draw solution, $C_{d,b}$ is the solute concentration in bulk draw solution, δ_d is the thickness of boundary layer on the draw side surface of the membrane. This phenomenon is known as dilutive external concentration polarization (DECP).

For solute transport over the surface of semipermeable membranes, the net solute flux at membrane surface is equal to the reverse solute flux at steady state. Thus, the expanded expressions for DECP and CECP can be obtained [90, 91],

$$C_{f,m} = C_{f,b} \cdot \exp\left(\delta_f \cdot \frac{J_w}{D}\right) + \frac{B}{J_w} (C_{d,m} - C_{f,m}) \cdot \left[\exp\left(\delta_f \cdot \frac{J_w}{D}\right) - 1 \right] \quad (\text{Eq 2.8})$$

$$C_{d,m} = C_{d,b} \cdot \exp\left(-\delta_d \cdot \frac{J_w}{D}\right) - \frac{B}{J_w} (C_{d,m} - C_{f,m}) \cdot \left[1 - \exp\left(-\delta_d \cdot \frac{J_w}{D}\right) \right] \quad (\text{Eq 2.9})$$

where k_f and k_d are the mass transfer coefficients in the flow channels feed side and draw side of the membrane, as defined by the following:

$$k_f = \frac{D}{\delta_f} \quad (\text{Eq 2.10})$$

$$k_d = \frac{D}{\delta_d} \quad (\text{Eq 2.11})$$

While it is possible to determine the mass transfer coefficient from experimental data, it can also be estimated from the following equation:

$$k = \frac{Sh \cdot D}{d_h} \quad (\text{Eq 2.12})$$

where Sh is the Sherwood number, and d_h is the hydraulic diameter of the flow channel. Depending on the flow regime and the geometry of the flow channel, the Sherwood number can be calculated,

For rectangular channel,

$$Sh = \begin{cases} 1.85 \cdot \left(Re \cdot Sc \cdot \frac{d_h}{L} \right)^{0.33} & (\text{laminar flow}) \\ 0.04 \cdot Re^{0.75} \cdot Sc^{0.33} & (\text{turbulent flow}) \end{cases} \quad (\text{Eq 2.13})$$

where Sc is the Schmidt number, Re is the Reynolds number, and L is the channel length. Nevertheless, it is possible to alleviate the adverse effects of ECP on membrane performance by increasing the crossflow velocity of solutions or by introducing turbulence over membrane surface [37], which increases the mass transfer coefficient at the membrane surface.

2.3.1.2 Internal concentration polarization (ICP)

Most of the membranes today possess asymmetrical structures, where only the thin and dense layer (also known as the selective layer) on one (or both side) of the surface of the membrane is selective. Therefore, the driving force of the ODMP is determined by the osmotic pressure difference across the selective layer of the asymmetrical membrane. On the other hand, the relatively thick and porous layer beneath the selective layer (i.e. the support layer) serves to provide mechanical support and maintain the structural integrity of the selective layer during handling and operation.

However, the support layer also forms a local unstirred region on one side of the selective layer that further hinders the solute transport between the bulk

solution and selective layer of the membrane [18]. Therefore, the CP within the support layer could result in substantially greater difference between the solute concentration at the surface of selective layer and that in bulk solution. This phenomenon is known as internal concentration polarization (ICP).

The effect of ICP may vary substantially with the operating orientation of the asymmetric membrane in ODMP [92]. For operation of membrane with active-layer-facing-feed-solution configuration (AL-FS, also known as FO mode), the selective layer is in contact with the feed solution directly, while the support layer of the membrane faces the draw solution. As such, the diffusion of draw solute toward the selective layer is hindered by the support layer, resulting in a lower solute concentration at the interface between the selective layer and support layer. Therefore, this phenomenon is known as dilutive internal concentration polarization (DICP) [37, 91]. The solute transport across the support layer can be described in similar way as equation 2.5,

$$J_s = C(x) \cdot J_w - D_s \cdot \frac{dC(x)}{dx} \quad (\text{Eq 2.14})$$

where D_s is the effective diffusion coefficient of solute inside the support layer. D_s accounts for the contribution of support layer characteristics and is related to the bulk diffusion coefficient as follows [90],

$$D_s = D \cdot \frac{\varepsilon}{\tau} \quad (\text{Eq 2.15})$$

where τ , and ε are the tortuosity and porosity of the support layer. At steady state, the net solute flux across the support layer of the membrane is equal to the reverse solute flux across the selective layer, and the following solution can be derived after integrating equation 2.14 with boundary conditions across the support layer,

$$\begin{aligned} \text{Boundary conditions: } C(x) &= \begin{cases} C_{s/s} , & x = 0 \\ C_{d,m} , & x = t \end{cases} \\ C_{s/s} &= C_{d,m} \cdot \exp\left(-\frac{J_w \cdot t \cdot \tau}{D \cdot \varepsilon}\right) - \frac{B}{J_w} (C_{s/s} - C_{f,m}) \cdot \left[1 - \exp\left(-\frac{J_w \cdot t \cdot \tau}{D \cdot \varepsilon}\right)\right] \end{aligned} \quad (\text{Eq 2.16})$$

where $C_{s/s}$ is the concentration of solute at selective layer-support layer interface, and t is the thickness of the support layer. Assuming that the van't

Hoff's Law (equation 2.1) applies, the governing equation for water flux in ODMP that solely accounts for DICP in asymmetric membrane can be obtained by solving equation 2.2 and equation 2.16 to give:

$$K = \frac{1}{J_w} \cdot \ln \left[\frac{(J_w + A \cdot \Delta P) \cdot \left(\frac{B}{J_w}\right) + A \cdot \pi_{d,m}}{(J_w + A \cdot \Delta P) + (J_w + A \cdot \Delta P) \cdot \left(\frac{B}{J_w}\right) + A \cdot \pi_{f,m}} \right] \quad (\text{Eq 2.17})$$

where $\pi_{d,m}$ and $\pi_{f,m}$ are the osmotic pressure at the membrane surface facing the draw solution and feed solution, respectively, and K is the resistance of the support layer towards solute diffusion. K is defined as follows:

$$K = \frac{t \cdot \tau}{\varepsilon \cdot D} \quad (\text{Eq 2.18})$$

The contribution of the support layer characteristics to ICP is often separately evaluated in terms of structure parameter, S , which is defined as follows,

$$S = \frac{t \cdot \tau}{\varepsilon} \quad (\text{Eq 2.19})$$

For operation of membrane with active-layer-facing-draw-solution configuration (AL-DS, also known as PRO mode), the selective layer faces the draw solution, while the support layer faces the feed solution. In this scenario, solutes from the feed solution are convectively transported into the support layer. This process leads to solute concentration build-up at the selective layer-support layer interface, and is known as concentrative ICP (CICP) [37, 90]. The solute concentration at selective layer-support layer interface can be derived in the same way as equation 2.15 with a different set of boundary conditions across the support layer:

$$\text{Boundary conditions:} \quad C(x) = \begin{cases} C_{f,m}, & x = 0 \\ C_{s/s}, & x = t \end{cases}$$

$$C_{s/s} = C_{f,m} \cdot \exp\left(\frac{J_w \cdot \tau \cdot t}{D \cdot \varepsilon}\right) + \frac{B}{J_w} (C_{d,m} - C_{s/s}) \cdot \left[\exp\left(\frac{J_w \cdot \tau \cdot t}{D \cdot \varepsilon}\right) - 1\right] \quad (\text{Eq 2.20})$$

Similar to equation 2.16, the governing equation for ODMP that solely accounts for CICP in asymmetric membrane can be obtained by substituting equation 2.20 into equation 2.2,

$$K = \frac{1}{J_w} \cdot \ln \left[\frac{(J_w + A \cdot \Delta P) + (J_w + A \cdot \Delta P) \cdot \left(\frac{B}{J_w}\right) + A \cdot \pi_{d,m}}{(J_w + A \cdot \Delta P) \cdot \left(\frac{B}{J_w}\right) + A \cdot \pi_{f,m}} \right] \quad (\text{Eq 2.21})$$

By taking the effects of both ECP and ICP into account, the effective solute concentration difference across the selective layer of an asymmetric membrane operating with AL-FS configuration at steady state can be determined by substituting equation 2.9 into equation 2.16 and subsequently subtract equation 2.8 from it,

$$\Delta C_{eff} = C_{d,s/s} - C_{f,m} = \frac{C_{d,b} \cdot \exp \left[-J_w \cdot \left(\frac{1}{k_d} + K \right) \right] - C_{f,b} \cdot \exp \left(\frac{J_w}{k_f} \right)}{1 + \frac{B}{J_w} \cdot \left\{ \exp \left(\frac{J_w}{k_f} \right) - \exp \left[-J_w \cdot \left(\frac{1}{k_d} + K \right) \right] \right\}} \quad (\text{Eq 2.22})$$

For asymmetric membrane operating with AL-DS configuration, the effective solute concentration difference across the selective layer of the membrane at steady state can be determined by substituting equation 2.8 into equation 2.20 and subsequently subtract equation 2.9 from it,

$$\Delta C_{eff} = C_{d,m} - C_{f,s/s} = \frac{C_{d,b} \cdot \exp \left(-\frac{J_w}{k_d} \right) - C_{f,b} \cdot \exp \left[J_w \cdot \left(\frac{1}{k_f} + K \right) \right]}{1 + \frac{B}{J_w} \cdot \left\{ \exp \left[J_w \cdot \left(\frac{1}{k_f} + K \right) \right] - \exp \left(-\frac{J_w}{k_d} \right) \right\}} \quad (\text{Eq 2.23})$$

By substituting equation 2.22 or 2.23 into equation 2.1 and 2.2, the water flux across asymmetric membrane operating with either AL-FS or AL-DS configuration can be expressed as the following,

AL – FS configuration:

$$J_w = A \left\{ \frac{\pi_{d,b} \cdot \exp \left[-J_w \cdot \left(\frac{1}{k_d} + K \right) \right] - \pi_{f,b} \cdot \exp \left(\frac{J_w}{k_f} \right)}{1 + \frac{B}{J_w} \cdot \left\{ \exp \left(\frac{J_w}{k_f} \right) - \exp \left[-J_w \cdot \left(\frac{1}{k_d} + K \right) \right] \right\}} - \Delta P \right\} \quad (\text{Eq 2.24})$$

AL – DS configuration:

$$J_w = A \left\{ \frac{\pi_{d,b} \cdot \exp \left(-\frac{J_w}{k_d} \right) - \pi_{f,b} \cdot \exp \left[J_w \cdot \left(\frac{1}{k_f} + K \right) \right]}{1 + \frac{B}{J_w} \cdot \left\{ \exp \left[J_w \cdot \left(\frac{1}{k_f} + K \right) \right] - \exp \left(-\frac{J_w}{k_d} \right) \right\}} - \Delta P \right\} \quad (\text{Eq 2.25})$$

On the other hand, the reverse solute flux can be estimated from the water flux by using equation 2.4, regardless of the orientation of the asymmetric membrane.

Unlike ECP, improving the hydrodynamic conditions at membrane surface by increasing crossflow velocity and inducing turbulence do not help to alleviate ICP, as the phenomena was caused by hindered mass transport within the support layer of the membrane. In order to suppress ICP, it is necessary to optimize structure of the support layer and reduce the mass transfer resistance of the membrane. The desirable characteristics of support layer includes high porosity, low thickness and low tortuosity. Besides that, improving the diffusion rate of draw solute by reducing solution viscosity or using draw solute with higher diffusivity may alleviate ICP as well.

2.3.2. Reverse solute diffusion

Due to concentration difference of draw solute across the membrane in FO process, there is always a small portion of draw solute that diffuses across the membrane from the draw solution side into the feed solution side. As the feed gets concentrated during the FO process, the concentration of solutes escaped from draw side will gradually build up in the feed solution. Consequently, the osmotic pressure of the feed solution could rise within a shorter period, which lowers the performance of FO process and limits the final water recovery. Contamination of feed solution by accumulated draw solutes could negatively impact the quality of the concentrated feed, which may require further treatment to remove the draw solute [61].

Moreover, reverse solute diffusion may contribute to water flux decline associated with ICP, depending on the operating orientation of the FO membrane [18]. In AL-DS orientation, reverse solute diffusion may promote the accumulation of draw solute within the support layer caused by CICI. As the result, the effective osmotic pressure difference across the FO membrane is further reduced. If the feed solution has relatively low osmotic pressure, the enhanced CICI due to reverse solute diffusion could result in more severe water flux decline. For FO membrane operated in AL-FS orientation, reverse solute

diffusion may speed up the loss of draw solute across the selective layer from the support layer into the feed solution. As the diffusion of draw solute into the support layer is already retarded by DICP in such membrane orientation, the occurrence of reverse solute diffusion may further reduce the concentration of draw solute at the interface between the support layer and the selective layer. As such, the effective osmotic pressure across the FO membrane may be suppressed by reverse solute diffusion as well, causing severe water flux decline. The impact of reverse solute diffusion can be evaluated in terms of the reverse solute flux and specific reverse solute flux of the membrane during the FO process [93]. As defined earlier in section 2.1, the reverse solute flux depends on the solute permeability coefficient and the solute concentration difference across the selective layer of the membrane, whereas specific reverse solute flux is related to the selectivity of the active layer of the membrane and should be independent of the draw solute concentration and the properties of the support layer [61]. A higher reverse solute flux indicates poorer selectivity and lower FO efficiency.

Reverse solute diffusion can be suppressed by improving the selectivity of the membrane, or by employing multivalent salts (e.g. CaCl_2 and MgCl_2) as the draw solutes [93]. However, the latter may also cause a reduction in the water flux due to increase severity of ICP, as the multivalent ions are greater in their molecular size and lower diffusion coefficient as compared to monovalent ions [94].

2.3.3. Membrane fouling

During the FO process, the water flux driven by osmotic pressure difference could generate convective movement of feed solution which carries the dissolved and suspended matters in the feed solution towards the membrane. Due to occurrence of CP, these substances will be concentrated at the membrane surface. As the result, some of these substances, including colloidal matters, organic macromolecules, sparingly soluble inorganic compounds, and microorganisms may deposit on the surface or within the membranes [73, 74]. This phenomenon is known as membrane fouling and could significantly deteriorate the performance of FO membranes. The impacts of membrane

fouling included water flux decline, lower water recovery, lower permeate quality and shortened membrane lifespan [18]. Therefore, membrane cleaning has to be carried out periodically to remove the deposited foulants and restore the performance of the membranes, which may increase the operating cost of the process.

Membrane fouling is a common problem in many membrane processes, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and RO [95-97]. A few studies on membrane fouling in FO processes reported fouling mechanisms that were similar to those in NF and RO processes [18]. Solution chemistry, foulant-foulant interactions, hydrodynamic conditions and membrane surface characteristics were found to influence membrane fouling in the FO process [98]. Membrane fouling may affect the FO performance of membranes in several ways [18]. The formation of cake layer from deposited foulants could increase the hydraulic resistance of the membrane and lead to a reduction in water flux. The cake layer also acts as an unstirred region that hinders the diffusion of solutes into the bulk feed solution. As a result, the CP at membrane surface is aggravated, which could increase the concentration of solute at the membrane surface facing the feed solution. Such a condition is known as cake-enhanced concentration polarization (CE-CP) and could cause water flux decline due to a reduction of the effective osmotic pressure difference across the membrane.

Membrane fouling in FO process is also influenced by ICP and reverse solute diffusion, which are phenomena that are unique to ODMP [99-101]. The impact of ICP in FO process is lower when water flux is lower. Therefore, a reduction of water flux in FO process caused by membrane fouling will be compensated by a slight increase in osmotic driving force due to lowered ICP. Such a self-compensation effect of ICP is often more pronounced when the membrane is operated in the AL-FS orientation. Reverse solute diffusion may aggravate membrane fouling in the FO process [102, 103]. The reverse diffusion of the draw solutes may interact with the organic foulants and scaling precursors in the feed solution and exacerbate membrane fouling [100, 101, 104, 105]. Reverse solute diffusion can also lead to increase in the ionic strength of the feed solution near the membrane surface, which destabilizes the foulants suspended in feed solution and accelerates the deposition of foulants [106].

Membrane fouling can take place at membrane surface or within the porous support layer of the membrane, depending on the operating orientation of the membrane in the FO process [18]. For membranes operated in the AL-FS orientation, where the dense selective layer is in contact with feed solution, foulants are mostly retained and accumulated on the membrane surface. Such condition is known as external fouling and could lead to formation of a cake layer on top of the selective layer. On the other hand, if FO membrane is operated in the AL-DS orientation, where the porous support layer is facing the feed solution, the fouling mechanism may vary with the size of the foulants. Foulants with size smaller than the pores of the support layer may infiltrate and accumulate within the support layer, and such a condition is known as internal fouling. External fouling may also take place when foulants of greater size are present. External fouling is more reversible as compared to internal fouling, as it can be controlled by varying the hydrodynamic conditions of surface of the membrane facing the feed solution, such as increasing the crossflow velocity [102, 107-109], using suitable feed spacers [107, 110, 111], applying air scouring [112] or changing flow patterns [107]. In contrast, the hydrodynamic condition within the porous support layer could not be manipulated directly, making internal fouling less reversible [113].

Depending on the characteristics of the foulants, the type of fouling can be categorized into colloidal fouling, organic fouling, inorganic scaling, biofouling, or a combination of them [18]. Colloidal fouling is caused by the deposition of colloidal particles on the membrane, whereas organic fouling is caused by the adsorption of macromolecular organic compounds on the membrane. Colloidal particles and organic macromolecular compounds are commonly found in wastewaters and natural waters [98, 108, 114-116]. Examples of commonly encountered colloidal and organic foulants include polysaccharides (alginate, xanthan and gellan, schizophyllan)[117], humic substances (humic acid) [118], proteins (bovine serum albumin (BSA), lysozyme) [119], and inorganic colloids (silica, aluminum silicates, ferric hydroxide) [118]. Inorganic scaling is another common fouling for membrane processes in wastewater reclamation and brackish water desalination [104, 120-122]. Inorganic scaling is caused by precipitation of sparingly soluble inorganic compounds on the membrane when

the concentration of the dissociated ions in the solution exceeds the supersaturation limit [123]. While colloidal fouling and organic fouling may occur even at low foulant concentration, inorganic scaling only occurs when the concentration of the sparingly soluble inorganic compounds exceed a critical value. Calcium carbonate (CaCO_3), calcium sulfate ($\text{CaSO}_4 \cdot x\text{H}_2\text{O}$), calcium phosphate (Ca_3PO_4) and aluminosilicates are the common scale-forming mineral compounds that are encountered in pressure-driven and osmotically driven membrane processes [18, 105, 123]. Most of the existing studies on inorganic scaling in FO process were carried out by using calcium sulfate as the model scaling precursor [18, 124, 125]. While formation of calcium sulfate scale is relatively independent of solution pH, inorganic scaling caused by calcium carbonate, calcium phosphate and silica-based precursors are strongly associated with the solution pH [18, 123]. Biofouling is caused by attachment and growth of microorganisms on the membrane. When nutrients are present, the microorganisms could multiply and secrete extracellular polymeric substances (EPS), which eventually form aggregated structures known as “biofilms” on the membrane surface [126, 127]. As such, biofouling can be a serious issue even if microorganism is present in very small numbers. Application of FO process that may be affected by biofouling included desalination, bio-product separation, and wastewater treatment processes [101, 110, 120, 128-132]. Other than introducing additional hydraulic resistance, the attached microorganisms may also break down the membrane material and accelerate the degradation of membranes [133].

2.3.4. Mechanical stability

In addition to perm-selectivity, FO membranes should possess good mechanical properties to maintain membrane integrity and ensure stable operations [134-137]. In order to minimize the impact of ICP on the performance of asymmetric membranes in the FO process, the support layer of the membrane has to be thin, highly porous and comprises highly interconnected pore structures. However, membranes which exhibit these characteristics often have poor mechanical stability. Therefore, FO membranes that were optimized to improve their water flux often have low mechanical strength. As such, the FO

membranes may be more vulnerable to mechanical deformation during process operations when subjected to fluctuations in operating pressure. The lack of mechanical durability could be a major drawback of FO membrane that hampers the advancement of FO process for practical applications.

2.3.5. Draw solute regeneration

As discussed, FO may be a potential alternative in water reuse and desalination, as FO process could achieve high water flux with low energy consumption. Yet, unlike RO and most of other hydraulic pressure driven membrane processes, which produce purified product water after retaining unwanted dissolved or suspended solids from feed, the products of FO process are concentrated feed and diluted draw solution. As such, a second process is required to extract water from the diluted draw solution and regenerate the draw solution in the FO process. Inorganic salts are often used as draw solutes as they create high osmotic pressure [138]. Yet, these draw solutes can only be recovered by means of RO or distillation process, which greatly increases the overall energy requirement of the processes.

Therefore, draw solutes which can be regenerated easily are required to recover the product water from the FO process in an energy-saving and cost-effective way [62]. A dozen of research studies have been carried on draw solutes that are responsive towards physical stimuli such as temperature, pH, electromagnetic field and light [46]. Ammonium bicarbonate is one of the most promising draw solutes, as it can produce high osmotic pressure and be regenerated by mild heating of the solution [17].

While the use of responsive draw solute enables the recovery of draw solute with physical stimuli such as temperature change, the net energy consumed in draw solute regeneration process may not be lower than the RO process [46]. However, the cost associated with regeneration of responsive draw solute may be significantly lower as expensive electrical energy consumption can be partially substituted with inexpensive energy such as industrial low-grade heat [46]. Therefore, FO process driven by using efficient responsive draw solutes may achieve significant cost-saving as compared to RO process.

2.4. Development of membrane for FO process

2.4.1. Desirable membrane characteristics

For early investigations on FO, the studies were carried out by using semipermeable cellulosic membranes which were designed for RO desalination process, and extremely low water flux were observed [37]. It was later found out that the unexpected low water flux was caused by unfavorable properties related to the structure of the membranes. While the thick and compact support layer of RO membranes provide excellent mechanical stability to resist mechanical deformation under a high pressure, it could largely hindering mass transfer and causing severe ICP within the support during FO [139]. Cath et al summarized the ideal characteristics of FO membrane that could help to improve the efficiency of the FO process [37]. The membrane should possess a dense selective layer which can effectively reject the solutes. In order to suppress ICP, the membrane should be thin, and consists of highly porous support layer. Also, the membrane should be hydrophilic to make it more resistant to membrane fouling. In cases where the membrane is subjected to elevated hydraulic pressure (e.g. PRO and PAO), the membrane should possess sufficiently high mechanical strength in order to resist deformation under the applied pressure. Currently, investigations on FO membrane fabrications were mostly focused on cellulosic membranes, thin-film composite (TFC) membranes and polyelectrolyte-based membranes [140].

2.4.2. Membrane materials and fabrication techniques

2.4.2.1. Cellulosic membranes

Hydration Technologies Inc. (HTI) developed the first commercial FO membranes, one of which was made of cellulose triacetate (CTA) and was embedded with thin polyester mesh support [37, 140, 141]. The thickness of the FO membrane is less than 50 μm , and the membrane lacks a thick support layer that is commonly present in RO membranes. This FO membrane has been used for investigations of FO and related processes [37]. Cellulose esters have been used extensively for fabrication of FO membrane due to its good mechanical

properties, commercial availability, relatively high hydrophilicity and resistance to chlorine attack [142, 143]. An overview on the development of cellulosic membrane for FO process is presented in Table 2.1.

Table 2.1. An overview on the development of cellulosic membranes for FO process.

Membrane materials	Objective of study	Membrane properties			FO performance			Ref.	
		A (LMH/ bar)	B (LMH)	S (μm)	Water flux (LMH)	Reverse solute flux (gMH)	Testing conditions		
CA/NMP/ Acetone	<ul style="list-style-type: none">Investigate the effect of substrate chemistry on membrane structurePrepare flat sheet FO membranes that with good rejection, high water flux and minimized ICP	0.17	0.07	54	10.3 ± 0.3 (AL-FS)	0.8 ± 0.1 (AL-FS)	2.0 M MgCl ₂ as draw; DI water as feed	[142]	
					17.3 ± 0.4 (AL-DS)	1.2 ± 0.2 (AL-DS)			
		0.13	0.09	51	9.8 ± 0.7 (AL-FS)	1.2 ± 0.3 (AL-FS)			
					14.7 ± 1.0 (AL-DS)	2.2 ± 0.4 (AL-DS)			
CA/ acetone/ formamide	<ul style="list-style-type: none">Develop CA nanofiltration hollow fiber membranes with high salt rejection as FO membranes	0.47	-	-	2.69±0.07 (AL-DS)	0.17±0.02 (AL-DS)	0.5 M MgCl ₂ as draw, DI water as feed	[144]	
CA/NMP/ acetone	<ul style="list-style-type: none">Studied membrane formation by non-solvent induced phase inversion process with the aid of positron annihilation spectroscopy (PAS)Studied the effects of polymer and substrate hydrophilicity, membrane thickness and solvent on the porosity, thickness and separation performance of membrane bottom layer	1.2 ±0.1	-	-	7.7 ± 0.4 (AL-FS)	3.8 ± 0.2 (AL-FS)	2.0M MgCl ₂ as draw; DI water as feed	[145]	
CTA/NMP/ acetone		-	-	-	9.4 ± 0.4 (AL-FS)	12.7 ± 0.8 (AL-FS)			
CAP/NMP/ acetone		-	-	-	7.6 ± 0.5 (AL-FS)	921 ± 21 (AL-FS)			
CAB/ NMP/ acetone		-	-	-	7.4 ± 0.3 (AL-FS)	1520 ± 35 (AL-FS)			
CAB/NMP/ acetone/ formamide	<ul style="list-style-type: none">Synthesized cellulose esters with different degree of substitution of functional groupsEvaluated the potential of the asymmetric FO membranes prepared from the cellulose esters via non-solvent induced phase inversion techniqueInvestigated the relationship among cellulose ester chemistry, physicochemical properties, casting conditions and FO performance	0.51	0.40	-	21.6 (AL-DS)	10.6 (AL-DS)	2.0 M NaCl as draw; DI water as feed	[146]	
					9.4 (AL-FS)	3.9 (AL-FS)	1.0 M NaCl as draw; DI water as feed		
CTA/NMP/ acetone	<ul style="list-style-type: none">Studied the effect of solvent systems on the performance of CTA FO membranes with the aid of advanced characterization tools (PAS, molecular simulations, FTIR)	-	-	-	11.2 ± 2.1 (TOP-DS)	101 ± 14 (TOP-DS)	2.0 M NaCl as draw; DI water as feed	[147]	
					15.3 ± 3.3 (BOT-DS)	125 ± 7.5 (BOT-DS)			
CTA/ dioxane/ acetone		-	-	-	1.5 ± 0.1 (TOP-DS)	2.4 ± 1.7 (TOP-DS)			
					3.6 ± 0.4 (BOT-DS)	1.3 ± 0.4 (BOT-DS)			
CTA/ dioxane/ acetone/ acetic acid		-	-	-	12.8 ± 0.6 (TOP-DS)	6.8 ± 0.2 (TOP-DS)			
CA/CTA/ boehmite/ dioxane/ acetone/ methanol/ lactic acid	<ul style="list-style-type: none">Investigated the effects of incorporating boehmite nanoparticles in the preparation of nanocomposite FO membranes	0.48 ± 0.03	0.10 ±0.004	1360 ± 70	5.5 ° (AL-FS)	2.5 ° (AL-FS)	1.0 M NaCl as draw; 10 mM NaCl as feed	[148]	
		1.1 ± 0.06	0.16 ±0.011	790 ± 40	10.8 ° (AL-FS)	3.3 ° (AL-FS)			
		1.43 ± 0.05	0.18 ±0.010	530 ± 50	15.2 ° (AL-FS)	4.7 ° (AL-FS)			
		1.51 ± 0.06	0.37 ±0.012	960 ± 80	10.9 ° (AL-FS)	9.0 ° (AL-FS)			

^a Abbreviations: CA (cellulose acetate), CAB (cellulose acetate butyrate), CAP (cellulose acetate propionate), CTA (cellulose triacetate), FTIR (Fourier transform infrared spectroscopy), NMP (N-methyl-2-pyrrolidone)

^b TOP-DS was referring to the testing orientation where the top layer of the membrane faces the draw solution, whereas BOT-DS was referring to the testing orientation where the bottom layer of the membrane faces the draw solution

^c The values of water flux and reverse salt flux were estimated from provided figures.

Cellulosic membranes are typically prepared by phase inversion via immersion precipitation method. The fabrication cellulosic membranes in both flat sheet and hollow fiber configuration has been reported in the literature [142, 144-148]. Zhang et al. fabricated CA flat sheet membranes with single and double dense layers and investigated the effect of casting substrate on the properties of the membrane [142]. The membrane with double dense layer was formed on glass substrate, whereas membrane with a dense top layer and porous bottom layer was formed on the Teflon substrate. The membrane with double dense layer was found to be more resistant to fouling by colloidal Al_2O_3 particles. When mixtures of NMP and water was used as intermediate coagulation bath, the top layer of the membrane would become porous, and the resulting membrane had a lower structural parameter. Su et al. fabricated cellulose acetate (CA) hollow fiber membrane with NF outer skin layer and investigated the effect of heat treatment on membrane properties and FO performance [144]. They found that heat treatment at 60 °C for 60 min had only slight effect on the membrane, whereas further heat treatment at 95 °C for 20 min caused significant membrane shrinkage, lower water permeability and significantly improved rejection to NaCl and MgCl_2 . However, the latter suffered severe ICP during the FO process. Ong et al. investigated the effect of the degree of substitution of cellulose esters with different functional groups on the properties of the membranes fabricated by the phase inversion process [146]. They found that highly hydrophobic cellulose esters produce membranes with defects due to rapid phase separation during membrane formation process, whereas cellulose esters that were too hydrophilic suffered high salt leakage due to significant swelling of polymer chains in water. Ong et al. investigated the effect of different solvents on the properties of CTA FO membranes [147]. It was found that membranes prepared by using dioxane as the solvent had a dense close-cell sublayer structure, whereas membranes prepared from NMP as solvent had a looser dense layer. The former exhibited high NaCl rejection but lower water flux than the latter. They also found that the addition of acetic acid in casting solution of CTA dissolved with dioxane/acetone could increase the free volume of the dense selective layer and create more porous open-cell sublayer, which showed better FO performance. Zirehpour et al. prepared a CTA/CA-based FO membrane that incorporated boehmite nanoparticles [148]. The incorporation of boehmite

nanoparticles reduced mean pore size, increased porosity and improved the hydrophilicity of the membrane. Thus, water permeability of the membranes was enhanced alongside the FO water flux while reducing the specific salt flux of the membrane in the FO process.

Nevertheless, membranes prepared from cellulose esters generally do not tolerate extreme pH, which could accelerate membrane degradation due to hydrolysis [73, 149]. Therefore, it is recommended to operate these membranes between pH 4-6 and maintaining the working temperature at below 35 °C [73, 149, 150]. Cellulose esters are prone to biological degradation as well, but chlorination can be adopted to control microbial growth when the feed contains significant loading of microorganisms [73, 150].

2.4.2.2. Polyamide thin-film composite membranes

Over the last decade, a large number of studies on the preparation and characterization of polyamide thin-film composite (TFC) membranes for FO process has been reported in literature [81, 82, 139, 151-174]. TFC membrane consists of a thin and dense selective layer that is laid on top of a microporous substrate. Owing to the extremely low thickness of the selective layer, TFC membranes could achieve significantly high selectivity while retaining decent permeability, making it a desirable choice for water purification and wastewater treatment processes. Polyamide TFC membranes have been widely applied to desalinate seawater and brackish water, or to remove heavy metals, hardness and micropollutants [175, 176]. An overview of the development of TFC membranes for FO process is presented in Table 2.2.

Table 2.2. An overview of the development of TFC membranes for FO process.

Membrane materials	Objective of study	Membrane properties			FO performance			Ref.
		A (LMH/bar)	B (LMH)	S (µm)	Water flux (LMH)	Reverse solute flux (gMH)	Testing conditions	
Support layer: PSI/NMP/ PVP Monomers used in IP: MPD, TMC	<ul style="list-style-type: none"> Investigated the effect of monomer concentrations used in interfacial polymerization (IP) on the separation properties and the FO performance of the TFC flat sheet membrane. 	0.8 ~ 5.7	-	710 ± 140	14.4 ~ 21.5 ° (AL-FS)	0.5 ~ 1.2 ° (AL-FS)	2.0 M NaCl as draw, 10 mM NaCl as feed	[153]
					35.5 ~ 37.2 ° (AL-DS)	0.5 ~ 2.7 ° (AL-DS)		

<u>Support layer:</u> PSf/DMAC/ HNTs <u>Monomers used in IP:</u> MPD, TMC	<ul style="list-style-type: none"> Incorporated HNT in the PSf support layer of TFN membrane. Incorporated g-C₃N₄ during interfacial polymerization to fabricate the selective layer of TFN flat sheet membranes. Investigated the effect of varying loading of g-C₃N₄ on the morphology, hydrophilicity, structural parameter and FO separation performances of the TFN membrane. 	0.78 ±0.16	0.19 ±0.04	1410 ±110	5.10±0.66 (AL-FS)	2.51±0.21 (AL-FS)	2.0 M NaCl as draw, DI water as feed	[177]
		2.0 ±0.14	0.43 ±0.05	850 ±70	10.1±0.54 (AL-FS)	2.70±0.12 (AL-FS)		
		2.17 ±0.18	0.39 ±0.06	370 ±90	18.9±0.35 (AL-FS)	2.74±0.15 (AL-FS)		
		2.42 ±0.23	0.47 ±0.07	200 ±140	20.4±0.78 (AL-FS)	3.53±0.25 (AL-FS)		
<u>Support layer:</u> PSf/DMF/ PVP <u>Monomers used in IP:</u> MPD, TMC	<ul style="list-style-type: none"> Incorporated MWCNTs functionalized with amine groups into the polyamide selective layer of TFN flat sheet membrane during IP. Investigated the effect of varying loading of MWCNTs on the morphology, hydrophilicity, structural parameter and FO separation performances of the TFN membrane. 	3.1 ±0.04	0.140 ±0.043	440 ±100	27.2 ^b (AL-FS)	3.23 ^b (AL-FS)	2.0 M NaCl as draw, 10 mM NaCl as feed	[159]
					37.8 ^b (AL-DS)	7.52 ^b (AL-DS)		
		3.44 ±0.2	0.130 ±0.029	420 ±50	28.7 ^b (AL-FS)	2.80 ^b (AL-FS)		
					66.7 ^b (AL-DS)	6.42 ^b (AL-DS)		
		3.6 ±0.16	0.103 ±0.014	380 ±30	30.8 ^b (AL-FS)	2.43 ^b (AL-FS)		
					73.4 ^b (AL-DS)	4.31 ^b (AL-DS)		
		4.47 ±0.24	0.170 ±0.025	410 ±100	39.1 ^b (AL-FS)	2.92 ^b (AL-FS)		
					95.2 ^b (AL-DS)	5.21 ^b (AL-DS)		
<u>Support layer:</u> PSf/DMF/ PVP <u>Monomers used in IP:</u> MPD, TMC	<ul style="list-style-type: none"> Investigated the effect of adding LiCl and spinning parameters during the fabrication of PEI hollow fiber substrate on the structural parameter and mechanical properties of the membrane. Incorporated AQP in the polyamide selective layer during IP and investigated its effect on the intrinsic separation properties and FO performance of the TFC membrane. 	7.64 ^b	0.53 ^b	172 ±6	49.1 (AL-FS)	4.7 (AL-FS)	1.0 M NaCl as draw, DI water as feed	[178]
					91.2 (AL-DS)	9.9 (AL-DS)		
<u>Support layer:</u> PSf/NMP/ DMF/PVP (with non-woven PET fabric) <u>Monomers used in IP:</u> MPD, TMC	<ul style="list-style-type: none"> Fabricated PSf substrates with systematically varied casting parameters (solvent composition, dope polymer concentration, substrate fabric wetting, and the gate height of the casting blade). Investigated the effect of casting parameters on the membrane transport and structural characteristics Evaluated the relationship between the membrane characteristics and the performance of the TFC membrane. 	0.66 ~ 1.90	0.20 ~ 0.84	312 ~ 7934	0.5 ~ 25.0 (AL-FS)	-	1.0 M NaCl as draw, DI water as feed	[174]
<u>Support layer:</u> PSf/NMP/ PEG/PVP (with non-woven PET fabric) <u>Monomers used in IP:</u> MPD, TMC <u>Additives used in IP:</u> TEA, CSA	<ul style="list-style-type: none"> Fabricated PSf substrates with systematically varied casting parameters (solvent composition, dope polymer concentration, substrate fabric wetting, and the gate height of the casting blade). Investigated the effect of casting parameters on PSf substrate characteristics (pore size, porosity, and hydrophilicity) Investigated the effects of varying substrate characteristics on the separation properties of TFC membranes 	1.14 ~ 6.90	0.197 ~ 1.007	-	-	-	-	[179]
<u>Support layer:</u> PES/NMP/ PEG/ DI water <u>Monomers used in IP:</u> MPD, TMC <u>Additives used in IP:</u> TEA, SDS	<ul style="list-style-type: none"> Investigated the effect of varying bore fluid composition during the fabrication of PES hollow fiber substrates on the structural characteristics, separation properties and FO performance of TFC membranes. 	1.18	0.135	219	32.1 (AL-FS)	6.15 (AL-FS)	2.0 M NaCl as draw, DI water as feed	[81]
					57.1 (AL-DS)	6.93 (AL-DS)		
		1.64	0.281	252	34.1 (AL-FS)	7.10 (AL-FS)		
					62.7 (AL-DS)	10.30 (AL-DS)		
		1.83	0.348	261	34.5 (AL-FS)	9.87 (AL-FS)		
					65.1 (AL-DS)	12.34 (AL-DS)		

<u>Support layer:</u> PES/ PES-co- sPPSU/ NMP/EG <u>Monomers used in IP:</u> MPD, TMC	<ul style="list-style-type: none"> Blended PES-co-sPPSU into casting solution for the fabrication of PES flat sheet substrate. Investigated the effect of varying PES-co-sPPSU content on the morphology and pore size distribution and mechanical properties of the PES substrate, as well as the separation properties and FO performance of the TFC membrane 	0.68	0.22	963	13.5 (AL-DS)	3.7 (AL-DS)	2.0 M NaCl as draw, DI water as feed	[152]
					10.5 (AL-FS)	3.1 (AL-FS)		
		0.72	0.23	512	21.0 (AL-DS)	3.7 (AL-DS)		
					16.5 (AL-FS)	3.1 (AL-FS)		
		0.73	0.25	324	33.0 (AL-DS)	2.8 (AL-DS)		
					21.0 (AL-FS)	2.2 (AL-FS)		
<u>Support layer:</u> PSf/SPEK/ NMP/DEG <u>Monomers used in IP:</u> MPD, TMC	<ul style="list-style-type: none"> Blended SPEK into casting solution for the fabrication of PSf flat sheet substrate. Investigated the effect of varying SPEK content on the morphology and pore size distribution and mechanical properties of the PSf substrate, as well as the separation properties and FO performance of the TFC membrane. Investigated the effect of heat treatment on the morphology and pore size distribution and mechanical properties of the PSf substrate, as well as the FO performance of the TFC membrane. 	0.50	0.041	182	38 (AL-DS)	6 (AL-DS)	2.0 M NaCl as draw, DI water as feed	[82]
					23 (AL-FS)	4 (AL-FS)		
		0.67	0.062	156	42 (AL-DS)	7 (AL-DS)		
					29 (AL-FS)	5 (AL-FS)		
		0.75	0.068	107	50 (AL-DS)	9 (AL-DS)		
					35 (AL-FS)	7 (AL-FS)		
<u>Support layer:</u> PPSU/ (or sPPSU) NMP/EG <u>Monomers used in IP:</u> MPD, TMC	<ul style="list-style-type: none"> Applied directly sulfonated PPSU as the substrate materials. Studied the morphology, pore size distribution and mechanical properties of flat sheet substrate prepared by using sPPSU with different degrees of sulfonation. Investigated the separation properties and FO performance of TFC membranes prepared with sPPSU substrates. 	12.53	5.78	2940	10 (AL-DS)	2.1 (AL-DS)	2.0 M NaCl as draw, DI water as feed	[158]
					10 (AL-FS)	2.3 (AL-FS)		
		3.23	1.05	652	54 (AL-DS)	8.8 (AL-DS)		
					48 (AL-FS)	7.6 (AL-FS)		
<u>Support layer:</u> Commercial CTA membrane <u>Monomers used in IP:</u> MPD, TMC	<ul style="list-style-type: none"> Applied commercial CTA membrane as the substrate for TFC membrane preparation. Used TMC, succinyl chloride and malonyl chloride to pretreat substrate, which act as the linker for creating covalent crosslinks between substrate and polyamide selective layer. Investigated the morphology, separation properties and FO performance of the TFC membranes prepared with the use of different linkers. 	0.29 ±0.03	-	-	2.4 ^b	49 ^b	2.0 M NaCl as draw, DI water as feed	[157]
		0.27 ±0.03	-		6.5 ^b	12 ^b		
		0.5 ~1.87	-		6.8 ^b	7.6 ^b		
<u>Support layer:</u> PSf/NMP/ PVP/LiCl/ Zeolite <u>Monomers used in IP:</u> MPD, TMC	<ul style="list-style-type: none"> Blended zeolite into PSf flat sheet substrate during phase inversion process Investigated the effect of varying zeolite loading on the morphology, pore size distribution, structural parameter of PSf substrate. Evaluated the separation properties and FO performance of TFC membranes. 	1.87	-	960 ±100	34 (AL-DS)	13 (AL-DS)	2.0 M NaCl as draw, DI water as feed	[163]
					13 (AL-FS)	6.5 (AL-FS)		
		3.30	-	340 ±60	86 (AL-DS)	57 (AL-DS)		
					40 (AL-FS)	29 (AL-FS)		
		4.27	-	370 ±20	-	-		
<u>Support layer:</u> PES/ DMAc/ PVP/ MWCNTs <u>Monomers used in IP:</u> MPD, TMC	<ul style="list-style-type: none"> Blended carboxylated MWCNTs into PES flat sheet substrates during phase inversion process. Investigated the effect of varying carboxylated MWCNTs loading on the morphology, pore size, hydrophilicity and mechanical properties of PES substrates, as well as the separation properties and FO performance of the TFC membranes. 	2.31 ±0.18	0.79 ±0.32	2340	11.9 (AL-DS)	-	2.0 M glucose as draw, 10 mM NaCl as feed	[180]

<u>Support layer:</u> PSf/NMP/ LiCl/PVP/ UiO-66 <u>Monomers used in IP:</u> MPD, TMC	<ul style="list-style-type: none">• Incorporate water stable UiO-66 nanoparticles into PSf flat sheet substrates during phase inversion process.• Investigated the effects of varying UiO-66 loading on the morphology, pore size distribution and hydrophilicity of PSf substrate, as well as the separation properties and FO performance of the TFC membranes.• Examined the stability of the separation properties of TFC membranes over 72 hours.	2.19 ±0.27	0.27 ±0.15	528	26 ^b (AL-DS)	-	1.0 M NaCl as draw, DI water as feed	[181]
		2.53 ±0.13	0.37 ±0.17	s477	17 ^b (AL-FS)	-		
					30 ^b (AL-DS)	-		
		2.87 ±0.23	0.52 ±0.14	443	19 ^b (AL-FS)	-		
					33 ^b (AL-DS)	-		
		3.31 ±0.26	0.53 ±0.19	351	20 ^b (AL-FS)	-		
40 ^b (AL-DS)	-							
25 ^b (AL-FS)	-							
2.58 ±0.09	0.47 ±0.02	427	29 ^b (AL-DS)	-				
			20 ^b (AL-FS)	-				
<u>Support layer:</u> PSf/DMAc/ PVP/HNTs <u>Monomers used in IP:</u> MPD, TMC	<ul style="list-style-type: none">• Incorporated HNTs in PSf flat sheet substrate during phase inversion process.• Investigated the influence of varying HNTs loading on the hydrophilicity, pore size, porosity, roughness and morphology of PSf substrates, as well as the separation properties and FO performance of TFC membrane.	1.12	0.117	950 ±100	13.3 (AL-FS)	6.02 (AL-FS)	2.0 M NaCl as draw, 10 mM NaCl as feed	[182]
		1.70	0.228	620 ±60	22.8 (AL-FS)	11.1 (AL-FS)		
		2.00	0.336	370 ±50	27.7 (AL-FS)	14.6 (AL-FS)		
		2.56	1.50	210 ±20	36.6 (AL-FS)	20.3 (AL-FS)		
<u>Support layer:</u> PES/NMP/ DMF (electrospun nanofiber, or phase inversion membrane) <u>Monomers used in IP:</u> MPD, TMC	<ul style="list-style-type: none">• Prepared and characterized TFC membranes from electrospun PES nanofiber substrate and phase inversion PES flat sheet substrates in terms of morphology and separation properties.• Compared the FO performance of the TFC membranes prepared from different substrates and a commercial cellulosic FO membrane.	1.70 ±0.10	-	80 ±6	37.8 (AL-FS)	-	0.5 M NaCl as draw, DI water as feed	[151]
		1.65 ±0.14	-	106 ±8	33.9 (AL-FS)	-		
		1.25 ±0.12	-	450 ±50	13.4 (AL-FS)	-		
<u>Support layer:</u> PAN/CA/ DMF (electrospun nanofiber) <u>Monomers used in IP:</u> MPD, TMC	<ul style="list-style-type: none">• Blended PAN and CA to prepare nanofiber mats by electrospinning and used them as the substrates for preparation of TFC membranes.• Evaluated the morphology, hydrophilicity, mechanical properties, separation properties and FO performance of the TFC membranes.	1.17 ±0.66	2.25 ±0.36	693 ±181	24 ^b (AL-DS)	5.7 ^b (AL-DS)	1.5 M NaCl as draw, DI water as feed	[156]
					13 ^b (AL-FS)	4.0 ^b (AL-FS)		
		1.29 ±0.27	0.56 ±0.33	624 ±62	36 ^b (AL-DS)	3.5 ^b (AL-DS)		
					15 ^b (AL-FS)	8.3 ^b (AL-FS)		
		1.80 ±0.14	0.58 ±0.22	311 ±63	43 ^b (AL-DS)	1.8 ^b (AL-DS)		
					27 ^b (AL-FS)	3.9 ^b (AL-FS)		
		2.04 ±0.95	1.57 ±1.16	291 ±53	52 ^b (AL-DS)	3.3 ^b (AL-DS)		
					29 ^b (AL-FS)	8.4 ^b (AL-FS)		

Abbreviations: AQP (aquaporin), CSA (camphor sulfonic acid), DMAc (N,N-dimethylacetamide), DMF (N,N-dimethylformamide), EG (ethylene glycol), HNTs (halloysite nanotubes), IP (interfacial polymerization), LiCl (lithium chloride), MPD (m-phenylenediamine), MWCNTs (multiwalled carbon nanotubes), NMP (N-methyl-2-pyrrolidone), PAN (polyacrylonitrile), PEG (polyethylene glycol), PEI (polyetherimide), PES (polyethersulfone), PES-co-sPPSU (block copolymers of polyethersulfone and sulfonated polyphenylenesulfone), PET (polyethyleneterephthalate), PSf (polysulfone), PVP (polyvinylpyrrolidone), PPSU (polyphenylenesulfone), SDS (sodium dodecylsulphate), SPEK (sulfonated poly(ether ketone)), TEA (triethylamine), TFN (thin-film nanocomposite), TMC (trimethylsilyl chloride)

^b The values were estimated from the provided figures.

2.4.2.2.1. Preparation and modification of polyamide selective layer

Polyamide TFC membranes are typically fabricated via a two-step process [183]. The first step involved the fabrication of a porous substrate, which is usually a polymeric membrane with relatively small pore size and exhibits MF to UF selectivity. The second step involves the deposition of the selective layer on top

of the porous substrate, which is often achieved by using a technique known as the interfacial polymerization (IP). The concept of IP was first proposed by Mogan in 1965 [176, 184], whereas Cadotte developed the first RO membrane that was fabricated based on the IP technique [185]. This technique involves the polycondensation reaction between monomers dispersed in two immiscible solvents that takes place at the interface of the solvents, forming an ultrathin layer of highly crosslinked polymeric structure. The selective layer prepared from IP technique usually consists of polyamide, which is formed by reacting diamines with aromatic acyl chlorides. Among the commonly used reactive monomers, the reaction between m-phenylenediamine (MPD) and trimesoyl chloride (TMC) is the most popular choice to prepare high-performance desalination membranes [176]. The two-step fabrication process made it possible to individually tune the characteristics of the selective layer and the support layer of TFC membrane, thus achieving desirable permeability, selectivity and mechanical strength [176].

The performances of polyamide TFC membrane are mainly determined by the thin-film structure (i.e. pore dimension, thickness, roughness and hydrophilicity) and its chemical properties (i.e. crosslinking, functional groups and bonds) [176]. The crosslinking degree and thickness of the selective layer are the main factors that affect the water permeability and selectivity of polyamide TFC membranes [186]. A few approaches have been explored to modify the characteristics of the selective layer in attempt to improve the FO performance of the polyamide TFC membranes. These approaches include varying the concentration of amine/acyl chloride monomer concentrations [153], and the addition of nanofillers [177] during the IP process. Wei et al. fabricated polyamide TFC FO membranes by using MPD and TMC as monomers and investigated the effect of monomer concentrations on the performance of TFC FO membranes [153]. With increasing TMC concentration, the permeability of the TFC membrane increased, but its salt rejection was decreased. The opposite trend was observed with increasing MPD concentration. Besides that, it was found that high reverse solute diffusion caused by poor salt rejection of the membrane could aggravate ICP and significantly reduce the water flux in the FO process. Based on the observed trade-off between water permeability and selectivity, it

was concluded that TFC FO membranes may have to be optimized differently depending on the main limiting factor that affects the water flux of the membrane under specific operating conditions. Rezaei-DashtArzhandi et al. prepared thin-film nanocomposite (TFN) membrane by incorporating graphitic carbon nitride (g-C₃N₄) nanoparticles into the polyamide selective layer [177]. By loading 0.05 wt/v% of g-C₃N₄ into MPD solution during IP process, the resulting TFN membrane exhibited higher water flux without increasing reverse solute flux during the FO process and experienced less water flux decline when tested with bovine serum albumin (BSA) as a model foulant. Amini et al. fabricated TFN membranes by incorporating amine functionalized multi-walled carbon nanotubes (F-MWCNTs) in the polyamide selective layer [159]. The surface hydrophilicity and roughness of TFN membranes increased with higher F-MWCNTs loadings in the TFN membranes. Compared to the TFC membrane fabricated without adding F-MWCNTs, the water permeability of the TFN membrane prepared with 0.1 wt% F-MWCNTs loading was 44% higher. The salt rejection of TFN membrane was higher than TFC membrane at low F-MWCNTs loadings of 0.01-0.05 wt% but decreased with higher F-MWCNTs loadings. The TFN membranes also exhibited higher water flux and lower reverse solute flux with increasing F-MWCNTs loading.

To overcome the trade-off between the permeability and selectivity of polyamide TFC membranes, one of the solutions was to incorporate aquaporins (AQP) and other equivalent water channels into the selective layer of the membrane [28]. AQP is a special class of protein which selectively facilitate water transport, and it exists in different forms in animals and plants [187]. The concept of biomimetic membrane is essentially to mimic the water transport mechanism in biological systems, which theoretically could achieve 100% rejection of all solutes except water if the proteins are properly embedded in a solute-impermeable matrix. Although the protein itself exhibit extremely high permeability and selectivity, the main challenge was to develop scalable membrane fabrication strategies which can effectively exploit the unique properties the proteins [188]. The performance of biomimetic membranes has been reported in several studies [178, 189-192], most of which exhibit higher permeability and selectivity as compared to other types of commercial FO membranes [139]. Yet, it should be noted that most of

the reported performance were characterized from very small membrane area [188].

2.4.2.2.2. Modification of the support layer by tuning phase inversion process

The FO performance of TFC membrane is also significantly affected by the characteristics of the support layer. As discussed earlier in **Section 2.3**, the impact of ICP of the water flux of the membrane in FO process is affected by the structural parameter of the support layer and is influenced by the porosity, tortuosity and thickness of the support layer. Besides that, the structure of the support layer could affect the formation of the selective layer, and therefore could substantially affect the performance of the membrane [140]. Tiraferri et al. investigated the influence of polysulfone support layer on the performance of the TFC membranes by varying the casting conditions of the polysulfone support layer formed by phase inversion process [174]. It was found that the structure, porosity, and hydrophobicity of the skin layer could affect the permeability and separation performance of the polyamide selective layer formed in IP process [179]. They concluded that the optimal FO membrane should possess a thin sponge-like top layer and a highly porous sublayer filled with macrovoids, and the structural dependence of each layer should be controlled independently during the fabrication of the microporous support. Yet, the influence of support layer morphology on the FO performance of TFC membranes is still debatable, as contradictory observations have been reported in the literature. Sukitpaneemit et al. fabricated macrovoid-free PES hollow fiber substrates by using dual-layer coextrusion technique and prepared TFC membrane from the substrate by the IP technique [81]. To achieve complete macrovoids suppression, water was added into the dope to bring it closer to the binodal boundary. Pure solvent was coextruded on the outer surface of the dope during membrane spinning process to create porous structures on the outer surface of the membrane. The macrovoid-free TFC membranes have a low structural parameter (219 – 261 μm) as compared to most membrane reported in the literature.

Various approaches have been taken to modify the characteristics of the microporous substrate of polyamide TFC membrane. One of the common

approaches is by blending commonly used polymers with hydrophilic materials during the fabrication of the microporous substrates [82, 152]. Widjojo et al. fabricated TFC membranes from substrates that were prepared from polyethersulfone (PESU) and sulfonated copolymer of polyethersulfone and polyphenylene sulfone (PESU-co-sPPSU) by the phase inversion process [152]. The TFC membranes prepared from substrates with 50 wt% sulfonated copolymer content exhibit fully sponge-like structure and produced higher water flux as compared to TFC membranes prepared from substrates with lower sulfonated copolymer content, although the latter exhibit fully finger-like structures. It was shown that the structural parameter of the TFC membrane decreased substantially with increasing sulfonated copolymer content in the substrate. The results implied that the hydrophilicity of the membrane substrate had significant impact on the structural parameter of the TFC membranes. Similar findings were reported by Han et al., who fabricated flat sheet membrane substrates for TFC membranes by blending polysulfone (PSU) with sulfonated poly(ether ketone) (SPEK) [82]. Partial substitution of PSU with SPEK changed the morphology of the membrane from finger-like to fully sponge-like structure. The PSU-SPEK blended membrane possessed significantly lower tensile strength and higher ductility. The structural parameter of the membrane was significantly reduced after blending 50 wt% SPEK into the substrate due to the improvement of hydrophilicity. It was concluded that substrate hydrophilicity and thickness have greater influence on the performance of TFC FO membranes as compared to membrane morphology. Other than the polymer blending approach, the hydrophilicity of membrane substrate can be tuned by controlling the proportion of sulfonated monomers used to synthesize the polymer for substrate fabrication. Widjojo et al. fabricated TFC membranes from substrates that were casted from sulfonated polyphenylenesulfone (sPPSU) comprising three different degrees of sulfonation [158]. The degree of sulfonation was controlled by varying the concentration of sulfonated monomer (sDCDPS) during polymer synthesis. The substrate prepared from the polymer synthesized with 2.5 mol% sulfonated monomer (sPPSU-2.5) possessed rather uniform sponge-like structure. The water flux and reverse salt flux of TFC membrane fabricated from sPPSU-2.5 were 54 L/m²/h when tested in PRO mode with 2 M NaCl as draw and DI water as feed. This was 5 times the water flux of the TFC membrane

fabricated from PPSU substrate. The structural parameter of the TFC membrane prepared from sPPSU-2.5 substrate (652 μm) was much lower than the TFC membrane prepared from PPSU substrate (2940 μm). However, the mechanical strength of the substrates decreased significantly with increasing degree of sulfonation.

Fabrication of polyamide TFC membrane from substrates prepared with more hydrophilic polymer has also been investigated. However, preparation of polyamide TFC membranes with hydrophilic substrates by the IP technique is often found to be unsuccessful, likely due to the poor adhesion of the polyamide layer and the hydrophilic substrate [157]. Alsvik et al. attempted to create covalent bonding between the polyamide selective layer and hydrolyzed CTA substrate by using TMC, succinyl chloride or malonyl chloride as the linking molecules. They investigated the effect of different linking molecules on the performance of the TFC membranes [157]. The selectivity of the TFC membrane prepared with TMC as the linking molecule was found to vary with salt concentration, which was attributed to membrane swelling due to the presence of high concentration of charged functional groups created by TMC. In comparison, the performance of TFC membranes prepared with succinyl chloride and malonyl chloride as the linking molecules showed less dependence on salt concentration.

The effect of blending nanofillers into the porous substrate has been investigated as well. Polyamide TFC membranes prepared from nanocomposite substrate exhibited less compaction and could maintain high water permeability [193]. The incorporation of nanofillers such as zeolites, titanium dioxide (TiO_2) nanoparticles, multiwalled carbon nanotubes (MWNTs), metal-organic frameworks (MOFs) and halloysite nanotubes (HNTs) in the support layer of TFC membrane has been shown to reduce the structure parameter of the membrane and increase the water flux of the membrane in the FO process [163, 166, 167, 180-182, 194]. The improvements were attributed to increased porosity, hydrophilicity and the formation of extra water passages by the embedded porous nanoparticles. Moreover, the TFC membranes fabricated from nanocomposite substrate possessed higher tensile strength. Ma et al. incorporated water-stable MOF (UiO-66) in the fabrication of the substrate for

the preparation of TFC-mixed matrix membranes (TFC-MMMs) [181]. With optimal UiO-66 loading of 6.5 wt%, they found that the TFC-MMMs possessed 51% higher water permeability and 34% lower structural parameter. Ghanbari et al. prepared TFN FO membrane by blending HNTs into PSU substrates [182]. They found that the performance of the FO membrane was optimal upon incorporation of 0.5 wt% HNTs in the substrate, which reduced the structure parameter from 0.95 mm to 0.37 mm.

2.4.2.2.3. Fabrication of TFC membrane on electrospun nanofiber membrane

Nanofiber membranes fabricated by the electrospinning technique is another type of substrate which can be used for fabrication of polyamide TFC membrane for FO process. Song et al. fabricated scaffold-like nanofiber support layers and used it as a substrate to prepare TFC membranes [151]. The tortuosity of the TFC membranes with nanofiber support was only 1.26 and 1.33, which was much lower than the TFC membrane prepared with support layer fabricated by phase inversion. Therefore, the TFC membrane with nanofiber support possessed much lower structural parameter and higher water flux in FO process. Bui et al. fabricated nanofiber mats with blends of polyacrylonitrile (PAN) and cellulose acetate (CA) and prepared polyamide TFC membranes by using the nanofiber mat as a substrate via the IP technique [156]. With increasing proportion of PAN in the substrate, the water flux of the TFC membranes increased significantly, and the structural parameter of the membranes decreased from 693.2 to 290.7 μm . The improvement was attributed to greater hydrophilicity of PAN, which increased porosity, reduced tortuosity and improved membrane wetting. The structural parameter of the nanofiber supported TFC membrane was further reduced to 109.1 μm after the removal of polyester nonwoven fabric sheet (PET) from the membrane.

2.4.2.3. Other types of membranes

Polyelectrolyte-based membranes have also been studied extensively in the FO process. Polyelectrolyte-based membrane is commonly prepared by layer-by-layer (LBL) assembly technique [195-198]. LBL assembly comprises sequential deposition of anionic polyelectrolyte and cationic polyelectrolyte on a porous

substrate by immersing the substrate in the solutions of the polyelectrolytes alternatively [195-198]. The alternating layers of anionic and cationic polyelectrolytes which are electrostatically adsorbed on the porous substrates form a dense network structure which interacts strongly with the permeating ions and exhibit highly selective ion transport properties [196, 199]. Moreover, alternate polyelectrolyte layers generally result in high water permeability, high solvent resistance and high thermal stability [199, 200].

Liu et al. prepared hollow fiber NF membranes via LBL deposition technique by using poly(styrenesulfonic acid) (PSS) and poly(allylamine hydrochloride) (PAH) as polyelectrolytes and evaluated the FO performance of the membrane by using MgCl_2 as the draw solute [195]. When tested in the AL-DS orientation with DI water and 0.5 M MgCl_2 as the feed and draw solutions, the hollow fiber membrane showed high water flux of $40.5 \text{ L/m}^2/\text{h}$ and low specific reverse solute flux of 0.201 g/L . Pardeshi et al. fabricated a FO membrane with LBL technique by using chitosan (CH) and polyacrylic acid (PAAc) as polyelectrolytes and the nanocomposite of polyvinyl alcohol (PVA) and methyl dihydroxyethyl hydrogenated tallow ammonium-modified montmorillonite clay (MMt-Ta) as the substrate [198]. The membrane showed water flux of $37.65 \text{ L/m}^2/\text{h}$ and very low reverse salt flux of $0.2813 \text{ g/m}^2/\text{h}$ when tested in the AL-DS orientation by using 2 M NaCl and DI water as the draw and feed solutions. Such high performance was attributed to the hydrophilicity of the porous substrate imparted by the intercalated layers of MMt-TA particles and PVA. Lee et al. synthesized FO membranes from PAN substrates blended with silica gel by LBL assembly, using PAH and PSS as the electrolytes [201]. The incorporation of silica gel significantly enhanced the water flux of the membrane in the FO process. This was attributed to presence of nanosized pores in the silica gel, which improved the porosity of the substrate. Water flux as high as $121 \text{ L/m}^2/\text{h}$ was achieved when tested with 2 M MgCl_2 as draw and DI water as feed.

In addition to the LBL assembly, FO membranes have also been fabricated through chemical modification of microporous substrates by using polyelectrolytes that can chemically react with the substrate [202, 203]. Setiawan et al. fabricated hollow fiber FO membranes with positively charged NF-like selective layer by treating microporous polyamide-imide (PAI)

substrates with polyethyleneimine. The FO membrane exhibited water flux of 9.74 L/m²/h and specific reverse solute flux of less than 0.4 g/L when tested in the AL-FS orientation with 0.5 M MgCl₂ and DI water as draw and feed. Setiawan et al. fabricated dual-layer hollow fiber substrates that consisted of PAI outer layer and PES inner layer and modified only the PAI layer with polyethyleneimine to prepare FO membranes with NF selectivity [204]. The dual-layer FO membrane possessed high water permeability of 15.9 L/m²/h/bar and rejected MgCl₂ at 89%. When the dual-layer FO membrane tested in the AL-FS orientation by using 0.5 M MgCl₂ and DI water as draw and feed solutions, it achieved water flux of 27.5 L/m²/h and specific reverse solute flux of 0.2 g/L. Goh et al. fabricated PAI hollow fiber substrate and deposited functionalized multi-walled carbon nanotubes (MWCNT) on the substrate by vacuum filtration before treating the substrate with polyethyleneimine [205]. The incorporation of MWCNT improved the water permeability of the polyethyleneimine modified membrane by 44% without significant increase in salt permeability. The FO water flux of the membrane containing MWCNT was 29% higher than the unfilled membrane with no MWCNT when tested in the AL-FS orientation with 0.5 M MgCl₂ and DI water as draw and feed solutions.

2.4.2.4. Summary

Overall, the studies carried out on FO membrane development were mainly focused on increasing the permeability and selectivity, while minimizing the structural parameter to improve the FO performance of the membrane. Membranes prepared via non-solvent induced phase inversion and interfacial polymerization techniques were extensively studied in large numbers of publications, where correlation between materials properties, fabrication parameters, membrane separation properties and the performance of membrane in FO process were systematically evaluated. The general characteristics of the three main classes of membranes frequently investigated in FO process are compared in **Table 2.3**.

Table 2.3. Summary on the main classes of FO membranes developed thus far.

Membrane	Fabrication techniques	Advantages	Disadvantages
Cellulosic asymmetric	Both support layer and selective layer of membrane are formed simultaneously by non-solvent induced phase inversion (mainly involved wet immersion precipitation process).	<ul style="list-style-type: none"> • Lower cost • Good chlorine resistance 	<ul style="list-style-type: none"> • Lower permeability • Narrow operating pH and temperature • Susceptible to biodegradation
Polyamide TFC	A microporous substrate that act as the support layer is first prepared by non-solvent induced phase inversion, which may involve wet immersion precipitation process or electrospinning technique. The selective layer is then formed on the surface of the substrate by interfacial polymerization technique.	<ul style="list-style-type: none"> • Higher permeability and selectivity • Can be operated over wider pH and temperature range • Support layer and selective layer may be optimized separately 	<ul style="list-style-type: none"> • Limited chlorine resistance • Lower fouling resistance
Polyelectrolyte based	A microporous substrate that acts as the support layer is first prepared by non-solvent induced phase inversion. The selective layer is formed by LBL assembly.	<ul style="list-style-type: none"> • High permeability • Solvent resistance • High thermal stability 	<ul style="list-style-type: none"> • Lower selectivity • Operating pH range vary with the chemical composition of the selective layer.

Increasing attention was paid to the structure and characteristics of the support layer of FO membranes, as well as the influence of these properties on the formation of the selective layer. Also, it has been increasingly recognized that the hydrophilicity of the support layer could substantially affect the structural parameter of FO membranes, in addition to the thickness and porosity of the support layer. On the other hand, most of the studies evaluated the FO performance of newly fabricated membranes with DI water or low concentration NaCl solution as the feed. Yet, it may be more practical to apply more realistic testing conditions to evaluate FO membranes that were intended for specific application.

Chapter 3 Investigating the Influence of Microporous Polyethersulfone Hollow Fiber Substrate on the Performance of Thin-Film Composite Membranes in Forward Osmosis Process

3.1. Introduction

Among the existing types of asymmetric membranes that have been studied for application in FO process, more attention was paid to polyamide TFC membrane as its selective layer and support layer could be optimized and modified separately to meet the requirements of the FO process [206]. TFC membranes can be fabricated with a few different geometries, including flat sheet, tubular, and hollow fibers [37]. Flat sheet membranes are widely applied in large-scale pressure-driven membrane processes and can be constructed in plate-and-frame or spiral-wound configurations [37]. However, the construction and operation of flat sheet membrane modules for FO process are relatively more complicated as the feed and draw solutions have to be circulated separately on two sides of the membrane [37]. In comparison, hollow fiber membrane exhibits several desirable characteristics as compared to flat sheet membranes when applied in FO process. It has a self-supported membrane geometry and can be packed into modules with flow channels to create suitable flow patterns for the FO process without the use of spacers [206-208]. In addition, the fabrication of hollow fiber module is less technically complex and high packing density can be achieved [206, 209].

For most of the reported studies on the fabrication of TFC hollow fiber membranes, the selective layer consisted of polyamide material that was formed on membrane surface in the lumen of the hollow fiber substrate [81, 206, 210-212]. The selective layer of TFC hollow fiber membrane can also be formed on the shell side of the hollow fiber substrate. Compared to inner-selective TFC hollow fiber membrane, outer-selective membrane has higher effective membrane area per unit length of membrane and is less vulnerable to severe

fouling [150, 209, 213]. However, the development of outer-selective membranes is relatively more challenging [209].

The support layer of TFC hollow fiber membranes is mostly formed via NIPS and is usually fabricated by a dry-jet wet spinning process [81, 206, 210-212]. During the fabrication process, the dope solution is prepared by dissolving polymer and additives in solvent before it is extruded from a spinneret. Bore fluid is pumped simultaneously from the center of the extruded dope to displace the dope solution to form the annular structure. The extruded solution travel across a small air gap before entering a bath containing non-solvents, where exchange of solvent and non-solvent leads to coagulation of the dope solution and forms the microporous hollow fiber substrate. The hollow fiber substrate is collected at a controlled rate by using a winding drum. Polymers that have been used to fabricate hollow fiber substrates via NIPS process included CTA [157, 214], cellulose acetate propionate (CAP) [215, 216], PSU [217], PES [81, 206, 210, 211], polyetherimide (PEI) [218], PAI [219], Matrimid [220], and polyacrylonitrile (PAN) [209]. Among the polymers above, PES is particularly suitable for the construction of the porous support layer of TFC membrane due to its thermal stability, wide pH tolerance and good mechanical strength [221]. Yet, PES is not as hydrophilic as compared to other materials like CTA and PAN.

Hydrophilic polymers such as polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP) are often used as additives in the dope solution to modify the properties of the microporous PES substrates [215, 222-225]. Idris et al prepared PES membranes with dimethylformamide (DMF) as the solvent and employed three types of PEG with different molecular weight (200 Da, 400 Da and 600 Da) as the additive [223]. They found that PEG with higher molecular weight improved the permeability of the membrane most significantly and increased the pore size of the membrane. In addition, they observed that increasing concentration of PEG 200 led to reduction in the permeability and reduced pore size of PES membrane, whereas increasing concentration of PEG 400 and PEG 600 led to increased permeability and increased pore size of PES membrane. Fathizadeh et al reported that PEG 600 significantly increased the water permeability of PES microporous substrate prepared with dimethylacetamide (DMAc) as the solvent [225], while the pore size of the

substrate was unaffected. Recently, Kahrs and Schwellenbach prepared PES membranes with four different solvents and used both PVP and PEG as the additives [226]. They found that the concentration of PEG has little effect on the permeability and solute retention properties of PES membrane, whereas increasing molecular weight of PEG led to increased permeability and decreased solute retention properties, regardless of the solvent used. In terms of membrane morphology, the addition of PEG was found to increase the size of macrovoids and reduce the thickness of the substrates [223, 224].

On the other hand, the effect of blending PVP into microporous membranes may vary substantially with the molecular weight and concentration of PVP. Miyano et al blended PVP with molecular weight of 10000 Da into casting solution of PES dissolved in dimethylsulfoxide (DMSO) and found that both permeability and pore size of prepared PES membrane decreased with increasing PVP content [227]. Fathizadeh et al added PVP K-90 into casting solution of PES in DMAc and reported similar observation as Miyano et al [225]. Al Malek et al and Vatsha et al investigated the effect of varying concentration of PVP in PES casting solutions prepared with n-methyl-2-pyrrolidone (NMP) as the solvent on the permeability and pore size of the PES membrane [228, 229]. Al Malek et al choose PVP with lower molecular weight (8000 Da) as the additive observed significantly enhanced membrane permeability with increasing PVP concentration, but when the concentration of PVP is higher than certain point, the membrane's permeability decreased instead [228]. Similar observation was reported by Kahrs and Schwellenbach[226]. The decrease in membrane permeability at high concentration of PVP was attributed to the formation of dense structure in the top layer of the membrane [228]. Vatsha et al selected PVP 40K as the additive and found that the permeability of PES membrane prepared with lower polymer concentration (16 wt%) increased with increasing PVP concentration [229]. Again, PES membranes that were prepared with higher polymer concentration (18%) showed reduction in permeability when the concentration of PVP exceed certain level. The contradictory observations regarding the effect of varying PVP concentration on the permeability of PES membrane may be caused by the influence of the solvent on the interaction between PES and PVP, as it is evident in the studies carried out by Kahrs and

Schwellenbach [226]. In terms of the effect of PVP on membrane morphology, Boom et al observed that the formation of macrovoids was suppressed with the addition of PVP into of the PES dope solution dissolved in NMP [230]. The opposite effect was observed when PVP was added into the PES dope solution that was dissolved in dimethylformamide (DMF) [231].

Despite having different effect on the properties of the substrates, both the incorporation of PEG and PVP during substrate fabrication reduced the water permeability and improved the salt rejection of TFC membrane [225]. Nonetheless, the effect of PEG and PVP as additives may vary with the molecular weight of the additive, concentration of the additive and the fabrication condition of the substrate [232].

Owing to the discrepancy and to optimize the TFC hollow fiber membranes for the FO process, the objective of this current study is to investigate the influence of the fabrication parameters on the properties of hollow fiber substrates and the performance of TFC hollow fiber membranes. Hollow fiber substrates were fabricated with three different dope compositions and varied concentration of solvent and pore-forming additive. Subsequently, inner-selective TFC hollow fiber membranes were fabricated by forming dense polyamide layer on the membrane surface at the lumen side of the hollow fiber substrates via IP process. The morphology, water permeability, pore size distribution and mechanical properties of hollow fiber substrates were characterized. The intrinsic separation properties of the TFC hollow fiber membranes were evaluated by low-pressure RO tests. The FO performance of the TFC hollow fiber membranes were assessed on a lab-scale FO setup. The current study aims to elucidate key characteristics of hollow fiber substrate which are associated with the perm-selective properties of the TFC membranes and their performance for the FO process.

3.2. Experimental

3.2.1. Materials

Polyethersulfone (PES, Gafone® 3000P, Solvay, Belgium), N-methyl-2-pyrrolidone (NMP, 99.5%, Merck Chemicals) and polyethylene glycol 200 (PEG, Merck Chemicals) were used the polymer, the solvent, and the pore-forming additive, respectively, in the fabrication of hollow fiber substrates. Tap water was used as the external coagulant. Dextrans standards (from *Leuconostoc mesenteroides*, Sigma-Aldrich) were used to determine the molecular weight cut-off (MWCO) of the substrate. Glycerol (85%, Merck Chemicals) was used for membrane post-treatment prior to storage. 1,3,5-Benzene-tricarbonyltrichloride (TMC, Sigma-Aldrich) and m-phenylenediamine (MPD, Sigma-Aldrich) were employed as the monomers in IP process. Cyclohexane (Merck Chemicals) was used as the solvent for TMC. Sodium chloride (NaCl, Merck Chemicals, Singapore) was used to prepare feed and draw solutions for FO experiments. Deionized (DI) water produced by Milli-Q system (Millipore, USA) was used to prepare all aqueous solutions in this study.

3.2.2. Fabrication of hollow fiber substrates

All hollow fiber substrates were fabricated by using a dry jet–wet spinning technique based on the NIPS process. The detailed procedures for hollow fiber spinning process can be found elsewhere [203, 218]. The polymer dopes used in spinning process were prepared by dissolving PES and PEG in NMP at 60°C with stirring until homogeneous mixtures were obtained. In order to investigate the influence of NMP and PEG concentrations in dope on the properties of hollow fiber membranes, polymer dopes with three different compositions were prepared. The first dope contained equal concentration of solvent and additive and was denoted as PES#1. The other dopes were prepared by adding either more NMP or more PEG into PES#1 and were denoted as PES#2 and PES#3, respectively. These two polymer dopes had the same polymer concentration while the NMP/PEG ratio varied. The composition of polymer dopes that were

employed to fabricate hollow fiber substrates is listed in **Table 3.1** and the fabrication conditions are provided in **Table 3.2**.

Table 3.1. Dope compositions and characteristics.

Dope ID	Composition (wt%) [PES/NMP/PEG]	Viscosity (Pa.s)	Cloud point (wt% of water)
PES#1	20.0/40.0/40.0	10.5	2.0
PES#2	19.0/38.0/43.0	8.0	2.5
PES#3	19.0/43.0/38.0	6.0	2.6

Table 3.2. Spinning conditions of PES hollow fiber membrane substrates.

Substrate ID	PES#1-1	PES#2-1	PES#3-1	PES#3-2
Spinneret dimension	ID = 0.5 mm, OD = 1.0 mm			
Dope composition	PES#1	PES#2	PES#3	PES#3
Dope flow rate (mL/min)	2.2	2.2	2.2	2.2
Bore fluid composition (wt% NMP/H ₂ O)	40/60	40/60	40/60	40/60
Bore fluid flow rate (mL/min)	2.1	2.1	2.1	1.5
Air gap (cm)	18	18	18	18
Take-up speed (m/s)	0.141	0.141	0.141	0.141
Coagulation bath	Tap water (23±1 °C)			

3.2.3. Fabrication of lab-scale modules

Laboratory-scale modules were used for all crossflow filtration, RO and FO experiments. The modules were packed by inserting 15 strands of hollow fibers into a Teflon® tube (3/8" inner diameter). The gap between the hollow fibers at both ends were sealed by using epoxy resin (Araldite Rapid 5 Minutes). The effective length of the hollow fibers in the module was around 26±1 cm.

3.2.4. Preparation of TFC hollow fiber membranes

All TFC hollow fiber membranes were prepared by performing IP on the lumen side of the PES hollow fiber substrates, based on the procedure described by Wang et al [206]. Firstly, the aqueous phase was prepared by dissolving MPD and additives in DI water, whereas the organic phase was prepared by dissolving TMC in cyclohexane. Under ambient temperature, the aqueous MPD solution was pumped through the lumen of post-treated hollow fiber membranes (packed in modules) and drained off after the solution was left standing in the membrane for 30 minutes. Then, the lumen of the hollow fiber was flushed with cyclohexane to remove excess aqueous MPD solution. Finally, the TMC solution was pumped through the lumen of the membrane, where the monomers react at the interface between immiscible phases and form a polyamide selective layer. The modules were immersed in DI water for 1 day prior to characterizations.

3.2.5. Hollow fiber substrates characterization

Keyence VHX500F Digital Microscope was used to observe the cross-section morphology and determine the dimension of PES hollow fiber substrates, where mean values were taken based on 10 replicate measurements using fresh hollow fibers before post-treatment in glycerol. JEOL JSM-7600F field emission scanning electron microscope (FE-SEM) was used to investigate the structure and morphology of the cross-section and surface of the hollow fiber membranes. After the hollow fiber samples are freeze-dried overnight and fractured in liquid nitrogen, they are mounted on the SEM stubs and sputter coated with platinum prior to observation under FE-SEM.

Bench-scale crossflow filtration setup was used to determine the pure water permeability (PWP) and MWCO of PES hollow fiber substrates. To determine PWP, pressurized DI water was circulated through the lumen side of module at 1 bar pressure. Permeate was collected and weighed after 45 min stabilization period. The PWP of PES hollow fiber substrates were calculated by using equation 3.1.

$$PWP = \frac{m_w}{\rho_w \cdot A_m \cdot \Delta t \cdot \Delta P} \quad (\text{Eq 3.1})$$

where m_w is the mass of collected permeate, ρ_w is the density of water, A_m is the effective membrane area, Δt is the time taken and ΔP is the transmembrane pressure recorded during permeate collection.

The MWCO of PES hollow fiber substrate was determined by crossflow filtration method using 200 ppm dextran solution which consisted of mixtures of different molecular weights ranged from 6 kDa to 500 kDa. The feed and collected permeate were analyzed by using gel permeation chromatography (GPC) on Polymer Laboratories-GPC 50 plus system with integrated refractive index detector (PD2020 light scattering detector), and rejection coefficient ($R(\alpha)$) was calculated by using the relationship:

$$R(\alpha) = \frac{C_f - C_p}{C_f} \times 100\% = \frac{I_f - I_p}{I_f} \times 100\% \quad (\text{Eq 3.2})$$

where C_f and C_p are the concentration of dextran molecule with molecular weight α in the feed and permeate, which are assumed to be linearly correlated to the respective signal intensity I_f and I_p in GPC spectrum. MWCO of hollow fiber substrate was defined as the molecular weight of dextran molecule rejected at 90%.

Based on the rejection characteristics of dextran determined from the experiments, the pore size distribution of each substrate can then be represented by using two-parameter log-normal distribution function $f(d)$ as described in the literature [233, 234]:

$$f(d) = \frac{1}{\ln(\sigma) \cdot a \cdot \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{\ln(a/D^*)}{\ln(\sigma)} \right)^2 \right] \quad (\text{Eq 3.3})$$

The geometric mean pore size (D^*) and geometric standard deviation (σ) of each membrane substrate can be obtained by solving the minimization problem:

$$\left(\sum_{i=1}^N \{R(a_i)_{\text{Expt.}} - R(a_i)_{\text{Calc.}}\}^2 \right)_{\text{Min}} \rightarrow (D^*, \sigma) \quad (\text{Eq 3.4})$$

where $R(a_i)_{Expt.}$ and $R(a_i)_{Calc.}$ are the experimentally determined rejection coefficient and theoretically determined rejection coefficient respectively for dextran molecules with diameter a_i . The theoretically determined rejection coefficient was calculated by using the relationship, which considered Poiseuille flow and steric interaction between solute molecules and membrane pores:

$$\begin{aligned}
 R(a) &= 1 - \frac{1}{2} \left\{ 1 + \operatorname{erf} \left[\frac{1}{\sqrt{2} \ln \sigma} \left(\ln \left(\frac{D^*}{a} \right) + 4(\ln \sigma)^2 \right) \right] \right\} \\
 &+ 2 \left(\frac{a}{D^*} \right)^2 \exp[-6(\ln \sigma)^2] \left\{ 1 + \operatorname{erf} \left[\frac{1}{\sqrt{2} \ln \sigma} \left(\ln \left(\frac{D^*}{a} \right) + 2(\ln \sigma)^2 \right) \right] \right\} \\
 &- 2 \left(\frac{a}{D^*} \right)^3 \exp \left[-\frac{15}{2} (\ln \sigma)^2 \right] \left\{ 1 + \operatorname{erf} \left[\frac{1}{\sqrt{2} \ln \sigma} \left(\ln \left(\frac{D^*}{a} \right) + (\ln \sigma)^2 \right) \right] \right\} \\
 &+ \frac{1}{2} \left(\frac{a}{D^*} \right)^4 \exp[-8(\ln \sigma)^2] \left\{ 1 \right. \\
 &\left. + \operatorname{erf} \left[\frac{1}{\sqrt{2} \ln \sigma} \ln \left(\frac{D^*}{a} \right) \right] \right\}
 \end{aligned} \tag{Eq 3.5}$$

The diameter of dextran molecules were calculated from the molecular weight (MW) by using the relationship:

$$a = 0.66 \cdot (MW)^{0.46} \tag{Eq 3.6}$$

where a is in unit of Å and MW in unit of Dalton.

The mechanical properties of hollow fiber substrates were assessed with Zwick 0.5 kN Universal Testing Machine. The tensile modulus, tensile strength and maximum elongation of the substrates were determined based on ten replicate measurements, where fresh PES hollow fiber substrates were clamped on sample holder with initial gap of 2.5 cm and subjected to constant stretching rate of 50 mm/min at room temperature. To determine the burst pressure of hollow fiber substrates, one end of the hollow fibers was sealed with epoxy and hydraulic pressure was increased stepwise by pumping water through the lumen of the membrane at interval of 1.0 bar every 3 minutes until the fibers burst.

3.2.6. TFC membrane characterization

The intrinsic properties of TFC membranes, such as water and salt permeability, were tested on laboratory-scale crossflow filtration system by passing respective feed solutions through the lumen of the modules under 2 bar pressure at ambient temperature (20-22 °C). DI water was used as the feed for determination of water permeability coefficient (A , L/m²/h/bar, LMH/bar), which was calculated by using the same relationship as given for PWP:

$$A = \frac{m_w}{\rho_w \cdot A_m \cdot \Delta t \cdot \Delta P} \quad (\text{Eq 3.7})$$

The salt rejection (R_s) of the TFC membranes was determined by using 500 ppm NaCl as the feed at 2 bar applied pressure, during which the conductivities of feed and permeate were measured by using conductivity meter (Mettler Toledo, Switzerland). Salt rejection was calculated by using the relationship derived from equation 2.3:

$$R_s = \left(1 - \frac{EC_p}{EC_f} \right) \times 100\% \quad (\text{Eq 3.8})$$

where EC_f and EC_p represent the conductivity of feed and permeate solution, which are assumed to be linearly correlated to NaCl concentration in solutions to the conductivity. The corresponding salt permeability coefficient (B , L/m²/h, LMH) is calculated from the experimentally determined A and R_s by using equation 2.4.

3.2.7. FO experiments

The schematic diagram of FO testing system employed in this study is presented in **Figure 3.1**. All FO experiments were carried out in AL-DS configuration unless stated otherwise. A diaphragm pump was used to continuously circulate draw solution through the lumen of TFC membranes. The pressure and flow rate of draw solution were controlled by the pressure regulator valve and needle valve. The pressure of draw solution at the inlet and outlet of the modules, denoted as P_1 and P_2 respectively, were constantly monitored by

pressure transducers connected to a computer and recorded on a data logging software.

Figure 3.1 Schematic diagram of the bench-scale FO testing setup.

The concentration of salt in the draw solution was monitored by changes in conductivity. The dilution of draw solution by water flux across the TFC membranes was compensated by constantly dosing the draw solution with concentrated salt solution. The temperature of draw solution was maintained at 22° C using submerged heat exchanger connected to a recirculation chiller.

For all FO experiments, 1.0 M NaCl solution was used as the draw solution and DI water was used as feed solution unless otherwise stated. Feed solution was circulated over the shell side of the module by using a peristaltic pump, and the flow rate was recorded and automatically adjusted by using a flow transmitter. Any changes in the weight of feed solution were monitored and compensated by automated dosing. Conductivity and temperature transducer probes were immersed in feed and draw solutions and connected to the computer to record the changes in the condition of the solution on data logging system. The flow rate of feed solution was controlled at 1.0 L/min and the flow rate of draw solution in the lumen of the hollow fiber membrane was adjusted to maintain crossflow velocity at 0.80 m/s.

During FO experiments, the hydraulic pressure in lumen was maintained at minimum level to achieve the stated crossflow conditions. Water flux (J_w , L/m²/h, LMH) across the TFC membrane was determined from the changes in feed mass (Δm_f) over certain time interval (Δt):

$$J_w = \frac{-\Delta m_f}{\rho_w \cdot A_m \cdot \Delta t} \quad (\text{Eq 3.9})$$

where A_m is the effective membrane area of the TFC membrane in the laboratory-scale module. The corresponding salt flux (J_s , g/m²/h, gMH) was calculated by the rate of increase of the amount of salt in the feed solution:

$$J_s = \frac{\Delta(C_F \cdot m_F)}{\rho_w \cdot A_m \cdot \Delta t} \quad (\text{Eq 3.10})$$

where C_F is the concentration of NaCl in feed solution based on conductivity and m_F is the mass of the feed.

Based on water flux determined in FO experiments, the structural parameter of each TFC membrane was calculated by using the following equation [206, 210, 235-237],

$$S = \left(\frac{D}{J_w} \right) \cdot \ln \left[\frac{(A \cdot \pi_D - A \cdot \Delta P - J_w) + B \cdot \left(\frac{A \cdot \Delta P}{J_w} + 1 \right)}{A \cdot \pi_F + B \cdot \left(\frac{A \cdot \Delta P}{J_w} + 1 \right)} \right] \quad (\text{Eq 3.11})$$

For all structural parameter calculations, a constant value of 1.61×10^{-9} m²/s was used for solute diffusivity of NaCl [206].

3.3. Results and discussion

3.3.1. Substrate characteristics

In this study, PEG was used as the main additive in polymer dopes, which have been shown to increase porosity and improve pore interconnectivity of the membrane [238]. Low molecular weight PEG is considered as a weak non-solvent to PES solution, as it can be added in large proportion without destabilizing the polymer dope. The SEM images of the hollow fiber substrates

are shown in **Figure 3.2**. All fabricated PES substrates exhibited similar cross-section morphologies, where finger-like macrovoids aligned orderly and formed a bilayer pattern. Previous studies have also shown that the addition of low molecular weight PEG alone does not suppress macrovoid formation [238]. However, the presence of macrovoids may have negative impact on the mechanical stability of the membrane [239]. Many studies had been carried out to understand the mechanism behind the formation of macrovoids and other morphologies in both flat sheet and hollow fiber membranes prepared by the NIPS process [41, 240-252]. It was shown that occurrence of instantaneous demixing during NIPS process generally encourages macrovoid formation [244, 252]. Smolders et al. [251] summarized the findings from their observations and other researchers derived a set of empirical rules to explain the mechanism of macrovoid formation. They proposed that the formation of macrovoids is initiated by a nuclei of polymer-lean phase that are formed at a certain distance from the film interface, where the precipitation conditions change from instantaneous to delayed onset of demixing. Subsequently, the diffusion of solvent expelled from the surrounding polymer-rich phase causes macrovoid growth.

On the other hand, the surface morphology of the hollow fiber substrates did not vary substantially with dope composition. In general, the inner surface of the substrates exhibited striations that were parallel to the direction in which the substrates were spun. Changing the proportion of PEG or the solvent in the dope has no apparent effect on the morphology of the inner surface of the substrate. With higher concentration of PEG in the dope, the outer surface of hollow fiber substrate appears to be more porous and rougher.

Figure 3.2 SEM images of PES hollow fiber substrates. The (a) overall cross-section, (b) magnified cross-section, (c) inner surface and (d) outer surface of (1) PES#1-1, (2) PES#2-1, (3) PES#3-1, (4) PES#3-2

The dimension, PWP, MWCO, pore size distribution and the mechanical properties of the hollow fiber substrates fabricated in the current investigation were listed in **Table 3.3**. There was no significant difference between the dimension of PES#1-1, PES#2-1 and PES#3-1, which implied that the composition of the dope has little effect on the dimension of the hollow fiber membranes. The three substrates also possessed similar PWP. However, the MWCO of PES#2-1 was found to be 160% higher than PES#1-1 substrate, while the MWCO of PES#3-1 substrate was negligibly different from PES#1-1 substrate. Such outcome indicated that increase in the concentration of PEG in dope could lead to substantial increase in the pore size of substrate, whereas slight reduction in polymer concentration has negligible effect on the pore size of the substrate. It is suggested that dilution of NMP content in the dope by increasing PEG concentration leads to a reduction in the rate of non-solvent

intrusion into the dope and slowed down the phase separation and vitrification process. It prolongs the progression of dope composition across the metastable region, where pore formation by nucleation and growth of polymer poor phase dominates [249]. It is suggested that such condition may have induced the formation of smaller numbers of bigger pores in the membrane, and possibly reduced the interconnectivity of pores in the substrate.

Table 3.3 Properties of hollow fiber substrates.

Substrate ID	PES#1-1	PES#2-1	PES#3-1	PES#3-2
Inner diameter, ID (um)	522 ± 4	510 ± 5	518 ± 4	436 ± 3
Outer diameter, OD (um)	731 ± 3	701 ± 8	721 ± 7	664 ± 5
Thickness, t (um)	105 ± 1	96 ± 3	101 ± 3	114 ± 2
t/ID ratio	0.20	0.19	0.19	0.26
Pure water permeability, PWP (LMH/bar)	343 ± 1	340 ± 20	319 ± 27	318 ± 1
Molecular weight cut-off, MWCO (kDa)	45	117	45	18
Geometric mean pore diameter (nm)	3.12	9.21	2.00	2.85
Geometric standard deviation	1.65	1.37	1.79	1.52
Tensile modulus, E_t (MPa)	129 ± 3	121±3	121±5	119 ± 7
Tensile strength, σ_t (MPa)	5.2 ± 0.1	5.0 ± 0.1	4.9 ± 0.1	4.9 ± 0.1
Maximum tensile elongation, ε_t (%)	47 ± 4	46 ± 6	51 ± 4	50 ± 6
Burst pressure (bar)	11	10	10	12

In terms of mechanical properties, both PES#2-1 and PES#3-1 substrates have slightly lower tensile modulus than PES#1-1 substrate due to a lower polymer concentration in the polymer dope prepared. Even though PES#3-1 substrate had a lower tensile strength, its tensile elongation was higher than PES#1-1 substrate. Such difference could be a result of better entanglement between PES chains in the substrate with less chain disruption when the concentration of PEG was lower.

Figure 3.3 Pore size distribution of PES hollow fiber substrates.

In order to investigate the influence of rate of phase separation on surface properties of substrate and PES-TFC membrane, a separate comparative study was carried out by varying the flow rate of bore fluid to control the rate of coagulation on the inner surface of the membrane. Based on the spinning conditions for PES#3-1 substrate, the flow rate of bore fluid was lowered by 29% to produce PES#3-2 substrate. Even though the decreased bore fluid flow rate has caused the thickness of substrate to increase, it has no influence on the PWP and only slightly increased the mean pore size of substrate. Apart from that, there was no noticeable change in the mechanical properties of the substrate when the bore fluid flow rate varied. When bore fluid flow rate was lower, less non-solvent was brought into contact with the extruded dope. Therefore, the rate of phase separation may be reduced when decreasing bore fluid flow rate. Since the polymer dope composition is relatively stable, the decrease in the rate of phase separation could promote pore formation by nucleation and growth mechanism, resulting in the formation of larger pores observed in PES#3-2 substrate.

However, it is believed that the change in bore fluid flow rate affects the precipitation kinetics of the top layer (which was in contact with the bore fluid) and the sublayer (region just beneath the top layer) on the lumen side of the extruded polymer dope during membrane formation process, as proposed by Machado et al. [253]. When the bore fluid contains significantly high non-solvent concentration, a dense film is usually formed immediately on the inner surface

of extruded polymer dope by a rapid vitrification process due to high solvent/non-solvent exchange rate at polymer dope/bore fluid interface. This process raises the mass transfer resistance across the nascent film/bore fluid interface and immediately impeded the exchange of solvent and non-solvent in the sublayer just below the nascent film.

It is suggested that a decrease in bore fluid flow rate under the given spinning condition slowed down the rapid vitrification process on the surface, forming a looser nascent film which has relatively lower mass transfer resistance. These changes lead to an increase in the non-solvent intrusion rate and solvent/non-solvent exchange rate in the sublayer of nascent fiber, which increase the overall porosity of substrate inner layer and reduce pore size distribution of the substrate.

3.3.2. Effect of substrate on TFC hollow fiber membrane performance

For TFC membranes designed for FO process, the conventional substrate is a thin porous structure, which sole purpose is to serve as the mechanical support for ultrathin selective layer. Other than the mechanical strength and chemical resistance of the substrate material, another major consideration in the development of ideal substrate for TFC membrane fabrication is the substrate characteristics, such as pore dimension, porosity, roughness, charge, etc. Ideally, the right combination of each of these characteristics could ensure the formation of selective layer with optimal performance and good adhesion to substrate. There have been a few research works which focus on the interaction between ultrathin selective layer and the surface of the underlying microporous support with respect to characteristics of the support layer [179, 254-256].

In order to evaluate the performance of each substrate in the osmotic process, a polyamide selective layer was formed via IP process on the lumen side of the substrates. The intrinsic properties of the respective TFC membranes were determined prior to any experiments which involves high transmembrane pressure to minimize the influence of pressure-induced deformation on the selective layer. Water permeability coefficient and salt permeability coefficients represents two of the main characteristic parameters which describe the

selectivity properties of the polyamide selective layer. As shown in **Table 3.3**, these two intrinsic properties of TFC membranes could vary significantly when different substrates were used. In general, there was no clear correlation between the PWP or pore size of substrate and the intrinsic properties of the selective layer.

Table 3.4 Properties of TFC hollow fiber membranes prepared from respective substrates.

Substrate ID	PES#1-1	PES#2-1	PES#3-1	PES#3-2
Water permeability, A^1 (LMH/bar)	3.58 ± 0.28	3.32 ± 0.10	3.07 ± 0.07	1.49 ± 0.31
NaCl rejection, R_s^1 (%)	97.2 ± 0.1	96.3 ± 0.1	95.2 ± 0.2	92.4 ± 0.7
Salt permeability, B^2 (LMH)	0.162 ± 0.010	0.204 ± 0.014	0.244 ± 0.005	0.190 ± 0.020
Selectivity, B/A (mbar)	45.1 ± 0.6	61.4 ± 2.4	79.6 ± 3.4	131.0 ± 13.6
Structural parameter, S^3 (μm)	536 ± 6	499 ± 11	448 ± 31	570 ± 22
Burst pressure (bar)	11.5	10	12	15

¹ Determined by RO experiments at 2 bar transmembrane pressure on bench-scale crossflow filtration system. DI water and 500 ppm NaCl were used as respective feed solutions to determine A and R_s .

² Calculated from experimentally determined A and R_s .

³ Calculated from FO results obtained using 1 M NaCl and DI water as the draw and feed solutions.

However, through a closer comparison between TFC membranes prepared from different substrates, it seems that the viscosity of the polymer dopes used to prepare the substrates has some influence on the characteristics of the selective layer. Even though all three substrates were fabricated under the same spinning conditions, the polymer dopes with higher viscosity experienced a higher level of shear stress when extruded through the spinneret, and this led to the formation of denser structure due to shear induced chain alignment. Since the surface of the substrate which experienced the highest shear stress, the skin layer became denser as the viscosity of polymer dope increased. Hence, it is suggested that a denser skin layer may encourage the formation of thin and uniform polyamide selective layer which possesses high water permeability while maintaining good solute rejection properties.

On the other hand, changes in bore fluid flow rate during hollow fiber substrate fabrication process appeared to have significant impact on the characteristics of

hollow fiber inner surface that strongly affects the properties of the polyamide selective layer. While the PWP and pore size of PES#3-2 and PES#3-1 substrates were similar, the intrinsic properties of TFC membrane prepared from these two substrates varied significantly. Apart from surface pore size distribution, it is suspected that the reaction kinetics controlling the formation of polyamide layer is also influenced by the porosity of the top layer on the inner surface of the substrate, which was shown to be higher at lower bore fluid flow rate.

One of the possible explanations is that the increased porosity just beneath the inner surface of the substrate causes it to trap a higher amount of MPD solution in the first step of selective layer coating process. Also, the higher porosity could impose lower mass transfer resistance on the movement of reactants in the top layer of membrane inner surface, which increases the availability of reactants at aqueous/organic interface and speed up the IP reaction, thus inducing the formation of a denser polyamide layer. As such, the overall mass transfer resistance of the polyamide selective layer becomes much higher and leads to reduction in both water permeability and solute permeability of the TFC membrane.

3.3.3. FO performance

In addition, the change in substrate properties due to varying dope compositions seems to have a significant influence on the FO performance of TFC membranes, as shown in **Figure 3.4**. Other than poorer intrinsic properties of the selective layer, the difference in the water flux in FO process is mainly associated with the ICP, which is affected by the structural parameter of each substrate.

Through FO experiments, it was found that the TFC membrane prepared from substrate with lower PEG/NMP ratio has a higher water flux in the FO process. As discussed in previous section, when PEG is used in high concentration, further increment in PEG concentration resulted in a significantly larger pore size but has little effect on the water permeability of the substrate. This is mainly attributed to lower pore density and pore interconnectivity. Lower pore

interconnectivity increases the tortuosity of the support layer, thus PES#2-1-TFC membrane exhibits larger structural parameter than PES#3-1-TFC membrane. Based on this observation it is suggested that the PEG/NMP ratio in PES/NMP/PEG dope system might have to be slightly lower than 1:1 in order to create pore structures with lower structural parameter.

Figure 3.4 Transition in FO performances of TFC hollow fiber membranes with different substrate fabrication conditions. All membranes were tested in AL-DS orientation with 1.0 M NaCl and DI water as the draw and feed solutions, respectively.

For substrates prepared from the same polymer dope formula, the FO performance of TFC membrane appeared to improve with increasing bore fluid flow rate during spinning process. The structural parameter of TFC membrane prepared from PES#3-2 is 28% higher than PES#3-1, even though the wall thickness of the former is only 13% greater. As previously suggested, lower bore fluid flow rate reduces the difference in precipitation rate across extruded polymer dope in radial direction and leads to formation of more uniform pore structures in the inner layer of PES#3-2. The larger mean pore size indicated that the overall rate of phase separation maybe lower, which may be associated to a lower pore interconnectivity. Such changes could result in higher tortuosity, which is suspected to be the additional factor that contributed to larger structural parameter of PES#3-2.

The performance of PES#3-1-TFC membrane was also assessed in AL-FS by using the 1.0 M NaCl and DI water as draw and feed solutions, which produced water flux of 41.2 LMH and specific reverse solute flux of 0.11 g/L. As compared to the FO membranes developed over the past few years, as shown in **Table 3.5**, PES#3-1-TFC membrane demonstrated a high water flux and low specific salt flux, which suggests that it might have greater potential in food product concentration and water reuse applications.

Table 3.5 Comparison of the performance of FO membranes in the literature.

Membrane type	Support layer material	Orientation	Water flux * (LMH)	Specific salt flux * (g/L)	Ref.
Inner-selective hollow fiber	PES	AL-FS	41.2	0.11	This work
Outer-selective hollow fiber	PAN	AL-FS	16.58	0.39	[209]
Outer-selective hollow fiber	PAN	AL-FS	17.01	0.34	[209]
Outer-selective hollow fiber	PAN	AL-FS	24.71	0.79	[209]
Flat sheet	CA	AL-FS	22.9	0.28	[257]
Inner-selective hollow fiber	PES	AL-FS	26.00	0.17	[81]
Inner-selective hollow fiber	-	AL-FS	10.00	0.36	[212]
Flat sheet	PSU/SPSU/PET	AL-FS	29.95	0.10	[258]
Flat sheet	PSU/LDH-NP	AL-FS	18.1	0.45	[259]
Flat sheet	PSU/PET/Si	AL-FS	31.0	0.24	[260]
Flat sheet	PTA-POD	AL-FS	37.5	0.15	[261]
Inner-selective hollow fiber	PES	AL-DS	74.9	0.10	This work
Outer-selective hollow fiber	PAN	AL-DS	25.86	0.42	[209]
Outer-selective hollow fiber	PAN	AL-DS	24.53	0.26	[209]
Outer-selective hollow fiber	PAN	AL-DS	36.57	0.52	[209]
Flat sheet	CA	AL-DS	46.4	0.54	[257]
Inner-selective hollow fiber	PES	AL-DS	37.50	0.14	[81]
Inner-selective hollow fiber	-	AL-DS	19.00	0.47	[212]
Outer-selective hollow fiber	PSU/PET/PDA	AL-DS	21.78	0.59	[262]
Outer-selective hollow fiber	PSU/PET/PDA	AL-DS	36.29	0.93	[262]
Outer-selective hollow fiber	PSU/PET/PDA	AL-DS	33.17	0.72	[262]
Flat sheet	PSU/SPSU/PET	AL-DS	66.89	0.10	[258]
Flat sheet	PSU/LDH-NP	AL-DS	34.6	0.36	[259]
Flat sheet	PSU/PET/Si	AL-DS	60.5	0.26	[260]
Flat sheet	PTA-POD	AL-DS	78.4	0.16	[261]

* The performance of the listed FO membranes was evaluated by using 1 M NaCl and DI water as the draw and feed solutions, respectively. Abbreviations: PES: polyethersulfone; PAN: polyacrylonitrile; CA: cellulose acetate; PSU: Polysulfone; SPSU: sulfonated polysulfone; PET: polyethylene terephthalate; LDH-NP: layered double hydroxide nanoparticle; Si: fumed silica powder; PTA-POD: hydroxyl functionalized polytriazole-co-polyoxadiazole copolymer; AL-FS: active layer facing feed solution; AL-DS: active layer facing draw solution.

3.4. Conclusions

In this study, inner-selective TFC hollow fiber membranes have been fabricated successfully via the phase inversion process and IP technique. When characterized in FO test by using 1.0 M NaCl as the draw solution and DI water as the feed solution, the TFC membrane prepared from PES hollow fiber substrate exhibited water flux of 41.2 LMH and 74.9 LMH when characterized in AL-FS and AL-DS orientations, respectively, which out-performed most FO membranes tested under the similar conditions. In addition, the specific reverse solute flux of the TFC membrane fabricated in this study were 0.11 g/L and 0.10 g/L in the respective orientations, which were also the lowest among reported performance as well.

The influence of dope composition used for fabrication of PES hollow fiber substrates on the characteristics of hollow fiber substrates and the respective TFC hollow fiber membranes were investigated. When using high concentration of PEG (40 wt%) as a pore-forming additive in the dope solution, the increase in the proportion of PEG in the dope increased the pore size and widened the pore size distribution of the substrate, whereas the opposite effect was observed when the proportion of solvent (NMP) in the dope was increased. Yet, the water permeability of the hollow fiber substrates was similar.

There is no clear correlation between the characteristics of the hollow fiber substrates and the intrinsic separation properties of TFC hollow fiber membranes. However, there seems to be a correlation between the viscosity of the dope that is used to fabricate the substrate and the perm-selectivity of the TFC hollow fiber membranes. TFC membrane prepared from hollow fiber substrate which was fabricated from the dope with highest viscosity, has the highest water permeability coefficient and lowest solute permeability coefficient, which was attributed to the formation of a dense skin layer on the substrate, leading to the formation of a thinner polyamide selective layer. While increasing both the proportion of PEG and solvent in dope led to a reduction in structural parameter of the TFC membrane, substrates spun from dope solutions with lower PEG/NMP ratio gave rise to a lower structural parameter.

Chapter 4 A Novel Thin Film Composite Hollow Fiber Osmotic Membrane with One- step Prepared Dual-Layer Substrate for Sludge Thickening

4.1. Introduction

Upon optimization of the hollow fiber substrate for the development of high-performance TFC membranes, the next focus is to target another Achilles heel of FO: internal membrane fouling. As discussed in section 2.3.3, internal membrane fouling is driven by infiltration and accumulation of small-sized foulants in the porous support layer when the membrane is operating in the AL-DS orientation. Comparative to fouling on the membrane surface, internal membrane fouling is unique to the FO process and is more challenging to deal with, owing to the limited strategies that can be used to mitigate fouling in the support layer. Hence, to address this problem, a co-extrusion technique is used to optimize the hollow fiber substrate with a denser layer on the shell side of the membrane. The denser layer on the shell side is designed to alleviate penetration of foulants into the support layer, while the polyamide layer acts as the inner-selective layer as described in Chapter 3. Herein, we optimize this double-skinned membrane for sludge volume reduction and nutrients retention using the FO process.

Large amounts of sewage sludge were generated worldwide, and sludge management may constitute more than 50% of the construction and operating costs of a wastewater treatment plant (WWTP) [263-265]. Sludge thickening may be performed prior to a digestion process to increase the organic content of sludge and improve the digestion efficiency [266]. Traditionally, sludge thickening was carried out by gravity settling, air flotation, rotary drum filtration, or by centrifugation, whereas sludge dewatering was usually achieved by filter belt press or plate-frame dewatering process [265, 267-269]. Traditional sludge thickening and dewatering technologies cannot retain the soluble matter, and nutrient-rich concentrate would be produced, which requires further treatment

to meet the discharge requirement [265]. FO process may be considered as a potential solution for sludge thickening and dewatering, as the high selectivity of FO membrane could effectively extract water from sludge while rejecting most soluble organic matter. The FO process may be operated by using seawater reverse osmosis (SWRO) brine or seawater as draw solutions [264, 265, 267], which renders the regeneration of the draw solution irrelevant, thus greatly reduces the overall energy consumption of the FO process. As the draw solution gets diluted during the FO process, it may be disposed directly without negative environmental impact associated with direct discharge of SWRO brine [267, 270].

A few studies on sludge concentration has been carried out by using FO flat sheet membranes operated in AL-FS orientation [264-267, 271]. However, in the AL-FS orientation, the greater-sized particulates in the sludge could easily clog the lumen of the hollow fiber (which has inner diameter of around 1 mm or less). Thus, AL-DS orientation is normally adopted for hollow fiber FO operation for sludge concentration, which opens the possibility of internal membrane fouling. In order to prevent penetration of foulants into the porous support layer, one solution is to narrow down the pore size by adjusting the fabrication conditions (such as increasing the polymer concentration in dope solution). However, it would inevitably reduce the overall porosity of the porous support layer. As a result, ICP may become more severe and membrane permeability would be relatively low. The design of a double-skinned FO membrane is deemed a better solution [272-276], with a primary selective layer providing sufficient selectivity to the draw solutes, while the secondary selective layer serves as a barrier against the penetration of foulants. The additional dense layer can be generally introduced on the shell side by either IP [275], chemical cross-linking [273] or LBL assembly [274, 277] before or after the formation of a selective layer at the lumen side. However, these methods required three or more fabrication steps, which inevitably increase the complexity of fabrication process and the cost of membrane production.

In this study, a novel double-skinned hollow fiber TFC FO membrane was fabricated by a two-step preparation. The substrate possessed a relatively

dense ultrafiltration(UF)-like outer skin layer and a relatively porous UF inner layer, which were formed simultaneously via a one-step co-extrusion technique based on the NIPS method [204]. The inner-selective layer was formed on the porous lumen-side support layer by the IP process. The newly developed double-skinned hollow fiber FO membrane was characterized by a series of standard protocols and its performance was benchmarked against the commercial membranes and double-skinned hollow fiber membranes reported in the literature. Particularly, the fouling mechanisms for the hollow fiber FO membrane in concentrating sludge were also illustrated. This study aims to explore an effective FO membrane fabrication technique and demonstrate the promising application of the double-skinned hollow fiber FO membrane in sludge concentration.

4.2. Experimental

4.2.1. Materials

Polyethersulfone (PES, Gafone™ 3000P, Solvay, Belgium), N-methyl-2-pyrrolidone (NMP, Merck Chemicals, USA), polyethylene glycol 200 (PEG, Mw = 200 g/mol, Merck Chemicals, USA), acetone (Merck Chemicals, USA), polyvinylpyrrolidone (PVP, Mw = 1,300,000 g/mol, Acros Organics, USA), glycerol (85%, Merck Chemicals, USA) and DI water was used for the fabrication of hollow fiber substrates. ϵ -caprolactam (Merck Chemicals, USA), cyclohexane, 1,3,5-benzenetricarbonyl trichloride (TMC, Sigma-Aldrich, USA), m-phenylenediamine (MPD, Sigma-Aldrich, USA), sodium dodecyl sulfate (SDS, Sigma-Aldrich, USA) and DI water were used in the fabrication of TFC membrane via IP process. Polyethylene glycol (PEG) of various molecular weights ranging from 200 to 20,000 g/mol (Merck Chemicals, USA) was used to characterize the MWCO and pore size distribution of hollow fiber substrates. Sodium chloride (NaCl, Merck Chemicals, USA), humic acid sodium salt (HA, Sigma-Aldrich, USA) were used for the preparation of draw and feed solutions used in the characterization of TFC membrane intrinsic properties and FO tests. Deionized (DI) water was obtained by a Milli-Q system (Millipore, USA) and used

to prepare all aqueous solutions in this study. A commercial FO membrane (OsmoF2O™, Fluid Technology Solutions Inc.) was characterized for benchmarking of FO membrane performance. The commercial membrane consisted of cellulose triacetate membrane with embedded mesh.

4.2.2. Fabrication of hollow fiber substrate

PES polymer was dried in the vacuum oven at 50°C overnight before it was used for the preparation of dope solution. To prepare the dope solution, PES was dissolved into NMP with constant stirring at 60 °C for 1 h. After the polymer was completely dissolved, the additives were added into the dope solution and the mixture was stirred until a homogeneous solution was obtained. Subsequently, the dope solutions were slowly cooled down to room temperature and degassed under vacuum overnight prior to the hollow fiber spinning process. The dope compositions used in fabricating PES hollow fiber substrate are listed in **Table 4.1**. To evaluate the stability of the polymer dopes, water was added slowly into polymer dopes (which were prepared separately) under constant stirring until clouding of polymer dope was observed. The mass concentration of water required to trigger the clouding phenomenon was recorded as the cloud point of the polymer dope.

Table 4.1 Dope compositions in fabricating hollow fiber substrate.

Polymer dope	Composition (wt%)						Cloud point (wt% of H ₂ O)
	PES	NMP	PEG	Acetone	PVP	DI water	
PES#1 (Inner dope)	20.0	40.0	40.0	-	-	-	4.2
PES#4 (Outer layer)	29.2	50.3	-	16.8	1.0	2.8	4.2

PES hollow fiber substrates were fabricated through a dry-jet wet-spinning process using the NIPS process. The details of the procedures can be found in the literature [206]. The fabrication process of dual-layer hollow fiber substrate is schematically illustrated in **Figure 4.1**. The substrate was prepared from a simultaneous co-extrusion of two different polymer dopes, where the skin structure on the shell side was densified through increased polymer concentration and exclusion of pore-forming additives to reduce the surface

pore size of the substrate. The detailed spinning conditions are listed in **Table 4.2**.

Figure 4.1 Fabrication of hollow fiber substrates by NIPS process with co-extrusion method.

Table 4.2 Spinning conditions for fabricating PES hollow fiber substrates

Spinneret dimension	
Bore channel inner diameter (μm)	360
Middle channel inner/outer diameter (μm)	620/890
Outer channel inner/outer diameter (μm)	1230/1420
Spinning conditions	
Bore fluid composition	DI water
Bore fluid low rate (mL/min)	10
Inner dope composition	PES#1
Inner dope flow rate (mL/min)	6.7
Outer dope composition	PES#4
Outer dope low rate (mL/min)	0.10
Take up speed (m/s)	0.27
Air gap (cm)	1.0
Room temperature ($^{\circ}\text{C}$)	23-24
Coagulation bath temperature ($^{\circ}\text{C}$)	22-23
Relative humidity (%)	70

4.2.3. Characterization of hollow fiber substrate

The standard protocol of hollow fiber substrate characterization was described previously [178, 206]. Specifically, the dimension of the hollow fiber membrane was determined with a digital optical microscope (Keyence, Japan). The structure and morphology of the hollow fiber membranes were measured by using a field emission scanning electron microscope (FE-SEM, JEOL, Japan) after the membranes were freeze-dried and coated with platinum. The average overall porosity of the hollow fiber substrate was determined using a gravimetric method by measuring the mass of water that was in the membrane pores.

The PWP of the hollow fiber substrate was examined by employing DI water circulating through the shell and lumen sides of the membrane module at 1 bar. The MWCO of the hollow fiber substrate was determined by using solute rejection experiments, in which 200 mg/L PEG solutions (with different molecular weights) was circulated over the hollow fiber substrate under 1 bar of transmembrane pressure (TMP) in the cross-flow filtration testing system. The feed and permeate samples were collected and analyzed by using a gel permeation chromatography (GPC) instrument equipped with refractive index (RI) detector (Polymer Laboratories-GPC 50 plus system, Agilent, USA). The MWCO, pore size and pore size distribution of hollow fiber substrate were then calculated from the solute rejection based on the procedures reported elsewhere [278, 279].

4.2.4. Interfacial polymerization on hollow fiber substrate

The PES hollow fiber substrate was immersed in a 50 wt% glycerol solution for 1 day and dried at room temperature for 1 day prior to being used for preparation of TFC membranes. Then, hollow fiber substrate modules were made by placing 5 strands of hollow fibers in each module casing assembled from two PP T-fittings connected by PTFE tubes (1/2 inch outer diameter, 3/8 inch inner diameter), where the gaps at two ends were sealed with epoxy adhesive (ARALDITE Rapid 5 minutes). The effective length of the hollow fibers in each module was around 25 cm, and the effective membrane area was around 38 cm². The polyamide selective layer was created on the lumen side of hollow

fiber substrate via IP process, based on the procedures described in section 3.2.4. First, the lumen of PES hollow fiber substrate was filled with MPD solution to allow the penetration of the monomer and additives into the substrate. After removing the residual MPD solution from the fiber lumen, the solution of TMC in cyclohexane was pumped through the fiber lumen of the membrane. The monomers react to form the polyamide layer on the lumen surface of the TFC membrane. The TFC membrane, denoted as “PES-HF-TFC”, was immersed in DI water for 1 day before use.

4.2.5. TFC hollow fiber intrinsic properties and FO membrane performance evaluation

Water permeability coefficient (A , L/m²/h/bar, LMH/bar) of the PES-HF-TFC membrane was determined and calculated in the same way as the PWP of the hollow fiber substrate. Salt rejection (R_s , %) of the PES-HF-TFC membrane was determined by circulating 500 ppm NaCl solution through the membrane lumen under 1 bar, where the conductivity of feed (EC_f) and permeate (EC_p) were measured using conductivity meters (Mettler Toledo, Switzerland). The detailed procedures for determination of salt rejection and salt permeability coefficient (B , L/m²/h, LMH) were described in section 3.2.6.

A bench-scale FO testing system was employed to examine the FO performance of the PES-HF-TFC membrane. The membrane was tested in AL-DS orientation by using a 0.5 M NaCl solution as draw solution, while DI water was used as feed. The details of the setup were described previously [280]. For the evaluation of FO performance, the osmotic-driven water flux (J_w , L/m²/h, LMH) was calculated from the mass change of feed by using equation 3.9, whereas the salt reverse flux (J_s , g/m²/h, gMH) was calculated with equation 3.10. Specific reverse salt flux (J_s/J_w , g/L) was calculated as the ratio of salt flux to water flux. Duplicate experiments ($n=2$) were performed and averaged data were presented in the table. The structural parameter (S , μm) of PES-HF-TFC membrane was calculated from the water flux of the membrane determined by FO tests by using equation 3.11.

To assess the fouling propensity of the PES-HF-TFC membrane, the model foulant, humic acid, (Sigma-Aldrich, 50 mg/L) was employed as a feed solution and 0.5 M NaCl was used as a draw solution. As shown in **Figure 4.2**, the feed solution was circulated over the shell side of the PES-HF-TFC membrane at a flow rate of 1.0 L/min (corresponding to crossflow velocity of 0.23 m/s) and the draw solution was circulated through the lumen side of the membrane at a flow rate of 190 mL/min (corresponding to crossflow velocity of 0.8 m/s), i.e., in the AL-DS orientation. Throughout each FO test, the concentration of draw solution was maintained by dosing 5.0 M NaCl when needed. After each 5-h FO experiment with humic acid-containing feed, physical cleaning was applied by flushing the shell side of the fiber for 30 sec with DI water, and then the recovered performance of the cleaned membrane was evaluated by using DI water as feed. For comparison, the FO performance of the commercially available FO membrane (OsmoF2O™ FO flat sheet membrane, Fluid Technology Solutions, Albany, OR; with effective membrane area of 40 cm²) was also evaluated in the AL-DS orientation using the same operation condition and cleaning protocol.

4.2.6. Compositions of feed sludge sample

Anaerobic digested sludge samples were collected from Ulu Pandan Water Reclamation Plant in Singapore and stored at 4 °C. The sludge was warmed to room temperature (22-23 °C) before use. The composition of the digested sludge is provided in **Table 4.3**.

Table 4.3 Compositions of digested sludge used as feed in sludge thickening process.

MLSS (g/L)	pH	Conductivity (mS/cm)	DOC (mg/L)	TN (mg/L)	NH ₄ ⁺ -N (mg/L)	PO ₄ ³⁻ P (mg/L)	Ca (mg/L)	Mg (mg/L)	Si (mg/L)	Osmolality (mOsm/kg)
15.5	7.23	5.15	9.3	543.3	670	558	86.6	40.8	28.9	108

4.2.7. Sludge thickening process by FO

A series of short-term FO sludge thickening experiments were carried out in the AL-DS orientation using 0.5 M NaCl as draw solution (**Figure 4.2**). The feed sludge was delivered to the shell side of the PES-HF-TFC membrane and the draw solution was delivered to the lumen side of the membrane at a flow rate of 1 L/min (corresponding to crossflow velocity of 0.23 m/s) and 190 mL/min (corresponding to crossflow velocity of 0.8 m/s), respectively. Physical cleaning was applied after 50 min of FO sludge thickening process operation, where the shell side of membrane was flushed with water at crossflow rate of 1.5 L/min for 5 minutes. At the same time, membrane backwashing was also carried out by circulating DI water on the lumen side of the membrane at 1 bar pressure. A total of six FO sludge thickening-cleaning cycles were performed.

4.2.8. Extraction of irreversible foulants from membranes

At the end of experiments, the fouled membranes were physically rinsed with DI water to remove loosely attached foulants (i.e., cake layer foulants) on membrane surface. After that, the fouled membranes were soaked into a NaOH solution (pH 12) under constant agitation (by using vortex mixer) for 2 h to extract the organic foulants accumulated inside the porous substrate layer (i.e., chemically removable foulants).

Figure 4.2. Schematic illustration of the experimental design of FO system operation.

4.2.9. Characterization of feed samples and foulants

Mixed liquor suspended solids (MLSS) was determined according to Standard Methods [281]. Conductivity and pH were examined by a conductivity/pH meter (Hanna, USA). The feed sample was filtered with a 0.45 μm filter (Pall Corporation, USA), and the dissolved total organic carbon (TOC) and total nitrogen were measured by a TOC/TN analyzer (Shimadzu, Japan). The concentration of NH_4^+ was determined by using commercial test kits and measuring colour intensity with a spectrophotometer (Hach, USA). Organic matter composition analysis was carried out by using a liquid chromatography-organic carbon detection (LC-OCD, DOC-Labor, Germany) [282].

4.3. Results and discussion

4.3.1. Characteristics of PES hollow fiber substrate

In this study, PES hollow fiber substrate with porous inner layer and dense outer skin was fabricated by a one-step co-extrusion technique with a variation of dope composition (**Table 4.1**) and spinning parameter (**Table 4.2**). As shown in **Figure 4.3**, the hollow fiber substrate exhibited finger-like cross-section morphology, where the macrovoids extended from both lumen and shell sides and intercepted at the center of the membranes. The thin layers of defect-free skin lying on the surface of both lumen and shell sides are formed, as a result of rapid vitrification (solid-liquid phase separation) during the initial contact between the polymer dope and strong non-solvent. Clearly, as shown in **Figure 4.3d**, the two layers formed from different dope compositions fused perfectly with no clear sign of delamination, similarly to those dual-layer membranes based on the simultaneous co-extrusion technique [283, 284]. Generally, similar shrinkage ratios of outer and inner layers in the NIPS process promote the formation of delamination-free structure. In this study, the difference in shrinkage ratio was minimized by employing the same polymer in both the outer and inner dopes. Also, the cloud point of the outer dope was adjusted to the same level as the inner dope by the addition of water into the dope, which is believed to have promoted the formation of a continuous phase at the interface.

In addition, the skin layer on shell side (i.e., tight UF skin layer) seems to be much thinner than that on the lumen side (i.e., loose UF skin layer). This could be associated with the fact that the higher polymer content in the outer layer dope solution impedes the inward diffusion of water and delays the vitrification process. Under this scenario, the formation of porous structure close to the skin layer is promoted, as driven by the nucleation and growth mechanism [285, 286].

Figure 4.3. SEM images displaying morphologies of the pristine PES-HF-TFC membrane. (a-b) Overall cross-section; (c) Cross-section on shell side; (d) Magnified cross-section on shell side (dense UF); (e) Magnified cross-section on lumen side showing polyamide selective layer.

The properties of the PES hollow fiber substrate are summarized in **Table 4.4**. It has an average inner and outer diameter of 999 μm and 1287 μm , respectively (i.e., a thickness of $144 \pm 3 \mu\text{m}$). While the substrate has a considerably high porosity of around 75%, its PWP is only 4.6 LMH/bar, which indicates that the outer skin layer has a much higher contribution to the overall mass transfer resistance. Under an outside-in filtration mode, the MWCO of the hollow fiber substrate is estimated to be around 1.2 kDa, suggesting that the outer surface of the membrane is completely and evenly covered by the dense skin layer. It is noted that the MWCO of the substrate under inside-out filtration mode is about 32 kDa, which is much higher than that under the outside-in filtration mode. It is well known that the dextran molecules in the feed solution could easily penetrate

the porous matrix of the membrane and accumulate underneath the outer dense skin, which result in CICP and thus a relatively lower apparent rejection.

Table 4.4 Properties of the pristine PES hollow fiber substrate.

Dimension (μm)			PWP (LMH)	MWCO (kDa)		Mean pore diameter (nm)	Geometric standard deviation	Porosity (%)
Inner diameter	Outer diameter	Thickness		[I-O] ^a	[O-I] ^b			
999 $\pm$ 6	1287 $\pm$ 9	144 $\pm$ 3	4.6 $\pm$ 1.5	32	1.2	1.25	1.35	74.6 $\pm$ 0.3

^a [I-O] indicates that the membrane properties was tested in inside-out configuration, where the pressurized feed solution was circulated on the lumen side of the membrane.

^b [O-I] indicates that the membrane properties was tested in outside-in configuration, where the pressurized feed solution was circulated on the shell side of the membrane.

The mean pore diameter was calculated from the solute rejection characterized under outside-in filtration mode, and the probability distribution function curve is shown in **Figure 4.4**. Based on the MWCO and pore size distribution, the selectivity of outer skin layer of the hollow fiber substrate can be considered to be within a tight UF range (with MWCO between 1 kDa to 3 kDa) [287]. The improved selectivity of the substrate may help to suppress membrane fouling caused by pore plugging, which is mostly irreversible through physical cleaning [288, 289]. Such characteristics could help to improve the fouling resistance of inner-selective TFC membrane prepared from this substrate when operating in AL-DS orientation, since the smaller pore size of the outer skin of the substrate layer deters the entry and deposition of high molecular weight organic foulants from the feed solution into the matrix of the membrane.

Figure 4.4. Pore size distribution of the outer skin layer of pristine dual-layer PES hollow fiber substrate.

Aside from the dual-layer hollow fiber substrate, a hollow fiber substrate without purposefully densified outer skin layer was also fabricated and denoted as PES-PSHF. The PWP and MWCO of the substrate were 262 LMH/bar and 32 kDa, respectively, when characterized by outside-in filtration experiments.

4.3.2. Characteristic and intrinsic performance of TFC hollow fiber membranes

4.3.2.1. Membrane morphology and intrinsic separation properties

The cross-section view of the polyamide selective layer on the inner surface of the PES-HF-TFC membranes is shown in **Figure 4.3e**. Similar to the TFC hollow fiber membranes reported in some other studies [178, 274, 290], the selective layer is laid on the porous support layer as an extra layer and displays a typical ridge and valley pattern.

The water permeability coefficient of PES-HF-TFC membrane was 2.29 LMH/bar, which is not superior as compared to most of the TFC FO membranes reported in the literatures [173, 274, 291-293]. The resistance of tight UF skin layer on the shell side of PES-HF-TFC membrane may have contributed to the lower water permeability. The solute permeability coefficient of PES-HF-TFC membrane was 0.16 LMH, which was comparable or lower than most reported TFC FO membranes with similar water permeability coefficient [173, 274, 292-294].

4.3.2.2. Membrane performance: DI water as feed solution

The performance of the PES-HF-TFC membrane with DI water as feed solution in the AL-DS orientation was characterized. When 0.5 M NaCl was used as the draw solution, the water flux and reverse salt flux of PES-HF-TFC membrane was 24.1 LMH and 8.4 gMH, respectively. Compared to other reported double-skinned FO membranes, the pure water performance of this membrane in terms of water and reverse salt fluxes was not superior (**Table 4.5**). Based on the experimental FO performance, the structural parameter of PES-HF-TFC membrane was estimated to be 1230 μm , which is substantially higher than the TFC membranes prepared in the previous study (section 3.3.2). The increased structural parameter may be caused by greater substrate thickness and

relatively higher mass transfer resistance of the tight UF skin layer on the shell side of the membrane, which impeded the diffusion of solutes across the support layer of the TFC membrane.

Table 4.5 Performance comparison of various TFC FO membranes evaluated by using humic acid as feed solution.

Membranes	Selective layer properties	Intrinsic properties			FO performance				Ref.
		A (LMH/bar)	R _s (%)	B (LMH)	Orientation	Draw	Feed	Water flux (LMH)	
Inner-selective PES-TFC hollow fiber membrane with densified outer skin	Tight-UF outer skin (PES), RO-like polyamide TFC (MPD-TMC) selective layer on inner surface	2.29	89	0.16	AL-DS	0.5 M NaCl	Humic acid (50 mg/L)	~14.1 after 5 h	Current work
Double-skinned flat sheet membrane	TFN (DA-TMC-CNT) selective layer on both top and bottom surface	-	-	-	AL-DS	2.0 M MgCl ₂	Humic acid (5 mg/L)	~9.9 ^g after 3 h	[295]
Double-skinned hollow fiber membranes	RO-like polyamide TFC (MPD-TMC) selective layer on inner surface, NF-like crosslinked LBL (PSS-PAH) selective layer on outer surface	2.01 ^a	95.4 ^b	0.16 ^b	AL-DS	0.5 M NaCl	Humic acid (200 mg/L) and 10 mM NaCl	~23.6 ^h after 4 h	[274]
Inner selective SPES-TFC FO membrane (Samsung Cheil Industries, Korea)	TFC selective layer on inner surface	-	-	-	AL-FS	2.0 M KCl	Humic acid (60 mg/L)	~13.9 ⁱ after 5 h	[296]
Asymmetric CTA flat sheet membrane (HTI, Albany, OR)	CTA selective layer (RO) with embedded polyester mesh	0.517 ^c	-	0.195 ^d	AL-FS	2.0 M NaCl	Humic acid (60 mg/L as DOC)	~13.1 ^j after 5 h	[297]
					AL-DS		Humic acid (60 mg/L as DOC)	~19.6 ^j after 5 h	
TFC FO membrane (Oasys Water, Boston, MA)	RO-like polyamide selective layer	4.70 ^e	-	0.164 ^f	AL-DS	1.0 M NaCl	Humic acid (100 mg/L in background electrolyte solution)	~15.5 ^k after 5 h	[291]

^a Test conditions: RO test at 2.0 bar applied pressure; DI water as feed.

^b Test conditions: RO test at 2.0 bar applied pressure; 500 ppm NaCl as feed.

^c Test conditions: RO test at 0 -15.5 bar applied pressure; DI water as feed.

^d Test conditions: RO test at 0-15.5 bar applied pressure; 10 mM NaCl as feed.

^e Test conditions: RO test at 8.62 bar applied pressure; feed temperature 20 °C; DI water as feed.

^f Test conditions: RO test at 8.62 bar applied pressure; feed temperature 20 °C; 2000 mg/L NaCl as feed.

^g Test conditions: crossflow velocity was 1.59 cm/s for both draw and feed.

^h Test conditions: crossflow velocity was 10 cm/s for both feed and draw, room temperature (23 °C), all solutions exhibited neutral pH of ~7.

ⁱ Test conditions: crossflow Reynolds number for feed and draw were 1900 and 700, respectively and temperature was 25 ± 0.5 °C.

^j Test conditions: crossflow rate was 0.19 L/min (crossflow velocity of 9.8 cm/s) for both feed and draw; with membrane supported by mesh; temperature at 20 °C; pH = 6.5; ionic strength = 1 mM.

^k Test conditions: crossflow rates of feed and draw were 1 L/min (corresponding to crossflow velocity of 9 cm/s); temperatures of feed and draw solutions were 25 ± 1 °C.

Nonetheless, it should be noted that such FO performance is not representative of real feed solutions. Therefore, the performance of the membrane was further assessed in the following section with humic acid and activated sludge as feed solutions.

4.3.2.3. Membrane performance: humic acid as feed solution

The FO membrane performance in the AL-DS orientation was examined by using humic acid, a model foulant which has been employed in several earlier studies [99, 295, 298]. The water flux profile of the PES-HF-TFC membrane in three FO filtration-physical cleaning cycles is presented in **Figure 4.5**. In the first cycle, the water flux decreased linearly over time, approaching 75% of the pristine membrane's water flux after 5 h. In the following two cycles, the water flux decline rate appeared to be slower than the first cycle. The drop of water flux might be caused by (1) deposition of the high molecular weight fraction of the humic acid, forming a thin cake layer, and the partial pore blocking by the low molecular weight fraction of the humic acid [99]; and (2) a decrease in the osmotic pressure due to the accumulation of draw solutes in the feed solution.

Figure 4.5 FO performance of PES-HF-TFC and OsmoF2O™ FO membrane with humic acid (50 mg/L) as feed. The crossflow velocity on lumen side and shell side was 0.8 m/s and 0.23 m/s, respectively. The shaded region indicate that physical cleaning was carried out and then the FO water flux of cleaned membrane was tested by using DI water as feed.

It should be noted that the short-term physical cleaning (30 sec) of the PES-HF-TFC membrane could contribute up to above 82% recovery of water flux during cycles 2 and 3, implying that cake layer fouling was predominant for the PES-HF-TFC membrane during the long-term operation. Nevertheless, after 15-h filtration, as compared to the commercial OsmoF2O™ membrane with humic acid as feed solution in the AL-DS orientation (water flux at ~5.6 LMH), the PES-HF-TFC membrane (water flux at >14.1 LMH) displayed much better membrane performance when the same concentration of draw solution (0.5 M NaCl) was employed (**Figure 4.5**).

To make a fair comparison, the same initial water flux of PES-HF-TFC and commercial OsmoF2O™ membranes were set by regulating the draw solution concentration (0.5 M NaCl for PES-HF-TFC membrane and 2 M NaCl for commercial OsmoF2O™ membrane) and the water flux of the two membranes using humic acid as feed was recorded in **Figure 4.5**. After 3 cycles, OsmoF2O™ membrane had a slightly higher water flux than the PES-HF-TFC membrane. However, short-term physical cleaning could only recover less than 7% of water flux for the OsmoF2O™ membrane, implying predominantly irreversible fouling. It is reported that humic acid could cause pore clogging in a porous support layer in the AL-DS orientation due to comparable sizes of the humic acid and support layer pore size, which resulted in enhanced ICP and increased membrane resistance [99]. Also, the rather pronounced water flux decline in PES-HF-TFC membrane tested with humic acid may be attributed to adsorptive fouling [299]. Due to the low hydrophilicity of PES, adsorption of humic acid onto the surface of PES outer skin layer occurs more readily and this leads to faster increase in membrane resistance.

These findings indicated that the dense outer skin of PES-HF-TFC membrane fabricated in the current study, which was purposefully modified to reduce the average surface pore size (with mean pore diameter of 1.25 nm), could effectively restrict the penetration of high molecular weight humic acids (its hydration radius was estimated to be between 2.3 nm and 7.7 nm solution [300]) into the support layer and mitigated internal fouling. It also reveals a possibility

to achieve sustainable long-term operation of PES-HF-TFC membrane by employing periodic physical cleaning.

4.3.2.4. Comparison with double-skinned FO membranes in literature

The FO performances of the double-skinned FO membrane developed in this study and those reported in the literatures using humic acid as the model foulant are summarized in **Table 4.5**. Apparently, although the osmotic pressures in these previous studies were much higher than that in this study, the permeate flux of the PES-HF-TFC membrane was higher than or comparable to most of previous studies using the double-skinned FO membranes [295] or commercial FO membranes [291, 296, 297]. However, Fang et al. [274] from our group reported a double-skinned hollow fiber membrane (RO-like polyamide TFC selective layer on inner surface and NF-like crosslinked polyelectrolyte LBL selective layer on outer surface) with a higher permeate flux (~23.6 LMH) at the same osmotic pressure (0.5 M NaCl) as in this study. This is likely due to (1) a much thinner LBL selective layer than the dense UF skin layer in this current study; (2) the stronger humic acid-PES membrane interaction because of a lower hydrophilicity of PES compared to the LBL layer, which leads to a faster deposition of humic acid on the outer surface of the membrane; and (3) the improved humic acid rejection effectiveness of the NF-like layer compared to the dense UF-like layer, which possibly resulted in less ICP and irreversible fouling. Nevertheless, it should be pointed out that the current method of making double-skinned hollow fiber membrane is less complex. The PES-HF-TFC membrane developed in this study exhibited moderate fouling reversibility, as depicted by the reproducible water flux profile over consecutive cycles of FO experiments (**Figure 4.5**). To further reduce irreversible fouling when the dual-layer FO membrane is operated in the AL-DS orientation, improving surface hydrophilicity and minimizing surface pore size of the secondary selective layer by optimization of membrane fabrication process is suggested. One simple approach to achieve such a goal is to blend hydrophilic additives (such as PES block-copolymers with hydrophilic segments) during the dope preparation process, such that inherently more hydrophilic substrates may be fabricated. In addition, such approach should be adopted to modify only the outer dope

composition when fabricating hollow fiber substrates with dual-layer co-extrusion technique.

4.3.3. FO performance in a sludge concentrating process

4.3.3.1. Membrane performance

Generally, activated sludge contains greater-sized solids (having sizes up to a few millimeters) and can easily clog the hollow fiber membrane lumen side (i.e., active layer) in the AL-FS direction. Therefore, in this study, the sludge concentrating tests were performed in the AL-DS orientation and the dense nature of UF skin on the feed solution side is expected to play a critical role in reducing the membrane fouling propensity.

The membrane performance in six filtration-physical cleaning cycles is recorded in **Figure 4.6**. The water flux of the PES-HF-TFC membrane dropped significantly during the first cycle. After that, slow declining water flux was observed. At the end of each cycle, physical cleaning (flushing with backwashing for 5 min) was applied, which resulted in a mere 2.6-4.8% water flux recovery. This hints that the cake fouling has a negligible contribution to the water flux decline, while irreversible fouling is predominant. To further explore the membrane fouling mechanism, after 5-min physical cleaning, the SEM images of the fouled membrane were taken (**Figure 4.7**). It is observed that little or no foulant layer were found deposited on the fouled membrane surface, which suggests that pore blocking or narrowing predominantly caused the flux decline rather than physical-irremovable cake layers (such as gel layers). This observation was inconsistent with the finding in concentrating sludge in the AL-FS direction, in which reversible cake layer fouling was found to be a major contributor to membrane flux decline [265, 267]. It appears that the operation orientation plays an important role in affecting membrane fouling mechanisms.

Figure 4.6 The PES-HF-TFC membrane performance with activated sludge as feed (0.5 L of feed sludge, 0.5 M NaCl was used as the draw solution. The crossflow velocity on lumen side and shell side was at 0.8 m/s and 0.23 m/s, respectively).

Figure 4.7 The SEM images of the feed side (tight UF) of the fouled membrane after the sludge concentrating test (300-min) and 5-min physical cleaning.

After 300-min of operation, the sludge was concentrated at 1.4 times and the water flux of PES-HF-TFC membrane was stabilized at ~5.2 LMH with ~24.6 bar of osmotic pressure driving force. The achieved water flux per osmotic pressure (~0.21 LMH/bar) in this study at the AL-DS orientation was higher than those using commercial TFC and CTA FO membranes in the AL-FS orientation,

as reported in the literature (~0.06-0.19 LMH/bar; **Table 4.7**). It is also worth noting that the initial sludge concentration (15.5 g/L) employed in this study was 1 to 7 times higher of those in the reported literatures. The PES-HF-TFC membrane is expected to achieve even higher permeate flux (> 5.2 LMH) when a lower concentration of sludge is used. The combination of high water flux and low fouling tendency offers the possibility for such membranes to be used in concentrating sludge or other high solid content feed solutions and in recovering valuable products.

In order to further investigate the effect of the pore size of shell side skin layer on the fouling resistance of the FO membrane in sludge thickening process, parallel experiments were also carried out by using hollow fiber TFC membranes fabricated without purposefully densified outer skin layer, denoted as PES-PSHF-TFC. The performance of the PES-PSHF-TFC membrane is shown together with the dual-skinned membrane in **Figure 4.8**.

Figure 4.8 Water flux profiles (a), normalized water flux profiles (b), and apparent resistance increment (c) of the PES-HF TFC membranes in sludge thickening experiments (0.5 M NaCl as draw solution, crossflow velocity in membrane lumen side at 0.8 m/s; 0.5 L of sludge at 15.5 g/L as feed, crossflow velocity in membrane shell side at 0.23 m/s).

Under the same testing conditions, PES-PSHF-TFC membrane exhibited a much higher initial water flux but experienced a more serious water flux decline over the first hour of FO experiment when using sludge as the feed. Both membranes exhibited similar patterns of water flux decline over the next few hours. The observed water flux decline may be attributed to increase in resistance of the membrane due to accumulation of foulants, which could be estimated by a simplified equation derived from Darcy's Law:

$$\Delta R = (R_f - R_0) = \frac{\Delta P}{\mu} \cdot \left(\frac{1}{J_{w,t}} - \frac{1}{J_{w,0}} \right) = \frac{\Delta \pi}{\mu} \cdot \left(\frac{1}{J_{w,t}} - \frac{1}{J_{w,0}} \right) \quad (Eq 4.1)$$

Table 4.6 A summary of operation conditions and membrane performances of various FO-based sludge thickening processes.

Membrane	Orientation	Draw solution	Draw osmotic pressure ^a (bar)	Initial MLSS (g/L)	Final MLSS (g/L)	Water flux (LMH) @ 5h	Ref.
TFC, hollow fiber	AL-DS	0.5 M NaCl	~24.6	15.5	21.8	5.2	This work
CTA, flat sheet (HTI, Albany, Oregon, US)	-	1.5 M MgCl ₂	~111	1.8	~2.5 ^b	-	[301]
CTA, flat sheet (HTI, Albany, Oregon, US)	AL-FS	Simulated SWRO retentate (mixed inorganic salts)	~40	7.3	~24 ^c	-	[267]
CTA, flat sheet (HTI, Albany, Oregon, US)	AL-FS	Simulated seawater (0.62 M NaCl)	~30.3	8.0	~14.9 ^c	~5.1 ^d	[265]
CTA, flat sheet (HTIs OsMem™, Albany, Oregon, US)	AL-FS	Simulated seawater (0.62 M NaCl)	~30.3	8.0	~13.4 ^c	~5.6 ^d	[264]
CTA, flat sheet (HTI, Albany, Oregon, US)	AL-FS	0.7 M EDTA sodium salt at pH 8	~68.9	8.0	~12.7 ^c	~6.0 ^d	[271]
TFC, flat sheet (HTI)	AL-FS	2.2 M MgCl ₂	~163	5.43	~6.5 ^b	~9 ^d	[266]

^a Osmotic pressure of the draw at room temperature (23°C) was estimated by using van't Hoff equation, where the van't Hoff factor of NaCl, MgCl₂, CaCl₂, NaHSO₄, Na₂SO₄ and EDTA sodium salt were taken as 2, 3, 3, 2, 3 and 4. Note that the estimated values may only be valid for dilute solutions.

^b Final MLSS after 5 h of FO sludge thickening experiments were calculated from reported initial MLSS and volume reduction of sludge, where the latter was estimated from the figures.

^c Final MLSS after 5 h of FO experiments were estimated from the figures.

^d FO water flux after 5 h of FO experiments were estimated from the figures.

where R_f and R_0 are the resistance of pristine membrane and fouled membrane, ΔP is the driving force across the membrane, μ is the viscosity of the water, $J_{w,o}$ and $J_{w,t}$ are the water flux of pristine membrane and the water flux of fouled membrane. For FO process, osmotic pressure difference ($\Delta\pi$) across the selective layer of TFC membrane is the sole driving force, which is estimated by the van't Hoff's equation. As shown in **Figure 4.8**, the increase in the resistance of PES-PSHF-TFC membrane was apparently higher than that of the double-skinned membrane, which indicates that foulant accumulation in the double-skinned membrane is indeed slower.

4.3.3.2. Characteristics of irreversible foulants

At the end of the FO experiments (300 min), the physically cleaned membranes were removed from the module and the organic foulants accumulated inside the FO membrane was extracted by NaOH solution (pH 12, for 2h). The LC-OCD results (**Figure 4.9**) revealed that the dense UF layer of the PES-HF-TFC membrane could effectively reduce the accumulation of the higher molecular weight substances such as biopolymers (>10 kDa), humic substances (~1 kDa), and building blocks (300-500 Da), which were 370%, 130% and 130% lower than those in the feed sludge, respectively. However, there was a tendency for low molecular weight neutrals (<350 Da) to be accumulated inside the FO membrane, which was 70% higher than that in the feed sludge. This finding highlights the importance in further minimizing the surface pore size of the secondary rejection layer of FO membranes in order to improve rejection efficiency of low molecular weight substances from the sludge samples.

Organic foulant analysis was also carried out by using PES-PSHF-TFC membrane that has been tested in parallel experiments as PES-HF-TFC membrane, as shown in **Figure 4.10**. It was found that a higher amount of organic foulants could be extracted from the former after sludge thickening experiments, as compared to the latter. In terms of foulant composition, it appears that the accumulation of humic acid in the PES-PSHF-TFC membrane was much more significant. This observation confirmed that the use of TFC membrane with smaller pore size on the shell side could effectively reduce the

deposition of high to medium molecular weight organic foulants in the membrane.

Figure 4.9 Composition ratios of organic substances in the feed sludge and irreversible foulants accumulated in the PES-HF-TFC membrane.

Figure 4.10 Compositions of organic foulants from both FO membranes.

4.4. Conclusions

This study furthers the effort in optimizing the hollow fiber substrate in Chapter 3 by designing a novel double-skinned (tight UF outer skin and RO inner skin) hollow fiber TFC FO membrane preparation process, i.e., fabricating a dual-layer PES substrate in one step, followed by interfacial polymerization to form the inner-selective polyamide layer. This membrane exhibited better performance in concentrating humic acid and activated sludge in the AL-DS orientation as compared to most of the commercial membranes and some self-prepared membranes reported so far. The tight UF-like outer layer has proven to reject greater-sized molecules, for example, reducing the accumulations of biopolymers, humic acids, and building blocks inside of the FO membranes in sludge thickening processes, and thus helps to suppress irreversible organic fouling of the membranes.

Chapter 5 Membrane Compaction in Forward Osmosis Process

5.1. Introduction

The double-skinned FO membrane developed in Chapter 4 is not without drawbacks. Apart from a potential reduction in the water flux of the membrane, the mechanical stability required for a sustainable long-term operation of the double-skinned membranes remains a topic yet to be fully comprehended. In general, polymeric membranes could experience certain degree of densification under the stress induced by applied hydraulic pressure, leading to gradual increase in mass transfer resistance and thus decrease in membrane permeability over time. Such a phenomenon is known as membrane compaction, and it could significantly reduce the flux of RO, NF and UF as well as gas separation membranes over the early stage of operation [302, 303]. Compaction of polymeric membranes is influenced by time-dependent phenomena such as plasticization, swelling and creep of the polymer [304-307]. Although compaction may take place slowly over long time of operation, the lack of proper assessment on the contribution of compaction on membrane performance could still negatively impact the results of lab-scale studies [302]. Currently, pre-compaction is a typical solution to isolate the influence of compaction and decoupled it from other factors that could affect membrane performance.

For FO membranes, little attention was paid to membrane compaction and its possible influence on the long-term performance as there is no external hydraulic pressure applied in the FO process. Thus, researchers commonly presumed that there is no significant stress exerted on the membrane. Also, the characterization of intrinsic FO performance of membranes were mostly carried out through short-duration experiments in the lab studies (<2 hours) [17, 308], where the reduction of effective osmotic gradient due to dilution of draw solution and draw solute accumulation in feed solution was normally not examined thoroughly. However, in our recent laboratory study, it was observed that the water flux of FO membrane decreased gradually when it was tested in the AL-

DS orientation over 24 hours. More importantly, due to the complex structure of the double-skinned FO membrane, a more significant difference in the water flux was observed using a high concentration draw solution. Hence, this brought us to wonder if a time-dependent transformation in membrane structure (i.e., membrane compaction) exists for double-skinned FO membrane but is often neglected due to the short-duration of experiments.

In order to confirm our hypothesis and understand the mechanism, three types of hollow fiber TFC membranes, including one with single-layered substrate and two with dual-layered substrates were specially designed and studied. The FO performance of the membranes were characterized by using draw solutions with different concentrations and their water and salt flux patterns over time were compared to elucidate the possible connections between the compaction behavior of TFC membranes and the mass transfer resistance of support layer, as well as the osmotic driving force presented across the membranes. Changes in membrane morphology, surface topography and structure during FO experiments were also analyzed through the inspection of the tested membranes under scanning electron microscope (SEM), transmission electron microscope (TEM) and atomic force microscope (AFM). The possible causes of compaction in FO process were proposed based on the experimental observations of TFC membranes. It is envisaged that this study could shed light on the important factors that should be taken into account during FO membrane fabrication and when establishing testing protocols for the characterization of FO membrane.

5.2. Experimental

5.2.1 Materials

For the preparation of polymer dope solutions, Veradel® 3000P Polyethersulfone (PES) was supplied by Solvay Advanced Polymers; N-methyl-2-pyrrolidone (NMP), polyethylene glycol 200 (PEG, $M_w = 200$ g/mol) and acetone (Ac) were purchased from Merck Chemicals; while polyvinylpyrrolidone (PVP, $M_w = 1,300,000$ g/mol) was purchased from Acros Organics. Glycerol

(85%) was obtained from Merck Chemicals for post-treatment of hollow fiber substrates. Cyclohexane, 1,3,5-benzenetricarbonyl trichloride (TMC) and m-phenylenediamine (MPD) were purchased from Sigma-Aldrich and used in the fabrication of TFC membrane. Dextran of various molecular weights were purchased from Sigma-Aldrich and used in crossflow filtration experiments for determination of molecular weight cut-off (MWCO) of the hollow fiber substrates. Sodium chloride (NaCl) was supplied from Merck Chemicals and used for the characterization of TFC membrane intrinsic properties and FO performances. Deionized (DI) water was used to prepare all aqueous solutions in this study, which was produced by Milli-Q system (Millipore, USA).

5.2.2 Hollow fiber membrane fabrication

5.2.2.1 Substrates and module preparation

Hollow fiber membranes which were used as the substrate for the preparation of TFC membranes in Chapter 4 were fabricated via the NIPS process [206, 309]. The fabrication process of hollow fiber substrate is schematically illustrated in **Figure 4.1**. In order to produce hollow fiber substrates with highly asymmetric structures, a co-extrusion method [204, 309] was employed through the use of a triple-channel spinneret during hollow fiber spinning process. Single-layer hollow fiber substrate denoted as “SL” was fabricated from a dope with lower concentration of polymer and high concentration of pore forming additive (PEG 200), which was extruded through the inner dope channel to form a highly porous structures upon phase inversion.

Prior to module preparation, the hollow fiber substrates were immersed in glycerol/water (50/50 wt%) mixture for 1 day. Then, the hollow fibers were dried in the air at room temperature for 1 day. The residual glycerol in the hollow fiber substrates served as the pore preserving agent. Five pieces of glycerol preserved membranes were then packed into laboratory-scale modules by using epoxy resin (Araldite® Rapid). Each module possesses an effective membrane length of around 25 cm with an effective membrane area between 37 cm² to 40 cm².

Table 5.1 Hollow fiber substrate spinning conditions.

Hollow fiber substrate	SL	DL#1	DL#2
Dope composition (wt%) (PES/NMP/PEG/PVP/Ac/H ₂ O)			
- inner layer	20/40/40/0/0/0	20/40/40/0/0/0	20/40/40/0/0/0
- outer layer	-	29.2/50.3/0/16.8/1.0/2.8	30.0/52.1/0/17.4/0.5/0
Spinneret dimension			
- bore fluid channel ID	360		
- inner dope channel ID/OD	620/890		
- outer dope channel ID/OD	1230/1420		
Inner dope flow rate (mL/min)	6.70		
Outer dope flow rate (mL/min)	-	0.30	0.30
Bore fluid composition	DI water		
Bore fluid flow rate (mL/min)	10.0		
Take-up speed (cm/s)	18.85		
Air gap (cm)	1.0		
Coagulation bath composition	Tap water		
Coagulation bath temperature (°C)	22-23		
Room temperature (°C)	22-24		
Relative humidity (%)	70-71		

5.2.2.2 TFC membranes preparation

Inner-selective hollow fiber TFC membranes were prepared by interfacial polymerization reaction, based on the procedures described in section 3.2.4. The hollow fiber membranes were first impregnated with MPD by filling the lumen of the modules with the aqueous solution for some time. Then, cyclohexane and TMC solutions were sequentially pumped through the lumen of the modules at constant flow rate, during which MPD and TMC reacted and formed a thin layer of polyamide on the membrane surface inside the lumen of the fiber. Finally, the TFC membranes were then rinsed and immersed in DI water for 1 day.

5.2.3 Membrane characterization

5.2.3.1 Intrinsic property of substrate and TFC FO membrane

Digital microscope (Keyence, Japan) was used to characterize the dimension of hollow fiber substrates. At least 12 measurements were taken with different sections of the membranes to obtain the average dimensions of each substrate. Pure water permeability (PWP) of the substrates were characterized via

crossflow filtration experiments, where DI water was circulated over the shell side of the hollow fibers at 1.0 bar applied pressure. PWP ($\text{L/m}^2/\text{h}/\text{bar}$) was calculated with equation 3.1.

The MWCO of the substrates were also determined by crossflow filtration experiments, where 2000 ppm dextran solutions (a mixtures of dextran standards with molecular weight range from 6 kDa to 650 kDa) was circulated on the shell side of the substrates at 1.0 bar applied pressure. The feed and permeates were analyzed on gel permeation chromatography (GPC) instrument equipped with refractive index (RI) detector (Polymer Laboratories-GPC 50 plus system, Agilent, USA). The MWCO of the substrates were calculated based on the rejection towards dextran molecules of different molecular weights, according to the procedures reported elsewhere [278, 279]. The porosity of substrates was calculated by gravimetric method.

5.2.3.2 TFC membranes performance evaluation

Water permeability coefficient (A , $\text{L/m}^2/\text{h}/\text{bar}$) of TFC membranes were characterized via crossflow filtration experiments, where DI water was circulated through the lumen of the module at 2.0 bar applied pressure. The water permeability coefficient of TFC membranes was calculated with equation 3.7 (see Section 3.2.6). Note that the effective membrane area used for the calculation of water permeability coefficient was estimated from the inner diameter of the TFC membranes instead. The salt rejection (R_s , %) and solute permeability coefficient (B , LMH) of TFC membranes was characterized via crossflow RO experiments. A 500 ppm NaCl solution was used as the feed solution and circulated on the lumen side of the TFC membranes at 2 bar applied pressure. The conductivity of permeate (EC_p) and feed (EC_f) were measured by using conductivity meter (ULTRAMETER II™, Cole-Parmer). Salt rejections were calculated with equation 3.8 (see Section 3.2.6). Solute permeability coefficients were calculated from water permeability coefficient and salt rejection by using equation 2.4 (see Section 2.1.2).

5.2.3.3 Inspection using SEM, AFM and TEM

The cross-section morphology of TFC membrane was examined under field-emission SEM (FE-SEM, JEOL, Japan). To prepare samples for SEM, wet

membranes were frozen and cleaved in liquid nitrogen to expose the fine structures of membrane cross-section. The samples were then freeze-dried overnight and sputter-coated with platinum (20 mA coating current, 45 sec coating time) prior to inspection under SEM (5 kV acceleration voltage).

The surface topography on the lumen side of TFC membranes was characterized by using AFM (Park Systems, Korea). The membranes were freeze-dried overnight prior to characterization under AFM. To expose the polyamide layer on the lumen side of TFC membranes, the membranes were sliced along the axis and mounted flat on sample disks with the aid of double-sided tapes. The topography images of the polyamide layer were obtained under non-contact mode (NCM) with PPP-NCHR cantilever loaded head. The raw images were processed by using the XEI program to generate 3D topographic images and calculate the average roughness of the membrane surface.

TFC membranes were characterized with a JEOL 1230 Transmission Electron Microscope (TEM) at an acceleration voltage of 120 kV. The membranes were embedded in LR White resin before they were cut into sections for TEM inspection, based on modified procedures from Tang et al [310]. Membrane samples were freeze dried overnight and immersed in 100% ethanol for 1 h. Then, samples were sequentially immersed in 50 wt% (1 h), 67 wt% (2 h), 100 wt% (4 h), and another 100 wt% (24 h) LR White resin. The 50% and 67% solutions were prepared by diluting fresh LR White resin with ethanol. Finally, the samples were transferred into gelatin capsules filled with 100% LR White resin and cured at 48 °C for 4 days. TEM sections (<100 nm thick) were prepared with Leica Ultracut S Ultramicrotome (Leica, Wetzlar, Germany).

5.2.4 Forward osmosis experiments

A schematic diagram of the experimental setup used for characterizing the FO performance of the TFC membranes is shown in **Figure 5.1**. All TFC membranes were characterized in the AL-DS configuration. DI water was used as the feed solution, while NaCl solutions with different concentrations were used as draw solution.

Figure 5.1 Schematic illustration of FO experimental setup.

During the FO experiments, feed solution was circulated on the shell side of the membranes at a cross-flow velocity of around 23 cm/s, while draw solution was circulated on the lumen side of the membranes at a cross-flow velocity of around 80 cm/s in a counter-current configuration. The temperature of draw and feed solutions were maintained at room temperature (22 – 24 °C) throughout the experiments. The conductivity and temperature of draw and feed solutions were monitored by using conductivity probes (Suntex, Taiwan). Dosing pump was used to maintain the concentration of the draw solution based on the conductivity. The mass of the feed solution was monitored by using mass balance (Shimadzu, Japan). The concentration of NaCl in feed and draw solutions were determined based on their conductivity.

The water flux (J_w , L/m²/h) of the membranes were determined based on the mass change of feed solution by using equation 3.9 (see Section 3.2.7). The reverse salt flux (J_s , g/m²/h) of the membranes were determined based on the change in the concentration of NaCl in feed solution (C_f , ppm) and the mass of feed solution by using equation 3.10 (see Section 3.2.7). Specific reverse salt flux (J_s/J_w , g/L) was determined by dividing the reverse salt flux with the water flux of the membrane at a given time.

In order to investigate the time-dependent process in the AL-DS orientation, the FO tests were carried out under near-ideal conditions for an extended duration.

To minimize the decrease in osmotic pressure difference between the draw and feed solutions, the concentration of draw solution was maintained by constant dosing with a 5.0 M NaCl solution. A relatively large volume of the feed solution was used in each FO tests to ensure that the accumulation of draw solute in the feed solution was slowed down significantly. In addition, to rule out the effect of draw solute accumulation in the feed solution on the membrane performance, the final FO performance of each TFC membrane was re-determined using fresh feed and draw solutions under initial testing conditions.

5.3. Results and discussion

5.3.1 Characteristics of membranes

5.3.1.1 Hollow fiber substrates and TFC membranes

The properties of the hollow fiber substrates fabricated in this study are summarized in **Table 5.2**. The PWP of the substrates varied significantly with the dope composition changed. The single-layer substrate, denoted as SL, possessed a PWP of 297 L/m²/h/bar, which was the most permeable among the three substrates fabricated. This is attributed to the use of high concentration of PEG 200, a pore-forming additive which induced the formation of highly porous skin layer on both shell and lumen sides of the SL substrate. The dual-layer substrates, denoted as DL#1 and DL#2, possessed PWP of 16.6 L/m²/h/bar and 2.83 L/m²/h/bar, respectively, which were around one to two orders of magnitude lower than the single-layer substrate. Such enormous differences in PWP were attributed to the presence of the relatively thin but significantly less porous layer on the shell side of the dual-layer hollow fiber substrates, which were formed from the dopes containing a higher polymer concentration and smaller amount of pore forming additives (see **Table 5.1**).

Table 5.2. Properties of hollow fiber substrates.

Hollow fiber substrates:	SL	DL#1	DL#2
Dimension (um)			
inner diameter	900±6	975±27	1013±7
outer diameter	1185±9	1260±22	1292±7
thickness	142±4	142±5	140±2
PWP (L/m ² /h/bar)	297±7	16.6±0.5	2.83±0.26
MWCO (kDa)	9.5	1.8	1.9
Porosity (%)	77	78	78

On one hand, all hollow fiber substrates possess relatively high porosity. The porosity of SL, DL#1 and DL#2 were 77% 78% and 78%, respectively. Despite that much higher polymer concentration was used in the second dope which formed the outer layer of the dual-layer substrates, their overall porosity did not vary substantially from the single-layer substrates. This is ascribed to the higher inner dope flow rate as compared to the outer dope flow rate during membrane fabrication. Due to the large difference between the dope flow rates, the dope extruded from the inner dope channel constituted a much larger portion of the extruded dopes. As the dope extruded from the inner dope channel contained high concentration of PEG as the pore forming agent, which forms the thicker but highly porous inner layer. In contrast, the dope with a higher polymer concentration and small amount of pore forming agent was extruded at a significantly lower flow rate to create an extremely thin but dense outer layer. As such, a highly asymmetric hollow fiber membrane with a critically densified top layer can be prepared without sacrificing the bulk porosity of the membrane. The porous support of the three substrates could thus be considered similar.

The intrinsic separation properties of the TFC membranes fabricated in this study are summarized in **Table 5.3**. The water permeability coefficient of TFC membranes prepared from SL, DL#1 and DL#2 were 4.07 L/m²/h/bar, 2.41 L/m²/h/bar and 1.38 L/m²/h/bar, while their NaCl rejections were 97.2%, 96.3% and 91.7%, respectively.

Table 5.3 Intrinsic properties of TFC hollow fiber membranes.

Hollow fiber TFC membrane	SL-TFC	DL#1-TFC	DL#2-TFC
Water permeability coefficient, A (L/m ² /h/bar)	4.07 ± 0.14	2.41 ± 0.24	1.38 ± 0.09
Salt rejection, R _s (%)	97.2 ± 0.1	96.3 ± 0.7	91.7 ± 0.6
Solute permeability coefficient, B (L/m ² /h)	0.18 ± 0.01	0.16 ± 0.02	0.21 ± 0.02

5.3.2 FO performance of TFC membrane with single-skinned FO membrane/

The performances of SL-TFC membrane over 24 hours of FO tests are shown in **Figure 5.2**, which are normalized with reference to the performance determined in the first 20 minutes. The initial water flux, reverse salt flux and specific reverse salt flux of SL-TFC membrane were 50.4 L/m²/h, 2.6 g/m²/h and 0.051 g/L, respectively, when 0.5 M NaCl was used as draw solution. On the other hand, when 2.0 M NaCl was used as a draw solution, the initial water flux, reverse salt flux and specific reverse salt flux of SL-TFC membrane were 110.6 L/m²/h, 9.2 g/m²/h, and 0.083 g/L, respectively. For both FO tests carried out with either 0.5 M NaCl or 2.0 M NaCl as draw solution, the water flux of SL-TFC membrane stabilized within 1 hour after the FO tests began. There was substantial increase in the reverse salt flux of SL-TFC membranes over the first hour of FO test when 0.5 M NaCl was used, which was likely due to the delay of conductivity measurement when the concentration of draw solute in the feed was extremely low.

Figure 5.2 FO performance of SL-TFC membrane characterized by using DI water as feed solution. The normalized water flux, normalized reverse salt flux and normalized specific reverse salt flux of the membrane are presented in logarithmic time scale. The final performance of the membrane after 24 hours of experiments are indicated by the bold shaded markers.

The water flux and reverse salt flux of SL-TFC membranes tested with draw solutions of different concentrations displayed similar patterns over 24 hours of FO test. Both water flux and reverse salt flux of the membrane remained relatively stable over the first 3 hours but started to decline linearly afterwards until the end of the FO tests. After the 24-hour test, the membrane was re-tested using fresh feed and draw solutions and results are shown in **Figure 5.2** (shaded points). It was found that the water flux of the used SL-TFC membrane were 9% and 21% lower, while the reverse salt fluxes were 16% and 66% lower than the initial values of the fresh membrane, with 0.5 M NaCl and 2.0 M NaCl as draw solutions, respectively. These results indicated that the FO performance of the TFC membrane did not recover completely even after the initial testing conditions were restored. It implied that both the water flux decline and reverse salt flux decline during FO tests were not entirely caused by the changes of feed and draw solutions (such as the accumulation of salt in feed solution due to salt back diffusion). It may suggest that the properties of the support layer changed during FO tests, such that the structural parameter increased, leading to more severe ICP.

In addition, the water flux decline and salt flux decline may also be associated with the decrease in the water permeability and solute permeability of the TFC membrane, which was probably caused by the change of the selective layer. It was also found that the reverse salt flux decreased more significantly than the water flux of SL-TFC membrane, leading to overall reduction in the specific reverse salt flux of 7% and 57% respectively when 0.5M NaCl and 2.0 M NaCl were used as draw solution. Such changes may be interpreted as improvement in membrane selectivity. These results imply that the FO performance that are typically measured through short-duration FO tests may not reflect the stable performance of TFC membranes over a long period of operation, particularly if the osmotic gradient across the membrane is high.

To determine if the reduction in both water flux and salt flux are related to the membrane deformation, membrane autopsy was carried out for SL-TFC membrane before and after FO tests. The SEM images showing the cross-section and the surface on the lumen side of SL-TFC membranes are shown in **Figure 5.3**. Despite that the FO performance of SL-TFC membrane had

changed substantially, there was no discernible difference in the morphology of SL-TFC membrane before and after the FO tests, regardless of the concentration of the draw solution used. This implies that the flux decline that occurred in SL-TFC membrane may be caused by microscopic deformations which were visually too minor to be identified.

Figure 5.3 SEM images of SL-TFC membrane before and after FO tests.

Nevertheless, the irreversible changes in the FO performance of SL-TFC membranes with operating time was observed, and the change was pronounced when the draw solution with higher concentration was used. To have a better understanding of these observations, two double-skinned membranes were fabricated and characterized for further investigations.

5.3.3 FO performance of TFC membrane with dual-layered support (DL#1-TFC)

The DL#1-TFC membrane was fabricated from a hollow fiber substrate with purposely densified skin layer on its shell side, similar to that in Chapter 4. The FO performance of DL#1-TFC membrane was tested for 24 hours, and its water flux, reverse salt flux and specific reverse salt flux are shown in **Figure 5.4**. For FO test carried out using 0.5 M NaCl as draw solution, the initial water flux, reverse salt flux and specific reverse salt flux of DL#1-TFC membranes were

36.7 L/m²/h, 5.3 g/m²/h and 0.15 g/L, respectively whereas, when 2.0 M NaCl was used as draw solution, the initial water flux, reverse salt flux and specific reverse salt flux of DL#1-TFC membranes were 60.1 L/m²/h, 24.8 g/m²/h and 0.41 g/L, respectively.

The initial specific reverse salt flux of DL#1-TFC membrane was significantly higher when 2.0 M NaCl was used as draw solution, which indicated that the selectivity of DL#1-TFC membrane had deteriorated immediately after it was brought into contact with 2.0 M NaCl solution.

When 0.5 M NaCl was used as draw solution, the water flux of DL#1-TFC membrane decreased almost linearly with time starting from the beginning of the test. As the concentration of draw solution was increased to 2.0 M NaCl, the water flux decline of DL#1-TFC membrane was even faster, which implied that the structure of DL#1-TFC membrane had experienced a greater change within a short duration. It was also observed that the DL#1-TFC membrane displayed similar salt flux decline patterns in both FO tests using 0.5 M NaCl and 2.0 NaCl as draw solutions, where the reverse salt fluxes were relatively stable within the first 3 hours but began to decrease logarithmically afterwards.

After the 24-hour FO tests, the used DL#1-TFC membrane was re-tested using fresh feed and draw solutions. It was found that its water flux decreased by 32% and 52%, whereas the reverse salt flux of the used membrane decreased by 14% and 47% using 0.5 M NaCl and 2.0 M NaCl as draw solutions, respectively, relative to the results of fresh DL#1-TFC membrane. Overall, the used DL#1-TFC membrane presented a more significant water flux decline and reverse salt flux decline when the draw solution of higher concentration was used in FO tests, similar to the SL-TFC membrane. Yet, the reverse salt flux decline of DL#1-TFC membrane was less significant than the water flux decline, which was different from the situation of the SL-TFC membrane. As a result, the specific reverse salt flux increased by 26% and 8% after the FO tests were carried out with 0.5 M NaCl and 2.0 M NaCl as draw solutions. These results implied that the rejection of DL#1-TFC membrane to NaCl has deteriorated during the FO tests.

Figure 5.4 FO performance of DL#1-TFC membrane characterized by using DI water as feed solution. The normalized water flux, normalized reverse salt flux and normalized specific reverse salt flux of the membrane are presented in logarithmic time scale. The final performance of the membrane after 24 hours of experiments are indicated by the bold shaded markers.

In order to investigate if the significant deterioration of FO performance is associated with the structural deformation of DL#1-TFC membrane, membrane autopsy was carried out right after the FO tests. The cross-section morphology of DL#1-TFC membrane before and after the FO tests were shown in the SEM images in **Figure 5.5**. It was found that the thickness of the polyamide layer became thinner and the surface grew more even. The surface of the polyamide layer surface exhibited loosely bound leafy appearance before the FO test, which seemed to become compressed and flattened after the FO test. These observations imply that the deterioration of FO performance is very likely associated with the microscopic deformation of TFC membrane during FO tests.

Figure 5.5 SEM images of DL#1-TFC membrane before and after FO tests.

In comparison with the case of SL-TFC membrane in Section 5.3.2, both SL-TFC and DL#1-TFC membranes with different support layer structures displayed irreversible decline in water flux and reverse salt flux during FO tests within 24 hours. In addition, the water flux decline of DL#1-TFC membrane was more significant than that of SL-TFC membrane, whose support layer was more permeable than the former. It is also noted that the initial water flux of DL#1-TFC membrane were lower than SL-TFC membrane. Thus, it is speculated that the osmosis-induced compaction of TFC membrane is associated with not only the polyamide layer, but also the support layer structure. A support layer with

low permeability may contribute high hydraulic resistance to water permeation, which may promote TFC FO membrane's compaction.

5.3.4 FO performance of TFC membrane with dual-layered support (DL#2-TFC)

To confirm the influence of the hydraulic resistance of support layer on the osmosis-induced compaction, DL#2-TFC membrane was prepared and characterized with the same testing conditions. Similar to DL#1-TFC membrane, DL#2-TFC membrane was prepared from a hollow fiber substrate that possessed a specially densified skin layer on the shell side. Yet, the water permeability of the substrate of DL#2-TFC membrane was 83% lower than that of DL#1-TFC membrane. Therefore, it was expected that the osmosis-induced compaction would have greater influence on the performance of the DL#2-TFC membrane.

Figure 5.6 shows the water flux, reverse salt flux and specific reverse salt flux of DL#2-TFC membrane in FO tests. When 0.5 M NaCl was used as the draw solution, the initial water flux, reverse salt flux and specific reverse salt flux of DL#2-TFC membranes were 17.0 L/m²/h, 7.2 g/m²/h and 0.42 g/L, respectively. Both water flux and reverse salt flux decreased logarithmically with time, which were similar to the flux patterns observed in the FO performance of DL#1-TFC membrane. On the other hand, the initial water flux, reverse salt flux and specific reverse salt flux of DL#2-TFC membranes were 5.7 L/m²/h, 6.1 g/m²/h and 1.02 g/L, respectively, when 2.0 M NaCl was used as the draw solution. The water flux of DL#2-TFC membrane decreased sharply within the first 5 minutes after the FO test began and stabilized shortly. The reverse salt flux of DL#2 membrane increased instantly after the FO test began and stabilized shortly after that. As a result, the initial specific reverse salt flux of DL#2-TFC membrane using 2.0 M NaCl as draw solution was close to 250% higher than when 0.5 M NaCl was used as draw solution. These unusual changes in the pattern of water flux and reverse salt flux over time may indicate that a substantial structural deformation occurred almost instantly on DL#2-TFC membrane when it was exposed to a highly concentrated draw solution. Hence, it is confirmed that the rejection of TFC membrane to NaCl could be seriously compromised due to

osmosis-induced compaction when operated over an extremely high osmotic pressure gradient.

Figure 5.6 FO performance of DL#2-TFC membrane characterized by using DI water as feed solution. The normalized water flux, normalized reverse salt flux and normalized specific reverse salt flux of the membrane are presented in logarithmic time scale. The final performance of the membrane after 24 hours of experiments are indicated by the bold shaded markers.

At the end of FO tests, the water flux of DL#2-TFC decreased by 65% and 4%, while reverse salt flux decreased by 35% and 1%, when 0.5 M NaCl and 2.0 M NaCl fresh draw solutions were used together with fresh feed water, respectively. As expected, the overall water flux reduction and reverse salt flux reduction of DL#2-TFC membrane were significant when 0.5 M NaCl was used as a draw solution. It suffered even more significant water flux decline than DL#1-TFC membrane, which confirmed again that osmosis-induced compaction is present in TFC membranes that possess a support layer with higher hydraulic resistance.

The cross-section morphology of DL#2-TFC membranes before and after FO tests were observed under SEM, as shown in the images in **Figure 5.7**. Similar to SL-TFC and DL#1-TFC membranes, the macroscopic morphology of DL#2-TFC membrane was featured by densely packed needle-like macrovoids with a bi-layered arrangement, which remained unchanged after the FO tests. However, visible changes in the cross-section morphology can be observed in the regions of the support layer which was lying directly beneath the polyamide selective layer. Before the FO tests, the sublayer resembled a highly porous sponge-like structure. After FO tests, the void volume in the sublayer appeared to be lower, and the apparent thickness of polyamide layer also decreased significantly. The changes in the morphology of the sublayer beneath the polyamide layer was more significant after the FO tests with 2.0 M NaCl as draw solution. It may imply that pore collapse in the sublayer have contributed to severe reduction in the FO performance of DL#2-TFC membranes.

The effect of osmosis-induced compaction on the structure of the membrane is also evident under TEM. The cross-section morphology of DL#2-TFC membrane near the polyamide layer before and after FO tests are shown in **Figure 5.8**. Before the FO tests, there were some voids in the support layer that were very close to the polyamide layer, and there was no apparent transition in porosity across the section. After the FO tests, the big pores within the support layer disappeared, and a visibly densified band appeared next to the polyamide layer, which confirmed that a serious compaction occurred around the skin layer of the TFC membrane. These observations confirmed that osmosis-induced compaction could affect the structure of TFC membrane, especially when there was significantly high osmotic pressure difference across the membrane.

Figure 5.7 SEM images of DL#2-TFC membrane before and after FO tests.

Figure 5.8 TEM images showing the cross-section morphology of DL#2-TFC membrane near the polyamide selective layer: (a) before FO test, and after 24-hours FO test carried out with either (b) 0.5 M NaCl or (c) 2.0 M NaCl as draw solution.

In addition, the characterization of DL#2-TFC membrane by AFM has revealed that the surface topography of the polyamide layer of the membrane has changed substantially after FO tests. As shown in **Figure 5.9**, the surface of the polyamide layer before FO test exhibited more spikes-like structures that spread out evenly across membrane surface, which well corresponded to the

characteristic ridge-and-valley structures observed under SEM. After FO tests using 0.5 M NaCl as draw solution, some of the protruding structure appeared to have collapsed and the surface became less uniform. After tested with 2.0 M NaCl as draw solution, the surface of polyamide layer was apparently flattened, and most of the visible structures observed in the pristine DL#2-TFC membrane were diminished. The average surface roughness (R_a) of the polyamide layer of DL#2-TFC has decreased from 299 nm to 248 nm and 96 nm after FO tests were carried out by using 0.5 M NaCl and 2.0 M NaCl as draw solutions, respectively. The substantial reduction in surface roughness may indicate that there was a substantial pressure difference across the membrane during the FO test, such that the polyamide layer was flattened under the stress exerted.

Figure 5.9 AFM images showing the surface topography of polyamide selective layer of DL#2-TFC membrane (a) before FO test, and after 24-hours FO tests carried out with either (b) 0.5 M NaCl or (c) 2.0 M NaCl as draw solution.

5.3.5 Mechanism of membrane compaction in FO process

The collapse of the pore structures beneath the polyamide layer and the smoothening of polyamide layer of DL#2-TFC membrane after FO tests confirmed membrane compaction in the FO process. This could be caused by a substantial mechanical stress imposed on the membrane despite no external hydraulic pressure applied on the membrane. In order to understand the possible mechanisms behind, the water transport across the membrane and corresponding hydrostatic pressure profile are schematically illustrated in **Figure 5.10**.

Figure 5.10 Schematic illustration of osmosis-driven compaction in forward osmosis membrane.

During the FO process, water was drawn across the polyamide selective layer of TFC membrane at a rate proportional to the osmotic pressure difference. Due to the cohesion force of water, water permeation across the support layer should occur at an equal rate as the osmosis-driven water flux to replenish the water lost into the draw solution. As the water permeates through the support layer, the hydraulic resistance of the support layer would induce pressure drop across the support layer which is proportional to the water flux [311]. Thus, there exists a steady-state pressure gradient across the support layer. The local pressure gradient could induce mechanical stress within the support layer, which may cause microscopic deformations of the pore channels such as narrowing and collapse of pores. Eventually, the deformations may obstruct water transport passages within the substrate, which leads to increased hydraulic resistance. As a result, the water flux of the TFC membrane would decrease during the FO process when operating under the AL-DS orientation.

Since SL-TFC membranes possess porous support layer with high water permeability, the resistance towards water flux through the support layer during FO may be relatively low. As such, when the osmotic water flux is low, the pressure drop across the support layer could be small. This explains the relatively minor water flux decline observed in the SL-TFC membrane during the FO tests. Nevertheless, the water flux decline of SL-TFC membrane became more significant when it is subjected to FO tests with higher osmotic pressure gradient. It shows that substantial mechanical stress could still occur within the TFC membrane that consists of a support layer with high water permeability if the osmotic water flux is sufficiently high. On the other hand, if there is a dense skin layer on the side of the support facing the feed solution, which imposes a high hydraulic resistance on the water transport across the support layer, the build-up of the mechanical stress within the TFC membrane could be more severe. The consequence would be a more significant water flux decline during the FO process, which were clearly observed on DL#1-TFC and DL#2-TFC membranes.

On the other hand, since there was no externally applied pressure in FO process, the hydrostatic pressure on both sides of the TFC membrane should be equal at around 1 atm (atmospheric pressure), as depicted in **Figure 5.10**. However, the hydrostatic pressure within the porous matrix of the support layer could vary significantly, since the lumen side of the support layer is completely segregated from the atmosphere by the polyamide layer. As the result, the pressure drop across the support layer could induce an equal hydrostatic pressure difference across the polyamide layer during the FO process. As the polyamide layer is extremely thin, the pressure gradient across the polyamide layer could be substantially higher than that across the support layer. Therefore, a significantly high stress is believed to be exerted on the polyamide layer towards the direction facing the support layer. This could explain the reduction in the thickness of the polyamide layer observed in DL#1-TFC (**Figure 5.4**) and DL#2-TFC (**Figure 5.6**) membranes, as well as the smoothening of polyamide layer of DL#2-TFC membrane (**Figure 5.8**) after the FO tests were carried out. Also, since the polyamide layer rests on the support layer, the mechanical stress exerted on the polyamide layer is also partly distributed to the support layer,

which may cause deformation of the support layer near the polyamide layer. This is also observed in DL#2-TFC membrane, where visible densification occurred around the region of the support layer that is in contact with the polyamide layer (**Figure 5.7**).

The pressure drop across the support layer of TFC membranes could also lead to occurrence of “negative pressure” within the porous matrix of the support layer during the FO process, as illustrated in **Figure 5.10**. In such situation, it is speculated that capillary pressure could maintain the continuity of water flow within the interconnected pores of the support layer. For example, from the SEM images of DL#2-TFC membrane, the pore diameter within the sponge-like structures near the skin layers on the shell side may be around 0.1 μm or less. This could translate to a capillary pressure of approximately 15 bar within the interconnected pores. It is possible that the capillary pressure may suppress the occurrence of vacuum-filled cavities within the interconnected pores, as long as the “negative pressure” created by the osmosis-driven water flux across the membrane does not exceed the capillary pressure. The water transport within these double-skinned membranes also closely resembles the water transportation system in plants, where the mechanism of water transport was explained by a cohesion-tension theory [312].

5.4. Conclusions

In this study, the deterioration of membrane performance has been observed during the FO process. TFC membranes experienced different extents of water flux decline and reverse salt flux decline after the FO test was carried out for 24 hours. It was deduced that the performance of TFC membranes was correlated to the resistance of the support layer of the membrane. As the hydraulic resistance of the support layer increased, the TFC membrane suffered a more severe water flux decline than reverse salt flux decline, which led to an increasingly more significant decrease in the selectivity of the TFC membranes.

The deterioration of FO performance was largely irreversible, which implied that the TFC membranes underwent structural changes during FO tests. Membrane

autopsies confirmed noticeable changes in the morphology of the cross-section and the surface of the polyamide layer of TFC membrane. The morphology transformation suggested that there was mechanical stress exerting on the TFC membrane during the FO tests. Based on these observations, it is deduced that osmosis-induced compaction was associated with microscopic deformation in the TFC membrane. Consequently, serious pore collapse increased the hydraulic resistance of the support layer and aggravated ICP, thus deteriorated the FO performance of TFC membranes.

The current study revealed that the properties of TFC membranes could be significantly affected by membrane compaction during FO process. Compaction of TFC membranes may be caused by a build-up of internal stress, which is associated with the hydraulic resistance of the membrane support layer and the rate of water permeation driven by osmosis. The observations also indicate that certain membrane structures (especially double-skinned membranes) may be more susceptible towards osmosis-induced compaction, which could lead to severe deterioration of FO performance. As such, it is suggested that FO experiments with longer testing duration should be applied to ensure that stabilized performance of the FO membranes can be acquired. Also, in analogy to the common practice on pre-compaction of RO membranes under high pressure, FO membranes may be pre-compacted by operating the membrane with draw solution of higher concentration for a short period of time to accelerate the compaction process and achieve stabilized performance with draw solution of low concentration thereafter.

Chapter 6 Conclusions and prospects

6.1. Conclusions

In this thesis, TFC hollow fiber membranes with high FO performance have been fabricated and characterized under various testing conditions to study the influence of the support layer characteristics on the performance of TFC hollow fiber membranes in FO process.

In Chapter 3, inner-selective TFC hollow fiber membranes that exhibit high water flux and low reverse salt flux have been fabricated successfully via phase inversion and IP technique. The influence of dope composition used for fabrication of hollow fiber substrates on the characteristics of the substrates and TFC hollow fiber membranes prepared from the substrates were briefly investigated. The conclusions are as follows,

1. When using high concentration of PEG (40 wt%) as pore-forming additive in dope, further increasing the concentration of PEG in the dope led to formation of hollow fiber substrate with greater pore size but did not affect its water permeability.
2. There was no clear correlation between the characteristics of the hollow fiber substrates and the intrinsic separation properties of TFC hollow fiber membranes. However, TFC membrane prepared from hollow fiber substrate which was fabricated from dope with highest viscosity has the highest water permeability coefficient and lowest solute permeability coefficient.
3. Both increasing the proportion of PEG and solvent in dope led to a reduction in structural parameter of the TFC membrane. Substrates spun from dope with lower PEG/NMP ratio give rise to lower structural parameter.
4. Decreasing bore fluid flow rate during the fabrication of hollow fiber substrate was found to have a negative impact on the intrinsic separation properties of TFC hollow fiber membrane and increasing the structural parameter of the membrane.

5. Higher dope viscosity and higher bore fluid flow rate may promote the formation of denser skin layer on the inner surface of the substrate, which may promote the formation of polyamide selective layer with high water permeability and high salt rejection.
6. Excessively high PEG concentration in dope and high dope viscosity may slow down phase separation and increase the tortuosity of the substrate, thus increases the structural parameter of the TFC membrane.

In Chapter 4, after optimizing the substrate, a novel double-skinned hollow fiber TFC FO membrane has been fabricated in two-step. A dual-layer PES substrate with dense outer layer was fabricated first, followed by the preparation of the inner-selective layer via interfacial polymerization. The conclusions are as follows,

1. The membrane exhibited better performance in concentrating humic acid and activated sludge in the AL-DS orientation as compared to most of the commercial membranes and some self-prepared membranes reported so far.
2. The tight UF-like outer layer had proven to reject greater-sized molecules. It could reduce the accumulations of biopolymers, humic acids, and building blocks inside the FO membranes in the sludge thickening processes. This helped to suppress irreversible organic fouling of the membranes.

In Chapter 5, to understand the long-term performance stability of the double-skinned FO membranes, three TFC hollow fiber membranes were fabricated and a series of experiments were carried to investigate the causes of the deterioration of membrane performance. It was found that TFC hollow fiber membranes experience membrane compaction which led to different extent of flux decline during FO process. The conclusions are as follows,

1. The deterioration of membrane performance was correlated to the resistance of the support layer of the membrane. As the hydraulic resistance of the support layer increased, the TFC membrane suffered more severe water flux decline than reverse salt flux decline, which led to increasingly more significant decrease in the selectivity of the TFC

membranes. The deterioration of FO performance was largely irreversible, which implied that the TFC membranes had undergone structural changes during FO tests.

2. Membrane autopsies confirmed noticeable changes in the morphology of the cross-section and the surface of the polyamide layer of TFC membrane. The morphology transformation suggested that there was mechanical stress exerting on the TFC membrane during FO test and implied that the deterioration of membrane performance was associated with microscopic deformation in the TFC membrane.
3. The properties of TFC membranes could be significantly affected by membrane compaction during FO process. Compaction of TFC membranes may be caused by a build-up of internal stress, which is associated with the hydraulic resistance of the membrane support layer and the rate of water permeation driven by osmosis.
4. Certain membrane structures (especially double-skinned membranes) may be more susceptible toward osmosis-induced compaction, which could lead to severe deterioration of FO performance.
5. FO experiments with longer testing duration should be applied to ensure that stabilized performance of the FO membranes can be acquired. Also, in analogy to the common practice on pre-compaction of RO membranes under high pressure, FO membranes ought to be pre-compacted by operating the membrane with draw solution of higher concentration for a short period of time to accelerate the compaction process and achieve stabilized performance with draw solution of low concentration afterwards.

6.2. Prospects and recommendations

6.2.1. Permeability or selectivity?

Development of asymmetric membranes with high water permeability, low solute permeability, low structural parameter and high fouling resistance has been one of the main goals of research in FO process. Among various type of developed membrane materials currently available, polyamide TFC membrane

exhibits the greatest potential for FO process as most of the desirable characteristics as mentioned above can be achieved by tuning the fabrication conditions at different stages of the fabrication process. FO TFC membranes developed over the past few years has achieved substantially higher water flux and comparable reverse solute flux as compared to the commercial membranes (**Figure 7.1a, b**) [313]. Nevertheless, the development of high-performance TFC membranes is limited by the permeability-selectivity trade-off relationship [314]. As shown in **Figure 6.1c**, the specific reverse solute flux of the newly fabricated FO membranes reported in recent years falls in the same range as the commercial membranes. The results imply that there has not been a significant consistent improvement in the selectivity of FO membranes.

Figure 6.1 The average (a) water flux and (b) reverse solute flux of commercial CTA, commercial TFC, and new TFC membrane reported in the literature (draw solution: 1 M NaCl), and (c) specific reverse solute flux (SRSF) reported in the literature (where NaCl was used as the DS). Adapted from a review by Zou et al. [313]

Although higher water flux may be obtained by increasing the water permeability of the membrane, the sacrifice on the selectivity could aggravate reverse solute diffusion and result in a poorer utilization of osmotic pressure gradient when employing low molecular weight draw solutes. Adopting draw solutes with higher molecular weight could be an alternative solution, but these solutes may afford lower osmotic pressure. Furthermore, ICP may have more severe impact on the membrane performances due to lower diffusivity and higher solution viscosity of high molecular weight draw solutes. In addition, simple dissolved inorganic and thermolytic salts remain the preferred draw solutes when dealing with high salinity feed, as they could generate sufficiently high osmotic pressure to [29].

Highly selective FO membranes is also required to ensure that low molecular weight species in feed solution can be well retained by the membrane. In closed-loop processes (such as FO-RO and FO-MD), the compounds from feed solution that pass through the membrane may accumulate in the draw solution and affect the quality of product water [315]. Therefore, the development of next generation FO membranes should prioritize on the selectivity of membrane. Also, the structural parameter of the membranes should be further reduced to suppress ICP and enable the membranes to utilize a greater portion of osmotic pressure gradient across the membranes, which could compensate for water flux reduction incurred by a lower water permeability of highly selective FO membrane.

6.2.2. Further optimization of double-skinned membranes

While FO may perform better than RO in treating impaired feed streams with high fouling tendency, membrane fouling remains the main cause of FO membrane deterioration in long-term operation. As demonstrated in Chapter 4, double-skinned FO membranes exhibited reversible membrane fouling in FO when dealing with feed solution containing macromolecular organic foulants. However, low molecular weight organic foulants and scaling precursors could easily penetrate the tight-UF like selective layer of the double-skinned membrane developed in this work and resulted in significant membrane fouling. Therefore, the selectivity of secondary selective layer needs to be improved to the NF range to effectively reject these foulants. Yet, increasing the selectivity

of the secondary selective layer could lead to a reduction in its water permeability. Apart from increasing the overall resistance of the membrane, a secondary selective layer with low water permeability could induce membrane compaction during the FO process, as demonstrated in Chapter 5 of this thesis. Therefore, further optimization of the double-skinned membranes should focus on identifying the trade-off relationship between permeability and selectivity of the secondary selective layer.

Although developing secondary selective layer by phase inversion process with the aid of coextrusion technique is a facile and scalable option, it could be extremely challenging to obtain a highly selective secondary selective layer with modest water permeability due to the stochastic nature of the phase inversion process. Nevertheless, it is speculated that blending nanofillers with well-defined micropores (such as MOF [316] and covalent organic frameworks (COF) [317]) into the secondary selective layer during phase inversion process could be a potential solution to improve water permeability while achieving the desired selectivity.

On the other hand, severe external fouling could occur in the FO process when the feed solution contains high concentration of suspended solids, which lead to a rapid formation of dense cake layer that is capable of causing substantial water flux reduction. Although the cake layer can be detached by increasing shear force through periodic flushing with water, higher membrane-foulant interaction could cause the cake layer to attach strongly to the membrane, which required higher cleaning frequency and intensity. As such, the hydrophilicity of the secondary selective layer should be increased to weaken the adhesion of foulant layer on membrane surface. The hydrophilicity of secondary selective layer may be improved by partially substituting the material of the secondary selective layer with hydrophilic polymers (such as SPES [318, 319], sPPSU [158, 161], SPSf [154]), blending hydrophilic nanofillers [293] (such as graphene oxide [320-322], zeolites [163, 323], TiO₂ [166, 194] and SiO₂ [260]) into the secondary selective layer, or modifying the surface of secondary selective layer with polydopamine [324-326] and other hydrophilic materials [327, 328]. The effect of these strategies on the perm-selective properties of the secondary selective layer should be investigated as well.

The impact of ICP on the performance of double-skinned membrane cannot be neglected as well. As DICP is eliminated when double-skinned membrane operating with the high selectivity (primary) selective layer facing the draw solution, the extent of ICP is expected to be less significant than single-skinned membrane operated in AL-FS orientation in most situations. Still, the extent of ICP in double-skinned membrane is proportional to the relative resistance of the secondary selective layer as compared to the primary selective layer [276]. As such, it was proposed that the permselective properties of the secondary skin layer should resemble low rejection NF membranes, which could prevent the infiltration of foulants into the support layer while retaining sufficiently high water permeability [276]. Alternatively, it is proposed to couple double-skinned membranes (which possess the mentioned perm-selective properties) with the use of large-size draw solutes that can be well rejected by the less selective skin layer of the membrane (such as ethylenediaminetetraacetic acid (EDTA) [271, 329, 330], polyacrylic acid sodium salts (PAA-Na) [331], poly (aspartic acid sodium salt) (PAspNa) [332], poly (sodium 4-styrenesulfonate) (PSS) [333] and polydiallyldimethylammonium chloride (PolyDADMAC) [334]). As such, it enables the operation of FO process with the less selective skin layer of the membrane facing the draw solution, which could significantly suppress ICP. Meanwhile, the skin layer with higher selectivity will be in direct contact with the feed solution, which enables the membrane to reject low molecular weight compounds in the feed solution and prevent the inter-contamination of draw and feed solutions. Nevertheless, the characteristics of the draw solute such as water solubility, achievable osmotic pressure, toxicity and the effective techniques for draw solute recovery have to be assessed in order to evaluate the feasibility of such strategy.

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