

**NANYANG**  
**TECHNOLOGICAL**  
**UNIVERSITY**

**DEVELOPMENT OF NOVEL COMPOSITE  
NANOFILTRATION HOLLOW FIBER MEMBRANES  
FOR NICHE APPLICATIONS**

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**SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING**

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NANOFILTRATION HOLLOW FIBER MEMBRANES  
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# ABSTRACT

Due to its unique ability to separate divalent and multivalent ions as well as low molecular weight organic species, nanofiltration (NF) has now become a widely applied separation technology. However, it is still challenging to develop NF membranes which could achieve competent permeation flux at ultrafiltration (UF)-range low operating pressure in order to reduce energy consumption and membrane fouling tendency. The objectives of this research were to develop novel composite NF hollow fiber membranes with UF-range low operating pressure, and to tailor the membrane properties for various niche applications. Specifically, this thesis presents the development of novel composite hollow fiber membranes with NF-like selectivity at operating pressure no greater than 2 bar, and appropriate surface properties and structures for applications including water softening and forward osmosis (FO) processes. Three different techniques including interfacial polymerization (IP), surface modification, and layer-by-layer (LBL) assembly were employed for the formation of NF-like selective layer.

Composite NF hollow fiber membranes desirable for water softening under UF-range low operating pressure have been successfully developed. The positively charged thin-film selective layer was formed through IP reaction on the inner surface of a polyethersulfone (PES) hollow fiber substrate with branched polyethylenimine (PEI) and trimesoyl chloride (TMC) employed as the two IP monomers. It is found that a proper molecular weight of PEI and the presence of sodium dodecyl sulfate (SDS) in the aqueous phase are important for a successful interfacial polymerization reaction. It is revealed that the PEI-TMC polymerized thin layer exhibits a combined separation mechanism of the Donnan exclusion and steric hindrance. It possesses pure water permeability (PWP) of about 17 l/m<sup>2</sup> h bar and a molecular weight cut-off (MWCO) of around 500 Da with MgCl<sub>2</sub> and MgSO<sub>4</sub> rejections of 96.7% and 80.6%, respectively, when tested for a feed solution containing 1000 ppm salt at 2 bar operating pressure. Additionally, for a 3000 ppm

total dissolved salt (TDS) feed stream containing salt mixtures, the membrane rejections for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions were found to be around 90% while the water flux was about  $20 \text{ l/m}^2 \text{ h}$  at 2 bar pressure, suggesting its potential for effective water softening application.

However, the above mentioned membrane experienced a substantial decrease in rejection to hard water metal ions when the feed solution contained divalent counterions such as  $\text{SO}_4^{2-}$ . To improve the situation, the IP thin film formation process was ameliorated to strengthen its capability for low-pressure softening of more concentrated and complex water sources. A mixture of PEI and piperazine (PIP) was employed as the monomers in the aqueous phase, and it was found that there was a synergetic effect of PEI and PIP on the formation of the selective layer. The water permeability and salt rejection of the resultant membrane were both enhanced with a small amount of PIP added into the PEI aqueous phase, but dropped quickly with a higher PIP to PEI ratio. The mixed PEI/PIP-based composite NF membrane possessed a tighter MWCO of 380 Da, and a higher PWP of  $18.2 \text{ l/m}^2 \text{ h bar}$ . Under an operating pressure of 2 bar, it exhibited rejection of 96.3% and 93.8% to 1000 ppm  $\text{MgCl}_2$  and  $\text{MgSO}_4$  feed solutions, respectively. This membrane demonstrates better water softening performance compared with the membranes made with PEI or PIP alone as the aqueous phase IP monomer, and is able to soften more concentrated and complex water sources.

On the other hand, novel thin-film composite FO hollow fiber membranes with an NF-like secondary selective skin were successfully developed for the first time. The fabrication procedures involved making UF hollow fiber substrate using polyamide-imide (PAI) polymer material via phase inversion method, followed by IP and surface modification on the inner and outer surfaces of the substrate to yield a polyamide RO-like inner skin layer and a positively charged NF-like outer skin layer, respectively. It was discovered that the preparation route was critical for obtaining high performance double skinned FO membranes. The sequence of conducting IP on the substrate inner surface prior to the chemical cross-linking of the outer skin was preferred in order to achieve better performance for the resultant

double-skinned hollow fibers. The double-skinned FO hollow fibers exhibited high water permeability of  $2.05 \text{ l/m}^2 \text{ h bar}$  and 85% rejection to NaCl at 1 bar pressure. It also presented superior FO water flux of  $41.3 \text{ l/m}^2 \text{ h}$  and a low ratio of salt flux over water flux of 0.126 g/L when using DI water and 2.0 M NaCl as feed and draw solutions, respectively, in the active layer facing draw solution (AL-DS) of membrane orientation. The double-skinned membrane was found to outperform single-skinned membrane when the feed contains divalent ions or the feed exhibits high scaling tendency to membrane. It suggested that the incorporation of NF-like secondary selective layer is an effective way to minimize the internal concentration polarization (ICP) effect, mitigate the membrane scaling and thus enhance the feasibility of FO processes for practical applications.

In addition, LBL assembly method was involved for the formation of NF-like secondary layer to substitute the chemical cross-linking method, and double-skinned hollow fiber membranes with further improved water permeability, salt rejection and FO performance were therefore developed. The resultant double-skinned hollow fiber membrane exhibited exciting organic fouling resistance because of its highly hydrophilic LBL NF-like secondary layer with minimal surface charge and tightened surface structure to mitigate possible substrate pore clogging and fouling layer formation. A stable water flux of around  $25 \text{ l/m}^2 \text{ h}$  was attained for DS#2.5 membrane using  $<0.5 \text{ M NaCl}$  as the draw solution and a water containing 200 ppm dextran (DEX) or Aldrich humic acid (AHA), or lysozyme (LYS) and 10 mM NaCl as the model feed in AL-DS membrane orientation, suggesting its capability for a wide range of practical FO applications.

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# LIST OF SYMBOLS

|                      |                                                                                                 |
|----------------------|-------------------------------------------------------------------------------------------------|
| $A, A_{out}, A_{in}$ | water permeability coefficient ( $\text{l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ )            |
| $A'_{out}$           | normalized water permeability coefficient ( $\text{l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ) |
| $B, B_{out}, B_{in}$ | NaCl salt permeability coefficient ( $\text{l m}^{-2} \text{ h}^{-1}$ )                         |
| $B'_{out}$           | normalized NaCl salt permeability coefficient ( $\text{l m}^{-2} \text{ h}^{-1}$ )              |
| $c$                  | solute concentration, $\text{mol l}^{-1}$                                                       |
| $C_f$                | concentration in feed, ppm                                                                      |
| $c_i$                | solute concentration in the membrane, $\text{mol m}^{-3}$                                       |
| $C_i$                | solute concentration in the bulk solution, $\text{mol m}^{-3}$                                  |
| $C_p$                | concentration in permeate, ppm                                                                  |
| $D_i$                | bulk diffusivity, $\text{m}^2 \text{ s}^{-1}$                                                   |
| $F$                  | Faraday's constant, $\text{C mol}^{-1}$                                                         |
| $J_i$                | solute flux, $\text{mol m}^2 \text{ s}^{-1}$                                                    |
| $J_s$                | solute flux, $\text{mol m}^2 \text{ s}^{-1}$                                                    |
| $J_v$                | volumetric flux, $\text{m s}^{-1}$                                                              |
| $K_{i,c}$            | steric hindrance factor for convection                                                          |
| $K_{i,d}$            | steric hindrance factor for diffusion                                                           |
| $L_p$                | solvent permeability, $\text{l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$                         |
| $L_s$                | solute permeability, $\text{m s}^{-1}$                                                          |
| $M_w$                | molecular weight of the solute, Da                                                              |
| $Q$                  | volumetric permeation flow rate, $\text{l h}^{-1}$                                              |
| $R$                  | ideal gas constant, $\text{J mol}^{-1} \text{ K}^{-1}$                                          |
| $R_a$                | surface roughness, nm                                                                           |
| $r_s$                | Stocks radius of a neutral solute molecule, nm                                                  |

|                 |                                                                   |
|-----------------|-------------------------------------------------------------------|
| $R_s$           | solute rejection, %                                               |
| $T$             | absolute temperature, K                                           |
| $V$             | solute velocity, m s <sup>-1</sup>                                |
| $X_m$           | effective volumetric membrane charge density, mol m <sup>-3</sup> |
| $z_i$           | valence of the solute                                             |
| $\Delta P$      | Hydraulic pressure difference, bar                                |
| $\Delta x$      | membrane thickness, m                                             |
| $\Delta \pi$    | osmotic pressure difference, bar                                  |
| $\Delta \psi_D$ | Donnan potential, V                                               |
| $\lambda$       | ratio of solute radius to effective pore radius                   |
| $\sigma$        | reflection coefficient                                            |
| $\Phi$          | steric partitioning factor                                        |
| $\psi$          | electric potential in axial direction, V                          |



# **CHAPTER 1**

## **Introduction**

### **1.1 Background**

#### **1.1.1 Membrane separation technology**

Since the first anisotropic reverse osmosis (RO) membrane was developed by Loeb and Sourirajan via phase inversion method using cellulose acetate in early 1960s (Loeb and Sourirajan 1963), membrane separation technology has drawn increasing attention in water industry including domestic and industrial water and wastewater treatment, seawater and brackish water desalination. Membrane separation has also been widely utilized in a variety of applications in chemical, pharmaceutical and food industry as well as energy conversion and storage systems. Comparing to conventional separation processes, membrane separation is able to operate without heating or addition of hazardous chemicals, and therefore provides the benefits including reduced chemical and energy consumption, preservation of thermal- or chemical-sensitive compounds, and lower environmental impact with increased operation safety (Mulder 1996).

Generally, a membrane is a selective barrier for separation with the input of energy, which serves as a driving force to separate a mixture. Typical driving forces for membrane separation include differences in pressure, concentration, thermal gradient and electrical potential across the membrane, and pressure-driven

membrane filtration processes are usually categorized according to the membrane pore sizes, which prescribe the size of the particles they are able to retain. Microfiltration (MF) and ultrafiltration (UF) membranes are commonly referred as porous membranes, since they possess pore sizes larger than 10 nm (Mulder 1996). In contrast, nanofiltration (NF) and RO membranes exhibit smaller pore sizes than UF and MF membranes and are usually considered non-porous membranes. Porous membranes function under low operating pressure during the MF and UF processes, however much higher pressure is required for NF and RO membranes in order to overcome the transport resistance provided by the tightened membrane pore size in addition to the osmotic pressure generated by the salt in the feed stream. General properties including pore size, operating pressure, etc. for the four types of pressure-driven membranes are presented in Table 1.1.

Table 1.1 Properties of membranes for pressure-driven processes (Mulder 1996; Schäfer, Fane *et al.* 2002).

| Membrane | Separation mechanism                    | Pore size            | Operating pressure | Removes                                      |
|----------|-----------------------------------------|----------------------|--------------------|----------------------------------------------|
| MF       | Size exclusion                          | 0.1-10 $\mu\text{m}$ | <2 bar             | Suspended solids/<br>bacteria                |
| UF       | Size exclusion                          | 10-100 nm            | 1-5 bar            | Macromolecules/<br>viruses                   |
| NF       | Size exclusion/<br>electrical exclusion | 0.5-2 nm             | 5-20 bar           | Multivalent ions/<br>natural organic matters |
| RO       | Solution-diffusion                      | <0.5 nm              | 10-100 bar         | Monovalent ions/<br>small organics           |

### 1.1.2 Nanofiltration: applications and challenges

Nanofiltration is a pressure-driven membrane separation process between ultrafiltration and reverse osmosis. The history of nanofiltration membranes can be traced back to the 1970s when RO membranes with higher water and solute permeation but relatively lower operating pressure were commercially available. The terms like “loose RO”, “selective RO” or “hybrid RO-UF” have been used to describe the process until FilmTec adopted the term “nanofiltration” in the 1980s

according to the typical pore size of 0.5 to 2.0 nm for NF membranes (Schäfer, Fane *et al.* 2002). Comparing to UF and RO membranes, NF membranes have several unique features: (1) relatively lower rejection (<90%) to NaCl and other monovalent ions, but very high rejection to divalent and multivalent ions; (2) rejection to uncharged solutes depends mostly on the solute molecular size and shape, while the membrane molecular weight cut-off (MWCO) usually ranges from about 100 to 1000 Da; (3) operation under pressure of 5 to 20 bar, which is lower than that for RO membranes but higher than that for UF membranes. In addition, NF membranes are generally negatively or positively charged so that the separation mechanisms of NF membranes involve both steric (size exclusion) and electrostatic (Donnan exclusion) effects.

Due to its unique ability to separate divalent and multivalent ions as well as low molecular weight organic species, the application of NF membranes has grown rapidly in the last few decades. The installed capacity of NF membranes in year 2000 was 10 times higher than in 1990, and NF-related research publications increased 400% from 1996 to 2006 (Li, Fane *et al.* 2008). At present, NF has become an important separation and purification technique not only in the field of water and wastewater treatment, but also in food, pharmaceutical, biomedical, petrochemical and other industries (Schäfer, Fane *et al.* 2002). In water industry, NF membranes has been widely applied in surface and groundwater softening (Duran and Dunkelberger 1995), pretreatment for desalination (Hilal, Al-Zoubi *et al.* 2004), removal of heavy metal (Favre-Reguillon, Lebuzit *et al.* 2008) and natural organic matters (Alborzfar, Jonsson *et al.* 1998). Membranes with an NF-like selective layer are also efficient in forward osmosis (FO) and pressure retarded osmosis (PRO) applications with divalent ions or organic macromolecules involved in the processes, which provide an alternative to conventional RO-type FO membranes (Yang, Wang *et al.* 2009; Setiawan, Wang *et al.* 2011).

Although nanofiltration has been implemented in a wide range of applications, it is expected that the evolution in NF will continue by solving problems that hinder the further development of NF technology. Challenges for nanofiltration at the current

stage include membrane fouling prediction and control, further treatment of concentrates, selective separation between different solutes, precise control of membrane pore size, chemical resistance (especially chlorine resistance for polyamide membranes) and limited lifetime of membranes, possibility in hollow fiber configuration, and the need for modeling and simulation tools to better understand the NF process, etc. (Li, Fane *et al.* 2008; Van der Bruggen, Manttari *et al.* 2008). Basically, the progress in membrane preparation is crucial to overcome those obstacles in the advancement of nanofiltration. Development of NF membranes with improved separation properties, chemical tolerance and fouling resistance has become and will always be the core issue of NF research globally.

Furthermore, even though the required trans-membrane pressure for NF membranes can be reduced comparing with RO process, the operating pressure for conventional NF membranes is still relatively high in order to create productive permeation flux. For niche applications like juice concentration in food industry and the treatment of certain pharmaceutical products, a high hydraulic pressure may break the concentrated organic molecules which are intended to be retained (Jiao, Cassano *et al.* 2004; Sun, Hatton *et al.* 2012). For other purification applications such as water softening, it is also challenging to develop such NF membranes which could achieve capable permeation flux at UF-range low operating pressure so as to reduce energy consumption and membrane fouling tendency.

### **1.1.3 Fabrication of nanofiltration membranes**

Two types of NF membranes are fabricated nowadays. Integral asymmetric NF membranes are generally prepared via phase inversion method using cellulose acetate, polysulfone, or other polymeric membrane materials (Mulder 1996; Schäfer, Fane *et al.* 2002). This type of one-step forming membranes carries the obvious advantages of easy fabrication and great mass production feasibility. However, since the whole membrane is made with the same material via a single-step formation, there is a limitation on the solute selectivity and water permeation that can be achieved by an integral asymmetric NF membrane simultaneously. In contrast, a

composite NF membrane is composed of a dense selective skin layer and a porous mechanical support layer, both of which are made separately via a two-step fabrication process. The main advantage of composite NF membranes over integral NF membranes is that the materials and properties of the two layers can be controlled and optimized individually during each step to achieve better overall separation properties for the final resulting membrane.

The support layer of the composite NF membrane is usually UF-like membranes made via phase inversion method, while the selective skin layer can be prepared by a variety of approaches. For instance, interfacial polymerization yields a highly controllable ultra-thin dense film, and is the most widely used and commercially systemized method for the formation of NF and RO selective skin layer (Petersen 1993). Besides, surface modification is also applied as a highly feasible technique to alter the surface pore size of RO and UF membranes towards NF-range, as the modification usually involves only a one-step chemical treatment (Schäfer, Fane *et al.* 2002). More recently, layer-by-layer assembly has been considered as an attractive technique for preparation of NF-like ultra-thin dense layers with highly tunable separation properties without the involvement of organic solvent or harsh treatment conditions (Hong, Miller *et al.* 2006). In addition, many other approaches like polymer solution dip-coating, gas phase plasma deposition, etc. have also been reported as the fabrication method for composite NF membranes, but their applications are limited mainly due to the fact that those approaches are likely to cause damage on the polymeric substrate layer (Van der Bruggen, Manttari *et al.* 2008).

In terms of module types, currently, most of NF membranes are flat-sheet membranes in the spiral wound configuration. Comparing to flat sheet membranes, hollow fiber membranes can provide better packing density, higher surface area to volume ratio and self-support capability as well as cost-effective large-scale production and operation (Futselaar, Schonewille *et al.* 2002). However, the application of NF hollow fiber membranes is still limited owing to the fact that the standard hollow fiber spinning process only produces integral asymmetric NF

hollow fibers with unsatisfactory water permeability and solute selectivity (Baker 2004; Wang, Chung *et al.* 2007). Due to the merit of composite NF membranes, more research inputs are urged to explore different approaches for the fabrication of composite NF hollow fibers for different application scenarios.

## **1.2 Objectives and scope**

The objectives of the research are to develop novel composite hollow fiber membranes with NF-like selectivity at low operating pressure, and to tailor the membrane structure and properties for various niche applications such as water softening and forward osmosis.

Specifically, the following tasks are intended to be carried out during the PhD study:

1. Prepare and characterize interfacially polymerized (IP) composite NF hollow fiber membranes with high permeation flux and high rejection of divalent metal ions at UF-range low operating pressures for water softening application.
2. Modify the IP thin film formation process of composite NF hollow fiber membranes to achieve improved rejection profile and strengthened capability for low-pressure softening of more concentrated and complex water sources.
3. Incorporate an NF-like secondary selective layer into the thin-film composite hollow fiber membrane via surface modification method to yield a double-skinned membrane for mitigating internal concentration polarization and scale formation in the FO processes.
4. Ameliorate the membrane preparation by forming a layer-by-layer assembled NF-like secondary skin layer to develop double-skinned hollow fibers with enhanced water permeation and organic fouling resistance, which is more competent in practical FO applications.

### 1.3 Thesis outline

Seven chapters are presented in this thesis, which are outlined as follows:

Chapter 1 provides background information regarding membrane separation technology, the major applications and challenges of nanofiltration. Research objectives and scope are presented in the chapter as well.

Chapter 2, as a literature review chapter, starts with a review of the nanofiltration separation mechanism, which basically involves steric hindrance and Donnan exclusion. This is followed by the review of composite NF membrane development. The fundamentals and recent progress for three membrane preparation methods including interfacial polymerization, layer-by-layer assembly and surface modification are reviewed correspondingly. The last part of the chapter discusses the general and specific membrane design criteria for the development of NF membranes with respect to niche applications like water softening and forward osmosis.

Chapter 3 presents the development of composite NF hollow fiber membranes with positive surface charges for low-pressure water softening application. The positively charged thin-film selective layer was formed through interfacial polymerization (IP) on the inner surface of a PES hollow fiber substrate with PEI and TMC employed as the two IP monomers. Results for membrane characterization and NF separation experiments operated under operating pressure as low as 2 bar with feed solutions containing various neutral solutes, inorganic salts and salt mixtures, are presented in the chapter.

Chapter 4 explores the modification of IP process to produce composite NF hollow fiber with improved rejection profile and strengthened capability for low-pressure softening of more concentrated and complex water sources. A mixture of PEI and PIP was employed as the monomers in the aqueous phase, and the influence of the aqueous co-monomer solution composition on the formation of IP thin film

selective layer was studied. Water softening capability of the resultant membrane was testified by simulated hard water feed solutions with different ionic compositions and total hardness under UF-range low operating pressure.

Chapter 5 investigates the incorporation of an NF-like secondary selective skin layer into the thin-film composite hollow fibers to yield a double-skinned membrane for mitigation of internal concentration polarization and scaling in the FO processes. The NF-like layer was prepared by modifying the outer surface of the PAI hollow fiber substrate via chemical cross-linking. The FO performance of the double-skinned membrane was examined by feed solutions containing divalent ions or exhibiting high scaling tendency to membrane.

Chapter 6 demonstrates a refined approach to integrate the NF-like secondary layer by introducing a layer-by-layer (LBL) assembled NF-like layer to avoid the modification of the support layer. The effect of the number of LBL assembled layers on the separation properties and surface characteristics of the NF-like skin layer was measured, while FO fouling tests were conducted on the resultant double-skinned fibers with three different organic foulant species so that the proficiency of the NF-like secondary layer on organic fouling mitigation was thoroughly evaluated.

Chapter 7 summarizes the important findings of the research, and provides recommendations for future work.

## CHAPTER 2

### Literature Review

#### 2.1 Nanofiltration separation mechanism

Nanofiltration is a pressure-driven membrane separation process between UF and RO, while neither the convective pore flow mechanism for UF nor the solution-diffusion mechanism for RO can fully describe the solute transport across the NF membrane. Unlike RO and UF membranes, the surface charge of the NF membrane plays an important role for the separation of charged solutes. Moreover, other properties of the solute like hydrophobicity, molecular shape and dipole moment, etc., may also influence the separation process (Li, Fane *et al.* 2008). As a result, the nanofiltration separation mechanisms involve at least pore-sieving, solution-diffusion and electrostatic interactions, and it is difficult to find a simple and universal mathematical model to thoroughly describe the solute transport in NF process.

##### 2.1.1 The extended Nernst-Planck equation

The extended Nernst-Planck equation is recognized as the basis for the description of the transport of charged and uncharged solute through the NF membranes with steric hindrance and electrostatic exclusion (Bowen, Mohammad *et al.* 1997; Schaep, Vandecasteele *et al.* 2001). The equation can be written as:

$$J_i = -K_{i,d}D_i \frac{dc_i}{dx} - \frac{z_i c_i K_{i,d} D_i}{RT} F \frac{d\psi}{dx} + K_{i,c} c_i V \quad (2.1)$$

with  $J_i$  the flux of solute  $i$ ,  $K_{i,d}$  the membrane steric hindrance factor for diffusion,  $D_i$  the bulk diffusivity,  $c_i$  the solute concentration in the membrane,  $z_i$  the valence of the solute,  $F$  Faraday's constant,  $R$  the ideal gas constant,  $T$  the absolute temperature,  $\psi$  the electric potential in axial direction,  $K_{i,c}$  the membrane steric hindrance factor for convection and  $V$  the solute velocity.

Although applying the equation is difficult due to the complexity to solve the equation mathematically, a qualitative indication of the solute transport process can be given by this universal equation. Basically, the three terms in the equation represent the solute transport due to diffusion, electric field gradient (Donnan potential) and convection, respectively. Since the two steric hindrance factors,  $K_{i,d}$  and  $K_{i,c}$ , are related to the ratio of solute size to membrane pore size (Bowen, Mohammad *et al.* 1997), smaller membrane pores can reduce the solute flux via diffusion and convection. Moreover, for ionic solutes, a strong electrical field created by the charged membrane can reduce the flux of solute with the same charge as the membrane.

### 2.1.2 Separation of uncharged solutes

For uncharged solutes where the transport of the solute is not influenced by electrostatic interactions, it is generally accepted that only the diffusive and convective flows affect the solute transport across the NF membrane. Therefore, the term for electric field gradient in the extended Nernst-Planck equation can be omitted and only the terms for diffusion and convection are left. A simplified phenomenological transport model is developed in the case by adopting irreversible thermodynamics. For a single solute feed solution, the volumetric flux ( $J_v$ ) and solute flux ( $J_s$ ) can be expressed as follows (Spiegler and Kedem 1966):

$$J_v = L_p(\Delta P - \sigma \cdot \Delta \pi) \quad (2.2)$$

$$J_s = L_s \Delta x \frac{dc}{dx} + (1 - \sigma) J_v c \quad (2.3)$$

where  $L_p$  and  $L_s$  are permeability of the solvent and solute,  $\Delta P$  and  $\Delta\pi$  are hydraulic and osmotic pressure difference across the membrane thickness  $\Delta x$ , and  $c$  is the solute concentration.  $\sigma$  is the reflection coefficient which represents the maximum rejection that the membrane can get for the solute at infinite high volumetric flux. With  $0 < \sigma < 1$ , larger  $\sigma$  indicates that lower portion of solute is transporting through convective flow and the membrane behaves more like RO membranes.

### 2.1.3 Separation of charged solutes

The separation of charged molecules i.e. ions by the NF membrane is contributed by Donnan exclusion (electrical effect) in addition to steric hindrance (size effect). According to the Donnan principle (Yaroshchuk 2001), in a charged membrane in contact with an electrolyte solution, ions with the same charge as the membrane (co-ions) will possess a lower concentration in the membrane than that in solution, whereas the ions with the opposite charge (counter-ions) have a concentration higher in the membrane than in the solution. The concentration difference of the ions generates a potential difference (Donnan potential) at the interface between the membrane and the solution to maintain electrochemical equilibrium between solution and membrane. The diffusion of co-ions into the membrane is therefore obstructed due to the Donnan potential, and counter-ions are also retained in the bulk solution to keep the electroneutrality of the electrolyte solution.

The conditions of electroneutrality in the bulk solution (feed or permeate) and inside the NF membranes are expressed respectively as:

$$\sum_{i=1}^n z_i C_i = 0 \quad (2.4)$$

$$\sum_{i=1}^n z_i c_i + X_m = 0 \quad (2.5)$$

with  $X_m$  the effective volumetric membrane charge density,  $z_i$  the valence of ion  $i$ , and  $c_i$  and  $C_i$  the concentration of the ion in the membrane and the bulk solution, respectively.

The Donnan equilibrium for ion  $i$  at the interface between the membrane and external solution can be written as (Peeters, Boom *et al.* 1998):

$$\frac{c_i}{C_i} = \exp\left(-\frac{z_i F}{RT} \Delta\psi_D\right) \quad (2.6)$$

where  $\Delta\psi_D$  is the Donnan potential i.e. the electrical potential difference between the electrical potential in the membrane and that in the bulk solution.

For a solution containing counter-ion A and co-ion B, the Donnan potential can be written as:

$$\Delta\psi_D = \frac{RT}{z_A F} \ln \frac{C_A}{c_A} = \frac{RT}{z_B F} \ln \frac{C_B}{c_B} \quad (2.7)$$

Combination of Eq. (2.7) with the conditions of electroneutrality gives the distribution of co-ion B in the membrane and external solution:

$$\frac{c_B}{C_B} = \left( \frac{|z_B| C_B}{|z_B| c_B + |X_m|} \right)^{\left| \frac{z_B}{z_A} \right|} \quad (2.8)$$

which reveals that the Donnan equilibrium is dependent on factors including ionic concentration of the solutes, effective charge density of the membrane and valence of co- and counter-ions.

However, the Donnan equilibrium does not consider the steric effect of the NF membrane i.e. influence of diffusion and convection to the solute transport. By combining the extended Nernst-Planck equation and the Donnan equilibrium theory, a hybrid model named the Donnan and steric partitioning pore model, or the Donnan-steric-pore model (DSPM), was derived to describe the transport of charged solute through the NF membrane (Bowen and Mukhtar 1996). It introduces a dimensionless steric partitioning factor,  $\Phi$ , to describe the extent of steric hindrance during the solute transport through the NF membrane. Therefore, combining the effect of Donnan equilibrium and steric hindrance gives the Donnan-steric partitioning equation as:

$$\frac{c_i}{C_i} = \Phi \exp\left(-\frac{z_i F}{RT} \Delta\psi_D\right) \quad (2.9)$$

where the factor  $\Phi$  only relates to the ratio between the solute radius and effective membrane pore radius, and can be experimentally measured in steric-interaction-only systems i.e. only uncharged solutes present on the feed solution. The DSPM model will be further discussed in subsequent chapters.

## 2.2 Preparation of composite NF membranes

Since Cadotte patented the first interfacially polymerized thin-film composite (TFC) membrane in 1981 (Cadotte 1981), composite membranes have come to dominate the RO desalination market. Most NF membranes available in the current market are composite membranes, which include NF series made by Filmtech, NTR series by Nitto-Denko, ESNA series by Hydranautics, Desal series by Osmonics, and UTC series by Toray Industries. Different from integral symmetric or asymmetric membranes with the whole membrane made from the same material in a single process, preparation of composite membranes involves a two-step process to form the dense selective skin layer and porous mechanical support layer separately. Materials and properties of the two layers can therefore be controlled and optimized individually during each step to achieve better overall separation performance as well as commercial feasibility (Baker 2004; Verissimo, Peinemann *et al.* 2005).

The porous support layer of composite membranes is usually fabricated via phase inversion method with or without further mechanical reinforcement depending on designated operating pressure applied on the membrane (Petersen 1993; Mulder 1996; Schäfer, Fane *et al.* 2002). On the other hand, a variety of approaches are employed to prepare the dense skin layer with NF-like selectivity, such as polymer solution dip coating (Kim, Chowdhury *et al.* 2000; He, Frank *et al.* 2008), gas phase plasma deposition (Wang, Fang *et al.* 2001), dual layer hollow fiber co-extrusion (He, Mulder *et al.* 2002; Yang, Wang *et al.* 2009), etc. Among those techniques, in-situ interfacial polymerization, membrane surface modification and polyelectrolyte layer-by-layer assembly have received the most research attention.

### 2.2.1 Interfacial polymerization

Back in 1965, the concept of in-situ interfacial polymerization (IP) was firstly introduced by Morgan (Morgan 1965). Nowadays, IP has become the most widely used technique for the formation of NF-like selective skin layer, and most commercial composite NF and RO membranes are manufactured using this method. In this section, basic principles of interfacial polymerization as well as recent progress in interfacially polymerized NF membranes are reviewed.

#### i) *Basic principles of interfacial polymerization*

An interfacially polymerized thin-film selective layer is usually developed on top of a UF membrane substrate through polymerization or polycondensation reaction between two different monomeric reactants. One of the monomers is dissolved in an aqueous phase and the other in an immiscible organic phase. When these two immiscible phases are brought into contact on top of the porous support layer, polymerization reaction occurs rapidly near the interface created by the two phases, and a thin film layer is formed. Fig. 2.1 shows the schematics of the thin film formation procedure via interfacial polymerization.

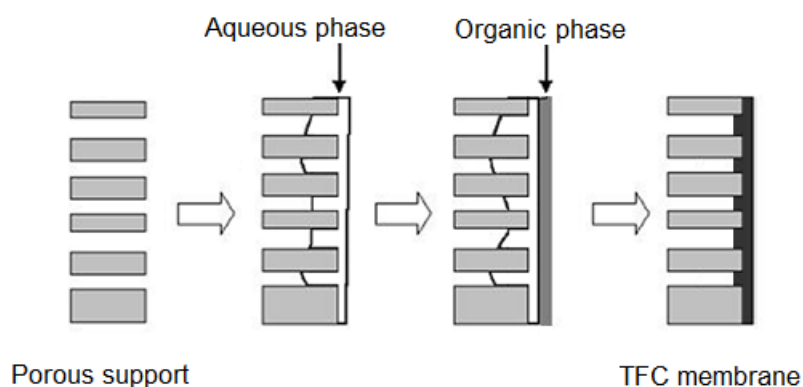


Fig. 2.1 Schematics of in-situ interfacial polymerization

The most common monomer pair for interfacial polymerization contains a polyfunctional amine and a polyfunctional acyl chloride, and the polymerization

reaction is actually amine acylation reactions occurring in the organic phase near the interface. Upon the two phases contact, both reactants and solvents tend to become partitioned with the opposing phase, yet water and the organic solvent are immiscible and acyl chloride has little solubility in water. As a result, amine in the aqueous phase has a potential to penetrate into the organic phase (Chai and Krantz 1994; Morgan and Kwolek 1996). The first portion of penetrated amine gets acylated at both ends by acyl chloride near the interface. The following amine then finds a layer of acid chloride-terminated oligomers. The reaction proceeds by an irreversible coupling of the oligomers by the amine. This is a rapid reaction so that the concentration and size of oligomers increases until a layer of high polymer is obtained. As the concentration of polymer species increases, inter-chain contacts increase until a contact network is formed and precipitates on the surface of the porous support layer (Morgan and Kwolek 1996; Freger 2005). It is worth noting that the growth of the cross-linked thin film often inhibits further contact between the two reactants at a later stage, which results in a self-limiting reaction process and an ultra-thin IP layer (Chai and Krantz 1994). Fig. 2.2 illustrates the reaction scheme between piperazine (PIP) and trimesoyl chloride (TMC), one of the most widely used pairs of monomers in NF membrane fabrication, whereas Fig. 2.3 schematically shows the relation of the concentration of amine and acyl chloride groups near the interface of aqueous and organic phases.

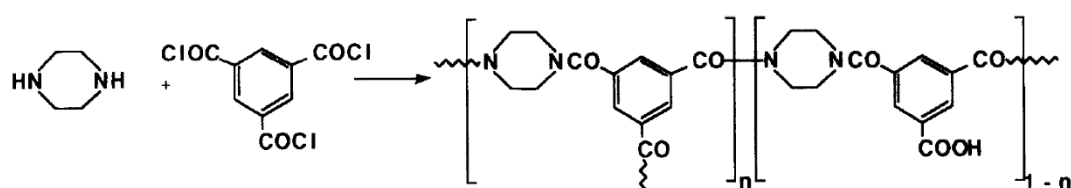


Fig. 2.2 Interfacial polymerization reaction between PIP and TMC (Petersen 1993)

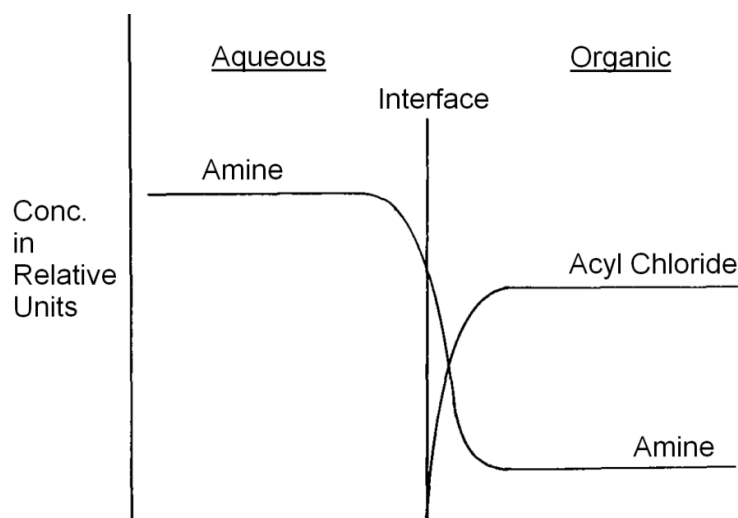


Fig. 2.3 Relationships of concentrations in an interfacial polymerization (Morgan and Kwolek 1996)

The polymerization parameters greatly influence the separation performance of the resultant IP thin film. High monomer concentrations, high reaction rates and long reaction time usually lead to lower water permeability and higher solute rejections (Kim, Kim *et al.* 2000; Jegal, Min *et al.* 2002; Freger 2005). Moreover, since the IP reaction occurs in the organic phase, the diffusion rate of monomers in the organic solvent also affects the thin film formation significantly. Different organic solvents or mixed solvents often result in altered membrane separation properties (Ghosh, Jeong *et al.* 2008; Kong, Kanezashi *et al.* 2010).

## ii) Recent progress in preparation of interfacially polymerized NF membranes

Considerable work has been done on the interfacial polymerization (IP) technique during last three decades, and previous work on IP membranes was reviewed comprehensively by several review papers (Hilal, Al-Zoubi *et al.* 2004; Lau and Ismail 2009; Lee, Arnot *et al.* 2011), especially the one published by Petersen (Petersen 1993) covering most commercially available NF and RO membranes thoroughly up to 1992. Therefore, this section only reviews recent research progress in the preparation of interfacially polymerized composite NF membranes.

### • Monomers

The nanofiltration performance of the IP membrane is mainly determined by the hydrophobicity, charge and structure of the IP active layer, which is basically controlled by the monomers that formed the layer. The effect of different monomers on the interfacial polymerization process and characteristics of the resulted IP layer has been thoroughly investigated. The most commonly used monomers are aromatic or aliphatic amines in the aqueous phase and acyl chloride in the organic phase. Aromatic amines generally yield membranes with better solute rejection but lower water fluxes than aliphatic amines (Oh, Jegal *et al.* 2001). And the most well-known commercially viable aromatic, aliphatic amine and acyl chloride for composite NF membrane development are m-phenylenediamine (MPD), piperazine (PIP) and trimesoyl chloride (TMC), respectively.

To further improve the separation performance of IP membranes, ample research effort has been taken on the investigation of newly synthesized monomers. For example, studies regarding 3,5-diamino-N-(4-aminophenyl)benzamide (Wang, Li *et al.* 2010) and 3,3',5,5'-biphenyl tetraacyl chloride (Li, Zhang *et al.* 2009) claimed that membranes with more than 30% improvement in permeation flux were successfully prepared. In addition to monomeric amines and acyl chlorides, polyamines and polymers with pendant acyl chloride groups like polyethyleneimine (Chiang, Hsub *et al.* 2009), polyamidoamine (Li, Wang *et al.* 2006) and polyvinylbenzylchloride (Pandey, Childs *et al.* 2001) were also used as the monomers for synthesis of the IP layer. Due to the excess amine or acyl chloride groups in the polymer chain, polymeric IP monomers usually yield NF membranes with lower cross-linking degree and higher permeation flux with lower solute retention.

The chlorine tolerance is always the key issue for application of polyamide membranes especially in the water industry. In order to protect the chlorination and hydrolysis of amide groups, aromatic amines with substituted groups such as m-phenylenediamine-4-methyl (Yu, Liu *et al.* 2009) were introduced. At the same time, membranes with polyester IP layer were prepared by different researchers (Jayarani and Kulkarni 2000; Tang, Huo *et al.* 2008), which all showed improved

chlorine tolerance comparing to polyamide membranes.

- *Additives*

The presence of additives in the aqueous or organic phases is also with great impact on the polymerization process and properties of the resultant interfacially polymerized thin film. Different additives like surfactants (Jegal, Min *et al.* 2002; Mansourpanah, Madaeni *et al.* 2009), acid acceptors (Yang, Zhang *et al.* 2007; Li, Zhang *et al.* 2009), non-reactive polymers (Sforca, Nunes *et al.* 1997), hydrophilic macromolecules (Abu Tarboush, Rana *et al.* 2008) and nanoparticles (Lind, Ghosh *et al.* 2009; Wu, Tang *et al.* 2010) are involved in the IP process to facilitate or hinder the polymerization reaction as well as to change the hydrophobicity, roughness, density, charge and anti-fouling properties of the resultant IP layer.

- *Substrates*

Up to date, polysulfone (PSf) and polyethersulfone (PES) porous membranes are the most frequently used substrates for the substrate of IP membranes due to their satisfactory mechanical and thermal stability, chemical tolerance as well as economic viability (Petersen 1993). Alternatively, other porous substrates made with modified polyvinylidene fluoride (PVDF) (Kim, Kim *et al.* 2009), polypropylene (PP) (Korikov, Kosaraju *et al.* 2006), polyacrylonitrile (PAN) (Oh, Jegal *et al.* 2001), polyetherimide (PEI) (Verissimo, Peinemann *et al.* 2005) or novel polymers like poly (phthalazinone ether sulfone ketone) (PPESK) (Wei, Jian *et al.* 2005), sulfonated poly (phthalazinone ether sulfone ketone) (SPPEsk) (Dai, Jian *et al.* 2002) are used as the substitution of PSf and PES towards better thermal and solvent stability.

Moreover, research efforts on IP membranes made from hollow fiber substrates are far less than flat sheet membranes. Handful studies (Liu, Xu *et al.* 2007; Wang, Shi *et al.* 2010; Sun, Hatton *et al.* 2012) were reported about NF hollow fiber membranes via outer skin interfacial polymerization, despite the fact that hollow fiber membranes give better packing density, higher surface area to volume ratio

and self-support capability as well as cost-effective large-scale production and operation (Futselaar, Schonewille *et al.* 2002). Although the selective layer is usually located at the shell side of the hollow fiber to utilize the larger surface area, hollow fiber membranes with a selective layer on the inner surface exhibit better hydraulic flow conditions, lower concentration polarization and fouling tendency (Baker 2004). The studies on conducting interfacial polymerization in the lumen of the hollow fiber (Verissimo, Peinemann *et al.* 2005; Yang, Zhang *et al.* 2007; Chou, Shi *et al.* 2010) have already shown that the process is more controllable and viable for scale-up fabrication as well, but the technology is still far away from mature and deserves great efforts and much attention.

### **2.2.2 Surface modification**

Surface modifications are often applied to UF or RO membranes in order to adjust the pore size, introduce different functional groups, alter the hydrophilicity and surface charge of the membrane, and NF membranes with enhanced separation performance, anti-fouling capability, solvent resistance and long-term stability can therefore be prepared. Important modification methods include polymer grafting, classical chemical treatment and chemical cross-linking.

#### *i) Polymer grafting*

Grafting is a process of covalent attachment of monomer or polymer onto the membrane surface. The process usually started with a UF membrane substrate with reactive ionic or radical positions generated by various energy sources, and monomers are grafted to the reactive sites on the membrane surface. Polymerization of the monomer may occur subsequently to form an NF-like selective layer. Membrane surface characteristics like hydrophilicity, surface charge, etc. can be altered as well by the grafted polymer layer.

Ultraviolet (UV) light or plasma is often used as the energy source for the generation of reactive sites on the membrane surface. For example, Akbari *et al.*

applied UV-photografting to modify polyethersulfone (PES) hollow fiber membrane using p-styrene sulfonate as a vinyl monomer, and the resultant NF membrane possessed a negatively charged selective layer and suitable for treatment of anionic dye solutions (Akbari, Desclaux *et al.* 2007). Whereas Zhao *et al.* induced grafting polymerization of acrylic acid onto polyacrylonitrile (PAN) UF flat-sheet membrane substrate by low-temperature plasma to yield hydrophilic composite NF membrane for water treatment (Zhao, Li *et al.* 2004). However, the grafting polymerization often presents a high extent of polymerization and results in a thick selective layer with low water permeability.

ii) *Classical chemical treatment*

Classical chemical treatments like sulfonation, nitration, acid/base treatment, organic solvent treatment, etc. can be applied to either UF or RO membranes to tighten or open the surface pores, respectively, and yield membranes with NF-like selectivity. For instance, polysulfone UF flat-sheet membranes were transformed to NF membranes by nitration with NO and NO<sub>2</sub> followed by amination (Chowdhury, Kumar *et al.* 2001). And polyamide (PA) composite RO membranes can be treated with protic acids to hydrolyze the carbonyl groups, open the cross-linked structure, create more charge and increase the water flux (Schäfer, Fane *et al.* 2002). Additionally, when PA membranes were treated with ethanol, the selective layer swelled and was partially dissolved, and a more porous PA layer with NF-like selectivity was produced (Oh, Jegal *et al.* 2001). The long-term stability of the resultant membrane from this method is yet to be assured due to the harsh treatment conditions that may have damaged the membrane.

iii) *Chemical cross-linking*

Chemical cross-linking is a straightforward treatment process employed on the membrane surface to interconnect the polymer chains, to tighten the pore size and to improve the NF-layer stability. Depending on the functionality of the membrane material and the choice of proper cross-linker, mild treatment conditions are usually involved, and additional functional groups can be introduced to adjust the surface

properties of the membrane. For example, Huang *et al.* prepared quaternized chitosan/PAN composite NF membrane by epichlorohydrin cross-linking. The membrane exhibited a MWCO of 560 Da with positive surface charge (Huang, Chen *et al.* 2007). Moreover, Jegal *et al.* fabricated poly(vinyl alcohol) (PVA) based composite NF membranes with enhanced chemical stability by cross-linking using glutaraldehyde (Jegal, Oh *et al.* 2001). In addition, polyelectrolyte LBL assembled NF membrane was also cross-linked by glutaraldehyde to improve the stability of the LBL multilayer as well as to enhance the rejection towards highly concentrated salt solutions (Qiu, Qi *et al.* 2011).

Specifically, polyimide or copolyimide based membrane surfaces are able to be cross-linked by diamine or polyamine cross-linkers to achieve NF-like selectivity, because imide rings tend to be opened up and connect with amine groups quite easily. Qiao *et al.* discovered that ethylenediamine was more effective in reaction with imide group than p-xylenediamine when performing cross-linking with P84 polyimide based flat-sheet membranes (Qiao and Chung 2006). Whereas Ba *et al.* utilized the multiple amine groups of branched polyethyleneimine (PEI) to functionalize the P84 polyimide flat sheet membrane and produced a positively charged NF membrane (Ba, Langer *et al.* 2009). Furthermore, PEI was adopted as the cross-linker by Setiawan *et al.* to modify poly (amide-imide) (PAI) so that PAI/PES based composite NF hollow fiber membranes were prepared, and the pendant amine groups from the cross-linker also led to its positive membrane surface charge (Setiawan, Wang *et al.* 2012b). The cross-linking reaction between PEI and PAI membrane is illustrated in Fig. 2.4.

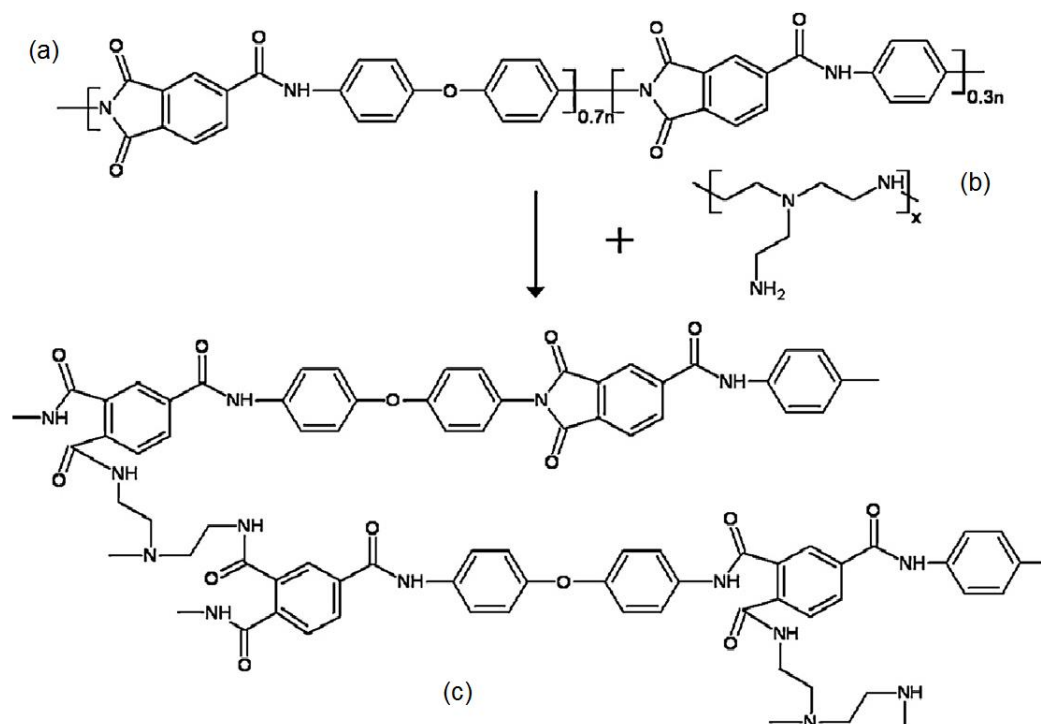


Fig. 2.4 Cross-linking reaction between (a) PAI and (b) PEI; (c) cross-linked PAI (Setiawan, Wang *et al.* 2011).

### 2.2.3 Layer-by-layer assembly

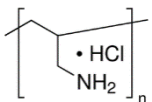
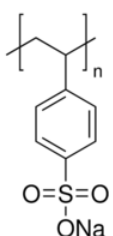
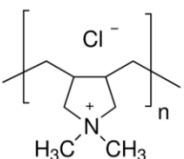
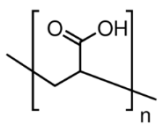
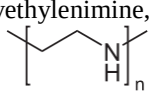
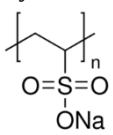
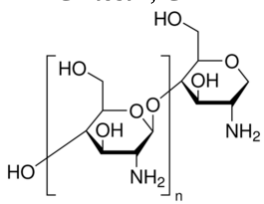
Polyelectrolyte layer-by-layer (LBL) assembly was firstly reported by Decher in 1997 to form thin-film multilayers (Decher 1997). Nowadays LBL assembly has become an attractive technique for preparation of ultra-thin dense layers with highly tunable separation properties, and LBL membranes are widely applied in nanofiltration (Hong, Miller *et al.* 2006; Ahmadiannamini, Li *et al.* 2010), reverse osmosis (Jin, Toutianoush *et al.* 2003; Park, Park *et al.* 2010), forward osmosis (Saren, Qiu *et al.* 2011; Liu, Fang *et al.* 2013), pervaporation (Krasemann and Tieke 1998; Zhang, Yan *et al.* 2007) and gas separation (Lev äsalmi and McCarthy 1997; Sullivan and Bruening 2002). The general procedure of LBL method involves the alternating adsorption of positively and negatively charged polyelectrolytes on the surface of a membrane substrate, and the multilayer thin film is assembled on the substrate due to the electrostatic attraction between the polycation and polyanion. The key merit of LBL assembly is the precise control of thin film thickness as well

as its surface properties by tuning the sequential adsorption steps.

i) *Polyelectrolytes and substrates for LBL assembly*

Polyelectrolytes correspond to polymers with charged or chargeable groups within the monomer repeat units. These electrolyte groups make the polymer soluble in water or aqueous solutions to become macromolecular ions, and dissolved polyelectrolytes with cationic or anionic charge groups are referred to as polycations or polyanions, respectively. Moreover, polyelectrolytes with charged groups that can fully dissociate in water are denoted as strong polyelectrolytes, while the charge dissociation of weak polyelectrolytes is partial and pH dependent. Polyelectrolytes that are commonly employed for LBL assembly are summarized in Table 2.1.

Table 2.1 Commonly used polyelectrolytes for LBL assembly.

| Polycations                                                                                                                                | Polyanions                                                                                                                |
|--------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------|
| <p>Poly(allylamine hydrochloride), PAH</p>              | <p>Poly(styrene sulfonate), PSS</p>  |
| <p>Poly(diallyldimethylammonium chloride), PDADMAC</p>  | <p>Poly(acrylic acid), PAA</p>       |
| <p>Polyethylenimine, PEI</p>                            | <p>Poly(vinyl sulfate), PVS</p>      |
| <p>Chitosan, CHI</p>                                    |                                                                                                                           |

A variety of substrate materials can be used for the formation of LBL thin film as long as the initial layer of polyelectrolyte is effectively attached on the substrate by electrostatic attraction. For example, porous alumina was adopted as the membrane substrate for LBL assembly due to its positive surface charge for the fine adsorption of initial polyanion layer (Stanton, Harris *et al.* 2003; Hong, Malaisamy *et al.* 2007). Whereas a plasma-treated porous polyacrylonitrile (PAN) membrane substrate with negative surface charge was employed for the preparation of LBL assembled NF membranes (Krasemann and Tieke 1999). In addition, polyethersulfone (PES) UF membranes, which usually possess neutral surface charge, were also used as the polyelectrolyte membrane substrate for NF membrane development (Malaisamy and Bruening 2005). The attachment of LBL multilayer on the PES membrane surface is mainly attributed to hydrophobic interaction.

ii) *Parameters that influence the LBL thin film formation*

Various factors such as charge density of polyelectrolyte, number of electrolyte layers, ionic strength and pH of the polyelectrolyte solution etc. have great influence on the formation of LBL thin film layer as well as its NF performance. Polyelectrolytes with higher charge density usually yield NF membranes with higher rejection to ionic species as the effect of Donnan exclusion is enhanced (Krasemann and Tieke 1999; Ouyang, Malaisamy *et al.* 2008). Whereas higher number of assembled electrolyte layers increases the solute transport resistance and strengthens the size effect, so that better solute rejection is generally achieved (Bruening, Dotzauer *et al.* 2008; Liu, Fang *et al.* 2013). Besides, ionic strength of the polyelectrolyte solution affects the thickness of the assembled layer significantly. When higher background salt concentration i.e. higher ionic strength is involved, the polyelectrolyte chain becomes more coiled because electrostatic repulsion within the polymer chain is weakened. As a result, thickness of the polyelectrolyte layers increases, and NF membranes with lower water permeability and higher solute rejection can be prepared (Lavalle, Gergely *et al.* 2002; Salomäki and Kankare 2008). Furthermore, since the charge density of weak polyelectrolytes is pH dependent, the structure of the polyelectrolyte multilayer can be fine-tuned by controlling the solution pH (Shiratori and Rubner 2000; Elzbieciak, Zapotoczny *et*

*al.* 2009).

### *iii) Preparation methods of LBL assembled membranes*

The preparation of LBL assembled multilayers on a membrane substrate can be conducted via different methods. Dip-coating, which involves alternate immersion of the membrane substrate into the polyelectrolyte solution followed by rinsing, is the most commonly adopted method for lab-scale LBL membrane preparation (Decher and Schlenoff 2012). However, dip-coating can be a tedious and time-consuming method when a large number of polyelectrolyte layers needs to be assembled. It is crucial to keep as few deposited layer as possible to develop a LBL assembled membrane with proper feasibility. Besides, various methods like spray-coating (Schlenoff, Dubas *et al.* 2000; Kolasinska, Krastev *et al.* 2008), spin-coating (Cho, Char *et al.* 2001; Jiang, Markutsya *et al.* 2004), etc. has been introduced to reduce the time needed for multilayer formation so that the LBL assembly technique could be more efficient in commercialized mass production.

## **2.3 Design of NF membranes for niche applications**

### **2.3.1 Criteria for NF membrane design**

In water-related industry, NF membranes have been widely applied in surface and groundwater softening (Duran and Dunkelberger 1995), pretreatment for desalination (Hilal, Al-Zoubi *et al.* 2004), removal of heavy metal (Favre-Reguillon, Lebuzzit *et al.* 2008) and natural organic matters (Alborzfar, Jonsson *et al.* 1998). Membranes with an NF-like selective layer are also feasible for forward osmosis (FO) and pressure retarded osmosis (PRO) applications with divalent ions or organic macromolecules involved in the processes, which gives an alternative to conventional RO-type FO membranes (Yang, Wang *et al.* 2009; Setiawan, Wang *et al.* 2011). Although higher water permeability, lower operating pressure, better economic feasibility, etc. are the universal requirements for higher productivity and lower energy consumption, specific membrane properties are required for niche

applications. For example, NF membranes for wastewater treatment should be designed to have high chlorine tolerance to withstand the free chlorine in the feed water, and negative or neutral surface charge for better fouling resistance. Oppositely, groundwater softening requires the NF membrane to have positive membrane surface charge for more effective retention of divalent metal ions, whereas no specific requirement on chlorine resistance is raised as the level of free chlorine in groundwater is deemed negligible. The following sections provide detailed discussion on membrane design of some niche applications.

### **2.3.2 Water softening**

Water softening, a process to remove abundant calcium and magnesium cations as well as other water hardening minerals from raw water stream, is not only indispensable to the domestic and industrial water supply, but also important as a pre-treatment process for brackish water and seawater desalination to improve water recovery by minimizing membrane scaling (Gabrielli, Maurin *et al.* 2006). Different from conventional water softening methods involving ion-exchange resin, zeolite or lime-soda ash treatments, water softening via membrane is a one-stage process that serves the role of hardness removal and the rejection of bacteria, virus, natural organic compounds and other undesirable chemical compounds simultaneously (Conlon, Hornburg *et al.* 1990). With the rapid development of nanofiltration (NF) technology in recent years, it becomes possible to selectively remove divalent cations from monovalent ions under an operating pressure much lower than typically applied pressure in reverse osmosis (RO). Thus membrane softening has great potential to supersede traditional water softening methods in terms of effectiveness and operating costs, especially for the effective removal of major hardness contributing ions from raw water with high salt concentration such as brackish water (Comstock 1989; Duran and Dunkelberger 1995), seawater (Song, Xu *et al.* 2011; Su, Dou *et al.* 2012) and desalination concentrate (Van der Bruggen, Lejon *et al.* 2003).

However, the application of low-pressure membrane softening is limited due to the

fact that the specialized NF membranes with exclusive characteristics for water softening are almost not available in the current commercial market. Most commercial NF membranes possess a polyamide active layer made from interfacial polymerization of PIP and TMC, which present negative surface charges when in contact with neutral pH feed water (Schaep and Vandecasteele 2001). Negatively charged NF membranes reject divalent metal ions by steric-hindrance exclusively so that the membranes have to be made with a tight structure and sharp pore size distribution to successfully reject divalent metal ions and allow monovalent ions to pass through at the same time. The water permeability of the NF membranes is thus sacrificed due to the dense membrane structure, and a relatively high operating pressure is required in order to achieve desired water softening productivity. The high operating pressure leads to additional energy consumption and thus hinders the breakdown of overall membrane softening cost-efficiency. In contrast, for NF membranes with positive surface charges, the separation mechanism involves electrostatic repulsion in addition to size exclusion for separating hard water metal ions from feed streams. According to Donnan exclusion principle, membranes with positive surface charges are more favorable in rejecting divalent cations than monovalent ions due to the higher charge density of divalent ions (Yaroshchuk 2001). This additional factor makes the membrane less dependent on tight pore size. Hence, a “looser” positively charged NF membrane with relatively large pore sizes can be used for water softening with higher water permeability while maintaining similar high rejection to divalent metal cations at lower operating pressure.

Alternatively, for feed stream with high salt concentration (TDS) like brackish water, seawater and RO brine, etc., especially when a large amount of divalent anions (such as  $\text{SO}_4^{2-}$ ) are presented, the surface charge of the NF membrane is likely to be neutralized by the high ionic strength or high valence of the counterion in the feed (Chaufer, Rabiller-Baudry *et al.* 1996). Tighter membrane pore size is therefore necessary to enhance the steric effect and maintain the salt rejection, but tightened pores may also raise the concentration of monovalent ions like  $\text{Na}^+$  and  $\text{Cl}^-$ . The osmotic pressure difference across the membrane would then be built up too high for the membrane to operate at low pressure. In this case, NF membranes should be

designed with narrower pore size distribution to make it highly selective to divalent ions and monovalent ions can pass though freely at the same time, while the membrane surface charge only possess minor effect on the water softening performance.

### **2.3.3 Forward osmosis**

Forward osmosis (FO) process has attracted much attention in recent years. Unlike pressure-driven process, the driving force for water transfer in FO arises from the osmotic pressure difference due to the concentration gradient between draw and feed solutions separated by a semi-permeable membrane. As a result, the energy consumption in FO can be reduced significantly in comparison with RO. If pressure is applied on the draw solution side to retard the natural osmosis, energy can then be generated from the excess osmotic pressure (pressure retarded osmosis, PRO). Nonetheless, when commercial RO membranes are used in FO/PRO process, severe internal concentration polarization (ICP) occurred in their thick and relatively dense substrates leads to extremely low water flux (Cath, Childress *et al.* 2006). In fact, the development of appropriate membranes with specialized properties for FO is one of the major challenges for the application of FO processes. Generally, a desired membrane for FO processes should have a highly dense active layer for high solute rejection, especially monovalent or divalent ion rejection. A thin support layer with small tortuosity and large porosity is desirable for lower degree of ICP and higher water flux. The membrane should also possess good anti-fouling/scaling capability for more practical FO applications. If the membrane is applied in PRO processes, high mechanical strength is required as well.

Similar to many other membrane processes, a great challenge that has to be tackled for FO/PRO applications is membrane fouling/scaling. Normally, when the active layer is facing the draw solution (AL-DS orientation or PRO mode), the membrane possesses a high fouling/scaling propensity if the feed solution contains organic macromolecules or inorganic scalants that can penetrate into the porous support layer easily. Due to the internal fouling and/ or pore clogging, the substrate structure

was altered, leading to enhanced ICP effect and mass transfer resistance, consequently, a sharp decreased water flux in the AL-DS orientation (Tang, She *et al.* 2010). In contrast, the membrane orientation with active layer facing the feed solution (AL-FS orientation or FO mode) offers the advantage of anti-internal fouling/scaling because of the dense active layer that prevents the penetration of foulants/scalants into the support layer. Yet the AL-FS operation experiences more severe reduction of effective driving force due to dilutive ICP (Chou, Shi *et al.* 2010; Wang, Shi *et al.* 2010). Furthermore, AL-DS is the more feasible orientation for PRO process, where a relatively high hydraulic pressure is applied in the draw solution side.

As a consequence, the concept of double-skinned FO membranes is developed in order to fully utilize the higher water flux of AL-DS orientation and mitigate the potential problem of internal fouling/scaling in the FO/PRO applications. In addition to the dense ultra-thin active layer, a secondary skin layer was proposed on the substrate to face the feed solution so as to prevent possible foulant/scalant penetration into the support layer. The secondary selective layer is also expected to obstruct the diffusion of solutes in the feed solution from diffusing into the substrate and give rise to further ICP effect. A mathematical model has been derived to analyze the mass transfer in the double-skinned FO membranes, which provides guidance for the membrane design (Tang, She *et al.* 2011), but very few studies were conducted to make double-skinned FO membranes.

An RO-like dense active layer is preferred for more efficient solute rejection, while the secondary selective layer of the double-skinned membrane can be NF-like with high water permeability to minimize the additional water transport resistance induced by this layer. Particularly, this NF-like selective skin layer should firstly possess sufficient rejection to organic macromolecules and inorganic scalants so that their penetration into the supporting layer can be prevented. Moreover, the surface characteristics of the NF-like layer including hydrophilicity, roughness and charge properties should be carefully adjusted so that fouling/scaling on the surface of the NF-like layer could be kept to a minimum.

## **CHAPTER 3**

# **Interfacially Polymerized Composite NF Hollow Fiber Membranes for Low-Pressure Water Softening**

### **3.1 Introduction**

Hard water is undesirable in either domestic water supply or industrial applications, as its high mineral content decreases the household cleaning efficiency, induces scaling and corrosion problems and causes serious failures in pipelines of boilers, heat exchangers and electrical appliances (Gabrielli, Maurin *et al.* 2006). Water softening is a water treatment process that serves the removal of calcium and magnesium cations as well as other divalent or multivalent metal ions in hard water. Compared with conventional water softening methods involving ion-exchange resin, zeolites or lime-soda ash treatments, water softening through nanofiltration (NF) has the potential to offer lower operating and by-product disposal costs, increased operation safety as well as less chemical and energy consumption (Duran and Dunkelberger 1995).

Most commercial NF membranes suitable for water softening are thin-film composite membranes, which are composed of an ultra-thin active layer responsible for separation and a porous substrate layer (usually a UF membrane made by PSf or PES) providing mechanical support. The key merit for composite membranes is that the characteristics of the active skin layer and porous support layer can be

independently optimized to achieve better commercial feasibility. The active separating barrier layer is developed on the top of the porous support layer through interfacial polymerization reaction between a polyfunctional amine and a polyfunctional acyl chloride. Since the active skin layer controls the water softening performance of the NF membrane in terms of water permeability and selectivity between divalent and monovalent ions under designated operating pressure, the interfacial polymerization process has been extensively studied in recent years. For example, new monomers were explored (Buch, Mohan *et al.* 2008; Tang, Huo *et al.* 2008; Li, Zhang *et al.* 2009), surfactants and other additives were introduced (Tarboush, Rana *et al.* 2008; Mansourpanah, Madaeni *et al.* 2009; Tang, Zou *et al.* 2010; Wu, Tang *et al.* 2010), and the reaction time and temperature as well as post-treatment conditions were investigated (Jegal, Min *et al.* 2002; Rao, Joshi *et al.* 2003; Ahmad, Ooi *et al.* 2004; Ghosh, Jeong *et al.* 2008).

However, to date the application of low-pressure membrane softening is still limited due to the fact that the specialized NF membranes with exclusive characteristics for water softening are almost not available in the current commercial market. Most commercial NF membranes possess a polyamide active layer with negative surface charge. Alternatively, as discussed in Chapter 2 Section 2.3.3, the separation mechanism for NF membranes with positive surface charge involves electrostatic repulsion (Donnan effect) in addition to size exclusion for separating hard water metal ions from feed streams, which makes the membrane less dependent on tight pore size. Hence, membranes with relatively large pore sizes can be used for water softening with higher water permeability while maintaining similar high rejection to divalent metal cations at lower operating pressure. Development of positively charged NF membranes via interfacial polymerization between other aliphatic amines and TMC has been reported in recent studies (Li, Wang *et al.* 2006; Verissimo, Peinemann *et al.* 2006; Chiang, Hsub *et al.* 2009), but further exploration is needed with respect to low-pressure water softening applications.

This study aims to develop composite NF hollow fiber membranes with low operating pressure, which are desirable for water softening. The thin-film skin layer

of the membrane is developed through interfacial polymerization on the inner surface of polyethersulfone (PES) UF hollow fiber membrane substrate. Instead of PIP, branched polyethyleneimine (PEI), a cationic polyelectrolyte rich in primary and secondary amine functional groups, is selected as one of polymerization monomers accompanied with TMC to yield a positively charged selective layer. The separation characteristics of the acquired NF hollow fiber membranes are evaluated by NF processes involving feed solutions containing various neutral solutes, inorganic salts and salt mixtures, operated under the trans-membrane pressure as low as 2 bar. It is interesting to notice that NF hollow fibers with such a UF-range low operating pressure have not been reported in the open literature especially for membrane softening applications.

## **3.2 Experimental**

### **3.2.1 Materials and chemicals**

Polyethersulfone (PES, Gafone<sup>®</sup> 3000P granular powder), supplied by Solvay Advanced Polymers, India, was used for hollow fiber substrate preparation. N-Methyl-2-pyrrolidone (NMP, >99.5%, CAS#872-50-4, Merck) was used as a solvent. Branched polyethyleneimine (PEI) with molecular weights of 800 and 750,000 (Sigma-Aldrich) and 50,000~100,000 (MP Biomedicals), trimesoyl chloride (TMC, 98%, CAS#4422-95-1, Sigma-Aldrich), sodium dodecyl sulfate (SDS, >95%, CAS#151-21-3, Reagents), and cyclohexane (CAS#110-82-7, Merck) were used for interfacial polymerization.

Neutral organic solutes such as glucose, sucrose, and raffinose as well as analytical grade inorganic salts including magnesium chloride (MgCl<sub>2</sub>, hexahydrate), magnesium sulfate (MgSO<sub>4</sub>, heptahydrate), sodium chloride (NaCl), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and calcium chloride (CaCl<sub>2</sub>, anhydrous) purchased from Merck were used to prepare various feed solutions. Deionized water (Milli-Q, 18MΩcm) was utilized for the preparation of aqueous solutions, and all the feed solutions exhibited pH from 6.5 to 7. All chemicals were used as received.

### 3.2.2 Membrane preparation

#### i) *Fabrication of hollow fiber substrates by phase inversion*

Substrates of the composite membranes were UF hollow fiber membranes, and fabricated via phase inversion method using a dry-jet wet spinning processes as reported previously (Wang, Shi *et al.* 2010; Loh, Wang *et al.* 2011). Basically, the PES polymer dope was prepared by dissolving the polymer into NMP solvent. The homogenously mixed dope solution was pressurized through a spinneret by nitrogen gas at a controlled rate, and went through a certain air gap before immersed into a coagulation bath. The newly formed hollow fibers were taken up by a roller at a free falling velocity and stored in a water bath to remove residual solvent.

#### ii) *Preparation of composite hollow fibers by interfacial polymerization*

The active skin layer of the composite hollow fiber membrane was prepared on the inner surface of the PES hollow fiber substrate through interfacial polymerization. Membrane modules were prepared by sealing four pieces of PES substrate fibers in a PTFE tube with a diameter of 6.35 mm and an effective length of 18 cm using epoxy resin prior to the interfacial polymerization experiment. A typical preparation procedure started with one membrane module that was held vertically. An aqueous solution containing 0.25 wt.% PEI and 0.1 wt.% SDS with pH adjusted to 11 by sodium hydroxide (NaOH) and hydrochloric acid (HCl) was introduced using a syringe into the lumen side of the substrate fibers in the module and in contact with the fiber inner surface for 30 min. The syringe and one end of the membrane module were connected with silicone tubing in order to introduce the solution into the lumen of four fibers simultaneously. After the removal of excess PEI solution by pure cyclohexane solvent purge using a peristaltic pump, a 0.13 wt.% TMC/cyclohexane solution was pumped through the lumen side of the fiber in the same manner for 120 s to allow the interfacial polymerization reaction to take place. Fibers with newly developed thin film active layer were then washed and kept in DI water.

### 3.2.3 Hollow fiber characterization

#### i) *Membrane morphology observation*

The cross-section and inner surface of the PES substrates and composite hollow fiber membranes were examined by a Zeiss EVO 50 Scanning Electron Microscope (SEM). Hollow fiber samples were fractured in liquid nitrogen and coated with gold using an EMITECH SC7620 sputter coater before the SEM observation.

#### ii) *FTIR analysis and streaming potential measurement*

The nature of the interfacial polymerization reaction was investigated using a Fourier transform infrared spectrometer (FTIR, Prestige-21, Shimadzu) via the attenuated total reflection (ATR) method, while membrane surface charge characteristics for the inner skin of the composite fiber and PES substrate were measured by streaming potential method using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria). The hollow fibers were cut open and flattened in advance so that the chemical composition and charge character of the substrate and composite fiber inner surfaces were able to be analyzed by the respective instruments. For streaming potential measurement, an electrolyte solution of 0.01 M potassium chloride (KCl) was utilized to provide the background ionic strength, and automatic titration was performed using 0.05 M HCl and 0.1 M NaOH solutions to investigate the effect of pH on the zeta potential as well as the isoelectric point of the membrane (Setiawan, Wang *et al.* 2011).

#### iii) *Measurement of dynamic contact angle and mechanical properties*

The hydrophobic/hydrophilic nature of the substrate and composite hollow fibers was determined by dynamic contact angle measurements using a tensiometer (DCAT11 Dataphysics, Germany). A hollow fiber sample with an effective length of 5 mm was held vertically and underwent 3 immersion-emersion cycles getting into and out of the DI water. The weight change of the fiber due to the membrane

surface tension was continuously recorded throughout the measurement process. The equilibrium contact angle for either inner or outer fiber surfaces was then calculated from the wetting force based on the Wilhelmy method (Wang, Shi *et al.* 2010).

Mechanical properties of the substrate and composite hollow fiber membranes were characterized by the tensile strength test using a Zwick 0.5 kN Universal Testing Machine. A hollow fiber sample with both ends fastened was pulled with a constant elongation velocity until breakage, and tensile modulus, yield stress and yield strain of the fiber were measured along with the elongation process.

iv) *Determination of molecular weight cut-off and effective pore size*

Rejection of the composite membrane to different neutral organic solutes (glucose, sucrose, and raffinose) was measured and plotted against the molecular weight so that the molecular weight cut-off (MWCO, molecular weight of solute with 90% rejection) of the composite NF membrane could be determined. More detailed information regarding the measurement of solute rejection will be provided Section 3.2.4.

The effective pore size of the NF membrane was estimated using the Donnan-Steric-Pore model (DSPM). Based on the model, the rejection to neutral organic solutes is given by (Bowen, Mohammad *et al.* 1997; Bowen and Mohammad 1998):

$$R = (1 - \Phi K_{i,c}) \times 100\% \quad (3.3)$$

where

$$\Phi = (1 - \lambda^2) \quad (3.4)$$

$$K_{i,c} = (2 - \Phi)(1.0 + 0.054\lambda - 0.988\lambda^2 + 0.441\lambda^3) \quad (3.5)$$

$\Phi$  is the steric partitioning factor,  $K_{i,c}$  is the steric hindrance factor, and  $\lambda$  is the ratio of solute radius to effective pore radius. Since the solute rejection is only related to  $\lambda$ , the effective pore radius of the membrane can be obtained based on the rejection to various solutes by knowing their solute radii through the following empirical equation (Bowen and Mohammad 1998):

$$\log r_s = -1.3363 + 0.395 \log M_w \quad (3.6)$$

where  $r_s$  is the Stocks radius of a neutral solute molecule (nm), and  $M_w$  is the molecular weight of the solute (Da).

### 3.2.4 Evaluation of membrane separation properties

#### i) *Pure water permeability*

Pressure-driven filtration experiments were carried out using a bench-scale pressurized cross-flow filtration setup (Setiawan, Wang *et al.* 2012a), where the same membrane modules used for interfacial polymerization were utilized in the filtration experiments. Since the active skin layer is located on the inner surface of the composite hollow fibers, the feed solution was circulated through the lumen side of the membrane module under an effective trans-membrane pressure of 2~7 bar, and the permeate stream exited was collected from the shell side of the module. The pure water permeability of the composite membrane, PWP ( $\text{l/m}^2 \text{ h bar}$ ), was obtained by employing DI water as the feed at first, which was calculated as follows:

$$PWP = \frac{J_v}{\Delta P} = \frac{Q}{A \Delta P} \quad (3.1)$$

where  $J_v$  is the permeation flux ( $\text{l/m}^2 \text{ h}$ ),  $\Delta P$  is the trans-membrane pressure drop (bar),  $Q$  is the volumetric permeation flow rate ( $\text{l/h}$ ), and  $A$  is the effective membrane filtration area ( $\text{m}^2$ ).

#### ii) *Permeation flux and solute rejection*

Once a stabilized water flux was achieved after the membrane went through compaction with DI water for about 1 h, various feed solutions containing neutral solutes, inorganic salts, or salt mixtures were applied to estimate the MWCO (molecular weight cut-off) and pore size, to characterize the charge properties and to evaluate the separating performance of the composite membrane. The permeation flux and solute rejection for each feed solution were measured correspondingly. Eq. (3.1) was applied for the determination of permeation flux, whereas the solute rejection,  $R_s$  (%), was calculated based on the following equation:

$$R_s = \frac{C_f - C_p}{C_f} \times 100\% \quad (3.2)$$

where  $C_f$  and  $C_p$  correspond to concentrations (ppm) of one specific solute (neutral solute or dissolved ions) or total solute concentrations in the feed and permeate solutions, respectively.

Concentrations of neutral organic solutes in the feed and permeate solutions were obtained through total organic carbon measurements using a TOC analyzer (TOC-VCSH, Shimadzu, Japan), whereas the salt concentration in single salt solutions were acquired based on conductivity measurements (Ultrameter II, Myron L Company, Carlsbad, Canada). The metal ion concentrations in mixed salt solutions were measured using an optical emission spectrometer (ICP-OES Optima 8000, Perkin Elmer, USA).

### 3.3 Results and discussion

#### 3.3.1 Characteristics of composite NF hollow fiber membranes

First of all, it should be noted that the PES hollow fiber substrates have an external diameter of 1.38 mm and inner diameter of 1.05 mm with porosity of 80%. The pure water permeability and the molecular weight cut-off (MWCO) of the substrate fibers were measured to be 280 l/m<sup>2</sup> h bar and 48 kDa, respectively. The measurement method for MWCO of UF membranes has been reported elsewhere (Wei, Wang *et al.* 2006). After thin film formation through interfacial polymerization, the best composite NF hollow fiber membranes developed (please refer to Section 3.2.2 for the corresponding preparation parameters) went through comprehensive membrane characterization including the studies of membrane morphology, chemical composition, surface charge and hydrophobic/hydrophilic properties as well as mechanical properties.

The morphologies of the PES UF substrate and developed composite NF hollow fiber membrane are shown in Fig. 3.1. Comparing the cross-section morphologies

of the composite fiber near the lumen surface (Fig. 3.1(c)) with the substrate (Fig. 3.1(e)), a dense thin-film layer fiber firmly attached to the inner surface of the substrate was observed. Moreover, before the interfacial polymerization, the inner surface of the PES substrate presented a smooth manner with uniformly distributed pores, as shown in Fig. 3.1(f). After the thin-film was formed, a rougher fiber inner surface (Fig. 3.1(d)) was observed without perceptible membrane pores.

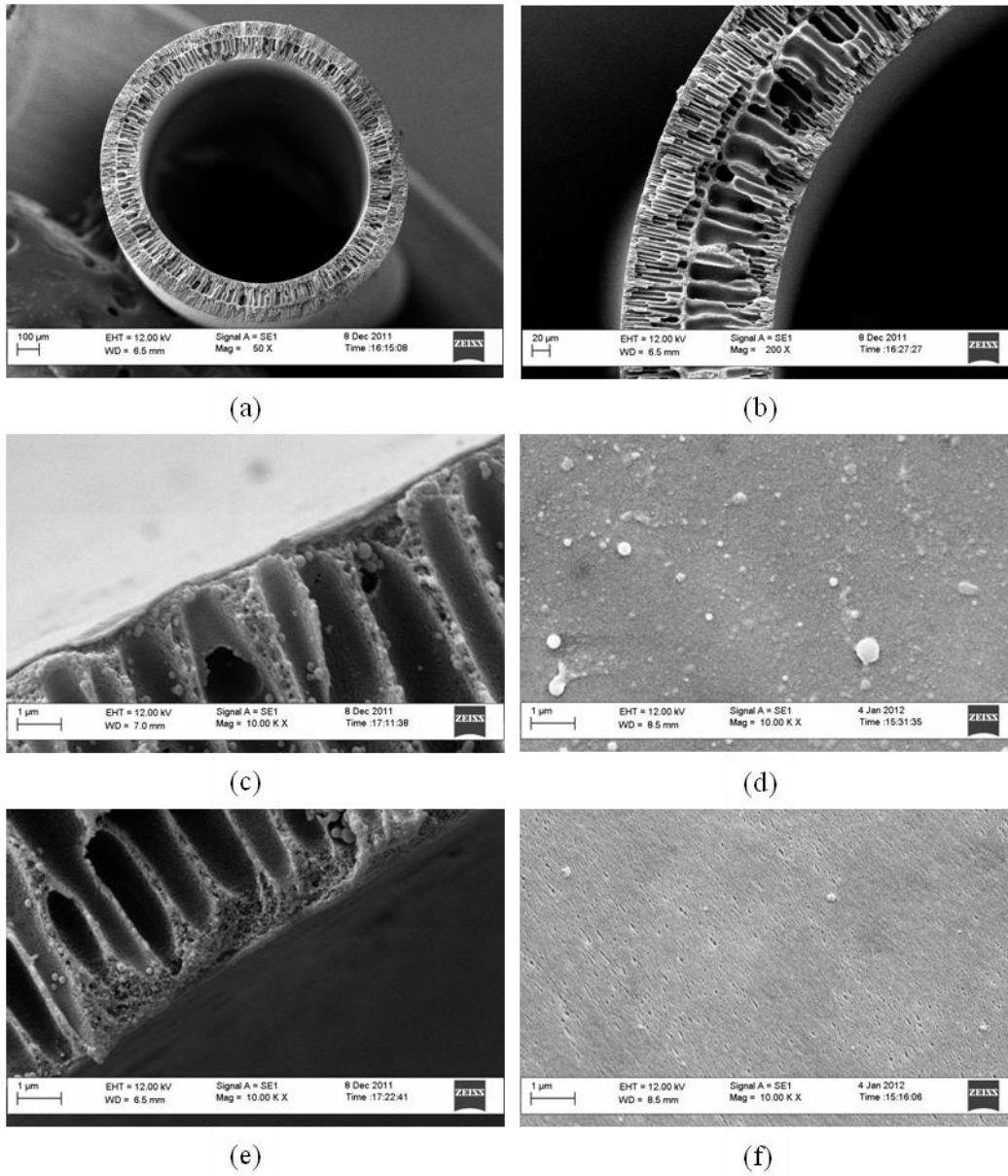


Fig. 3.1 Morphology of composite NF hollow fiber membrane: (a) cross-section; (b) enlarged cross-section; (c) enlarged lumen side cross-section; (d) inner surface; Morphology of PES hollow fiber substrate: (e) enlarged lumen side cross-section; (f)

inner surface.

The nature of the polymerization reaction as well as chemical composition of resultant thin-film layer was analyzed by comparing FTIR spectra of the PES hollow fiber substrate before and after interfacial polymerization, which are illustrated in Fig. 3.2.

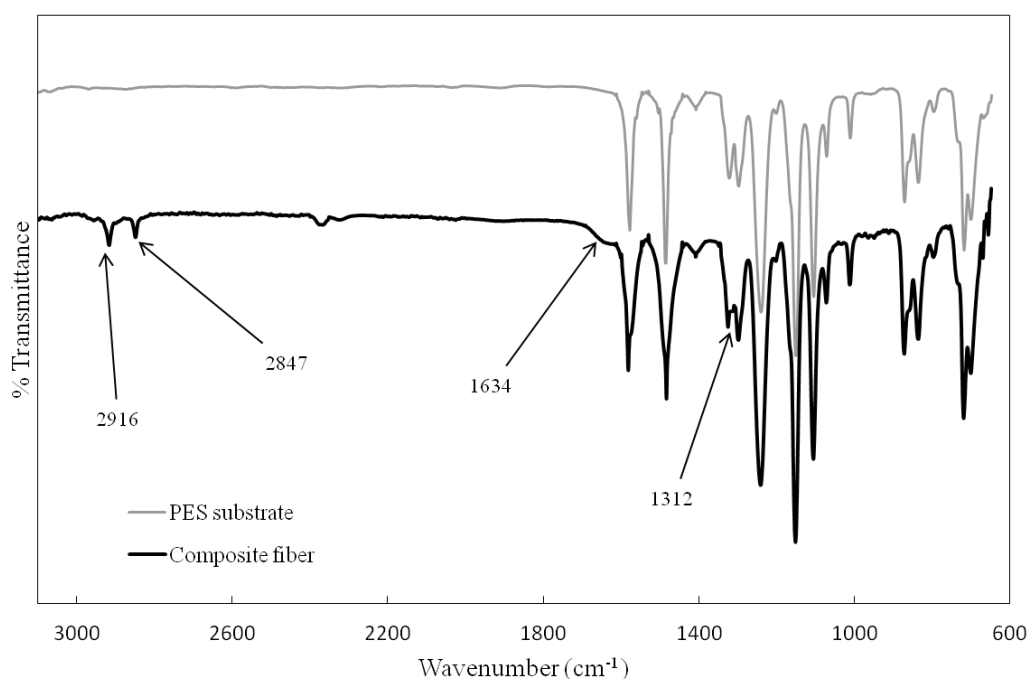


Fig. 3.2 FTIR spectra of PES substrate and composite hollow fiber membrane (aqueous amine solution: 0.25 wt.% PEI, 0.1 wt.% SDS, pH = 11; organic solution: 0.13 wt.% TMC; reaction time = 240 s).

From the spectra shown in Fig. 3.2, several new peaks were noticed after the reaction. The characteristic peak of amide was detected at about 1634 cm<sup>-1</sup>, indicating the successful polymerization between amine groups from PEI and acyl chloride groups from TMC. In addition, the new -COO<sup>-</sup> peak at 1312 cm<sup>-1</sup> signified that unreacted acyl chloride groups from TMC presented in the developed thin-film and was hydrolyzed to carboxyl groups. Furthermore, the characteristic peaks of protonated primary and secondary amines (-NH<sub>3</sub><sup>+</sup> and -NH<sub>2</sub><sup>+</sup>) were identified at 2916 cm<sup>-1</sup> and 2847 cm<sup>-1</sup>, respectively (Lin-Vien, Colthup *et al.* 1991). Those peaks

indicated that excess primary and secondary amine groups from PEI were remained in the thin-film layer after the polymerization reaction, and protonated in storage DI water with neutral pH. The substantial presence of protonated amine groups also revealed the cationic nature of the thin-film layer at neutral pH. Based on the FTIR analysis, the reaction scheme and possible structure of interfacially polymerized PEI/TMC network were illustrated in Fig. 3.3.

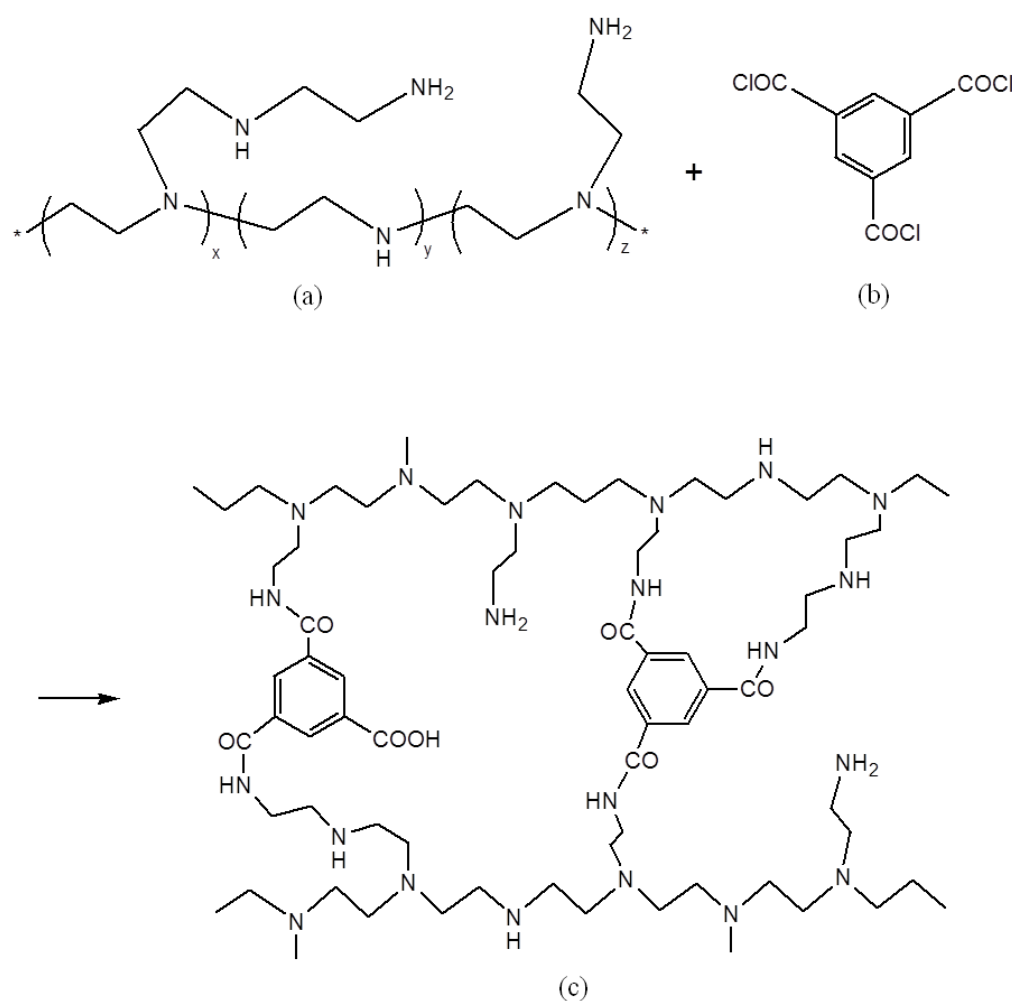


Fig. 3.3 Reaction scheme between (a) branched polyethylenimine (PEI) and (b) trimesoyl chloride (TMC); (c) possible structure of PEI/TMC network.

The surface charges of the composite hollow fiber and PES substrate were measured by streaming potential method with their zeta potential at pH ranging from 3 to 11 shown in Fig. 3.4. It is found that the isoelectric point of the hollow fiber membrane shifted from lower than 3 to 7.2 after the formation of the thin-film

active layer. As interpreted by the FTIR spectra analysis, both amine and carboxyl groups presented in the thin-film layer. At pH below the isoelectric point, protonation of the amine groups led to a positive membrane surface, whereas the composite fiber possess negative surface charges at pH above the isoelectric point due to the presence of deprotonated carboxyl groups. The zeta potential data of the composite fiber indicates that the membrane exhibits positive charges at the pH range (6.5~7) of the feed solutions involved in the current study.

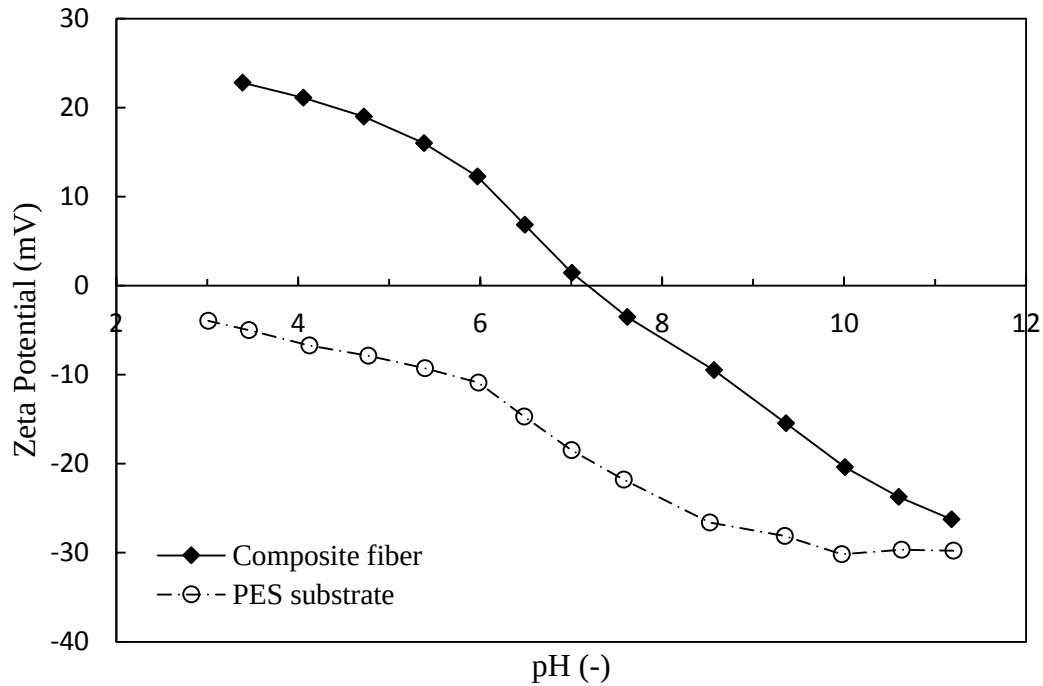


Fig. 3.4 Zeta potential of PES substrate and composite hollow fiber membrane (aqueous amine solution: 0.25 wt.% PEI, 0.1 wt.% SDS, pH = 11; organic solution: 0.13 wt.% TMC; reaction time = 240 s).

The equilibrium contact angle of the PES hollow fiber substrate as well as interfacially polymerized composite membrane was measured and listed in Table 3.1. According to the table, the contact angle of the fiber lumen surface dropped from 76.2° down to 40.9° after the interfacial polymerization, indicating the highly hydrophilic nature of the developed thin-film. The high contents of amine and carboxyl groups introduced from the two monomers, respectively, contribute to the enhanced hydrophilicity and give rise to the water permeability of the composite

membranes.

Table 3.1 Contact angle and mechanical properties of PES substrate and composite hollow fiber membrane<sup>+</sup>

| Membrane        | Contact angle<br>(°) | Tensile modulus<br>(MPa) | Yield stress<br>(MPa) | Yield strain<br>(%) |
|-----------------|----------------------|--------------------------|-----------------------|---------------------|
| PES substrate   | 76.2 ± 1.7           | 90.3 ± 1.5               | 5.1 ± 0.2             | 57.6 ± 3.7          |
| Composite fiber | 40.9 ± 0.8           | 95.4 ± 1.6               | 5.8 ± 0.2             | 63.0 ± 4.5          |

<sup>+</sup>Aqueous amine solution: 0.25 wt.% PEI, 0.1 wt.% SDS, pH = 11; organic solution: 0.13 wt.% TMC; reaction time = 240 s.

Table 3.1 also summarized the mechanical properties of the substrate and composite hollow fibers including tensile modulus, yield stress and yield strain. It can be concluded that the mechanical strength of composite hollow fibers depends essentially on the characteristics of the UF substrate. Although the addition of a dense thin-film layer created marginal reinforcement on the mechanical properties of the fiber, the nature of the substrate material and structural conformation of the fiber dominated the mechanical strength of the composite fiber ultimately.

### 3.3.2 Effects of interfacial polymerization parameters

The separation performance of a composite NF hollow fiber membrane is mainly determined by the property of the interfacially polymerized thin-film active skin layer. Therefore, with other interfacial polymerization parameters kept the same as the ones described in Section 3.2.2, the influences of individual parameters were investigated to identify the optimal conditions for the best active skin. Performance of the resultant composite hollow fibers was evaluated in terms of PWP and salt rejection using a 1000 ppm MgCl<sub>2</sub> feed solution under trans-membrane pressure of 2 bar.

#### i) PEI molecular weight and SDS concentration

With the same concentration of PEIs involved, the effects of different molecular weights of PEI and different concentrations of SDS in aqueous amine solution on the formation of selective layer were investigated and summarized in Table 3.2.

Table 3.2 Effect of PEI molecular weight and SDS concentration on composite hollow fiber membrane performance<sup>+</sup>

| PEI molecular weight (Da) | SDS concentration (wt.%) | PWP (l/m <sup>2</sup> h bar) | MgCl <sub>2</sub> rejection* (%) |
|---------------------------|--------------------------|------------------------------|----------------------------------|
| 800                       | -                        | 10.2                         | 50.7                             |
|                           | 0.1                      | 1.7                          | 96.5                             |
| 50,000~100,000            | -                        | 29.7                         | 31.7                             |
|                           | 0.05                     | 15.6                         | 95.7                             |
|                           | 0.1                      | 16.5                         | 96.5                             |
|                           | 0.2                      | 11.9                         | 94.3                             |
|                           | 0.4                      | 15.1                         | 49.7                             |
| 750,000                   | -                        | 46.0                         | 26.5                             |
|                           | 0.1                      | 31.8                         | 64.9                             |

<sup>+</sup>Aqueous amine solution: 0.25 wt.% PEI, pH = 11; organic solution: 0.13 wt.% TMC; reaction time = 120 s.

\*Obtained using 1000 ppm MgCl<sub>2</sub> feed solution under hydraulic pressure of 2 bar.

The experimental results reveal that a proper selection of molecular weight of the PEI used as a monomer is important for a successful interfacial polymerization reaction. It seems that the PEI with a small molecular weight of 800 Da formed a skin layer with a highly tightened structure suggested by its extremely low PWP, while the membrane made of 750,000 Da PEI exhibited higher water permeability but poor salt rejection. The composite membrane made of PEI with a molecular weight of 50,000~100,000 Da appeared to have the best performance in terms of water flux and salt rejection.

It has been reported that interfacial polymerization reaction takes place at the organic phase side of the interface instead of the aqueous phase because of the highly non-favorable partition coefficient for the acyl chloride, which limits the availability of the acid chloride in the aqueous phase (Freger 2005). As a result, the

diffusion rate of PEI molecules from the aqueous phase into the organic phase controls the extent of polymerization reaction. A high molecular weight might lead to an ineffective diffusion of PEI and thus slow the polymerization reaction. Consequently, an insufficiently polymerized thin-film layer could be formed with defects.

In addition, it can be seen from Table 3.2 that SDS, as an additive in the aqueous phase, plays a crucial role in the formation of thin-film skin layer. The resulting membranes from three types of PEI experienced a dramatic boost in  $\text{MgCl}_2$  rejection when SDS was introduced into the aqueous amine solution. The presence of SDS in the aqueous phase enhanced the miscibility of the two phases and helped with PEI diffusion, and facilitated the attachment of the polymerized thin-film layer to the PES substrate so that a uniform and defect-free dense skin layer could be synthesized (Jegal, Min *et al.* 2002). However, at a high SDS concentration (0.4 wt.%), an increase in PWP and a reduction in salt rejection were observed, because of the formations of the polyamide-SDS complex and free micelles, which results in defects and cracks occurring in the thin-film layer (Mansourpanah, Madaeni *et al.* 2009). In the current study, the membranes developed from PEI with molecular weight of 50,000~100,000 Da with either 0.05 or 0.1 wt.% SDS as the additive exhibited superior performance. The SDS concentration was therefore kept at 0.1 wt.% for remaining efforts of the current work.

#### ii) TMC and PEI concentrations

Fig. 3.5 shows the effect of TMC concentration on the performance of composite hollow fibers with constant PEI concentration. With the increase of TMC concentration, the PWP of the resultant membranes decreased continuously and salt rejection increased until a plateau at ~98%  $\text{MgCl}_2$  rejection was reached when the TMC concentration was greater than 0.2 wt.%. This observation is consistent with the typical nature of organic monomers reported in literature (Verissimo, Peinemann *et al.* 2005; Yang, Zhang *et al.* 2007; Li, Zhang *et al.* 2009), where the increase of monomer concentration only gave rise to more intense polymerization reaction and yielded a denser selective layer with lower PWP and better salt rejection.

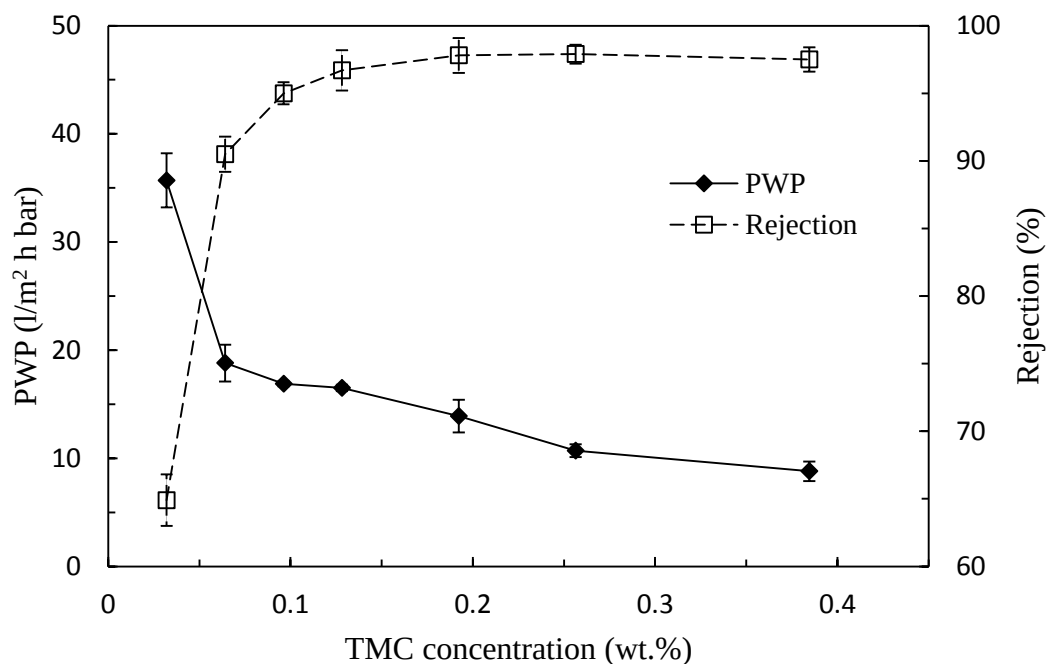


Fig. 3.5 Effect of TMC concentration on composite hollow fiber membrane performance (aqueous amine solution: 0.25 wt.% PEI, 0.1 wt.% SDS, pH = 11; reaction time = 120 s; rejection was obtained using 1000 ppm  $\text{MgCl}_2$  feed solution under hydraulic pressure of 2 bar).

In contrast, a different trend was observed for the impact of increasing PEI concentration. Fig. 3.6 illustrates the effect of PEI (50,000~100,000 Da) concentration with other preparation parameters kept constant. as shown in the figure, when the PEI concentration was low, the increase of PEI concentration led to slightly decreased PWP and increased salt rejection, which was similar to the effect of increasing TMC concentration. However, once the PEI concentration was higher than 0.5 wt.%, the water permeability increased with elevated PEI concentration sharply, but there was a significant loss of salt rejection. It was found that best combination of water permeability ( $16.5 \text{ l/m}^2 \text{ h bar}$ ) and  $\text{MgCl}_2$  rejection (96.5%) was attained when the TMC and PEI concentrations were 0.13 wt.% and 0.25 wt.%, respectively.

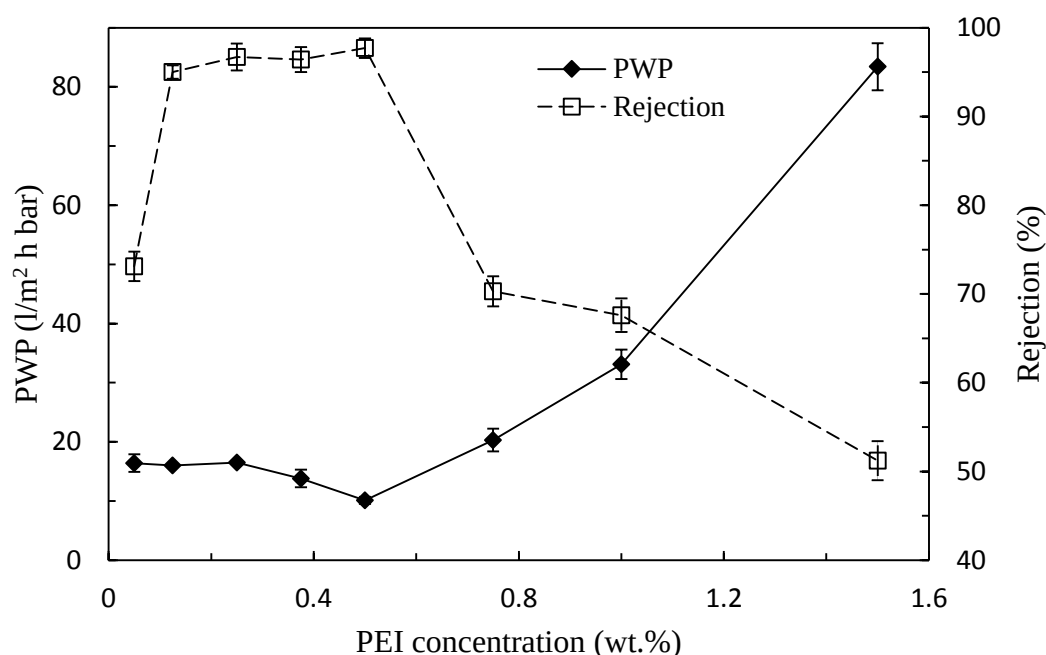


Fig. 3.6 Effect of PEI concentration on composite hollow fiber membrane performance (aqueous amine solution: 0.1 wt.% SDS, pH = 11; organic solution: 0.13 wt.% TMC; reaction time = 120 s; rejection was obtained using 1000 ppm  $\text{MgCl}_2$  feed solution under hydraulic pressure of 2 bar).

The elevation of membrane water flux with high PEI concentrations is most likely attributed to the polymeric nature of PEI, which is different from other monomers with small molecules. Other than the polymerization of two monomers with small molecules, the PEI as a polymer are cross-linked by the TMC molecules during the polymerization reaction, and the TMC molecules play the role of a cross-linker. When a high PEI concentration is involved, the supply of TMC is in deficit, which results in a thin-film layer with low crosslinking density, high water permeability and low salt rejection. A large amount of unreacted amine groups is therefore left in the polymer chain and the resultant thin-film. Whereas the thin-film with higher cross-linking density, lower water flux and higher salt rejection could be obtained providing a lower PEI concentration in the aqueous amine solution. Due to the high degree of cross-linking, the presence of excess amine groups is minimal.

The amount of excess amine groups greatly influence the membrane surface charge

characteristics, which could be measured precisely by streaming potential measurements. Surface charge characteristics for membranes prepared with different PEI concentrations were therefore examined with zeta potential data provided in Fig. 3.7. It can be seen that a higher PEI concentration (1.5 wt.%) led to a higher isoelectric point (10.0), while a lower PEI concentration (0.25 wt.%) corresponded to a lower isoelectric point (7.4). This observation is in accordance with the interpretation that a higher PEI concentration results in a thin-film with lower cross-linking density and a greater amount of unreacted amine groups, which provide extra positive charges at low pH and drift the isoelectric point to a higher value.

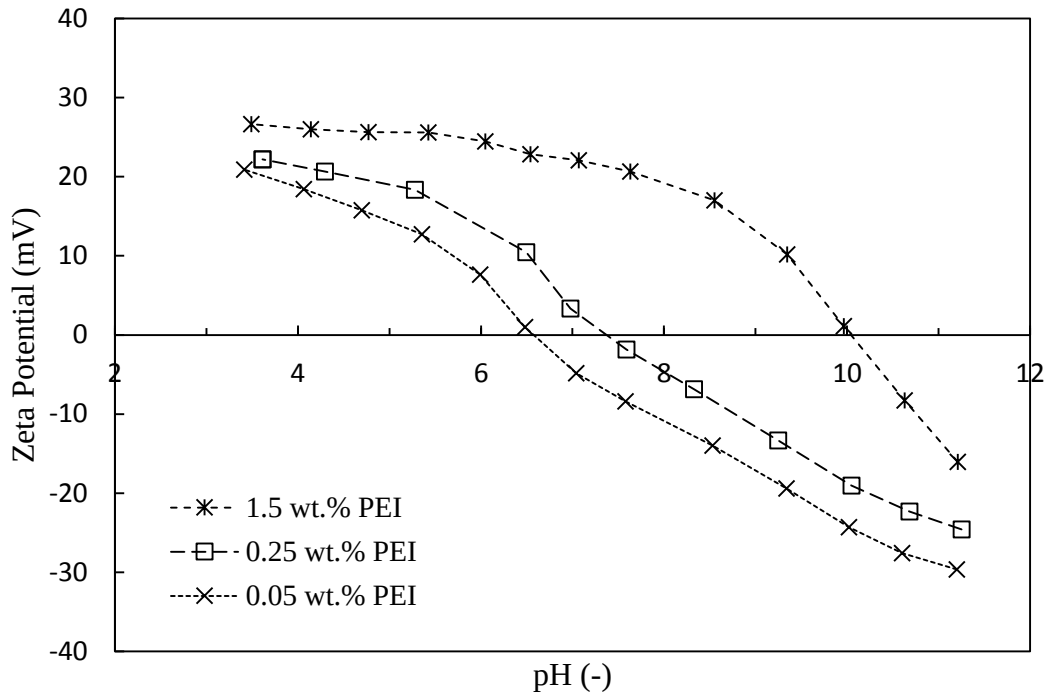


Fig. 3.7 Effect of PEI concentration on membrane surface charge characteristics (aqueous amine solution: 0.1 wt.% SDS, pH = 11; organic solution: 0.13 wt.% TMC; reaction time = 120 s).

### iii) *pH of aqueous amine solution*

The effect of aqueous amine solution pH on the performance of composite hollow fibers was examined and illustrated in Fig. 3.8. With the pH increased from 9 to

11.5, the resulting hollow fibers were able to achieve enhanced salt rejection at the cost of inferior water permeability, and membrane performance reached the highest rejection at pH of around 11. It is well-understood that the polymerization of amines and acyl chlorides produces HCl. The increased alkalinity of the aqueous phase by adjusting the pH would neutralize the HCl effectively and help the reaction moving towards the forward direction. In the meantime, more PEI amines in the aqueous solution, which was initially protonated at lower pH, were deprotonated and retrieved the reactivity with TMC at higher pH. Hence, the polymerization was boosted to a higher degree, leading to a denser thin film with better salt rejection. However, with further increase of pH, the membrane performance dropped quickly. This should be attributed to the fact that acyl chloride could be easily hydrolyzed to carboxylic acid at a high pH, which ultimately lost the rapid reactivity with amines (Li, Zhang *et al.* 2009).

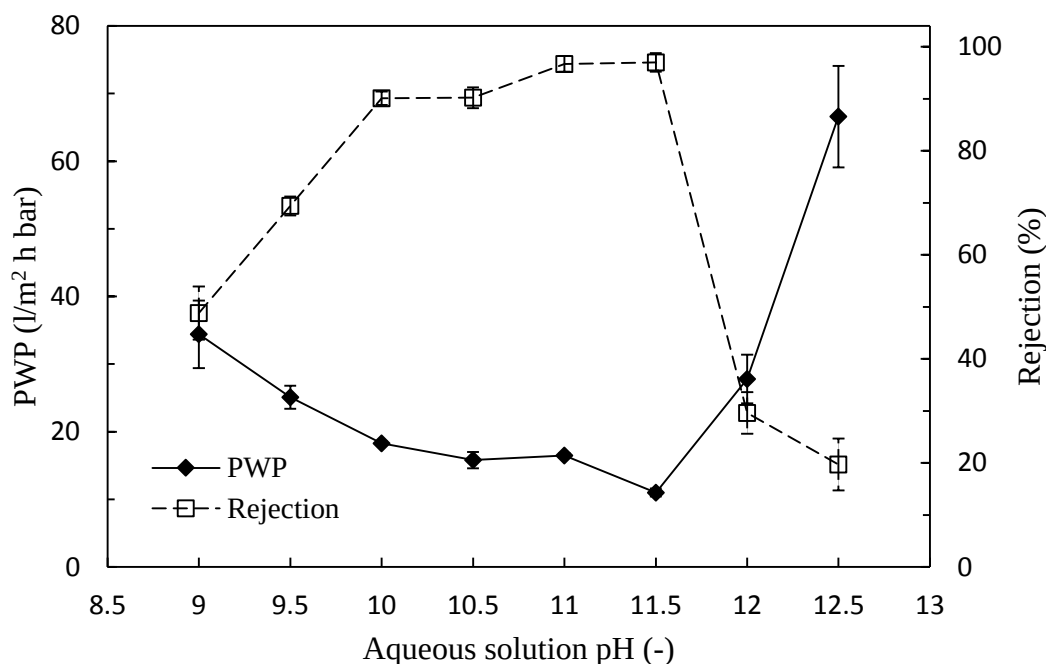


Fig. 3.8 Effect of aqueous solution pH on composite hollow fiber membrane performance (aqueous amine solution: 0.25 wt.% PEI, 0.1 wt.% SDS; organic solution: 0.13 wt.% TMC; reaction time = 120 s; rejection was obtained using 1000 ppm  $\text{MgCl}_2$  feed solution under hydraulic pressure of 2 bar).

iv) *Polymerization reaction time*

The influence of polymerization reaction time i.e. the flow duration of the TMC organic solution through the fiber lumen was explored with results presented in Fig. 3.9. It was noticed that even with a short reaction time of 20 s, a dense thin-film layer was successfully developed and the PWP dropped rapidly from 280 l/m<sup>2</sup> h bar for the PES UF substrate to 13.0 l/m<sup>2</sup> h bar with MgCl<sub>2</sub> rejection of 93.1% for the resulting NF membrane. However, 20 s is too short to control the experimental procedure precisely. It can be seen that with a slight variation in salt rejection, the membrane water permeability increased significantly when the reaction time prolonged from 20 to 240 s. The best membrane performance with PWP of 17.1 l/m<sup>2</sup> h bar and MgCl<sub>2</sub> rejection of 96.7% was achieved at reaction time of 240 s. Decline of PWP was then observed when the reaction time further extended to 360 s.

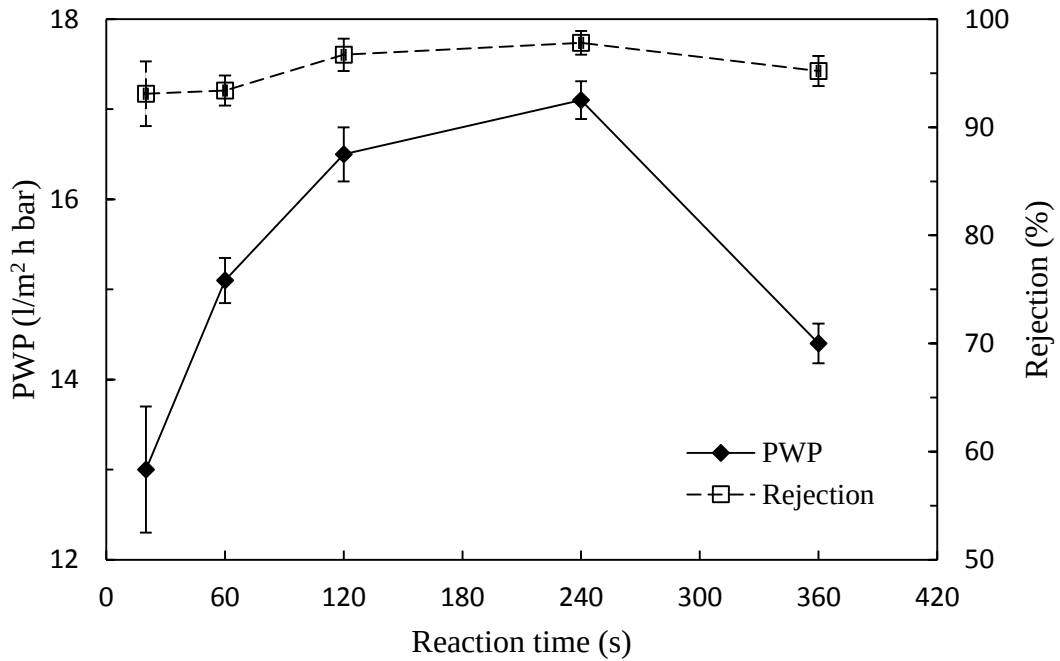


Fig. 3.9 Effect of reaction time on composite hollow fiber membrane performance (aqueous amine solution: 0.25 wt.% PEI, 0.1 wt.% SDS, pH = 11; organic solution: 0.13 wt.% TMC; rejection was obtained using 1000 ppm MgCl<sub>2</sub> feed solution under hydraulic pressure of 2 bar).

According to literature (Chai and Krantz 1994), the growth of interfacially polymerized polyamide thin-film layer was self-limited because the formation of the dense active layer hindered further diffusion of the monomer from the aqueous

phase into the organic phase. In the current work, PEI, as a bulky molecule, was obstructed more easily even the primary thin-film was not tightened to the RO range. This explained the consistency of membrane performance in terms of salt rejection. Meanwhile, as the reaction time was prolonged, more un-reacted acyl chloride groups were introduced by the dynamic flow of TMC solution and eventually hydrolyzed to carboxyl groups (Song, Sun *et al.* 2005). Those acid groups enhanced the hydrophilicity of the thin-film layer and led to improved membrane water permeability. On the other hand, the degree of cross-linking between the two monomers increased with the reaction time and resulted in further growth of the thin-film layer after 300 s (Chai and Krantz 1994). That could be the reason why reduced PWP was observed after 360 s reaction.

The above interpretation was verified by examining the surface charge characteristics of the composite membranes prepared with different reaction times. As indicated by the zeta potential data shown in Fig. 3.10, composite hollow fibers prepared with reaction time of 20, 120 and 240 s possessed the isoelectric points of 8.2, 7.4 and 7.2, respectively, indicating the presence of less amine groups or more carboxyl groups. This observation is in accordance with the interpretation that more carboxyl groups were introduced to the polymerized thin-film layer prepared with a longer reaction time.

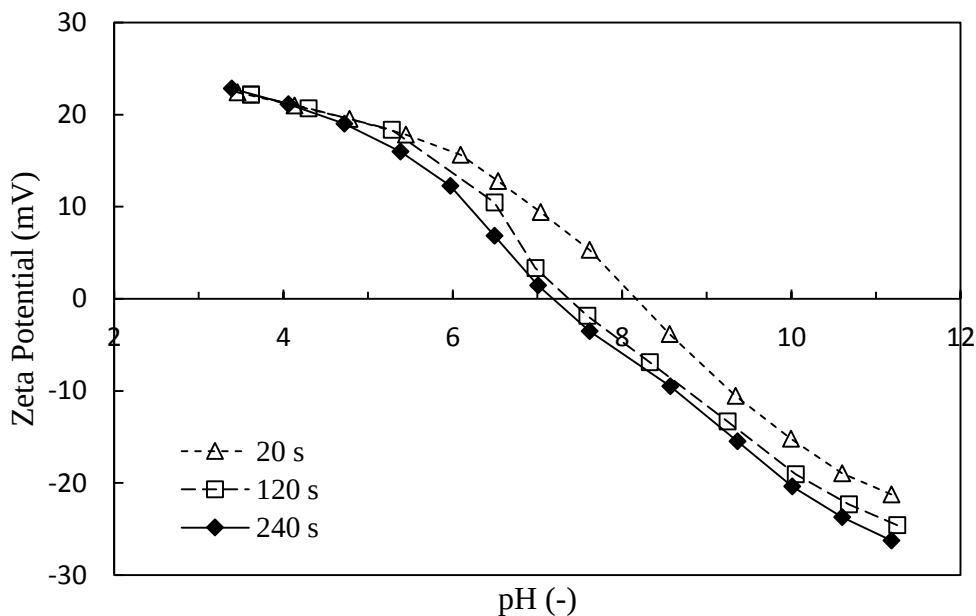


Fig. 3.10 Effect of reaction time on membrane surface charge characteristics (aqueous amine solution: 0.25 wt.% PEI, 0.1 wt.% SDS, pH = 11; organic solution: 0.13 wt.% TMC).

In summary, the optimized thin-film active layer preparation procedure involved an aqueous solution containing 0.1 wt.% SDS and 0.25 wt.% PEI with molecular weight of 50,000~100,000 Da, and the solution pH was adjusted to 11. The TMC was at 0.13 wt.% in the cyclohexane solution and passed through the fiber lumen for the reaction time of 240 s. With the above interfacial polymerization parameters applied, the developed composite hollow fiber membrane was able to achieve a performance with PWP of 17.1 l/m<sup>2</sup> h bar and MgCl<sub>2</sub> rejection of 96.7% under operating pressure of 2 bar. This batch of hollow fibers was utilized for subsequent membrane characterization and further NF applications.

### 3.3.3 Separation properties of composite NF hollow fibers

#### i) Separation of neutral solutes

The nanofiltration performance of the best composite hollow fiber membranes developed was evaluated using 200 ppm feed solutions containing single neutral solute of glucose, sucrose and raffinose, respectively, under 2 bar pressure. The permeation flux and solute rejection are listed in Table 3.3.

Table 3.3 Separation properties of composite NF hollow fibers<sup>+</sup> to neutral solutes.

| Solute    | Molecular weight (Da) | Stokes radius (nm) | Permeation flux* (l/m <sup>2</sup> h) | Solute rejection* (%) |
|-----------|-----------------------|--------------------|---------------------------------------|-----------------------|
| Glucose   | 180                   | 0.359              | 31.7                                  | 81.8                  |
| Sucrose   | 342                   | 0.462              | 28.8                                  | 89.6                  |
| Raffinose | 504                   | 0.538              | 28.6                                  | 90.2                  |

<sup>+</sup>Aqueous amine solution: 0.25 wt.% PEI, 0.1 wt.% SDS, pH = 11; organic solution: 0.13 wt.% TMC; reaction time = 240 s.

\*The permeation flux and solute rejection were obtained using 200 ppm feed solutions under hydraulic pressure of 2 bar.

It was found in the table that the solute rejection increased with the increase of the molecular weight of the solute, while the permeation flux declined with the elevated rejection. Similar results have been attributed to the solute-membrane affinity (Verliefde, Cornelissen *et al.* 2009; Shi, Chou *et al.* 2011). Generally, neutral organic solutes possess higher affinity with polymeric materials than inorganic salts. When high solute rejection is achieved, the solute concentration is highly polarized near the membrane surface, and solutes with high solute-membrane affinity attach to and accumulate on the membrane surface easily. The increased mass transport resistance leads to the decline of permeation flux.

According to the measured solute rejections listed in Table 3.3, the membrane MWCO of around 500 Da was obtained by plotting rejection against solute molecular weight. The Stokes radii of the three solutes were also calculated and listed in Table 3.3. The mean value of effective pore radius attained based on the membrane rejections to 3 different solutes revealed that the effective pore size of the composite membrane was around 0.647 nm in radius or 1.29 nm in diameter. The obtained MWCO and the pore size are within the range of NF membranes.

#### *ii) Separation of inorganic salts*

The separation behavior of the developed composite NF hollow fibers to different inorganic salts was examined by a series of nanofiltration experiments conducted under operating pressure of 2 bar. Each type of feed solutions contains one of the four salts ( $\text{MgCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$ ) with a concentration of 1000 ppm. The respective membrane permeation flux and salt rejection are illustrated in Fig. 3.11.

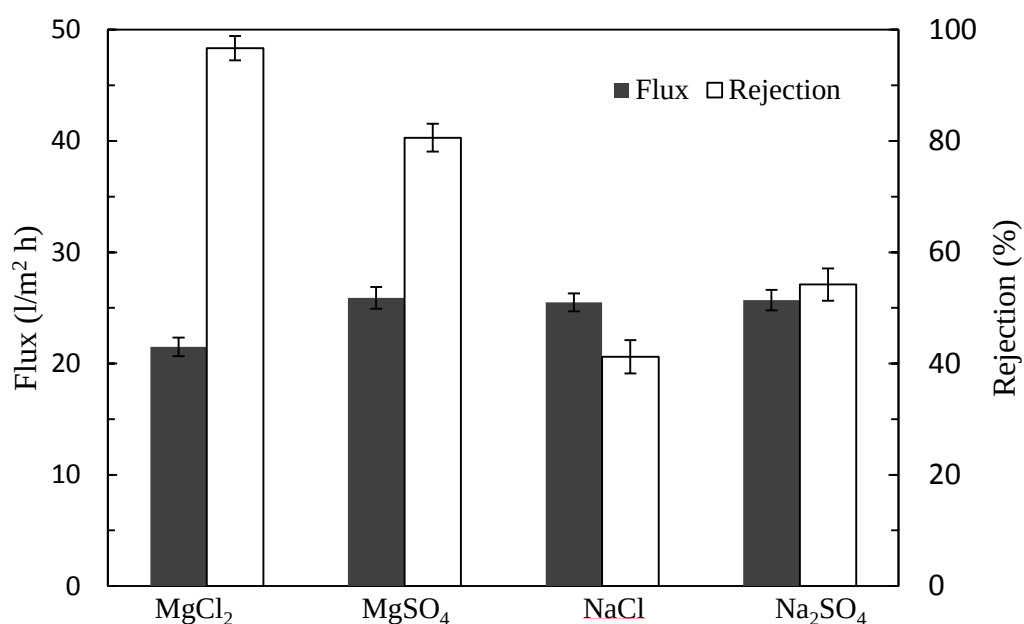


Fig. 3.11 Separation behavior of composite hollow fibers to various inorganic salts (testing using 1000 ppm feed solutions under hydraulic pressure of 2 bar; aqueous amine solution: 0.25 wt.% PEI, 0.1 wt.% SDS, pH = 11; organic solution: 0.13 wt.% TMC; reaction time = 240 s).

It can be seen from the figure that the membrane possessed higher rejection to MgCl<sub>2</sub> (96.7%) than Na<sub>2</sub>SO<sub>4</sub> (54.2%), which suggested that the thin-film layer is positively charged, as stated by the Donnan exclusion principle (Yaroshchuk 2001). This implication is in accordance with the zeta potential data provided in Section 3.3.1 that the composite membrane is positively charged at feed solution pH of 6.5~7. Moreover, the rejection of Na<sub>2</sub>SO<sub>4</sub> is higher than that of NaCl, which is contradictory to the Donnan exclusion principle. In this circumstance, the effect of steric hindrance must be considered. According to the hydrated ion radii summarized in Table 3.4, SO<sub>4</sub><sup>2-</sup> ion has a larger ion size than Cl<sup>-</sup> ion. As the pore size of the composite membrane is close to the size of hydrated SO<sub>4</sub><sup>2-</sup> ion, it gives greater transport resistance to the SO<sub>4</sub><sup>2-</sup> ion and help with the membrane rejection to Na<sub>2</sub>SO<sub>4</sub>. In the meantime, as listed in the same table, the diffusion coefficient of Cl<sup>-</sup> is much larger than SO<sub>4</sub><sup>2-</sup>, which facilitates the solute transport through the membrane. Furthermore, the rejection of the membrane to MgSO<sub>4</sub> (80.6%) was observed to be in between MgCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> rejections. The membrane has poorer

MgSO<sub>4</sub> rejection than MgCl<sub>2</sub> because of the presence of divalent SO<sub>4</sub><sup>2-</sup> ions that greatly affects the cationic electric field provided by the membrane surface and minimizes the effect of Donnan exclusion (Schaep, Van der Bruggen *et al.* 1998), while the better MgSO<sub>4</sub> rejection comparing to Na<sub>2</sub>SO<sub>4</sub> is attributed to the larger size of hydrated Mg<sup>2+</sup> ions. Clearly, the developed composite hollow fiber separates inorganic salts through both Donnan exclusion and steric hindrance, and exhibits typical characteristics of positively charged NF membranes.

Table 3.4 Radius and diffusion coefficient of divalent and monovalent ions.

| <b>Ion</b>                    | <b>Ionic radius<sup>+</sup><br/>(nm)</b> | <b>Hydrated radius<sup>+</sup><br/>(nm)</b> | <b>Diffusion coefficient*<br/>(10<sup>-9</sup> m<sup>2</sup>/s)</b> |
|-------------------------------|------------------------------------------|---------------------------------------------|---------------------------------------------------------------------|
| Mg <sup>2+</sup>              | 0.065                                    | 0.428                                       | 0.706                                                               |
| Ca <sup>2+</sup>              | 0.099                                    | 0.412                                       | 0.792                                                               |
| Na <sup>+</sup>               | 0.095                                    | 0.358                                       | 1.334                                                               |
| Cl <sup>-</sup>               | 0.181                                    | 0.332                                       | 2.032                                                               |
| SO <sub>4</sub> <sup>2-</sup> | 0.290                                    | 0.379                                       | 1.065                                                               |

<sup>+</sup>The ionic and hydrated radii were reported by (Nightingale 1959).

<sup>\*</sup>The diffusion coefficients were reported by (Samson, Marchand *et al.* 2003).

The separation characteristics of the composite hollow fiber with respect to operating pressure were explored and the permeation flux and rejection to a 1000 ppm MgCl<sub>2</sub> feed solution under operating pressure from 2 to 7 bar was plotted in Fig. 3.12. When the same membrane was applied to a 1000 ppm MgCl<sub>2</sub> feed solution, the water permeability dropped from 17.1 for pure water to around 11 l/m<sup>2</sup> h bar (the water flux is 21.8 l/m<sup>2</sup> h at 2 bar pressure, as shown in Figure 9). This is because a 1000 ppm MgCl<sub>2</sub> solution has an osmotic pressure of 0.78 bar, thus the effective driving force is less than 1.3 bar for a high rejection membrane, leading to reduced water permeation.

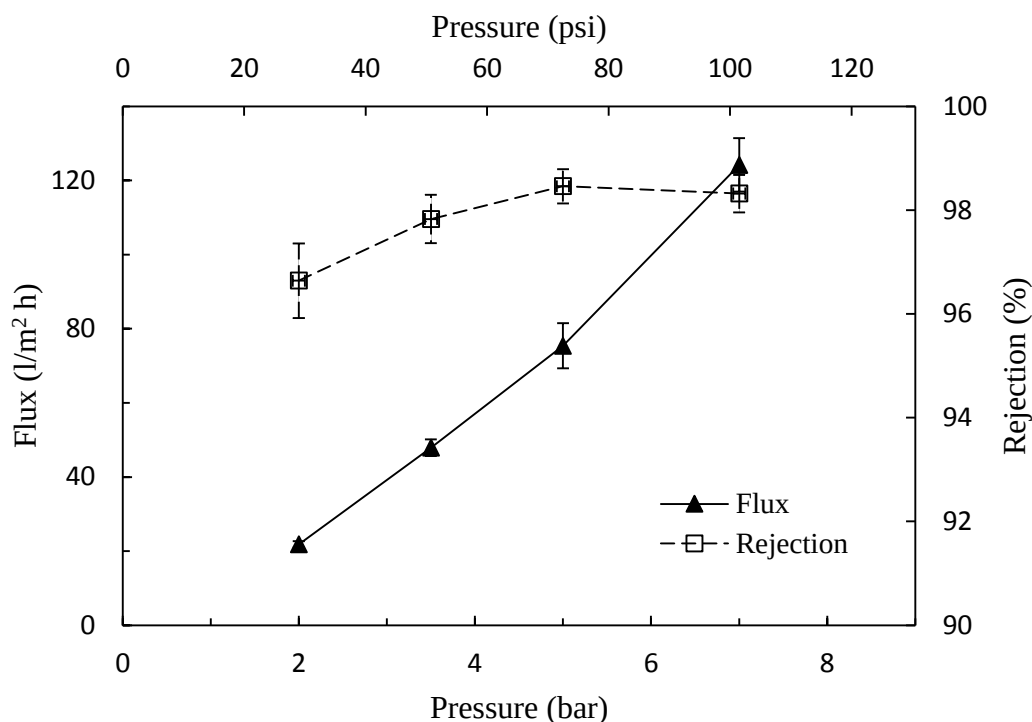


Fig. 3.12 Permeation flux and  $\text{MgCl}_2$  (1000 ppm) rejection of composite hollow fibers under different operating pressures (aqueous amine solution: 0.25 wt.% PEI, 0.1 wt.% SDS, pH = 11; organic solution: 0.13 wt.% TMC; reaction time = 240 s).

It is also observed that permeation flux of the membrane increased from  $21.8 \text{ l/m}^2 \text{ h}$  at 2 bar to  $75.4 \text{ l/m}^2 \text{ h}$  at 5 bar, and the rejection also improved from 96.7% to 98.5%. However, a further increase of operating pressure to 7 bar resulted in a flux jump to  $124.2 \text{ l/m}^2 \text{ h}$  without any rejection increment. Additional permeation flux and  $\text{MgCl}_2$  rejection of the membrane was measured at 3.5 bar after testing at 7 bar, and it was found that the flux was increased from 47.9 to  $52.3 \text{ l/m}^2 \text{ h}$ , and the salt rejection dropped from 96.9% to 94.3% i.e. salt permeation increased from 3.1% to 5.7%. One could interpret from the above observations that the rejection of the membrane reaches the plateau at 98.5%, and operating pressure higher than 5 bar may lead to a structural alteration of the hollow fiber that promote the water permeation by  $\sim 10\%$  at the price of almost doubled salt permeation. Therefore, operating pressure higher than 5 bar could possibly affect the stability of the membrane performance during long-term operation.

The comparison of the composite NF hollow fiber developed in the current work

with several NF membranes reported in the literature is shown in Table 3.5. The reported membranes are all interfacially polymerized and claimed to exhibit positive surface charges. It is observed that the separation performance of the hollow fiber membranes obtained in the current work surpasses the reported cationic composite membranes in terms of both permeation flux and  $\text{MgCl}_2$  rejection at comparable operating pressure and feed solution concentration. Moreover, Table 3.5 also lists the separation performance of various commercial NF flat-sheet membranes. The permeation flux of the resultant hollow fiber appears to be competitive at much lower operating pressure of 2 to 3.5 bar. Superior flux is achieved at 7 bar which is still lower than the pressure applied in most commercial membranes. As for salt rejection, as most commercial NF membranes possess anionic charges, they exhibit higher  $\text{Na}_2\text{SO}_4$  rejections and lower  $\text{MgCl}_2$  rejections comparing to the hollow fiber developed in the current work. The only exception is the UTC-20 membrane. It has a cationic selective skin as claimed by the manufacturer, and thus presents a high  $\text{MgCl}_2$  rejection. It was noted that its performance parameters were obtained under a high operating pressure of 10 bar.

Table 3.5 Comparison of various composite NF membranes.

| Membranes                                   | Permeation flux* (l/m <sup>2</sup> h) | Solute rejection <sup>#</sup> (%) |      |                                 | Operating pressure (bar) | Solute concentration (ppm) | Ref.                                         |
|---------------------------------------------|---------------------------------------|-----------------------------------|------|---------------------------------|--------------------------|----------------------------|----------------------------------------------|
|                                             |                                       | MgCl <sub>2</sub>                 | NaCl | Na <sub>2</sub> SO <sub>4</sub> |                          |                            |                                              |
| Composite NF hollow fiber <sup>a+</sup>     | 21.8                                  | 96.7                              | 41.2 | 54.2                            | 2                        |                            |                                              |
|                                             | 47.9                                  | 97.8                              | -    | -                               | 3.5                      | 1000                       | Present work                                 |
|                                             | 124.2                                 | 98.3                              | -    | -                               | 7                        |                            |                                              |
| TFC NF dual-layer hollow fiber <sup>b</sup> | 24.5                                  | 96.2                              | 85.5 | 61                              | 5                        | 100                        | (Sun, Hatton <i>et al.</i> 2012)             |
| DAPP-TMC flat-sheet <sup>b</sup>            | 32                                    | -                                 | 57   | 35                              | 10                       | 3000                       | (Verissimo, Peinemann <i>et al.</i> 2006)    |
| HPEI/TMC flat-sheet <sup>a</sup>            | 39                                    | 80                                | 45   | 51                              | 4                        | 1000                       | (Chiang, Hsub <i>et al.</i> 2009)            |
| PEK-C NF flat-sheet <sup>c</sup>            | 68.2                                  | 95.7                              | 72.5 | 58.2                            | 6                        | 1000                       | (Li, Wang <i>et al.</i> 2006)                |
| NF-40 <sup>c</sup>                          | 43                                    | 70                                | 45   | 95                              | 20                       | 2000                       | (Nystrom, Kaipia <i>et al.</i> 1995)         |
| NF-270 <sup>d</sup>                         | 53                                    | -                                 | 50   | 98                              | 4.8                      | 2000                       | (Liu, Yu <i>et al.</i> 2008)                 |
| NTR-7450 <sup>c</sup>                       | 92                                    | 13                                | 51   | 92                              | 10                       | 5000                       | (Nystrom, Kaipia <i>et al.</i> 1995)         |
| SU-600 <sup>c</sup>                         | 28                                    | -                                 | 55   | -                               | 3.5                      | 500                        | (Yang, Zhang <i>et al.</i> 2007)             |
| UTC-20 <sup>a</sup>                         | 97                                    | 98                                | 55   | 93                              | 10                       | 1500                       | (Schaep, Van der Bruggen <i>et al.</i> 1998) |

<sup>+</sup> Aqueous amine solution: 0.25 wt.% PEI, 0.1 wt.% SDS, pH = 11; organic solution: 0.13 wt.% TMC; reaction time = 240 s.

\*Permeation flux were obtained using (a) MgCl<sub>2</sub>, (b) pure water, (c) NaCl, or (d) Na<sub>2</sub>SO<sub>4</sub> feed solution.

<sup>#</sup>The “-” sign in the table indicates no test performed or no data reported in the referred literature.

### 3.3.4 Performance of composite NF hollow fibers for low-pressure water softening

Typical hard water streams not only exhibit high contents of hard water metal ions like  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , but also possess modest monovalent cation concentration. Water softening performance of the membrane should therefore assess the permeation of monovalent ions in addition to the rejection of divalent cations. Moreover, the feed solutions with both divalent and monovalent cations better simulate the real water softening application scenario where the interaction among different ions plays an important role in membrane separation. For the current work, the composite hollow fibers with optimal separation performance were challenged by mixed salt solutions with different compositions and concentrations of divalent and monovalent cations with total dissolved salt (TDS) ranging from 200 to 3000 ppm, and the results are summarized in Table 3.6. It is worthy to note that the 2000 ppm TDS mixed salt feed solution was composed of 1000 ppm of  $\text{MgCl}_2$  and 1000 ppm of  $\text{NaCl}$ , while concentrations of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Na}^+$  for the 3000 ppm TDS feed solutions (with and without  $\text{SO}_4^{2-}$ ) were similar to one source of brackish water in Florida (Conlon, Hornburg *et al.* 1990).

Table 3.6 Separation performance of composite NF hollow fibers<sup>+</sup> for feed solution with various ion compositions.

| Feed solution<br>TDS (ppm) | Ion composition (ppm) |                  |               |               |                    | Permeation<br>flux* ( $\text{l/m}^2 \text{ h}$ ) | Ionic rejection* (%) |                  |               |
|----------------------------|-----------------------|------------------|---------------|---------------|--------------------|--------------------------------------------------|----------------------|------------------|---------------|
|                            | $\text{Mg}^{2+}$      | $\text{Ca}^{2+}$ | $\text{Na}^+$ | $\text{Cl}^-$ | $\text{SO}_4^{2-}$ |                                                  | $\text{Mg}^{2+}$     | $\text{Ca}^{2+}$ | $\text{Na}^+$ |
| 200                        | 51                    | -                | -             | 149           | -                  | 31.3                                             | 99.4                 | -                | -             |
| 500                        | 128                   | -                | -             | 372           | -                  | 27.1                                             | 97.8                 | -                | -             |
| 1000                       | 255                   | -                | -             | 745           | -                  | 21.8                                             | 96.7                 | -                | -             |
| 2000                       | 260                   | -                | 390           | 1350          | -                  | 21.1                                             | 94.9                 | -                | 26.6          |
| 3000                       | 128                   | 325              | 629           | 1918          | -                  | 19.9                                             | 91.1                 | 88.8             | 15.2          |
| 3000                       | 128                   | 325              | 595           | 1614          | 338                | 21.2                                             | 84.8                 | 81.0             | 14.3          |

<sup>+</sup>Aqueous amine solution: 0.25 wt.% PEI, 0.1 wt.% SDS, pH = 11; organic solution: 0.13 wt.% TMC; reaction time = 240 s.

\*The permeation flux and ionic rejection were obtained under hydraulic pressure of 2 bar.

As shown in Table 3.6, the developed NF hollow fibers achieved an exceptional water softening performance with flux about 30 l/m<sup>2</sup> h and Mg<sup>2+</sup> rejection over 97.8% when the TDS in the feed solution was lower than 1000 ppm. However, both water flux and Mg<sup>2+</sup> rejection declined to around 20 l/m<sup>2</sup> h and 91% as the TDS increased to 3000 ppm. The decreases of water flux and salt rejection were due to different reasons. The rejection of hard water metal cations is influenced by the ionic strength of the feed solution. The influence of Donnan exclusion is weakened when the membrane is challenged by a high TDS feed with high ionic strength, and steric hindrance becomes the dominant separation mechanism (Chaufer, Rabiller-Baudry *et al.* 1996). More specifically, the high concentration of counter-ions (Cl<sup>-</sup>) shielded the electric field created by the positive membrane charges from repulsing the cations (Mg<sup>2+</sup>) in the feed stream, and consequently, the Mg<sup>2+</sup> rejection reduced. On the other hand, the decrease of permeation flux was owing to the enhanced osmotic pressure difference brought by higher feed TDS. For low-pressure water softening, osmotic pressure difference across the membrane must be taken into consideration, as the driving force provided by the applied pressure is limited comparing to high-pressure RO and NF applications. As long as the rejection was maintained at a high level, the increased osmotic resistance induced by hard water metal ions in high TDS feed streams would result in the decline of permeation flux.

It is also noticed from Table 3.6 that the composite hollow fibers possess high selectivity between monovalent and divalent cations. The rejection for Na<sup>+</sup> ion was as low as 15% while Mg<sup>2+</sup> and Ca<sup>2+</sup> ions were kept above 80% for the 3000 ppm TDS feed streams. It effectively cut down the osmotic pressure difference across the membrane because of the transfer of Na<sup>+</sup> ions to the permeate side. Such separation characteristics benefit the water softening performance of the membrane, especially when a high extent of monovalent cations presents in hard water feed stream.

In addition, it is shown in Table 3.6 that the permeation flux of the membrane increased slightly (from 19.9 to 21.2 l/m<sup>2</sup> h) with about 7% decline in Mg<sup>2+</sup> and Ca<sup>2+</sup> ion rejections when the feed solution possessed the same TDS of 3000 ppm but contained a substantial amount of SO<sub>4</sub><sup>2-</sup>. As discussed in Section 3.3.3, the

decrease of divalent cation rejection was attributed to the presence of divalent  $\text{SO}_4^{2-}$  ions that affected the cationic surface charge of the membrane and further weakened the effect of Donnan exclusion.

Referring to Table 3.6 again, although the  $\text{Ca}^{2+}$  rejection for the 3000 ppm TDS feed was slightly lower than the  $\text{Mg}^{2+}$  rejection due to the marginally smaller hydrated ion radius and higher diffusivity of  $\text{Ca}^{2+}$  ions, it is within the application range for membrane water softening. Clearly, the newly developed composite hollow fiber is applicable for efficient low-pressure water softening with a feed stream TDS as high as 3000 ppm.

### 3.4 Conclusions

Composite NF hollow fiber membranes desirable for water softening under UF-range low operating pressure (<2 bar) were successfully developed. The thin-film selective layer of the composite hollow fiber was formed through interfacial polymerization on the inner surface of a PES UF membrane substrate with branched PEI and TMC employed as the monomers in aqueous and organic phases, respectively.

The influences of various interfacial polymerization parameters on the separation performance of resulting membranes were investigated. A proper molecular weight of PEI and the presence of SDS in the aqueous phase are important for a successful interfacial polymerization reaction when PEI, a polyelectrolyte, is involved as the monomer instead of the monomers with small molecules. The PEI concentration also affected the membrane performance differently comparing to the effect of TMC concentration. In addition, adjusting aqueous amine solution pH towards higher alkalinity helped with the polymerization and yielded higher solute rejection, and the polymerization reaction was observed to be self-limited with respect to a prolonged reaction time.

With optimized preparation parameters, the developed thin-film selective layer

possesses a highly hydrophilic nature with a contact angle of  $40.9^\circ$ . The membrane also exhibits MWCO of 500 Da with an effective pore diameter of 1.29 nm and positive charges. With combined separation mechanism of the Donnan exclusion and steric hindrance, they are able to achieve a PWP of  $17.1 \text{ l/m}^2 \text{ h bar}$  and  $\text{MgCl}_2$  (1000 ppm) rejection of 96.7% under 2 bar operating pressure. For a 3000 ppm TDS feed stream containing salt mixtures, the membrane rejections for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions were kept at around 90% while the water flux was around  $20 \text{ l/m}^2 \text{ h}$  at 2 bar pressure, suggesting the potential of the newly developed composite hollow fibers for effective water softening application. However, the hard water metal ion rejections are found to increase substantially when the feed solution contains the  $\text{SO}_4^{2-}$  group, as the membrane positive charge is neutralized by the divalent counterions, which leads to weakened electrostatic repulsion to the divalent metal ions.

## CHAPTER 4

# Mixed Polyamide-Based Composite NF Hollow Fiber Membranes with Improved Low-Pressure Water Softening Capability

### 4.1 Introduction

Most commercial NF membranes with water softening capability such as NF series manufactured by Filmtec, Desal series by GE-Osmonics, and ESNA series by Hydranautics, are thin-film composite flat sheet membranes with an interfacially polymerized polyamide selective layer (Petersen 1993; Schäfer, Fane *et al.* 2002). The water softening performance of the composite NF membrane is mainly determined by the hydrophilicity, charge and structure of the thin-film active layer, which is basically controlled by the interfacial polymerization (IP) monomers that formed the layer. As a result, the effect of different IP monomers on the polymerization process and the characteristics of the resulted thin film were thoroughly investigated in the past decade. Although piperazine (PIP) and trimesoyl chloride (TMC) were accepted as the most established monomer pair for commercial NF membrane fabrication, various types of amine (Verissimo, Peinemann *et al.* 2006; Yu, Liu *et al.* 2009; Wang, Li *et al.* 2010), acyl chloride (Pandey, Childs *et al.* 2001; Li, Zhang *et al.* 2009), alcohol (Tang, Huo *et al.* 2008) and isocyanate (Huang, Chen *et al.* 2006) were also studied as the IP monomers to develop novel composite NF membranes with improved permeation flux and divalent ion rejection at lower operating pressure, better chemical tolerance and fouling resistance.

As an alternative to PIP and other monomeric amine monomers, polymeric amines such as polyethyleneimine (PEI) (Chiang, Hsub *et al.* 2009), polyamidoamine (Li, Wang *et al.* 2006) and polyvinylamine (Yu, Ma *et al.* 2011) were used as the aqueous phase monomers for the thin film synthesis. Due to the excess amine groups in the polymer chain, polymeric amines usually yield polyamide thin-film active layer with a lower cross-linking degree. NF membranes with higher permeation flux could therefore be obtained, which are able to reduce the required operating pressure for water production and reduce energy consumption. Moreover, unlike conventional negatively charged polyamide thin film made from monomeric IP monomers, the excess amine groups also result in positively charged membrane surfaces. This unique feature makes the membrane better at rejecting divalent metal cations and more favorable for water softening applications, which has been demonstrated in Chapter 3.

In Chapter 3, a type of positively charged NF membrane was prepared with suitable characteristics for water softening under ultrafiltration (UF)-range low operating pressure. The polyamide thin-film selective layer was formed through IP technique on the inner surface of a polyethersulfone (PES) UF hollow fiber membrane substrate with branched PEI and TMC employed as the monomers in aqueous and organic phases, respectively. As an extension of the work presented in the previous chapter, the fabrication of mixed polyamide-based composite NF hollow fiber membranes were reported in this study. By introducing PIP as a co-monomer into the PEI aqueous phase, the resultant hollow fiber membrane was found to exhibit improved low-pressure water softening performance comparing to NF hollow fibers prepared with PEI or PIP alone as the aqueous IP monomer in the IP process, and thus capable for softening of more concentrated and complex water sources. The synergetic effect of PEI and PIP on the formation of the selective layer was also investigated thoroughly in this chapter.

## **4.2 Experimental**

### **4.2.1 Membrane material and chemicals**

The polyethersulfone (PES) UF hollow fiber membrane substrate was fabricated by the phase inversion method through a dry-jet wet spinning process, which is similar to the procedure reported in Chapter 3 Section 3.2.2. The inner and outer diameters of the hollow fiber substrate are 1.01 and 1.37 mm, whereas the pure water permeability and molecular weight cut-off (MWCO) of the substrate fibers are around 270 l/m<sup>2</sup> h bar and 45 kDa, respectively.

Branched polyethyleneimine (PEI) with molecular weights of 50,000~100,000 (MP Biomedicals), piperazine (PIP, Merck), trimesoyl chloride (TMC, Sigma-Aldrich), sodium dodecyl sulfate (SDS, Reagents), and cyclohexane (Merck) were used for the synthesis of thin-film selective skin layer. Other materials have been listed in Chapter 3 Section 3.2.1.

### **4.2.2 Preparation of composite NF hollow fibers by interfacial polymerization**

An aqueous solution was prepared to contain a mixture of PEI and PIP with total amine concentration ranging from 0.05% to 1% (w/v) by varying their mixing ratio, and SDS (0.1% (w/v)) at a solution pH ranging from 9 to 12 adjusted by adding sodium hydroxide and hydrochloric acid. This solution was firstly brought into the lumen of the substrate fibers and in contact with the fiber inner surface for 30 min. After purging the excess aqueous amine solution with pure cyclohexane, a TMC organic solution (0.1% (w/v) in cyclohexane) was then pumped through the fiber lumen for 2 min to allow the IP reaction to take place so that an IP thin-film layer was formed on the fiber inner surface. The detailed procedure for the preparation of interfacially polymerized composite NF hollow fiber membranes can be found in Chapter 3 Section 3.2.2.

### **4.2.3 Hollow fiber characterization and membrane performance evaluation**

The physiochemical properties of the composite NF hollow fiber membranes made from mixed PEI/PIP were examined thoroughly via a series of standard characterization techniques as described in Chapter 3 Section 3.2.3, and compared with composite fibers made using PEI or PIP alone as the aqueous phase monomer. Briefly, the morphology of hollow fiber membranes was observed by a field emission scanning electron microscope (FESEM, JEOL, Japan), while the membrane surface topology and roughness were examined using an atomic force microscope (AFM, Park system, Korea) via the noncontact mode. Besides, the chemical composition of the thin-film selective layer was analyzed using a Fourier transform infrared spectrometer (FTIR, Shimadzu, Japan) via the attenuated total reflection (ATR) method, whereas membrane surface charge characteristics were measured by streaming potential method using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria). Furthermore, the wettability of the membrane was determined by dynamic contact angle measurements using a tensiometer (Data Physics, Germany), and the fiber mechanical properties were characterized by the tensile strength test using a universal testing machine (Zwick, United Kingdom).

Nanofiltration experiments were carried out as described in Chapter 3 with DI water as feed to examine the PWP of the composite NF hollow fiber membranes. Various feed solutions containing neutral solutes, inorganic salts, or salt mixtures were also applied under operating pressure of 2 bar to estimate the pore size, characterize the charge properties and evaluate the water softening performance of the composite membrane, where the permeation flux and solute rejection for each feed solution were measured correspondingly.

## **4.3 Results and discussion**

### **4.3.1 Hollow fiber membrane characteristics**

#### *i) Morphological study*

The cross-sectional and surface morphologies of the PES UF hollow fiber substrate are shown in Fig. 4.1, while the morphologies of composite membranes made with PEI only, PIP only and mixed PEI/PIP as the aqueous phase IP monomer are shown in Fig. 4.2.

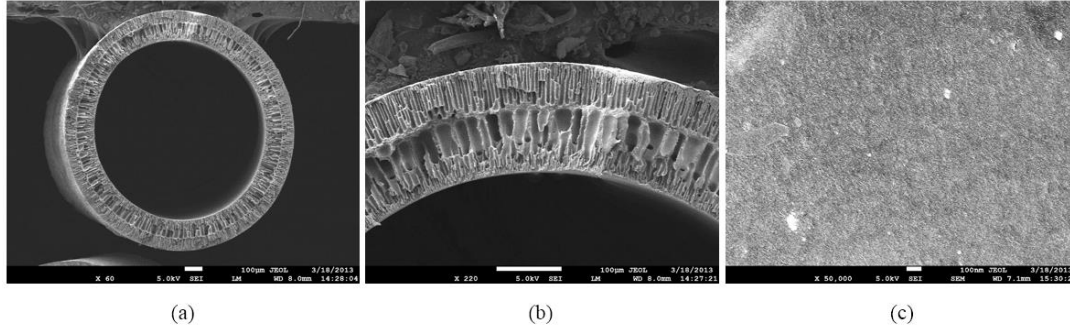


Fig. 4.1 Morphology of PES hollow fiber substrate: (a) cross-section at 50X; (b) enlarged cross-section at 200X; (c) inner surface at 50,000X.

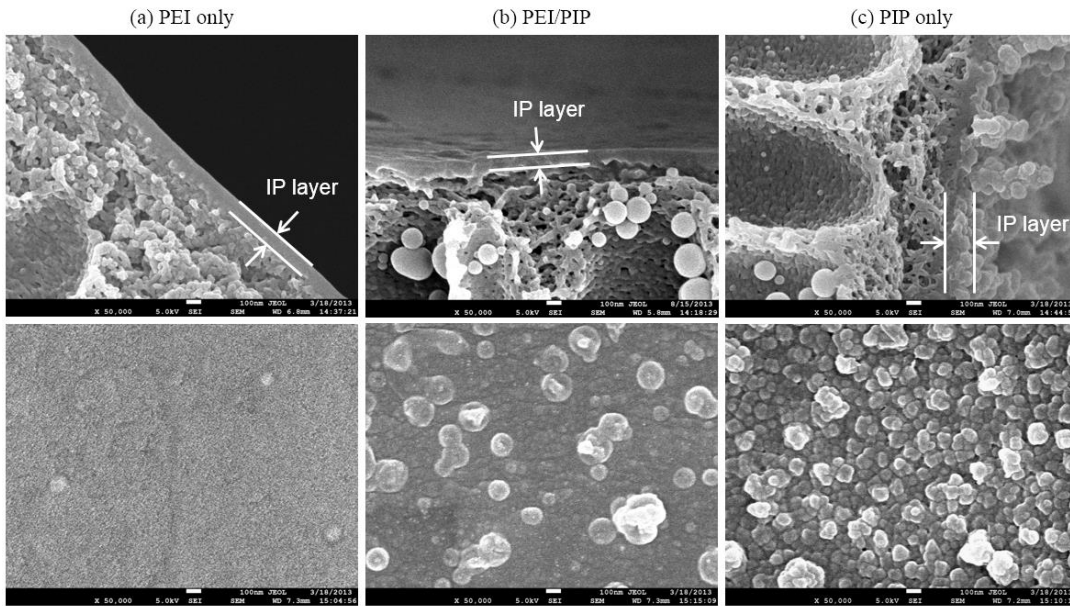


Fig. 4.2 Cross-sectional and surface morphologies of IP thin film formed with (a) PEI only; (b) mixed PEI/PIP and (c) PIP only as the aqueous phase IP monomer.

According to Fig. 4.1, the PES substrate fiber possesses a highly porous cross-sectional structure to minimize the resistance for water transport, and a relatively smooth and tight inner surface without observable cavities to support the formation

of defect-free thin film (Shi, Chou *et al.* 2011). From Fig. 4.2, the IP layer developed from PIP only has the greatest thickness ( $\sim 200$  nm) among the three types of membranes, while the other two membranes possess IP layers with much thinner thickness ( $\sim 100$  nm). As a thicker layer leads to a higher mass transfer resistance, a thinner IP layer is generally preferable in achieving higher water permeation.

In addition, the surface topologies of the three types of composite membranes as well as the PES support fiber were examined via AFM observation with images presented in Fig. 4.3.

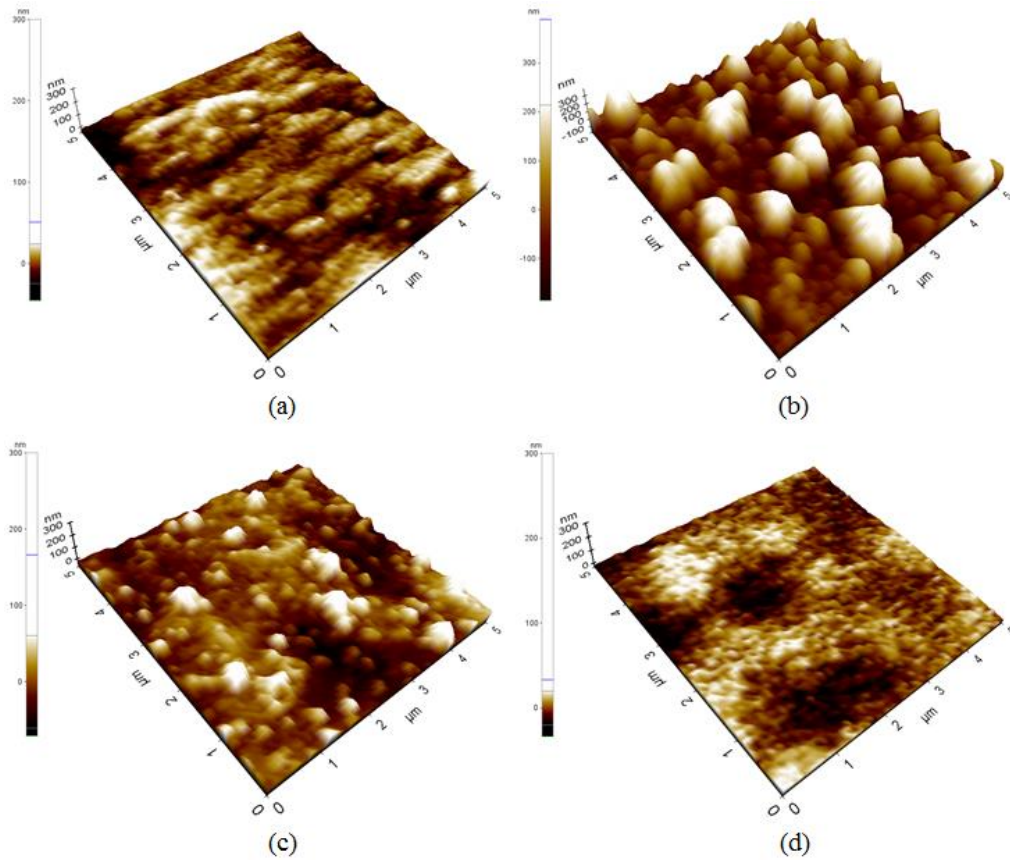


Fig. 4.3 AFM images of the fiber inner surface: (a) PEI only membrane; (b) PIP only membrane; (c) PEI/PIP membrane and (d) PES hollow fiber substrate.

As shown in the figure, the PEI only membrane possesses a smooth surface morphology, while the PIP only membrane has a much rougher surface. These

phenomena should be associated with the nature of the polymerization reaction. According to the discussions in Chapter 3 Section 3.3.2, smaller aqueous phase monomers (PIP) may diffuse more easily into the organic phase and react more rapidly than macromolecular monomers (PEI), hence resulting in a rougher and thicker IP layer on the surface. In addition, the AFM analysis deduced that the surface roughness ( $R_a$ ) of the mixed PEI/PIP membrane (22.4 nm) is in between of the smoother PEI only membrane (11.5 nm) and the rougher PIP only membrane (77.6 nm). This is also in accordance with the SEM observation in Fig. 4.2. Higher surface roughness is considered beneficial to enhance the water permeability of the membrane because it enlarges the effective surface area of the membrane (Hirose, Ito *et al.* 1996).

## ii) FTIR analysis

The chemical compositions of the three types of composite membranes prepared were analyzed by comparing their respective FTIR spectra with the PES support fibers, which are illustrated in Fig. 4.4.

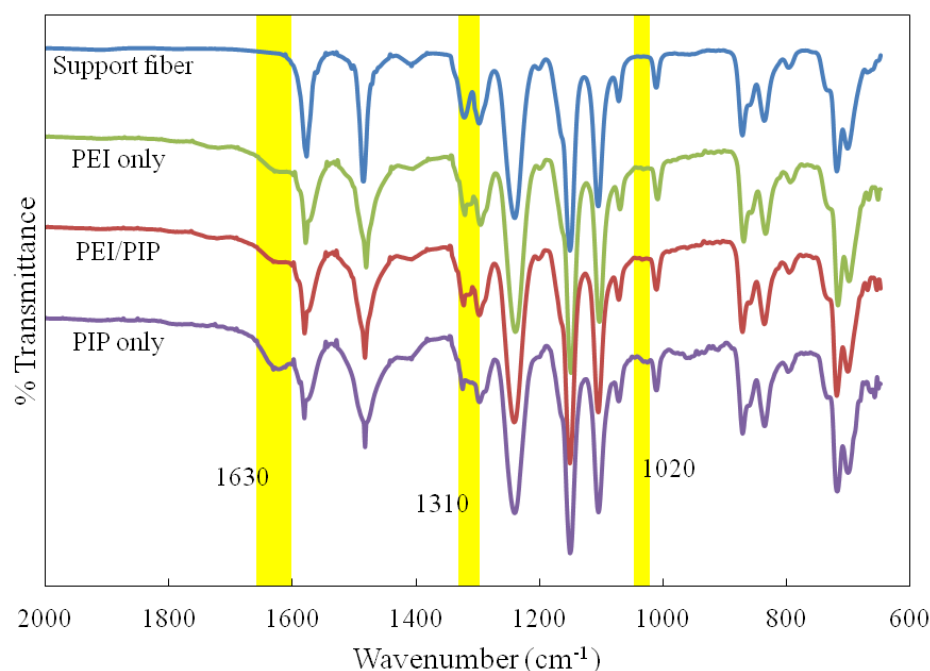


Fig. 4.4 FTIR spectra of PES substrate and composite hollow fiber membranes made using single or mixed amine monomers.

From the spectra shown in Fig. 4.4, the characteristic peak of amide group was detected for all composite membranes ( $\text{C}=\text{O}$  stretch at around  $1630\text{ cm}^{-1}$ ), which confirmed the polymerization reaction between amine groups from PEI and/or PIP and acyl chloride groups from TMC. Among the three composite membranes, the amide peak for PIP only membrane was noted to have the highest intensity, which is consistent with the FESEM observation that the membrane possess the IP thin-film layer with the greatest thickness. Meanwhile, the characteristic peaks of unreacted amine groups ( $\text{C}-\text{N}$  stretch at around  $1020\text{ cm}^{-1}$ ) from PEI and/or PIP as well as hydrolyzed acyl chloride groups ( $\text{C}-\text{O}$  stretch at around  $1310\text{ cm}^{-1}$ ) from TMC (Lin-Vien, Colthup *et al.* 1991) were also spotted for all the composite membranes. Based on the FTIR analysis, the IP reaction scheme between mixed PEI/PIP and TMC as well as possible structure of the resultant mixed polyamide network are illustrated in Fig. 4.5.

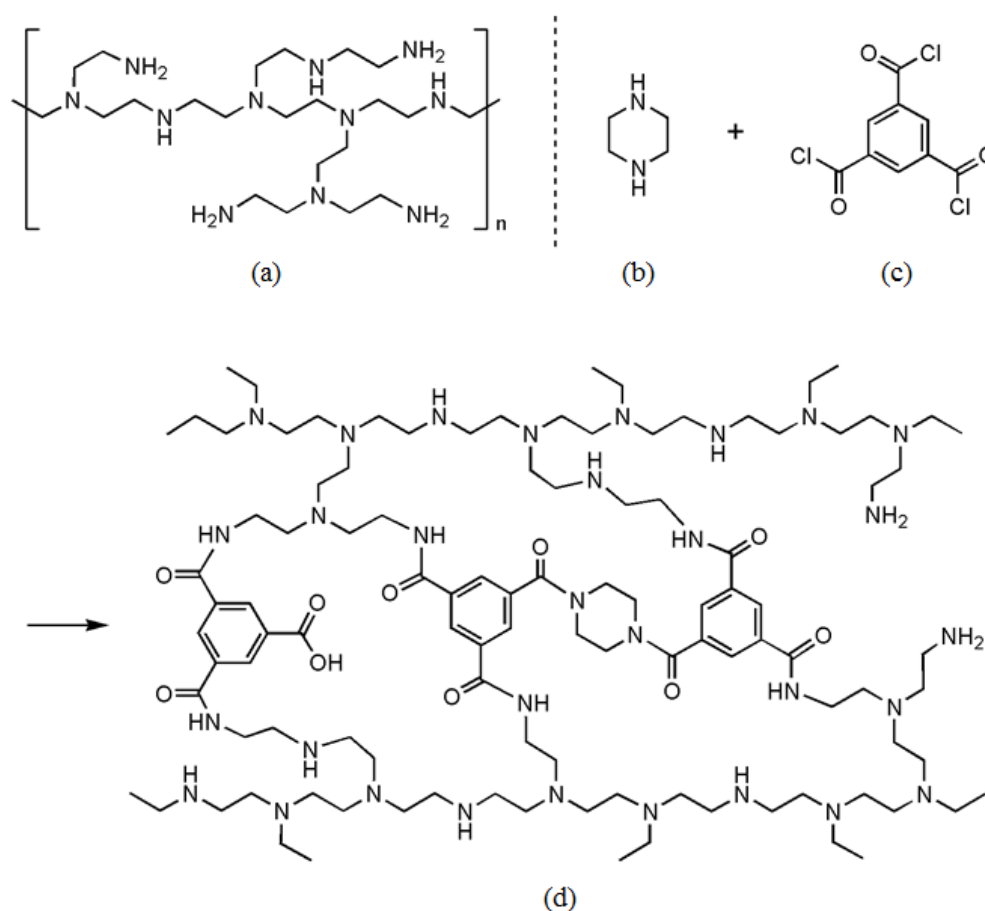


Fig. 4.5 Interfacial reaction scheme between (a) PEI, (b) PIP and (c) TMC; (d) possible structure of resultant mixed polyamide network.

iii) *Zeta potential, contact angle and fiber tensile strength*

The surface charge characteristics of the NF hollow fiber membrane developed from mixed PEI/PIP were measured by streaming potential method, and its zeta potential at pH ranging from 3 to 11 is shown in Fig. 4.6 and compared with the zeta potential of PEI only, PIP only and PES support membranes, whereas the isoelectric point obtained for the four membranes are listed in Table 4.1.

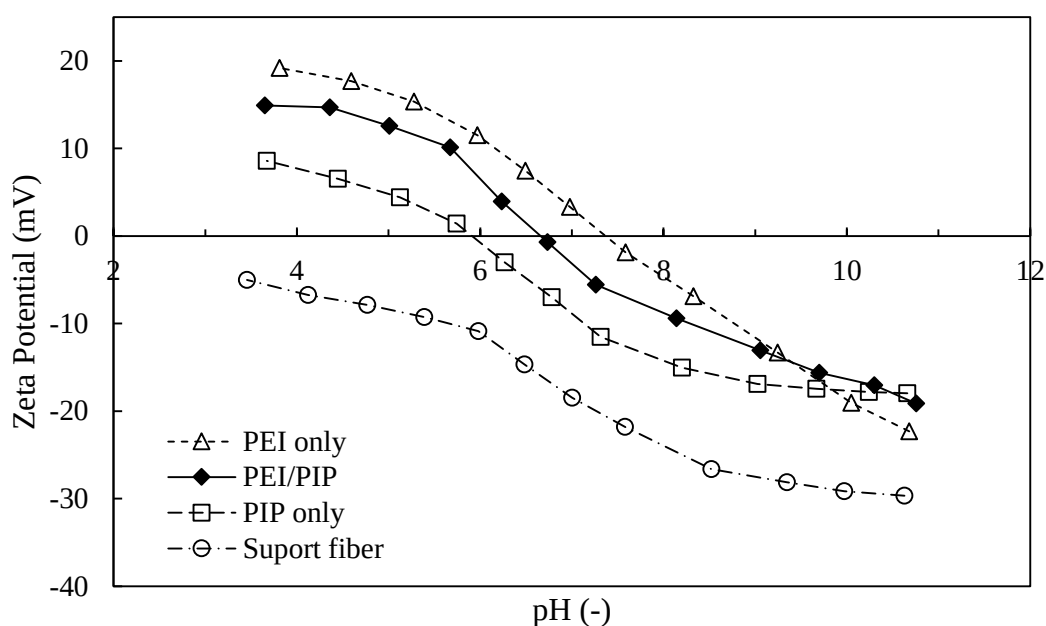


Fig. 4.6 Zeta potential of PES substrate and composite hollow fiber membranes made using single or mixed amine monomers.

Table 4.1 Isoelectric point, contact angle and tensile strength of PES substrate and composite hollow fiber membranes made using single or mixed amine monomers.

| Membrane      | Isoelectric point (pH) | Contact angle (deg) | Tensile modulus (MPa) | Stress at break (MPa) | Strain at break (%) |
|---------------|------------------------|---------------------|-----------------------|-----------------------|---------------------|
| Support fiber | < 3.5                  | 75.4                | 88.2                  | 4.9                   | 63.5                |
| PEI only      | 7.4                    | 39.6                | 95.7                  | 5.6                   | 60.2                |
| PEI/PIP       | 6.7                    | 42.2                | 107.3                 | 5.8                   | 55.9                |
| PIP only      | 5.9                    | 47.7                | 99.6                  | 5.9                   | 58.4                |

Compared with the PES substrate, the three composite membranes have isoelectric points shifted towards a larger pH, and exhibit cationic surface charge characters at pH below the isoelectric point. This is attributed to the protonation of unreacted amine groups brought from PEI and PIP immobilized on the polymerized thin film. Besides, when more PIP and less PEI were presented in the aqueous phase solution, the resultant IP layer became less positively charged in an acidic pH environment. The isoelectric point also went down from 7.4 for the PEI only membrane to 6.7 for the PEI/PIP membrane, and further down to 5.9 for the PIP only membrane. In comparison with the macromolecular PEI, the involvement of small PIP molecules could have increased the degree of polymerization so that the less portion of amine groups are left unreacted to provide the positive charge. Additionally, based on the isoelectric points of the three composite membranes, the PEI only and mixed PEI/PIP membrane surfaces were positively charged, while the PIP only membrane exhibited anionic surface charges within the feed solution pH range (~6.5) for this study.

Moreover, as indicated by the contact angle data listed in Table 4.1, the IP thin-film layer of the three composite hollow fiber membranes were highly hydrophilic compared to the PES support due to the abundant amine and carboxyl groups presented in the IP layer. And the contact angle of the IP layer was found to increase once a higher portion of PIP was involved during the thin film formation. This is in accordance with the zeta potential testing results that more PIP led to a higher degree of polymerization and less unreacted amine groups were on the IP layer to give rise to either the polarity or wettability of the membrane surface.

The mechanical properties of the composite membranes and PES support fibers are also summarized Table 4.1. It revealed that the IP layer increased the tensile strength of the hollow fiber, while the mixed PEI/PIP membrane possessed superior mechanical strength among the three composite fibers. However, the overall mechanical properties of the hollow fiber membrane were dominated by the PES substrate, as the enhancement from the thin-film layer is considered marginal (less

than 20% increase in tensile modulus and yield stress).

#### **4.3.2 Effect of amine solution composition on thin film formation**

Since the separation performance of a composite NF membrane is dominated by the character of its IP thin-film layer, controlling the interfacial polymerization parameters plays a key role to achieve the optimal performance of the resultant composite hollow fibers. The influence of individual IP parameters for the single aqueous phase monomer system has been thoroughly investigated in our previous work presented in Chapter 3, while the aqueous amine solution composition is crucial to the formation of mixed PEI/PIP-based IP thin film. Therefore, with other IP parameters remaining unchanged, the impacts of PEI/PIP mixing ratio, total amine concentration and amine solution pH were examined in sequence. It is worth mentioning that at least two independent experiments were carried out for each preparation condition to ensure the repeatability of results, and the variations in flux and rejection were within 5% and 2%, respectively.

##### *i) Effect of PEI/PIP mixing ratio*

When the total amine concentration was kept at 0.25% (w/v), the effect of PEI/PIP mixing ratio on the performance of resultant composite hollow fiber membrane is illustrated in Fig. 4.7. It can be seen that when the amount of PIP increased from 0% to 5% (w/w) of total amine, both PWP and  $\text{MgSO}_4$  rejection of the membrane increased. According to the discussion in the previous section, the increased surface roughness could explain the improved water permeation with a small amount of PIP addition into the PEI aqueous phase solution, while the enhancement in solute rejection should be attributed to the higher cross-linking density brought by the incorporation of PIP into the PEI-TMC network as confirmed by the FTIR analysis in Section 4.3.1.

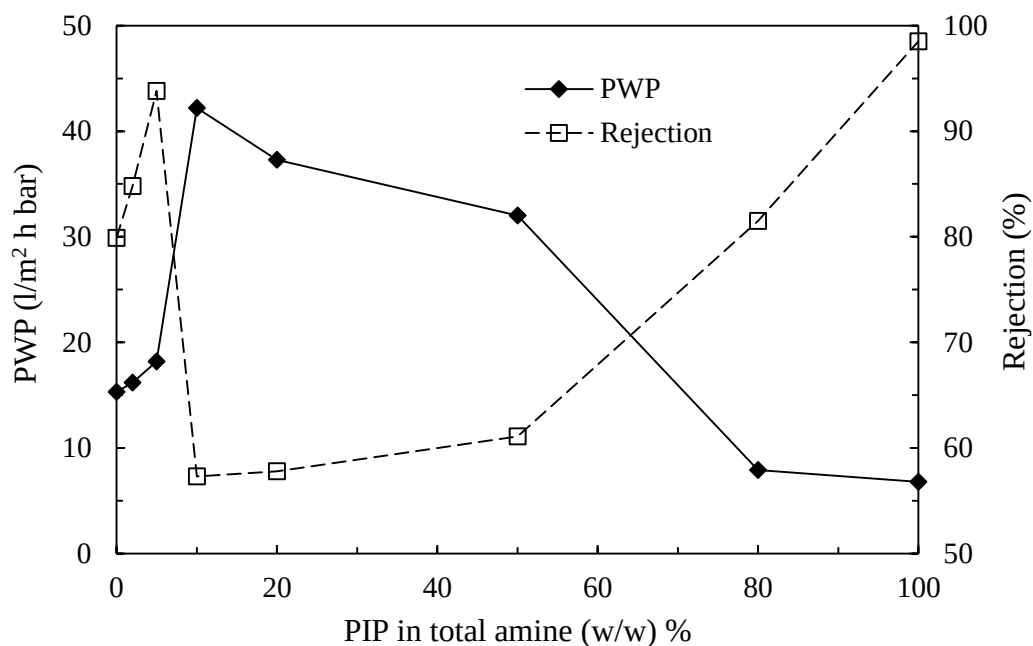


Fig. 4.7 Effect of PEI/PIP mixing ratio on composite hollow fiber membrane performance (total amine concentration = 0.25% (w/v), amine solution pH = 11; rejection obtained via 1000 ppm  $\text{MgSO}_4$  feed solution with operating pressure of 2 bar).

Nevertheless, an increase in PIP amount from 5% to 10% of total amine resulted in a drastic elevation of permeability and a significant drop of solute rejection. However, with a further increase of PIP amount from 10% to 100% of total amine, the resultant membranes went through a gradual rise in solute separation and decrease in water permeation. The interpretation from these two phenomena is probably that the membrane lost its NF scale performance when a comparable amount of PIP and PEI are presented in the aqueous phase at the same time. Due to the competing effect between the two amine monomers, the whole cross-linking reaction was retarded, and the extent of polymerization was therefore reduced. Rather than forming a fully established dense thin film which was the cases for single amine monomer systems, a relatively loose and immature thin film layer was developed for the case of PIP with 5% to 10% of total amine concentration. The competing effect between two amine monomers has been reported in several studies (Ahmad, Ooi *et al.* 2004; Saha and Joshi 2009; Yoon, Hsiao *et al.* 2009). Afterwards,

the quality of the IP layer was believed to be improved gradually.

ii) *Effect of total amine concentration*

As illustrated in Fig. 4.8, when total amine concentration increased from 0.05% to 0.25% (w/v) while the PEI/PIP mixing ratio was kept at 95/5 (w/w), the  $\text{MgSO}_4$  rejection of the resultant mixed PEI/PIP-based composite membrane increased from about 72% to over 93%. However, a 25% decline of water permeability was observed probably due to the fact that a higher monomer concentration leads to more intense IP reaction and results in a denser thin film structure (Verissimo, Peinemann *et al.* 2005; Yang, Zhang *et al.* 2007; Li, Zhang *et al.* 2009). A further increment of total amine concentration in the aqueous phase solution resulted in elevated PWP and reduction in salt rejection. This is in agreement with the trend observed for PEI only as the aqueous phase monomer in Chapter 3. Since the macromolecular PEI was cross-linked by the TMC molecules during the polymerization reaction, a high PEI concentration gave a deficit in TMC, resulting in a thin-film layer with lower cross-linking density, higher water permeability and lower salt rejection as a consequence.

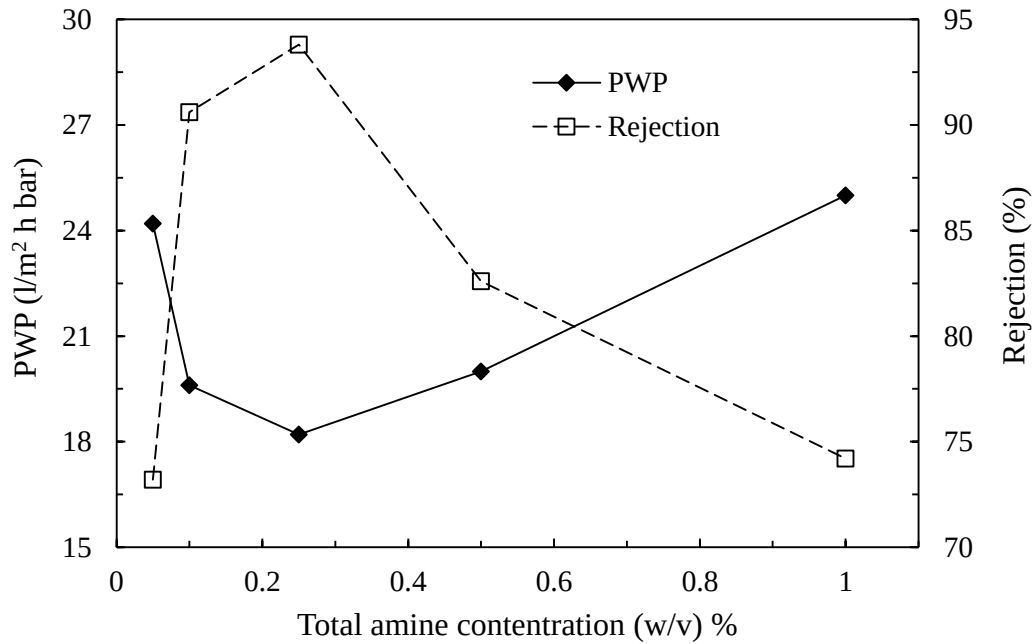


Fig. 4.8 Effect of total amine concentration on composite hollow fiber membrane

performance (PEI/PIP mixing ratio = 95/5 (w/w), amine solution pH = 11; rejection obtained via 1000 ppm  $\text{MgSO}_4$  feed solution with operating pressure of 2 bar).

### iii) Effect of amine solution pH

When the pH of mixed PEI/PIP aqueous solution increased from 9 to 11.5, the resultant composite hollow fiber experienced a drop in water permeability but an enhancement in  $\text{MgSO}_4$  rejection, as revealed in Fig. 4.9. By increasing the pH, the capability for the amine solution to neutralize the hydrochloric acid produced during the reaction between amine and acyl chloride was enhanced, so that the polymerization was promoted toward a higher extent and a tighter thin-film layer with lower permeation to both water and solutes was produced (Yu, Ma *et al.* 2011). In addition, the drop in membrane rejection was observed with a jump in water permeation when the amine solution pH was further increased to 12, which was owing to the hydrolysis of TMC acyl chloride under strong alkaline environment (Ghosh, Jeong *et al.* 2008; Li, Zhang *et al.* 2009).

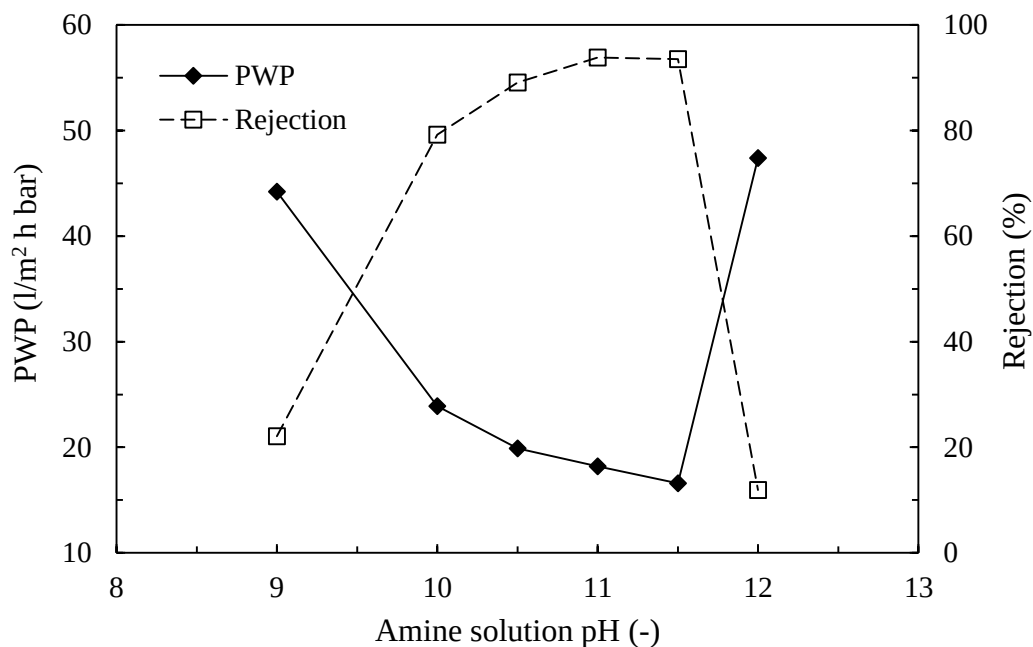


Fig. 4.9 Effect of amine solution pH on composite hollow fiber membrane performance (total amine concentration = 0.25% (w/v), PEI/PIP mixing ratio = 95/5 (w/w); rejection obtained via 1000 ppm  $\text{MgSO}_4$  feed solution with operating

pressure of 2 bar).

Based on the results shown in Figs. 4.7 to 4.9, the PIP amount of 5% in total amine or the PEI/PIP mixing ratio of 95/5 (w/v) with 0.25% (w/v) total amine concentration at solution pH 11 yielded the mixed PEI/PIP-based membranes with the best combination of PWP and solute rejection. This batch of hollow fibers was utilized for subsequent characterization and separation performance evaluation, and compared with single aqueous phase monomer (PEI only or PIP only) membranes made using the identical conditions of amine concentration, solution pH and all other preparation parameters.

### 4.3.3 Separation properties of mixed PEI/PIP-based membrane

#### i) Neutral solute rejection

The rejection behavior of the newly developed composite hollow fiber membranes to neutral solutes was examined using 200 ppm single solute feed solutions containing glucose, sucrose or raffinose, respectively, under 2 bar operating pressure. The Stokes radii of the three neutral solutes as well as their corresponding rejections are listed in Table 4.2.

Table 4.2 Rejection of current composite hollow fiber membranes to various neutral solutes.

| Solute    | Molecular weight (Da) | Stokes radius (nm) | Solute rejection* (%) |         |          |
|-----------|-----------------------|--------------------|-----------------------|---------|----------|
|           |                       |                    | PEI only              | PEI/PIP | PIP only |
| Glucose   | 180                   | 0.359              | 79.1                  | 84.7    | 72.7     |
| Sucrose   | 342                   | 0.462              | 87.0                  | 89.5    | 98.5     |
| Raffinose | 504                   | 0.538              | 89.8                  | 91.0    | 98.8     |

\* Total amine concentration = 0.25% (w/v), amine solution pH = 11 for all three membranes and PEI/PIP mixing ratio = 95/5 (w/w) for PEI/PIP membrane; The solute rejection was obtained using 200 ppm single solute feed solutions under operating pressure of 2 bar.

It can be seen that the PEI/PIP membrane possessed higher rejection to neutral solutes than the PEI only membrane. Since the rejection of NF membranes to neutral solutes is solely based on size exclusion, it suggests that the mixed PEI/PIP monomer yielded a tighter IP thin-film layer comparing to the situation where only PEI involved in the polymerization process.

The MWCO and pore size of the three composite membranes were determined based on the data listed in Table 4.2 and calculated according to the solute transport method described in Chapter 3 Section 3.2.3. The MWCO of the PEI only, PEI/PIP and PIP only membranes were found to be 530, 380 and 270 Da, while the effective pore diameter for the three membranes were around 1.34, 1.27 and 1.09 nm, respectively. All three membranes exhibited MWCO and pore size within the range of NF membranes (Schäfer, Fane *et al.* 2002). It was also discovered from the above data that the PEI/PIP membrane had a small pore size than the PEI only membrane, whereas the PIP membrane possessed the tightest IP thin-film layer. Referring to the discussion regarding the FTIR spectra, the introduction of PIP into the PEI aqueous phase provided additional cross-linking to the original PEI-TMC network, and resulted in a denser pore structure. Likewise, the PIP only membrane exhibited the highest degree of polymerization as interpreted from the FTIR analysis, so its smallest MWCO and pore size were deemed plausible.

#### ii) *Separation of electrolyte solutions*

A series of electrolyte feed solutions with 1000 ppm of  $\text{MgCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{NaCl}$  or  $\text{Na}_2\text{SO}_4$  as the single solute were employed for filtration under an operating pressure of 2 bar, and the respective rejections for the three membranes are illustrated in Fig. 4.10.

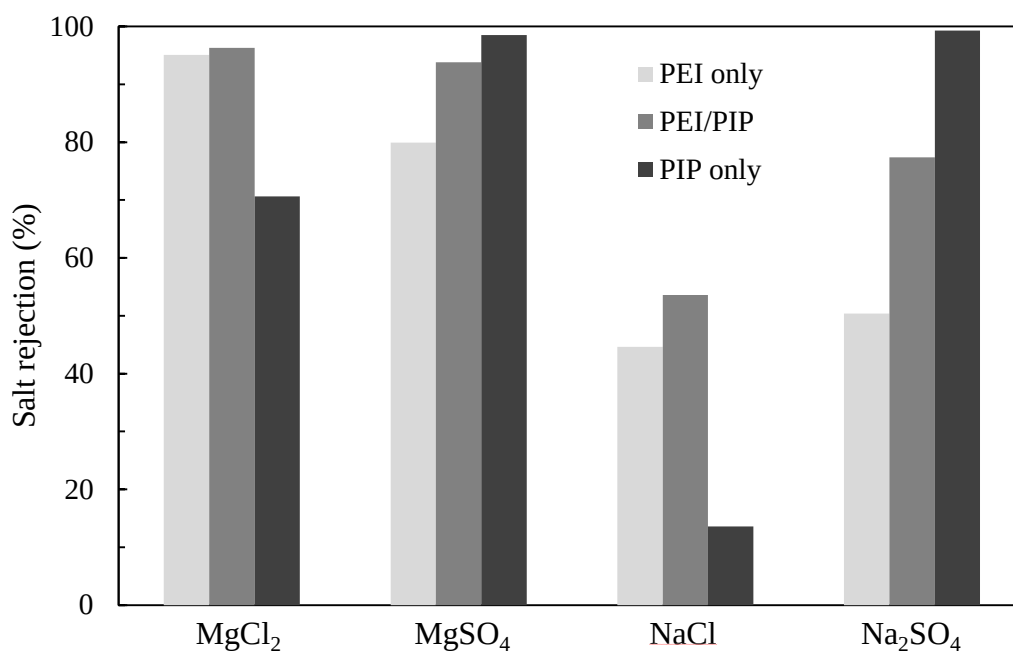


Fig. 4.10 Rejection of three types of composite hollow fiber membranes to different salts (total amine concentration = 0.25% (w/v), amine solution pH = 11 for all three membranes and PEI/PIP mixing ratio = 95/5 (w/w) for PEI/PIP membrane; rejections obtained using 1000 ppm single salt feed solutions under operating pressure of 2 bar).

As shown in the figure, the salt rejections for both PEI only and PEI/PIP membranes decreased in the order of  $R(\text{MgCl}_2) > R(\text{MgSO}_4) > R(\text{Na}_2\text{SO}_4) > R(\text{NaCl})$ , while PIP membrane possessed salt rejections in the order of  $R(\text{Na}_2\text{SO}_4) > R(\text{MgSO}_4) > R(\text{MgCl}_2) > R(\text{NaCl})$ . According to the Donnan exclusion principle, cationic membranes exhibit higher  $\text{MgCl}_2$  rejection than  $\text{Na}_2\text{SO}_4$ , which is opposite to the rejection behavior of anionic membranes (Yaroshchuk 2001). Therefore, the PEI only and PEI/PIP membranes were both positively charged, and the PIP only membrane possessed negative surface charges. The interpretation about the membrane surface charge character is in agreement with the zeta potential data of these membranes provided in Section 4.3.1. In addition, the NaCl rejection was found to be lower than  $\text{Na}_2\text{SO}_4$  for both PEI only and PEI/PIP membranes, and lower than  $\text{MgCl}_2$  rejection for the PIP only membrane. The above rejection behavior is opposing the Donnan exclusion principle, so that the effect of steric hindrance must have been involved during the NF separation. Briefly, the  $\text{Na}^+$  and

$\text{Cl}^-$  ions are smaller in hydrated radii, and receive less hindrance by the membrane pores comparing to the larger  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ions in the aqueous feed solution (Fang, Shi *et al.* 2013).

Furthermore, for all three membranes, the  $\text{MgSO}_4$  rejection appeared to be in between of  $\text{MgCl}_2$  and  $\text{Na}_2\text{SO}_4$  rejections. For cationic PEI only and PEI/PIP membranes, the positive electric field was greatly affected by  $\text{SO}_4^{2-}$ , the divalent counter-ion, and the Donnan effect was weakened. The  $\text{MgSO}_4$  rejection was thus lowered comparing to the case of  $\text{MgCl}_2$ . The higher  $\text{MgSO}_4$  rejection comparing to  $\text{Na}_2\text{SO}_4$  is however attributed to the larger size of hydrated  $\text{Mg}^{2+}$ , the divalent co-ion (Schaep, Van der Bruggen *et al.* 1998). For the PIP only membrane, similar rationale could explain the  $\text{MgSO}_4$  rejection except that the co-ion and counter-ion switched, as the membrane is negatively charged. In summary, for all three currently developed membranes, both surface charge and pore size influenced the salt rejection behavior of the membrane, and neither the effect of Donnan exclusion nor steric hindrance could fully determine the rejection.

Meanwhile, by comparing the rejection data between PEI only and mixed PEI/PIP membranes, it was found that the addition of PIP resulted in improvement of rejection to all four salts, especially  $\text{MgSO}_4$  and  $\text{Na}_2\text{SO}_4$  rejections. As the introduction of PIP into the PEI-TMC network made the resultant IP thin film structure denser, the  $\text{SO}_4^{2-}$  ions could be better retained by the tightened membrane pores through size exclusion. It is therefore expected that the mixed PEI/PIP-based composite NF hollow fiber membrane could be more capable for water softening applications especially when abundant  $\text{SO}_4^{2-}$  or other divalent anions present in the hard water feed stream.

Pure water permeability and salt rejections of the three composite NF hollow fibers are compared in Table 4.3 and benchmarked with several NF membranes available in the commercial market. All the commercial membranes listed in the table are flat-sheet membranes in the configuration of spiral wound modules, and are interfacially polymerized membranes designed for low-pressure operations, as claimed by the

manufacturer (Schaep, Van der Bruggen *et al.* 1998; Nghiem and Hawkes 2007; Liu, Yu *et al.* 2008; Park, Cho *et al.* 2010; Zazouli, Ulbricht *et al.* 2010). According to the table, the mixed PEI/PIP-based membrane possesses the highest water permeability among the three currently developed membranes, and is superior to all the commercial NF membranes in terms of PWP. Its  $\text{MgCl}_2$  rejection is also higher than most of the listed membranes except UTC20 membrane from Toray. However, it should be noted that the high rejections for UTC20 were achieved with 5 times higher operating pressure at 10 bar, and that all the other membranes operates under higher operating pressures than the current study does, even though lower than 10 bar pressure has already been commonly considered as low-pressure NF operation (Schäfer, Fane *et al.* 2002). Regarding the water permeability, NF270 from Dow-Filmtec and TFC-SR2 from Koch, the two commercial NF membranes with higher water permeation, have similar PWP to the current PEI only membrane. However, their rejection behavior and zeta potential data revealed that the membranes are negatively charged at neutral pH (Nghiem and Hawkes 2007), so that they might not be suitable for low-pressure water softening applications due to the ineffectiveness in removing divalent cations. In fact, the rejection profile of the current PIP only membrane is comparable to most of the negatively charged commercial NF membranes.

Table 4.3 Comparison of current composite hollow fibers to various commercially available low-pressure NF membranes.

| Membranes            | PWP (l/m <sup>2</sup> h<br>bar) | Solute rejection (%) |                   |      |                                 | Operating<br>pressure<br>(bar) | Solute<br>concentration<br>(ppm) | Ref.                                            |
|----------------------|---------------------------------|----------------------|-------------------|------|---------------------------------|--------------------------------|----------------------------------|-------------------------------------------------|
|                      |                                 | MgCl <sub>2</sub>    | MgSO <sub>4</sub> | NaCl | Na <sub>2</sub> SO <sub>4</sub> |                                |                                  |                                                 |
| PEI only             | 15.3                            | 95.1                 | 79.9              | 44.6 | 50.4                            |                                |                                  |                                                 |
| PEI/PIP              | 18.2                            | 96.3                 | 93.8              | 53.6 | 77.4                            | 2                              | 1000                             | Present work                                    |
| PIP only             | 6.8                             | 70.6                 | 98.5              | 13.6 | 99.3                            |                                |                                  |                                                 |
| Dow-Filmtec NF90     | 6.7                             | -                    | 97                | 90   | -                               | 4.8                            | 2000                             | (Nghiem and Hawkes<br>2007)                     |
| Dow-Filmtec NF270    | 13.2                            | 60                   | 97                | 51   | 98                              | 4.8                            | 2000                             | (Liu, Yu <i>et al.</i> 2008)                    |
| GE-Osmonics HL       | 6.9                             | -                    | 97                | 33   | -                               | 7.6                            | 1000                             | (Park, Cho <i>et al.</i> 2010)                  |
| Hydranautics ESNA1   | 7.5                             | 89                   | -                 | 93   | -                               | 5.2                            | 500                              | (Park, Cho <i>et al.</i> 2010)                  |
| Koch TFC-SR2         | 14.5                            | -                    | 92                | 20   | -                               | 5                              | 600                              | (Zazouli, Ulbricht <i>et al.</i><br>2010)       |
| Nitto-Denko NTR-7450 | 10.9                            | 16                   | 48                | 53   | 92                              | 10                             | 1000                             | (Schaep, Van der Bruggen<br><i>et al.</i> 1998) |
| Toray UTC20          | 10.2                            | 98                   | -                 | 55   | 93                              | 10                             | 1500                             | (Schaep, Van der Bruggen<br><i>et al.</i> 1998) |

#### 4.3.4 Performance of mixed PEI/PIP-based composite hollow fiber membranes for low-pressure water softening

Water softening performance of the NF membrane is greatly influenced by the quality of feed water with a variety of ionic species. Other than a single electrolyte feed solution, interactions among different ion charges affect the solute transport through the membrane. The rejection of a typical hard water metal ion, i.e. the hardness removal efficiency of the membrane is affected by the presence of other co-ions, concentration and valence of the counter-ions, and total ionic concentration within the feed water (Garcia-Aleman and Dickson 2004). Hence it is necessary to apply feed solutions with a mixture of ionic species in addition to single salt feed solutions in order to better evaluate the membrane water softening performance. Three types of simulated hard water with total dissolved salt (TDS) ranging from 1000 to 5000 ppm and hardness from about 500 to 2000 mg/l as  $\text{CaCO}_3$  were employed as the feed solutions, and their detailed ionic compositions and other properties are listed in Table 4.4. It is worthy to note that Feed 1 was composed of 500 ppm of  $\text{CaCl}_2$  and 500 ppm of  $\text{NaCl}$ , whereas Feed 2 and Feed 3 were prepared according to the ionic concentration of one source of well water in Florida (Reese, District *et al.* 2004) and RO concentrate from an inland desalination plant in Oman (Mohamed, Maraqa *et al.* 2005), respectively.

Table 4.4 Characteristics of simulated hard water feed solutions.

| Parameter                                | Feed 1 | Feed 2 | Feed 3 |
|------------------------------------------|--------|--------|--------|
| TDS (ppm)                                | 1000   | 3000   | 5000   |
| Conductivity ( $\mu\text{S}/\text{cm}$ ) | 2040   | 5840   | 8910   |
| Hardness (mg/l as $\text{CaCO}_3$ )      | 451    | 691    | 1923   |
| $\text{Mg}^{2+}$ (ppm)                   | -      | 102    | 204    |
| $\text{Ca}^{2+}$ (ppm)                   | 180    | 108    | 433    |
| $\text{Na}^+$ (ppm)                      | 197    | 870    | 1104   |
| $\text{Cl}^-$ (ppm)                      | 623    | 1582   | 2515   |
| $\text{SO}_4^{2-}$ (ppm)                 | -      | 338    | 744    |

Table 4.5 Water softening performance of newly developed composite hollow fiber membranes at 2 bar operating pressure.

| Hard water              | Membrane | Permeability<br>(l/m <sup>2</sup> h bar) | Hardness<br>removal (%) | Conductivity<br>removal (%) | Ionic rejection (%) |                  |                 |                 |                               |
|-------------------------|----------|------------------------------------------|-------------------------|-----------------------------|---------------------|------------------|-----------------|-----------------|-------------------------------|
|                         |          |                                          |                         |                             | Mg <sup>2+</sup>    | Ca <sup>2+</sup> | Na <sup>+</sup> | Cl <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> |
| Feed 1                  | PEI only | 9.8                                      | 94.0                    | 69.5                        | -                   | 94.0             | 42.1            | 68.7            | -                             |
|                         | PEI/PIP  | 13.4                                     | 97.4                    | 71.0                        | -                   | 97.4             | 41.0            | 70.0            | -                             |
|                         | PIP only | 6.4                                      | 86.7                    | 42.8                        | -                   | 86.7             | -6.6            | 41.2            | -                             |
| Feed 2                  | PEI only | 8.7                                      | 82.1                    | 34.4                        | 83.3                | 80.2             | 19.0            | 28.8            | 80.3                          |
|                         | PEI/PIP  | 12.8                                     | 90.2                    | 34.3                        | 92.9                | 86.0             | 17.8            | 28.2            | 94.0                          |
|                         | PIP only | 5.8                                      | 82.3                    | 25.2                        | 85.7                | 76.9             | 7.6             | 16.3            | 98.5                          |
| Feed 3                  | PEI only | 7.1                                      | 75.6                    | 32.6                        | 77.8                | 73.8             | 6.7             | 29.0            | 75.3                          |
|                         | PEI/PIP  | 10.0                                     | 86.9                    | 36.7                        | 91.4                | 83.4             | 6.1             | 31.7            | 89.6                          |
|                         | PIP only | 4.7                                      | 77.9                    | 30.2                        | 83.2                | 73.8             | 1.0             | 21.5            | 97.8                          |
| Morocco<br>groundwater* | NF90     | 4.1                                      | 96                      | -                           | 84                  | 97               | 85              | 96              | -                             |
|                         | NF270    | 9.2                                      | 40                      | -                           | 45                  | 40               | 14              | 43              | -                             |

\*Elazhar *et al.* (Elazhar, Habbani *et al.* 2013). Operated at 10 bar operating pressure.

Water softening performance of the mixed PEI/PIP-based composite hollow fibers when dealing with the three types of simulated hard water feed solutions under 2 bar operating pressure is listed in Table 4.5, and compared with the performance of the other two membranes made with PEI or PIP alone as the aqueous phase IP monomer. As shown in the table, the PEI/PIP membrane exhibited greater water softening capability than the other two membranes in term of higher water permeability as well as better hardness removal for all the three types of feed water. Specifically, both PEI only and PEI/PIP showed over 90% hardness removal for Feed 1, while the PEI/PIP membrane possessed better water permeation. Comparing to the other two, the PIP only membrane had poorer rejection to  $\text{Ca}^{2+}$  due to its anionic membrane surface charges.

As for the case of Feed 2, the hardness removal for PEI only membrane decreased to about 82%, while PEI/PIP membrane remained the hardness removal at around 90%. Comparing to Feed 1, an additional divalent counter-ion ( $\text{SO}_4^{2-}$ ) was introduced in Feed 2. The presence of  $\text{SO}_4^{2-}$  ions neutralized the positive charge of the PEI only membrane so that the rejections of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions via Donnan effect were greatly affected. The water softening performance of the PEI only membrane was thus dropped significantly. Whereas the PEI/PIP membrane possesses smaller pore size and the rejection of divalent cations are less dependent on the positive membrane charge but rely more on size exclusion. The hardness removal of PEI/PIP membrane was therefore less interfered by the presence of  $\text{SO}_4^{2-}$  ions.

When the membranes were further challenged by Feed 3, the water permeability for all three membranes declined substantially. The hardness removal for both PEI only and PIP only membranes dropped to less than 80%. The only capable membrane for the effective softening of Feed 3 remained the mixed PEI/PIP-based membrane, with hardness removal kept at about 87%. The reduction in both water permeation and hard water metal ion rejection were mainly attributed to the elevated osmotic pressure difference. According to Table 4.4, the concentration of both co-ions and counter-ions in Feed 3 were higher than the first two types of feed solution, which

resulted in higher osmotic pressure difference during NF operations. When operating pressure was kept as low as 2 bar for the current study, the effective driving force across the membrane reduced significantly, and led to decrease in water permeation as well as the overall ionic rejection.

Table 4.5 also presents one set of water softening data reported in the literature using commercial NF90 and NF 270 membranes with 10 bar operating pressure (Elazhar, Habbani *et al.* 2013). The hard water adopted for the study was from one groundwater source in Morocco. The feed water exhibited TDS of about 2300 ppm, hardness of 1100 mg/l as  $\text{CaCO}_3$ , and the ionic species presented were similar to the Feed 2 in the current study. The result showed that NF270 is ineffective in water softening with only 40% removal of total hardness. NF90 possessed high rejection to hard water metal ions, but the water permeation was lower than the currently developed mixed PEI/PIP-based composite membrane. Moreover, as revealed in the table, NF90 presented high rejection to monovalent ions like  $\text{Na}^+$  and  $\text{Cl}^-$ , whereas the three membranes developed in the current work exhibited much lower rejection to monovalent ions. High rejection to monovalent ions is unfavorable for low-pressure water softening, because it further increases the osmotic pressure difference, which produces an extra energy barrier and affect the water permeation as well as the permeate water quality. The high monovalent ionic rejection also produces highly concentrated brine, and the membrane could thus subject to the problems of severe membrane fouling.

## 4.4 Conclusions

Mixed polyamide-based composite NF hollow fiber membranes with suitable characteristics for water softening under UF-range low operating pressure were successfully developed in the current study. The thin-film selective layer of the composite fiber was formed via interfacial polymerization on the inner surface of a microporous PES hollow fiber substrate with TMC being the organic phase monomer, and a mixture of PEI and PIP were employed as the monomers in the aqueous phase.

The influence of aqueous amine solution composition on the formation of mixed PEI/PIP-based IP thin film was investigated thoroughly. It was found that the mixing ratio of PIP to PEI should be kept relatively large, as the membrane water permeability and salt rejection were enhanced with a small amount of PIP added into the PEI aqueous phase. It was also observed that both the total amine concentration and amine solution pH play important roles in the thin film formation and separation performance of the resultant membrane.

As revealed by the zeta potential and contact angle measurements, the mixed PEI/PIP-based thin-film selective layer exhibited positive surface charges with a highly hydrophilic nature. The optimized NF membrane possessed MWCO of 380 Da, an effective pore diameter of 1.27 nm, and pure water permeability (PWP) of 18.2 l/m<sup>2</sup> h bar. Under the operating pressure of 2 bar, the membrane exhibited rejection of 96.3% and 93.8% to 1000 ppm MgCl<sub>2</sub> and MgSO<sub>4</sub> feed solutions, respectively. The capability of the newly developed membrane for low-pressure water softening were evaluated by employing simulated hard water feed solutions with different ionic compositions and total hardness. By the combining effect of electrostatic repulsion and size exclusion, the mixed PEI/PIP-based composite hollow fiber offers better water softening performance compared with the membranes made with PEI or PIP alone as the aqueous phase IP monomer, and is therefore competent for softening of more concentrated and complex water sources.

## **CHAPTER 5**

# **Composite FO Hollow Fiber Membranes: Integration of RO- and NF-Like Selective Layers to Enhance Membrane Properties of Anti-Scaling and Anti-Internal Concentration Polarization**

### **5.1 Introduction**

In Chapters 3 and 4, the development of composite NF hollow fiber membranes for low-pressure water softening application was explored. Starting from Chapter 5, the NF membrane technology will be applied in forward osmosis (FO) process to assist in the mitigation of internal concentration polarization and scaling in the FO processes. FO-based separation process, that utilizes osmotic pressure difference across the membranes as the driving force, has drawn growing interest for its wide range of potential applications including osmotic power generation (Loeb 2002; McGinnis and Elimelech 2008; Chou, Wang *et al.* 2013), seawater/brackish water desalination (McCutcheon, McGinnis *et al.* 2005; Choi, Choi *et al.* 2009; Elimelech and Phillip 2011), wastewater treatment (Cornelissen, Harmsen *et al.* 2008; Achilli, Cath *et al.* 2009; Cath, Hancock *et al.* 2010), liquid food concentration (Petrotos and Lazarides 2001; Jiao, Cassano *et al.* 2004) and pharmaceutical processing (Nayak and Rastogi 2010; Wang, Teoh *et al.* 2011). Compared with conventional pressure-driven membrane processes, the FO process provides numerous benefits such as lower energy consumption, less membrane fouling and minimal disturbance

to sensitive components in the feed solution, etc. (McCutcheon and Wang 2013).

However, one of the major barriers that hinder the application of FO processes is the lack of optimized membranes that possess high water flux, low salt leakage and good anti-fouling/anti-scaling property during FO operations. From the perspective of mass transfer through the membrane, a desired FO membrane should have an asymmetric structure consisting of an ultra-thin dense active layer for salt rejection and a very thin and porous substrate that not only provides mechanical support, but also mitigates internal concentration polarization (ICP) (Cath, Childress *et al.* 2006). The ICP phenomenon describes the dilution of draw solution inside the substrate (dilutive ICP) when the active layer is placed against the feed solution (AL-FS orientation), or the concentration of feed solution (concentrative ICP) inside the substrate due to the salt leakage when the active layer is facing the draw solution (AL-DS orientation) (Loeb, Titelman *et al.* 1997; Gray, McCutcheon *et al.* 2006; McCutcheon and Elimelech 2006). The ICP occurred in the thick and relatively dense RO substrate has been identified to be the main factor responsible for extremely low water flux of RO membranes when used in FO process (Cath, Childress *et al.* 2006).

Extensive efforts have been made to develop high performance FO membranes, which include commercial FO flat sheet membranes developed by Hydration Technologies Inc. (HTI) (Cornelissen, Harmsen *et al.* 2008; Achilli, Cath *et al.* 2009), thin film composite (TFC) FO hollow fiber membranes (Chou, Shi *et al.* 2010; Wang, Shi *et al.* 2010; Shi, Chou *et al.* 2011), TFC FO flat sheet membranes (Yip, Tiraferri *et al.* 2010; Wei, Qiu *et al.* 2011), FO hollow fibers and flat sheet membrane with an NF-like skin layer (Setiawan, Wang *et al.* 2011; Qiu, Setiawan *et al.* 2012), and dual-layer hollow fibers for FO applications (Yang, Wang *et al.* 2009).

Nevertheless, these efforts are far from sufficient for bringing the FO technology to practical applications. Similar to many other membrane processes, a great challenge that has to be tackled for FO application is membrane fouling/scaling. As discussed in Chapter 2 Section 2.2.3, the AL-DS membrane orientation usually generates a

higher water flux than the AL-FS orientation, but possesses a high fouling/scaling propensity if the feed solution contains organic macromolecules or inorganic scalants that can penetrate into the porous support layer easily, and results in sharply decreased water flux. The concept of double-skinned FO membranes was developed with a secondary skin layer proposed on the substrate to face the feed solution to prevent possible foulant/scalant penetration into the support layer, and the high water flux of AL-DS orientation could thus be fully utilized. The secondary selective layer is also expected to obstruct the diffusion of solutes in the feed solution from diffusing into the substrate and give rise to further ICP effect.

A mathematical model has been derived to analyze the mass transfer in the double-skinned FO membranes, which provides guidance for the membrane design (Tang, She *et al.* 2011), but only a handful of study was conducted to make double-skinned or double dense-layer FO flat-sheet membranes as well as to study their anti-fouling performance (Wang, Ong *et al.* 2010; Zhang, Wang *et al.* 2010; Qi, Qiu *et al.* 2012). This study aims to develop composite FO hollow fiber membranes by integrating RO- and NF-like two selective skins on each side of an ultrafiltration (UF) hollow fiber substrate, and to evaluate its FO performance under certain application scenarios. This double-skinned FO hollow fiber is expected to present better anti-scaling property when the feed solution exhibits high scaling tendency to membrane, or better anti-ICP effect if the feed solution contains divalent salts. To the best of the author's knowledge, no composite FO hollow fiber membranes with an RO-like and an NF-like skin layers have yet been reported.

## 5.2 Theory

Although a comprehensive modeling of double-skinned FO membranes has been provide by Tang et al. (Tang, She *et al.* 2011), the model is based on flat-sheet configuration and the geometric effect of hollow fiber membrane is not taken into consideration. This section aims to specifically fill this gap and quantify the effect of hollow fiber dimension in the modeling of double-skinned FO membranes.

Different from a single-skinned FO membrane, the two skin layers of a double-skinned FO hollow fiber membranes contribute to the overall water and salt permeability coefficients ( $A$  and  $B$  values, respectively) by following the principle of the resistance-in-series model. Unlike double-skinned membranes in flat-sheet configuration, the surface areas of the two selective skins are different for a hollow fiber membrane. Therefore, the water and salt permeability coefficients for the NF-like outer skin need to be normalized as the current study is based on the RO-like inner skin:

$$A'_{out} = \frac{D_o}{D_i} A_{out} \quad (5.1)$$

$$B'_{out} = \frac{D_o}{D_i} B_{out} \quad (5.2)$$

where  $A'_{out}$  and  $B'_{out}$  are the normalized water and salt permeability coefficients for the NF-like outer skin, while  $D_o$  and  $D_i$  are outer and inner diameters of the hollow fiber. Assuming the resistance of the porous support layer is negligible, the formula for the calculation of overall  $A$  and  $B$  is derived as

$$\frac{1}{A} = \frac{1}{A_{in}} + \frac{1}{A'_{out}} = \frac{1}{A_{in}} + \frac{1}{(D_o / D_i) A_{out}} \quad (5.3)$$

$$\frac{1}{B} = \frac{1}{B_{in}} + \frac{1}{B'_{out}} = \frac{1}{B_{in}} + \frac{1}{(D_o / D_i) B_{out}} \quad (5.4)$$

where  $A$  and  $B$  are the overall water and salt permeability coefficients for the double-skinned hollow fibers, whereas  $A_{in}$  and  $B_{in}$ ,  $A_{out}$  and  $B_{out}$  are the water and salt permeability coefficients for the RO-like inner skin and NF-like outer skin, respectively. It should be pointed out that this calculation is also based on the assumption that no concentration polarization takes place inside the substrate structure between the two skins.

The theoretical calculation of NaCl rejection was based on the solution-diffusion model using the  $A$  and  $B$  computed from Eqs. (5.3) and (5.4). As a result, this value indicated the expected overall NaCl rejection throughout the two skin layers in series if no concentration polarization occurred inside porous support layer sandwiched by the two layers.

## 5.3 Experimental

### 5.3.1 Membrane materials and chemicals

Torlon® 4000T (copolymer of amide and imide) (PAI), supplied by Solvay Advanced Polymers (Alpharetta GA), was used for UF hollow fiber substrate preparation. N-Methyl-2-pyrrolidone (NMP, >99.5%, CAS#872-50-4, Merck Chemicals, Singapore) and Lithium chloride (LiCl, anhydrous, CAS#7447-41-8, MP Biomed) were used as a solvent and pore former, respectively.

M-Phenylenediamine (MPD, ≥99%, CAS#108-45-2, Sigma Aldrich), ε-Caprolactam (≥99%, CAS#203-313-2, Merck), trimesoyl chloride (TMC, >99%, CAS#4422-95-1, Sinopharm Chemical Reagent), hexane (>99.9%, CAS#110-82-7, Merck Chemicals, Singapore) were used for interfacial polymerization. Polyethyleneimine (PEI) ethylenediamine end-capped (Sigma Aldrich) was used for chemical modification of the hollow fiber substrate.

Sodium chloride (NaCl, ≥ 99%, Merck) were used to prepare draw solutions with a concentration ranging from 0.5 M to 2.0 M, while 5.0 M NaCl solution was prepared to simulate a brine solution for the dosing system. In addition to NaCl, magnesium chloride (MgCl<sub>2</sub>, hexahydrate), calcium chloride (CaCl<sub>2</sub>, dihydrate), and dipotassium hydrogen phosphate (K<sub>2</sub>HPO<sub>4</sub>, anhydrous) purchased from Merck were involved during the feed solution preparation. Deionized water (Milli-Q, 18MΩcm) was used for the preparation of solutions. All chemicals were used as received.

### 5.3.2 Preparation of double-skinned composite FO hollow fiber membranes

The double-skinned composite FO hollow fiber membrane was made through a three-step preparation. The hollow fiber substrate was firstly fabricated via phase

inversion method. Afterwards, the RO-like active skin layer was prepared on the inner surface of the hollow fiber substrate via interfacial polymerization, and the NF-like outer skin layer was made through chemical modification. Since polyamide-imide (PAI) is a more active polymeric material than polyethersulfone (PES), the chemical modification of PAI membrane can be performed in a milder condition without reaction initiator, high energy source or harsh treatment environment that is needed for the modification of PES membranes (Van der Bruggen 2009; Setiawan, Wang *et al.* 2011). PAI was therefore used as the membrane substrate material in this chapter.

i) *Fabrication of PAI hollow fiber substrates*

The polymer dope of PAI/LiCl/NMP (14/4/82 wt.%) was prepared by dissolving the Torlon® 4000T into NMP solvent. The detailed preparation procedure of polymer dope solution was described by Setiawan *et al.* (Setiawan, Wang *et al.* 2011). Two types of PAI hollow fiber substrates, denoted as PAI#1 and PAI#2, were fabricated by the dry-jet wet spinning method using the same dope composition but different spinning conditions, which are listed in Table 5.1. The details of fabrication method were reported elsewhere (Shi, Wang *et al.* 2007; Shi, Wang *et al.* 2008). The fabricated hollow fibers were soaked in tap water followed by 50% glycerol aqueous solution for 48h, respectively. The membranes were then dried in the air and stored at room temperature for characterization and further use.

Table 5.1 Spinning conditions and parameters

| Parameters                                   | PAI#1     | PAI#2     |
|----------------------------------------------|-----------|-----------|
| Dope composition (PAI/LiCl/NMP) (wt.%)       | 14/4/82   | 14/4/82   |
| Dope flow rate (g min <sup>-1</sup> )        | 6.0       | 6.0       |
| Bore fluid (NMP/H <sub>2</sub> O) (vol.%)    | 25/75     | 25/75     |
| Bore fluid flow rate (mL min <sup>-1</sup> ) | 7.0       | 6.0       |
| Air gap (cm)                                 | 5.0       | 2.0       |
| Take up speed                                | free fall | free fall |
| External coagulant                           | tap water | tap water |
| Spinning temperature (°C)                    | 23        | 23        |
| Spinneret diameter (mm)                      | 1.50      | 1.50      |
| ID of bore fluid needle (mm)                 | 0.70      | 0.70      |

## ii) *Formation of two skin layers*

The RO-like inner skin layer of the double-skinned FO hollow fiber membranes was synthesized by interfacial polymerization (IP) using MPD and TMC as the two basic monomers. The detailed procedures are similar to that used for making thin film composite single layer FO hollow fibers, which were reported previously (Wang, Shi *et al.* 2010; Shi, Chou *et al.* 2011). The NF-like outer skin layer was achieved through the surface modification of the outer surface of PAI hollow fiber substrate. The PAI hollow fiber substrates were immersed into a 1% (w/w) PEI aqueous solution for 90 min at temperature of 70°C to allow the chemical cross-linking between PAI and PEI to occur and eventually formed a dense skin layer on the fiber outer surface.

## iii) *Routes for double-skinned FO membrane preparation*

A double-skinned FO hollow fiber membrane can be prepared through two different routes. A route, designated as –NF/RO route, started with the chemical modification on the outer surface of the PAI UF hollow fiber substrate to produce a chemically cross-linked NF-like intermediate membrane, followed by interfacial polymerization conducted on the inner surface of the NF-like membrane to form an RO-like thin film, resulting in a double-skinned FO hollow fiber membrane. Another route, designated as –RO/NF route, took the reverse preparation procedure, which let interfacial polymerization take place on the substrate lumen first to yield a thin-film composite RO-like intermediate membrane. The outer surface of the RO-like intermediate membrane was chemically cross-linked subsequently to yield the double-skinned FO hollow fibers.

In this study, three types of double-skinned FO hollow fiber membranes were prepared and their designations are listed in Table 5.2 along with that of single-skinned intermediate membranes. For instance, DS#1-NF/RO membrane refers to the membrane made using PAI#1 hollow fiber as the substrate, and the –NF/RO route for an NF-like skin via chemical modification (step 1) and then an RO-like

skin via Interfacial polymerization (Step 2); while PAI#2-RO membrane refers to the RO-like intermediate membranes using PAI#2 hollow fiber as the substrate. All the hollow fiber membranes were stored in DI water prior to characterization and further applications.

Table 5.2 Routes for preparation of single- and double-skinned FO hollow fiber membranes

| Sample     | Substrate | Route  | Preparation step 1         | Preparation step 2         |
|------------|-----------|--------|----------------------------|----------------------------|
| DS#1-NF/RO | PAI#1     | –NF/RO | Chemical modification      | Interfacial polymerization |
| DS#1-RO/NF | PAI#1     | –RO/NF | Interfacial polymerization | Chemical modification      |
| DS#2-RO/NF | PAI#2     | –RO/NF | Interfacial polymerization | Chemical modification      |
| PAI#1-RO   | PAI#1     | –RO    | Interfacial polymerization | -                          |
| PAI#2-RO   | PAI#2     | –RO    | Interfacial polymerization | -                          |
| PAI#1-NF   | PAI#1     | –NF    | Chemical modification      | -                          |
| PAI#2-NF   | PAI#2     | –NF    | Chemical modification      | -                          |

### 5.3.3 Measurements of double-skinned FO hollow fibers

#### i) *Hollow fiber characterization*

PAI substrates, RO-like and NF-like intermediate membranes as well as double-skinned hollow fibers were characterized by a series of standard protocols with detailed procedures described in (Wang, Shi *et al.* 2010), including morphology observation, measurements of pore size and pore size distribution, porosity, contact angle, zeta potential, mechanical strength, etc. The pure water permeability (PWP) and molecular weight cut-off (MWCO) of the PAI hollow fiber substrate were determined by the filtration method (Ren, Li *et al.* 2006). It should be pointed out that the contact angle data of the hollow fiber were measured on an average basis, as neither the lumen side nor the shell side was blocked or covered.

#### ii) *Measurement of membrane intrinsic separation properties*

The intrinsic separation properties of the RO-like and NF-like skin layers as well as

the double-skinned FO membranes were evaluated in the RO mode tested using a bench-scale cross-flow filtration setup. A membrane module was made by sealing five fibers using epoxy in a PTFE tube with a diameter of 6.35 mm and an effective length of 25 cm. DI water with hydraulic pressure up to 1.5 bar was introduced as feed to determine the water permeability coefficient ( $A$  value) of the hollow fibers. For salt permeability coefficient ( $B$  value), salt rejection tests were carried out using 500 ppm NaCl and MgCl<sub>2</sub> aqueous solutions, respectively, and the calculation was based on conductivity measurements (Ultrameter II, Myron L Company, Carlsbad, CA) of the permeate and feed solutions.

To determine the  $A$  and  $B$  values of the RO-like inner skin layer, the feed solution flowed through the lumen of the RO-like intermediate membranes (PAI#1-RO and PAI#2-RO); while for the NF-like intermediate membranes (PAI#1-NF and PAI#2-NF), the feed solution flowed through the shell side of the module to obtain the  $A$  and  $B$  values of the NF-like outer skin layer. The overall  $A$  and  $B$  values of the double-skinned FO hollow fiber membranes were attained through inside-out RO mode test based on the surface area of the inner skin layer.

### iii) *FO performance evaluation*

A lab-scale FO cross-flow setup similar to the unit in (Chou, Shi *et al.* 2010) was used to conduct the FO performance test, and the same membrane modules for RO mode testing were used. Both the AL-DS and AL-FS orientations were evaluated at ~23 °C, presuming the RO-like inner skin layer as the dense active layer for draw solute rejection.

In addition to the three double-skinned FO membranes, the FO tests for RO-like intermediate membranes (PAI#1-RO and PAI#2-RO) were also conducted. The RO-like intermediate membranes are actually a thin-film composite FO membrane with PAI hollow fiber as the substrate, which has not been reported previously in the literature. Compared with the double-skinned FO membrane, the RO-like intermediate membrane has the identical RO-like inner skin and substrate structure, but a UF-like outer skin instead of the NF-like skin for the double-skinned FO

membrane. With the comparison of their performances, the influence of the NF-like secondary skin on overall performance of the double-skinned hollow fibers can be evaluated.

## **5.4 Results and discussion**

### **5.4.1 Characteristics of double-skinned composite FO hollow fiber membranes**

#### *i) PAI hollow fiber substrates*

The cross-section morphologies of two PAI hollow fiber substrates are shown in Fig. 5.1. It can be seen that finger-like structures were developed simultaneously from the outer and inner surfaces of the two substrates without forming large spherical macro-voids. Although these two kinds of macro-voids may produce similar porosity, finger-like structure provides better self-support and mechanical durability as compared with large spherical macro-voids. However, the sponge-like structure in the middle of the cross-section of PAI#2 substrate is thinner than that of PAI#1, which was mainly attributed to the shorter air gap used for PAI#2 during hollow fiber spinning (Table 5.1). A shorter air gap allowed the extruded dope to get in contact with the external coagulant (water) earlier. Since the bore fluid used was softer than the external coagulant, the finger-like structure developed from the outer surface was able to grow deeper towards the inner surface of the fiber. A small portion of sponge-like structure is favorable as it may contribute to lower tortuosity, higher porosity and thus better performance in subsequent FO applications.

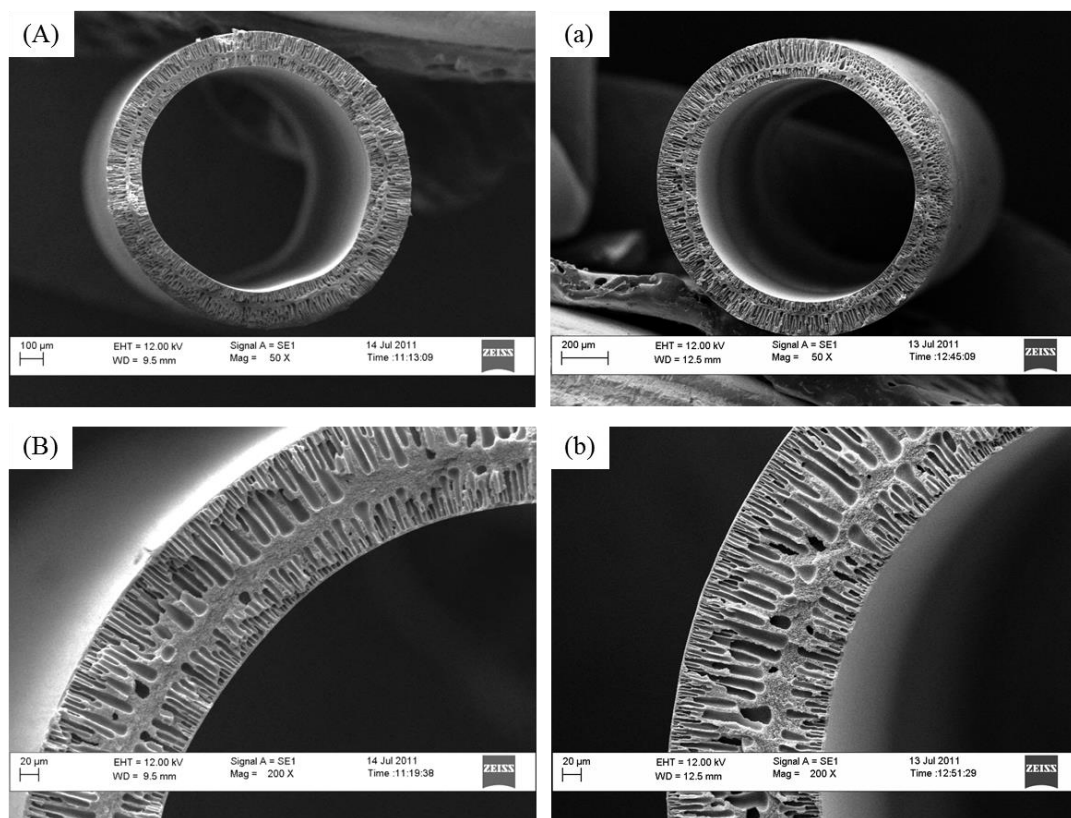


Fig. 5.1 Cross-section morphologies of PAI hollow fiber substrates: (A) PAI#1 at 50X; (B) PAI#1 enlarged at 200x; (a) PAI#2 at 50x; (b) PAI#2 enlarged at 200x.

The characteristics of PAI hollow fiber substrates (PAI#1 and PAI#2), including fiber dimensions, PWP, MWCO and porosity, are listed in Table 5.3. According to the table, the two substrates possess a slightly different porosity because of a larger portion of sponge-like structure of the PAI#1. The inner and outer skin MWCOs of the two substrates suggest that the substrates fall in the range of tight UF membranes. The smaller PWP of the PAI#2 membrane may be caused by the tighter structure of its outer surface, which was suggested by its smaller outer skin MWCO of 21 kDa. These characteristics of the substrates are closely related to the development and performance of subsequent double-skinned FO hollow fiber membranes.

Table 5.3 Characteristics of PAI hollow fiber substrates

| Characteristics                             | PAI#1 | PAI#2 |
|---------------------------------------------|-------|-------|
| Fiber outer diameter (mm)                   | 1.38  | 1.35  |
| Fiber inner diameter (mm)                   | 1.04  | 1.00  |
| Fiber wall thickness ( $\mu\text{m}$ )      | 170   | 175   |
| PWP ( $\text{L}/\text{m}^2 \text{ h bar}$ ) | 130   | 98    |
| Outer skin MWCO (KDa)*                      | 37    | 21    |
| Inner skin MWCO (KDa) <sup>+</sup>          | 33    | 48    |
| Porosity (%)                                | 71    | 78    |

\*Dextran filtration was performed from the shell side of the module.

<sup>+</sup>Dextran filtration was performed from the lumen of the fiber.

## ii) FO hollow fibers with two skin layers

The properties of the double-skinned FO hollow fiber membranes are contributed by the two skin layers as well as the PAI substrates. In order to examine the individual characters of the two skin layers, the NF-like and RO-like intermediate membranes were also characterized in addition to the double-skinned hollow fibers.

Fig. 5.2 shows the cross-section morphologies of double-skinned FO hollow fiber membrane DS#1-RO/NF as well as PAI#1 substrate from which the DS#1-RO/NF membrane was developed. By comparing the cross-section morphologies of the DS#1-RO/NF and PAI#1 membranes near the inner surface of the fibers (Fig. 5.2 (A) and (a)), the RO-like thin-film skin layer with a thickness of around 300 nm was found with a high roughness based on a rough estimation. This is a typical morphology of interfacially polymerized polyamide skin layers reported in the literature (Wang, Shi *et al.* 2010). On the other hand, the NF-like secondary skin layer can be observed on the cross-section near the outer surface of the DS#1-RO/NF (Fig. 5.2 (B)). Compared to PAI#1 substrate (Fig. 5.2 (b)), the outer skin of the DS#1-RO/NF possesses a much denser structure with a thickness of around 200 nm, produced by the chemical cross-linking reaction.

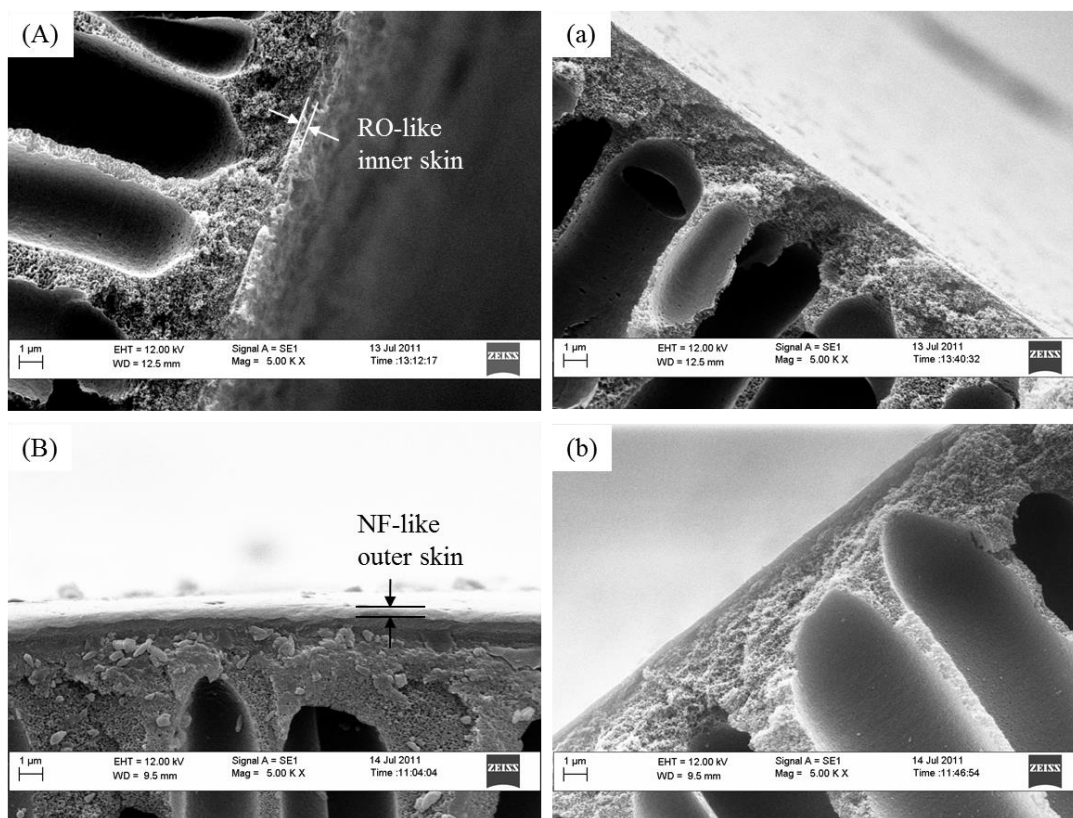


Fig. 5.2 Cross-section morphology of DS#1-RO/NF double-skinned FO hollow fiber: (A) inner skin at 5000x; (B) outer skin at 5000x; Cross-section morphology of PAI#1 hollow fiber substrate: (a) inner skin at 5000x; (b) outer skin at 5000x.

The membrane surface charge for PAI#1 hollow fiber substrate and PAI#1-NF intermediate membrane were examined by streaming potential measurements and the results are shown in Fig. 5.3. The PAI#1 substrate had an isoelectric point of 4.3 and was negatively charged when pH was higher than 4.3 due to the deprotonation of the end-capped carboxyl group (Childress and Elimelech 2000). However, the protonation of amine group drove the membrane to be positively charged when pH fell below the isoelectric point. For the PAI#1-NF membrane, its isoelectric point shifted to pH 9.7 because of the cross-linking reaction occurred on the outer surface, where the imide ring was opened by the PEI amine group and more amine groups from the bulk PEI molecular chains were therefore localized in the cross-linked outer skin layer. Consequently, the resultant NF-like skin exhibited a higher positive charge density. Similar results were reported in the literature (Setiawan, Wang *et al.* 2011; Sun, Hatton *et al.* 2011).

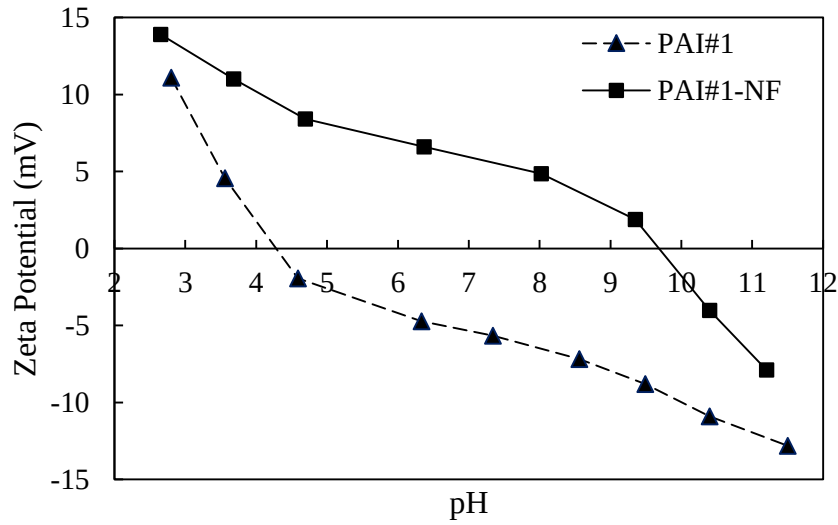


Fig. 5.3 Zeta potential of PAI#1 hollow fiber substrate and PAI#1-NF intermediate membrane.

Table 5.4 lists the dynamic contact angle data of various hollow fiber membranes. The contact angle of the PAI#1 substrate was measured to be  $80 \pm 1^\circ$ , which is similar to the value of PAI hollow fiber membrane reported in the literature (Sun, Hatton *et al.* 2011). The PAI#1-NF intermediate hollow fiber membrane exhibited a contact angle of  $66 \pm 1^\circ$ , which was attributed to enhanced hydrophilicity of its NF-like outer skin because of large number of attached amine groups. The contact angle of PAI#1-RO intermediate membrane also decreased to  $61 \pm 1^\circ$  due to the influence of the highly hydrophilic RO-like inner skin. The contact angle of the resultant double-skinned hollow fiber DS#1-RO/NF was then further decreased to as low as  $46 \pm 2^\circ$  as the two skin layers are more hydrophilic than the PAI substrate. The hydrophilic nature of the two skin layers has positive impacts on FO applications, as it can reduce the resistance for water permeation through the membrane and consequently result in an enhancement of water flux.

Table 5.4 Dynamic contact angle of various hollow fiber membranes

| Membrane                           | PAI#1      | PAI#1-NF   | PAI#1-RO   | DS#1-RO/NF |
|------------------------------------|------------|------------|------------|------------|
| Dynamic contact angle ( $^\circ$ ) | $80 \pm 1$ | $66 \pm 1$ | $61 \pm 1$ | $46 \pm 2$ |

#### 5.4.2 Performance of the double-skinned hollow fibers in the RO mode

##### i) *Intrinsic separation properties of single-skinned hollow fibers*

Table 5.5 summarizes the intrinsic separation properties of the two skin layers in terms of  $A$  and  $B$  values as well as rejection to NaCl and MgCl<sub>2</sub>. It can be seen that the polyamide inner skin had good intrinsic separation properties with water permeability above 2 L/m<sup>2</sup> h bar and NaCl rejection of above 80% at hydraulic pressure of 1 bar. The rejection to MgCl<sub>2</sub> is over 99%, attributed to the larger hydrated radius of Mg<sup>2+</sup> ions comparing to that of the Na<sup>+</sup> ions (Peeters, Boom *et al.* 1998). This also confirmed that the inner skin is a dense RO-like thin-film with the size exclusion being the major rejection mechanism. It was also found from the table that the chemically modified outer skin layer exhibited typical characteristics of NF membrane in terms of water permeability and salt retention. The positive surface charges which were discussed in Section 5.4.1 (Fig. 5.3) contributed to the rejection of Mg<sup>2+</sup> ions in addition to the size effect.

Table 5.5 Intrinsic separation properties of single-skinned hollow fibers

| Sample   | Water permeability,<br>$A$ (L/m <sup>2</sup> h bar) | Salt permeability,<br>$B^*$ (L/m <sup>2</sup> h) | NaCl rejection <sup>+</sup><br>(%) | MgCl <sub>2</sub> rejection <sup>+</sup><br>(%) |
|----------|-----------------------------------------------------|--------------------------------------------------|------------------------------------|-------------------------------------------------|
| PAI#1-RO | 2.09                                                | 0.234                                            | 85.1                               | 99.3                                            |
| PAI#2-RO | 3.04                                                | 0.211                                            | 89.9                               | 99.5                                            |
| PAI#1-NF | 9.30                                                | 43.40                                            | 20.8                               | 83.9                                            |
| PAI#2-NF | 8.99                                                | 22.00                                            | 32.3                               | 90.4                                            |

\*Salt permeability coefficient,  $B$ , refers to the permeability of NaCl.

<sup>+</sup>The NaCl and MgCl<sub>2</sub> rejection were obtained under hydraulic pressure of 1 bar.

In comparison of the membranes made from two types of PAI substrates, the NF-like outer skin developed from the two types of substrates possessed similar water permeability, but PAI#2-NF had a lower salt permeability due to the smaller MWCO and tighter structure of the UF-like outer skin of PAI#2 substrate. The RO-like inner skin formed on the PAI#2 substrate also exhibited better intrinsic properties. It can thus be expected that the double-skinned FO membranes prepared using PAI#2 as the substrate would achieve better intrinsic separation performance.

ii) *Intrinsic separation properties of double-skinned hollow fibers*

The experimentally measured and theoretically calculated  $A$  and  $B$  values and NaCl rejection for the three types of double-skinned FO membranes are listed in Table 5.6.

Table 5.6 Intrinsic separation properties of double-skinned FO hollow fibers.

| Membrane                             | Water permeability, $A$ (L/m <sup>2</sup> h bar) | Salt permeability, $B^*$ (L/m <sup>2</sup> h) | NaCl rejection | Remark                           |
|--------------------------------------|--------------------------------------------------|-----------------------------------------------|----------------|----------------------------------|
| DS#1 (calculated)                    | 1.79                                             | 0.233                                         | 83.3%@ 1 bar   |                                  |
| DS#2 (calculated)                    | 2.43                                             | 0.209                                         | 87.9%@ 1 bar   |                                  |
| DS#1-NF/RO                           | 0.60                                             | 0.101                                         | 79.6%@ 1 bar   | Present work                     |
| DS#1-RO/NF                           | 1.48                                             | 0.249                                         | 79.7%@ 1 bar   |                                  |
| DS#2-RO/NF                           | 2.05                                             | 0.226                                         | 85.3%@ 1 bar   |                                  |
| Double dense-layer flat sheet        | 0.17                                             | 0.07                                          | 92.0% @ 5 bar  | (Zhang, Wang <i>et al.</i> 2010) |
| CA double-selective layer flat sheet | 0.78                                             | 0.46                                          | 58% @ 1 bar    | (Wang, Ong <i>et al.</i> 2010)   |
| HTI-FO flat sheet                    | 0.80                                             | 0.61                                          | 82% @ 3.5 bar  | (Tang, She <i>et al.</i> 2010)   |

\*Salt permeability coefficient,  $B$ , refers to the permeability of NaCl.

Experimental results listed in the table revealed that the DS#1-NF/RO membrane exhibited the poorest water permeability which was much lower than the theoretical value obtained using Eq. (5.3) (0.60 vs. 1.79 L/m<sup>2</sup> h bar) though its salt permeability was also low. This result might be caused by the preparation route through which the double-skinned membrane was made. As described in Section 5.3.2, the DS#1-NF/RO membrane was prepared via –NF/RO route, i.e., chemical modification of the fiber outer skin followed by interfacial polymerization on the fiber inner surface. When chemical modification was completed, a large number of free amine groups from PEI were attached on the cross-linked outer skin. During subsequent interfacial polymerization reaction, it was likely that the excess TMC molecules penetrated into the substrate and eventually were in contact and reacted with those free amines. The rapid cross-linking reaction between TMC and PEI was

reported in the literature (Chiang, Hsub *et al.* 2009). A denser outer skin layer was thus resulted from this additional reaction, leading to increased mass transport resistance which contributed to the lower than expected water and salt permeability of resultant double-skinned FO membranes. In contrast, if the interfacial polymerization was taken place first, the excess TMC molecules were quickly converted to carboxylic acid and lost their reactivity before subsequent PEI amine groups were introduced. As a result, the formation of the two skin layers in –RO/NF route has less interference one other and can be controlled easily. The experimental water permeability data of double-skinned membranes, DS#1-RO/NF and DS#2-RO/NF, both made though the –RO/NF route were close to corresponding theoretical values, which confirmed the above deduction.

However, as also shown in Table 5.6, the experimentally obtained  $B$  values for DS#1-RO/NF and DS#2-RO/NF were slightly larger than the computed values, and measured NaCl rejections were a bit lower than the calculated ones. This result was believed to be associated with the concentration polarization inside the porous support between the two skin layers during the salt rejection test. When water flowed from the RO-like inner skin towards the NF-like outer skin, some  $\text{Na}^+$  and  $\text{Cl}^-$  ions would penetrate across the RO-like inner skin and accumulated near the NF-like secondary skin as long as the NF-like secondary skin had a rejection to salts in certain degree. Hence, the salt concentration in the final permeate water would increase.

The intrinsic properties of two reported FO membranes with double-selective layers as well as commercial FO membrane from HTI are also listed in Table 5.6 for comparison. It can be seen that the newly developed DS#1-RO/NF and DS#2-RO/NF double-skinned FO hollow fibers have much larger water permeability. Their salt permeability was also smaller than that of the CA double-skinned flat sheet (Wang, Ong *et al.* 2010) and the HTI membrane (Tang, She *et al.* 2010). The large  $A$  value and small  $B$  value are desirable for FO process, which will be discussed in the following section.

### 5.4.3 FO performance with pure water as feed

The FO performances of three types of double-skinned FO hollow fiber membranes were evaluated using NaCl solutions from 0.5 M to 2.0 M as the draw solution and DI water as the feed solution. The water flux and the ratio of salt flux over water flux ( $J_s/J_v$ ) as a function of draw solute concentrations are shown in Fig. 5.4. It was found that the DS#2-RO/NF membrane has the highest water flux for both AL-DS and AL-FS orientations. Since the DS#2-RO/NF possesses better intrinsic water permeability than other two membranes and the PAI#2 substrate is more porous than the PAI#1 substrate, it is not surprising to see higher water flux of the DS#2-RO/NF membrane.

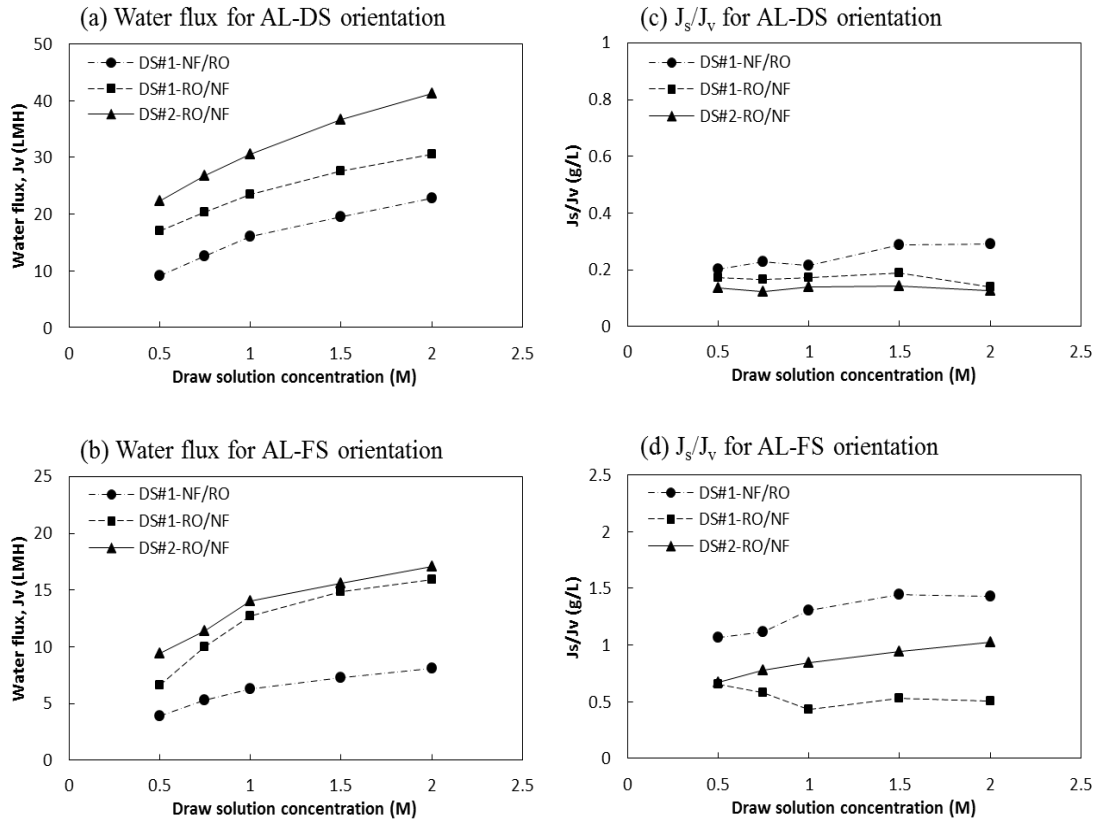


Fig. 5.4 FO performance of double-skinned FO hollow fiber membranes. Draw solution: 0.5-2.0 M NaCl; feed: DI water.

The ratio of the salt flux and water flux,  $J_s/J_v$ , is a parameter suggesting the separation property of the membrane during FO processes and is more indicative

than the absolute salt flux without considering the contribution of FO water flux. According to Fig. 5.4, the  $J_s/J_v$  ratio appeared to be almost stable regardless of the increase of water flux when higher draw solution concentrations were used. This observation is consistent with the conclusion made in (Tang, She *et al.* 2010) that the  $J_s/J_v$  ratio is proportional to the  $B/A$  ratio, which represents the intrinsic property of the membrane and does not change with the variation of draw solution concentration. In addition, for all of the three double-skinned membranes, the  $J_s/J_v$  ratio for the AL-FS configuration was found to be higher than that for the AL-DS configuration, indicating a more severe salt leakage for the same amount of water produced. When the NF-like skin layer was against with the draw solution (the AL-FS orientation), the electric repulsion between the positively charged NF-like skin layer and the salt ions inside the substrate facilitated the salt transport as the repulsion and salt flux were in the same direction towards the feed solution. Whereas for the AL-DS configuration, the salt flux and salt repulsion were in opposite directions, which hindered the salt transfer and resulted in a lower  $J_s/J_v$  ratio. Similar phenomenon was reported with detailed discussions in (Setiawan, Wang *et al.* 2011). Therefore, the AL-DS orientation is more desired for the double-skinned FO hollow fibers not only because of the higher water flux, but also due to less back salt diffusions than the AL-FS orientation.

#### **5.4.4 Effect of the NF-like secondary skin on FO applications**

The purpose of introducing an NF-like secondary selective skin is to minimize the ICP occurred in the support layer and to enhance the fouling/scaling resistance for FO applications without sacrificing the higher water flux under the AL-DS orientation. To testify the real function of the NF-like skin layer, FO test was conducted using a feed solution containing divalent ions ( $\text{MgCl}_2$ ) or a mixed feed solution containing calcium chloride ( $\text{CaCl}_2$ ) and dipotassium hydrogen phosphate ( $\text{K}_2\text{HPO}_4$ ) operated in the AL-DS orientation.

##### *i) Feed solution containing divalent metal ions*

Fig. 5.5 shows the water flux of the DS#2-RO/NF (double skinned) and PAI#2-RO (single-skinned) membranes as a function of total dissolved salts (TDS) of  $\text{MgCl}_2$  in feed solution ranging from 0 to 1000 ppm. Although the single-skinned PAI#2-RO hollow fiber membrane exhibited superior water flux of  $31.5 \text{ L/m}^2 \text{ h}$  when DI water was used as the feed, its water flux decreased dramatically when the feed contained dissolved salts. In contrast, the water flux of double-skinned DS#2-RO/NF membrane remained almost unchanged with the variation of salt concentration in the feed. When the TDS of the feed solution was further increased, the water flux of the PAI#2-RO membrane eventually became lower than that of the DS#2-RO/NF membrane. This indicated that once the feed contained dissolved salts, severe ICP was built up inside the porous substrate of the PAI#2-RO membrane and the driving force across the RO-like skin layer was reduced significantly, as there was no relatively dense skin layer presented on the side of the porous substrate facing the feed solution.

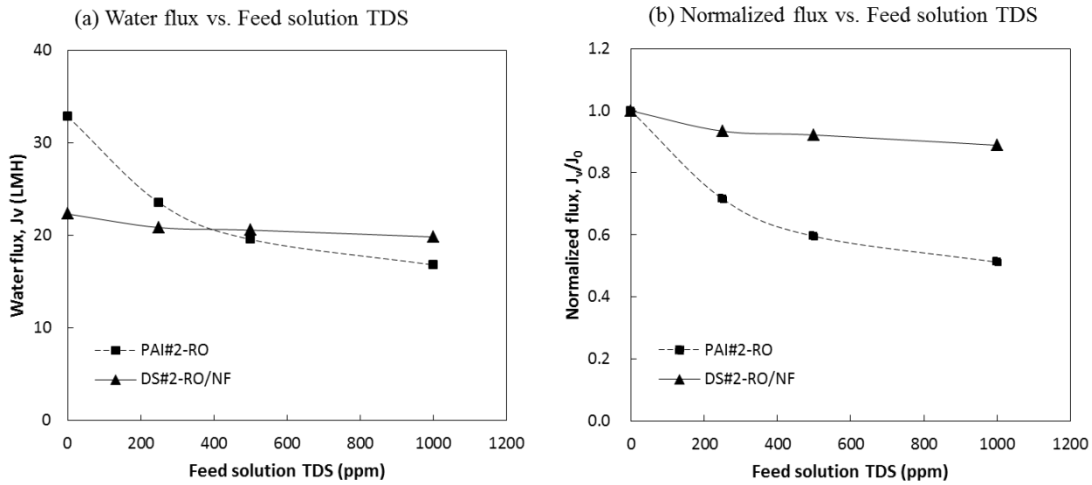


Fig. 5.5 FO water flux at different total dissolved salts (TDS) in feed solution. Draw solution: 0.5M NaCl; feed:  $\text{MgCl}_2$  solution; in AL-DS configuration.

Referring back to Table 5.5, the NF-like outer skin of the DS#2-RO/NF membrane was highly selective to divalent ions, and hence prevented the instant penetration of  $\text{MgCl}_2$  into the porous substrate. As a result, the salt concentration inside the DS#2-RO/NF porous substrate would be much lower than that of the PAI#2-RO membrane, and the ICP was able to be minimized. The normalized water flux

shown in Fig. 5.5 (b) illustrated clearly that the percentage decrease of water flux for the double-skinned hollow fiber was much less than that for the single-skinned one. For the DS#2-RO/NF membrane, the water flux was reduced only by 11% when 1000 ppm  $\text{MgCl}_2$  solution was used as the feed, whereas the reduction for the PAI#2-RO membrane was as high as 49%.

ii) *A mixed feed solution with high scaling tendency to membrane*

Phosphorous compounds exist commonly in water and wastewater streams. When membrane processes are applied for municipal wastewater treatment, phosphate scaling was likely to occur due to the low solubility of calcium phosphate and calcium hydrogen phosphate ( $\text{CaHPO}_4$ ) (Xie, Gomez *et al.* 2004). The current work used a mixed solution containing calcium chloride ( $\text{CaCl}_2$ ) and dipotassium hydrogen phosphate ( $\text{K}_2\text{HPO}_4$ ) as the feed to conduct the FO experiment. The mixed feed solution had a concentration of 100 ppm TDS with equal concentration of  $\text{CaCl}_2$  and  $\text{K}_2\text{HPO}_4$  by weight, which is closed to the solubility limit of  $\text{CaHPO}_4$ . The  $\text{CaHPO}_4$  precipitation and crystallization would occur once the solution was further concentrated. 0.5 M NaCl was used as the draw solution in the AL-DS orientation so that the NF-like secondary skin was placed against the feed solution.

Fig. 5.6 shows the FO water flux of the DS#2-RO/NF and PAI#2-RO membranes verses operating time in the FO experiment using above-mentioned mixed solution as the feed. According to the figure, the water flux of the two membranes dropped with operating time, indicating that both membranes were subjected to inorganic scaling. However, the percentage reduction of the DS#2-RO/NF membrane was less than that of the PAI#2-RO membrane (40% vs. 70%), which implied that the NF-like skin played a role of reducing the degree of scaling. As shown in Fig. 5.6(a), the DS#2-RO/NF membrane ended up with a higher water flux after 40 mins of operation and possessed better long-term application capability.

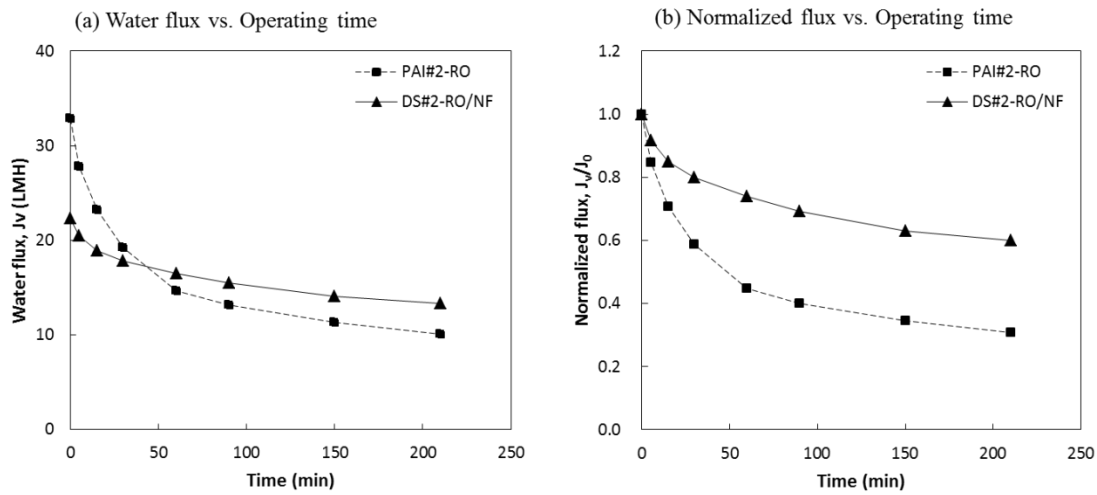


Fig. 5.6 FO water flux over operating time. Draw solution: 0.5 M NaCl; feed: mixed salt solution with high scaling tendency; in AL-DS configuration.

The scaling of the two membranes was believed to have different characteristics due to the existence of the NF-like outer skin. The scaling of PAI#2-RO should mainly occur inside the substrate, while an external scaling should be the case for the DS#2-RO/NF membrane. To confirm this, following experiments were performed. To recover the water flux of the membranes after inorganic scaling, a cross-flow flush on the outer surface of the scaled hollow fiber membranes using DI water was conducted without applying hydraulic pressure and creating water permeation, followed by back wash from the lumen side of the fibers using DI water at 1 bar. The FO water flux of the membranes after cleaning was measured and the results are shown in Fig. 5.7.

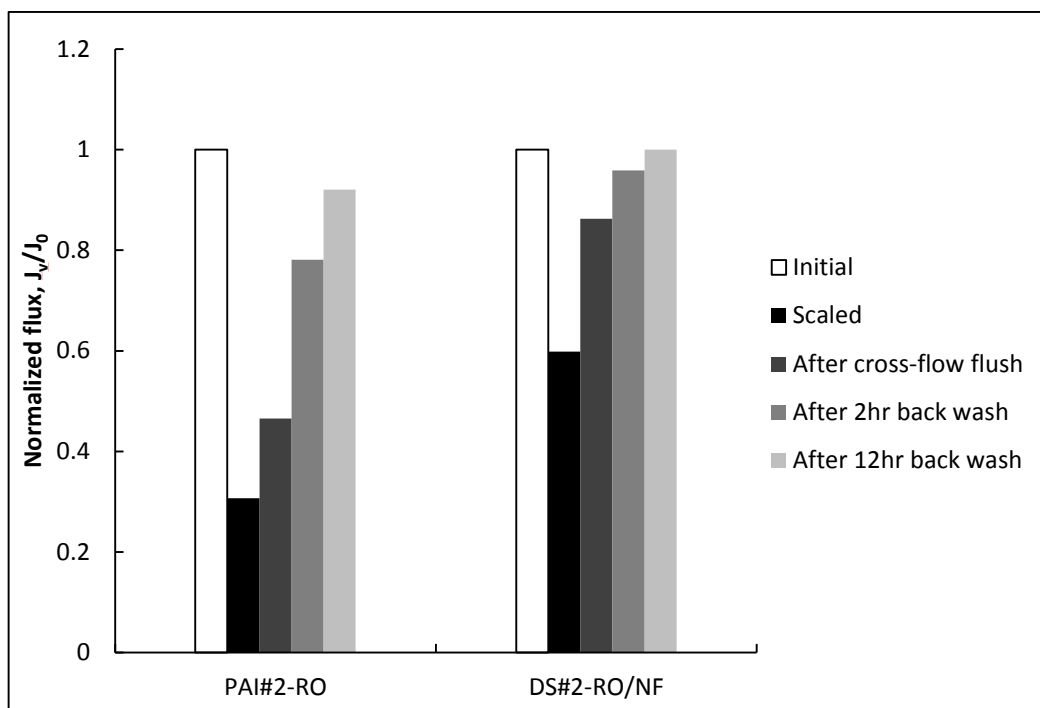


Fig. 5.7 Effect of cleaning on scaled FO hollow fiber membranes.

It can be seen that after 1 hr cross-flow flush, the water flux of the DS#2-RO/NF membrane was quickly recovered to 86% of the initial water flux, while the recovery rate for the PAI#2-RO membrane was only up to 47%. After 2 hr back wash, the water flux of the DS#2-RO/NF membrane further increased to 96% of the initial value, and eventually retrieved back to 100% after continuous cleaning. In contrast, the PAI#2-RO membrane achieved 78% of the initial water flux after 2 hr back wash, and the water flux increased to 92% after 12 hr back wash. It can be concluded that the scaling in the PAI#2-RO membrane was more persistent and difficult to clean, as the scaling probably occurred severely inside the porous substrate of the PAI#2-RO membrane. Whereas for the DS#2-RO/NF membrane, the NF-like secondary skin had a high rejection to divalent ions, the scaling of  $\text{CaHPO}_4$  might take place mainly on the surface of the outer skin, which could be easily cleaned up by the cross-flow flush and back wash.

#### 5.4.5 Comparison of various FO membranes

The FO performance of composite FO hollow fiber membranes with double or

single selective skins developed in the current work are listed in Table 5.7 along with other FO membranes reported in the literature.

Table 5.7 Comparison of various FO membranes\*

| Membranes                                         | Water flux (LMH) | Salt flux /water flux (g/L) | Draw solution           | Feed                                                          | Ref.                                  |
|---------------------------------------------------|------------------|-----------------------------|-------------------------|---------------------------------------------------------------|---------------------------------------|
| DS#2-RO/NF hollow fiber (double-skinned)          | 22.3             | 0.137                       | 0.5 M NaCl              | DI water                                                      | Present work                          |
|                                                   | 41.3             | 0.126                       | 2.0 M NaCl              | DI water                                                      |                                       |
|                                                   | 19.8             | -                           | 0.5 M NaCl              | 1000 ppm MgCl <sub>2</sub>                                    |                                       |
|                                                   | 13.4             | -                           | 0.5 M NaCl              | 100 ppm CaCl <sub>2</sub> and K <sub>2</sub> HPO <sub>4</sub> |                                       |
| PAI#2-RO hollow fiber (single-skinned)            | 31.5             | 0.167                       | 0.5 M NaCl              | DI water                                                      | (Zhang, Wang <i>et al.</i> 2010)      |
|                                                   | 46.3             | 0.164                       | 2.0 M NaCl              | DI water                                                      |                                       |
|                                                   | 16.8             | -                           | 0.5 M NaCl              | 1000 ppm MgCl <sub>2</sub>                                    |                                       |
|                                                   | 10.1             | -                           | 0.5 M NaCl              | 100 ppm CaCl <sub>2</sub> and K <sub>2</sub> HPO <sub>4</sub> |                                       |
| Double dense-layer flat sheet <sup>+</sup>        | 11.2             | 0.39                        | 2.0 M NaCl              | DI water                                                      | (Wang, Ong <i>et al.</i> 2010)        |
| CA double-selective layer flat sheet <sup>+</sup> | 19               | 0.71                        | 2.0 M NaCl              | DI water                                                      | (Wang, Shi <i>et al.</i> 2010)        |
| TFC FO hollow fiber                               | 32.2             | 0.11                        | 0.5 M NaCl              | DI water                                                      | (Yang, Wang <i>et al.</i> 2009)       |
|                                                   | 46.0             | 0.10                        | 2.0 M NaCl              | DI water                                                      | (Wei, Qiu <i>et al.</i> 2011)         |
| Dual-layer (PBI-PES) hollow fiber                 | 15.7             | 0.030                       | 1.0 M MgCl <sub>2</sub> | DI water                                                      | (Gray, McCutcheon <i>et al.</i> 2006) |
| TFC flat-sheet membrane                           | 20.5             | 0.29                        | 0.5 M NaCl              | 10 mM NaCl                                                    | (Tang, She <i>et al.</i> 2010)        |
| HTI-FO flat sheet                                 | 18.6             | -                           | 0.5 M NaCl              | DI water                                                      |                                       |
|                                                   | 17               | 0.85                        | 0.5 M NaCl              | 10 mM NaCl                                                    |                                       |

\*All data is reported in AL-DS orientation at 20-25°C.

<sup>+</sup>Data were retrieved from published figures.

As shown in the Table, the single-skinned PAI#2-RO hollow fiber membrane exhibited superior FO performance than most of reported FO membranes. It was comparable with the thin film composite FO hollow fiber developed by Wang *et al.* previously (Wang, Shi *et al.* 2010), though the two membranes were made by

different hollow fiber substrates. With the incorporation of the NF-like secondary skin layer, the double-skinned DS#2-RO/NF hollow fiber membrane was able to outperform single-skinned FO membrane when the feed solution contained divalent metal ions or the feed solution had a high tendency of scaling to membrane. In addition, the DS#2-RO/NF hollow fiber membrane was found to possess much better FO permanence of higher water flux and much lower salt leakage than other double-selective layer flat sheet membranes under the same test conditions.

## 5.5 Conclusions

Novel composite FO hollow fiber membranes with an RO-like selective skin and an NF-like secondary selective skin were successfully developed for the first time. The fabrication procedures involved making UF hollow fiber substrate using PAI polymer material via phase inversion method, followed by interfacial polymerization and chemical modification on the inner and outer surfaces of the substrate to yield a polyamide RO-like inner skin layer and a positively charged NF-like outer skin layer, respectively.

It was found that the preparation route was critical for obtaining high performance double skinned FO membranes. The sequence of conducting interfacial polymerization on the substrate inner surface prior to the chemical modification of the outer skin was preferred, which made the resultant double-skinned hollow fibers possess better intrinsic properties and FO performance as compared with the reverse route.

The newly developed double-skinned DS#2-RO/NF membrane exhibited high water permeability of 2.05 L/m<sup>2</sup> h bar and 85% rejection to NaCl at 1 bar pressure. The hydrophilic nature of the two skin layers reduced the contact angle of the membrane from 80 ± 1° for the PAI hollow fiber substrate to 46 ± 2° for the composite FO membrane. The double-skinned composite hollow fiber, DS#2-RO/NF, presented high water flux of 41.3 L/m<sup>2</sup> h and low  $J_s/J_v$  ratio of 0.126 g/L when using DI water and 2.0 M NaCl as feed and draw solutions, respectively, in the AL-DS orientation,

which are superior to commercial HTI FO membranes as well as other double-selective layer membranes reported in the literature.

Furthermore, comparing with single-skinned membranes, the introduction of NF-like secondary layer offers the advantages of minimized ICP when the feed contains divalent ions, and lower propensity to inorganic scaling when the feed exhibits high scaling tendency to membrane. As a result, the double-skinned DS#2-RO/NF hollow fiber membrane was able to outperform single-skinned PAI#2-RO membrane in these application scenarios, suggesting that the integration of RO- and NF-like two selective skins in FO membrane is an effective way to enhance the feasibility of FO processes for practical applications.

## CHAPTER 6

# Composite Forward Osmosis Hollow Fiber Membranes: Integration of RO- and NF-Like Selective Layers for Enhanced Organic Fouling Resistance

### 6.1 Introduction

As discussed in Chapter 5, an NF-like secondary selective skin is introduced in addition to the RO-like primary active skin layer in order to fully utilize the higher water flux of AL-DS orientation and enhance the membrane fouling resistance at the same time. In this double-skinned membrane structure, the primary active layer is placed against the draw solution to produce osmotic driving force, while the secondary skin layer is facing the feed solution to prevent possible foulant penetration into the porous substrate so that a stable water flux could be achieved (Tang, She *et al.* 2011). To date, only a few studies have reported double-skinned FO membranes in flat-sheet (Wang, Ong *et al.* 2010; Zhang, Wang *et al.* 2010; Qi, Qiu *et al.* 2012) or in hollow fiber configuration (Fang, Wang *et al.* 2012; Su, Chung *et al.* 2012), while hollow fiber FO membranes are capable to offer better packing density, higher effective surface area and self-support capability than flat-sheet membranes (Chou, Shi *et al.* 2010; Wang, Shi *et al.* 2010; Shi, Chou *et al.* 2011).

Interfacial polymerization (IP) is to date the most widely used technique to prepare

FO membranes with an RO-like active layer (Chou, Shi *et al.* 2010; Wang, Shi *et al.* 2010; Yip, Tiraferri *et al.* 2010; Shi, Chou *et al.* 2011; Wei, Qiu *et al.* 2011; Wang, Chung *et al.* 2012). Alternatively, a variety of other methods have been involved to yield FO membranes with an NF-like selective layer, which include phase inversion (Wang, Chung *et al.* 2007; Yang, Wang *et al.* 2009), chemical post-treatment (Setiawan, Wang *et al.* 2011; Qiu, Setiawan *et al.* 2012; Setiawan, Wang *et al.* 2012b) and multilayer polyelectrolyte deposition (Qiu, Qi *et al.* 2011; Saren, Qiu *et al.* 2011; Liu, Fang *et al.* 2013; Setiawan, Wang *et al.* 2013).

In Chapter 5, a composite FO hollow fiber membrane with two selective skin layers was reported. The RO-like active skin layer was prepared on the inner surface of the hollow fiber substrate via interfacial polymerization, while the NF-like outer skin layer was made through chemical cross-linking. As verified in the chapter, the double-skinned FO hollow fibers exhibited a lower degree of concentrative ICP and internal scaling during the AL-DS operation. In this study, another type of double-skinned hollow fibers with improved FO performance was successfully developed. With the formation of the RO-like primary skin layer remaining unchanged, the NF-like secondary skin layer was prepared via polyelectrolyte layer-by-layer (LBL) assembly. Compared to the post-treatment method reported in the previous chapter, the formation of the NF-like layer via LBL assembly approach does not involve the chemical modification of support layer. As the substrate structure directly determines the extent of ICP effect (Gray, McCutcheon *et al.* 2006; McCutcheon and Elimelech 2006), it is important to keep the substrate pore structure unaffected. In addition, surface properties such as electrical charge, roughness as well as separation performance of the NF-like skin layer can be tailored more effectively by altering the LBL deposition conditions (Jin, Toutianoush *et al.* 2003; Malaisamy and Bruening 2005).

The newly developed double-skinned FO hollow fibers are expected to render better organic fouling control property when they are used for applications where the feed contains elements that present high fouling tendency. It is well recognized that feed water composition may vary depending on water sources. Natural organic matters

(NOM), mostly humic substances, are identified as the major organic foulant in surface water (Hong and Elimelech 1997; Schäfer, Fane *et al.* 2000), while the most common organic foulants in wastewater are polysaccharides and proteins (Ho and Zydney 2000; Lim and Bai 2003; Lee, Ang *et al.* 2006). Therefore, three organic compounds including Aldrich humic acid (AHA), dextran (DEX) and lysozyme (LYS) with negative, neutral and positive electric charges, respectively (Tang, Chong *et al.* 2011), were employed as the model foulants in this study to give a complete presentation of organic foulant species as well as electrostatic interactions. The capability of organic fouling control of the newly developed double-skinned FO hollow fibers were evaluated thoroughly in the current study.

## 6.2 Experimental

### 6.2.1 Materials and chemicals

Commercial polymer polyethersulfone (PES) was used for preparation of hollow fiber substrate. M-phenylenediamine (MPD) and trimesoyl chloride (TMC) supplied by Sigma-Aldrich were used for interfacial polymerization. Poly(styrenesulfonic acid) sodium salt (PSS, 500,000 Da, Alfa Aesar) and poly(allylamine hydrochloride) (PAH, 120,000-200,000 Da, PolyScience) were used for layer-by-layer assembly, and glutaraldehyde (GA, Sigma-Aldrich) was used to improve the stability of the polyelectrolyte deposition.

Sodium chloride (NaCl), magnesium chloride (MgCl<sub>2</sub>), and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) purchased from Merck were used in determining membrane separation properties. NaCl was also used to prepare draw solutions with various concentrations. Aldrich humic acid (AHA, Aldrich H16752), dextran from *Leuconostoc mesenteroides* (DEX, Sigma D9260) and lysozyme from chicken egg white (LYS, Fluka 62971) were involved in the preparation of FO feed solution. According to the manufacturer, molecular weight for AHA, DEX and LYS are 4-23, 9-11 and 14.3 kDa, respectively. Deionized water (Milli-Q, 18MΩcm) was used for the preparation of solutions.

### 6.2.2 Membrane preparation

Preparation of double-skinned hollow fiber membranes involved three steps, which include fabrication of the hollow fiber substrate, RO-like active layer and NF-like secondary selective layer, sequentially. The fabrication of PES hollow fiber substrate and the formation of RO-like polyamide active skin layer have been described previously (Shi, Chou *et al.* 2011; Fang, Wang *et al.* 2012). Generally, the substrate fiber was fabricated by the phase inversion method through a dry-jet wet spinning process, and the RO-like active layer was then formed on the inner surface of the substrate fiber via interfacial polymerization (IP) with MPD and TMC as the two basic monomers.

The intermediate single-skinned membranes with an RO-like selective layer were subject to subsequent polyelectrolyte layer-by-layer (LBL) deposition to develop the NF-like secondary selective layer on the fiber outer surface. The procedures of the LBL deposition were similar to a previous work (Liu, Fang *et al.* 2013), in which only the fiber outer surface was immersed into the polyanion (0.02 M PSS with 0.5 M NaCl) and polycation (0.02 M PAH with 2.5 M NaCl) solutions alternately to form the polyelectrolyte bilayers. The contact time for the two solutions was 3 and 5 min, respectively, with 4 min DI water rinse in between to remove the excess polyelectrolytes. It is worth noting that one pair of PSS/PAH deposition is considered as one bilayer of polyelectrolytes so that “n bilayers” refers to n pairs of PSS/PAH deposition with PAH as the terminating layer, whereas “n.5 bilayers” of deposition has an additional PSS layer on top of the n bilayers of polyelectrolytes. When a desired number of bilayers was achieved, the nascent LBL layers were cross-linked by 0.1% (w/v) GA solution post-treatment for 25 min to improve the stability of the assembled multilayers (Qiu, Qi *et al.* 2011). Finally, the newly fabricated double-skinned membranes were rinsed and stored in DI water prior to further application.

It is difficult to measure the properties of the NF-like secondary skin layer independently in a double-skinned membrane, as the solute rejection is dominated by the RO-like selective layer. Single-skinned hollow fiber membranes with only

NF-like outer skin layer were thus prepared so that separate measurements could be applied. The formulation of the polyelectrolyte multilayers could also be optimized before integrating with the RO-like polyamide layer to yield the double-skinned membranes. In addition, the RO-like single-skinned membrane was also utilized to compare the FO performance with the double-skinned FO membranes.

### **6.2.3 Hollow fiber characterization**

Characterization of the hollow fiber substrate and composite membranes followed a standard protocol as reported in previous chapters, where membrane morphology, surface charge, contact angle, substrate PWP and MWCO, etc. were examined accordingly. Moreover, membrane intrinsic separation properties including water permeability and rejections to various salts were measured via RO mode tests as described in Chapter 5 Section 5.3.3. It is difficult to measure the properties of the NF-like secondary skin layer independently in a double-skinned membrane, as the solute rejection is dominated by the RO-like selective layer. Single-skinned hollow fiber membranes with only NF-like outer skin layer were thus prepared so that separate measurements could be applied. The formulation of the polyelectrolyte multilayers could also be optimized before integrating with the RO-like polyamide layer to yield the double-skinned membranes. In addition, the RO-like single-skinned membrane was also utilized to compare the FO performance with the double-skinned FO membranes.

### **6.2.4 FO performance evaluation**

FO performance of the double-skinned hollow fibers was evaluated in both the AL-DS and AL-FS orientations (the RO-like inner skin layer was considered as the active layer for draw solution rejection) using a lab-scale FO cross-flow setup, similar to the unit described previously (Chou, Shi *et al.* 2010). Concentrated NaCl solutions (0.25 to 1.0 M) were used as the draw solution, and either DI water or 10 mM NaCl solution was employed as the feed water. The single-skinned hollow fiber membrane with an RO-like skin layer was also tested out, and influence of the

secondary NF-like skin layer on the overall FO performance of the double-skinned membrane could thus be revealed.

FO fouling tests were conducted on the double-skinned FO hollow fibers and single-skinned RO-like hollow fibers in the AL-DS orientation. The feed solution contained 10 mM NaCl and one of the three types of organic macromolecules, AHA, DEX or LYS, with a concentration of 200 ppm. The membranes were equilibrated with a 10 mM feed solution for 30 min with water flux adjusted to be  $\sim 25 \text{ l/m}^2\text{h}$  by altering the NaCl draw solution concentration between 0.25 and 0.5 M. The foulant was then added into the feed solution and the experiment was continued for 4 hours. All FO tests were carried out at room temperature of  $\sim 23^\circ\text{C}$  with a cross-flow velocity of 10 cm/s for both feed and draw solutions, and all solutions exhibited neutral pH of  $\sim 7$ .

## **6.3 Results and discussion**

### **6.3.1 Morphology and properties of PES hollow fiber substrate**

The morphology of the PES hollow fiber substrate is shown in Fig. 6.1, while detailed characteristic parameters of the substrate fiber are listed in Table 6.1. It can be seen from the figure that the finger-like pores were developed from both the outer and inner fiber surfaces to achieve a high porosity of 75%. Such a pore structure leads to relatively low mass transport resistance, which is believed to be beneficial for the mitigation of ICP in subsequent FO applications. Moreover, as shown in Fig. 6.1 (c) and (d), both the fiber inner and outer surfaces present a relatively smooth surface and uniformly distributed pores. The inner and outer skin layers of the substrate fiber have the MWCO of around 90 kDa, and possess a narrow pore size distribution as indicated by the small standard deviation (1.08 nm) of mean pore size (12.7 nm). Since the molecular weight of the polyelectrolytes employed in this study was larger than 100 kDa, the tight outer skin layer could minimize the penetration of the polyelectrolytes into the substrate fiber. The LBL multilayer may only formed on the fiber outer skin surface. Consequently, the pore

structure of the PES substrate could be preserved.

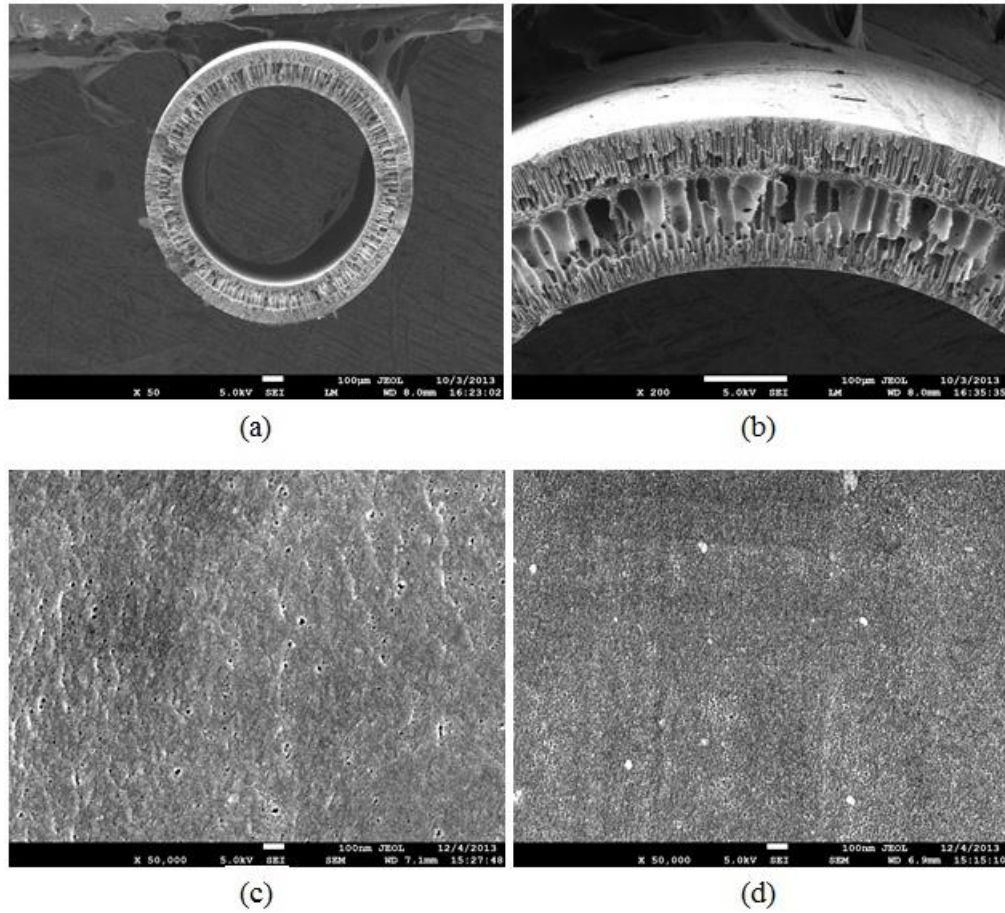


Fig. 6.1 Morphology of PES hollow fiber substrate: (a) cross-section at 50x; (b) enlarged cross-section at 200x; (c) inner surface at 50,000x; (d) outer surface at 50,000x.

Table 6.1 Characteristics of PES hollow fiber substrate.

| Characteristics              | Substrate fiber |
|------------------------------|-----------------|
| Fiber outer diameter (mm)    | 1.32            |
| Fiber inner diameter (mm)    | 0.96            |
| Fiber wall thickness (µm)    | 180             |
| Mean pore size (nm)          | 12.7            |
| Standard deviation (nm)      | 1.08            |
| PWP (L/m <sup>2</sup> h bar) | 280             |
| Outer skin MWCO (KDa)        | 88              |
| Inner skin MWCO (KDa)        | 90              |
| Porosity (%)                 | 75              |

### 6.3.2 Effect of LBL deposition on NF-like skin layer formation

The effects of the LBL deposition conditions such as polyelectrolyte concentration, solution pH and deposition time, etc. on the skin layer formation were explored previously (Qiu, Qi *et al.* 2011; Liu, Fang *et al.* 2013). In current study, only the influence of bilayer number on the separation properties of resultant LBL layer was investigated. The LBL assembled hollow fiber membranes with 0.5 to 3.0 bilayers were prepared, and their PWP and the rejection to different salts are listed in Table 6.2.

Table 6.2 Effect of bilayer number on PWP and salt rejections of resultant LBL assembled membranes.

| Membrane      | PWP (l/m <sup>2</sup> h bar) | NaCl rejection* (%) | MgCl <sub>2</sub> rejection* (%) | Na <sub>2</sub> SO <sub>4</sub> rejection* (%) |
|---------------|------------------------------|---------------------|----------------------------------|------------------------------------------------|
| PES substrate | 280                          | -                   | -                                | -                                              |
| 0.5-bilayer   | 189                          | 3.2                 | 1.4                              | 27.0                                           |
| 1.0-bilayer   | 58.0                         | 4.1                 | 17.0                             | 1.9                                            |
| 1.5-bilayer   | 6.72                         | 18.5                | 78.1                             | 81.9                                           |
| 2.0-bilayer   | 4.58                         | 42.4                | 90.4                             | 42.5                                           |
| 2.5-bilayer   | 3.47                         | 19.3                | 87.6                             | 82.2                                           |
| 3.0-bilayer   | 2.39                         | 58.8                | 95.0                             | 48.1                                           |

\*Salt rejections were obtained with 500 ppm single salt solutions under operating pressure of 2 bar.

It was found that the PWP of the LBL membrane decreased with the increasing number of deposited layers, but the membranes were ineffective in salt rejections until at least 1.5 bilayers of LBL deposition were applied. Moreover, a higher MgCl<sub>2</sub> rejection was perceived for the LBL membranes with 2.0 and 3.0 deposited bilayers, which indicates positive membrane surface charges according to Donnan exclusion principle (Schaep, Van der Bruggen *et al.* 1998). This observation was consistent with the fact that these LBL membranes were terminated with the cationic PAH as the last deposited layer. Meanwhile, a high NaSO<sub>4</sub> rejection was

noticed for 1.5- and 2.5-bilayer LBL membranes due to the polyanion termination. Furthermore, the highest NaCl rejection was observed for the LBL membrane with the most polyelectrolyte layers (3.0-bilayer) assembled, indicating the formation of a tight selective layer with high mass transport resistance. This also contributed to its low water permeability.

Based on their separation properties, the NF-like skins with 1.5, 2.0 and 2.5 bilayers were selected for the fabrication of double-skinned FO hollow membranes denoted as DS#1.5, DS#2.0 and DS#2.5, respectively. Although the 3.0-bilayer LBL membrane exhibited decent salt rejections, its low water permeability and high hydraulic resistance affected the overall performance of the resultant double-skinned membrane significantly. It was therefore omitted in the subsequent discussions on double-skinned FO membranes.

### **6.3.3 Characteristics of double-skinned FO hollow fiber membranes**

#### *i) SEM observation*

The SEM image of the interfacially polymerized RO-like skin layer is shown in Fig. 6.2 (a), while Figs. 6.2 (b) to (d) present the surface morphology of LBL assembled NF-like skin layer with 1.5, 2.0 and 2.5 bilayers of polyelectrolyte deposition, respectively. Comparing to the surface morphologies of the PES hollow fiber substrate shown in Fig. 6.1, the membrane pores can no longer be observed, and both the RO- and NF-like skin surfaces possess a rougher appearance. Specifically, the ridge-and-valley structure is observed for the RO-like skin, which is a typical morphology for interfacially polymerized polyamide membranes (Chou, Shi *et al.* 2010; Wei, Qiu *et al.* 2011). In contrast, the NF-like skin surface presents in a smoother manner, and it is interesting to notice that the 2.0-bilayer LBL deposition yielded a rougher surface than those with 1.5 and 2.5 deposited bilayers.

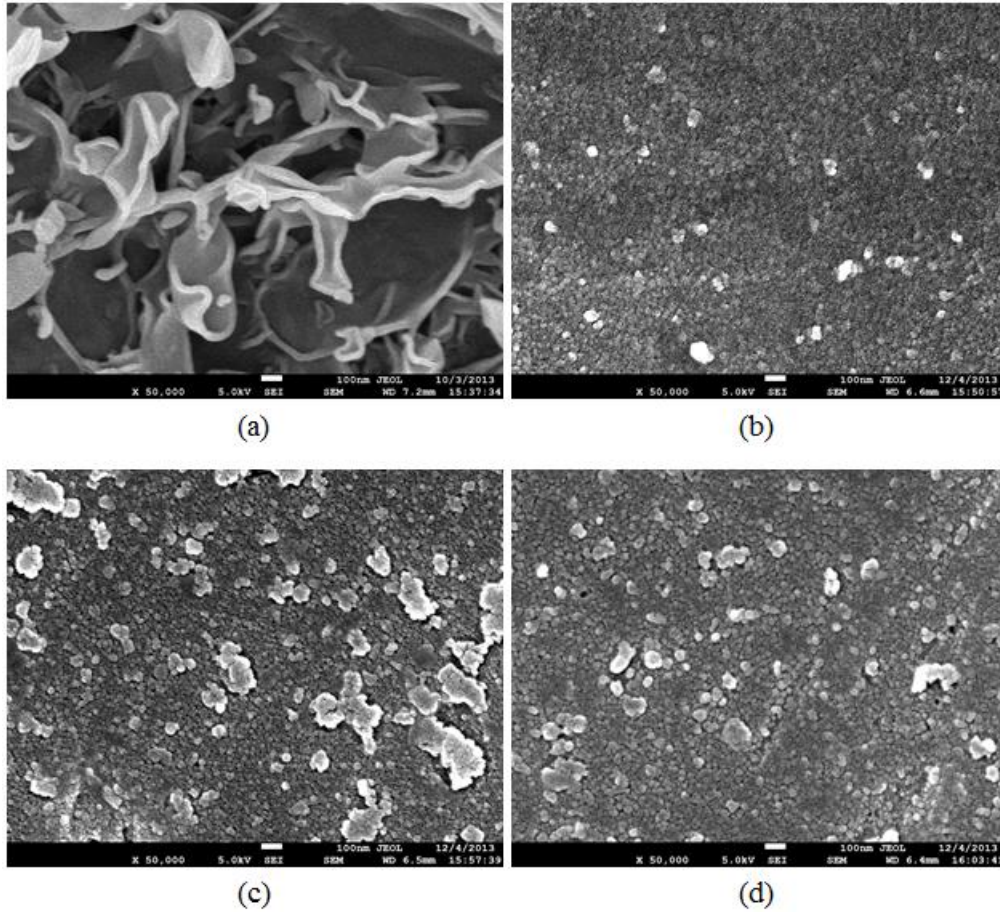


Fig. 6.2 Surface morphology of RO-like IP inner skin layer: (a) at 50,000x; Surface morphology of NF-like LBL assembled outer skin layer: (b) 1.5 bilayers at 50,000x; (c) 2.0 bilayers at 50,000x; (d) 2.5 bilayers at 50,000x.

ii) *Contact angle, surface roughness and zeta potential*

The wettability of the double-skinned FO hollow fibers were examined by dynamic contact angle measurements, and the results are shown in Table 6.3. According to the table, both RO- and NF-like selective skins possess a more hydrophilic nature in comparison with the PES substrate, as the contact angles for both the inner and outer skins of all three FO membranes are much smaller than the substrate fiber. Specifically, the outer skin of DS#2.5 membranes is more hydrophilic than DS#2.0 and DS#1.5, which may be due to the higher content of deposited hydrophilic polyelectrolytes that have contributed to the reduction of contact angle.

Table 6.3 Surface characteristics of PES substrate and double-skinned FO hollow fibers.

| Membrane          | Surface | Contact angle (deg) | Roughness (nm) | Isoelectric point* (pH) | Zeta potential* (mV) |
|-------------------|---------|---------------------|----------------|-------------------------|----------------------|
| DS#1.5, 2.0 & 2.5 | Inner   | 43.8                | 234            | 5.4                     | -7.3                 |
| DS#1.5            | Outer   | 38.2                | 16.1           | 6.4                     | -5.9                 |
| DS#2.0            | Outer   | 41.7                | 45.4           | 8.3                     | 12.2                 |
| DS#2.5            | Outer   | 26.5                | 35.3           | 7.1                     | 1.9                  |

\*Measurements were carried out with 0.01 M KCl from pH 4 to 9, and the zeta potential data were obtained at pH 7.

Moreover, as also listed in Table 6.3, the two selective skins of the composite membranes possess larger surface roughness values as compared with the PES substrate. The RO-like skin exhibits higher roughness than all the NF-like skins, while DS#2.0 possesses a rougher NF-like skin than DS#1.5 and DS#2.5. The roughness data is in good accordance with the observation from SEM images as discussed in the previous section.

In addition, the surface charge properties of the double-skinned membranes were characterized by streaming potential measurements with isoelectric point and zeta potential (at pH 7) of the respective skin layers summarized in Table 6.3. It is found that the NF-like skin of DS#1.5 is negatively charged, while DS#2.0 possesses a cationic NF-like skin. Differently, DS#2.5 exhibits minimal surface charge under neutral pH environment. Together with hydrophilicity and roughness, these membrane surface characteristics play an important role in determining the fouling behavior of the double-skinned membrane during FO applications, which will be further exemplified in Section 6.3.5.

### iii) *Intrinsic separation properties*

The intrinsic separation properties of the double-skinned membranes including water permeability (*A* value), salt permeability (*B* value) and NaCl rejection are listed in Table 6.4, and compared with the single-skinned membrane comprising only the

RO-like selective layer. It is observed that the water permeability of the membrane dropped significantly with the addition of a secondary NF-like selective layer, as the  $A$  value decreased from 3.45 l/m<sup>2</sup> h bar for the RO only membrane to 2.01 l/m<sup>2</sup> h bar for the DS#2.5 membrane. This is consistent with the modified resistance-in-series model with the dimension effect of hollow fiber taken into account, which was proposed in Chapter 5 Section 5.2. Nevertheless, the incorporation of NF-like skin has minimal influence on the membrane salt permeability due to the reason that the NF-like layer has a low rejection to NaCl and the essential salt rejection is still contributed by the RO-like active layer.

Table 6.4 Intrinsic separation properties of double-skinned FO hollow fibers.

| Membrane                                 | Water permeability, $A$ (l/m <sup>2</sup> h bar) | Salt permeability, $B$ (l/m <sup>2</sup> h) | NaCl rejection | Remark                           |
|------------------------------------------|--------------------------------------------------|---------------------------------------------|----------------|----------------------------------|
| RO only                                  | 3.45                                             | 0.14                                        | 97.6 @ 2 bar   | Present work                     |
| DS#1.5                                   | 2.64                                             | 0.14                                        | 96.2 @ 2 bar   |                                  |
| DS#2.0                                   | 2.49                                             | 0.13                                        | 96.8 @ 2 bar   |                                  |
| DS#2.5                                   | 2.01                                             | 0.16                                        | 95.4 @ 2 bar   |                                  |
| DS#2-RO/NF hollow fiber (double-skinned) | 2.05                                             | 0.23                                        | 85.3 @ 1 bar   | Previous work in Chapter 5       |
| Double dense layer flat sheet            | 0.17                                             | 0.07                                        | 92.0 @ 5 bar   | (Zhang, Wang <i>et al.</i> 2010) |
| CA double selective layer flat sheet     | 0.78                                             | 0.46                                        | 58 @ 1 bar     | (Wang, Ong <i>et al.</i> 2010)   |
| HTI FO flat sheet                        | 0.80                                             | 0.61                                        | 82% @ 3.5 bar  | (Tang, She <i>et al.</i> 2010)   |

The separation properties of double-skinned FO hollow fiber membranes reported in Chapter 5 and other similar types of FO membranes from literature (Tang, She *et al.* 2010; Wang, Ong *et al.* 2010; Zhang, Wang *et al.* 2010) are also summarized in Table 6.4 for comparison. The newly fabricated DS#1.5, DS#2.0 and DS#2.5 are found to possess improved water permeability and reduced salt permeability, as much higher  $A$  value and better NaCl rejection are perceived for DS#1.5, DS#2.0 and DS#2.5 membranes.

### 6.3.4 Effect of NF-like secondary skin layer on FO performance

The FO performances of the newly developed double-skinned FO hollow fiber membranes were evaluated using NaCl solutions from 0.25 to 1.0 M as the draw solution and DI water as the feed solution, and compared with the single-skinned membrane with only the RO-like selective skin. The water flux and ratio of salt flux over water flux ( $J_s/J_v$ ) as a function of draw solute concentration for both the AL-DS and AL-FS configuration are shown in Fig. 6.3.

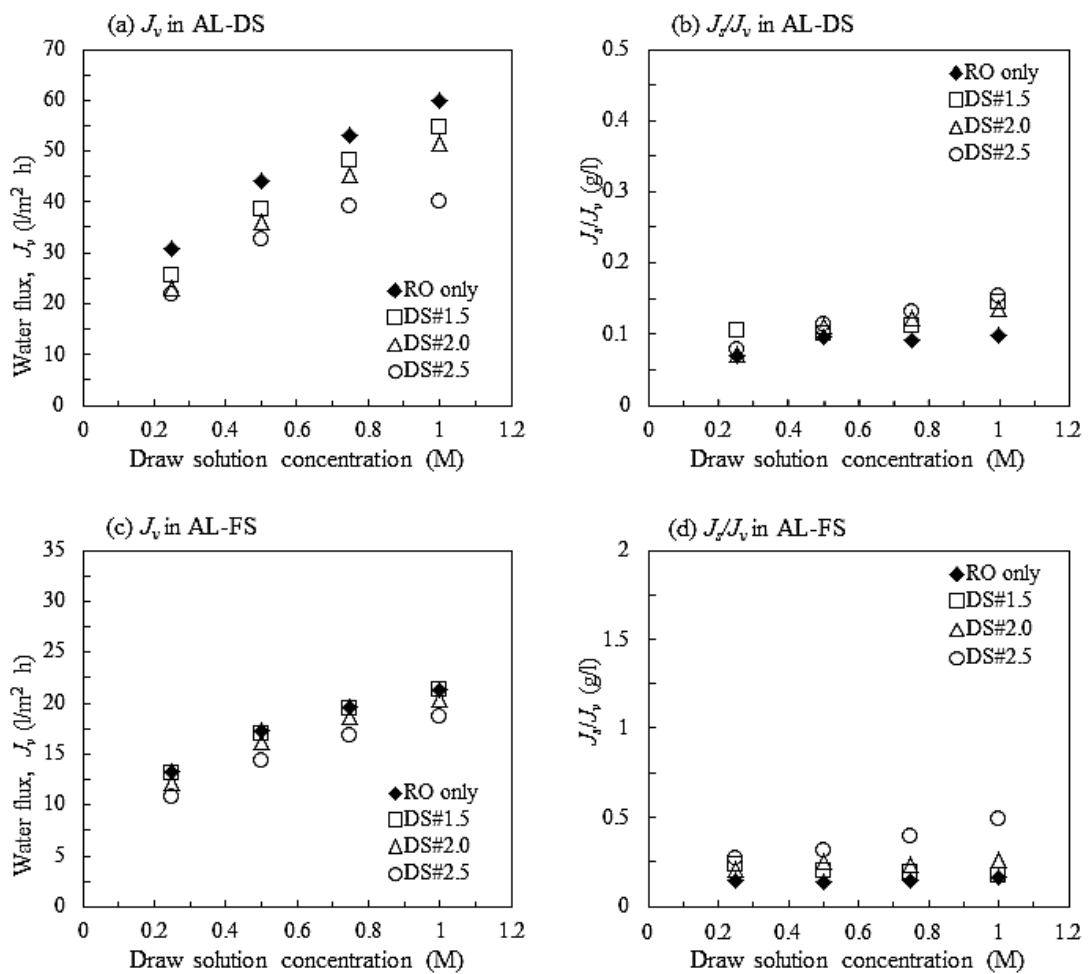


Fig. 6.3 FO performance of double-skinned hollow fiber membranes in the two orientations. Draw solution: 0.25-1 M NaCl; feed: DI water.

It can be seen that the FO water flux is affected when a secondary selective skin layer is incorporated into the membrane, as all the three double-skinned membranes have a lower water flux than the RO-like single-skinned membrane for both AL-DS

and AL-FS orientations. Similar phenomenon has been reported previously (Tang, She *et al.* 2011; Qi, Qiu *et al.* 2012), and was attributed to the additional water transport resistance introduced by the NF-like skin layer. When more polyelectrolyte layers are deposited for the NF-like skin formation, decreased water flux is observed for both membrane orientations. This is in agreement with the decreased intrinsic water permeability ( $A$  value) from DS#1.5 to DS#2.5 as deliberated in the preceding section. Furthermore, as illustrated in Figs. 6.3 (b) and (d), the ratio of salt flux and water flux ( $J_s/J_v$ ) for double-skinned hollow fiber membranes are generally larger than that for single-skinned membrane in both AL-DS and AL-FS configurations. Since the salt rejection is dominated by the RO-like selective layer and the contribution by the NF-like skin is insignificant, the overall salt flux for double-skinned membranes remains at the same level, but the decline of overall water flux for the double-skinned membranes leads to enlarged  $J_s/J_v$  ratios consequently. Finally, in comparison with AL-FS configuration, all the double-skinned membranes possess higher water flux and lower salt leakage in the AL-DS configuration, which are also in line with the trend for RO/NF double-skinned membranes reported in Chapter 5 Section 5.4.3. Therefore, the merit of AL-DS orientation in terms of higher water flux is effectively maintained by the newly fabricated double-skinned membranes when the feed used is DI water.

The FO performance of the three double-skinned hollow fibers in AL-DS orientation with DI water or 10 mM NaCl as feed is summarized in Table 6.5, and compared with other reported FO membranes with double selective layers. It is found that the FO water flux of all the three membranes reduce substantially when the feed water contains 10 mM NaCl, while the extent of salt back diffusion remain unchanged. The decline of water flux in AL-DS orientation with the increased feed solution concentration is caused by the enhanced ICP effect in the membrane porous support layer, which has been thoroughly investigated in different studies (Chou, Shi *et al.* 2010; Qi, Qiu *et al.* 2012). It is also noticed that the newly developed double-skinned hollow fibers possess superior water flux and less salt leakage than the commercial HTI FO membranes as well as all the RO-like double-skinned FO membranes reported in the literature.

Table 6.5 FO performance of double-skinned hollow fiber membranes.

| Membrane                                          | Water flux,<br>(l/m <sup>2</sup> h) | $J_s/J_v$ (g/l) | Draw solution | Feed solution | Remark                                |
|---------------------------------------------------|-------------------------------------|-----------------|---------------|---------------|---------------------------------------|
| DS#1.5                                            | 38.4                                | 0.10            | 0.5 M NaCl    | DI water      | Present work                          |
|                                                   | 30.1                                | 0.10            | 0.5 M NaCl    | 10 mM NaCl    |                                       |
| DS#2.0                                            | 36.0                                | 0.11            | 0.5 M NaCl    | DI water      |                                       |
|                                                   | 29.7                                | 0.10            | 0.5 M NaCl    | 10 mM NaCl    |                                       |
| DS#2.5                                            | 32.7                                | 0.11            | 0.5 M NaCl    | DI water      |                                       |
|                                                   | 27.0                                | 0.11            | 0.5 M NaCl    | 10 mM NaCl    |                                       |
| DS#2-RO/NF hollow fiber (double-skinned)          | 22.3                                | 0.14            | 0.5 M NaCl    | DI water      | Previous work in Chapter 5            |
| Double dense-layer flat sheet <sup>+</sup>        | 11.2                                | 0.39            | 2.0 M NaCl    | DI water      | (Zhang, Wang <i>et al.</i> 2010)      |
| CA double-selective layer flat sheet <sup>+</sup> | 19                                  | 0.71            | 2.0 M NaCl    | DI water      | (Wang, Ong <i>et al.</i> 2010)        |
| HTI-FO flat sheet                                 | 18.6                                | -               | 0.5 M NaCl    | DI water      | (Gray, McCutcheon <i>et al.</i> 2006) |
|                                                   | 17                                  | 0.85            | 0.5 M NaCl    | 10 mM NaCl    | (Tang, She <i>et al.</i> 2010)        |

\*All data is reported in AL-DS configuration at 20-25 °C.

### 6.3.5 Membrane organic fouling controlled by the NF-like secondary skin layer

Three organic compounds of Aldrich humic acid (AHA), dextran (DEX) and lysozyme (LYS) were used as the model foulants to test the capability of the NF-like secondary skin layer against the organic fouling. 4-hour FO fouling test was conducted for each individual foulant in AL-DS orientation so that the NF-like skin was placed against the feed solution. As initial water flux has great impact on the fouling behavior of FO membranes (Mi and Elimelech 2008; Tang, She *et al.* 2010), the draw solution concentration was adjusted accordingly so that all the membranes have the same initial flux of ~25 l/m<sup>2</sup> h. It is worth mentioning that the baseline testing results without any foulant in the feed solutions were not shown in this work. A dosing system as described previously (Chou, Shi *et al.* 2010) was utilized to

maintain the draw solution concentration, and the water flux are thus unchanged throughout the baseline testing period. The fouling behaviors of the double-skinned hollow fibers by AHA, LYS and DEX are signified by FO water flux over operating time as shown in Figs. 6.4 (a), (b) and (c), respectively.

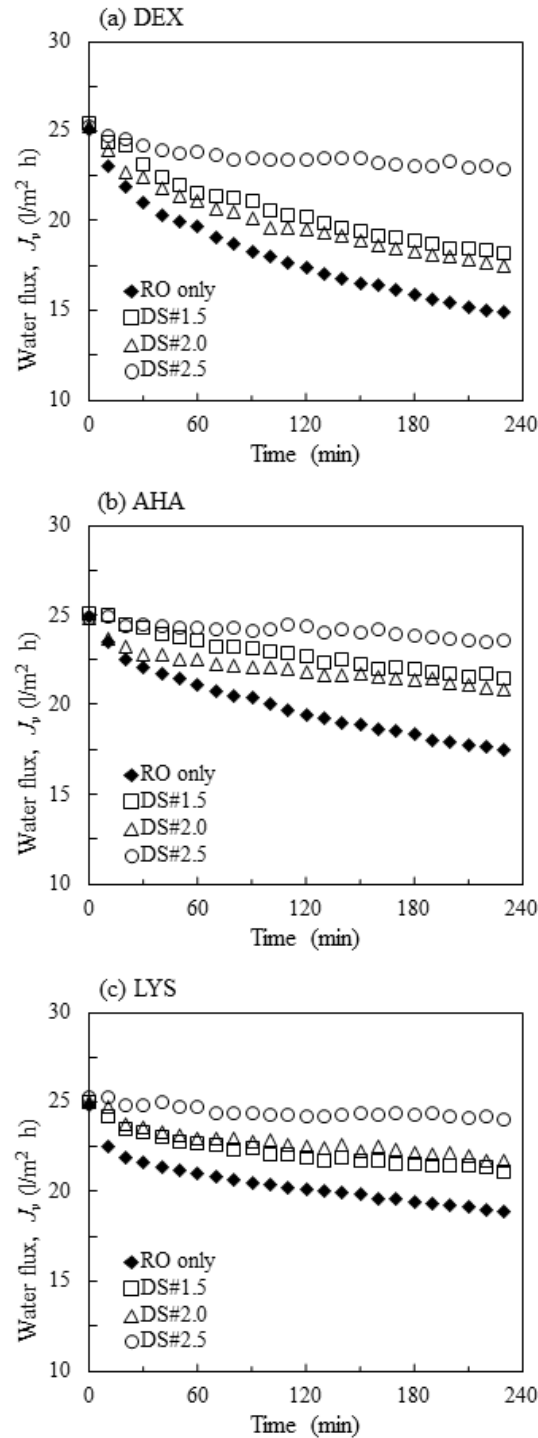


Fig. 6.4 Fouling behavior of double-skinned FO hollow fiber membranes by (a)

DEX, (b) AHA and (c) LYS. Draw solution: NaCl solutions ranged from 0.25 to 0.5 M to achieve the same initial flux ( $\sim 25 \text{ l/m}^2 \text{ h}$ ) for all membranes; feed solution: 200 ppm AHA and 10 mM NaCl; cross-flow velocity: 10 cm/s; in AL-DS configuration.

In general, the decline of water flux for all the three double-skinned membranes by organic fouling are less severe than the RO-like single-skinned membrane, which proves the presumption that the NF-like secondary skin provides an extra barrier to prevent the direct contact between the feed solution and the porous support layer, and to mitigate the possible pore clogging by the foulant.

Nevertheless, the fouling behaviors of the three double-skinned membranes deviate from each other quite considerably. It seems that their resistances to organic fouling are not only determined by the membrane surface characteristics, but also influenced by the properties of encountered foulants. It can be seen from Fig. 6.4 (a) that DS#2.5 membrane exhibited the highest water flux ( $22.8 \text{ l/m}^2 \text{ h}$ ) after 4 h DEX fouling test, followed by DS#1.5 membrane ( $18.2 \text{ l/m}^2 \text{ h}$ ) and DS#2.0 membrane ( $17.5 \text{ l/m}^2 \text{ h}$ ). Since dextran is a polysaccharide macromolecule with neutral electric charge, the dextran fouling may be mainly governed by the wettability and roughness of the membrane surface (Vrijenhoek, Hong *et al.* 2001; Lee, Amy *et al.* 2004; Susanto, Franzka *et al.* 2007). As discussed in Section 6.3.3, DS#2.5 membrane has the most hydrophilic NF-like skin with a much smaller contact angle ( $26.5^\circ$ ) than DS#1.5 and DS#2.0 membranes (both around  $40^\circ$ ), which might lead to its superior dextran fouling resistance. Apart from the similar wettability, the difference in dextran fouling behavior for DS#1.5 and DS#2.0 membranes may be associated to their surface roughness. DS#2.0 membrane possesses a rougher NF-like skin surface (almost 3 times of the roughness of DS#1.5 membrane) so that it is more susceptible to dextran fouling than DS#1.5 membrane.

In contrast, the membrane fouling by AHA and LYS are strongly influenced by the surface charge properties of the NF-like skin layer, which may supersede the effect of surface roughness. As also revealed in Section 6.3.3, DS#1.5 and DS#2.0

membranes possess an NF-like skin with negative and positive surface charges, respectively, in neutral pH environment. In addition to the high roughness of DS#2.0 membrane, the electrostatic attraction between its cationic skin surface and negatively charged AHA molecules would facilitate the formation of fouling layer, resulting in more severe AHA fouling. This interpretation is confirmed by the AHA fouling results shown in Fig. 6.4 (b), as the water flux of DS#2.0 membrane after 4 h testing was lower than DS#1.5 membrane. Similar behaviors are observed for LYS fouling in Fig. 6.4 (c), where DS#1.5 membrane with a negatively charged NF-like secondary skin experienced more severe fouling by the cationic LYS molecules even though DS#1.5 membrane has a relatively smoother NF-like secondary skin layer than that of DS#2.0 membrane. Again, DS#2.5 membrane appears to be more resistant to fouling by either AHA or LYS than the other two membranes, as the least decline in water flux (~5%) is perceived for DS#2.5 membrane in both Figs. 2 (b) and (c). Since DS#2.5 membrane possesses an NF-like secondary skin with minimal surface charge, its electrostatic interaction with AHA and LYS is insignificant. Together with the highly hydrophilic nature of the NF-like secondary layer, DS#2.5 membrane provides the best anti-fouling capability among the three double-skinned hollow fiber membranes developed in the current study, suggesting its great potential for practical FO applications.

## 6.5 Conclusions

In the present study, composite FO hollow fiber membranes with two selective skin layers were developed. The PES hollow fiber substrate was firstly fabricated by the phase inversion method. The RO-like polyamide skin layer was then prepared on the inner surface of the hollow fiber substrate via interfacial polymerization, while the NF-like outer skin layer was prepared via polyelectrolyte layer-by-layer assembly.

The newly developed double-skinned membranes presented a much more hydrophilic nature than the PES hollow fiber substrate. The zeta potential data showed that the surface charge of the 1.5- and 2.0-bilayer NF-like LBL skins were

negative and positive, respectively, while the 2.5-bilayer skin exhibited minimal surface charge under neutral pH environment. All the three double-skinned membranes possessed water permeability greater than  $2 \text{ l/m}^2 \text{ h bar}$  and NaCl rejection higher than 95% under 2 bar pressure, and have superior water flux and less salt leakage than the commercial HTI FO membranes as well as all the reported double-skinned FO membranes with RO-like selective layers.

In addition, the organic fouling resistance of the double-skinned membranes was examined by utilizing AHA, DEX and LYS as the model foulants. It was discovered that the NF-like secondary skin can effectively prevent the direct contact between the feed solution and the porous support layer, and mitigated possible pore clogging by the foulant. Moreover, DS#2.5 membrane provided the most exciting anti-fouling capability because of its highly hydrophilic NF-like secondary layer with minimal surface charge. A stable water flux of around  $25 \text{ l/m}^2 \text{ h}$  was attained for DS#2.5 membrane using  $<0.5 \text{ M}$  NaCl as the draw solution and a water containing 200 ppm DEX or AHA or LYS and  $10 \text{ mM}$  NaCl as the feed in AL-DS configuration, suggesting its great potential for practical FO applications.

## CHAPTER 7

### Conclusions and Recommendations

#### 7.1 Overall conclusions

This thesis presents the development of novel composite hollow fiber membranes with NF-like selectivity at low operating pressure, as energy consumption and membrane fouling tendency can be reduced significantly while remaining competent water permeation flux and solute rejection at UF-range low operating pressure. A series of novel NF composite membranes were prepared with structures and surface properties tailored for the niche applications of water softening and forward osmosis, respectively.

Three different techniques including interfacial polymerization (Chapter 3 and 4), surface modification (Chapter 5), and layer-by-layer assembly (Chapter 6) were employed for the formation of NF-like selective layer. An interfacially polymerized (IP) composite NF hollow fiber membranes with high permeation flux and high rejection of divalent metal ions at UF-range low operating pressures was developed for water softening application, then the IP thin film formation process was modified to achieve improved rejection profile and strengthened capability for low-pressure softening of more concentrated and complex water sources. On the other hand, an NF-like secondary selective layer was integrated into the thin-film composite hollow fiber membrane via surface modification method to yield a double-skinned membrane for mitigation of internal concentration polarization and

scaling in the FO processes. Subsequently, the preparation process of double-skinned membrane was ameliorated by involving a layer-by-layer assembled NF-like secondary skin layer to enhance the membrane water permeation and organic fouling resistance so that a membrane capable for a wide range of practical FO applications was developed.

The major findings and conclusions are summarized as follows:

- Composite NF hollow fiber membranes desirable for water softening under UF-range low operating pressure have been successfully developed. The positively charged thin-film selective layer was formed through interfacial polymerization (IP) on the inner surface of a PES hollow fiber substrate with PEI and TMC employed as the two IP monomers.
- A proper molecular weight of PEI and the presence of SDS in the aqueous phase are important for a successful interfacial polymerization reaction when PEI, a polyelectrolyte, is involved as the monomer instead of the monomers with small molecules. The PEI concentration also affected the membrane performance differently comparing to the effect of TMC concentration. In addition, the polymerization reaction is observed to be self-limited with respect to a prolonged reaction time.
- It is revealed that the PEI-TMC polymerized thin film exhibits a combined separation mechanism of the Donnan exclusion and steric hindrance. It possesses a PWP of about 17 l/m<sup>2</sup> h bar and a MWCO of around 500 Da with MgCl<sub>2</sub> and MgSO<sub>4</sub> rejections of 96.7% and 80.6%, respectively, when tested for 1000 ppm MgCl<sub>2</sub> or MgSO<sub>4</sub> feed solutions at 2 bar operating pressure. Additionally, for a 3000 ppm TDS feed stream containing salt mixtures, the membrane rejections for Mg<sup>2+</sup> and Ca<sup>2+</sup> ions were found to be around 90% while the water flux was about 20 l/m<sup>2</sup> h at 2 bar pressure, suggesting its potential for effective water softening application.

- However, the rejections to hard water metal ions are found to decrease substantially when the feed solution contains the  $\text{SO}_4^{2-}$  group, as the membrane's positive charges are neutralized by the divalent counterions, thus leading to weakened electrostatic repulsion to the divalent metal ions.
- Novel mixed PEI/PIP-based composite NF hollow fiber membranes with improved rejection profile and strengthened capability for low-pressure softening of more concentrated and complex water sources were successfully developed via interfacial polymerization with TMC being the organic phase monomer, and a mixture of PEI and PIP being the monomers in the aqueous phase.
- It was found that there was a synergetic effect of PEI and PIP on the formation of the selective layer. The water permeability and salt rejection of the resultant membrane were both enhanced with a small amount of PIP added into the PEI aqueous phase, but dropped quickly with a higher PIP to PEI ratio.
- The mixed PEI/PIP-based composite NF membrane possessed a MWCO of 380 Da, and pure water permeability (PWP) of  $18.2 \text{ l/m}^2 \text{ h bar}$ . Under an operating pressure of 2 bar, the membrane exhibited rejections of 96.3% and 93.8% to 1000 ppm  $\text{MgCl}_2$  and  $\text{MgSO}_4$  feed solutions, respectively. By the effective softening of simulated hard water feed solutions with high total hardness and high content of  $\text{SO}_4^{2-}$ , the membrane demonstrates better water softening performance compared with the membranes made with PEI or PIP alone as the aqueous phase IP monomer, and is therefore competent for softening of more concentrated and complex water sources.
- Novel thin-film composite FO hollow fiber membranes with an NF-like secondary selective skin were successfully developed for the first time. The fabrication procedures involved making UF hollow fiber substrate using PAI polymer material via phase inversion method, followed by IP and surface modification on the inner and outer surfaces of the substrate to yield a

polyamide RO-like inner skin layer and a positively charged NF-like outer skin layer, respectively.

- It was discovered that the preparation route was critical for obtaining high performance double skinned FO membranes. The sequence of conducting IP on the substrate inner surface prior to the chemical cross-linking of the outer skin was preferred in order to achieve better performance for the resultant double-skinned hollow fibers.
- The double-skinned FO hollow fibers exhibited high water permeability of 2.05 l/m<sup>2</sup> h bar and 85% rejection to NaCl at 1 bar pressure as well as superior FO water flux of 41.3 l/m<sup>2</sup> h and low ratio of salt flux over water flux of 0.126 g/L when using DI water and 2.0 M NaCl as feed and draw solutions, respectively, in the active layer facing draw solution (AL-DS) orientation.
- The double-skinned membrane was found to outperform single-skinned membrane when the feed contains divalent ions or the feed exhibits high scaling tendency to membrane which suggested that the incorporation of NF-like selective layer is an effective way to minimize the ICP effect, mitigate the membrane scaling and thus enhance the feasibility of FO processes for practical applications.
- Polyelectrolyte layer-by-layer (LBL) assembly method was involved for the formation of NF-like secondary layer to substitute the chemical cross-linking method, and double-skinned hollow fiber membranes with improved water permeability, salt rejection and FO performance was therefore developed.
- The double-skinned DS#2.5 hollow fiber membrane exhibits exciting organic fouling resistance because of its highly hydrophilic LBL NF-like secondary layer with minimal surface charge and tightened surface structure to mitigate possible substrate pore clogging and fouling layer formation. A stable water flux of around 25 l/m<sup>2</sup> h was attained for DS#2.5 membrane using <0.5 M NaCl as

the draw solution and a water containing 200 ppm dextran (DEX) or Aldrich humic acid (AHA), or lysozyme (LYS) and 10 mM NaCl as the model feed in AL-DS configuration, suggesting its capability for a wide range of practical FO applications.

## 7.2 Recommendations for future research

The following tasks are suggested to be extended to in the future research:

- It is more challenging to apply low-pressure NF membranes in softening highly concentrated feed streams such as seawater and SWRO brine. As the membrane surface charge is less effective for the rejection of a highly concentrated feed, a denser structure and tighter pore size is required for the NF-like selective layer, and water permeability of the layer is likely to be compromised. Nanoparticles like zeolite (Lind, Ghosh *et al.* 2009) and carbon nanotube (Wu, Tang *et al.* 2010) may therefore be incorporated in the NF-like selective layer to enhance the water permeation without loosening the pore structure. The anti-fouling nature of the nanoparticles also improves the long-time performance of the membrane when a high amount of foulants is presented in the feed stream (Sun, Su *et al.* 2009).
- Apart from the discussions in Chapters 5 and 6, the AL-FS orientation is a more viable orientation for composite membranes with single selective layer to be applied in FO applications. Although more severe flux decline is induced by the dilutive ICP, the dense active layer prevents the penetration of foulants from the feed stream into the support layer so that more sustainable water flux could be accomplished (Yip, Tiraferri *et al.* 2010; Wei, Qiu *et al.* 2011). In this case, composite membranes with highly water permeable active layer and good anti-ICP substrate are needed to achieve productive FO performance. In this case, single-skinned composite membranes with an NF-like selective layer could be adopted for FO applications with AL-FS orientation, as their higher-than-RO pure water permeability should provide higher FO water fluxes than RO-like

membranes.

- Investigation on the preparation of thin-film active layer with NF-like selectivity is the primary focus of the thesis as the separation properties of the composite membrane is principally controlled by the selective layer. However, the surface pore structure and properties of the hollow fiber substrate have great impacts on the formation of selective layer as well as the performance of resultant composite membranes. Influences of substrate material, dimension, surface pore size and pore size distribution, hydrophobicity and charge character on the formation of NF-like layer via different methods could be studied accordingly.
- According to the specific requirement for the niche applications, the overall porosity, fiber thickness and tortuosity, etc. of the hollow fiber substrates could be further adjusted. For instance, PVDF hollow fibers with MF-range pores can possess higher porosity than UF PES membranes (Ji, Zhu *et al.* 2008; Rajabzadeh, Maruyama *et al.* 2008). It is therefore worthwhile to explore the possibility of adopting such hollow fibers as the substrates for the development of composite NF membranes for forward osmosis applications.
- Since the membranes developed in this study are intended for niche applications, further tests in actual field applications are recommended. As such, it shall be necessary to extend the current work from lab-scale towards pilot- and full-scales. This can be challenging because adjustments might be required on the fabrication techniques to assure the performance of the scaled-up NF membranes. Moreover, performance of the composite NF hollow fibers also needs to be examined for different operating parameters like recovery level, flow rate, operating time, extent of backwash, etc. so that the membrane performance profile towards actual field applications could thus be obtained.

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