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**Module scale-up and performance evaluation of thin film composite hollow fiber
membranes for pressure retarded osmosis**

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Abstract

Pressure retarded osmosis (PRO) demonstrates great potential in energy harvesting when combining with seawater reverse osmosis. However, the lack of suitable membrane modules and the issue caused by the membrane fouling greatly impede the practical application of PRO to a larger scale. In this study, two-inch thin film composite hollow fiber modules were fabricated by using in-house developed PRO membranes. 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 performance tests were also carried out using the developed two-inch modules 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 improving the module design in the further endeavor.

Keywords: pressure retarded osmosis; pilot scale PRO; PRO membrane fouling; external concentration polarization; two-inch module design

Highlights:

- Development of PRO hollow fiber modules from lab to pilot scales was demonstrated.
- External concentration polarization is a crucial factor for module scale-up.
- Several module designs were made to improve PRO performances and stability.
- A power density of 9 W/m^2 was obtained using pretreated wastewater retentate as feed solution in a pilot PRO setup.

1. Introduction

Over the last century, the soaring world's population and global economy have intensified the ever-increasing demand for freshwater [1, 2], promoting fast growth in desalination technologies such as seawater reverse osmosis (SWRO) [3]. However, large energy consumption in the process is a key concern for sustainable deployment of SWRO plants [4]. Pressure retarded osmosis (PRO), a process where energy could be harvested when water permeates through a semipermeable membrane from a low salinity stream to a pressurized high salinity stream, was proposed in 1970s and now is widely recognized as a potential effective energy reduction measure when combined with SWRO process [5].

Many attempts have been made to demonstrate PRO potential for energy reduction in hybrid configurations [6-9]. Altaee et al. reported that up to 31% of energy cost could be saved through SWRO-PRO process based on their simulation results [10]. Four different SWRO-PRO hybrid systems were discussed by Kim et al. with respect to energy/water consumption [7]. 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 [11]. Though PRO shows fast advancement recently [6, 10, 12-17], the lack of suitable membrane modules [18] and the issue caused by the membrane fouling [8, 19, 20] greatly impede practical application of PRO to a larger scale.

The production of hollow fiber (HF) modules is well developed in industry in terms of fiber packing [21, 22], module potting [23, 24], and tubesheets supporting [25]. Nevertheless, fabricating suitable HF modules for PRO remains challenging due to the unique requirement raised from its process. Ren et al. tried to fabricate a PRO module based on the commercial

HF ultrafiltration (UF) modules from Koch Membrane Systems Inc. [26]. A polyamide layer was synthesised by interfacial polymerization in the lumen. A flux of $17.5 \text{ L/m}^2 \text{ h}$ was obtained in the active layer facing draw solution (AL-DS) mode with a salt flux of $5.52 \text{ g/m}^2 \text{ h}$. This work demonstrated the possibility of fabricating an active layer on a UF module with 300 fibers. Wan et al. had also successfully fabricated a PRO module with 300 fibers from in-house made hollow fibers [27]. 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 defect 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 test. 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) [28]. The lack of suitable PRO modules greatly hinders the development of the PRO process. This calls for more research efforts in engineering PRO module that can support larger-scale operation of PRO process. A systematic development of PRO module in a large scale is necessary to facilitate the practical applications of PRO process.

In Singapore where water resources are limited, the utilization of wastewater retentate from water reclamation process as feed in PRO was proposed to save river water or surface water that are more precious [29]. However, fouling with the wastewater retentate was found to severely reduce the water flux in PRO [29-31]. Since the wastewater retentate is a pressurized stream ($>5 \text{ bar}$), low-pressure nanofiltration (NF) seems to be a cost-effective strategy to mitigate the fouling in PRO via pre-treating the wastewater retentate. However, this idea has not been tested in a pilot scale yet.

This work aims to develop PRO hollow fiber modules from lab scale to pilot scale with the considerations of the impacts of ECP and the variation of the selective layer properties caused by module scale-up. The developed pilot-scale modules were also tested using actual wastewater retentate 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.

2. Materials and methods

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 [32]. 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 [33, 34]. 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 Fig. 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 a 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, interfacial polymerization (IP) was carried out in the lumen of the substrates to produce a polyamide selective layer. The produced module was soaked in an *m*-phenylenediamine (MPD, CAS# 108-45-2, Sigma-Aldrich) solution and then purged with cyclohexane (CAS# 110-82-7, Merck Chemicals, Singapore) to remove excessive MPD solution on the surface of the membrane. 1,3,5-Benzenetricarbonyl trichloride (TMC, CAS# 4422-95-1, Sigma-Aldrich) solution was then pumped through the lumen to form a thin polyamide layer on the membrane surface. 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.

Fig. 1 Schematic drawing of fabrication procedure of modules with (a) 150 fibers and (b) 500 fibers and above

2.2. PRO module performance

A typical RO filtration setup similar to that in the study of Wang et al. [35] was used to determine the water permeability and salt rejection of the PRO modules. DI water was circulated in the lumen of the fibers at 2 bar for pure water permeability (PWP) measurement. Rejection of these modules was tested using a 500 ppm NaCl solution at 2 bar. 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.

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 [34, 36, 37]. A commonly used industrial practice shown in Fig. 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.

Fig. 2. Schematic drawing of industrial practice of defect detection and repairing of HF modules

2.4. Pretreatment of PRO feed solution

In this study, one of the feed solutions used for PRO testing is the wastewater retentate from a local wastewater treatment plant that produces NEWater. As fouling and scaling are the major issues affecting the PRO performance [30], low pressure pretreatment was adopted to improve the feed water quality for PRO. A commercial NF membrane (NF-4, Axion Water Technologies, USA) operated at 5 bar was used to pretreat the wastewater retentate or NEWater brine (NB).

2.5. PRO performance in lab scale and pilot scale

A typical lab-scale PRO setup described in our previous study [32] 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 AL-DS orientation. 1 M sodium chloride (NaCl, CAS# 7647-14-5, Merck Chemicals, Singapore) solution was used as the draw solution, while either 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. A 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.

A pilot-scale setup, as shown in Fig. 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. 1 M 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 1 M 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.

Fig. 3. (a) 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

2.6. ECP evaluation using water flux prediction model

It is well-known that water flux in PRO process is highly affected by the ICP and the ECP. A schematic diagram to illustrate the effects of the ICP and the ECP is shown in **Error! Reference source not found.** 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 following water flux prediction model for PRO accounting the ICP and the ECP effects was used [38] :

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

where J_w is the water flux across the membrane, A is the intrinsic PWP of the membrane, B is the intrinsic solute permeability of the membrane, $\pi_{D,b}$ and $\pi_{F,b}$ are the osmotic pressures in the bulk of draw and feed solutions, respectively, ΔP is the transmembrane hydrostatic pressure, S is the structural parameter of the membrane substrate, D_F is the solute diffusion coefficient in the feed side, k_D and k_F are the mass transfer coefficient in the draw and feed sides, respectively. 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 (1) 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. Therefore, the concentration change effect was not considered in this work for simplicity.

Fig. 4. Schematic drawing of the effects of ICP and ECP in PRO. The green line indicates the ECP effect, the red line indicates the ICP effect and the yellow line indicates the effective osmotic pressure difference across the membrane, which is the difference between $\pi_{D,m}$ (osmotic pressure of the draw solution at the active layer surface) and $\pi_{R,S}$ (the osmotic pressure at the boundary of the rejection layer and support layer). $\pi_{F,m}$ is the osmotic pressure of the feed solution at the interface between the membrane substrate and the feed solution.

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 [38]. (1) could thus be simplified below when excluding ECP effect:

$$J_w = A \left\{ \frac{\pi_{D,b} - \pi_{F,b} \exp\left[J_w \left(\frac{S}{D_F}\right)\right]}{1 + \frac{B}{J_w} \left\{ \exp\left[J_w \left(\frac{S}{D_F}\right)\right] - 1 \right\}} - \Delta P \right\} \quad (2)$$

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 module were determined by independent RO experiments as described in Section 2.2. The S value was obtained by substituting the experimentally determined water flux of 15-fiber module into (1). 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. The mass transfer coefficient in both sides of membrane can be determined by $k = (Sh \times D)/d_h$, where d_h is the hydraulic diameter at the lumen or shell sides of the membrane, and Sh is the Sherwood numbers which are determined from the following correlations [39]:

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

$$Sh_s = 1.25 Sc^{1/3} \left(Re \frac{d_h}{L}\right)^{0.93} \quad (4)$$

where Sh_l and Sh_s are the Sherwood numbers at the lumen and shell sides, respectively; L is the module length; Sc and Re are the Schmidt and Reynolds numbers, respectively.

In order to quantify the extent of the ECP effect, the ECP modulus, defined as the ratio of osmotic pressure on the membrane surface to that in the bulk solution, can be expressed by the following equations:

$$\frac{\pi_{D,m}}{\pi_{D,b}} = \exp\left(-\frac{J_w}{k_D}\right) \quad (5)$$

$$\frac{\pi_{F,m}}{\pi_{F,b}} = \exp\left(\frac{J_w}{k_F}\right) \quad (6)$$

In an ideal case of no ECP effect, the ECP modulus is equal to 1. In reality, a dilutive ECP is expected at the draw solution side and thus $\pi_{D,m}/\pi_{D,b}$ will show a value of smaller than 1. In contrast, $\pi_{F,m}/\pi_{F,b}$ will be greater than 1 since the feed side experiences concentrative ECP.

3. Results and discussion

3.1. Performance evaluation of PRO modules using lab-scale setup

PRO modules with 15, 150, 500 and 1000 fibers were successfully fabricated with their filtration characteristics summarized in Table 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 Fig. 5.

Table 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 in feed solution (m/s)/ draw solution
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 ^c	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 bars; b. Tested using 500ppm NaCl solution at 2 bars; c. Smaller effective length due to wicking of glue

Fig. 5. 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.

Fig. 6 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 Fig. 6 (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/m² h 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 selective layer properties, which will be discussed in section 3.3, and (2) more severe ECP at the lumen and shell sides of the membranes (see the following section).

Fig. 6. PRO performances of HF modules with (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, tested with the lab-scale setup using DI water as feed and 1M NaCl solution as draw

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 [38]. The magnitude of the ECP is not easily measurable, but it can be

calculated from experimental data using (1). 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 [39]. Therefore, to validate the choice of Sherwood number correlation and the accuracy of the (1), 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 **Error! Reference source not found.**. 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 (2)) and ICP+ECP cases (calculated from (1)). 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 Fig. 7 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.

Fig. 7. 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 Fig. 8. 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 Fig. 8 (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 Fig. 8 (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. 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.

Fig. 8. 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)

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 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 [40]. 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 (1, 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 **Error! Reference source not found.**, 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.

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

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/m^2 using tap water as in Fig. 9 (a) from 11.1 W/m^2 using DI water (Fig. 6 (d)).

Fig. 9. PRO performances of HF modules with 1000 fibers in 2-inch 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

Considering the issues of flux reduction with larger scale PRO modules as discussed in previous section, effort should be made on mitigating ECP effect of the PRO modules. One possible way is to modify module design to improve uniformity of fiber distribution and thus the water flow distribution. The 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 initial flux was observed between the one-bundle (Fig. 9 (b)) and the four-bundle design (Fig. 9 (c)). It is worth noting that the 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 [41], 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 $20.3 \text{ L/m}^2 \text{ h}$ at 15 bar was observed with four-bundle design and produced a power density of 8.6 W/m^2 . In addition, the four-bundle design is preferable as it is beneficial for the identification of leaked fibers during defect detection.

Schematic diagrams of distribution baffle as another module design are shown in Fig. 10 (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 $20.3 \text{ L/m}^2 \text{ h}$ to $21.3 \text{ L/m}^2 \text{ h}$ 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 ECP.

Fig. 10. Schematic drawing of side view (top figures) and cross section view (bottom figures) of (a) distribution baffle 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 Fig. 10 (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 3.4.3.

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 (1, and the results are presented in Fig. 11. Fig. 11 (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 the water flux is mainly limited by the ECP at the feed side, which is in accordance to the ECP

modules as shown in Fig. 8. Fig. 11 (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.

Fig. 11. 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 Fig. 11 (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% [26]. 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.

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 **Error! Reference source not found.** 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 **Error! Reference source not found.** However, ECP mitigation strategies adopted in current study such as increasing cross flow velocity and modifying module design (as in **Error! Reference source not found.**) were not effective in enhancing water flux. A more effective way to improve the flow distribution in the shell channel is imperative to alleviate the ECP and compensate the significant flux drop (34%) in scaling up PRO modules.

Table 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	Draw (NaCl)	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	Lab-scale	-	70.1	49.8	20.8
150	0.75	0.18	0.034	DI	1M	Lab-scale	one bundle	46.8	37.2	11.6
500	2	0.4	0.251	DI	1M	Lab-scale	one bundle	43.1	32	13.3
1000	2	0.4	0.503	DI	1M	Lab-scale	one bundle	47	26.7	11.1
1000	2	0.4	0.503	Tap water	1M	Pilot-scale	one bundle	29.7	17.7	8.6
1000	2	0.4	0.503	Tap water	1M	Pilot-scale	four bundles	27.6	20.3	8.5
1000	2	0.4	0.503	Tap water	1M	Pilot-scale	Distribution baffle	28.2	21.3	8.9
1000	2	0.4	0.503	Tap water	1M	Pilot-scale	Distribution tube	31	N.A.	N.A.
2000	2	0.4	1.005	tap water	1M	Pilot-scale	Seven bundles	25.7	N.A.	N.A.

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 the 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 [27]. 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 Fig. 12, 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.

Fig. 12. Schematic drawing of PRO module 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 the production of even larger-scale module. This is also illustrated by the 2000-fiber modules fabricated in the current study (**Error! Reference source not found.**), where the module with FO flux of $\sim 25.7 \text{ L/m}^2 \text{ h}$ 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.

3.5. Exploration of 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/m^2 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 other PRO tests using

wastewater retentate as feed in the literature [29, 30], water flux drops significantly to 7-8 L/m² h 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 (126.7mg/L), silica (19.76 mg/L), etc. 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) [42]. As such, low-pressure NF pretreatment of the feed solution can be proposed to take advantage of the pressurized NB and to enhance the PRO performance. A commercial NF module with high rejection to multi-valent salts was selected for the pretreatment, and the characteristics of the NF module are tabulated in Table 3. The PRO performances of the HF modules with NF-treated NB are summarized in Fig. 13. A much higher PRO flux of larger than 20 L/m² h 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 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 retentate 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 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 NF	Spiral wound	5 bars	~2.5	~8.9	99.5%	93.7%

Note: a. Tested at 5 bar using NB as feed

Fig. 13. PRO performances of HF modules with 1000 fibers using tight NF-treated NEWater brine as feed and 1 M NaCl solution as draw

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.

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