EFFECT OF MEMBRANE STRUCTURE ON THE PERFORMANCE OF NANOFILTRATION HOLLOW FIBER MEMBRANE USED IN FORWARD OSMOSIS

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Introduction

Along with the global water scarcity, less and less access to clean water has become a world-wide issue afflicting people, especially in the developing and industrialized nations. More and more effort has been put into evaluating the potential techniques to recover fresh water from wastewater and sea water/brine desalination with low capital costs. Even though the reverse osmosis (RO) process has replaced conventional thermal distillation processes as the dominant desalination technology after 40 year development, the high oil prices have shadowed its future potential because high hydraulic pressures must be provided in the RO process to overcome the osmotic pressure of feed solutions. In addition, the low water recovery by RO is another disadvantage during sea water desalination. Membrane separation technology, important for non-thermal separation, has been becoming more attractive to avoid thermodynamically imposed efficiency limitations on heat utilization. Recently, forward osmosis (FO) has drawn much attention by researchers and its applications have been developed in various fields, such as wastewater treatment [1], pharmaceutical and juice concentration [2-4], desalinating seawater [5, 6], even in the power generation [7-9] and the potable water reuse in space [10, 11]. Forward osmosis process, which is a natural process, utilizes the osmotic pressure gradient generated by a highly concentrated solution (draw solution) to allow water to diffuse through a semi-permeable membrane from a saline feedwater, which has a relatively low concentration. By employing the osmotic pressure as a driving force, forward osmosis can operate without high hydraulic pressures which are necessary in the reverse osmosis process. Therefore, less energy is required for the FO process compared to the RO process. In addition, FO may offer the advantages of high rejection of a wide range of contaminants and lower membrane-fouling propensities than traditional pressure-driven membrane processes. Because the osmotic forces from draw solutions in FO are greater than the trans-membrane pressures used in RO, potentially higher water productivity and recoveries may be achievable.

Membrane, as the barrier between the draw solution and the feed solution to transport water and reject solute, play an important role on the realization of forward osmosis. However, most available membranes used in the forward osmosis are either from dense semi-permeable membranes available in the reverse osmosis industry or cellulose triacetate based FO membrane developed by Hydration Technologies Inc. (Albany, OR) through coating cellulose triacetate on the non-woven fabric [5]. In addition, almost all FO studies were mainly based on the flat membrane configuration. As compared to flat sheet membrane, hollow fiber membranes have been widely used for liquid phase separation due to their high surface area to volume ratio and ability to self-support. Because nanofiltration (NF) membranes have much higher rejections to di-valent ions but partially permit the mono-valent ions get through due to the Donnan electrostatic exclusion, they can be employed to fractionate electrolyte

mixtures [12]. Nanofiltration membranes have been widely used for the separation of small neutral and charged molecules in aqueous solutions through their active charged nano-scale pores, with the estimated pore sizes of around 0.5 ~ 2 nm in diameter. As a pressure-driven process, nanofiltration has become an effective means for the removal of heavy metals ions and divalent anions from wastewater [13]. It is possible to develop NF membrane with applicable nano-scale pore size and narrow pore size distribution in the forward osmosis to obtain desirable permeation flux and high separation performance [14].

Polybenzimidazole is a generic name of a class of heterocyclic polymers, and the most commonly concerned is the poly-2, 2′ - (m-phenylene)-5, 5′ -bibenzimidazole (PBI). PBI are a class of heterocyclic polymers that were commercially developed by the Celanese Corporation in 1983 [15, 16], In addition to higher moisture affinity and high glass transition temperature (Tg, 425 ~ 435°C), PBI was known to possess outstanding thermal, physical and chemical stability over a wide range of pH. Since hollow fiber configuration has the advantage of self-support and provides a higher ratio of membrane area over unit module volume [17], fabricating PBI NF hollow fiber membranes may have greater potential in the water recovery with high productivity. Moreover, the relatively low cost of fabricating the hollow fibers make it of interest for large-scale industrial applications.

In this study, hydrophilic polybenzimidazole hollow fiber membranes through dry-jet wet phase inversion and its modified patterns were fabricated with different structures, for instances, wall thickness, microstructure and pore size in order to investigate the effects of membrane morphology on the membrane performance during FO process. It has been acknowledged that the support layer structure have the important effect on the water transport due to the serious internal concentration polarization in the porous support layer.

Experimental

The first batch PBI hollow fiber (A) was produced from the polymer dope of PBI/DMAc/LiCl (22.6/75.6/1.8 wt%). The selective layer was formed on the shell side of hollow fiber. After immersing in tap water for three days in order to remove the residual DMAc and LiCl, the fabricated hollow fiber membranes were soaked in a 50 wt% glycerol aqueous solution for 48 hrs and then air-dried at room temperature. SEM images illustrate the hollow fiber structure which consists of four types of morphologies, namely: asymmetric outer selective skin layer, finger-like macrovoids, sponge-like substructure, and porous inner skin layer. The outer and inner diameters of fiber are 273 and 137 microns, respectively. During PBI hollow fiber spinning, water is applied as the external coagulant to form the nano-porous outer selective layer. The formed sponge-like substructure near inner skin is due to the delayed phase separation induced by the solvent enriched bore fluid of DMAc/ethylene glycol mixture. This kind of microstructure makes PBI hollow fiber mechanically strong to sustain high trans-membrane pressure during nanofiltration except that the substructure may produce internal concentration polarization and seriously influence the water recovery during forward osmosis. The second batch PBI hollow fiber (A) was produced from the polymer dope of PBI/DMAc/LiCl (22.0/76.3/1.7 wt%). The as-spun PBI hollow fiber (B) was dipped in fresh methanol for three times to replace water. Then, the membrane was dipped in the solution of substituting agent *p*-Xylylene dichloride (1.0 wt%) in ethanol for 2.0 and 9.0 hours. After taking out of *p*-Xylylene dichloride solution, the modified PBI membrane was rinsed by ethanol again, and then kept in water [18]. The solute transport experiments were conducted to characterize the pore size distribution. 200 ppm solutions

containing glycerol, glucose, saccharose or raffinose with known Stokes radius r_s were used to measure the solute rejection.

Membrane characterization

SEM images illustrate the hollow fiber structure which consists of four types of morphologies, namely: asymmetric outer selective skin layer, finger-like macrovoids, sponge-like substructure, and porous inner skin layer, as shown in Fig. 1. The outer and inner diameters of fiber are 273 and 137 microns, respectively. During PBI hollow fiber spinning, water is applied as the external coagulant to form the nano-porous outer selective layer. The formed sponge-like substructure near inner skin is due to the delayed phase separation induced by the solvent enriched bore fluid of DMAc/ethylene glycol mixture. This kind of microstructure makes PBI hollow fiber mechanically strong to sustain high trans-membrane pressure during nanofiltration except that the substructure may produce internal concentration polarization and seriously influence the water recovery during forward osmosis. The pure water permeability is 0.5 liter m^{-2} bar^{-1} hr^{-1} measured at 10 bar. From the solute transport method [19], the mean effective pore radius of PBI NF hollow fiber membrane was 0.32 nm.

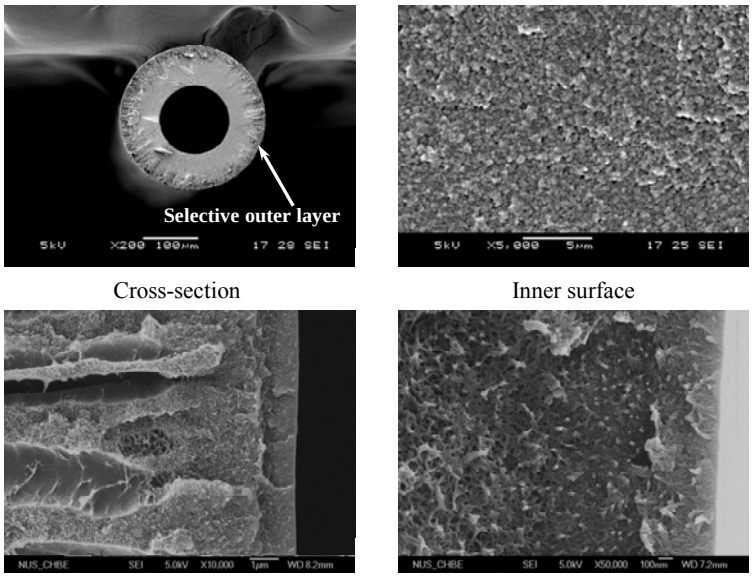

Figure 1 Morphology of PBI hollow fiber A

The PBI hollow fiber B from second batch has the same structure as the PBI fiber A, as shown in Fig. 2. The wall thickness was designed to be thin as 40 μm to reduce the mass transport resistance. The outer and inner diameters of the formed fiber B are 293 and 213 microns, respectively. Following table 1 lists the pure water permeability, mean pore size and MWCO of the polybenzimidazole membrane as a function of modifying period in the *p*-Xylylene dichloride/ethanol solution. After the p-xylylene dichloride modification, the PBI membrane has a decreased mean pore size and a narrowed pore size distribution which lead to an enhanced selectivity for the separation of solutes, as shown in Fig. 3. This suggests that the membrane structure and subsequent separation performance can be effectively controlled through the chemical modification.

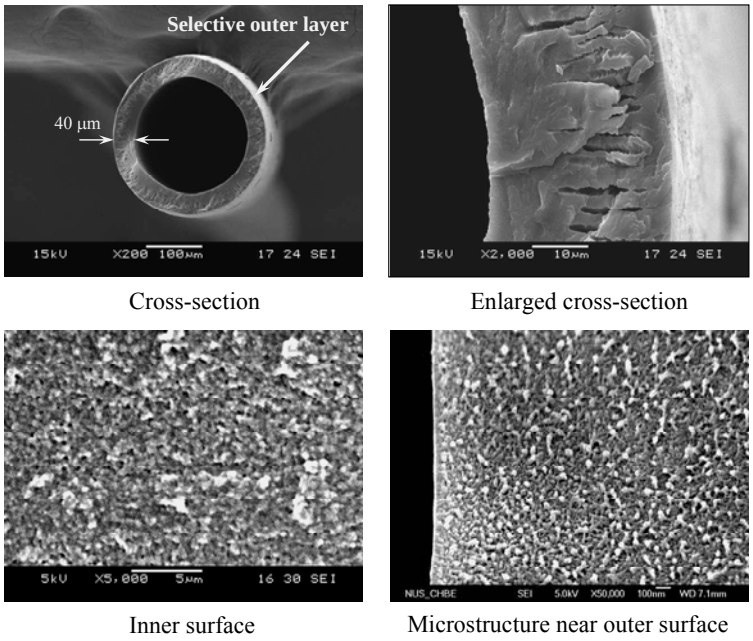

Figure 2 Morphology of PBI hollow fiber B

Table 1 properties of PBI fiber B vs. *p*-xylylene dichlororide modification

PBI NF hollow fiber membrane (B)	PWP ($l\ m^{-2}\ bar^{-1}\ hr^{-1}$)	r_p (nm)	MWCO (Da)
Original membrane	2.43	0.41	993
Modified membrane (2 hour)	1.53	0.34	528
Modified membrane (9 hour)	1.25	0.29	354

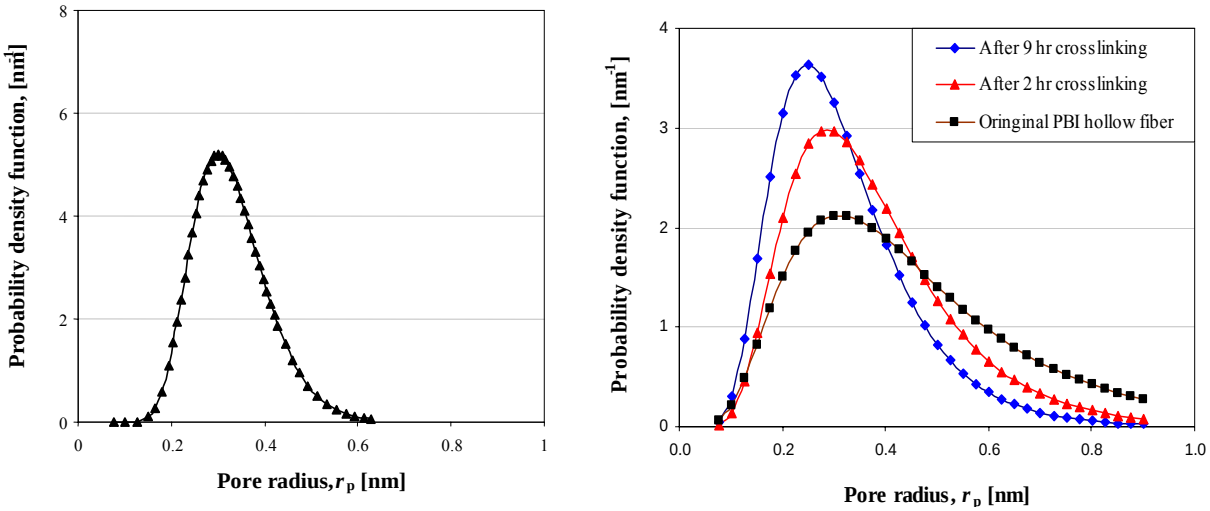

Figure 3. Pore size distribution probability density of the PBI hollow fiber A (left) and B (right)

Forward osmosis based on the PBI NF membrane

Forward osmosis experiments were conducted on a lab-scale circulating filtration unit, as shown in Fig. 4. In addition, membrane orientations have an obvious influence on the water permeation flux resulting from effects of membrane structure and concentration polarization; namely, the pressure retarded osmosis (PRO) mode for when the draw solution flows against the selective layer, and the forward osmosis (FO) mode for when the draw solution flows against the porous support layer. When draw solution flows against the outer selective layer of the hollow fiber (PRO mode), the water permeation is much higher than the other way that draw solution flows against the inner porous support layer of the hollow fiber (FO mode) when two streams are under laminar flow. This is attributed to the lack of internal concentration polarization when DI water flows against the inner porous layer in PRO mode. On the other hand, when draw solution flows against the porous support layer, the dilutive internal concentration polarization due to the porous support structure of asymmetric membrane seriously decreases the net driving force. This leads to the reduced water permeation flux although there is no external concentration polarization because the feed is the DI water in FO mode.

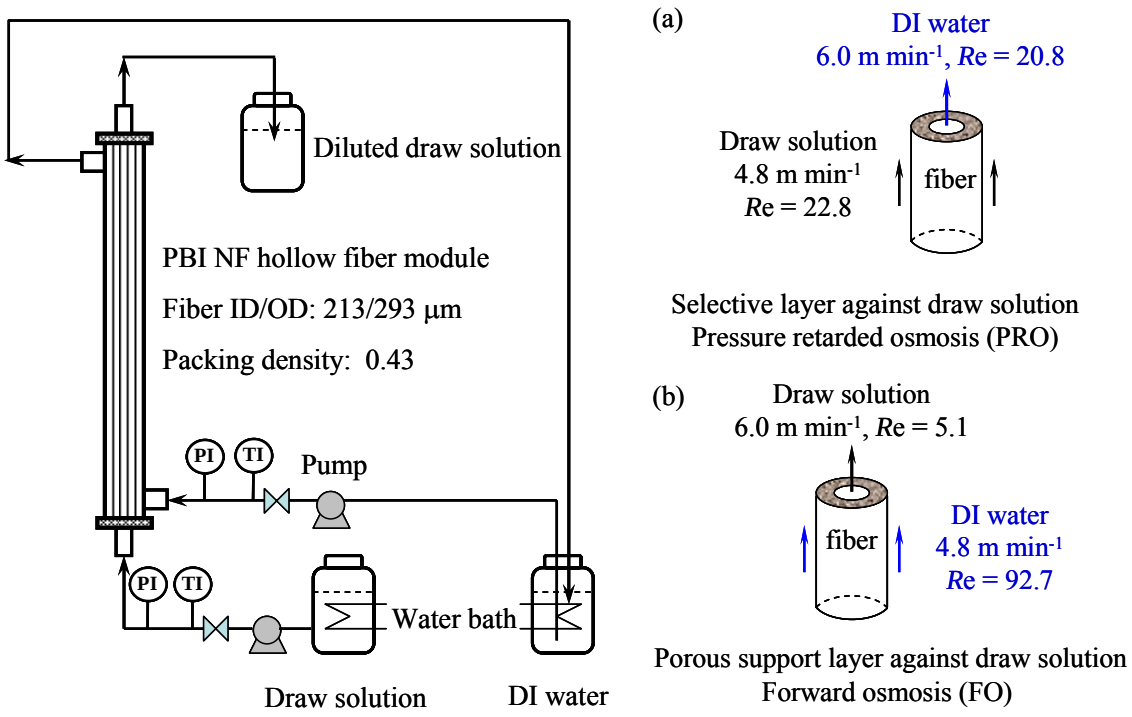

Figure 4. Schematic of forward osmosis set-up and membrane orientations

The dependence of water permeation flux on draw solution concentration for two different membrane orientations inside the membrane module is plotted in Fig. 5 and 6. The water transport through the PBI membrane goes up with an increase in draw solution concentration. The draw solution concentration dominates the membrane performance because the osmotic pressure is the driving force in the forward osmosis process.

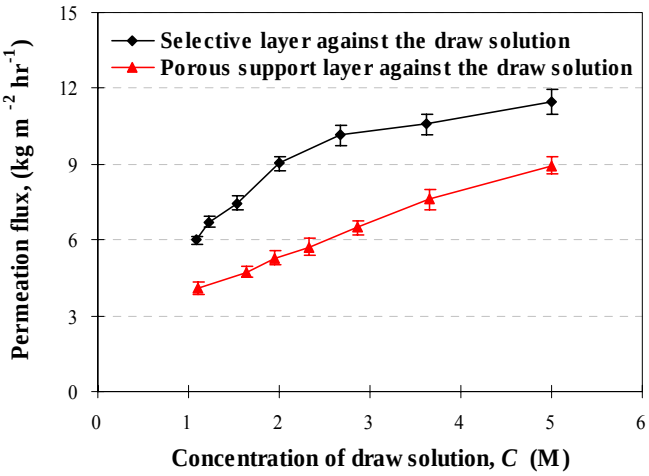

Figure 5 Effect of $MgCl_2$ draw solution concentration on the water flux (fiber A)

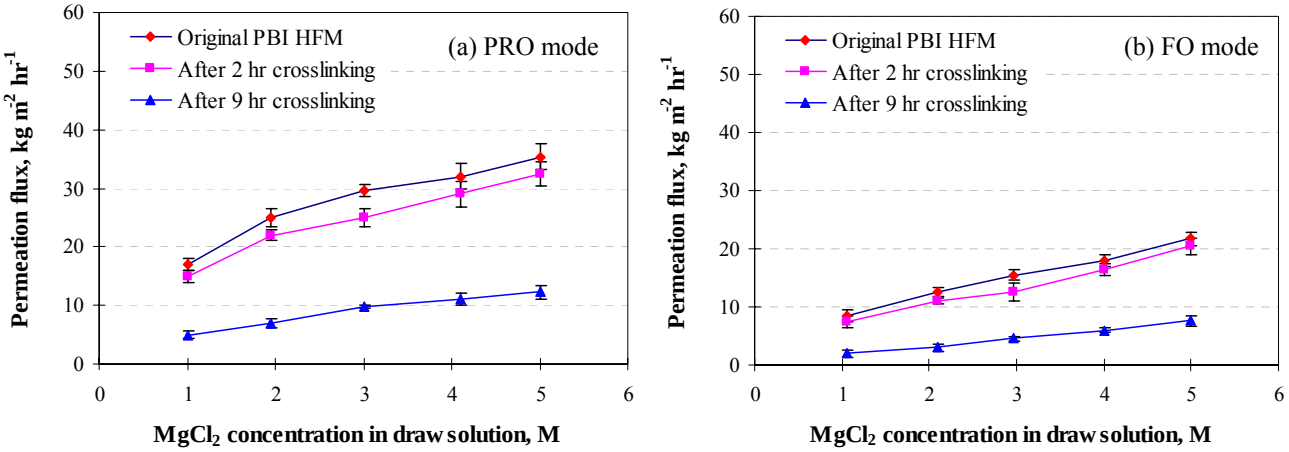

Figure 6 Effect of $MgCl_2$ draw solution concentration on the water flux (fiber B)

Compared to PBI fiber A, the flux of the newly developed PBI NF membranes B is almost double because of the thin wall effect. Flux slightly decreases for the 2-hr chemical modification sample even though its reject rates for ions improve significantly. The 9-hr chemical modification may not only narrow the pore size but also increase substructure resistance; as a result, it has the lowest flux.

Conclusions

This study has demonstrated that through *p*-xylylene dichloride modification the asymmetric PBI nanofiltration hollow fiber membranes can adjust the mean effective pore size to a level which can be used for forward osmosis. The 2-hr modified PBI nanofiltration membrane with high permeation flux and improved salt selectivity may be used for water recovery from wastewater whereas a longer cross-linking time may make the PBI membrane applicable for the seawater desalination. The PBI NF hollow fiber designed with a thin wall has an improved water permeation flux because of reduced transport resistance. Compared with the PBI fiber with thick wall, the water permeation flux is greatly increased. The internal concentration polarization has a serious influence on the water permeation flux

when the draw solution flows against the membrane porous support layer. As a result, the pore size, membrane structure, draw solution concentration, membrane orientation and operating conditions will influence the water transport flux and salt back-diffusion through the membrane. Future studies will further optimize the nanofiltration hollow fiber structure to decrease the internal concentration polarization and investigate their performance in the seawater desalination.

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