Development of hollow fiber membranes with high power density for pressure retarded osmosis

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**DEVELOPMENT OF HOLLOW FIBER MEMBRANES
WITH HIGH POWER DENSITY FOR PRESSURE
RETARDED OSMOSIS**

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INTERDISCIPLINARY GRADUATE SCHOOL
SINGAPORE MEMBRANE TECHNOLOGY CENTRE
NANYANG ENVIRONMENT AND WATER RESEARCH
INSTITUTE**

2017

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS	i
TABLE OF CONTENTS	iii
LIST OF PUBLICATIONS	vii
LIST OF FIGURES.....	ix
LIST OF TABLES	xv
LIST OF SYMBOLS	xvi
SUMMARY	xix
Chapter 1 Introduction	1
1.1 Background.....	1
1.2 Statement of problems	3
1.3 Objectives	5
1.4 Thesis outline.....	6
Chapter 2 Literature review	9
2.1 Power production in PRO	9
2.2 Development of PRO applications.....	12
2.3 Key challenges for PRO process.....	14
2.3.1 External concentration polarization in PRO	14
2.3.2 Internal concentration polarization in PRO	17
2.3.3 Mechanical strength.....	19
2.3.4 Membrane fouling in PRO.....	21

2.4	Desired PRO membranes	23
2.5	Current PRO membranes development	25
2.5.1	Integral asymmetric membranes.....	26
2.5.2	Composite membranes	27
2.5.3	Fouling mitigation in PRO	32
2.5.4	PRO hollow fiber module development	35
2.6	Summary	36
Chapter 3	Identification of safe and stable operation conditions for pressure retarded osmosis with high performance hollow fiber membrane	38
3.1	Introduction	38
3.2	Experimental Methods	39
3.2.1	Materials.....	39
3.2.2	Fabrication of PRO hollow fiber membranes and modules	40
3.2.3	Characterization and analysis.....	40
3.2.4	Performance in PRO process.....	43
3.3	Results and discussion.....	44
3.3.1	Substrate characteristics	44
3.3.2	Morphology of composite PRO hollow fiber membranes	47
3.3.3	Intrinsic properties of PRO hollow fiber membrane	48
3.3.4	PRO performance.....	51
3.3.5	Stability test.....	55

3.4	Conclusion	61
Chapter 4	Enhancing pressure retarded osmosis performance with low-pressure nanofiltration pretreatment: membrane fouling analysis and mitigation.....	63
4.1	Introduction.....	63
4.2	Materials and methods	64
4.2.1	Chemicals and membranes.....	64
4.2.2	Characterizations and analysis	66
4.2.3	Performance evaluation in PRO process.....	67
4.3	Results and discussion	68
4.3.1	Characteristics of NF membranes	68
4.3.2	Characteristics of PRO feed solutions.....	69
4.3.3	PRO fouling with NB.....	71
4.3.4	PRO fouling with NF pretreated waters.....	74
4.4	Conclusion	80
Chapter 5	Module scale-up and performance evaluation of thin film composite hollow fiber membranes for pressure retarded osmosis	82
5.1	Introduction.....	82
5.2	Materials and methods	83
5.2.1	Fabrication of PRO membranes and modules.....	83
5.2.2	PRO module performance.....	85

5.2.3	Defect identification and repair	85
5.2.4	Pretreatment of PRO feed solution.....	86
5.2.5	PRO performance in lab scale and pilot scale	86
5.2.6	Prediction of PRO water flux using mathematical model	88
5.3	Results and discussions	90
5.3.1	Performance evaluation of PRO module in a lab-scale setup	90
5.3.2	Effects of ECP on PRO flux.....	93
5.3.3	Effects of change in selective layer properties	96
5.3.4	Performance evaluation and ECP mitigation of PRO module in a pilot-scale setup.....	98
5.3.5	Exploration for pilot-scale PRO operation with actual wastewater	105
5.4	Conclusions	107
Chapter 6	Conclusions and recommendations	109
6.1	Overall conclusions	109
6.2	Recommendations for future research.....	111
Reference		114
Appendix		134
Appendix A.	Organic components in different PRO feed solutions.	134
Appendix B.	Calculation of effect of concentration change in pilot PRO modules.	135
Appendix C.	Calculated ECP modulus when considering the concentration change effect	137

LIST OF PUBLICATIONS

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LIST OF FIGURES

Figure 1.1. Direction of water transportation in FO (from low salinity to high salinity), RO (from high salinity to low salinity) and PRO (from low salinity to high salinity).....	2
Figure 1.2. Schematic drawing of PRO power generation process using a hollow fiber (HF) module. The draw solution is pressurized in the lumen of the HF module while the feed solution is pumped in the shell of the HF module.	3
Figure 2.1. Maximum theoretical extractable energy from different saline water source (adapted from (Helfer et al. 2014b)).	10
Figure 2.2. Power density in the FO, RO and PRO process. Energy is required in a RO process while energy is produced for a PRO process.	11
Figure 2.3. Concentration profile in a typical PRO membrane. The draw solution and feed solution operate in the countercurrent direction. Water permeates from the feed solution side to the draw solution side while the back-diffused solute transports from the draw to the feed.....	15
Figure 2.4. Chemical structure of PEI.	21
Figure 2.5. Schematic drawing of membrane fouling in (a) AL-FS and (b) AL-DS orientation.....	22
Figure 2.6. Schematic drawing of HF PRO membrane (a) with selective layer in the lumen; (b) with selective layer in the outer layer in AL-FS orientation.	25

Figure 2.7. A typical IP process using MPD and TMC. The reaction occurs in the interface of the organic phase and solvent phase where TMC and MPD slowly diffuse to the interface. 28

Figure 3.1. Morphologies of PEI hollow fiber membrane substrate: (a1) cross-section; (a2) cross-section near the inner surface; (a3) inner surface; thin film composite (TFC) – PEI hollow fiber membrane before PRO testing (b1) cross-section; (b2) cross-section near the inner surface; (b3) inner surface. 45

Figure 3.2. Morphologies of TFC – PEI HF membrane: (a) cross-section near inner surface and (b) polyamide layer on the inner surface, after PRO testing at different hydraulic pressures: (1) 12.5 bar; (2) 15.0 bar; (3) 22.0 bar; (4) 12.5-18.0 bar for 180 h. 48

Figure 3.3. PRO water flux (Δ) and power density ($\square$) of the TFC-PEI hollow fiber membrane at various operating pressures from 5 to 24 bar. Testing conditions: 1.0 M NaCl solution as the draw solution and DI water as the feed water at ambient temperature. 49

Figure 3.4. Water permeability A ($\square$), salt permeability B ($\blacksquare$), B/A ($\bullet$) and NaCl rejection ($\blacktriangle$) as a function of hydraulic pressure of the feed, which implies the creeping occurred at 18 bars. Testing conditions: 2000 ppm NaCl solution as the feed at ambient temperature, operating pressure of 5-18 bar. 51

Figure 3.5. Water permeability A ($\square$), salt permeability B ($\blacksquare$), B/A ($\bullet$) and NaCl rejection ($\blacktriangle$) as a function of hydraulic pressure of the feed. Testing conditions:

2000 ppm NaCl solution as the feed at ambient temperature, operating pressure of 5-15 bar.	51
Figure 3.6. (a) water flux (J_w) and J_s/J_w and (b) power density as a function of hydraulic pressure of the draw solution. One cycle consists of ascending (●, ▲, ■) and descending (○, △, □) pressure. (1) and (2) are first and second cycle, respectively. PRO testing conditions: 1.0 M NaCl as draw solution and DI water as the feed at ambient temperature; maximum pressure is 22 bar.	53
Figure 3.7. (a) water flux (J_w) and J_s/J_w and (b) power density as a function of hydraulic pressure of the draw solution. One cycle consists of ascending (●, ▲, ■) and descending (○, △, □) pressure. (1) and (2) are first and second cycle, respectively. PRO testing conditions: 1.0 M NaCl as draw solution and DI water as the feed at ambient temperature; maximum pressure is 20 bar.	54
Figure 3.8. Surface morphologies of thin film composite (TFC) – PEI hollow fiber membrane after PRO testing at maximum pressures of 22 and 20 bar.	55
Figure 3.9. Power density and water flux (●, ▲, ■) and hydraulic pressure of the draw solution (○, △, □) as a function of time. PRO testing was performed continuously using 1.0 M NaCl as draw solution and DI water as the feed at ambient temperature at hydraulic pressures of 12.5 (○), 15 (△) and 18 (□) bar.	57
Figure 3.10. Atomic force microscope (AFM) images showing measured topography after indentation tests on the inner surface of hollow fiber membranes: (a) PEI substrate, (b) TFC-PEI, (c) TFC-PEI after long term PRO testing.....	58

Figure 3.11. (a) Water flux (J_w) and salt flux over water flux (J_s/J_w); (b) power density and pressure as a function of time. PRO testing was performed using 1.0 M NaCl as draw solution and DI water as the feed at ambient temperature at maximum hydraulic pressure of 15 bar 60

Figure 4.1. PRO water flux profile for (a) DI water and (b) NB feed water. The pressure stepping was performed for precise recording of the water flux..... 72

Figure 4.2. SEM images of (from left to right) inner surface, cross-section near inner layer, outer surface, and cross-section near outer layer of (a) DI-PRO membrane and (b) NB-PRO membrane. The scale bar applies to all figures above. 73

Figure 4.3. Low vacuum EDX element mapping images of carbon, oxygen, phosphorus, calcium, silicon, sulfur and magnesium (from left to right) of cross section inner layer of the (a) DI-PRO membrane and (b) NB-PRO membranes and cross section outer layer of (c) DI-PRO membrane and (d) NB-PRO membrane. White color stands for the highest element signal detected while black color denotes the lowest element signal. The scale bar applies to all figures above... 74

Figure 4.4. PRO flux profile of PRO membranes using (a) NF270/P, (b) S-NF/P, (c) L-NF/P as feed and 1M NaCl solution as draw and (d) enlarged water flux profile of (a-c) in the first 50 mins operation. 75

Figure 4.5. EDX element mapping images of carbon, oxygen, phosphorus, calcium silicon and sulfur (from left to right) of cross section near inner layer of

the (a) NF270/P -PRO, (b) S-NF/P-PRO and (c) L-NF/P -PRO membranes respectively. The scale bar applies to all figures above.	76
Figure 4.6. XPS depth profiling starting from surface of active layer of (a) DI-PRO; (b) NB-PRO; (c) S-NF/P-PRO; (d) L-NF/P-PRO membranes.	77
Figure 4.7. Plot of estimated SiO ₂ concentration in the PRO membrane substrate as a function of membrane water flux.	79
Figure 5.1. Schematic drawing of fabrication procedure of modules with (a) 150 fibers and (b) 500 fibers and above.	84
Figure 5.2. Schematic drawing of industrial practice of defect detection and repair of HF modules.	86
Figure 5.3. Schematic drawing of pilot setup, which could be operated with 200 L draw/feed solution tank (yellow/green loop); with 1000 L draw/feed tank (red/blue loop); and with pressure exchanger or hydro turbines.	88
Figure 5.4. Photo images of cross-section (top row) of PRO modules with (a) 15 fibers, (b) 150 fibers, (c) 500 fibers, (d) 1000 fibers in one bundle, (e) 1000 fibers in four bundles, (f) 2000 fibers in seven bundles; and top view (bottom picture) of these modules.	91
Figure 5.5. PRO performance using a lab-scale setup of HF modules of (a) 15 fibers in 0.5- inch housing, (b) 150 fibers in 0.75-inch housing (c) 500 fibers in 2-inch housing and (d) 1000 fibers in 2-inch housing using DI water as feed and 1M NaCl solution as draw.	92

Figure 5.6. Calculated and experimental water fluxes of different modules at an operating pressure of 15 bar (draw: 1M NaCl; feed: DI water)	94
Figure 5.7. Calculated ECP modulus at (a) draw and (b) feed sides in different modules (modelling at 15 bar with 1M NaCl as draw solution and DI water as feed)	96
Figure 5.8. PRO performances of HF modules with 1000 fibers in 2-inch housing using a pilot-scale setup with (a) one bundle design, (b) four bundles design, and (c) a distribution baffle, using tap water as feed and 1M NaCl solution as draw.	99
Figure 5.9. Schematic drawing and photo images of (a) distribution baffles and (b) distribution tubes in a HF module.....	100
Figure 5. 10. Calculated water flux with different cross flow velocities at (a) the draw (cross flow velocity of feed solution =1.9 cm/s) and (b) the feed sides (cross flow velocity of draw solution = 12 cm/s) in the 1000-fiber module (operating pressure: 15 bar; draw: 1M NaCl; feed: tap water; red dots indicate cross flow velocity used in this study)	102
Figure 5.11. Schematic drawing of PRO modules with perforated feed diffuser (a) side view and (b) cross section view	104
Figure 5.12. PRO performances of HF modules with 1000 fibers using tight NF-treated NEWater brine as feed and 1 M NaCl solution as draw.....	107

LIST OF TABLES

Table 2.1. Tensile strengths of materials adopted in membrane fabrication.....	21
Table 2.2. Recent PRO membrane performances	30
Table 2.3. Summary of recent studies about membrane fouling in PRO.....	33
Table 3.1. Properties of PEI HF membranes.....	46
Table 3.2. Mechanical and structural properties of PEI HF membranes.	47
Table 3.3. Comparison of PRO performance.....	52
Table 4.1. Summary of denotations of PRO feed solutions and PRO membranes.	65
Table 4.2. Chracteristics of membrane NF270, S-NF and L-NF.	69
Table 4.3. Summary of ionic compositions in different solutions.	70
Table 4.4. Summary of PRO performance using different feed solutions.	80
Table 5.2 Characteristics of PRO modules.	91
Table 5.3. Summary of characteristics and performance of PRO modules.	105
Table 5.4. Characteristics of NF module used in pretreatment.	107

LIST OF SYMBOLS

Letters

A	Pure water permeability of the membrane, L/m^2hbar
A_m	Effective membrane area of the hollow fiber membrane, m^2
B	Solute permeability of the membrane, L/m^2h
c	The molar concentration M(mol/L)
c_F	Salt concentration in the feed water tank, mol/L
C_i	Silica concentration at the boundary layer (x), mol/L
C_b	Silica concentration at $x=0$, mol/L
C_{db}	Bulk concentration on the draw side, mol/L
C_{dm}	Bulk concentration on the draw solution-membrane boundary concentration, mol/L
C_{RS}	Concentration of the boundary between rejection layer and support layer, mol/L
C_{fm}	Concentration at the feed solution-membrane boundary layer, mol/L
C_{fb}	Concentration at the bulk feed solution, mol/L
d_h	Hydraulic diameter of the flow channel, m
D	Diffusion coefficient, m^2/s
D_s	Diffusion coefficient of the solute, m^2/s
i	Van't Hoff factor
J_s	Salt flux through a thin film, L/m^2h
J_w	Volumetric water flux through a thin film, L/m^2h
k	Mass transfer coefficient in the bulk solution, L/m^2h
K_m	Mass transfer coefficient inside membrane, L/m^2h
k_D	Mass transfer coefficient in the draw side, L/m^2h

k_F	Mass transfer coefficient in the feed side, L/m ² h
L	Module length, m
P	porosity of the membrane, %
P_i	Applied pressure on the inner surface of the HF membranes, bar
ΔP	Imposed external pressure, bar
Q_{D1}	Flow rate of the draw solution at the inlet of the module, m ³ /s
Q_{D2}	Flow rate of the draw solution at the outlet of the module, m ³ /s
Q_{F1}	Flow rate of the feed solution at the inlet of the module, m ³ /s
Q_{F2}	Flow rate of the feed solution at the outlet of the module, m ³ /s
r_o	outer diameter of the membranes, m
r_i	inner diameter of the membranes, m
R	The universal gas constant, J/molK
Re	Renolds number
S	Structural parameter of the membrane, m
Sc	Schmidt number
Sh_l	Sherwood number in the lumen of the membrane
Sh_s	Shewood number of the flow in the shell
Δt	Predetermined time interval, hr
V_T	True specific volume, cm ³ /g
V_A	apparent specific volume cm ³ /g
V_F	volume of the feed water, m ³
ΔV_{DF}	volume change of the dosing feed, m ³
W	Power density, W/m ²

Greeks

π	Osmotic pressure, bar
$\Delta\pi$	Difference in the osmotic pressure through the membrane, bar
π_b	Osmotic pressure at the bulk solution, bar
π_m	Osmotic pressure at the membrane-bulk solution surface, bar
π_D	Osmotic pressure on the draw side, bar
π_F	Osmotic pressure on the feed side, bar
$\pi_{D,b}$	Osmotic pressure of the bulk draw solution, bar
$\pi_{F,b}$	Osmotic pressure on the bulk feed solution, bar
$\pi_{D,m}$	osmotic pressure of the draw solution at the active layer surface, bar
$\pi_{F,m}$	osmotic pressure of the feed solution at the interface between the membrane substrate and the feed solution, bar
τ	Tortuosity of the membrane
μ	Poisson's ratio
α	Effective membrane area of the module, m ²

SUMMARY

Energy shortage and water scarcity are worldwide challenges, which drive the exploitation of sustainable alternative energy sources. Among various options, osmotic energy has attracted much attention in recent years as a renewable energy that could be harvested by a pressure retarded osmosis (PRO) process, where energy is produced when water permeates naturally from a low salinity stream to pressurized high salinity stream. However, challenges like concentration polarization, membrane fouling and lack of commercial PRO membranes have greatly impeded the practical application of PRO process for energy harvesting. Therefore, proper design of optimized PRO modules with high performance is vital for practical PRO operations.

Firstly, a novel thin-film composite hollow fiber PRO membrane with high PRO performance was fabricated. As the hollow fiber membrane is made from polymeric materials, it may gradually deform over time under high pressure loading, or membrane “creeping”, where hollow fiber membranes are severely stretched due to applied pressure in the lumen and thus lose its selectivity, will occur. An attempt to analyze the membrane creeping phenomenon was conducted. The membrane creeping was evaluated via nanoindentation by using an atomic force microscopic (AFM) technique. A non-stop 200 hours PRO test and integrity evaluation were carried out to investigate the membrane performance under various operating pressures. The results showed that the membrane was able to produce a stable power density output of 19.2 W/m^2 at 15.0 bar, using 1.0 M NaCl as the draw solution and DI water as the feed water. Membrane creeping was observed when the applied pressure exceeded the safe operation limit or the flux

turning point, where the membrane flux started to increase with increasing applied pressure in the PRO mode. This caused an irreversible damage to the membranes. Essentially, this work identified a safe operating boundary for the in-house produced PRO hollow fiber membranes so as to achieve optimized PRO performances. It also provides guidance for practical applications of polymeric hollow fiber membranes in the PRO process.

Secondly, the feasibility of the produced PRO membranes for practical PRO operation was examined. It was found that the fouling was severe when a real wastewater retentate from a local water reclamation plant was used as the feed solution of the PRO process. Therefore, low pressure nanofiltration (NF) pretreatment was adopted to treat the wastewater brine prior to feeding it into the PRO process. Three NF membranes were compared in terms of their membrane properties, quality of the NF permeates (i.e., PRO feed) and PRO membrane performances. Results showed that the PRO water flux could increase to 30.5 L/m²h at 16 bar applied pressure by using in-house made low-pressure NF hollow fiber membranes on the pretreated solution, in contrast to a lower water flux of 9 L/m²h in the case of untreated wastewater retentate. A systematic analysis of the water chemistry and various membrane characterization such as electron dispersed X-ray (EDX) and X-ray photoelectron spectroscopy (XPS) depth profiling has revealed that calcium salts, organic compounds, and silica were main contributors of membrane fouling in the PRO process. Low-pressure NF was found to be able to mitigate the fouling potential from multivalent ions and organic matters, but silica scaling in PRO remains a challenge which needs to be further addressed.

Furthermore, the PRO membranes were also scaled-up to a two-inch module from a lab-scale half-inch module for a pilot-scale study. The produced PRO modules have a maximum effective area of 0.5 m². By assessing the PRO performances of the modules with different sizes, external concentration polarization (ECP) was found to have significant impact on the flux reduction during module scale-up. Different module designs, including fiber bundles, distribution baffles and distribution tubes, were thus adopted as an attempt to boost the membrane performance. A power density of 8.9 W/m² at 15 bar was obtained using tap water as feed and 1M NaCl solution as draw solution. PRO was also carried out using the developed two-inch module on a pilot-scale setup with actual wastewater retentate as feed solution. Low pressure nanofiltration was selected as the pretreatment of the wastewater retentate to mitigate fouling. A power density of larger than 8 W/m² was obtained when pretreated wastewater retentate was used as the feed solution, implying high potential of PRO in the pilot scale. Nevertheless, full potential of PRO can only be realized by mitigating ECP, which could be achieved by proper module designs and will be conducted in the further endeavor.

CHAPTER 1 INTRODUCTION

1.1 Background

Over the last century, the soaring world's population and global economy have intensified the ever-increasing demand for freshwater and exploitable energy. To address this call, a paradigm shift towards sustainability where renewable energy resources have a big role to play is highly imperative. Potentially, a significant amount of osmotic energy can be harvested as a renewable energy from two streams of different salinities by using a pressure retarded osmosis (PRO) system. This concept was first proposed by Loeb in 1970s (Loeb 1975). However, due to limited availability of commercial membranes in the market, few PRO experiments were conducted to improve the technology (Lee et al. 1981b, Mehta and Loeb 1978). Recently, the PRO technology has gained increasing popularity as a result of advancement in membrane fabrication technology, which offers a compelling solution for the dwindling world's resources.

Based on the osmotic process type, membranes can be classified as reverse osmosis (RO), forward osmosis (FO) or direct osmosis (DO) and PRO as shown in Figure 1.1. RO utilizes hydraulic pressure to overcome the osmotic pressure difference and push freshwater from a high salinity solution to a low salinity solution across a semi-permeable membrane. To this end, RO has been extensively studied and utilized for seawater desalination and waste water reclamation (Fritzmann et al. 2007b, Greenlee et al. 2009, Petersen 1993). FO, on the other hand, is a concentration-driven process where water diffuses

naturally from a low salinity solution to a high salinity solution across a semi-permeable membrane. In spite of its inability to produce freshwater directly, FO has attracted much attention recently and boasts several potential applications and hybrid systems (Cath et al. 2006, Gray et al. 2006b, McCutcheon and Elimelech 2006, N. Y. Yip 2010, Wang et al. 2010). Similar to the FO process, PRO is an osmotic energy-recovering process that derives from the natural phenomenon of osmosis to transfer water from a low salinity solution at ambient pressure via a selectively permeable membrane to a pressurized high salinity solution. The increased volume of pressurized solution is then able to drive a turbine for power generation (Loeb 1976).

Figure 1.1. Direction of water transportation in FO (from low salinity to high salinity), RO (from high salinity to low salinity) and PRO (from low salinity to high salinity).

A brief illustration of the power generation theory in the PRO process is shown in Figure 1.2. Seawater and freshwater are pumped counter-currently to increase the efficiency and ensure stable performance of the system. The water naturally permeated from the low salinity will get pressurized in the high salinity side. As such, the total volume of pressurized solution has increased and the osmotic energy could thus be harvested. In the process, the brine gets diluted and a portion of the diluted brine is then recirculated to maintain the high-pressure

condition necessary for the system to operate while the remaining portion is used to drive the turbine for power generation.

Figure 1.2. Schematic drawing of PRO power generation process using a hollow fiber (HF) module. The draw solution is pressurized in the lumen of the HF module while the feed solution is pumped in the shell of the HF module.

1.2 Statement of problems

Though PRO has been intensively studied recently (Achilli et al. 2009, Altaee et al. 2014b, Bui and McCutcheon 2014, Chou et al. 2013, Gang Han 2013), many problems remain to be addressed. Concentration polarization is believed to have severe effect on the water flux reduction during the PRO process (Yip and Elimelech 2011). Meanwhile, membrane robustness is another limiting factor for optimization of PRO (Chou et al. 2012). Moreover, membrane fouling

is found to compromise power density significantly when using real wastewater as feed solution (Wan and Chung 2015). Last but not the least, upscale possibility of the PRO modules is a must for the pilot and commercial usage of the PRO process.

Studies on PRO processes reveal that experimental PRO water flux tends to be significantly lower than theoretical predictions due to the internal concentration polarization (ICP) effect. The presence of ICP reduces the effective osmotic driving force resulting in a lower power density (Chou et al. 2012). ICP was first discussed in the late 1970s (Mehta and Loeb 1978), and was further developed into a conceptual model in the early 1980s. According to the model developed by Lee *et al.*, it is possible to eliminate ICP if the mass transfer resistance is minimized (Lee et al. 1981b). Subsequently, the ideal support layer for PRO is thought to be as thin and porous as possible (Helfer et al. 2014b).

On the other hand, the membrane should possess an excellent mechanical strength to withstand high hydraulic pressures and long-term operation. Theoretically, a maximum power density exists when the hydrostatic pressure difference is equal to half of the osmotic pressure difference, suggesting that the working condition for a PRO system has to be optimized carefully.

In addition, river and impaired water are usually used as feeds in the PRO process. Another concern is therefore the high fouling propensity of these types of water which could increase the capital cost of the PRO power plant as a result of poorer membrane performance and lower energy output from the membranes.

In previous studies, the flat sheet (FS) configuration is widely used in the

PRO process though the performance is not as good as expected (Achilli et al. 2009). Meanwhile, due to the high packing density, the hollow fiber (HF) configuration seems to be a viable option for the PRO development (Li et al. 2012). However, HF membranes fabricated so far have not been able to achieve optimization for the PRO process. The PRO membrane modules are thus under slow development as well. Production of HF PRO modules in a large scale is more challenging and calls for more research efforts.

To sum up, optimized HF membranes with excellent membrane performances, less internal concentration polarization, low fouling tendency, large mechanical strength and upscale possibility are essential to the PRO process.

1.3 Objectives

In order to address the problems mentioned above, efforts should focus on producing a thin film composite (TFC) HF membrane that is suitable for practical PRO operation. This thesis mainly involves membrane fabrication and modification methods as well as potential application of these membranes. The main objectives of the study are defined as such:

- i). Fabricate HF membrane that can withstand high pressure loading with high permeability.
- ii). Characterize the membrane performance in the PRO operation and evaluate the membrane stability under high pressure loading over a long-term period.

- iii). Explore the feasibility of the produced membrane in practical PRO operation with real wastewater as feed.
- iv). Analyze the fouling potential of the NEWater brine (NB) as feed in the PRO operation.
- v). Propose an effective fouling mitigation strategy for a practical PRO operation.
- vi). Develop pilot-scale PRO HF modules.
- vii). Demonstrate the practicability of the HF module in a pilot PRO test.

1.4 Thesis outline

The main focus of the work is to develop a HF membrane which can provide a high power density and explore its feasibility using real wastewater. The thesis includes 6 chapters, which are highlighted as follows:

- Chapter 1 ***Introduction*** – This chapter briefly introduces the concept of pressure retarded osmosis, as well as background, objective and outline of the study.
- Chapter 2 ***Literature review*** - The chapter provides a comprehensive understanding about the PRO process and its development. The key factors in the PRO and its applications are highlighted together with a detailed description of the major challenges in the PRO development which include ICP, ECP, mechanical strength and membrane fouling. At the end, a recent progress in the PRO membrane advancement is reviewed.

- Chapter 3 *Identification of safe and stable operation conditions for pressure retarded osmosis with high performance hollow fiber membrane*
 - This chapter highlights the importance of mechanical stability and membrane creeping during high pressure operation. A high performance PRO membrane with excellent pressure resistance and water permeability was fabricated to analyze the membrane creeping at high pressure loading. Furthermore, a long-term study was conducted to examine the stability of the produced module in terms of water flux and solute back diffusion. To avoid membrane creeping, a safe and stable operating pressure especially in the long-term PRO operation will be proposed.
- Chapter 4 *Enhancing pressure retarded osmosis performance with low-pressure nanofiltration pretreatment: membrane fouling analysis and mitigation* – This chapter describes the PRO fouling with real wastewater as feed and possible fouling mitigation strategies. The membrane produced in the previous chapter was used for a PRO feasibility evaluation using real wastewater brine as feed. Low pressure NF was utilized as a pretreatment to mitigate the fouling tendency. The fouling mechanism was also systematically elucidated using different techniques.
- Chapter 5 *Module scale-up and performance evaluation of thin film composite hollow fiber membranes for pressure retarded osmosis* – This chapter demonstrates the development process of the lab-scale module to pilot-scale modules. The membrane from previous chapter was further developed into a commercial sized module. This included a detailed

discussion of the developmental process so as to shed light about scaling up the membrane module. Several module designs were used to optimize the module performance. The modules were also tested in a pilot setup to demonstrate the feasibility of PRO using real wastewater in a larger scale.

- Chapter 6 *Overall conclusions and recommendations* - The important findings of the work are summarized and some recommendations about future work are also made.

CHAPTER 2 LITERATURE REVIEW

This review starts with background of the PRO process and its applications. This chapter also focuses on the critical challenges in the PRO membrane, followed by a summary of desired characteristics of a high performance PRO membrane. Two major categories of the current PRO membranes are also reviewed in current section. At the end, a review of the fouling mitigation and PRO HF module development is provided.

2.1 Power production in PRO

Osmotic power is the energy that is released when streams with different salinity are mixed together. In a natural osmotic process, water permeates spontaneously from a low concentrated side to a high concentrated side until the chemical potential across the membrane reaches equilibrium. Osmotic pressure could be calculated using the Van't Hoff equation as follows:

$$\pi = icRT \quad \text{Eq. 1}$$

where i is the Van't Hoff factor, c (mol/L) represents the molar concentration, R (J/molK) stands for the universal gas constant and T (K) is the absolute temperature. In an osmotic process, the difference between osmotic pressure of the feed solution (low concentrated side) and draw solution (high concentrated side) drives the water to move from the feed solution to the draw solution. For the seawater and pure water pair, the osmotic pressure difference is about 27 bars,

which theoretically contains energy equivalent to hydro power of 270 m water column, or 0.75 kWh/m³. As such, a large amount of energy could be harvested by PRO for different high salinity streams in theory as shown in Figure 2.1.

For an ideal osmosis process, only water can diffuse through the partially permeable film while all the solutes and ions are completely rejected. Generally, the water flux in such a process is expressed below:

$$J_w = A \times (\Delta\pi - \Delta P) \quad \text{Eq. 2}$$

where J_w (L/m²h) represents volumetric water flux through a thin film; A (L/m²h bar) stands for pure water permeability (PWP); $\Delta\pi$ (bar) and ΔP (bar) are the difference in the osmotic pressure through the membrane and imposed external pressure, respectively. As water diffuses from freshwater to high salinity stream in FO by nature, ΔP is equal to zero in the FO process. When the brine is under an external force or a hydrostatic pressure (ΔP) which is equal or larger than the osmosis pressure ($\Delta\pi$), the RO process occurs. Contrastingly, when the ΔP is less than $\Delta\pi$, the PRO process occurs instead.

Figure 2.1. Maximum theoretical extractable energy from different saline water source (adapted from (Helfer et al. 2014b)).

The energy production is generally measured by the power density, W (W/m^2) which is described as the product of the water flux permeating across the membrane (J_w) and the external pressure imposed on the draw solution (ΔP). The relationship is described as follows:

$$W = J_w \times \Delta P = A \times (\Delta\pi - \Delta P) \times \Delta P = -A \left(\frac{\Delta\pi}{2} - \Delta P \right)^2 + A \frac{\Delta\pi^2}{4} \quad \text{Eq. 3}$$

The power density in the FO, RO and PRO process is shown in Figure 2.2, which also indicates that energy production in the PRO process is theoretically feasible. The optimum situation for the PRO plant operation occurs when ΔP is equal to half of $\Delta\pi$ as illustrated in the Eq. 3. At this point, the largest W is achieved. As the salinity of the solution gets higher, larger ΔP is required for an optimal energy production in PRO as shown in Figure 2.2. Therefore, a robust membrane is a prerequisite for the PRO process.

Figure 2.2. Power density in the FO, RO and PRO process. Energy is required in a RO process while energy is produced for a PRO process.

2.2 Development of PRO applications

At the beginning stage of PRO, the process was proposed as an energy production technique (Loeb 1976, Loeb et al. 1976). The seawater was pressurized as the draw solution while the river water was used as feed water. Energy was then harvested when the water flows through the semi-permeable membrane and get pressurized at the seawater side (Loeb 1976). Membrane distillation (MD), where clean water is produced when water permeates from the semi-permeable membrane driven by the vapor pressure difference, was then explored to operate together with the traditional PRO process to improve the osmotic energy harvesting (Han et al. 2015, Lin et al. 2014). MD was incorporated for regenerating the high and low concentration streams so as to ensure continuous power production from PRO. Both Han et al. and Lin et al. have demonstrated the potential of the PRO-MD system with low-grade heat in osmotic energy harvesting and clean water generation. A multi-stage vacuum membrane distillation (MVMD) system was integrated with the PRO system, where the concentrated brine from MVMD was used as draw solution in PRO to harvest the energy (Lee et al. 2015). PRO was also coupled with a multi-effect distillation (MSD) process to analyze its feasibility in energy recovery (Touati et al. 2015). It was found that 14% of energy could be recovered when the high concentrated brine is operated at 60 °C. However, the energy consumption in the MD/MSD is still a major concern impeding its further development.

FO-PRO and PRO-FO systems were also compared in terms of power generation efficiency (Altaee and Hilal 2014). The FO was used for reduction of

the total dissolved solids in the hypersaline solution and production of clean water. Based on their simulation results, PRO-FO system has a 2.65 times higher power production than FO-PRO systems with the identical diluted draw solution concentration. A dual stage PRO system was also studied by Altaee et al., and they concluded that the PRO system has higher energy production when brackish water and wastewater effluent are used in the first and second stage though more membrane area is needed in the system. (Altaee et al. 2014a) The system was further explored into four configurations and discussed by He et al. (He et al. 2015). From their dimensionless analysis, compared to the single stage PRO, advantageous energy capacity of the dual PRO system is obtainable when the feed or draw solution alone was divided into two streams and pumped into to the two PRO systems simultaneously.

With the advancement of technology, a hybrid process with seawater desalination was widely accepted for practical PRO application. PRO was proposed to reduce the energy consumption in the desalination technologies such as seawater reverse osmosis (SWRO) (Fritzmann et al. 2007a) , and is recognized as a potential effective energy reduction strategy when combined with the SWRO process (Helfer et al. 2014a) as in Figure 1.2. For this strategy, the PRO process plays an instrumental role in energy reduction (Kim et al. 2015, Kim et al. 2013, Kim and Elimelech 2013, Yip and Elimelech 2012). Altaee et al. reported that up to 31% of energy cost could be saved through the SWRO-PRO process based on their simulation results (Altaee et al. 2014b). Prante et al. used a similar model as Altaee et al. and found the SWRO-PRO system could theoretically reduce 40% energy consumption when the RO system has a specific energy consumption of

2 kWh/m³ (Prante et al. 2014). Four different SWRO-PRO hybrid systems were also discussed by Kim et al. with respect to energy/water consumption (Kim et al. 2013). In Singapore, PRO has also been proposed to be coupled with SWRO in a hybrid process to not only reduce energy consumption of SWRO but also dilute the RO brine for disposal (Li et al. 2013a). However, lack of suitable membrane modules and the issue caused by the membrane fouling greatly impede practical usage of PRO at a larger scale (Straub et al. 2016).

2.3 Key challenges for PRO process

Though PRO is under fast development as water sources are abundant and the process exhibits high energy harvesting potential as in Figure 2.1, there are many challenges yet to be resolved, such as ICP, external concentration polarization (ECP), solute reverse diffusion, membrane fouling and low mechanical strength (Achilli et al. 2009, Chou et al. 2010b, Guo et al. 2012, She et al. 2013b)

2.3.1 External concentration polarization in PRO

Concentration polarization is one of the major limiting factors in PRO membrane performance, where accumulation or reduction of solutes around the interface occurs (Achilli et al. 2009). The effective driving force is thus compromised due to reduction in effective osmotic pressure difference and thus the driving force of the process. A schematic drawing of the concentration profile

in a typical PRO membrane is illustrated in Figure 2.3.

Figure 2.3. Concentration profile in a typical PRO membrane. The draw solution and feed solution operate in the countercurrent direction. Water permeates from the feed solution side to the draw solution side while the back-diffused solute transports from the draw to the feed.

In this figure, C_{db} denotes the bulk concentration on the draw side; draw solution-membrane boundary concentration (due to ECP) is represented by C_{dm} ; C_{RS} stands for the concentration of the boundary between the rejection layer and support layer; the concentration at the feed solution-membrane boundary layer and the bulk feed solution is C_{fm} and C_{fb} , respectively; $\Delta\pi_{eff}$, $\Delta\pi_{dECP}$, $\Delta\pi_{ICP}$ and $\Delta\pi_{cECP}$ correspond to effective osmotic pressure difference and the osmotic pressure loss due to dilutive ECP, ICP and concentrative ECP, respectively. The ECP arises due to the boundary layer effect near the membrane-bulk solution where the convective flow drags the solute from the bulk solution to the membrane boundary (McCutcheon and Elimelech 2006). As the water permeates to the membrane from the feed solution, the solutes are left behind and this contributes to a higher concentration, leading to concentrative ECP. On the

contrary, when water transports from the membrane to the bulk draw solution, the convective flow displaces and drags the dissolved salt away from the membrane surface, leading to dilutive ECP.

The ECP effect could be described by the concentration polarization modulus, which is defined as the ratio of osmotic pressure at the bulk solution (π_b) and membrane-bulk solution surface (π_m), and can be calculated as:

$$\frac{\pi_b}{\pi_m} = \exp\left(-\frac{J_w}{k}\right) \quad \text{Eq. 4}$$

where k is the mass coefficient in the bulk solution, and defined as:

$$k = \frac{ShD}{d_h} \quad \text{Eq. 5}$$

where D is the diffusion coefficient, d_h is the hydraulic diameter of the flow channel and Sh_l stands for the Sherwood number in the lumen of the HF membrane, which is related to the Renolds number (Re) and Schmidt number (Sc), and calculated as in (Shen et al. 2010):

$$Sh_l = 1.62Sc^{1/3}Re^{1/3}\left(\frac{d_h}{L}\right)^{1/3} \quad \text{Eq. 6}$$

for a tubular flow regime and L stands for the module length. For the Shewood number of the flow in the shell, it is defined as,

$$Sh_s = 1.25Sc^{1/3}\left(Re\frac{d_h}{L}\right)^{0.93} \quad \text{Eq. 7}$$

Although the ECP effect is generally considered insignificant in the PRO operation as compared to ICP, it may still play a crucial role in the pilot module where the flow condition is much more dynamic and thus complicated (Yip and Elimelech 2011).

2.3.2 Internal concentration polarization in PRO

ICP is a critical challenge for the osmosis processes, in which the salt accumulates around the selective layer and thus reducing the effective osmotic pressure in the osmotic driven membrane process. The water flux is then compromised as a result of a reduction in the driving force. From the concentration profile in Figure 2.3, it could be observed that the severe flux reduction is expected due to the ICP effect. Loeb developed a model to define the flux of water through the membrane in an osmotic driven membrane process (Loeb et al. 1997), which could be expressed as:

$$J_w = K_m \ln \frac{\pi_D}{\pi_F} \quad \text{Eq. 8}$$

where K_m denotes mass transfer coefficient inside the membrane; osmotic pressure on the draw side and the feed side are respectively represented by π_D and π_F , and K_m is defined as:

$$K_m = \frac{D_s P}{\tau t} = \frac{D_s}{S} \quad \text{Eq. 9}$$

where τ is the tortuosity of the membrane while t and P stand for the thickness and porosity of the membrane, respectively. All of the three factors describe intrinsic properties of the membrane, which defines the structure parameter S , as defined in $\frac{\tau t}{P}$. D_s is the property of the solute which represents the diffusion coefficient of the solute in water.

As illustrated in Figure 2.3, ICP dominates in the active layer facing draw solution (AL-DS) orientation, and the water flux was modeled as:

$$\ln \left[\frac{A\pi_D + B - J_w}{A\pi_F + B} \right] = \frac{J_w}{K_m} \quad \text{Eq. 10}$$

where B stands for the solute permeability of the membrane. Different from the FO operation, membranes usually adopt an AL-DS orientation in the PRO mode. The main motivation behind this practice is to ensure that the support layer of the membrane is capable of providing sufficient mechanical support under a high pressure condition. The water flux was thus described as follows, (Xu et al. 2010):

$$\ln \left[\frac{(A\pi_D - A\Delta P - J_w) + B \left(\left(\frac{A\Delta P}{J_w} \right) + I \right)}{A\pi_F + B \left(\left(\frac{A\Delta P}{J_w} \right) + I \right)} \right] = \frac{J_w}{K_m} \quad \text{Eq. 11}$$

Combining Eq. 3 and Eq. 11, the power density of the PRO membranes is modeled as:

$$W = J_w \times \Delta P = K_m \ln \left[\frac{(A\pi_D - A\Delta P - J_w) + B \left(\left(\frac{A\Delta P}{J_w} \right) + I \right)}{A\pi_F + B \left(\left(\frac{A\Delta P}{J_w} \right) + I \right)} \right] \times \Delta P \quad \text{Eq. 12}$$

The equation highlights the importance of K_m and the operating pressure in the PRO process. In order to achieve the highest power density, both K_m and ΔP must be optimized. However, high K_m indicates that the membrane should be thin and porous, which can result in a support with a low mechanical property. Therefore, a proper optimization about the substrate structure is vital for PRO membrane fabrication.

Another factor that contributes to the ICP effect is the solute back diffusion (Cath et al. 2006, McCutcheon and Elimelech 2006). The solute back diffusion could reduce the effective osmotic pressure by increasing the concentration at the active layer-substrate boundary, or C_{RS} as in Figure 2.3. A simulation model discussed by Bui et al. demonstrated the different effect of ICP,

ECP and solute back diffusion on the power production in PRO (Bui et al. 2015). They also deduced a model accounting for all three effects, which is given as follows:

$$W = A \left\{ \frac{\pi_D \exp\left(-\frac{J_w}{k_D}\right) - \pi_F \exp\left[J_w \left(\frac{1}{k_F} + \frac{S}{D_s}\right)\right]}{1 + \frac{B}{J_w} \left\{ \exp\left[J_w \left(\frac{1}{k_F} + \frac{S}{D_s}\right)\right] - \exp\left(-\frac{J_w}{k_D}\right) \right\}} - \Delta P \right\} \Delta P \quad \text{Eq. 13}$$

where k_D and k_F are the mass transfer coefficient in the draw and feed sides, respectively. From the equation above, it is clear that the optimal power density occurs when A is maximum while B is the minimum for a given substrate of the membrane. This suggest another criterion in the fabrication of the PRO membrane active layer, i.e., a thin and dense film that has a high permeability and high rejection of solutes simultaneously. Moreover, the ICP effect results in an optimal applied pressure that is slightly higher than half of the osmotic pressure difference (Banchik et al. 2014, Yip and Elimelech 2011, Zhang and Chung 2013). This implies the need of a mechanically stronger substrate to harvest energy in a PRO process.

2.3.3 Mechanical strength

Currently, a lot of materials are adopted to produce different types of HF membranes for various commercial and industrial applications. However, as discussed in the previous chapter, PRO is a process that operates at a relatively high pressure, thus higher mechanical strength is required to withstand the higher hydraulic loading during operation. The osmotic pressure difference between the seawater and freshwater is as high as 29 bar (simulated as 0.59 M NaCl solution),

and the ideal maximum power density of the PRO membranes occurs at half of the osmotic pressure. As such, the HF membranes are supposedly able to operate at pressure as high as 14.5 bar. Furthermore, in a SWRO-PRO system, the optimal operation pressure is about 25 bar. Apart from the difference in the osmotic pressure, the actual operating pressure is usually slightly higher than the ideal operation pressure for reasons already discussed in section 2.3.2. This implies that very small deformation of the membrane is allowed at high applied pressure so as to ensure its integrity, which means that high tensile modulus is essential for the PRO HF membranes (Sukitpaneemit and Chung 2012). Furthermore, Chou et al. reported that membrane properties could vary when imposed at a high pressure loading (Chou et al. 2013). In order to improve the mechanical strength of the membranes, different types of polymers are tested to produce mechanically tough HF membranes. Table 2.1 shows the tensile modulus of some representative materials that are currently adopted to fabricate these membranes.

PAI has the largest tensile modulus in Table 2.1. Nevertheless, the high cost of PAI makes it unfavorable for industrial application. For this reason, PEI is an attractive alternative for PRO membrane fabrication owing to low cost, high tensile modulus and good chemical resistance. The chemical structure of PEI is shown in Figure 2.4.

Table 2.1. Tensile strengths of materials adopted in membrane fabrication

Material	Acronym	Brand name	Tensile modulus (Gpa)
Polyetherimide	PEI	TECAPEI	3.2
Polytetrafluoroethylene	PTFE	TECAFLON PTFE	0.8
Polypropylene	PP	TECAFINE PP	1.5
Polyethylene	PE	TECAFINE PE	1.0
Polyvinylidene fluoride	PVDF	TECAFLON PVDF	2.0
Polyamide-imide	PAI	TECATOR	4.8
Polyether sulfone	PES	TECASON E	2.7

Figure 2.4. Chemical structure of PEI.

2.3.4 Membrane fouling in PRO

Membrane fouling is one of the critical challenges in membrane operation, where foulants/scalants accumulate on/in membrane and lead to flux reduction as illustrated in Figure 2.5. Fouling in PRO is expected to be more severe as the porous support layer is facing the foulants/scalants directly as in Figure 2.5 (b). Much efforts have been devoted to developing PRO technology from various aspects, including novel membrane fabrication, and process integration and optimization (Altaee et al. 2015, Chou et al. 2013, Han et al.

2013b, Lin et al. 2014, Yip et al. 2010). It is noted that most of the studies were based on lab-scale studies using synthetic high salinity solutions as draw solutions and deionized (DI) water or other synthetic low salinity solutions as feed solutions. Among the many existing challenges, membrane fouling remains as one of the major concerns stifling the practical application of the PRO processes (Chen et al. 2016a, Kim et al. 2015, She et al. 2016, She et al. 2013b, Zhang et al. 2016).

Figure 2.5. Schematic drawing of membrane fouling in (a) AL-FS and (b) AL-DS orientation.

PRO membrane is normally placed in the AL-DS orientation where internal fouling in the support layer (facing untreated feed water) easily occurs, making it difficult to clean (Li et al. 2017, She et al. 2012a). Moreover, PRO membranes generally have a thicker or denser structure than FO membranes in order to withstand a high pressure loading (Chen et al. 2016b, Chou et al. 2012). Therefore, more severe internal concentration polarization (ICP) tends to enhance the fouling propensity (She et al. 2012a, Tang et al. 2010). In addition, the high pressure loading at the draw solution side is also found to contribute to

severe reverse solute diffusion that further exacerbates the problem. Many prior studies have reported that various components in the feed water, such as divalent ions, humic substance, alginate, silica, etc. could accumulate in the porous membrane substrate, reducing the membrane water flux to a great extent (Kim et al. 2015, She et al. 2013b, Thelin et al. 2013, Wang et al. 2016, Zhang et al. 2016, Zhang et al. 2014a), and the synergetic effect of different foulants is also believed to further impede the water flux (Chen et al. 2016a, Kim et al. 2015, She et al. 2013b). In fact, there are some reports exemplifying severe fouling in PRO using wastewater as feed, which challenges the feasibility of its practical application (Chen et al. 2016a, Kim et al. 2015). A cost-effective strategy is therefore vital to implement the idea of using wastewater in the PRO process.

2.4 Desired PRO membranes

In order to improve the PRO membrane performance, many materials are adopted to produce the membranes using various fabrication methods. As the power density is expressed as the product of water flux and applied pressure, two major approaches to enhance the PRO performances are proposed. The first is to increase the mechanical properties of the support substrate to allow the membrane to withstand higher pressure loading. The second is to increase the water permeability of the selective layer without compromising the membrane selectivity. Spongy-like structure in the substrate is well-known for increased mechanical properties of the support layer (Chou et al. 2012). In contrast, macro-void structure is not preferred owing to the weak polymer network which can

become a potential defect during high pressure loading. A study by Li and Chung suggested that P84 co-polyimide membrane with small dimensions demonstrated an increase in the pressure resistance of the HF membranes (Li and Chung 2014). The produced fibers can withstand a pressure of 21 bar with a power density of 12 W/m^2 .

Many methods were employed to improve the water permeability of the PRO membranes as well. Ethanol was used to swell the polymer chains and thus increase the water permeability as shown by Zhang et al. (Zhang et al. 2013). They also found that ethanol was useful in improving the mechanical properties of the membranes after treatment. Besides, sodium dodecyl sulfate (SDS) was proven to improve the formation of the PA layer on the substrate, thus optimizing the PRO performance (Cui et al. 2014). Specifically, a combination of SDS pretreatment on the substrate and N,N-dimethylformamide (DMF) post-treatment on the PA layer can greatly improve the permeability of the membrane so that a high power density of 18.09 W/m^2 at 22 bar is attainable. In addition, a 39.8 wt% of polyethylene glycol (PEG) 400 was used as an additive in a PES system (Zhang et al. 2014b) to produce a highly porous HF membrane. The membrane can produce a power density of 24.3 W/m^2 at 20 bar.

The PRO orientation is also crucial for practical PRO operation as severe membrane fouling is expected when AL-DS orientation is adopted (see earlier section). If PRO membrane is to operate in active layer facing feed solution (AL-FS) orientation, as in Figure 2.6, the HF membrane should be mechanically tougher to withstand the pressure from the shell side or ideally possess a high performance selective layer on the outer surface (Figure 2.6). Nonetheless,

fabrication of RO-like active layer on the outer surface of the HF membrane is quite challenging and only few works have successfully been reported to date (Sun and Chung 2013).

To sum up, a desired PRO membrane should possess a mechanically tough substrate with high permeability to minimize ICP effect and fouling tendency, and a thin and dense selective layer with high salt rejection and water permeability.

Figure 2.6. Schematic drawing of HF PRO membrane (a) with selective layer in the lumen; (b) with selective layer in the outer layer in AL-FS orientation.

2.5 Current PRO membranes development

Among the challenges mentioned earlier, developing the ideal PRO membrane is at the core of realizing the potential to produce clean and renewable energy by the PRO process. At present, there are mainly two types of PRO membranes which researchers use in the laboratory: asymmetric and composite membranes.

2.5.1 Integral asymmetric membranes

Proposed and discussed by Loeb (S. Loeb 1963), non-solvent induced phase separation (NIPS) method is a widely used technique to produce integral asymmetric membranes. These membranes are fabricated with the same type of materials but have an anisotropic morphology consisting of a thick support layer and a thin skin layer. This category can be further divided into cellulosic and non-cellulosic membranes.

Commonly used materials to fabricate cellulosic membranes are cellulose acetate (CA) and cellulose triacetate (CTA). They are widely used to produce PRO membranes due to their high robustness, hydrophilicity and chlorine resistance (Zhang et al. 2010). These features are desired for membrane casting since it can enhance the water flux, reduce the fouling tendency and prolong membrane lifetime. Most of these membranes are fabricated by phase inversion and heat treatment (Kai Yu Wang 2010, Su et al. 2010). She et al. analyzed the effect of spacers in the PRO performance using a CTA commercial membrane from HTI (She et al. 2013a). He embedded the membrane on a polyester woven mesh to increase its mechanical property. As a result, the membrane was able to withstand a hydraulic pressure of 17 bar and a power density of 5.8 W/m^2 (She et al. 2013a). A poly (vinyl chloride)-g-poly (3-sulfopropyl methacrylate) (PVC/PVC-g-PSPMA) graft copolymer was also used to prepare an asymmetric flat sheet membrane (Patel et al. 2014). However, the membrane was too dense and could only produce 0.88 W/m^2 power at 15 bar given the low water flux. A polybenzimidazole (PBI)-based membrane, PBI-polyacrylonitrile (PAN) dual

layer hollow fiber membrane, was first fabricated using the NIPS method by Fu et al. (Fu et al. 2013). After thermal annealing, the as-produced membrane also exhibited a low water flux and the peak power density was about 2.47 W/m² at 7 bar.

In summary, the integral asymmetric membranes are normally fabricated through phase inversion and then post-treated to produce a support sub-layer and selective skin layer. However, the properties of these two layers are hard to optimize simultaneously. From the data shown above, most of the membranes have a low water flux, thus resulting in a low power density.

2.5.2 Composite membranes

Composite membranes are membranes that have different functional layers which are fabricated in separate steps so that the layers can be manipulated separately. In general, a substrate is first prepared and an active layer is then formed above the substrate. To fabricate the active layer, the substrate is first immersed in a diamine aqueous solution, followed by the application of air or solvent to remove the excessive solution on the surface. After that, the substrate is immersed in an acyl chloride/solvent solution. A thin polyamide (PA) film is then formed on the interface and attached onto the substrate surface. This process is known as interfacial polymerization (IP). A typical IP process using m-phenylenediamine (MPD) and trimesoyl chloride (TMC) is illustrated in Figure 2.7.

Figure 2.7. A typical IP process using MPD and TMC. The reaction occurs in the interface of the organic phase and solvent phase where TMC and MPD slowly diffuse to the interface.

Conventional TFC membranes are generally prepared by a phase inversion method to produce a porous substrate and then a selective layer by IP. Many attempts have been made to fabricate high performance osmotic-driven membranes both in HF and FS configurations. For a typical TFC FO/PRO membrane, it consists of an RO-like selective layer supported by a permeable layer with a much lower mass transfer resistance. A FS TFC membrane using polysulfone (PSf), MPD and TMC was fabricated (N. Y. Yip 2010) and this was soon followed by a HF membrane using PES (Wang et al. 2010). Both membranes were prepared by the method mentioned above. In addition, HF support made from polyethersulfone (PES) was also used to prepare a TFC membrane. It was found that the finger-like structure of pores in the support layer was able to greatly mitigate the ICP effect (Chou et al. 2010b). This method was further improved to fabricate a PRO membrane with a power density of 11 W/m^2 at 9 bar (Chou et al. 2012). Moreover, to further enhance the mechanical strength, PEI was used as the substrate material and the structure of the HF membrane was manipulated to give a sponge-like morphology. Due to this synergistic effect, the

membrane was able to achieve a power density of 20.9 W/m^2 at 15.1 bar operating pressure (Chou et al. 2013). Zhang *et al.* also developed TFC PES HF membranes with power density of 24.3 W/m^2 at 20 bar by using 1.0 M NaCl as the concentrated brine and DI-water as the feed water (Zhang et al. 2014b). In a different study, Matrimid 5218 was used to fabricate a spongy-like substrate and a selective layer was formed using IP. A power density of 18.06 W/m^2 was reached at 22 bar (Han and Chung 2014). However, the membrane was suspected to deform during the process and a long-term evaluation is needed to confirm the membrane stability. A TFC nanofiber membrane was also produced by an electron-spun PAN substrate and MPD/TMC formed PA layer. The membrane has a high water permeability but low pressure resistance. As such, it broke at a relatively lower pressure loading of 12 bar (Bui and McCutcheon 2014).

A summary of recent PRO membranes developed is shown in Table 2.2. Compared to integrated asymmetric membranes, properties of composite membranes are easier to control as the performance of the substrate and rejection layer could be optimized individually. Although most of these studies have reported high power production in the PRO operation, the polymeric materials used for fabrication could be a concern during long term study as the polymer structures are highly susceptible to changes at high pressure loading over time (Chou et al. 2013). Therefore, besides separation performances, a long-term operation and membrane stability test is essential to give a balanced appraisal of polymeric membranes for PRO application.

Table 2.2. Recent PRO membrane performances

Membrane type	Material	Power density (W/m ²)	Pressure (bar)	Feed solution	Draw solution	Reference
Asymmetric FS	PVC/PVC-g-PSPMA graft copolymer	0.88	15	DI water	0.6 M NaCl	(Patel et al. 2014)
dual-layer HF	PBI-PAN dual layer	2.47	7	10 mM NaCl	1M NaCl	(Fu et al. 2013)
TFC FS	PAN with nonwoven fabric	2.6	8	DI water	3.5% NaCl	(Zhang et al. 2013)
TFC FS	Torlon 4000T-MV PAI	2.84	6	DI water	3.5% NaCl	(Li et al. 2013b)
TFC HF	PES	2.98	7	DI water	0.6 M NaCl	(Ingole et al. 2014)
Asymmetric FS	HTI CTA	5.8	17.2	10 mM NaCl	1M NaCl	(She et al. 2013a)
TFC HF	P84	6	9	DI water	1 M NaCl	(Li and Chung 2014)
TFC FS	P84	6	9	DI water	1 M NaCl	(Li and Chung 2013)
TFC HF	Matrimid 5218 (PA layer on outer surface)	7.63	20	DI water	2 M NaCl	(Sun and Chung 2013)
TFC HF	PES	10.6	9	40mM NaCl	1M NaCl	(Chou et al. 2012)

TNC membrane	PAN nanofibers on polyester nonwoven fabric	8	10.3	DI water	0.5 M NaCl	(Bui and McCutcheon 2014)
TFC FS	Matrimid 5218	12	15	DI water	1M NaCl	(Gang Han 2013)
TFC HF	Matrimid 5218	14	16	tap water	1M NaCl	(Han et al. 2013a)
TNC membrane	PAN nanofiber	15.2	15.2	0.9mM NaCl	1.06 M NaCl	(Song et al. 2013)
TFC HF	Matrimid 5218	16.5	15	DI water	1 M NaCl	(Han and Chung 2014)
TFC FS	Matrimid 5218 substrate	18.09	22	DI water	1 M NaCl	(Cui et al. 2014)
TFC HF	PEI	20.9	15.1	1 mM NaCl	1 M NaCl	(Shuren Chou 2013)
TFC HF	PES	24	20	10 mM NaCl	1M NaCl	(Zhang and Chung 2013)
TFC HF	PES	24.3	20	DI water	1 M NaCl	(Zhang et al. 2014b)

2.5.3 Fouling mitigation in PRO

Many efforts have been attempted to mitigate membrane fouling in PRO due to its severe effect on flux reduction. Changing the orientation of the PRO membrane to AL-FS may seem to be advantageous for reducing fouling tendency (Gray et al. 2006a, She et al. 2013b), but the pressure loading in this orientation could likely damage the active layer of traditional TFC membranes as discussed in Section 2.4. While surface modifications such as grafting hyper-branched polyglycerol (HPG) (Li et al. 2014a)/zwitterionic copolymers (Cai et al. 2016) on top of the membrane surface has shown promise in fouling resistance of bovine serum albumin (BSA), *E. coli* and so on., scalability of such membranes remains a great concern. On the other hand, utilization of anti-scalants is effective in mitigating scaling, but it is not cost-effective (Kim et al. 2015, Wang et al. 2016). Moreover, although hydraulic cleaning was reported to be beneficial in mild fouling conditions, it may not work well for a dense fouling layer according to Mi et al. (Mi and Elimelech 2008). As for ultrafiltration (UF) pretreatment, though simple and inexpensive, a majority of the scaling precursors is unable to get retained by the UF pretreatment (Kim et al. 2015).

A brief summary about recent studies on PRO fouling is shown in Table 2.3. Although these studies have proposed fouling mechanisms in different feed water, it may not be representative of all real wastewater owing to its complex chemical make-up. A more detailed and systematic analysis is still required for PRO operation using different real wastewater. Moreover, a cost-effective method to mitigate membrane fouling has yet to be found, especially in a practical operation where real wastewater is used.

Table 2.3. Summary of recent studies about membrane fouling in PRO

Feed solution	Draw solution	Membrane type	Proposed fouling mechanism	Mitigation strategy	Comments	Reference
Synthetic solution with Suwannee river NOM (SRNOM) and other salts	Simulated seawater (NaCl only)	PSf FS TFC	NOM fouling	Osmotic backwashing	44% flux recovery	(Yip and Elimelech 2013)
Synthetic brine	Synthetic seawater brine (NaCl only)	Commercial CTA	Reverse solute enhanced fouling	-	At high pressure, the fouling is related to decreased water flux and increased back solute diffusion.	(She et al. 2013b)
Synthetic solution with different gypsum saturation index	NaCl/CaCl ₂ solution	Commercial CTA FO	Gypsum scaling	-	Gypsum scaling is related to feed/draw concentration, operation pressure, water flux and membrane orientation.	(Zhang et al. 2014a)
Synthetic solution with alginate and calcium salts	1M NaCl solution	PES TFC HF	Gypsum scaling, alginate gelation	-	Alginate fouling is dominant while gypsum scaling is inhibited under high pressure.	(Chen et al. 2015)
Synthetic wastewater with SRNOM, alginate, BSA, calcium and magnesium salts	Synthetic seawater and brine	CTA FS	Inorganic fouling	Hydrodynamic cleaning/anti-scalant	Hydraulic cleaning is not effective while anti-scaling is useful.	(Kim et al. 2015)
Conditioned raw water from Mostadmark water work	Synthetic seawater	CA and TFC	ICP and reverse salt diffusion enhanced fouling	-	Fouling propensity is independent of NOM concentration/CA has less organic fouling tendency than TFC membranes.	(Thelin et al. 2013)

DI water with BSA	Synthetic seawater (NaCl only)	PES HF	Organic fouling	Membrane grafting modification	Antiprotein adsorption and antibacterial adhesion was achieved.	(Li et al. 2014a)
Real wastewater brine	Real seawater brine	PES HF	-	NF and UF pretreatment	Seawater brine has negligible effect on the fouling while significant fouling is observed in the wastewater brine side.	(Wan and Chung 2015)
Real wastewater brine	Real seawater brine	PES HF	Organic and inorganic fouling	Outer skinned selective layer/osmotic back washing/chemical cleaning/anti-scalant and pH treatment	Fouling with wastewater brine is complicated due to both organic and inorganic fouling, and the fouling is highly irreversible.	(Han et al. 2016)
Real wastewater brine/ simulated wastewater brine	1M NaCl	PES HF	Silica fouling and phosphate fouling	EDTA pretreatment with bubbling and back washing	Silica fouling is dominant in the wastewater brine while phosphate scaling occurs at interface facing draw solution.	(Chen et al. 2016a)

2.5.4 PRO hollow fiber module development

The production of HF modules is well developed in industry in terms of fiber packing (Henry 1969, Kohl 1971), module potting (Geary Jr et al. 1970, Schäfer et al. 2011), and tubesheets supporting (Clark 1977). Nevertheless, fabrication of suitable HF modules for PRO remains challenging due to the unique requirements of PRO membranes such as high robustness, high salt rejection and good anti-fouling properties as stated in Section 2.3. There are two main ways to achieve successful PRO module fabrication: 1) fabricate HF-membranes with RO-like skin directly and pot them into modules or 2) pot the substrates into the module and cast a RO-like skin layer afterwards. For the first method, asymmetrical membranes are commonly used but their performance is normally hard to control. For the second method, casting the RO-like layer on top of the HF surface is challenging and still at the developmental stage.

Commercial HF modules were used by Kumano et al. to test the PRO performance (Kumano et al. 2016). The 5-inch CTA hollow fiber module from TOYOBO was operated in the AL-FS orientation to reduce membrane fouling. The small outer diameter of 0.2 mm enables the membrane to withstand the high pressure loading of 18-26 bar from the shell side. However, the small inner diameter induces an entry pressure of the feed and a 1-2 bar pressure was required in the lumen during operation. Moreover, usage of CTA may be less advantageous in PRO application involving pH variations and microbial degradation (Edgar et al. 2001, Lee et al. 2011).

Ren et al. tried to fabricate a PRO module based on the commercial HF

UF modules with 300 fibers from Koch Membrane Systems Inc. (Ren and McCutcheon 2017). A polyamide layer was synthesised by IP in the lumen. A flux of 17.5 L/m²h was obtained in the AL-DS mode with a salt flux of 5.52 g/m² h. This work demonstrated the possibility of fabricating an active layer on a UF module.

Wan et al. had also successfully fabricated a PRO module with 300 fibers from in-house made hollow fibers (Wan et al. 2017). A typical centrifugal potting was used to prevent the wicking of the fibers during module fabrication. However, it was found that the repair of the defective fibers was needed after the PRO module was produced. Also, the fibers in the outmost and central regions were more vulnerable to bursting during high pressure tests.

The lack of suitable PRO modules greatly hinders the development of the PRO process. This calls for more research efforts in engineering PRO modules that can support larger-scale operations of the PRO process. A systematic development of PRO modules on a large scale is necessary to facilitate PRO practical applications.

2.6 Summary

In the commercialization of PRO application, ICP is commonly recognized as one of the key challenges in the membrane fabrication as severe flux reduction is expected owing to accumulation of solute in the membrane substrate (Achilli et al. 2009, Chung et al. 2012, Gray et al. 2006a). The PRO membrane is thus required to be thin and porous for the fast mass transport in the

support layer. However, high mechanical strength is a prerequisite for PRO membranes as the process is operated at a high pressure by nature. Therefore, a trade-off between the membrane permeability and mechanical strength should be carefully considered when designing PRO membranes. Spongy-like structures with highly interconnected pores are thus favored in the PRO membrane fabrication due to a good balance between structure parameter and robustness of the substrate (Chou et al. 2013). Furthermore, composite membranes shows great potential in PRO membrane development as the support layer and rejection could be designed separately thus achieving optimal PRO performance. Nonetheless, deformation of PRO membranes under high pressure loading due to their polymeric nature, is another consideration in PRO operation. Consequently, long term stability and integrity check is needed for evaluation of the PRO membranes in practical applications.

Membrane fouling is another concern that has challenged the feasibility of practical PRO recently when real river water or impaired water is used as the feed solution (Straub et al. 2016). Though many researchers have reported the fouling in the PRO process, most of studies focus on the fouling mechanisms in synthetic water rather than real river water/impaired water. The complex composition of real river water/impaired water thus requires further systematic analysis of the fouling mechanism. Therefore, an economical fouling mitigation measure is essential to demonstrate the feasibility of PRO. Moreover, a scale-up module is required to examine the PRO operation at a larger scale.

CHAPTER 3 Identification of safe and stable operation conditions for pressure retarded osmosis with high performance hollow fiber membrane

3.1 Introduction

As described in Chapter 2, a suitable PRO membrane should possess good mechanical properties and high permeability. Though there are many attempts to fabricate the PRO membranes, it should be pointed out that while different types of PRO membranes have been developed, the long-term PRO performance of resultant membranes and comprehensive integrity check were not reported in the literature. Investigations on membrane stability tested over long-term operation have been elusive. It is well understood that due to its polymeric nature, polymeric membrane may gradually deform over time under high pressure loading, or membrane “creeping” will occur. The creeping phenomenon would eventually damage the membrane and deteriorate the membrane performance to complete failure.

The current chapter aims to investigate the stability of an in-house made high performance PRO hollow fiber membrane in order to identify safe and stable operating conditions over long term testing under a high hydraulic pressure. The support layer was made of PEI, providing an excellent mechanical support and low trans-membrane mass-transfer resistance. The selective layer of polyamide was prepared by interfacial polymerization. The PRO hollow fiber membrane was pressurized at various hydraulic pressures in RO and PRO modes in order to understand its performance behavior. After obtaining an entire picture, the

membrane was pressurized at specific hydraulic pressures for a long period of time to study the time effect. The PRO hollow fiber membranes were then characterized using various techniques including nanoindentation by using AFM for membrane creeping evaluation. The performance of the PRO hollow fiber membranes was tested on a laboratory scale PRO setup. This work is believed to be the first effort to investigate the creeping phenomenon of PRO hollow fiber membrane due to high pressure loading and to report PRO membrane performance over a long term test of 200 hours. It is expected to provide guidance for practical applications of polymeric hollow fiber membranes in PRO process.

3.2 Experimental Methods

3.2.1 Materials

Polyetherimide (PEI Ultem 1000, GE Plastic, USA) was used to make the porous hollow fiber substrates. N-methyl-2-pyrrolidone (NMP, > 99.5%, CAS#872-50-4, Merck Chemicals, Singapore) was used as the solvent. Polyethylene glycol (PEG, CAS#25322-68-3, Merck Chemicals, Singapore) was used as a pore former for the substrate. Purified water by a Milli-Q system (18 MΩ cm) and tap water were used as the bore fluid and the external coagulant, respectively. Dextrans with different molecular weights (6,000-500,000 Da; (C₆H₁₀O₅)_n, Sigma Aldrich) were used to determine the molecular weight cut off (MWCO) of the substrate. Glycerol (85%, CAS#56-81-5, Merck Chemicals, Singapore) was used to post-treat the membrane for storage purposes. 1,3,5-Benzenetricarbonyl trichloride (TMC, CAS# 4422-95-1, Sigma-Aldrich) and *m*-

phenylenediamine (MPD, CAS# 108-45-2, Sigma-Aldrich) were used as the monomers for the interfacial polymerization. Cyclohexane (CAS# 110-82-7, Merck Chemicals, Singapore) was used as the solvent for TMC. Sodium chloride (NaCl, CAS# 7647-14-5, Merck Chemicals, Singapore) was used to prepare the feed and draw solutions.

3.2.2 Fabrication of PRO hollow fiber membranes and modules

PEI hollow fiber substrates were fabricated based on NIPS method by a dry jet-wet spinning technique. The polymer and the additive were completely dissolved in NMP prior to spinning. The details of the hollow fiber spinning process and post-treatment can be found elsewhere (Chou et al. 2013, Setiawan et al. 2011).

Fifteen pieces of hollow fibers were potted into a tube with effective length of 22 cm and sealed by epoxy. The active-selective layer was subsequently developed on the inner surface of the PEI hollow fiber substrates by interfacial polymerization of TMC and MPD at ambient temperature as described in the literature (Wang et al. 2010). The hollow fiber membranes with the selective layer would be known as PRO-PEI HF.

3.2.3 Characterization and analysis

The dimension of PEI hollow fiber substrates was measured by a Keyence VHX 500F Digital Microscope. A mean value was obtained based on the

measurement of ten different fibers. The structure and morphology of the fiber cross-section and surface were examined by a Jeol JSM-7600F field emission scanning electron microscope (FE-SEM). The wet hollow fiber membranes were dried in a freeze drier overnight prior to be fractured in liquid nitrogen. The samples were subsequently mounted on the SEM stubs followed by platinum sputter coating.

PWP and molecular weight cut off (MWCO) of PEI hollow fiber substrates were tested by using a bench scale cross-flow filtration system at a constant pressure of 1 bar. Ten pieces of hollow fiber substrates were potted into a tube (with effective length of 25 cm) and sealed by epoxy. Distilled water was circulated through the lumen side of the module to get PWP. The MWCO of PEI hollow fiber substrate was determined by the filtration method using a 2000 ppm dextran solution and analyzed by gel permeation chromatography (GPC) on a Polymer Laboratories-GPC 50 plus system. The dextran solution was made by a mixture of several different molecular weights from 6,000 to 500,000 Da.

After the active selective layer has been formed on the inner surface of the fiber, the intrinsic properties of PRO-PEI HF membranes, such as water and salt permeability, were tested in RO-mode by using a laboratory scale cross-flow filtration unit at ambient temperature. The hydraulic pressure varied from 5 to 22 bar was applied on the lumen side of the membrane modules. Water permeability coefficient (A) can be obtained using DI water as the feed at variable pressure. The salt rejection experiment was carried out using a 2000 ppm salt solution (~0.034 M NaCl solution) based on conductivity measurements (Mettler Toledo) of permeate and feed water at variable pressure. Details can be found elsewhere

(Chou et al. 2013).

Mechanical properties of the hollow fiber substrates were assessed in term of tensile modulus, stress at break, strain at break, and burst pressure. The tensile modulus, stress and strain at break were performed using a Zwick 0.5 kN Universal Testing Machine at room temperature. To test the membrane burst pressure, two hollow fiber modules were made. Every module consisted of fifteen fibers with an effective length of 22 cm. Interfacial polymerization of polyamide was carried out prior to the test. A hydraulic pressure at the interval of 2.5-5 bar was applied on the lumen side of the membrane modules until the fibers burst.

Inner surface topography and mechanical properties of PRO hollow fiber membranes were studied using an atomic force microscope (AFM, NX10, Park Systems). Loading forces of 5-50 μN were applied on the inner surface of three hollow fiber membranes: substrate, TFC-PEI, and TFC-PEI after long term PRO testing to assess the change in the mechanical properties before and after exposure to high pressure.

The porosity of PEI hollow fiber substrate was determined using gas pycnometer (Ultrapyc 1200e, Quantachrome, USA). Certain amounts of sample with known apparent volume were put into the sample chamber. High purity compressed nitrogen gas was used for measurement of sample's true volume. Porosity (P) can be calculated by:

$$P = \left(1 - \frac{V_T}{V_A}\right)100\% \quad \text{Eq. 14}$$

where V_T is true specific volume (cm^3/g) and V_A is apparent specific volume (cm^3/g).

3.2.4 Performance in PRO process

The schematic diagram of a laboratory scale PRO unit used in this study is similar to our previous work (Chou et al. 2012). The orientation of the hollow fiber module for the reported data is active layer facing draw solution, unless otherwise stated. Since the active selective layer is on the inner surface of the fiber, the pressurized draw solution was pumped through the fiber lumen by using a high pressure diaphragm pump. Pressure regulator valve and back pressure regulator were used in the draw solution loop for adjusting the pressure and the flow rate. Upstream and downstream pressures for draw solution are described as P_1 and P_2 , respectively, which can be monitored on a computer. Hydraulic pressure ranging from 5 to 22 bar was applied in the draw solution side. A concentrated salt solution was used to dose the draw solution to compensate the dilution of the draw solution during the experiments. It was controlled by the change in conductivity of the draw solution. Recirculation chillers connected to a submerged coil tube in the draw solution tank was used to remove heat generated by the high pressure pump. The temperature of the draw solution is maintained constant at 23 ± 1 °C. A 1.0 M NaCl solution was used as the draw solution. The feed solution was circulated using a peristaltic pump with a flow transmitter connected to a computer for flow rate adjustment. Dosing feed is controlled by the weight changing of the feed solution. The setup, thus, ran on the constant volume of feed. DI water was used as the feed water unless otherwise stated. The conductivity and temperature of the feed and draw solutions were monitored by probes connected to a data logging system. The flow rates of feed and draw solutions were maintained constant at 1.0 ± 0.05 L/min and 0.2 ± 0.05 L/min,

respectively, throughout PRO testing. All PRO tests were conducted at temperature of 23 ± 1 °C.

Water flux (J_w) during PRO process through a semi-permeable membrane can be quantified by the volume change of the dosing feed (ΔV_{DF}) in a predetermined time interval (Δt).

$$J_w = \frac{\Delta V_{DF}}{A_m \Delta t} \quad \text{Eq. 15}$$

where A_m is the effective membrane area of the hollow fiber membrane. The salt flux (J_s) was determined by the change in the total amount of salt in the feed water in a certain time interval per membrane area (Chou et al. 2013)

$$J_s = \frac{\Delta(c_F V_F)}{A_m \Delta t} \quad \text{Eq. 16}$$

where c_F is the salt concentration in the feed water tank based on the conductivity; V_F is the volume of the feed water. The power density (W) is determined by the water flux (J_w) and the corresponding hydraulic pressure difference over the membrane (ΔP).

3.3 Results and discussion

3.3.1 Substrate characteristics

The hollow fiber membrane substrate was fabricated by the NIPS method. It has an asymmetric structure as depicted in Figure 3.1. It is shown that the dense skin on the inner surface is supported by a highly porous sublayer. The substrate has a fully sponge-like structure providing an excellent mechanical strength to

withstand hydraulic pressure during PRO operation. Sponge-like structure, however, contributes to a severe ICP attributable to its lower porosity and higher tortuosity. Consequently, lower PRO water flux could be expected because of lower effective driving force. Therefore, an effort has been made to compensate for the membrane structure by reducing the thickness of the membrane wall. As seen in Figure 3.1(a1), the substrate has a uniform wall thickness of $101 \pm 3 \mu\text{m}$. Reducing wall thickness, however, would weaken the mechanical strength of the membrane. Hence, the hollow fiber membrane in the current study was designed to possess a significantly smaller outer and inner diameter of $628 \mu\text{m}$ and $427 \mu\text{m}$, respectively. The properties of PEI hollow fiber substrates are given in Table 3.1.

Figure 3.1. Morphologies of PEI hollow fiber membrane substrate: (a1) cross-section; (a2) cross-section near the inner surface; (a3) inner surface; thin film composite (TFC) – PEI hollow fiber membrane before PRO testing (b1) cross-section; (b2) cross-section near the inner surface; (b3) inner surface.

The PEI substrate has a pure water permeability (PWP) of $260 \text{ L/m}^2\cdot\text{h}\cdot\text{bar}$ and a porosity of 73%. The MWCO of the inner surface is bigger than 500 kDa . The mechanical properties of the PEI hollow fiber substrate are summarized in

Table 3.2. The membrane has a tensile modulus of 159 MPa as compared to 248 MPa for the previous PEI hollow fiber membrane. The stress and strain at break, representing stretch resistance and ductility respectively, are comparable to those of the previous PEI hollow fiber membrane. However, the current PEI membrane has much higher burst pressure of up to 24 bar.

Table 3.1. Properties of PEI HF membranes.

Sample	Dimensions				Porosity (%)	PWP (L/m ² .h .bar)	MWCO (KDa)	Reference
	OD (μm)	ID (μm)	Thickness (μm)	Thickness/ID				
PEI HF	628 ± 4	427 ± 6	101 ± 3	0.24	73 ± 3	260 ± 4	>500	Current work
PRO-PEI	1260	975	143	0.15	72 ± 2	360 ± 10	321 ± 30	(Chou et al. 2013)
PRO-PES	1380	980	200	0.20	80	273	45	(Chou et al. 2012)
FO-#C-PES	1370	960	205	0.21	82	278	39	(Chou et al. 2010a)

The stretching stress, σ_s , on the inner surface of the hollow fiber membrane is given by,

$$\sigma_s = \left(\frac{2}{(r_o/r_i)^2 - 1} + \mu + 1 \right) P_i \quad \text{Eq. 17}$$

where r_o , r_i represents the outer and inner diameter of the membranes, respectively; μ is the Poisson's ratio, and P_i is the applied pressure on the inner surface of the HF membranes (Chou et al. 2013). Based on the calculation using the equation, the previous PEI hollow fiber had a ratio of thickness over ID of 0.15, and thus the stretching stress at 16.5 bar is 70 bar. The current PEI hollow fiber has a ratio of thickness over ID of 0.24. The current fiber has similar stretching stress of 70 bar at a higher hydraulic pressure of 23 bar. The stretching stress increases as the ratio of thickness over diameter decreases. Consequently,

the previous PEI fiber has a lower burst pressure.

Table 3.2. Mechanical and structural properties of PEI HF membranes.

Sample	Tensile modulus (MPa)	Stress at break (MPa)	Strain at break (%)	Burst pressure –lumen ^a (bar)	Structural parameter (um)	Reference
PEI HF	159 ± 9.8	8.8 ± 0.3	39 ± 7.9	23.5	527	Current work
TFC-PEI	248 ± 8.0	8.6 ± 0.3	38.5 ± 4.0	16.5	610	(Chou et al. 2013)
TFC-PES	103	5.6	66.6	9.5	460	(Chou et al. 2012)
FO-#C-PES	93	4.0	47.3	5.0	550	(Chou et al. 2010a)

Note:

a. Applied pressure from the lumen where the membrane lose its selectivity

3.3.2 Morphology of composite PRO hollow fiber membranes

A polyamide selective layer can be interracially polymerized onto the surface of a membrane. A number of commercial products have been developed based on this technique due to their high flux and salt rejection (Petersen 1993). In this study, TFC and MPD have been used as the monomers to develop the polyamide RO-like skin on the inner surface of the PEI hollow fiber substrate. Figure 3.1 (b2) shows the cross-section near the inner surface of the hollow fiber membrane. The polyamide layer can be seen as an extra layer on the top of the porous support. Figure 3.1 (b3) shows that the inner surface was covered uniformly by the typical ridge and valley morphology. The same surface morphology has been reported in the literature (Chou et al. 2010b, Chou et al.

2013, Wang et al. 2010).

The morphologies of TFC-PEI hollow fiber membranes after PRO testing are shown in Figure 3.2. It can be seen that the typical ridge and valley structure has flattened due to compaction as compared to and Figure 3.1 (b2) before PRO testing. With higher operating pressures and longer testing processes (eg. 200 h), the TFC layer became more compacted (Figure 3.2 (a3)). These SEM images were taken on randomly chosen parts of the membranes. The pictures presented can be taken as representatives for each sample.

Figure 3.2. Morphologies of TFC – PEI HF membrane: (a) cross-section near inner surface and (b) polyamide layer on the inner surface, after PRO testing at different hydraulic pressures: (1) 12.5 bar; (2) 15.0 bar; (3) 22.0 bar; (4) 12.5-18.0 bar for 180 h.

3.3.3 Intrinsic properties of PRO hollow fiber membrane

The initial PRO tests were performed to evaluate the membrane performance with regard to the burst pressure by applying hydraulic pressure on the draw solution side from 5 to 24 bar with membrane oriented with the active layer facing the draw solution. These experiments tested the PRO water flux and

power density as a function of operating pressure as shown in Figure 3.3. The burst pressure was observed to be around 23.5 bar. Theoretically, the effective driving force across the active layer should decrease as the hydraulic pressure increases resulting in a decrease in PRO water flux, as previously reported (Chou et al. 2012, She et al. 2013a, She et al. 2012b). Indeed, the flux decreased as expected in the low pressure range (5-15 bar). Interestingly, there is a turning point where the water flux started to increase as the pressure exceeded 15 bar.

Figure 3.3. PRO water flux ($\triangle$) and power density ($\square$) of the TFC-PEI hollow fiber membrane at various operating pressures from 5 to 24 bar. Testing conditions: 1.0 M NaCl solution as the draw solution and DI water as the feed water at ambient temperature.

Since PRO water flux is closely associated with the water permeability of the membrane (A), following experiments have been designed to study the intrinsic properties of the membrane when the membrane was pressurized beyond the turning point (18 bar) and at the turning point (15 bar).

The permeation properties such as water permeability (A) and salt

rejection were measured in pressure driven RO-mode in a cross-flow cell. The experiments were performed at different pressures. The ascending pressures were carried out from 5 to 18 bar and the descending pressure from 18 to 5 bar. The experimental results are shown in Figure 3.4. It can be seen that the water permeability increased from 3.3 to 5.3 L/m².h.bar as the pressure increased from 5 to 18 bar. However, when the pressure was decreased back to 5 bar, the water permeability remained stable at around 5.1 L/m².h.bar. This might be due to physical deformation of the fibers at high pressure. As the membrane has been compacted, the polyamide selective layer becomes thinner (as shown in Figure 3.2), at the same time, the free volume of the polyamide layer may increase, leading to an increase in the water permeability of the membrane. Similar phenomenon has been discussed in the literature (Blandin et al. 2013, Chou et al. 2013). It is shown that an excellent salt rejection of >98% could be sustained over the entire testing period, despite increasing the operating pressure. This also indicates that the ratio of salt permeability over water permeability (B/A) was maintained constant at 0.09 ± 0.02 bar against various hydraulic pressures.

Similar testing of the membrane permeation properties was performed at a lower pressure range of 5 to 15 bar. It is interesting to see that the water permeability, A, is stable at around 4 L/m².h.bar as shown in Figure 3.5. When the fiber was tested at the maximum pressure near the turning point, the stretching stress on the membrane matrix is less damaging. In this range, the membrane is also able to maintain high salt rejection (> 98%) and low salt permeability (B).

Figure 3.4. Water permeability A (□), salt permeability B (■), B/A (●) and NaCl rejection (▲) as a function of hydraulic pressure of the feed, which implies the creeping occurred at 18 bars. Testing conditions: 2000 ppm NaCl solution as the feed at ambient temperature, operating pressure of 5-18 bar.

Figure 3.5. Water permeability A (□), salt permeability B (■), B/A (●) and NaCl rejection (▲) as a function of hydraulic pressure of the feed. Testing conditions: 2000 ppm NaCl solution as the feed at ambient temperature, operating pressure of 5-15 bar.

3.3.4 PRO performance

Further PRO experiments were conducted to evaluate the effects of the

maximum operating pressure on the water flux, specific salt flux and power density. A short comparison of PRO performance between current work and reported work is shown in Table 3.3. It can be seen that the newly developed membrane has similar or better performance as compared with previous works, and shows proven strong mechanical strength. In each experiment, the membranes were pressurized from low to maximum pressure and back to low pressure. This was considered as one cycle. Each module tested underwent two cycles of ascending and descending pressure.

Table 3.3. Comparison of PRO performance.

Salty water	Fresh water	Operation pressure ΔP (bar)	Water flux J_w (L/m ² h)	Power density W (W/m ²)	Specific salt flux J_s/J_w (g/L)	Membrane	Reference
1.0M NaCl	DI water	15.0	48.5	20.2 (10 hrs testing)	-	TFC-PEI HF	Current work
1.0M NaCl	1 mM NaCl	15.1	49.9	20.9	1.7	TFC-PEI HF	(Chou et al. 2012)
	10 mM NaCl	15.1	44.7	18.7	1.7		
1.0M NaCl	10 mM NaCl	8.4	47.2	11.0	-	TFC-PES HF	(Chou et al. 2013)

The initial PRO test showed that the burst pressure is around 23.5 bar. Firstly, the membrane was challenged to the maximum pressure near the burst pressure. PRO results were summarized in Figure 3.6. When the pressure increased from 5 to 22 bar, it is shown in Figure 3.6 (a1) that the PRO water flux decreased and then increased again. At 22 bar, the PRO water flux and power density are 50 L/m².h and 29 W/m², respectively. The pressure was subsequently decreased to 5 bar. Since the membrane has been significantly stretched, the water

flux at 5 bar increased by 46% from 50 to 73 L/m².h. As a result, the power density was also increased. However, the specific salt flux (J_s/J_w) shows good stability over the first whole cycle. On the second cycle, the membrane was pressurized from 5 to 22 bar. It can be seen that the water flux decreased significantly and peak power density was shifted to 15 bar pressure. During the ascending part of second cycle, the membrane showed a dramatic increase in the specific salt flux as the pressure increased from 5 to 20 bar. This indicates that the membrane selective layer has been damaged. As expected, the membrane burst at 20 bar.

Figure 3.6. (a) water flux (J_w) and J_s/J_w and (b) power density as a function of hydraulic pressure of the draw solution. One cycle consists of ascending (●, ▲, ■) and descending (○, △, □) pressure. (1) and (2) are first and second cycle, respectively. PRO testing conditions: 1.0 M NaCl as draw solution and DI water as the feed at ambient temperature; maximum pressure is 22 bar.

On the other hand, at a lower maximum pressure, two pressure cycles could be completed without bursting as showed in Figure 3.7. Similar to the previous test, the PRO water flux increased after the membrane was pressurized

at 20 bar during the first cycle. The flux turning point is around 15 bar. During the second cycle, the ascending and descending pressure curves were very closely matched. It is also shown that the membrane possesses identical peak power density of 28 W/m² at 20 bar. There was a slight increase in the specific salt flux during the second cycle when the membrane was pressurized at 20 bar. The membrane lost its selectivity when tested under 1 bar using 500 ppm NaCl solution after the PRO test. The two tests show that the creeping is highly dependent on pressure. When the applied pressure was higher than the safe operation limit, membrane creeping will occur. The creeping is more severe when the applied pressure is higher as the membrane pressurized under 22 bar cannot survive the second cycle.

Figure 3.7. (a) water flux (J_w) and J_s/J_w and (b) power density as a function of hydraulic pressure of the draw solution. One cycle consists of ascending (●, ▲, ■) and descending (○, △, □) pressure. (1) and (2) are first and second cycle, respectively. PRO testing conditions: 1.0 M NaCl as draw solution and DI water as the feed at ambient temperature; maximum pressure is 20 bar.

After PRO tests were completed, the module was opened and the hollow fiber membranes were subsequently viewed under the SEM to examine the membrane morphology after high pressure PRO tests. As depicted in Figure 3.8, the active layer of polyamide is delaminated (broken) after testing at the maximum pressure of 22 bar. Referring to the initial morphology of polyamide in Figure 3.1 (b3), the active layer of polyamide was significantly stretched after pressurizing at 20 bar (shown in Figure 3.8 (b)). It is obvious that pre-conditioning the membrane by pressurizing at high pressure results in an increase in water flux and power density. However, further testing is needed to determine the ability of the membrane to endure the stress for a long period of time, which is to be discussed in the following section.

Figure 3.8. Surface morphologies of thin film composite (TFC) – PEI hollow fiber membrane after PRO testing at maximum pressures of 22 and 20 bar.

3.3.5 Stability test

Stability tests were performed to evaluate the membrane behavior over

long term testing at high pressure. Briefly, hydraulic pressures of 12.5 (below turning point), 15.0 (turning point) and 18.0 bar (above turning point) were applied on the draw solution side. For each operating pressure, the membrane was run continuously for at least 60 h. This provides an insight into the optimum pressure for the PRO membrane and the behavior of the membrane under continuous high pressure conditions. Figure 3.9 shows a representative curve of power density, water flux, the specific salt flux and pressure with time at three different pressures. As can be seen from the figures, the membrane performance is stable for more than 60 h, with the power density, water flux and specific salt flux at $15.7 \pm 0.3 \text{ W/m}^2$, $45 \pm 0.9 \text{ L/m}^2\cdot\text{h}$ and $0.01 \pm 0.001 \text{ M}$, respectively, when the hydraulic pressure was set at 12.5 bar (below the flux turning point). When the pressure was increased to 15 bar, the power density increased to 19.2 W/m^2 . A slight increase in water flux was observed. This result shows that the applied pressure of 15 bar is the utmost pressure before the membrane starts to experience a creeping phenomenon. After 60 h running continuously, the pressure was increased to 18 bar which is above the turning point but it is still considerably lower than the burst pressure. It can be seen that there is a rapid increase in power density and water flux for the first 24 h. The membrane possesses an initial power density of 21 W/m^2 and PRO water flux of $43 \text{ L/m}^2\cdot\text{h}$ at the operating pressure of 18 bar. After 24 h, the power density and water flux of the membrane are stabilized at 27 W/m^2 and $54 \text{ L/m}^2\cdot\text{h}$, respectively. As can be seen from Figure 3.9, the membranes are able to maintain the specific salt flux as low as 0.01 M throughout 200 h PRO testing. In addition, the water flux of the membrane increased significantly when the pressure is reduced to lower pressure. The same

modules were then tested in RO-mode by using a laboratory scale cross-flow filtration unit. It was interesting to observe that the membrane lost its selectivity to NaCl. This implied that membrane creeping due to high pressure loading might induce irreversible damage to the membrane. As such, an integrity test should be conducted to find out the safe operation pressure for the PRO hollow fiber membranes.

Figure 3.9. Power density and water flux (●, ▲, ■) and hydraulic pressure of the draw solution (○, △, □) as a function of time. PRO testing was performed continuously using 1.0 M NaCl as draw solution and DI water as the feed at ambient temperature at hydraulic pressures of 12.5 (○), 15 (△) and 18 (□) bar.

Nanoindentation is an effective and powerful tool to evaluate polymer creeping in term of Young's modulus, hardness, etc. (Gibson 2014). In this study, nanoindentation was performed by using AFM. The tip was pushed into the surface of the membrane at certain force to investigate the mechanical behavior of the membrane matrix. Four loading forces ranging from 5 to 50 μN were applied on the inner surface of three different membranes (PEI substrate, TFC-PEI before compaction, TFC-PEI after long term PRO testing) as shown in Figure

3.10. When the loading force of 50 μN was applied, the indent depths of the membrane are ~ 0.2 , 0.7 and 1.3 μm for substrate, TFC-PEI before pressurization and TFC-PEI after PRO testing, respectively. The indent depth of 0.7 μm for TFC-PEI before high pressure loading can be explained from Figure 3.1 (b3). The thin film is very porous and thus, can be indented easily. Therefore, the indent depth is a combination of the thin film layer and the substrate. In contrast, the TFC-PEI hollow fiber after long term exposing to high pressure might become very soft due to the stretching effect at high pressure. This is confirmed by the indent depth of 1.3 μm .

Figure 3.10. Atomic force microscope (AFM) images showing measured topography after indentation tests on the inner surface of hollow fiber membranes: (a) PEI substrate, (b) TFC-PEI, (c) TFC-PEI after long term PRO testing.

From the data obtained through AFM, the hardness of the membrane can be calculated by Oliver-Pharr model (Díez-Pascual et al. 2015). The PEI hollow fiber substrate and TFC-PEI before compaction have similar hardness of 68 and 59 MPa, respectively. After long term PRO testing at high operating pressure, the

hardness of the hollow fiber membrane drops significantly to 5.2 MPa. These facts are consistent with the experimental PRO testing in which the membrane selective property deteriorated and the fibers burst easily.

In the real PRO operation, applied pressure will be relieved intermittently for backwashing to remove foulants. As such, an intermittent pressure should be applied to assess the integrity of the membranes after the pressure loading. This intermittent test could be considered as a good approach to justify the membrane integrity. In the experiment, the pressure was gradually increased until 15 bars and maintained for about 8 hours, after which the pressure was gradually removed until 0 bars. Another cycle was conducted again after 10 hours, and the results of water flux, specific salt flux and power density are summarized in Figure 3.11. It can be seen that the cycles were closely matched, indicating that the membrane integrity was well maintained at 15 bar. This shows that the membrane is safe to operate at the flux turning point. As shown previously, the creeping occurred when the pressure reached 18 bar. For that reason, it could be pronounced that it is safe to operate hollow fiber membranes at or below flux turning point for real PRO applications.

In a PRO process, when the applied pressure is relatively low (below the operating limit or the compaction zone), some slight membrane compaction-related effects can be observed. Figure 3.11 demonstrates that these effects are totally reversible. Time-dependent deformations of the membrane (creeping) will hardly be observed under these conditions as permanent deformation of the substrate does not occur when the operating pressures are low (Seltzer et al. 2012). However, the creep zone is encountered when the applied pressure exceeds the

mechanical limits of the substrate. Under these conditions, the membrane will start to creep over time. Deformation of the selective layer occurs as the mechanical support layer is unable to completely resist high pressure loadings. As the membrane gradually deforms and its mechanical properties deteriorate, it would eventually lose its functionality. A safe operating limit can be found in between these two zones. Successful and sustainable application of a PRO process thus depends on identifying and using an applied pressure that is compatible with the long-term, stable operation of the membrane, while also maximizing the energy density of the overall process.

Figure 3.11. (a) Water flux (J_w) and salt flux over water flux (J_s/J_w); (b) power density and pressure as a function of time. PRO testing was performed using 1.0 M NaCl as draw solution and DI water as the feed at ambient temperature at maximum hydraulic pressure of 15 bar

3.4 Conclusion

Most of the PRO tests for lab-made hollow fiber membranes reported in the literature did not present long-term PRO testing results and there was almost no integrity check. Thus it is difficult to judge the suitability and potential of the resultant PRO membrane for practical PRO application. The current work is believed to be the first effort to investigate the creeping phenomenon of PRO hollow fiber membrane due to high pressure loading and to report PRO membrane performance over a long term test of 200 hours. The major findings of the work can be summarized as follows:

- Membrane creeping was clearly observed when a non-stop 200 hr PRO testing was conducted, where the water flux gradually increased at 18 bar. The creeping phenomena resulted in irreversible damage to the membranes as the membrane lost most of its selectivity after the testing under high operating pressure. Nanoindentation by using AFM was applied to investigate the mechanical behaviour of the membrane matrix before and after experiencing the high pressure, which demonstrated to be an effective tool to verify the membrane creeping.
- A flux turning point (15 bar) was observed during the PRO testing, and it was proved to be safe to operate the hollow fiber membrane at or below the flux turning point through an intermittent PRO testing.
- Membrane creeping is dependent on both pressure and time. Membrane creeping occurs when the applied pressure exceeds the safe operation limit

and the effect of high pressure will accumulate over time thus resulting in permanent deformation in creep zone.

- A stable power density of 19.2 W/m^2 at 15 bar was achieved while the membrane integrity is ensured.

CHAPTER 4 Enhancing pressure retarded osmosis performance with low-pressure nanofiltration pretreatment: membrane fouling analysis and mitigation

4.1 Introduction

As discussed in Section 2.3.4, membrane fouling could be a serious issue for practical PRO operation when real wastewater was used. In Singapore, where water resources are limited, utilization of wastewater brine from water reclamation process as feed in PRO was proposed to save river water or surface water that are more precious (Wan and Chung 2015). However, fouling with the wastewater brine was found to severely reduce the water flux in PRO (Chen et al. 2016a, Wan and Chung 2015). A cost-effective strategy is vital to implement the idea of using wastewater in the PRO process. Compared to the fouling mitigation strategies discussed in Section 2.5.3 such as utilization of anti-scalant, UF pretreatment etc., NF has been widely used in wastewater treatment and pretreatment for reverse osmosis (RO) processes, with relatively high pressure ranging from 10 to 40 bar (Hassan et al. 2000, Košutić et al. 2007, Nghiem et al. 2004). However, the energy consumption may not be an issue by utilizing the novel low pressure NF membranes. According to our previous work (Liu et al. 2015a, b), low pressure NF membranes could achieve a considerably high water flux at only 2 bar applied pressure with excellent multivalent ion and small organic rejection. This strategy has high potential to work well in the pretreatment of wastewater for PRO process. Furthermore, the wastewater brine from a local water reclamation plant is a pressurized stream with ~5 bars (Qin et al. 2010),

which offers a favorable condition for the NF pretreatment installation.

The current chapter aims to demonstrate the feasibility of practical PRO application using NF pretreated real wastewater RO brine as feed solution. In specific, three low pressure NF membranes, including two in-house made NF hollow fiber membranes and one commercial flat-sheet membrane, were compared in terms of membrane property, NF permeates quality, and the succeeding PRO performance. A comprehensive analysis of PRO fouling mechanism by wastewater was made through the characterization of PRO feed waters and the fouled PRO membranes. It is expected that this study can shed some light on the feasibility of using wastewater RO brine in the PRO process to harvest salinity gradient energy.

4.2 Materials and methods

4.2.1 Chemicals and membranes

The wastewater retentate used in the study was collected from a Singapore's NEWater plant, and was denoted as Newater brine (NB). Three types of NF membranes were used to pretreat the NB prior to the PRO process. They were DOW filmtecTM NF270 membrane, in-house made polyelectrolyte deposited small NF (S-NF) module based on our previous work (Liu et al. 2015a) and large-scale 2-inch NF (L-NF) module with improved selectivity. The NF membranes were characterized using standard filtration test setup (Labban et al. 2017) with DI water (Milli-Q, Millipore Integral 10 Water Purification System), glucose (180 Dalton, Sigma Aldrich), and magnesium chloride (MgCl₂, Merck Chemicals)

solutions. The isoelectric point (IEP) of membranes was calculated using rejection with a 1000 ppm sodium chloride (NaCl, Merck Chemicals) solution at a series of pHs as reported in (Szoke et al. 2003).

All NF pretreatment experiments were operated at 2 bar, and the water permeates from NF270, S-NF and L-NF modules were denoted as NF270/P, S-NF/P and L-NF/P, respectively. The PEI PRO HF membranes from Chapter 3 were used for the PRO tests. NaCl was used to prepare the draw solutions in the PRO test. DI water, NB, NF270/P, S-NF/P and L-NF/P were then used as feeds to evaluate the PRO performance and to understand the effect of the NF pretreatment on mitigating PRO fouling. The PEI PRO membranes after PRO tests using the feed solution of DI water, NB, NF270/P, S-NF/P and L-NF/P, were named as DI-PRO, NB-PRO, NF270/P-PRO, S-NF/P-PRO and L-NF/P-PRO, respectively. The denotations for the membranes and PRO feed solutions (NF permeates) are summarized in Table 4.1.

Table 4.1. Summary of denotations of PRO feed solutions and PRO membranes.

NF membranes for pretreatment	PRO feed solution ^a	PRO membranes after test
-	DI	DI-PRO
-	NB	NB-PRO
NF270	NF270/P	NF270/P-PRO
S-NF	S-NF/P	S-NF/P-PRO
L-NF	L-NF/P	L-NF/P-PRO

Note:

a. NEWater brine (NB) was received from a wastewater plant in Singapore. NF270/P, S-NF/P and L-NF/P were the permeates collected from respective NF membranes at applied pressure of 2 bar.

4.2.2 Characterizations and analysis

The structure and morphology of the fiber cross-section and surface were examined by a field emission scanning electron microscope (FE-SEM, Jeol JSM-7600F) at 5 kV. The membrane samples were dried in a freeze drier overnight prior to platinum sputter coating. In addition, electron dispersive X-ray (EDX) analysis was conducted in the low-vacuum mode at 10 kV for membranes without freeze drying and coating. All the membrane cross-sections were prepared by fracturing in liquid nitrogen. Low-vacuum mode EDX was used in this study to analyze the elemental composition of the possible foulants. The advantage of low-vacuum mode lies in the preservation of the integrity of membrane surface morphology as no conductive coating is needed. In addition, it also eliminates the interference of platinum coating which has an indivisibly close energy peak with phosphorus (RoBINSoN and Nickel 1979, Toth et al. 2003).

The anion composition of the solution was analyzed using ion chromatography system (DIONEX ICS-1000) while the cations were analyzed using optical emission spectrometer (PerkinElmer optima 8300). The solution conductivity was measured using conductivity meter (Mettler Toledo). The carbon content in solutions was measured using total organic carbon (TOC) analyzer (Shimadzu TOC-V CSH). A detailed analysis of organic carbon content was conducted using liquid chromatography-organic carbon detection (LC-OCD). X-ray photoelectron spectroscopy (XPS) microscope (PHI Quantera II scanning) was used for elemental composition depth profiling of PRO membranes on a 1.5 x 1.5 mm sputtered area. Ion gun was utilized to etch membrane in a

series of sampling depth with 4 nm interval from the active surface (depth of 0) and in total 147 times of XPS scans (etching) were performed for each sample (i.e., membrane composition information from 0 to ~590 nm depth was obtained).

The solutes from the feed solution tend to accumulate in the substrate due to transport discontinuity when rejected by active layer of PRO membranes. In order to analyze the silica concentration in the substrate, the mass balance relationship between the silica entering the substrate via convection and silica diffused back to the bulk solution due to concentration gradient could be expressed below (Wang et al. 2016).

$$J_w C - D \frac{dC}{dx} = 0 \quad \text{Eq. 18}$$

The silica concentration C_i could be solved by integrating the boundary layer thickness x from the interface of the boundary layer and feed solution ($x = 0$) to the interface of boundary layer and active layer ($x = S$), as shown below:

$$C_i = C_b \exp\left(\frac{J_w S}{D}\right) \quad \text{Eq. 19}$$

where C_b is the silica concentration at $x = 0$, S is the structural parameter representing the length scale for concentration polarization, J_w is the volumetric water flux and D is the silica diffusion coefficient.

4.2.3 Performance evaluation in PRO process

The PRO test setup and methods are similar to that in previous chapter. In order to record the flux profile precisely in the first several minutes, none pressurized operation was preferred at the beginning and pressure stepping was

thus adopted. Water flux was stabilized for about 50 min with no pressure applied on the lumen side. The pressure increment was ~5 bar in every ~25 min until the pressure reached ~16 bar. The PRO operation was stabilized at 16 bar for about 80 min and was then slowly released in the similar procedure of increasing pressure. The power density (W) was determined by the product of water flux (J_w) and the corresponding hydraulic pressure difference across the membrane (ΔP).

4.3 Results and discussion

4.3.1 Characteristics of NF membranes

The membrane characteristics of NF270, S-NF and L-NF are listed in Table 4.2. The glucose rejection was used to compare the indicative pore size of the three membranes (Artuğ et al. 2007, Bowen and Mohammad 1998). A higher glucose rejection of S-NF suggests that it has smaller pore size than NF270. The L-NF membrane has even smaller pore size with a 93% glucose rejection, despite the trade-off of lower pure water permeability (PWP) (10 L/m²/h/bar for L-NF and ~15 L/m²/h/bar for S-NF and NF270). Compared to the commercial NF270, it is expected that the membrane S-NF and L-NF would exhibit a higher rejection of organic carbon in the pretreatment of NB.

Isoelectric point is a good indicator for the NF membrane surface charge where the membrane is considered to be uncharged at this pH value. Beyond this point the NF membranes are generally negatively charged and vice versa (Xu and Lebrun 1999). Therefore, NF270 is negatively charged while S-NF and L-NF are positively charged at neutral pH. The positively charged hollow fiber membranes

would show higher rejection to Ca^{2+} and Mg^{2+} ions (Childress and Elimelech 2000). In addition, it has been reported that the selectivity of multivalent ions in a mixed ion solution is also highly dependent on the dielectric exclusion and steric hindrance where smaller pore size would result in a better rejection (Labban et al. 2017). Therefore, the highly selective L-NF/P membrane was expected to produce better quality feed water to PRO.

Table 4.2. Characteristics of membrane NF270, S-NF and L-NF.

	PWP ^a (L/m ² h /bar)	Glucose ^b (% rejection)	MgCl ₂ ^c (% rejection)	Isoelectric point ^d (pH)
NF270	15.3	84.0	42.9	4
S-NF	15.5	88.5	98.2	8
L-NF	10	93.2	99.2	9

Note:

a. Tested at 1 bar using DI water.

b. Tested at 1 bar using 200 ppm Glucose (180 Dalton).

c. Tested at 2 bar using 1000 ppm MgCl₂ respectively.

d. Tested with 1000 ppm NaCl at various pH.

4.3.2 Characteristics of PRO feed solutions

The compositions of the four different feed solutions named NB, NF270/P, S-NF/P and L-NF/P are presented in Table 4.3. The NB is a transparent brownish solution in nature with some suspending flocs, agreeing well with the existence of large amount of humic substances (see Appendix A). It is observed in Table 3 that the NB was rich in potential membrane foulants/scalants such as organic contents and divalent ions. Ca^{2+} (~112 ppm) and SO_4^{2-} (~301 ppm) ions were the dominant cation and anion, respectively. Nevertheless, the scales due to the precipitation of PO_4^{3-} and CO_3^{2-} are likely to occur due to their much lower

solubility.

After NF270 filtration, about half of calcium and magnesium, >95% of sulphate and >70% phosphate were removed (shown as NF270/P in Table 4.3). The in-house made S-NF and L-NF showed much higher calcium rejection (85.9% and 96.5%) than that of NF270 (49.8%) and similar sulfate and phosphate rejections (as compared with NF270). The positive surface charges of the S-NF and L-NF membranes were mainly accounted for the higher rejection of divalent cations. It is expected that the inorganic fouling in the subsequent PRO process could be mitigated to a certain extent as most of the divalent cations are removed by the S-NF and L-NF membranes. However, silicon concentration in the NF permeates almost remained unchanged for all the three membranes, which could be an issue for the PRO process. In addition, the leftover inorganic carbon content was still high, with the lowest inorganic carbon content of 20 ppm in L-NF/P. The rejection of organic content was consistent with the glucose rejection results. The membrane L-NF showed the highest organic carbon rejection (~ 91%) followed by S-NF (77%) and NF270 (70%).

Table 4.3. Summary of ionic compositions in different solutions.

PRO feed solution ^a	Cations (ppm)					Anions (ppm)		Carbon content ^b (ppm)		Conductivity (us/cm) @ 25 °C
	Ca	Mg	Si	K	Na	SO4	PO4	IC	TOC	
NB	112.1	16.2	15.3	78.2	315.5	301.4	17.4	36.5	41.3	2520 ± 5
NF270/P	56.3	8.4	14.5	62.7	303.9	13.3	4.4	36.8	12.3	2240 ± 6
S-NF/P	15.8	0	14.2	70.7	280.4	20.7	6.7	32.2	9.6	1750 ± 4
L-NF/P	3.9	0	14.1	60.4	286.0	8.5	4.8	20.0	3.8	1432 ± 8

Note:

a. All PRO feed solution had a pH of 7-8.

b. IC: inorganic carbon; TOC: total organic carbon.

4.3.3 PRO fouling with NB

4.3.3.1 PRO flux performance with NB as feed

The water flux using DI water and NB as feed is as shown in Figure 4.1. The intrinsic PRO water flux profile using DI water (Figure 4.1 (a)) demonstrates that the membrane is safe to operate under 16 bar as the water flux is identical when releasing the pressure from 15 bar to lower pressure. In contrast, a fast flux decline is observed during the first several minutes of none pressurized operation for NB-PRO. This is presumably due to the fast pore clogging of the microporous substrate by the organic substances and the scales of divalent ions and organic carbons in the support layer near the active layer at a high initial water flux (She et al. 2013b). After the fast flux drop, it seems the increase in applied pressure thereafter did not affect the water flux, unlike the significant variation of flux upon pressure change in Figure 4.1 (a). The water flux was almost stabilized at $\sim 9 \text{ L/m}^2\text{h}$ at 16 bar, producing a power density of 4.4 W/m^2 . This value was much smaller than the 23.6 W/m^2 obtained using DI feed water. Moreover, the flux could not be recovered when slowly releasing the pressure from 16 bar, indicating that the regain in the driving force could not compensate the flux loss due to severe membrane fouling, which could be attributed to the greatly increased structural parameter (S value) of the PRO membrane.

Figure 4.1. PRO water flux profile for (a) DI water and (b) NB feed water. The pressure stepping was performed for precise recording of the water flux.

4.3.3.2 Characteristics of NB-PRO membrane

The SEM images in Figure 4.2 (a-b) show the morphologies of the membranes after the PRO tests using DI water and NB as feed solution, respectively. In contrast to the porous outer surface of DI-PRO membrane (almost a fresh membrane), a layer of deposited foulants could be spotted on the outer surface of the NB-PRO membrane. The observed foulants were likely to be a mixture of organic foulants and inorganic scales. The views from the active surface and the cross-section do not provide obvious information on foulant deposition.

A comparison of EDX mapping images of the cross-section between the DI-PRO membrane and NB-PRO membrane is illustrated in Figure 4.3. The colors in the pictures represent the relative signal strength of the elements, with white representing the highest strength while black indicating the lowest. In Figure 4.3 (a) of carbon mapping, the green line near the edge of the membrane is likely an indication of the selective layer. The green region in Figure 4.3 (b) is wider for a NB fouled membrane, which could be attributed to the interference of

other elements accumulated near the selective layer. Strong signals of calcium, oxygen and phosphorus are observed at the same region in their respective mapping images, suggesting that one of the dominating foulants could be the different forms of calcium phosphate, which are widely reported as scalants during wastewater RO process (Bartels et al. 2005, Chesters 2009, Kim et al. 2015). In addition, the presence of S, Mg and Si can be also observed by comparing with the clean membrane, suggesting the scale formation of CaSO_4 , silica and magnesium salts. The carbonate salts were not easily analyzed from the EDX mapping images, but its existence cannot be neglected (inorganic carbon of ~36 ppm).

Figure 4.2. SEM images of (from left to right) inner surface, cross-section near inner layer, outer surface, and cross-section near outer layer of (a) DI-PRO membrane and (b) NB-PRO membrane. The scale bar applies to all figures above.

It is interesting to note that no centralized scale formation at the outer surface of the NB-PRO membrane according to EDX mapping images in Figure 4.3 (d). The presence of P, Ca, Si, S and Mg can be observed from the scattered signals, providing the evidence of scale formation across the membrane support layer. The formed scale in the support layer together with the deposited organic substances greatly reduced the porosity and increased the tortuosity of substrate,

thereby resulting in severe flux decline (Figure 4.1 (b)).

Figure 4.3. Low vacuum EDX element mapping images of carbon, oxygen, phosphorus, calcium, silicon, sulfur and magnesium (from left to right) of cross section inner layer of the (a) DI-PRO membrane and (b) NB-PRO membranes and cross section outer layer of (c) DI-PRO membrane and (d) NB-PRO membrane. White color stands for the highest element signal detected while black color denotes the lowest element signal. The scale bar applies to all figures above.

4.3.4 PRO fouling with NF pretreated waters

4.3.4.1 PRO flux performance using NF pretreated waters

The PRO water flux performance with different NF-treated feed waters is presented in Figure 4.4. It is observed that the water flux significantly increased after NF pretreatment compared to the case of untreated NB water (Figure 4.1 (b)). However, similar to the case of NB fouled membrane (Figure 4.1 (b)), the variance of applied pressure did not affect the water flux significantly when the membranes were already fouled. By taking a closer look of the initial flux (Figure 4.4 (d)), the feed solution NB and NF270/P caused significant flux drop at the beginning of the run, where the real initial flux was hard to be recorded. The water treated by the L-NF membrane corresponded to a much milder initial flux decline. The stabilized water flux at 16 bar was about 18 L/m²h, 24 L/m²h and 30.5 L/m²h

for NF270/P, S-NF/P and L-NF/P as feed, respectively, corresponding to the power density of 8.2, 10.7 and 13.5 W/m². The water flux performance was highly related to the quality of the PRO feed waters. The lesser the foulants and scaling precursors in the feed solution, the higher water flux the PRO process could achieve. L-NF/P was the feed solution containing the least organic matters and inorganic solutes among the four feed waters (Table 4.3), thanks to the highly selective L-NF membrane.

Figure 4.4. PRO flux profile of PRO membranes using (a) NF270/P, (b) S-NF/P, (c) L-NF/P as feed and 1M NaCl solution as draw and (d) enlarged water flux profile of (a-c) in the first 50 mins operation.

4.3.4.2 Characteristics of fouled PRO membranes

The EDX images of the NF270/P-PRO, S-NF/P-PRO and L-NF/P-PRO membranes are shown in Figure 4.5. Compared to the fouled NB-PRO membrane (Figure 4.3 (b)), both NF270/P-PRO and S-NF/P-PRO membranes demonstrated weakened Ca, P signals (Figure 4.5 (a-b)), indicating the less precipitation of

calcium salt. The membrane L-NF/P-PRO shows even weaker signals of Ca/P (Figure 4.5 (c)), which is consistent with the better quality of the L-NF/P feed water and the higher PRO water flux. However, all the three fouled PRO membranes (Figure 4.5) shows increased Si signal at the interface of active layer and support layer, as compared to the NB fouled PRO membrane (Figure 4.3 (b)).

Figure 4.5. EDX element mapping images of carbon, oxygen, phosphorus, calcium silicon and sulfur (from left to right) of cross section near inner layer of the (a) NF270/P-PRO, (b) S-NF/P-PRO and (c) L-NF/P-PRO membranes respectively. The scale bar applies to all figures above.

Similarly, elemental compositions were also observed from the XPS depth profiling analysis near the inner layer, shown in Figure 4.6. The changes in carbon and oxygen contents at 0-100 nm depth (Figure 4.6 (a)) indicate the location of polyamide rejection layer, agreeing well with the EDX images in Figure 4.3(a). In comparison, the NB fouled PRO membrane showed markedly different elemental profile, with significant increase in O, Ca, and P elements. This observation is also consistent with the EDX mapping results. In Figure 4.6 (c), the percentage of P was greatly decreased for membrane S-NF/P-PRO; the presence of Ca/O also decreased after 200 nm depth, suggesting a narrowed scaling layer close to the active layer, as compared to that of the NB fouled membrane. The

relatively high content of O might suggest the substantial presence of CaCO_3 , as the inorganic carbon content in the S-NF/P was still high (32 ppm). Consistent with the Ca content in L-NF/P and EDX results, the Ca content in Figure 4.6 (d) was minimized to less than 5%. The percentage of Si content was obviously increased from <5% to ~20% (agreeing with the strong signal in Figure 4.5 (c)), indicating the dominant scaling by silica.

Figure 4.6. XPS depth profiling starting from surface of active layer of (a) DI-PRO; (b) NB-PRO; (c) S-NF/P-PRO; (d) L-NF/P-PRO membranes.

The increased silica scaling for NF-pretreated feed water was probably caused by the increased water flux (Figure 4.4 (d)). It has been reported that the solute concentration in the membrane support layer is affected by the water flux and the membrane S value for an osmotically driven membrane (Wang et al. 2016). The silica concentration in the membrane support layer was estimated

using the similar method documented in our previous study (Wang et al. 2016). The estimated silica concentration in substrate as a function of membrane water flux was plotted in Figure 4.7. Higher water flux resulted in higher silica concentration in the substrate. Theoretically, SiO_2 scaling could occur when the concentration is beyond its solubility of 120-150 mg/L (pH < 8, 25 °C) (Morey et al. 1964). In the case of NB-PRO membrane, although the initial flux was higher than 20 L/m²h, it dropped rapidly to less than 20 L/m²h within 5 min and after 50 min it was stabilized at ~10 L/m²h. The relatively low water flux led to minimal silica scaling; therefore it is hardly to observe a distinct silica layer adjacent to the active layer (Figure 4.3 (b)). In contrast, the increased water flux for the case of NF270/P-PRO (>20 L/m²h) triggered higher internal silica concentration in the substrate and more severe silica scaling. Consequently, silica scaling was most significant for the L-NF/P-PRO membrane due to the highest water flux (>30 L/m²h). Although this rule is also applied to other salts/foulants, their bulk concentration was prominently reduced after NF-pretreatment, which might not result in more precipitation/deposition at higher water flux. However, it also revealed that an even higher level of cleanness of PRO feed is required when PRO is operated at higher water flux.

A summary of all the PRO performance using different feed solutions is presented in Table 4.4. It can be seen that a significant improvement was made by adopting the NF pretreatment strategy. Due to the high concentration of various foulants in NB, a rapid flux decline was observed in the first several minutes' operation and a water flux of 9 L/m²h at 16 bar was achieved. The pretreatment with NF270 membrane removed most of the organic components

and the majority of multivalent ions, a doubled water flux was produced in PRO. The in-house made NF membranes S-NF and L-NF had even higher selectivity, and the pretreatment with them could lead to improved PRO performance, i.e. the corresponding water fluxes were 24.1 L/m²h and 30.5 L/m²h, respectively. The use of most promising 2-inch L-NF membrane helped to increase the PRO power density to ~13.5 W/m² from 4.4 W/m² (untreated NB feed). Compared to the method of ethylenediaminetetraacetic acid (EDTA) dosing (1 mM) together with air bubble assisted back washing adopted in a prior study (Chen et al. 2016a), the NF pretreatment may provide a more cost-effective approach for enhancing PRO performance, as the NB from the previous RO process is a pressurized stream (~5 bar) and no extra energy input is required for the NF pretreatment (Qin et al. 2010).

Figure 4.7. Plot of estimated SiO₂ concentration in the PRO membrane substrate as a function of membrane water flux.

Table 4.4. Summary of PRO performance using different feed solutions.

Feed solution	Draw solution	Flux (L/m ² h)	Power density (W/m ²)	Membrane	Reference
DI water	1M NaCl	53 @16 bar	23.6	PEI TFC	Previous work (Chen et al. 2016b)
NB	1M NaCl	9 @16 bar	4.4	PEI TFC	Current work
NF270/P	1M NaCl	19 @16 bar	8.2	PEI TFC	Current work
S-NF/P	1M NaCl	24.1 @16 bar	10.7	PEI TFC	Current work
L-NF/P	1M NaCl	30.5 @16 bar	13.5	PEI TFC	Current work
Wastewater RO brine with 1 mM EDTA dosing	1M NaCl	24.1 ^a @20bar	13.4 ^a	PES TFC	(Chen et al. 2016a)

Note:

a. Air bubbling and DI water back washing was applied at 23.3 cm/s for 30 min for every 1000 min operation. Normalized water flux and power density is estimated for 2000 min operation.

4.4 Conclusion

This study provides the first systematic investigation on the NF pretreatment of wastewater for practical PRO practice. The PRO fouling mechanism was thoroughly analyzed through NF-treated wastewater quality, PRO performance and fouled PRO membrane characterization. Results showed that organic substances, inorganic calcium salts and silica played an important role in PRO fouling. The in-house made NF hollow fiber membrane modules (S-NF and L-NF) could remove most of the multivalent ions and organic substrates at low pressure operation. The NF-pretreated water as the PRO feed significantly mitigated the PRO fouling, which led to PRO water flux increment of 3 times and the produced power density increased from 4.4 to 13.5 W/m². Nevertheless, the silica could not be effectively removed by NF filtration, which limited the

attainable water flux and power density. More effort shall be put on silica removal if higher water flux is demanded. Future work shall be also focused on long term PRO run for understanding the issues associated with a practical PRO operation.

CHAPTER 5 MODULE SCALE-UP AND PERFORMANCE EVALUATION OF THIN FILM COMPOSITE HOLLOW FIBER MEMBRANES FOR PRESSURE RETARDED OSMOSIS

5.1 Introduction

Though microfiltration/UF HF modules are well developed in the industrial sector as discussed in Section 2.5.4, there is still a huge gap in terms of RO/PRO module fabrication, especially for TFC modules. The great potential of PRO in power harvesting and energy reduction is thus hindered owing to lack of suitable large-scale modules. Apart from the difficulties in scaling up the PRO modules, external concentration polarization (ECP) may play a crucial role in the large module where the flow condition is much more dynamic and thus complicated though its effect is generally considered insignificant in the PRO operation as compared to internal concentration polarization (ICP) (Yip and Elimelech 2011). At present, the studies published has only demonstrated the possibility of scaling up of PRO HF modules (Ren and McCutcheon 2017, Wan et al. 2017), and a detailed development process about PRO modules in a larger scale is essential to facilitate the practical PRO operation.

Meanwhile, the great potential of PRO using NF-treated wastewater brine as feed in a lab-scale study has been demonstrated and helped clear some doubts about viability of PRO as demonstrated in Chapter 4 (Kim et al. 2015, Straub et al. 2016). However, the effectiveness of the proposed fouling mitigation strategy is still questionable in larger scale. A pilot study using similar method is therefore needed to explore the feasibility of PRO in a larger scale.

This work aims to develop PRO hollow fiber modules from lab scale to pilot scale with the considerations of the impacts of ECP and selective layer properties caused by module scale-up. The developed pilot-scale modules were also tested using retentate of an actual wastewater treatment process as feed together with nanofiltration (NF) pretreatment as fouling mitigation strategy. The study is expected to shed lights on the module development for PRO process to demonstrate the PRO feasibility in pilot scale.

5.2 Materials and methods

5.2.1 Fabrication of PRO membranes and modules

Polyetherimide (PEI, Ultem 1000, Sabic, Saudi Arabia) and N-Methyl-2-pyrrolidone (NMP, CAS#872-50-4, Merck Chemicals, Singapore) were used as the polymer and solvent to prepare polymer dope. The polymer dope solution was pre-filtered before spinning to remove contaminants. Detailed fabrication procedure of the hollow fiber substrates in current work could be found in our previous study (Chen et al. 2016b). The produced substrates were dried in 50 wt% glycerol (Merck Chemicals, Singapore) / water solution.

A lab-scale PRO module was fabricated by potting 15 fibers into a tube with an effective length of 22 cm directly with both end sealed by fast-cured epoxy. However, a two-step potting was adopted when a large number of fibers was involved in the potting process as wicking of potting material was likely to compromise the effective length of membrane and seal integrity (Macheras et al. 2001, Tigner 1979). The bundle of the fibers was firstly aligned uniformly and

cut smoothly at the end and then sealed with fast-cured epoxy. For the module with 150 fibers, static potting was then carried out, where the module was put vertically with slow-cured epoxy filled in its end, as shown in Figure 5.1 (a). Centrifugal potting was utilized when preparing modules with 500 fibers and above. The steps were similar to that of modules with 150 fibers except that centrifugal force was introduced to dispense slow-cured epoxy evenly into the end of the module. Moreover, wicking of potting material was also less expected with this method. After potting of module, IP was carried out in the lumen of the substrate to create a PA selective layer using the similar method as in previous chapter. The parameters in the fabrication process, such as flow rate of TMC solution, were proportional to the numbers of the fibers per module. The produced module was stored in de-ionized (DI) water for later usage.

Figure 5.1. Schematic drawing of fabrication procedure of modules with (a) 150 fibers and (b) 500 fibers and above.

5.2.2 PRO module performance

The characterization of the PWP and salt rejection are similar to the method used in previous chapter. The nominal packing density was defined by the ratio of cross sectional area occupied by the fibers to that of the inner chamber of the module. Four different types of module design were also developed to improve the module performance, i.e., one-bundle design, four-bundle design, distribution baffle and distribution tube.

5.2.3 Defect identification and repair

Leakage due to the presence of membrane/selective layer defects is a common problem in the large-scale hollow fiber module fabrication process and it has been widely reported in the industrial field (Macheras et al. 2001, Nagashima 1995, Pedersen and Cote 2001). A commonly used industrial practice shown in Figure 5.2 was used in the current study. The module to be examined was soaked in a water bath and the shell side of the fibers was slightly pressurized with nitrogen gas. Bubbles could be observed at the end of fiber lumen if a fiber leaked. A wire with glue was then filled in the fiber to seal the identified leaking fiber.

Figure 5.2. Schematic drawing of industrial practice of defect detection and repair of HF modules.

5.2.4 Pretreatment of PRO feed solution

In this study, one of the feed solutions used for PRO testing is wastewater retentate from a local wastewater treatment plant that produces NEWater. As mentioned earlier in Section 2.3.4, fouling and scaling are the major issues affecting the PRO performance. Therefore, low pressure pretreatment was adopted to improve the feed water quality for PRO. A commercial tight NF membrane (NF-4, Axion Water Technologies, USA), operated at 5 bar, was used to pretreat the NB for the pilot study. The commercial module was selected to due to (1) higher rejection of silica and (2) commercially available for larger production.

5.2.5 PRO performance in lab scale and pilot scale

A typical lab-scale PRO setup described in previous Chapter was used to

evaluate PRO performance of the modules with 15 fibers, 150 fibers, 500 fibers and 1000 fibers. All modules were operated in the orientation of AL-DS. 1 M sodium chloride (NaCl, CAS# 7647-14-5, Merck Chemicals, Singapore) solution was used as the draw solution, while DI water or tap water was used as the feed solution in the test. The pressure at the upstream and downstream of the module and the weight of feed solution were recorded by a data logging system. 5 M NaCl solution was automatically dosed to the draw solution to maintain its conductivity at around 84 mS/cm. A circulation chiller was also used to keep the temperature of draw solution at around $23 \pm 1^\circ\text{C}$. Water flux was calculated by weight change of feed solution per unit time per unit membrane area while power density was determined by product of water flux and operating pressure. It should be noted that the test duration for the 500-fiber module and 1000- fiber module at each pressure was only about 5-10 minutes when using lab scale setup, due to limited feed tank capacity.

A pilot-scale setup, as shown in Figure 5.3, was also used in current study to demonstrate the feasibility of PRO operation in a larger scale. The setup was able to test up to nine modules simultaneously with two sets of draw/feed solution tanks with 1000-L and 200-L capacity, respectively. 1M NaCl solution was pumped and pressurized through the lumen of the fibers while the feed solution (tap water, NB, or NF-treated NB) was pumped through the shell side of the fibers. The concentration of the draw solution was maintained at around 1M NaCl by slowly dosing concentrated NaCl solution. Water flux was determined by the difference between the feed flow rates at the upstream and downstream of the module, which were recorded by digital flowmeters. The pressure was maintained

stable for at least 30 minutes for each pressure point.

Figure 5.3. Schematic drawing of pilot setup, which could be operated with 200 L draw/feed solution tank (yellow/green loop); with 1000 L draw/feed tank (red/blue loop); and with pressure exchanger or hydro turbines

5.2.6 Prediction of PRO water flux using mathematical model

It is well known that water flux in PRO process is highly affected by the ICP and the ECP, or as shown in Figure 2.3. While the ICP is highly dependent on the structure of the membrane substrate and thus may remain similar regardless of module size, the ECP is expected to be varied during module scale-up since hydrodynamic conditions can be significantly different. The water flux prediction model developed in 2.3.2 or the Eq. 13, which accounts for the ICP and the ECP in PRO operation, was used to evaluate the ECP in the modules with different fibers. Calculation of the water flux based on this model could be expressed as,

$$J_w = A \left\{ \frac{\pi_{D,b} \exp\left(-\frac{J_w}{k_D}\right) - \pi_{F,b} \exp\left[J_w \left(\frac{1}{k_F} + \frac{S}{D_F}\right)\right]}{1 + \frac{B}{J_w} \left\{ \exp\left[J_w \left(\frac{1}{k_F} + \frac{S}{D_F}\right)\right] - \exp\left(-\frac{J_w}{k_D}\right) \right\}} - \Delta P \right\} \quad \text{Eq. 20}$$

In full-scale PRO operation, the osmotic pressures vary in the module

along the flow direction as the transports of water and solute across the membrane can cause dilution and concentration of the draw and feed solutions, respectively. To incorporate the effect of concentration changes, $\pi_{D,b}$ and $\pi_{F,b}$ in Eq. 20 should be corrected based on the mass balances of water and solute in the module. However, in the current study, it was found that the water flux was reduced by merely around 10% when the effect of concentration changes was incorporated in the calculation, as the modules used was only in the semi-pilot scale. Details of the calculation of the effect of the concentration change could be found in Appendix B. Therefore, the concentration change effect was not considered in this work for simplicity.

To reflect the actual osmotic concentrations at the surfaces of the membrane selective layer that contribute to the effective driving force, the osmotic concentrations at the bulk solutions are corrected in the equation. Specifically, the ICP effect in the substrate is corrected by introducing the “ $\exp\left(-\frac{S}{D_F}\right)$ ” term, while the ECP effects on the feed side and draw side are corrected by introducing the “ $\exp\left(\frac{J_w}{k_F}\right)$ ” term and “ $\exp\left(-\frac{J_w}{k_D}\right)$ ” term, respectively (Bui et al. 2015). Eq. 20 could thus be simplified below when excluding ECP effect:

$$J_w = A \left\{ \frac{\pi_{D,b} - \pi_{F,b} \exp\left[J_w \left(\frac{S}{D_F}\right)\right]}{1 + \frac{B}{J_w} \left\{ \exp\left[J_w \left(\frac{S}{D_F}\right) - 1 \right] \right\}} - \Delta P \right\} \quad \text{Eq. 21}$$

In the application of this model to predict water flux, the A , B , and S values are the intrinsic properties of the membrane. A and B values of each modules were determined by experiments as described in Section 5.2.2. The S value was

obtained by substituting the experimentally determined water flux of 15-fiber modules into Eq. 20. As the membrane substrate used was the same in all modules regardless of module size, the calculated S value of 0.5 mm was used in calculation for all cases. Combined with Sherwood estimation model in the fiber lumen (Eq. 6) and in the shell (Eq. 7), the water flux could be calculated given the operating conditions such as module dimensions, pressure, flow rates, and solute concentrations.

5.3 Results and discussions

5.3.1 Performance evaluation of PRO module in a lab-scale setup

PRO modules with 15, 150, 500 and 1000 fibers were successfully fabricated with their filtration characteristics summarized in Table 5.1. It is not surprising to observe that the PWP of these modules decreased with increasing fibers packed per module. The reduction of PWP could be attributed to the non-ideal reaction condition during interfacial polymerization due to the longer module length and less uniform flow of reacting solutions among fibers. Nevertheless, all the fabricated modules showed high salt rejection of at least 95%, indicating that the prepared composite membranes were defect-free. We believe this is the first time that a successful fabrication of pilot scale (membrane area up to 0.5 m²) defect-free hollow fiber modules with RO-like selective layer was reported for PRO application. Photo images of these modules from cross-section and top view are shown in Figure 5.4.

Figure 5.4. Photo images of cross-section (top row) of PRO modules with (a) 15 fibers, (b) 150 fibers, (c) 500 fibers, (d) 1000 fibers in one bundle, (e) 1000 fibers in four bundles, (f) 2000 fibers in seven bundles; and top view (bottom picture) of these modules.

Table 5.1 Characteristics of PRO modules.

PRO module	Pure water permeability ^a (L/m ² h /bar)	Rejection ^b (%)	Housing diameter (inch)	Effective length (m)	Membrane area (m ²)	Nominal packing density (%)	Cross flow velocity of feed solution (m/s)	Cross flow velocity of draw solution (m/s)
15 fibers	3.8 ± 0.3	>97	0.5	0.24	0.004	3.6	0.14	1.2
150 fibers	3.6 ± 0.2	>97	0.75	0.18	0.034	15.9	0.14	0.24
500 fibers	3.1 ± 0.4	>97	2	0.4	0.25	7.4	0.02	0.12
1000 fibers	2.5 ± 0.8	>95	2	0.4	0.50	14.9	0.02	0.12

Note:

a. Tested using DI water at 2 bar

b. Tested using 500ppm NaCl solution at 2 bar

Figure 5.5 presents the water flux and power density of different modules tested under 0 to 15 bar. For all the modules, the water flux showed a typical decreasing trend with increasing operating pressure from 0 to 15 bar, due to a decrease in the net driving force. When comparing water flux across Figure 5.5

(a) to (d) at the same operating pressure, it can be seen that the water flux and power density decreased as the module size increased. For instance, water flux at an operating pressure of 15 bar decreased from 49.8 to 26.7 L/m²h when the number of fiber in the module increased from 15 to 1000. As the hollow fiber substrates used to make the PRO membranes were the same for all the modules regardless of their sizes, it is believed that the effect of ICP on flux decline should be similar in different modules. The decreased performances could thus be attributed to (1) lower PWP of membranes caused by difference in active layer properties (2) deduction of effective driving force due to concentration dilution in the draw solution and (3) more severe ECP at the lumen and shell sides of the membranes. The three aspects will be discussed in sequence in the following sections.

Figure 5.5. PRO performance using a lab-scale setup of HF modules of (a) 15 fibers in 0.5- inch housing, (b) 150 fibers in 0.75-inch housing (c) 500 fibers in 2- inch housing and (d) 1000 fibers in 2-inch housing using DI water as feed and 1M NaCl solution as draw.

5.3.2 Effects of ECP on PRO flux

The ECP at both lumen and shell sides of hollow fibers can have significant impacts on FO and PRO fluxes (Bui et al. 2015). The magnitude of the ECP is not easily measurable, but it can be calculated from experimental data using Eq. 20. However, the equation involves the estimation of dimensionless Sherwood number at the shell side of the membranes, which brings uncertainty to the accuracy of the predictions. This is because the mass transfer at the shell side is often complicated by various parameters such as flow conditions, module geometry, and packing density, resulting in huge discrepancies among different empirical correlations of Sherwood number with Reynolds and Schmidt numbers in literature (Shen et al. 2010). Therefore, to validate the choice of Sherwood number correlation and the accuracy of the Eq. 20, the predicted PRO flux for individual module containing 150, 500 or 1000 pieces of fibers was compared with the experimental results. As mentioned in section 2.6, the A and B values of each module were determined by independent RO experiments, and the S value was obtained using the experimental data of 15-fiber module. Thus the comparison should exclude the results for the 15-fiber module.

The experimental PRO water fluxes and calculated values with different assumptions at an operating pressure of 15 bar using DI water as the feed are presented in Figure 5.6. It can be seen that the calculated water flux fitted well with the experimental data when both ICP and ECP were taken into account in the calculation. This validates the applicability of the flux prediction model in the current study. The effect of ECP on water flux can be seen clearly by comparing

the calculated water fluxes between ICP-only (calculated from Eq. 21) and ICP+ECP cases (calculated from Eq. 20). Decrease in water flux due to ECP became more pronounced when the number of fiber per module increased. The predicted water flux of different modules with ECP modulus equivalent to that of the 15-fiber module was also plotted as the red circles in Figure 5.6 to demonstrate the impact of the change in selective layer properties. The predicted water flux was calculated by adjusting the cross flow velocity of the draw and feed solutions such that the ECP modulus at both the draw and feed sides in these modules are equal to those in the 15-fiber module. The details will be discussed in Section 3.3.

Figure 5.6. Calculated and experimental water fluxes of different modules at an operating pressure of 15 bar (draw: 1M NaCl; feed: DI water)

The ECP modulus at the draw and feed sides, which was calculated based on experimental water flux of different modules, are presented in Figure 5.7. It can be seen that ECP at the draw side was not negligible even in the 15-fiber module (with the highest cross flow velocity among the different modules) was used. When the scale of modules increased, it is not practical to use a high cross

flow velocity as it is in the lab-scale module from the economical point of view. Therefore, the cross flow velocity was decreased from 1.2 m/s in the lab-scale module to 0.1 – 0.2 m/s in the larger-scale modules. A reduced ECP modulus, although not significant, was observed for the modules with 150 or more fibers, as shown in Figure 5.7 (a). On the other hand, the 15-fiber and 150-fiber modules experienced insignificant ECP at the feed side as evidenced by the close-to-unity ECP modulus as shown in Figure 5.7 (b). However, the ECP modulus at the feed side increased significantly in the larger-scale modules. For instance, the osmotic pressure on the substrate surface was 8 times higher than that in the bulk of the feed solution for 500-fiber module. Similar to the draw side, the enhanced ECP at the feed side was mainly due to the lower cross flow velocity used in the larger modules. Moreover, even in the situation where the concentration change effect was considered, the ECP modulus at both feed and draw sides shows similar trend in current study (see Appendix C). It was also difficult to achieve a uniform distribution of water flow in the module channel as the number of fiber increased. In addition, the use of a high cross flow velocity can cause damage of the hollow fibers, especially when the fibers are experiencing high pressure in the lumen.

It is worth noting that although the changes in ECP modulus at the draw side seem to be insignificant, its slight reduction could result in a larger decline in effective driving force compared with the impact from the ECP modulus changes at the feed side. This is because the draw solution has a much higher osmotic pressure (~48.6 bar for 1M NaCl), and a reduction of ECP modulus from 0.75 (~36.4 bar on membrane surface) to 0.6 (~29 bar on membrane surface)

translates to a decline in effective osmotic pressure of 7.4 bar. Therefore, a decline in water flux in the larger modules could be attributed to ECPs from both the draw and feed sides.

Figure 5.7. Calculated ECP modulus at (a) draw and (b) feed sides in different modules (modelling at 15 bar with 1M NaCl as draw solution and DI water as feed)

5.3.3 Effects of change in selective layer properties

In addition to the ECP, the difference in polyamide selective layer's property in the different modules might also be a reason contributing water flux decline in the larger-scale modules. As discussed earlier in Section 5.3.1, the PWP decreased with increasing number of fiber in a module mainly due to change in selective layer properties. As the fabrication conditions of the IP layer in the lumen of the modules are exactly the same in different modules (same reagent compositions, solvent flow velocity, etc.), the reduction of the permeability of the larger-scale HF modules might be attributed to different fluid dynamics caused by the increasing module scale. The effective length of the pilot-scale modules (0.4 m) was almost double of the lab-scale modules (~0.2 m), resulting in a more

significant decrease in reagent concentration along the fiber lumen during IP. This in turns resulted in a larger variation in formation conditions for the selective layer along the fibers in the larger modules. The formed selective layer was thus less uniform since the structure of the polyamide layer is highly dependent on the first several seconds of the reaction, which is closely related the reagent concentration (Song et al. 2005). A systematic analysis about this effect is needed in the future study in order to increase the permeability of the modules.

The impact of selective layer properties on PRO water flux can be examined by excluding the effect of ECP in the larger-scale modules, and assuming that the ICP in membrane substrate remained to be similar regardless of the module size. Using the model described in Eq. 20, the predicted water flux of different modules was calculated by adjusting the cross flow velocity of the draw and feed solutions such that the ECP modulus at both the draw and feed sides in these modules are equal to those in the 15-fiber module. As such, the driving force reduction due to the ECP can be considered the same in different modules, and thus the difference in water flux among different modules can be considered as the effect mainly caused by the variation of selective layer properties. As presented in Figure 5.6, water flux does not decrease as significant as that observed in experiments if the ECP modulus of the larger-scale modules is the same as the lab-scale module. It indicates that while the decrease in PWP of membranes would result in water flux decline in PRO, the enhancement in ECP remained to be the main contributor to the lower PRO performances in our attempts of scaling up hollow fiber modules.

5.3.4 Performance evaluation and ECP mitigation of PRO module in a pilot-scale setup

5.3.4.1 Mitigating ECP by improving module design

Tap water was used as the feed instead of DI water in this experiment due to the large consumption of feed solution in the pilot-scale setup. Compared with PRO using DI water as feed, a reduction of PRO flux was observed due to ionic components in the tap water that contributed to a higher osmotic pressure in the feed solution. Therefore, the power density of the 1000-fiber module was reduced to 8.6 W/m² using tap water as in Figure 5.8 (a) from 11.1 W/m² using DI water (Figure 5.5 (d)).

Considering the abovementioned issue of flux reduction with larger scale PRO modules, effort should be made to mitigate the ECP effects of the PRO modules. One possible way is to modify module design to improve uniformity of fiber distribution and thus the water flow distribution. Four-bundle design was employed in an attempt to enhance the mixing of feed solution in the shell side and higher PRO flux was thus expected. However, a similar FO flux was observed between one-bundle (Figure 5.8 (b)) and four-bundle design (Figure 5.8 (c)). It is worth noting that reduction of PRO flux due to increasing pressure was less obvious with the four-bundle design. As solute back diffusion became more severe under a high operating pressure in PRO process (She et al. 2012a), the effective solute transport at the feed side was more important to mitigate the ECP and to maintain higher effective driving force. Due to the more uniform fiber distribution in the module, the four-bundle design was believed to enhance the

effective contact between hollow fibers and feed solutions and thus promoted faster solute transport from substrate to bulk feed solution, resulting in less severe ECP. Therefore, a higher PRO flux of 20.3 L/m²h at 15 bar was observed with four-bundle design and produced a power density of 8.6 W/m². In addition, the four-bundle design is preferable as it is beneficial for the identification of leaked fibers during defect detection.

Figure 5.8. PRO performances of HF modules with 1000 fibers in 2-inch housing using a pilot-scale setup with (a) one bundle design, (b) four bundles design, and (c) a distribution baffle, using tap water as feed and 1M NaCl solution as draw.

Schematic diagrams and photo images of distribution baffle as another module design are shown in Figure 5.9 (a). The baffle located at the feed inlet was aimed to make the flow direction more in line with the fiber alignment and at the same time protect the fibers near the feed inlet as they were brittle due to wicking of the glue. Compared with the four-bundle design, a marginal increase in PRO flux from 20.3 L/m² h to 21.3 L/m² h at ~15 bar was observed with the distribution baffle design. A possible explanation for the insignificant improvement in the flux

is that, while introducing the baffle might locally enhance cross flow velocity along the fibers, it might also cause the flow in the shell to be non-evenly distributed, resulting in bypassing and channeling of the flow. Nonetheless, distribution baffles still seem necessary for protection of brittle fibers near the feed inlet, but the design of the baffles needs to be further optimized to mitigate feed ECP.

Figure 5.9. Schematic drawing and photo images of (a) distribution baffles and (b) distribution tubes in a HF module

The distribution tube, located along the center of the module, was designed to introduce axial flow through the orifices on the tube into the module, thus mitigating channeling and bypassing of flow and improve solution mixing in the module, as depicted in Figure 5.9 (b). A slight increase in the water flux (~9.9%) was found compared with that of the distribution baffle design. A possible problem with the tube is that water might be mostly flow out of the orifices near the end of the tubes, resulting in uneven water flow distribution along the module length. In addition, local turbulence created near the orifices of the tube was more likely to damage the fibers nearby. The module had severe salt leakage when pressurized at 10 bar. As such, it is not recommended to operate the

PRO modules with high turbulence in the shell side or distribution tube with optimized location and size of orifices introduced to achieve uniform flow conditions. Based on our current observation, a better module design to promote solution mixing and distribute the flow evenly without introducing local turbulence is required for the future study, which will be discussed in Section 5.3.4.3

5.3.4.2 Mitigating ECP by increasing cross flow velocity

Another method to mitigate ECP is to increase cross flow velocities at both sides of the hollow fibers, so that a more effective solute mass transfer on the membrane surfaces can be achieved. The effect of increasing cross flow velocity on mitigating ECP was examined via modelling in the 1000-fiber module using Eq. 20, and the results are presented in Figure 5. 10. Figure 5. 10 (a) reveals that increasing the cross flow velocity of the draw solution does not significantly mitigate the ECP. There is merely 7% or less increase in water flux by doubling the velocity in the range of examination. The insignificant effect of increasing flow of the draw solution might be because of its lower mass transfer coefficient at high solute concentration. Figure 5. 10 (b) shows that increasing the cross flow velocity of the feed solution has a more significant improvement in water flux. A 36% increase in water flux is expected when the cross flow velocity is increased from 1.0 to 1.9 cm/s. However, the water flux enhancement becomes less pronounced at 21% by further doubling the velocity to 3.8 cm/s. The benefit brought by increasing flow diminishes even more rapidly beyond this point.

Apparently, there exists an optimum cross flow velocity where beyond that point the energy input for delivering higher flow will exceed the energy harvested from water flux improvement.

Figure 5. 10. Calculated water flux with different cross flow velocities at (a) the draw (cross flow velocity of feed solution = 1.9 cm/s) and (b) the feed sides (cross flow velocity of draw solution = 12 cm/s) in the 1000-fiber module (operating pressure: 15 bar; draw: 1M NaCl; feed: tap water; red dots indicate cross flow velocity used in this study)

Based on the above modeling results, experiments were carried out by manipulating the cross flow velocity inside the module at different levels to mitigate the ECP at the shell side of the fibers. Similar to the trend observed in Figure 5. 10 (b), it was found that doubling the cross flow velocity from 1.9 to 3.8 cm/s could improve the PRO flux (at 0 bar) by merely ~16 % (from 20.3 L/m² h to 23.5 L/m² h). Similar observation was also reported by Ren *et al*, who found that doubling cross flow velocity in a 300-fiber module increased the PRO flux by ~30% (Ren and McCutcheon 2017). Apparently, the slight improvement of water flux might not worth the additional energy consumption for doubling the cross flow velocity. Moreover, high cross flow velocity creates violent turbulence in the module that could damage the brittle fibers near the potting area, and thus is not a good strategy to adopt. Experiments showed that a cross flow velocity of

larger than 4 cm/s easily led to dysfunction of the module (severe salt leakage) even at 0 bar. The situation could worsen when high operating pressure was applied in the lumen side. As such, the cross flow velocity was maintained at around 1.8-2 cm/s in the current pilot study. The observation on increasing cross flow velocity reveals that it has limitations on mitigating ECP, and thus future effort should still be focused on improving module design, as discussed in the following section.

5.3.4.3 Design considerations for future development of PRO module scale-up

Based on our experimental results from previous sections, the permeability and the ECP seems to contribute the most to the flux reduction in scaling up modules, or as summarized in Table 5.2. An optimization of the IP conditions (pumping flowrate, operating pressure and concentration of the reagents) is thus vital to preparing high-performance pilot PRO modules. Meanwhile, the ECP effect seems to dominate the flux reduction for 1000-fiber module based on the difference between our modeling data that excluded the ECP effect (40.6 L/m² h) and the experimental data (26.7 L/m² h) as in Figure 5.6. However, ECP mitigation strategies adopted in current study such as increasing cross flow velocity and modifying module design (as in Table 5.2) were not effective in enhancing water flux. A more effective way to improve the flow distribution in the shell channel and membrane lumen is imperative to alleviate the ECP and compensate the significant flux drop (34%) in scaling up PRO modules.

Another concern that has also aroused during our trial of ECP mitigation was the membrane damage due to violent turbulence in the feed channel. As the fibers were stretched or at tense due to high pressure loading in the lumen in a PRO process, the flow condition at the shell side is likely to have crucial impact on the fibers. In current study, the feed was pumped into the modules from the side and thus the flow was perpendicular to the hollow fiber alignment at the inlet, resulting in an induced force to the fibers nearby. Consequently, the fibers near the feed inlet are susceptible to physical damage induced by the turbulent flow (Wan et al. 2017). In order to ensure the membrane integrity and mitigate the ECP at the same time, the feed inlet is preferably in the same direction of the fiber alignment and the feed solution should be evenly pumped into different parts of cross section of the modules. A module design that could achieve the mentioned flow conditions is depicted in Figure 5.11, the feed inlet is embedded in the tube sheet and has perforated diffuser to distribute the flow evenly in the same direction of the fiber alignment.

Figure 5.11. Schematic drawing of PRO modules with perforated feed diffuser (a) side view and (b) cross section view

Moreover, it is important to use the industrial practice in sealing the defects in the large module production as more defects are expected when it comes to production of even larger-scale module. This is also illustrated by the 2000-fiber modules fabricated in the current study (Table 5.2), where the module with FO flux of ~ 25.7 L/m²h using tap water as feed and 1M NaCl solution as

draw easily burst at around 9-10 bar. A better practice to identify defects and strategy to facilitate repair needs to be developed for larger module fabrication. In addition, more effort is needed to improve fiber distribution, uniformity of water flow, etc. through better module design.

Table 5.2. Summary of characteristics and performance of PRO modules.

No. of fibers per module	Housing diameter (inch)	Effective length (m)	Membrane area (m ²)	Feed solution	Draw solution	Test setup	Module design	Flux at 0 bar (L/m ² h)	flux at 15 bars (L/m ² h)	Power density at 15 bars
15	0.5	0.24	0.004	DI	1M NaCl	Lab-scale	-	70.1	49.8	20.8
150	0.75	0.18	0.034	DI	1M NaCl	Lab-scale	One bundle	46.8	37.2	11.6
500	2	0.4	0.251	DI	1M NaCl	Lab-scale	One bundle	43.1	32	13.3
1000	2	0.4	0.503	DI	1M NaCl	Lab-scale	One bundle	47	26.7	11.1
1000	2	0.4	0.503	Tap water	1M NaCl	Lab-scale	One bundle	41.8	20.6	8.6
1000	2	0.4	0.503	Tap water	1M NaCl	Pilot-scale	One bundle	29.7	17.7	8.6
1000	2	0.4	0.503	Tap water	1M NaCl	Pilot-scale	Four bundles	27.6	20.3	8.5
1000	2	0.4	0.503	Tap water	1M NaCl	Pilot-scale	Distribution baffle	28.2	21.3	8.9
1000	2	0.4	0.503	Tap water	1M NaCl	Pilot-scale	Distribution tube	31	N.A.	N.A.
2000	2	0.4	1.005	tap water	1M NaCl	Pilot-scale	Seven bundles	25.7	N.A.	N.A.

5.3.5 Exploration for pilot-scale PRO operation with actual wastewater

Despite the decreased PRO performance during scaling up of membrane modules which requires further improvement, the developed modules still showed a reasonably high power density of 8.9 W/m² using tap water as feed, as mentioned earlier. In this section, feasibility of PRO to harvest energy was further

examined by running pilot-scale PRO with the developed 2-inch module using actual NEWater brine (NB) as the feed. Similar to our previous PRO tests using wastewater brine as feed in Section 4.3.3, water flux drops significantly to 7-8 L/m²h in the first several minutes of operation in the pilot setup due to membrane fouling. The high fouling tendency is expected as NB is rich in calcium, silica and etc., as discussed in Section 4.3.3 . A power density of 1-2 W/m² was thus produced at 15 bar. Therefore, a proper fouling mitigation strategy is vital in the pilot PRO operation.

In a typical NEWater production process, the NB is expected to possess a pressure of around 5 bar (or above) (Qin et al. 2010). As such, low-pressure NF pretreatment was proposed to take advantage of the pressurized NB and to enhance the PRO performance. A commercial tight NF module with high rejection to multi-valent salts was selected for the pretreatment for the pilot study, and the characteristics of the NF module are tabulated in Table 5.3. The PRO performances of the HF modules with NF-treated NB are summarized in Figure 5.12. A much higher PRO flux of larger than 20 L/m²h at 15 bar was observed when using the NF-treated NB as the pretreatment removes most all of the multi-valent ions and silica. Hence, a high power density of larger than 8 W/m² was obtained. This is close the the PRO performance using tap water as the feed, implying that the quality of the treated NB is actually comparable to the tap water in terms of PRO fouling tendency. The experiments demonstrated that while our developed 2-inch PRO modules could be further improved by mitigating ECP, reasonably high power density was still be able to achieved using actual wastewater brine as the feed when proper pretreatment was employed.

Nevertheless, cost analysis taking pretreatment process into consideration will still be required to demonstrate its economic feasibility. This will be carried out after our long-term pilot study in near future.

Table 5.3. Characteristics of NF module used in pretreatment.

NF module	Module Configuration	Operating pressure (bar)	Membrane area (m ²)	Pure water permeability (L/m ² h/bar)	Calcium rejection ^a	Silica rejection ^a
Commercial tight NF	Spiral wound	5 bars	~2.5	~8.9	99.5%	93.7%

Note:

a. Tested at 5 bar using NB as feed

Figure 5.12. PRO performances of HF modules with 1000 fibers using tight NF-treated NEWater brine as feed and 1 M NaCl solution as draw.

5.4 Conclusions

For the first time, the development process of PRO modules from lab-scale 15-fiber module to pilot-scale 1000-fiber module is demonstrated. It is thus expected to shed some light on the large-scale HF modules fabrication process. ECP was found to play a crucial rule in the flux reduction during the scaling up of the modules. Current work has thus exemplified several module designs in 2-

inch HF module fabrication, where bundle design and distribution baffle could slightly improve the overall module performance.

In addition, this work has firstly examined the feasibility of PRO using actual NF-treated wastewater retentate as feed in pilot scale. NF pretreatment proved to be effective to remove the possible foulants and scalants in wastewater retentate and a power density of more than 8 W/m² was thus obtained with the treated solution as feed, demonstrating the possibility of practical PRO operation in a pilot scale. The similar power density production using tap water and NF-treated NB as feed further highlights the importance of mitigating ECP to realize full potential of PRO during scaling up of PRO modules. Moreover, the effect of concentration change along the module length could play a significant role in the scaling-up of the PRO modules due to the increased membrane areas. Future study should focus more on the module design to mitigate ECP and examine the concentration change effect in the full-scale PRO modules.

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Overall conclusions

This thesis presents the development of high performance hollow fiber membrane for the PRO process from lab-scale to pilot-scale study using real wastewater. As both mechanical strength and permeability are required for a high performance PRO membrane, the HF membrane was designed with a porous spongy-like structure and had a thin and dense PA layer. However, membrane creeping remained a serious problem of the membrane due to its polymeric nature. Observation of this phenomenon was thus conducted to monitor HF membrane behavior under a high pressure loading (Section 3.3.5). The produced membrane was then used to study the fouling behavior when real wastewater was used as feed (Chapter 4). Finally, the membrane was further developed into a 2 inch PRO module to demonstrate its feasibility in a pilot-scale (Chapter 5). The major achievements and findings of the thesis are summarized as follows,

In Chapter 3:

- (1) A novel thin-film composite hollow fiber PRO membrane with high performance was successfully fabricated.
- (2) Membrane creeping was first studied for a HF membrane under high pressure loading. Membrane creeping is likely to occur when the applied pressure exceeds certain limit (flux turning point). Creeping slowly damage the membrane and compromise its performance over time under high pressure loading.

- (3) A 200-hour test demonstrated a good relationship between pressure loading, time and membrane creeping.
- (4) A stable power density of 19.7 W/m^2 was produced under a safe PRO operation condition (under flux turning point). Practical PRO operation pressure should be no larger than this flux turning point.

In Chapter 4:

- (5) When real wastewater brine was used as feed in PRO, a severe flux reduction could be observed (about 83% in current work).
- (6) Humic substance, calcium salts and silica are the major contributors in the fouling process.
- (7) Low pressure NF could be a cost-effective way to mitigate the fouling as the wastewater brine from the local water plant is a pressurized stream ($\sim 5 \text{ bar}$). A 110%, 167% and 239% flux increase was observed using commercial NF 270, small lab-scale module and large lab-scale module as pretreatment respectively compared with the flux when using wastewater brine as feed.
- (8) The calcium fouling contributes to most of the flux reduction when NF270 and lab-scale NF pretreatment were used while silica fouling was dominant when large-scale NF pretreatment was used.
- (9) A power density of 13.5 W/m^2 was produced when large-scale NF pretreated wastewater brine was used as feed.

In Chapter 5:

- (10) Modules with 150 fibers (3/4 inch), 500 fibers (2 inch) and 1000 fibers (2 inch) were successfully fabricated. The development process involves module fabrication, module repair and module design.
- (11) The best 2-inch module has an effective area of 0.5 m², power density of 8.9 W/m² when using tap water as feed and 1 NaCl solution as draw with a pilot-scale setup.
- (12) A commercial tight NF module was found to be more effective to treat the wastewater brine, and a 93.7% silica removal was achieved.
- (13) A power density of >8 W/m² was produced using the tight NF pretreated wastewater brine as feed in a pilot-scale setup. This suggested a high potential of the produced module in practical PRO operation when combined with proper NF pretreatment.

6.2 Recommendations for future research

A PRO membrane with higher pressure resistance is essential for PRO membrane development as the optimal operation pressure in PRO was slightly higher than 25 bar when seawater brine was used as feed. Therefore, future PRO membrane should be made to be more robust and the flux turning point should be pushed to be higher than 15 bar. Based on the estimation of stretching stress σ_s near the inner surface of hollow fibers as in Eq. 17 (Chou et al. 2013), the

stretching stress imposed on the HF membrane is lower when the ratio of the thickness and inner diameter of the fibers is larger. Manipulation of thickness and inner diameter of the substrate is a quite interesting topic to obtain PRO membrane with higher pressure resistance. A HF membrane of large thickness and small inner diameter but with uniformly finger-like structure could be a potential design for the optimal PRO membranes. In addition, more efforts should focus on searching for hydrophilic and robust membrane materials that help to enhance water flux and allow higher operating pressure in PRO process. Furthermore, incorporating the additional water channels into the selective layer of the PRO membrane, such as aquaporin (AQP) (Li et al. 2015, Li et al. 2014b, Qi et al. 2016, Zhao et al. 2012), could also contribute to significant flux increase without compromising the salt rejection and thus enhance the power production. In addition, recent studies also demonstrate the stable performance of the AQP embedded membranes over long term study (Qi et al. 2016).

As NF pretreatment is proposed as fouling mitigation strategy for current study, the fouling of the NF membrane is another concern in the practical operation. Future work should include the fouling behavior of the NF membrane as well. A long-term continuous operation of the NF-PRO system, rather than the batch test in the lab, is required for the appraisal of the effectiveness of the proposed fouling mitigation measure.

For the scale-up of the HF module, the IP conditions for the module need to be further optimized as the module is much longer and a simple amplification of the fabrication parameter is not sufficient. Moreover, there is still a technology gap in identifying defects and strategies to repair needs to be developed for larger

module fabrication. In addition, more effort is needed to improve fiber distribution, uniformity of water flow, etc. through better module design.

Last but not the least, a proper economic analysis of the PRO operation cost is needed based on our current and future studies. Although there are many studies about PRO modelling and analysis (Achilli et al. 2009, Altaee et al. 2015, Altaee et al. 2014b, Sharqawy et al. 2011, Straub et al. 2016, Straub et al. 2014, Yip and Elimelech 2012) (Kim and Elimelech 2013), few studies were conducted regarding the cost estimation of PRO plant, owing to absence of large-scale PRO modules and plants (Dinger et al. 2012, Kleiterp 2012, Lee et al. 1981a, Loeb 1998). The cost in a PRO plant mainly involves membrane module, intake and outfall systems and pretreatment, and the unit energy cost of PRO is estimated as 0.12 USD/kWh and 0.07 USD/kWh for a 25 MW and 200 MW PRO plant (Kleiterp 2012), which is comparable to that of wind energy (0.16USD/kWh- 0.28USD/kWh) (Tanioka et al. 2012) and solar energy (0.3 USD/kWh-0.74 USD/kWh) (ArifSyed et al. 2010) . However, low performance PRO modules (power density less than 5 W/m²) are used in most of these economic analysis conducted previously. Furthermore, the membrane cost has been reduced gradually with the advancement of membrane technology (Kleiterp 2012). A systematic economic analysis regarding the PRO plant cost using the most updated PRO performance and pilot data could be done in the future.

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APPENDIX

Appendix A. Organic components in different PRO feed solutions.

To have a good understanding about the organic components in the feed solutions, detailed analyzed results by using LC-OCD are summarized in Table A. 1. It is observed that the received NB was rich in humic substances. NF pretreatments were highly effective to remove the humic substances, while the low molecular weight molecules can be still found in the treated waters in ppm level. In addition to the hydrophobic organic carbons, hydrophilic carbon could also be found in the treated water in a few hundred ppb, although after 90% removal.

Table A. 1 Summary of organic carbon in different solutions.

Feed solution	CDOC (ppb)					HOC (ppb)	
	total	biopolymer	humic substance	building blocks	LMW Neutrals	LMW acids	total
NB	45430	640	10870	6280	27630	n.q.	13360
NF270/P	3850	n.q.	n.q.	90	3710	50	985
S-NF/P	3180	5	n.q.	115	3025	35	950
L-NF/P	2681	6	n.q.	180	2495	n.q.	494

Note:

CDOC: hydrophobic organic carbon;

HOC: hydrophilic organic carbon;

LMW: low molecular weight.

n.q.: not quantifiable

Appendix B. Calculation of effect of concentration change in pilot PRO modules.

Due to small membrane area used, osmotic pressure of the draw and feed solutions remains almost constant in lab-scale PRO modules. However, in large-scale PRO operation, the osmotic pressures can significantly change in the module along the flow direction as simultaneous transport of water and solute causes dilution and concentration of draw and feed solutions, respectively (Straub et al. 2014). To incorporate the effect of concentration changes, $\pi_{D,b}$ and $\pi_{F,b}$ in Eq. 20 should be corrected by considering the mass balance of water and solute in the module. Eq. 22 and Eq. 23 show the mass balance of water for the draw and feed solutions, respectively, whereas Eq. 24 and Eq. 25 show the mass balance of solute for the draw and feed solutions, respectively.

$$Q_{D2} - Q_{D1} = J_w \alpha \quad \text{Eq. 22}$$

$$Q_{F2} - Q_{F1} = -J_w \alpha \quad \text{Eq. 23}$$

$$Q_{D2}C_{D2} - Q_{D1}C_{D1} = -J_s \alpha \quad \text{Eq. 24}$$

$$Q_{F2}C_{F2} - Q_{F1}C_{F1} = J_s \alpha \quad \text{Eq. 25}$$

where Q is the flow rate, α is the effective membrane area of the module, C is the solute concentration of the bulk solution, the subscripts 1 and 2 refer to the module locations of inlet and outlet of the flowing direction, respectively. The average solute flux of the module, J_s , can be expressed by the following equation:

$$J_s = B \left\{ \frac{C_{db} \exp\left(-\frac{J_w}{k_D}\right) - C_{fb} \exp\left[J_w\left(\frac{1}{k_F} + \frac{S}{D_F}\right)\right]}{1 + \frac{B}{J_w} \left\{ \exp\left[J_w\left(\frac{1}{k_F} + \frac{S}{D_F}\right)\right] - \exp\left(-\frac{J_w}{k_D}\right) \right\}} \right\} \quad \text{Eq. 26}$$

Similar to Eq. 20, ICP and ECP effects have also been accounted in this salt flux equation. For simplicity, the average concentrations of the draw and feed solutions, C_{db} and C_{fb} , were treated as the average value of the inlet and outlet of the bulk draw solution and feed solution, respectively. $\pi_{D,b}$ and $\pi_{F,b}$ in Eq. 20 were then calculated based on C_{db} and C_{fb} .

Due to the larger membrane area for the large PRO module, the dilution of draw solution concentration caused by the larger amount of water permeating through the membrane could play a significant role in the deduction of the effective driving force. Based on the mathematical models illustrated above, PRO flux under the ICP only and ICP+ concentration change could be calculated as illustrated in Figure B. 1.

The effect of concentration dilution on the water flux can be observed by comparing the ICP-only and the ICP+concentration change scenarios. Though the concentration dilution effect seems contributes little to the flux reduction in the small PRO modules (15-fiber module and 150-fiber module), the effect increases with the size of the modules. This result is anticipated since larger membrane area results in higher amount of water permeated and thus causing reduction of the draw solution concentration. The effect of the concentration dilution is thus anticipated to play a more significant role when the module size (module length or membrane area) further increase and should be considered in our future work.

Figure B. 1. Calculated and experimental water fluxes of different modules at an operating pressure of 15 bar (draw: 1M NaCl; feed: DI water)

Appendix C. Calculated ECP modulus when considering the concentration change effect

When considering the concentration change effect as discussed in Appendix B, the calculated ECP modulus at the draw side and feed side is shown in Figure C. 1. Compared with the calculated ECP modulus when excluding the concentration change effect as in Figure 5.7, the ECP modulus shows similar trend in both scenarios. Marginal difference between this two scenarios shows that the concentration change effect may not be significant in current study with the semi-pilot modules. However, the concentration change effect could be crucial when further scaling up the modules with large membrane areas or module length.

Figure C. 1. Calculated ECP modulus at (a) draw and (b) feed sides in different modules when considering the concentration change effect (modelling at 15 bar with 1M NaCl as draw solution and DI water as feed)