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Emerging membrane technologies developed in NUS for water reuse and desalination applications: membrane distillation and forward osmosis

May May Teoh, Kai Yu Wang, Sina Bonyadi, Qian Yang and Tai-Shung Chung*

Department of Chemical & Biomolecular Engineering, National University of Singapore
4 Engineering Drive 4, Singapore 117576, Singapore

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Abstract. The deficiency of clean water is a major global concern because all the living creatures rely on the drinkable water for survival. On top of this, abundant of clean water supply is also necessary for household, metropolitan inhabitants, industry, and agriculture. Among many purification processes, advances in low-energy membrane separation technology appear to be the most effective solution for water crisis because membranes have been widely recognized as one of the most direct and feasible approaches for clean water production. The aim of this article is to give an overview of (1) two new emerging membrane technologies for water reuse and desalination by forward osmosis (FO) and membrane distillation (MD), and (2) the molecular engineering and development of highly permeable hollow fiber membranes, with polyvinylidene fluoride (PVDF) and polybenzimidazole (PBI) as the main focuses for the aforementioned applications in National University of Singapore (NUS). This article presents the main results of membrane module design, separation performance, membrane characteristics, chemical modification and spinning conditions to produce novel hollow fiber membranes for FO and MD applications. As two potential solutions, MD and FO may be synergistically combined to form a hybrid system as a sustainable alternative technology for fresh water production.

Keywords: membrane distillation; forward osmosis; desalination; hollow fiber membranes; separation; nanofiltration.

1. Introduction

Clean water scarcity is one of the major worldwide concerns resulting from resource depletion, pollution of surface and underground water, global warming, escalating world population and demand, as well as intensified competition among users. Fresh water shortage is especially severe in the developing and industrialized nations, such as Europe, USA, China, India and Middle East countries (Shannon *et al.* 2008). According to the report of World Resources Institute, 41% of Earth's population (estimated 2.3 billion) live in water-stressed areas and it is expected to exacerbate to ~3.5 billion in year 2025 (Service 2006).

Among many potential solutions, the advance in membrane technology is one of the most direct, effective and feasible approaches to solve this complex issue. Tremendous efforts in terms of manpower and developments have been put forth by both governments and industries to identify novel methods to (1) reduce water demand and spillage, (2) recycle and reuse water, and (3) develop low-

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* Corresponding author, Professor, E-mail:chencts@nus.edu.sg

energy desalination technologies. Desalination, a workable but energy-intensive process, is a promising resource to make available clean water as most Earth's water takes the form of salt water in oceans, seas, and lakes (Kelter *et al*. 2003). Even though the reverse osmosis (RO) process has surpassed and replaced conventional thermal distillation processes as the dominant desalination technology since 1999 (Drioli and Romano 2001), RO is an energy intensive process and ~50% of the operational cost is attributed to energy consumption (Semiat 2008). In addition, the RO based desalination still suffers many drawbacks such as fouling, chlorine attack and low water recovery that cannot be easily overcome.

Lately, membrane distillation (MD, temperature driven) and forward osmosis (FO, osmotic pressure driven) have received worldwide attention from both academia and industries as the alternative and emerging membrane technologies for water reclamation and seawater desalination. Combining these two processes in an integrated system can make use of their advantages to produce fresh water through recycling the draw solution used in FO by MD (Cath *et al*. 2005b, Cath *et al*. 2007), thus it may (1) decrease membrane fouling and scaling which commonly happens in RO and, (2) utilize low grade heat energy. However, presently available commercial membranes which specially designed for MD and FO are limited. It is necessary to conduct in-depth investigation on the design and fabrication of desirable membranes.

In this paper, we will review and summarize (1) the development of hollow fiber membranes for MD and FO, as well as (2) the molecular engineering of membrane materials and fabrication to produce high performance membranes in the membrane research laboratory, National University of Singapore (NUS). Hollow fiber membranes were deliberately chosen as the membrane type due to their high ratio of membrane surface to unit module volume, self-supporting capability, and easy module assembly (Strathmann 2001). Additionally, the relatively low cost of hollow fiber production attracts enormous interests for large scale industrial application. However, the fabrication of hollow fiber membrane through the phase inversion is a complicated process.

2. Membrane distillation

MD combines both membrane contactor technology and evaporation processing in a single unit. It has great potential to replace conventional desalination technologies such as thermal distillation and multistage flash (MSF) because MD offers the attractiveness of (1) small footprint, (2) operation at atmosphere pressure and low temperatures (30–90°C), and (3) theoretical ability to achieve 100% rejection of non-volatile ionic solutes and macromolecules (Lawson and Lloyd 1997, Curcio and Drioli 2005). If MD can be operated with the aid of low-cost solar and geothermal energy, or industrial wasted heat, it may potentially achieve cost and energy efficiency superior to RO (Burgoyne and Vahdati 2000). Several studies have been reported on the feasibility of solar thermal MD processes (Martínez *et al*. 2001, Ding *et al*. 2005, Hanemaaijer *et al*. 2006, Charcosset 2009) and coupling of vacuum MD device with waste-heat generated by vessel engine (Xu *et al*. 2006).

Typically, a nonwetting, microporous and hydrophobic membrane serves as the barrier between the feed and permeate solutions. Generally, pore sizes in the range of 0.1–1.0 μm are considered favorable for direct contact MD (DCMD) (Lawson and Lloyd 1997, Curcio and Drioli 2005) and the recommended maximum pore radius is about 0.5–0.6 μm (Drioli *et al*. 1987, Schneider *et al*. 1988). MD separation is based on a combination of the convective and diffusive mechanisms of relative volatility of various components in the feed solution across the membrane using partial pressure gradients as the driving forces for their mass transfers. For desalination, it involves the transport of water vapor through the pores of hydrophobic membranes and directly condenses into the cold stream. So far, MD has shown promising as a perspectives processer for seawater desalination (Lawson and Lloyd 1996, Drioli *et al*. 1999, Al-Obaidania *et al*. 2008, Curcio *et al*. 2010, Garcia-Payo *et al*. 2010), food processing (Kozák *et al*. 2009), wastewater treatment (Cath *et al*. 2005b, Karakulski *et al*. 2009), tap water purification (Gryta 2010), acid concentration (Tomaszewska 1993), biomedical application (Sakai *et al*. 1998, Ding *et al*. 2008) removal of volatile organic compounds (VOCs) (Zhen *et al*. 2006), and oxygen isotopic water separation (Kim *et al*. 2009).

However, there are some reasons that the industries have not yet fully embraced MD; namely, (1) low water flux (*i.e*., productivity), (2) shortage of long-term performance data, (3) limited availability of waste energy, (4) highly fluctuated oil price, and (5) moderate oil price. The first reason arises from the fact that most commercially available hydrophobic flat-sheet and hollow fiber membranes utilized in MD, such as polypropylene (PP), polyethylene (PE), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF), may not be applicable for MD process because they are originally manufactured for other applications, such as microfiltration or ultrafiltration. Owing to these low flux characteristics, fluctuation and uncertainty in future energy price, as well as difficulties in economic prediction, the incentives for industries to conduct long-term performance tests of MD were dampened. Breakthroughs on materials design and fabrication of high-performance hollow fibers with a much enhanced flux are vital to rejuvenate the industrial interests of MD's research and development (R&D) with greater future.

In addition to microporous PP hollow fibers, PVDF has been often chosen as the membrane material because it is a commercially available hydrophobic polymer and can be easily dissolved in many common organic solvents used for membrane fabrication. Moreover, PVDF fabrication through the non-solvent induced phase inversion processes provides an effective tool to manipulate membrane morphology and porosity compared to the melt spinning and sintering processes (that produce PP and PTFE fibers with porosity of 30~70%). Hitherto, our team have produced three generations of PVDF hollow fiber membranes, *i.e*. generation #1 (single-layer PVDF fiber), generation #2 (single-layer composite PVDF fiber), and generation #3 (dual-layer composite PVDF fiber). These fibers are intentionally fabricated for seawater desalination via DCMD process. DCMD is one of the MD configurations whereby the hydrophobic membrane comes into direct contact with two liquid streams (*i.e*., the hot feed and cold permeate streams). The model seawater used in the laboratory contains 3.5 wt% sodium chloride (NaCl).

2.1 Membrane module design

Engineering designs of novel membrane modules with lower polarizations in concentration and temperature, and molecular manipulation of membrane morphology with enhanced permeation properties are two essential but distinctive approaches to produce high productivity MD membranes. An ideal module must have good flow patterns that can maintain turbulence among the fibers and minimize the undesirable temperature polarization which leads to a lower driving force and vapor flux across the membrane (Lawson and Lloyd 1997, Li and Sirkar 2004, El-Bourawi *et al*. 2006). Hence, we started the MD research aiming at flux enhancement by module designs. A series of systematic module configurations via spacers/baffled design, modified hollow fiber geometries (twisted and braided), and combination the aforesaid designs were conducted for the optimization study (Teoh *et al*. 2008). Fig. 1 shows various hollow fiber module designs as well as the schematic

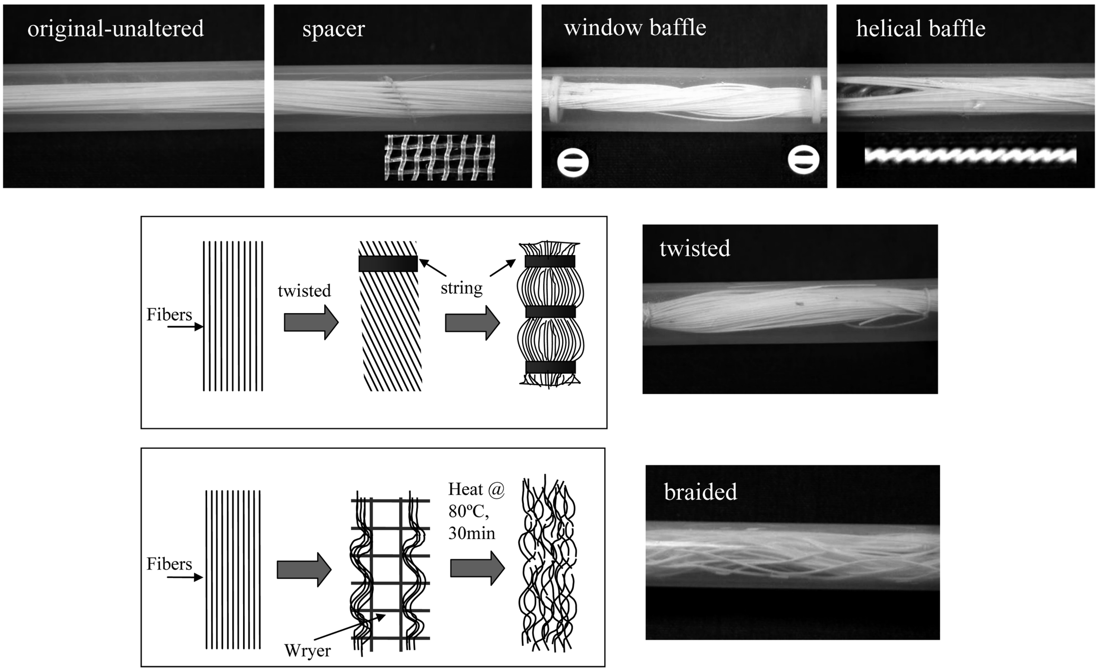


Fig. 1 Various hollow fiber module design and configurations (reproduced with permission from J. Membrane Sci. 311, 371 (Elsevier) Teoh *et al.* 2008)

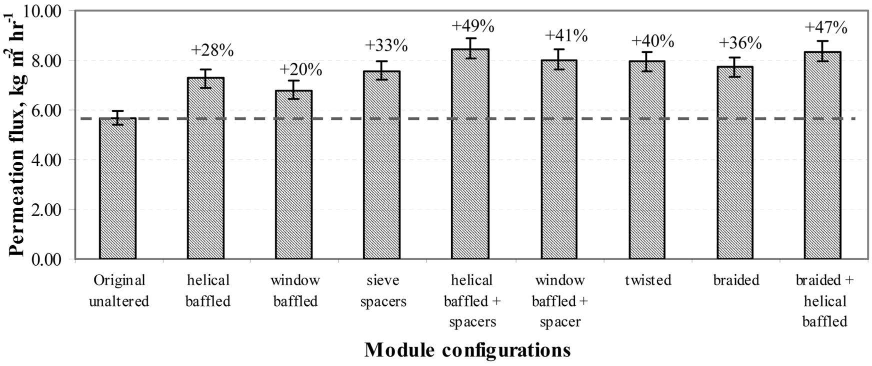


Fig. 2 Summary of the flux obtained with different module designs and configurations; salt solution: 75ºC, flow rate 0.86 m s^{-1}; cold distillate water: 17-20ºC, flow rate 0.72 m s^{-1} (reproduced with permission from J. Membrane Sci. 311, 371 (Elsevier) Teoh *et al.* 2008)

diagrams of modified hollow fiber geometries with their final module configurations.

Fig. 2 summarizes the overall performance, in terms of the total permeation flux obtained, for different module designs and hollow fiber geometries. Ultimately, advances in membrane module designs show an impressive permeate flux enhancement up to ~50% (feed inlet at 75ºC). This may be attributed to the generation of turbulence (helical baffle), effects of cross-flow (window baffle), increase in effective membrane surface area (spacers, braided and twisted), as well as enhancement in heat and mass transfer coefficients (baffles, braided and twisted). Nevertheless, the improvement

Table 1 Characteristic properties of single- and dual-layer PVDF hollow fibers

Membrane ID	Porosity (%)	Outer/inner diameter (μm)	Thermal efficiency (*EE*) @ 80°C (%)	Contact angle (°)	Average pore size (μm)
PVDF - Method #1	74	820/600	63	112	0.16
PVDF - Method #2	65	1100/860	58	130	0.08
PVDF (without PTFE)	86	960/680	82	88	0.16
Composite PVDF-PTFE	74	750/530	86	103	0.12
PVDF (without Clay)	90	1340/1020	70	80	< 0.05 (outer surface) < 1 (inner surface)
Composite PVDF-Clay	87	1380/1020	78	86	< 0.05 (outer surface) < 1 (inner surface)
Dual-layer - Approach #1	80	1200/520	90	Outer layer: 137, 140* Inner layer: 50*	0.41
Dual-layer - Approach #2	80	1100/860	74	137	0.44

*Note: contact angle measured using flat sheet membranes

is still too limited due to the poor initial membrane permeability. Clearly, the lack of commercially available membranes with superior MD performance is the immediate barrier for MD to compete with RO in addition to uncertain energy/economical issues (El-Bourawi *et al.* 2006). Consequently, the obtained results have driven researchers to fabricate novel MD membranes with (1) low heat conductivity to improve the thermal efficiency, (2) low vapor transport resistance to enhance the permeate flux, and (3) high membrane wetting resistance, anti-fouling characteristics and reasonable mechanical strength to conduct long time operation. The following summarizes their progresses and Table 1 tabulates the characteristic properties of single- and dual-layer PVDF hollow fibers.

2.2 Single-layer PVDF hollow fiber membranes (Generation #1)

At the outset, we spun our single-layer PVDF hollow fiber membranes (method #1), but the permeation flux was notably low due to a lower porosity as well as dense structure at the outer surface-outer edge and outer surface, as shown in Fig. 3 (a) (Wang *et al.* 2008). However, an effective approach to modify the PVDF membrane morphology was adopted through adding additives in the spinning dopes, to induce pores, and alter the phase inversion process. Ethylene glycol (EG) was selected because of its miscibility properties with water (coagulant) and *N*-methyl-pyrrolidone (NMP, solvent) in all proportions and it has been known as a powerful pore forming agent. Owing to its characteristics of low molecular weight and high miscibility with water, EG can effortlessly be removed from the nascent membrane after spinning. The as-spun fiber spun from dopes containing EG non-solvent demonstrated an exciting flux enhancement about 4.5-fold to 42.5 kg m^{-2} h^{-1} at 79°C (Fig. 4 (a)). This impressive enhancement is mainly attributed to a lower vapor transfer resistance with increased bulk and outer surface porosities, narrower pore size distribution as well as ultra-thin outer skin (less than 10 nm) and porous supportive layer. Generally, the permeation flux across the membrane increases exponentially with the feed inlet temperature; this observation is consistent with the driving force enhancement in consequence of exponential behavior of water vapor pressure against temperature.

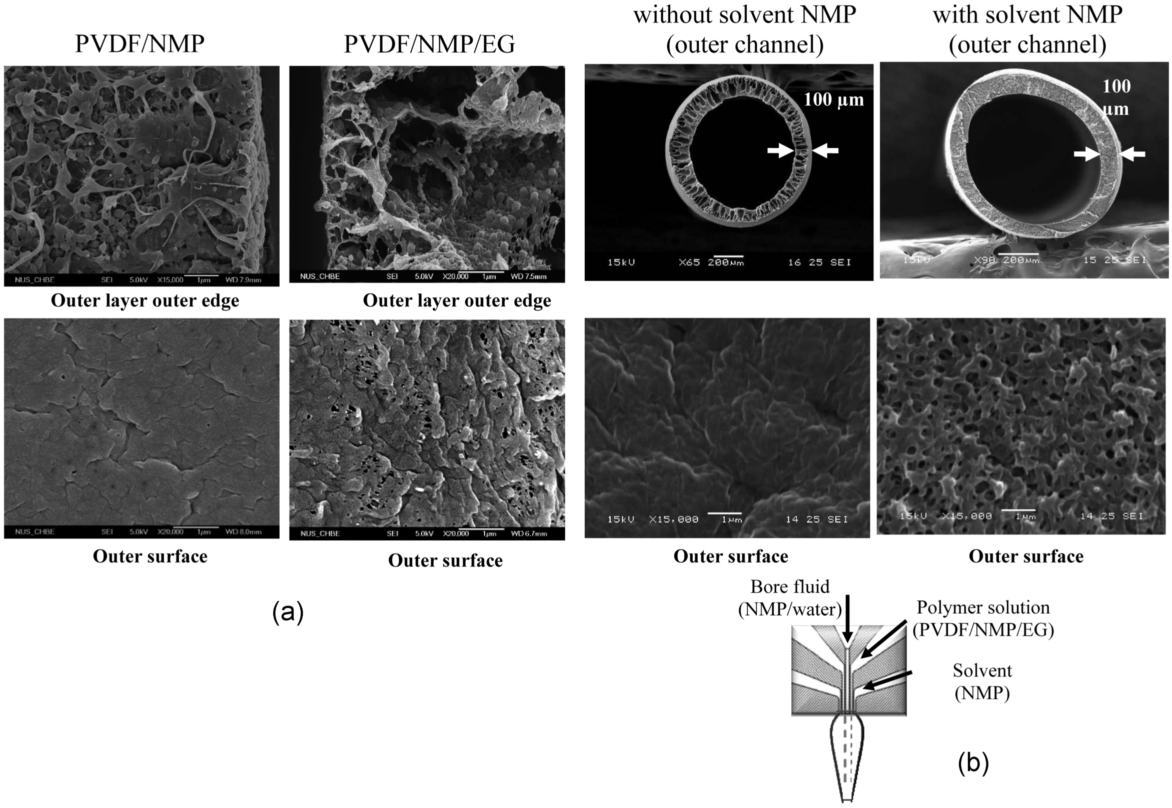


Fig. 3 Morphology of single-layer PVDF hollow fibers (a) method #1, and (b) method #2 (Reproduced with permission from Chem. Eng. Sci., 63, 2587 (Elsevier) Wang *et al.* 2008, and J. Membrane Sci. 331, 66 (Elsevier), Bonyadi and Chung 2009)

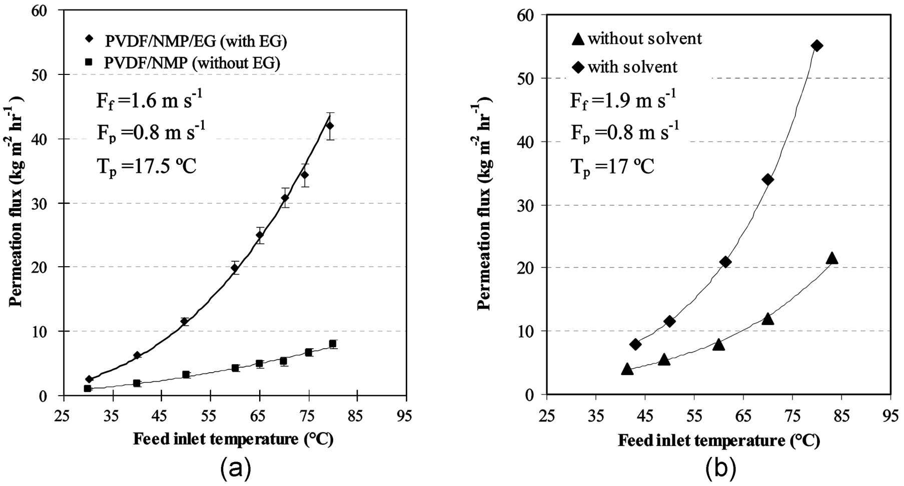


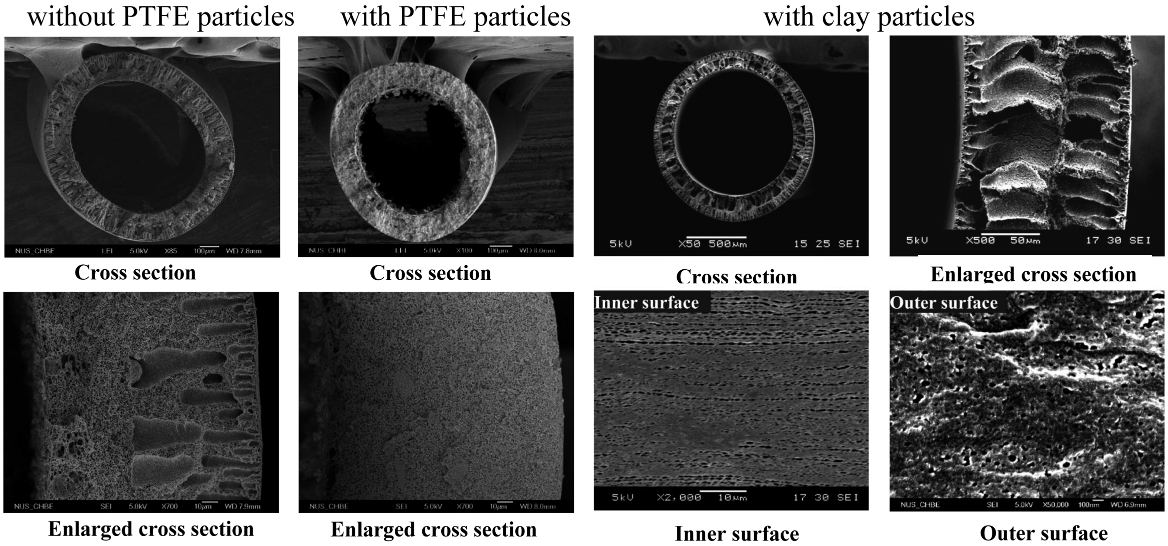
Fig. 4 Permeation flux obtained for single-layer PVDF hollow fibers: (a) method #1, and (b) method #2 (Reproduced with permission from Chem. Eng. Sci., 63, 2587 (Elsevier), Wang *et al.* 2008, and J. Membrane Sci. 331, 66 (Elsevier), Bonyadi and Chung 2009)

Next, a high surface porosity fiber was fabricated by applying a two-phase flow consisting of a solvent and a dope solution in the air-gap region of spinning (Bonyadi and Chung 2009). In this approach, the dope solution (PVDF/EG/NMP) and solvent (NMP) are co-extruded from the middle and outer channels of a triple orifice spinneret, respectively, prior entering the coagulant (water). Fig. 3 (b) illustrates the morphology of single-layer PVDF (method #2). The fiber spun with NMP flowing at the outer channel demonstrated a macrovoid-free, sponge-like and open-cell structure. This may attribute to two factors: (1) NMP has significantly lowered the outer skin polymer composition and created the delay demixing or spinnodal decomposition, and (2) the outward convection of NMP into the coagulation bath may hinder the intrusion of non-solvent (*i.e.*, water) into the nascent fiber. Furthermore, the introduction of the two-phase flow greatly increased the outer surface porosity of the PVDF fibers possibly due to the spinnodal decomposition and the Marangoni effect (Sternling and Scriven 1959). As a result, the permeation flux increased about 2.8-fold (67 kg m^{-2} h^{-1} at 80°C) compared to the standard dry-jet wet spun fibers. In terms of membrane permeability, macrovoids may seem to form desirable membrane structures with low tortuosity and high porosity. On the other hand, from a long-term performance point of view, macrovoids could be undesirable structures that enhance the membrane pore wetting and consequently reduce the membranes' long-term stability.

2.3 Single-layer composite PVDF hollow fiber membranes (Generation #2)

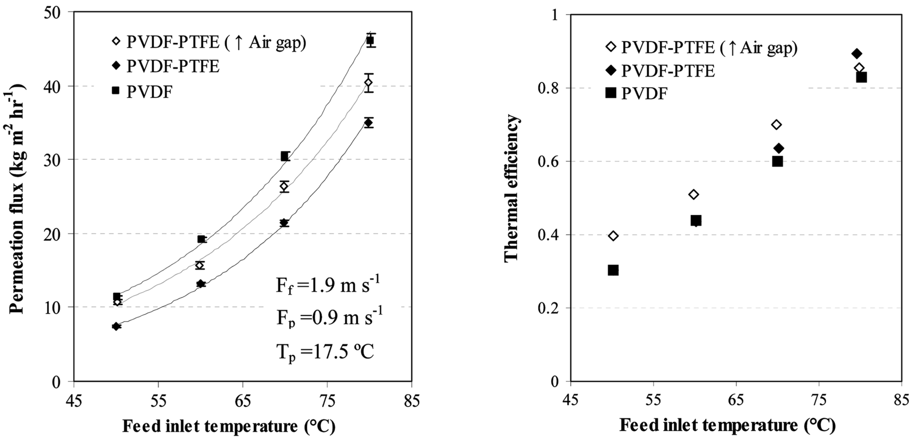
Composite membranes consisting of embedded micro- and/or nano-particles provide a potentially feasible and promising approach to overcome deficiencies in physicochemical properties (hydrophilicity and/or hydrophobicity) of membrane materials (Yan *et al*. 2003, Chung *et al*. 2007, Jiang *et al*. 2009, Shao *et al*. 2009). PTFE particles (<1 μm) were purposely selected as the disperse phase because of their superior physicochemical properties (*i.e.*, super-hydrophobic in nature) as well as stupendous stability in many organic and inorganic solvents. Incorporating hydrophobic PTFE particles into the PVDF matrix not only significantly enhanced the outer surface hydrophobicity (contact angle of 88° and 105° for the neat and composite fibers, respectively) (Teoh and Chung 2009), but also effectively suppressed the formation of macrovoids, as shown in Fig. 5 (a). This is due to the fact that increased dope viscosity can impede penetration of internal and external coagulants during membrane formation (Tsai *et al*. 2000, Xiao *et al*. 2006). Nevertheless, composite PVDF-PTFE membranes displayed a moderate decrease in permeation flux, which may attribute to higher water transport resistance and lower porosity in the non-macrovoid structure (compared to the PVDF fiber, as illustrated in Fig. 6). On the other hand, the thermal efficiency (*EE*) (which is defined as the fraction of feed brine thermal energy that has been used to evaporate water) is slightly increased with the incorporation of PTFE particles. *EE* is a crucial parameter for MD performance and usually MD systems with high flux and *EE* are preferable.

Hydrophobic clay particles (Cloisite 20A) were also incorporated into the PVDF matrix to form composite PVDF-Clay hollow fiber (Wang *et al*. 2009a). It was found that adding clay particles not only reinforce fiber mechanical strength, but also control the coefficients of thermal expansion and heat insulation by forming a kind of mixed matrix membrane embedded with a dispersed inorganic phase (Merkel and Murtagh 1993, Chung *et al*. 2007). Fig. 5 (b) illustrates the sandwich structure of composite PVDF-Clay fibers where a thin and sponge-like porous layer located between two thick layers full of finger-like macrovoids. This fiber demonstrated superior water flux of 79.2 kg m^{-2} h^{-1} at 81.5°C. Similar to the aforementioned PVDF-PTFE fibers, the addition of clay particles resulted in a slender reduction in permeation flux. However, experimental results showed that membrane



(a) (b)

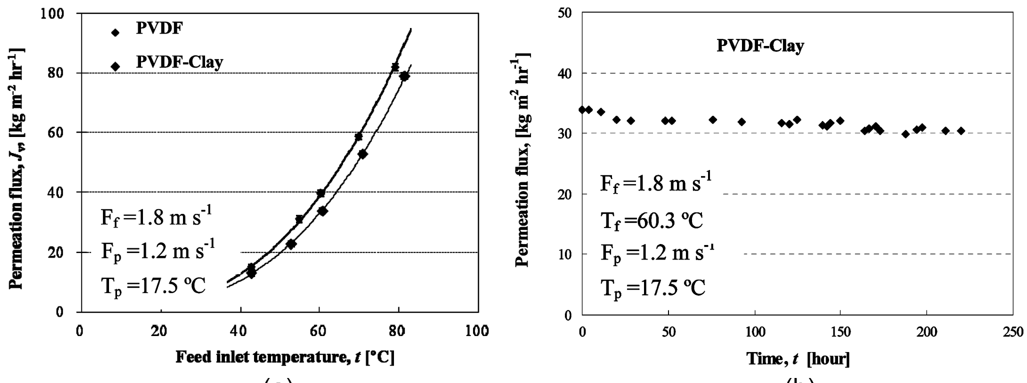
Fig. 5 Cross section of single-layer composite (a) PVDF-PTFE, and (b) PVDF-Clay hollow fibers (reproduced with permission from Sep. Purif. Technol. 66, 229 (Elsevier) Teoh and Chung 2009, and Ind. Eng. Chem. Res. 48, 4474 (American Chemical Society) Wang *et al.* 2009)



(a) (b)

Fig. 6 (a) Permeation flux obtained, and (b) thermal efficiency of single-layer composite PVDF-PTFE hollow fibers (reproduced with permission from Sep. Purif. Technol. 66, 229 (Elsevier) Teoh and Chung 2009)

with clay particles significantly enhanced long-term stability as illustrated in Fig. 7 (b). The water flux declined by 10% in the first 20 h and had almost no further decay for the next 200 h. The causes of this highly permeable fiber that could withstand a long-term continuous study are due to (1) the unique structure: low transport resistance (a high porosity of ~87% and uniform nanoscale pore less than 50 nm at the outer surface) and (2) reasonable mechanical strengths (a thin sponge-like porous middle layer with the aid of clay particles).



(a) (b)

Fig. 7 (a) Permeation fluxed obtained, and (b) long term performance of single-layer composite PVDF-Clay hollow fibers (reproduced with permission from Ind. Eng. Chem. Res. 48, 4474 (American Chemical Society) Wang *et al.* 2009)

2.4 Dual-layer approach for single-layer and dual-layer hydrophilic-hydrophobic PVDF hollow fiber membranes (Generation #3)

For the first time, we have utilized the state-of-the-art dual-layer spinning technology to minimize the thickness of the hydrophobic functional layer through additional hydrophilic layer as the support (dual-layer approach #1) (Bonyadi and Chung 2007, Bonyadi *et al.* 2008). This work was inspired by Cheng and Wiersma (1982, 1983), who described the use of MD composite membranes in a series of patents. Generally, the membrane surface physicochemical properties can be modified via plasma polymerization (Kong *et al.* 1992), radiation graft polymerization (Cheng and Wiersma 1982, 1983, Wu *et al.* 1992), and migration of hydrophobic macromolecules (SMM) to the membrane surface (Suk *et al.* 2002, 2006).

Due to the hydrophobic property in nature of outer layer, the membrane prevents pores wetting when in contact with the feed, while permeated water will fully wet the hydrophilic layer and lead to the reduction of water vapour mass-transfer resistance across membrane. Thus, the condensation of water vapour is occurred at the hydrophilic-hydrophobic interfaces, as illustrated in Fig. 8. In this work, hydrophobic clay particles were added in the outer layer and a water contact angle of ~137° has obtained (Table 1). On the other hand, hydrophilic clay particles, polyacrylonitrile (PAN) together with PVDF were formulated as the inner layer polymer dope. Inspiringly, the fabricated fibers (dual-layer approach #1) exhibited a desirable sponge-like microstructure, with a comparatively thin functional hydrophobic layer of ~50 μm (Fig. 9 (a)), can achieve permeation flux as high as 55 kg m^{-2} h^{-1} at 90°C.

The dual-layer hollow fibers fabrication technology was also utilized to produce completely sponge-like single-layer fibers with a small wall thickness (120 μm) (dual-layer approach #2) (Bonyadi *et al.* 2009). A normal dual-layer spinning process was adopted but due to the delamination between the two layers of the fibers, it allowed to effortlessly remove the inner supporting layer after drying the fibers, as shown in Fig. 9 (b). This phenomenon is attributed to the difference in shrinkage percentage between the outer and inner layer as well as the thermodynamically incompatibility between the inner (hydrophilic) and outer (hydrophobic) dope solutions. As a result, the as-spun outer and inner fibers could be separated easily and the outer layer exhibited superior performance

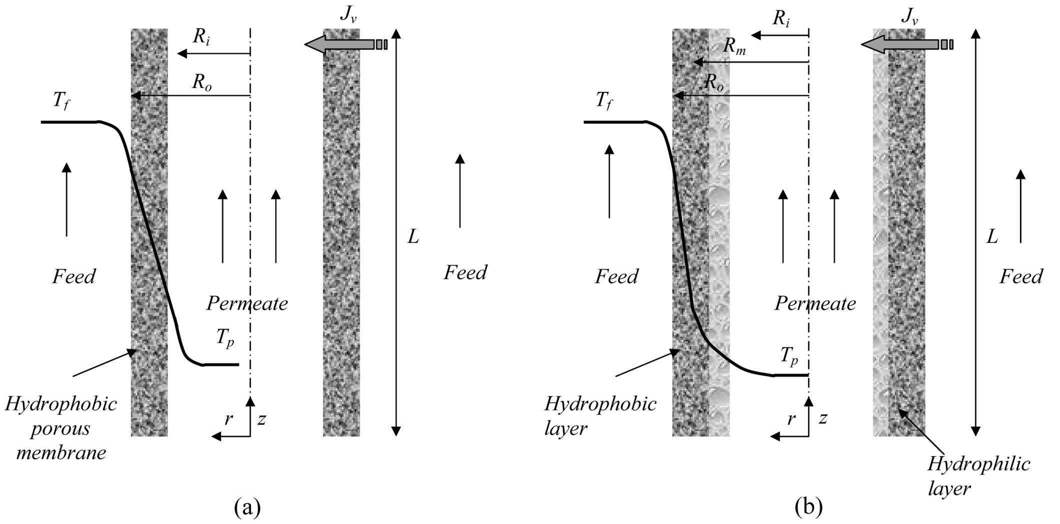


Fig. 8. Schematic direct contact membrane distillation process for (a) single-layer hydrophobic, and (b) dual-layer hydrophilic-hydrophobic hollow fibers (reproduced with permission from J. Membrane Sci. 306, 134 (Elsevier) Bonyadi and Chung 2009)

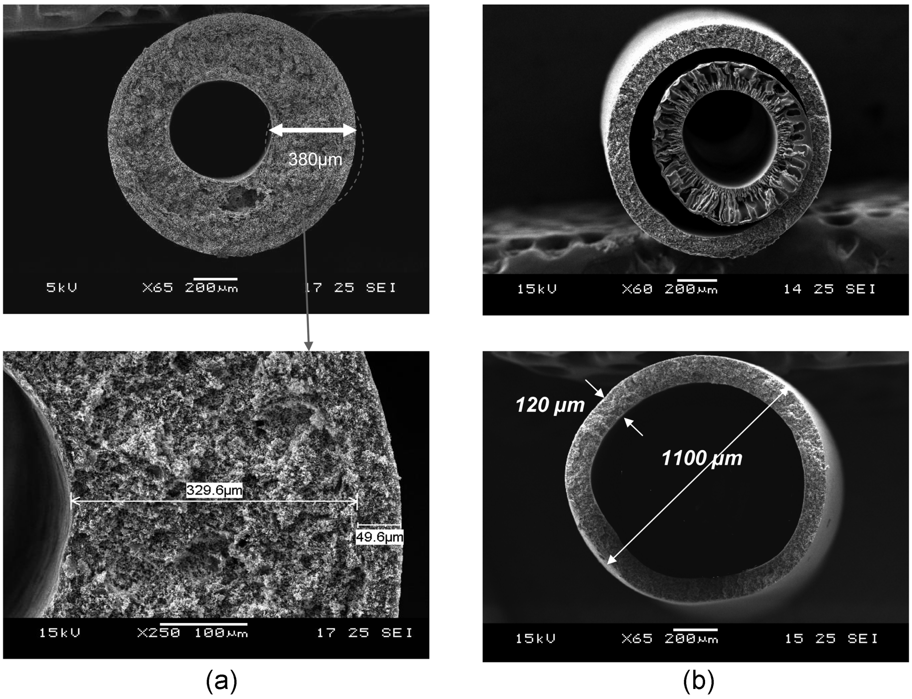


Fig. 9. Cross section of dual-layer composite PVDF hollow fibers: a) approach #1, and b) approach #2 (reproduced with permission from J. Membrane Sci. 306, 134 (Elsevier) Bonyadi and Chung 2009, and AIChE J., 55, 828 (John Wiley and Sons) Bonyadi *et al.* 2009)

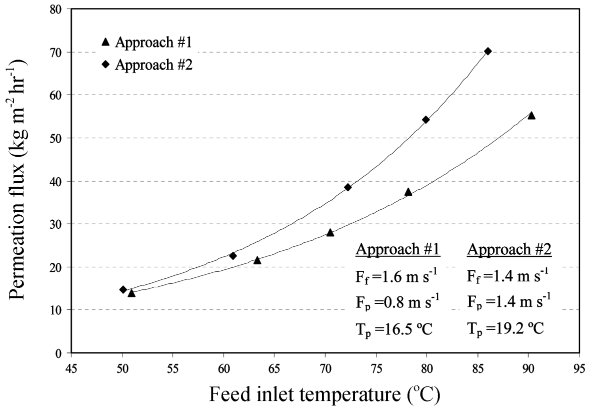


Fig. 10 Permeation flux obtained for dual-layer composite PVDF hollow fibers (reproduced with permission from J. Membrane Sci. 306, 134 (Elsevier) Bonyadi and Chung 2009, and AIChE J., 55, 828 (John Wiley and Sons) Bonyadi *et al.* 2009)

with a remarkable water flux of 70.1 kg m^{-2} h^{-1} at 86°C (Fig. 10).

2.5 Separation performance of MD membrane for desalination

The characteristic properties of our self-fabricated PVDF hollow fibers are tabulated in Table 1. Clearly, three generations of PVDF hollow fibers show desirable porosity (65~90%), hydrophobicity (with contact angle of 80°~140°) and pore size 50~410 nm at the membrane outer selective layer for MD applications. Furthermore, a reasonable high *EE* performance of above 74% can be achieved for single-layer composite fiber while dual-layer composite membranes show an impressive *EE* of 90% (at 80°C hot feed solution). Usually, the *EE* performance varies with membranes characteristics, testing conditions and module/system designs, such as morphology, wall and selective layer thicknesses, surface and bulk porosity, packing density, thermal conductivity, flow rates,

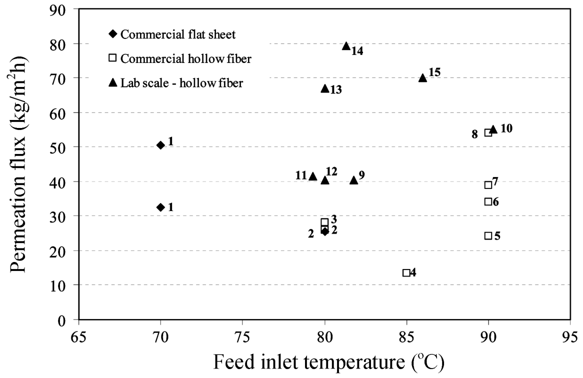


Fig. 11 Comparison of desalination performance (1. Phattaranawik *et al.* (2003); 2. Gryta and Barancewicz (2010); 3. Khayet *et al.* (2005); 4. Gryta *et al.* (2001); 5. Song *et al.* (2008); 6. Gryta (2007); 7. Song *et al.* (2007); 8. Li and Sirkar (2004); 9. Hou *et al.* (2009); 10. Bonyadi and Chung (2007); 11. Teoh and Chung (2009); 12. Wang *et al.* (2008); 13. Bonyadi and Chung (2009); 14. Wang *et al.* (2009a); 15. Bonyadi *et al.* (2009)

Table 2 Comparison of hollow fiber membranes for desalination used in DCMD

Membrane	Thickness or OD/ID (μm)	Feed solution			Permeate solution		Permeate flux* (kg m^{-2} hr^{-1})	Ref
			T in (ºC)	flow rate (m s^{-1})	T in (ºC)	flow rate (m s^{-1})		
Commercial flat sheet membranes								
GVHP PVDF, Millipore	126	Distillated water	70	2.59	20	4.67	32.4	Phattaranawik *et al*. (2003)
PTFE , Gore	70	Distillated water	70	2.59	20	4.67	50.4	Phattaranawik *et al*. (2003)
PTFE, Fluoropore FGLP, Milipore	200	1000 ppm NaCl	80	-	20	0.75-0.85	25.4	Gryta and Barancewicz (2010)
Commercial hollow fibers								
PP, Membrana GmbH	630/330	1.0 wt% NaCl	90	2.29	15-17	1.66	54^	Li and Sirkar (2004)
PP, Membrana coated with silicon-fluoropolymer	630/300	3.0 wt% NaCl	90	0.04	17	0.49	38.8^	Song *et al*. (2007)
PP, Membrana coated with silicon-fluoropolymer	630/300	3.5 wt% NaCl	90	0.14	20	0.81	24.1^	Song *et al*. (2008)
Accurel PP, Membrana GmbH	1800/1000	Concentrated tap water (~650 μS/cm)	80	1.35	20	0.25	29.2	Khayet *et al*. (2005)
Accurel PP S6/2, Akzo Novbel	2600/1800	3.5 wt% NaCl	85	0.37	20	-	13.5	Gryta *et al*. (2001)
Accurel PP S6/2, Akzo Novbel	2600/1800	Concentrated tap water (~650 μS/cm)	90	0.96	20	0.29	34.0	Gryta (2007)
PVDF, PV390, Memtek	600/370	1000 ppm NaCl	80	0.11	20	1.85	25.8	Gryta and Barancewicz (2010)
Lab scale hollow fibers								
PVDF	1200/940	3.5 wt% NaCl	81.8	0.5	20	0.15	40.5	Hou *et al*. (2009)
PVDF-Method #1	820/600	3.5 wt% NaCl	79.3	1.6	17.5	0.8	41.5	Wang *et al*. (2008)
PVDF-Method #2	1100/860	3.5 wt% NaCl	80.0	1.9	17	0.8	67.0	Bonyadi and Chung (2009)
Composite PVDF-PTFE	750/530	3.5 wt% NaCl	79.5	1.9	17.5	0.9	40.4	Teoh and Chung (2009)
Composite PVDF-Clay	1380/1020	3.5 wt% NaCl	81.5	1.8	17.5	1.2	79.2	Wang *et al*. (2009a)
Dual-layer - Approach #1	1200/520	3.5 wt% NaCl	90.3	1.6	16.5	0.8	55.2	Bonyadi and Chung (2007)
Dual-layer - Approach #2	1100/860	3.5 wt% NaCl	86.0	1.4	20.5	1.4	70.1	Bonyadi *et al*. (2009)

^The original data reported was based on the ID of fibers, and have been converted the permeate flux based on membrane OD for comparison

*All the permeate flux calculated using the OD of fibers temperatures, air gap, sweeping gas and vacuum pressure (Cheng *et al.* 2008, 2009).

Fig. 11 and Table 2 summarizes the separation performance of hydrophobic membranes for desalination. In overall, the performance of the self-fabricated hollow fibers membranes is comparable to or surpasses most of the commercially available hollow fibers, indicating that the newly developed PVDF membranes have great potential for the desalination of salt solution. All the fibers showed a substantial high rejection of 99.8% salt rejection, calculated based on the following equation

$$\beta = \left(1 - \frac{C_p}{C_f}\right) \times 100 = \left(1 - \frac{\zeta_{p2} - \zeta_{p1}}{\zeta_f}\right) \times 100$$

where β is the separation faction, C_p is the salt concentration in the permeate side, C_f is the salt concentration in the feed side, ξ_{p1} and ξ_{p2} are conductivities of permeate stream before and after the test, respectively, and ξ_f is the conductivity of the feed stream. Future work should focus on the long term performance study, effect of membrane scaling as well as temperature and concentration polarizations on heat and mass transfers.

3. Forward osmosis

Other than MD, FO also receives global attention as an emerging new membrane desalination technology (Cath *et al.* 2006). FO is a comparatively simple process because it makes use of the natural osmotic pressure gradient across the membrane to induce a net flow of water through the membrane. Compared to the traditional pressure-driven membrane processes in which membrane fouling cannot be disregarded in nanofiltration (NF) and RO under high pressures (Peng *et al.* 2004, Escobar and Ritchie 2008), FO may offer the advantages of higher rejection to a wide range of contaminants and lower membrane-fouling propensities (Cath *et al.* 2006, Hancock *et al.* 2009, Achilli *et al.* 2009a). FO has drawn much attention from researchers and its applications have been explored in wastewater treatment (Cath *et al.* 2006, Holloway *et al.* 2007, Cornelissen *et al.* 2008), desalinating seawater (Kessler and Moody 1976, McCutcheon *et al.* 2005, Choi *et al.* 2009), water purification in arid environments (Salter 2005), potable water reuse in space (Cath *et al.* 2005a, 2005b), concentration of fruits, protein and pharmaceuticals (Petrotos and Lazarides 2001, Jiao *et al.* 2004, Yang *et al.* 2009b), even in the power generation (Lee *et al.* 1981, Seppălă and Lampinen 1999, Jellinek and Masuda 2001, Loeb 2001, Achilli *et al.* 2009b) and control release drug devices (Bhatt 2004).

Alike the RO process, FO utilizes of a semi-permeable membrane and efficiently separates the fresh water from its solutes. The semi-permeable membrane acts as a barrier that allows water to pass through while blocks larger molecules like salts, sugars, starches, proteins, viruses, bacteria, parasites, and etc. Hence, FO offers the advantages of high rejections of wider range of contaminants and lower membrane-fouling propensities compared to traditional pressure-driven processes (Cornelissen *et al.* 2008). In addition, instead of using high hydraulic pressures in RO, the osmotic pressure driven FO process has been demonstrated to be advantageous in regards to membrane fouling and cleaning (Mi and Elimelech 2010a, 2010b). However, most available membranes used in FO are either dense semi-permeable membranes available in the RO industry or cellulose triacetate based FO membranes in flat sheet configuration developed by Hydration Technologies Inc. (Albany, OR) through coating cellulose triacetate on the woven mesh fabric (McCutcheon *et al.* 2005). Thus, it is necessary to develop unique FO membranes that can adapt for the FO application.

We adopted the strategy of fabricating NF membranes for FO applications because of their molecular-size pores (around 0.30~2 nm in diameter) on the selective layer and their high rejection rates for multi-valence ions and larger molecules. Polybenzimidazole (PBI), a unique heterocyclic class polymer, is chosen because of its self-charged characteristics in aqueous solutions, superior hydrophilicity and high water take-up (Chung 1997a, 1997b). These characteristics make PBI less susceptible for membrane fouling and provide great potential for water reuses. Till date, three generations of PBI NF hollow fiber membranes have been produced for FO studies. They are named as: generation #1, #2, and #3 as single-layer PBI (A), ultra-thin single-layer PBI (B) with chemical modification, and dual-layer PBI/PES hollow fiber membranes, respectively.

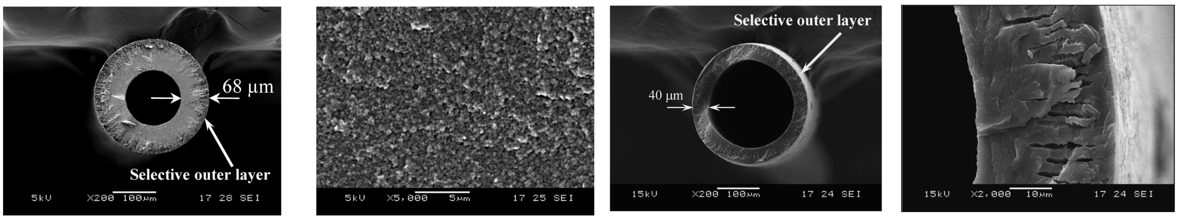
3.1 Single-layer PBI hollow fiber membranes (Generations #1 and #2)

The NUS membrane research team led by Prof. Chung has conducted pioneering research and reported the first study of NF hollow fiber membranes for osmotically driven membrane processes (Wang *et al.* 2007). The first generation of PBI (A) NF hollow fiber was produced by the dry-jet wet-spun process and the outer selective layer of the resultant fibers has a mean effective pore

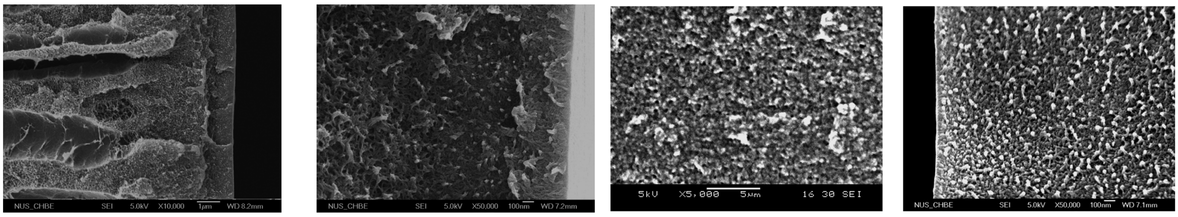
Table 3 Properties of single- and dual-layer PBI NF hollow fiber membranes

Membrane ID	PWP (l/m^2-bar-h)	r_p (nm)	MWCO (Da)	$MgCl_2$ rejection (%)
PBI-A	0.50 (10 bar)	0.32	365	92.4±0.3
PBI-B (Original membrane)	2.43 (2 bar)	0.41	993	76.3±0.6
PBI-B (Modified membrane – 2-h)*	1.53 (2 bar)	0.34	528	86.8±0.5
PBI-B Modified membrane – 9-h)*	1.25 (2 bar)	0.29	354	95.4±0.7
Dual-layer PBI/PES	1.74 (1 bar)	0.40	338	87.2±0.8

*Note: Chemically cross-linking modification of PBI-B fibers with *p*-xylylene dichlororide



Cross-section Inner surface Cross-section Enlarged cross-section



Enlarged outer layer Microstructure near outer surface Inner surface Microstructure near outer surface

PBI (A) PBI (B)

Fig. 12 Morphology of PBI (A) and PBI (B) hollow fibers (reproduced with permission from J. Membrane Sci., 300, 6 (Elsevier) Wang *et al.* 2007, and Chem. Eng. Sci., 64, 1577 (Elsevier) Wang *et al.* 2009) radius of 0.32 nm according to the solute transport method (Matsuura 1994, Singh *et al.* 1998). The pure water permeability was 0.5 liter m^{-2} bar^{-1} h^{-1} measured at 10 bar, as shown in Table 3. The production of the second generation PBI (B) membranes was intended to 1) enhance permeation flux by reducing fiber's wall thickness, and 2) reduce membrane pore size and improve salt selectively by chemically cross-linking modification via *p*-xylylene dichloride (Wang *et al.* 2009b, 2009c).

Fig. 12 illustrates the morphology of PBI (A) and PBI (B) fibers. These membranes have nano-porous outer selective layers and sponge-like substructure near the inner skin. This kind of microstructure makes PBI hollow fibers mechanically strong to sustain high trans-membrane pressures during NF operation. However, the major drawback of the asymmetric structure at the porous support layer which may result in internal concentration polarization and seriously influence the water recovery during the FO operation mode. These two batches of PBI fibers have similar membrane structure; except that the fibers' wall thickness for PBI (B) fibers was intentionally designed to be as thin as 40 μm to reduce the mass transport resistance.

In order to produce a desirable pore size for FO application, the resulted membranes were introduced to chemical cross-linking modification, one of the most direct, feasible and effective methods, to finely tune the mean pore size and lead to salt selectivity enhancement. The as-spun PBI (B) hollow fiber was firstly dipped in fresh methanol three times, following by dipping in the solution of substituting agent *p*-xylylene dichloride (1.0 wt%)/ethanol for 2-h and 9-h, respectively. Then, the

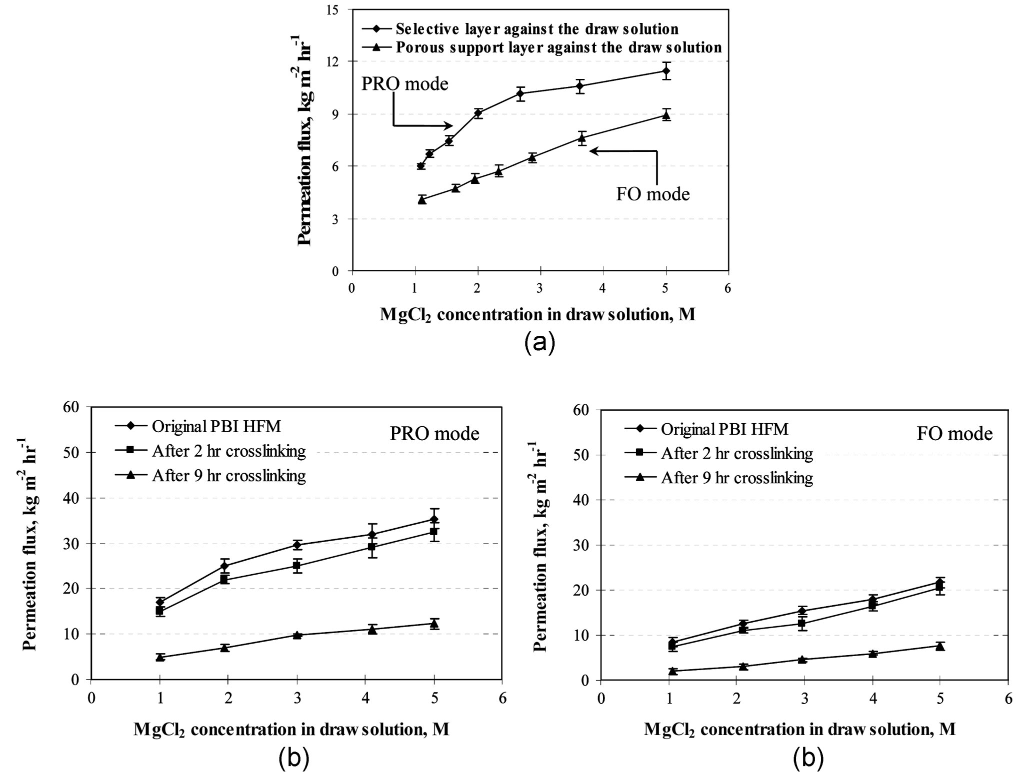


Fig. 13 Effect of $MgCl_2$ draw solution concentration on water flux: a) PBI (A) and b) PBI (B) fibers (reproduced with permission from J. Membrane Sci., 300, 6 (Elsevier) Wang *et al.* 2007, and Chem. Eng. Sci., 64, 1577 (Elsevier) Wang *et al.* 2009)

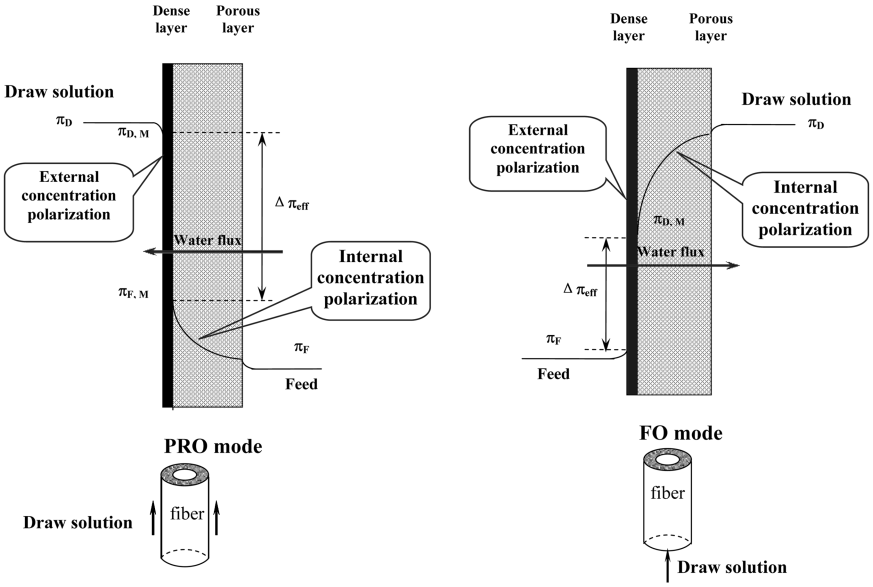


Fig. 14 Effect of concentration polarization under different membrane orientations (reproduced with permission from Ind. Eng. Chem. Res. 49, 4824 (American Chemical Society) Wang *et al.* 2010)

membrane was rinsed with fresh ethanol, and then kept in water for testing. Table 3 lists the pure water permeability, mean pore size and MWCO of the PBI membrane as a function of modifying period in the *p*-xylylene dichloride/ethanol solution. After the modification, the PBI (B) membrane has a decreased mean pore size and much narrowed pore size distribution, leading to an enhanced selectivity for the separation of solutes.

The dependence of water permeation flux on draw solution concentration for two different membrane orientations inside the membrane module is plotted in Fig. 13. As illustrated in Fig. 14, the pressure retarded osmosis (PRO) mode is the condition when the draw solution flows on (or against) the selective layer, while the FO mode operates as the draw solution flows on the porous support layer. Usually, the FO mode experiences a slightly lower water permeation flux than the PRO mode. This is attributed to severer dilutive internal concentration polarization of the draw solution in the porous substructure of the asymmetric membrane in the FO mode. As a result, a serious decrease in the net osmotic driving force occurs in the FO mode as displayed in the right diagram of Fig. 14 (Mehta and Loeb 1978, Cath *et al.* 2006, McCutcheon and Elimelech 2006). Similarly, an accumulation of salt concentration may take place in the porous substructure of the asymmetric membrane because water is drawn out of the feed in the PRO mode as displayed in the left diagram of Fig. 14. For diluted feed solutions, the dilutive internal concentration polarization (draw solution side) is generally severer than the concentrated internal concentration polarization (feed side). Thus the PRO mode tends to have a higher water flux than the FO mode. In addition, the water transport across the PBI membrane increases with an increase in draw solution concentration due to the increased effective osmotic pressure as the driving force.

The PBI (A) fiber exhibited a water permeation flux of 11.2 LMH (PRO mode, 5M $MgCl_2$) and substantial low salt leakage to divalent ions, as shown in Fig. 13 (a). This clearly demonstrates that the first generation NF membrane has a great potential for water reclamation and concentrating

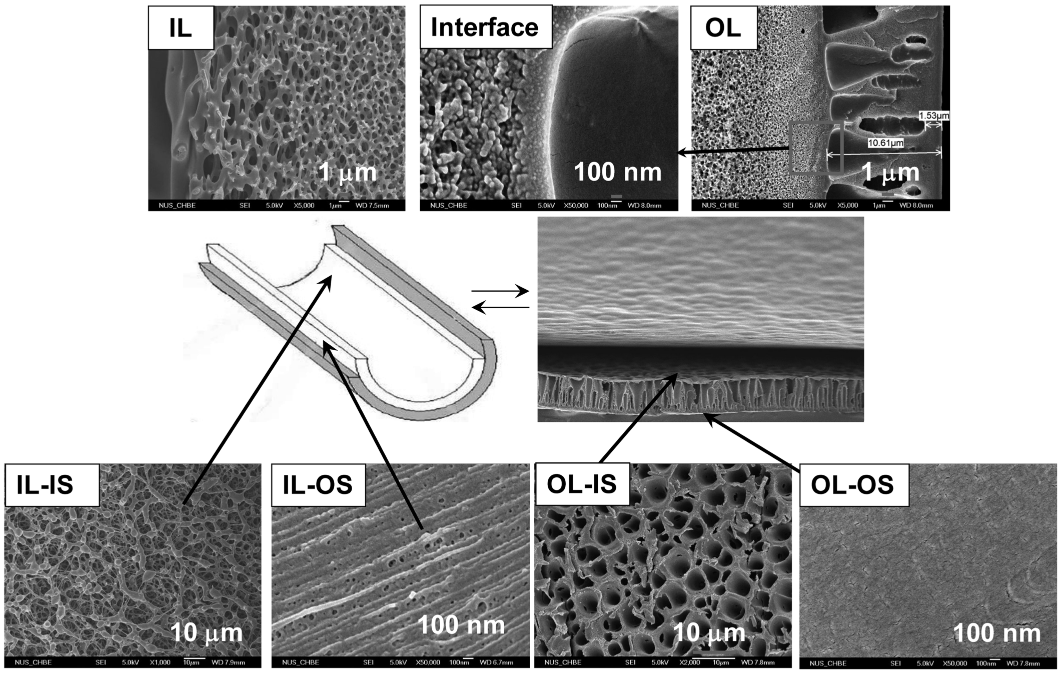


Fig. 15 SEM morphology of PBI/PES dual-layer hollow fiber membranes (reproduced with permission from Environ. Sci. Technol., 43, 2800 (American Chemical Society) Yang *et al*. 2009)

various feed solutions. Compared to the PBI (A) fiber, the permeation flux of the second generation PBI (B) NF membrane was almost double owing to the effect of thinner membrane wall. However, this membrane showed a poorer salt selectively as a result of bigger pore sizes. Thus, a further chemical modification was employed to reduce the salt transport. The permeation flux slightly decreased for the 2-h chemical modification sample even though its reject rates for ions improved significantly. However, the 9-h chemical modification not only narrowed the pore size but also

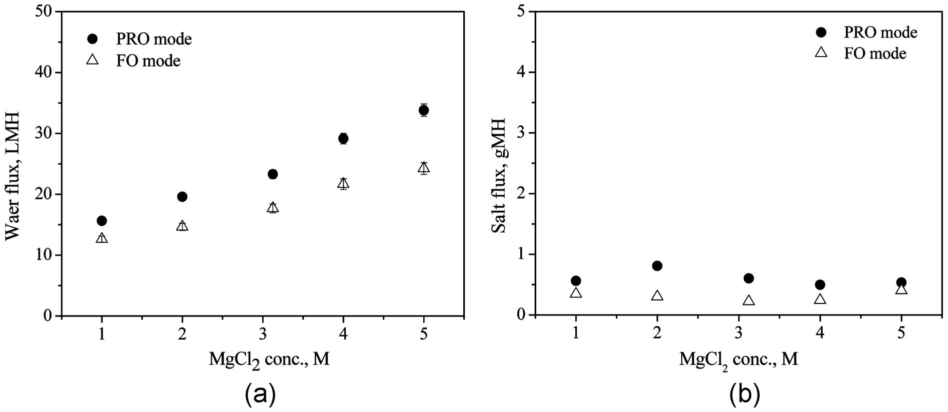


Fig. 16 Effect of $MgCl_2$ draw solution concentration on: (a) water flux, (b) salt leakage for dual-layer PBI/PES fibers (reproduced with permission from Environ. Sci. Technol., 43, 2800 (American Chemical Society) Yang *et al*. 2009)

increased substructure resistance; as a result, it had the lowest flux. In view of that, the 2-h modified PBI NF membrane with high permeation flux and improved salt selectivity may be useful for water recovery whereas the 9-h modified PBI NF membrane has high potential to be used for seawater desalination.

3.2 Dual-layer PBI hollow fiber membranes (Generation #3)

The water permeation flux of the aforementioned PBI NF single-layer hollow fiber membrane may not be satisfactorily high. This is due to the fact that the resultant single-layer membranes possesses a thicker dense PBI selective layer and tighter substructure. Consequently, the third generation PBI NF hollow fiber membrane utilized the state-of-the-art dual-layer membrane fabrication via co-extrusion technology to create an ultra-thin selective layer (Yang *et al*. 2009a, 2010). The outstanding PBI material was still selected as the outer selective layer, while polyethersulfone (PES) was chosen as the inner supporting layer because of its tendency to form porous and open cell structure with good mechanical properties. The addition of polyvinylpyrrolidone (PVP) was needed to modify the hydrophobic nature of PES (Lafreniere *et al*. 1987).

Fig. 15 shows the morphology of dual-layer PBI/PES hollow fiber membranes consisting of a PBI ultra-thin selective dense skin (around 1.5 μm after deducing the thickness of the macrovoid structure),

Table 4 Comparison of membranes used in FO process

T (°C)	Membranes	Draw solution (osmotic pressure, atm)	Flow rate	Flux (LMH)	Ref.
Commercial membranes					
20	Polyamide RO membrane with the fabric layer removed, Dow Filmtec	1.5M NaCl (73.2)	0.21m/s	8.1	McCutcheon and Elimelech (2008)
20	Cellulosic RO membrane with the fabric layer removed, GE Osmonics	1.5M NaCl (73.2)	0.21m/s	36.0	
20	FO flat sheet membrane, HTI.	1.5M NaCl (73.2)	0.21m/s	43.2	
20±2	FO flat sheet membrane, HTI.	0.5M NaCl (22.6)	5.5 l/min	8.5	Cornelissen *et al*. (2008)
22.5	FO flat sheet membrane, HTI.	0.5M NaCl (22.6)	0.3 m/s	18.6	Gray *et al*. (2006)
25	Permasep B-19 hollow fiber, DuPont	Net driving force @ 37atm	-	2.8	Mehta and Loeb (1978)
Single-layer hollow fibers (our works)					
22.5	PBI (A)	5M $MgCl_2$ (1148)	0.56 cm/s	11.2	Wang *et al*. (2007)
23	PBI (B) (original)	5M $MgCl_2$ (1148)	0.08 m/s	36.5	Wang *et al*. (2009b, 2009c)
23	PBI (B) (2-h cross-linking)	5M $MgCl_2$ (1148)	0.08 m/s	32.4	Wang *et al*. (2009b, 2009c)
Dual-layer hollow fibers (our works)					
23	PBI-PES	5M $MgCl_2$ (1148)	6.73 cm/s	33.8	Yang *et al*. (2009a, 2010)
38.5	PBI-PES	5M $MgCl_2$ (1148)	0.73 cm/s	45.6	Yang *et al*. (2009a, 2010)

Note: Operational mode: PRO; Feed: DI water a PES microporous sponge-like supporting structure and a delamination-free interface. Moreover, there is no much transport resistance because there are fully porous (1) inner-layer inner-surface (IL-IS), (2) inner-layer outer-surface (IL-OS), (3) outer-layer inner-surface (OL-IS) as well as (4) plenty of macrovoids directly and openly connected to the underneath of the PBI selective layer. As a consequence, water can rapidly diffuse across the ultrathin selective layer by the osmotic pressure gradient. In addition, with its sharp pore size distribution, the dual-layer hollow fiber can achieve a water flux as high as 33.8 LMH without elevated operation temperatures and a salt flux less than 1.0 gMH (PRO mode, 5M $MgCl_2$), as shown in Fig. 16. The properties of single- and dual-layer PBI NF hollow fiber membranes are summarized in Table 2.

3.3 Comparison of membranes used in FO process

A comparison between membranes used in the FO process is summarized in Table 3. As compared with commercial membranes, the PBI hollow fiber membranes achieve comparable or higher water flux. The FO membrane designed by Hydration Technologies Inc. has a much higher water flux while the commercial hollow fiber membrane (Permasep B-10 hollow fiber from DuPont) showed a lower water flux in FO process. This clearly suggests that the desirable hollow fiber membranes for FO need special innovative designs on the membrane structure that is different from the traditional RO membranes. However, the internal concentration polarization within the fiber porous support layer must be minimized.

4. Conclusions

Water is vital for life and all life-forms are dependent on water for survival. Woefully, the clean water supply in many counties is a pressing issue as the demands go beyond the supply at alarming proportion. Therefore, tremendous effort has been put forth to solve this intricate issue for a sensible water future. Up to now, RO and MSF are the most preponderant processes for desalination (>80% of desalination capacity), but their energy requirements are heavily associated with the oil price. With oil depletions in the foreseeable future and highly fluctuated oil price, there is an imperative need to identify new solutions for economically viable desalination processes. In this respect, FO and MD have received immense attention from both industries and academia as emerging and feasible approaches to produce clean, reliable and renewable water.

We have summarized the recent research activities at National University of Singapore aiming at the development of high-performance hollow fiber membranes for MD and FO. It is expected that by molecularly designing single- and dual-layer membranes with unique morphology and materials, one should be able to further reduce the selective layer thickness, control the pore size and pore size distribution, manipulate surface and bulk porosities, reduce the support layer thickness and optimize hydrodynamic flow conditions. As a result, the permeation water flux and salt rejection can be further enhanced. Future research directions in MD include (1) the integration of MD driven by renewable and waste energies, (2) ways to enhance energy efficiency and flux, and (3) lconducting long-term performance tests and methods to minimize fouling, while in FO comprise (1) developing novel membranes with minimized concentration polarization, (2) identifying new draw solutions and recovery methods to bring these technologies closer to industrialization, and (3) the study of fouling and anti-fouling. Also, hybrid technologies of FO/RO, FO/MD, MD/RO and etc. could be potential solutions to synergistically combine the strengths of each individual technology because as generally there is no single best method for fresh water production.

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Nomenclatures

FO = forward osmosis
IL = inner layer
IS = inner surface
MD = membrane distillation
MWCO = molecular weight cut-off, Da
OL = outer layer
OS = outer surface
PRO = pressure retarded osmosis
PWP = pure water permeability, $\mathrm{l\ m^{-2}\ h^{-1}\ bar^{-1}}$
EE = thermal efficiency
C = salt concentration
β = separation faction
ξ = conductivities
r_p = mean pore size, nm
$\Delta\pi$ = difference of effective osmotic pressure (Pa)
J_v = water permeation flux, $\mathrm{kg\ m^{-2}\ h^{-1}}$
r = radial coordinate (m)
R = fiber radius (m)
T = temperature (°C)
Z= axial coordinate (m)

Subscripts

f = feed
i = inner
o = outer
m = membrane
p = permeate

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