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Mixed polyamide-based composite nanofiltration hollow fiber membranes with improved low-pressure water softening capability

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Abstract

Mixed polyamide-based composite nanofiltraiton (NF) hollow fiber membranes with suitable characteristics for water softening under ultrafiltration (UF)-range low operating pressure were successfully developed. The thin-film selective layer of the composite membrane was formed via interfacial polymerization on the inner surface of a microporous polyethersulfone (PES) hollow fiber substrate with trymesoyl chloride (TMC) being the organic phase monomer, and a mixture of branched polyethyleneimine (PEI) and piperazine (PIP) being the monomers in the aqueous phase.

In was found that there was a synergetic effect of PEI and PIP on the formation of the selective layer. The water permeability and salt rejection of the resultant membrane were both enhanced with a small amount of PIP added into the PEI aqueous phase, but dropped quickly with a higher PIP to PEI ratio. The optimized NF membrane possessed a molecular weight cut-off (MWCO) of 380 Da, an effective pore diameter of 1.27 nm, and pure water permeability (PWP) of 18.2 l/m^2 h bar. Under an operating pressure of 2 bar, the membrane exhibited rejection of 96.3% and 93.8% to 1000 ppm $MgCl_2$ and $MgSO_4$ feed solutions, respectively. The capability of the newly developed membrane for low-pressure water softening were evaluated by employing simulated hard water feed solutions with different ionic compositions and total hardness. By the combining effect of electrostatic repulsion and size exclusion, the mixed PEI/PIP-based composite hollow fiber offered superior water softening performance compared with the membranes made with PEI or PIP alone as the aqueous phase IP monomer.

Keywords: nanofiltration; mixed aqueous phase monomers; interfacial polymerization; composite hollow fiber membrane; water softening; low operating pressure.

1. Introduction

Water softening, a process to remove abundant calcium and magnesium cations as well as other water hardening minerals from raw water stream, is not only indispensable to the domestic and industrial water supply, but also important as a pre-treatment process for brackish water and seawater desalination to improve water recovery by minimizing membrane scaling [1]. Different from conventional water softening methods involving ion-exchange resin, zeolite or lime-soda ash treatments, water softening via membrane is a one-stage process that serves the role of hardness removal and the rejection of bacteria, virus, natural organic compounds and other undesirable chemical compounds simultaneously [2]. With the rapid development of nanofiltration (NF) technology in recent years, it becomes possible to selectively remove divalent cations from monovalent ions under an operating pressure much lower than typically applied pressure in reverse osmosis (RO). Thus membrane softening has great potential to supersede traditional water softening methods in terms of effectiveness and operating costs, especially for the effective removal of major hardness contributing ions from raw water with high salt concentration such as brackish water [3, 4], seawater [5, 6] and desalination concentrate [7].

Most commercial NF membranes with water softening capability such as NF series manufactured by Filmtec, Desal series by GE-Osmonics, and ESNA series by Hydranautics, are thin-film composite flat sheet membranes with an interfacially polymerized polyamide selective layer [8, 9]. The water softening performance of the composite NF membrane is mainly determined by the hydrophilicity, charge and structure of the thin-film active layer, which is basically controlled by the interfacial polymerization (IP) monomers that formed the layer. As a result, the effect of different IP monomers on the polymerization process and the

characteristics of the resulted thin film were thoroughly investigated in the past decade. Although piperazine (PIP) and trymesoyl chloride (TMC) were accepted as the most established monomer pair for commercial NF membrane fabrication, various types of amine [10-12], acyl chloride [13, 14], alcohol [15] and isocyanate [16] were also studied as the IP monomers to develop novel composite NF membranes with improved permeation flux and divalent ion rejection at lower operating pressure, better chemical tolerance and fouling resistance.

As an alternative to PIP and other monomeric amine monomers, polymeric amines such as polyethyleneimine (PEI) [17], polyamidoamine [18] and polyvinylamine [19] were used as the aqueous phase monomers for the thin film synthesis. Due to the excess amine groups in the polymer chain, polymeric amines usually yield polyamide thin-film active layer with a lower cross-linking degree. NF membranes with higher permeation flux could therefore be obtained, which are able to reduce the required operating pressure for water production and reduce energy consumption. Moreover, unlike conventional negatively charged polyamide thin film made from monomeric IP monomers, the excess amine groups also result in positively charged membrane surfaces. This unique feature makes the membrane more favorable for water softening applications, as divalent metal cations could be better rejected by the positively charged membrane through electrostatic interaction (Donnan exclusion) in addition to the normal steric (size exclusion) effect [20].

In our previous work [21], a type of positively charged NF membrane was prepared with suitable characteristics for water softening under ultrafiltration (UF)-range low operating pressure. The polyamide thin-film selective layer was formed through IP technique on the inner surface of a polyethersulfone (PES) UF hollow fiber membrane substrate with branched

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PEI and TMC employed as the monomers in aqueous and organic phases, respectively. As an extension of our previous work, the fabrication of mixed polyamide-based composite NF hollow fiber membranes were reported in current study. The resultant hollow fiber membrane was found to exhibit improved low-pressure water softening performance comparing to NF hollow fibers prepared with PEI or PIP alone as the aqueous IP monomer in the IP process. The synergetic effect of PEI and PIP on the formation of the selective layer was investigated thoroughly.

2. Experimental

2.1 Membrane material and chemicals

The PES UF hollow fiber substrate was fabricated by the phase inversion method through a dry-jet wet spinning process, which has been reported elsewhere [22, 23]. The inner and outer diameters of the hollow fiber substrate are 1.01 and 1.37 mm, whereas the pure water permeability and molecular weight cut-off (MWCO) of the substrate fibers are around 270 l/m^2 h bar and 45 kDa, respectively.

Branched polyethyleneimine (PEI) with molecular weights of 50,000~100,000 (MP Biomedicals), piperazine (PIP, Merck), trimesoyl chloride (TMC, Sigma-Aldrich), sodium dodecyl sulfate (SDS, Reagents), and cyclohexane (Merck) were used for the synthesis of thin-film selective skin layer. A series of neutral solutes including glucose, sucrose, and raffinose, and different analytical grade salts including $MgCl_2$, $MgSO_4$, NaCl, Na_2SO_4 and $CaCl_2$ (Merck) were involved in the preparation of various single and mixed solute feed solutions with pH of around 6.5. Deionized water (Milli-Q, 18MΩcm) was employed for the aqueous solution preparation, and all chemicals were used as received.

2.2 Preparation of composite NF hollow fibers by interfacial polymerization

The detailed procedure for the preparation of interfacially polymerized composite NF hollow fiber membranes was reported in our previous work [21]. In the current study, an aqueous solution was prepared to contain a mixture of PEI and PIP with total amine concentration ranging from 0.05% to 1% (w/v) by varying their mixing ratio, and SDS (0.1% (w/v)) at a solution pH ranging from 9 to 12 adjusted by adding sodium hydroxide and hydrochloric acid. This solution was firstly brought into the lumen of the substrate fibers and in contact with the fiber inner surface for 30 min. After purging the excess aqueous amine solution with pure cyclohexane, a TMC organic solution (0.1% (w/v) in cyclohexane) was slowly pumped through the fiber lumen (30 ml/min) for 2 min to allow the IP reaction to take place. The fibers with an IP thin-film layer formed on the fiber inner surface were rinsed with and stored in DI water afterwards for further uses.

2.3 Hollow fiber characterization

The physiochemical properties of the composite NF hollow fiber membranes made from mixed PEI/PIP were examined thoroughly via a series of standard characterization techniques as described previously [21, 24], and compared with composite fibers made using PEI or PIP alone as the aqueous phase monomer. Briefly, the morphology of hollow fiber membranes was observed by a field emission scanning electron microscope (FESEM, JEOL, Japan), while the membrane surface topology and roughness were examined using an atomic force microscope (AFM, Park system, Korea) via the noncontact mode. Besides, the chemical composition of the thin-film selective layer was analyzed using a Fourier transform infrared spectrometer (FTIR, Shimadzu, Japan) via the attenuated total reflection (ATR) method, whereas membrane surface charge characteristics were measured by streaming potential

method using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria). Furthermore, the wettability of the membrane was determined by dynamic contact angle measurements using a tensiometer (Data Physics, Germany), and the fiber mechanical properties were characterized by the tensile strength test using a universal testing machine (Zwick, United Kingdom).

2.4 Nanofiltration experiments

The lab-scaled membrane module was made by potting 4 pieces of hollow fibers into a PTFE tube with an effective length of 18 cm. NF experiments were initiated by circulating DI water through the lumen of the membrane module under a trans-membrane pressure of 2 bar, while the permeate was collected from the shell of the module. After the membrane went through compaction with DI water for about 1 h, the membrane pure water permeability, PWP (l/m^2h bar), was measured under consistent operating pressure (2 bar) and calculated as follows:

$$PWP = \frac{F}{\Delta P} = \frac{Q}{A\Delta P} \qquad (1)$$

where F is the permeation flux (l/m^2 h), ΔP is the trans-membrane pressure (bar), Q is the volumetric permeation flow rate (l/h), and A is the effective membrane filtration area (m^2).

Afterwards, the newly developed composite NF hollow fiber membranes were further tested by applying various single solute feed solutions successively. Membrane pore size and molecular weight Cut-off (MWCO) were estimated by the rejection to neutral organic solutes, whereas membrane charge properties were characterized by inorganic salt feed solutions. Finally, the water softening performance of the membrane was evaluated via a series of simulated hard water feed solutions with a mixture of ionic species. All solute separation

experiments were conducted under the same low operating pressure (2 bar), and the solute

rejection, R (%), was calculated based on the following equation:

$$R = \frac{C_f - C_p}{C_f} \times 100\%$$ (2)

where C_f and C_p are the solute concentrations (ppm) in the feed and permeate solutions, respectively.

Total organic carbon measurements were conducted to determine the concentration of neutral organic solutes using a TOC analyzer (Shimadzu, Japan), while conductivity measurements were involved to find out the salt concentration in single salt solutions by a conductivity meter (Myron L Company, Canada). The concentrations of individual ions in the mixed salt solution were measured using an inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin Elmer, United States).

3. Results and discussion

3.1 Hollow fiber membrane characteristics

3.1.1 Morphological study

The cross-sectional and surface morphologies of the PES UF hollow fiber substrate are shown in Fig. 1, while the morphologies of composite membranes made with PEI only, PIP only and mixed PEI/PIP as the aqueous phase IP monomer are shown in Fig. 2. According to Fig. 1, the PES substrate fiber possesses a highly porous cross-sectional structure to minimize the resistance for water transport, and a relatively smooth and tight inner surface without observable cavities to support the formation of defect-free thin film [25]. From Fig. 2, the IP layer developed from PIP only has the greatest thickness (~200 nm) among the three types of

membranes, while the other two membranes possess IP layers with much thinner thickness (~100 nm). As a thicker layer leads to a higher mass transfer resistance, a thinner IP layer is generally preferable in achieving higher water permeation. As also presented in Fig. 3, which shows the surface topologies of the three types of composite membranes as well as the PES support fiber examined via AFM, the PEI only membrane possesses a smooth surface morphology, while the PIP only membrane has a much rougher surface. These phenomena should be associated with the nature of the polymerization reaction. According to our previous study [21], smaller aqueous phase monomers (PIP) may diffuse more easily into the organic phase and react more rapidly than macromolecular monomers (PEI), hence resulting in a rougher and thicker IP layer on the surface. In addition, the AFM analysis deduced that the surface roughness (R_a) of the mixed PEI/PIP membrane (22.4 nm) is in between of the smoother PEI only membrane (11.5 nm) and the rougher PIP only membrane (77.6 nm). Higher surface roughness is considered beneficial to enhance the water permeability of the membrane because it enlarges the effective surface area of the membrane [26].

3.1.2 FTIR analysis

The chemical compositions of the three types of composite membranes prepared were analyzed by comparing their respective FTIR spectra with the PES support fibers. From the spectra shown in Fig. 4, the characteristic peak of amide group was detected for all composite membranes (C=O stretch at around 1630 cm^{-1}), which confirmed the polymerization reaction between amine groups from PEI and/or PIP and acyl chloride groups from TMC. Among the three composite membranes, the amide peak for PIP only membrane was noted to have the highest intensity, which is consistent with the FESEM observation that the membrane possess the IP thin-film layer with the greatest thickness. Meanwhile, the characteristic peaks of unreacted amine groups (C-N stretch at around 1020 cm^{-1}) from PEI and/or PIP as well as

hydrolyzed acyl chloride groups (C-O stretch at around 1310 cm^{-1}) from TMC [27] were also spotted for all the composite membranes. Based on the FTIR analysis, the IP reaction scheme between mixed PEI/PIP and TMC as well as possible structure of the resultant mixed polyamide network are illustrated in Fig. 5.

3.1.3 *Zeta potential, contact angle and fiber tensile strength*

The surface charge characteristics of the NF hollow fiber membrane developed from mixed PEI/PIP were measured by streaming potential method, and its zeta potential at pH ranging from 3 to 11 is shown in Fig. 6 and compared with the zeta potential of PEI only, PIP only and PES support membranes, whereas the isoelectric point obtained for the four membranes are listed in Table 1. Compared with the PES substrate, the three composite membranes have isoelectric points shifted towards a larger pH, and exhibit cationic surface charge characters at pH below the isoelectric point. This is attributed to the protonation of unreacted amine groups brought from PEI and PIP immobilized on the polymerized thin film. Besides, when more PIP and less PEI were presented in the aqueous phase solution, the resultant IP layer became less positively charged in an acidic pH environment. The isoelectric point also went down from 7.4 for the PEI only membrane to 6.7 for the PEI/PIP membrane, and further down to 5.9 for the PIP only membrane. In comparison with the macromolecular PEI, the involvement of small PIP molecules could have increased the degree of polymerization so that the less portion of amine groups are left unreacted to provide the positive charge. Additionally, based on the isoelectric points of the three composite membranes, the PEI only and mixed PEI/PIP membrane surfaces were positively charged, while the PIP only membrane exhibited anionic surface charges within the feed solution pH range (~6.5) for this study.

Moreover, as indicated by the contact angle data listed in Table 1, the IP thin-film layer of the three composite hollow fiber membranes were highly hydrophilic compared to the PES support due to the abundant amine and carboxyl groups presented in the IP layer. And the contact angle of the IP layer was found to increase once a higher portion of PIP was involved during the thin film formation. This is in accordance with the zeta potential testing results that more PIP led to a higher degree of polymerization and less unreacted amine groups were on the IP layer to give rise to either the polarity or wettability of the membrane surface.

The mechanical properties of the composite membranes and PES support fibers are also summarized Table 1. It revealed that the IP layer increased the tensile strength of the hollow fiber, while the mixed PEI/PIP membrane possessed superior mechanical strength among the three composite fibers. However, the overall mechanical properties of the hollow fiber membrane were dominated by the PES substrate, as the enhancement from the thin-film layer is considered marginal (less than 20% increase in tensile modulus and yield stress).

3.2 Effect of amine solution composition on thin film formation

Since the separation performance of a composite NF membrane is dominated by the character of its IP thin-film layer, controlling the interfacial polymerization parameters plays a key role to achieve the optimal performance of the resultant composite hollow fibers. The influence of individual IP parameters for the single aqueous phase monomer system has been thoroughly investigated in our previous work [21], while the aqueous amine solution composition is crucial to the formation of mixed PEI/PIP-based IP thin film. Therefore, with other IP parameters remaining unchanged, the impacts of PEI/PIP mixing ratio, total amine concentration and amine solution pH were examined in sequence. It is worth mentioning that at least two independent experiments were carried out for each preparation condition to

3.2.1 Effect of PEI/PIP mixing ratio

When the total amine concentration was kept at 0.25% (w/v), the effect of PEI/PIP mixing ratio on the performance of resultant composite hollow fiber membrane is illustrated in Fig. 7. It can be seen that when the amount of PIP increased from 0% to 5% (w/w) of total amine, both PWP and $MgSO_4$ rejection of the membrane increased. According to the discussion in Section 3.1.1, the increased surface roughness could explain the improved water permeation with a small amount of PIP addition into the PEI aqueous phase solution, while the enhancement in solute rejection should be attributed to the higher cross-linking density brought by the incorporation of PIP into the PEI-TMC network as confirmed by the FTIR analysis in Section 3.1.2.

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

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amine monomers has been reported in several studies [28-30]. Afterwards, the quality of the IP layer was believed to be improved gradually.

3.2.2 Effect of total amine concentration

As illustrated in Fig. 8, when total amine concentration increased from 0.05% to 0.25% (w/v) while the PEI/PIP mixing ratio was kept at 95/5 (w/w), the $MgSO_4$ rejection of the resultant mixed PEI/PIP-based composite membrane increased from about 72% to over 93%. However, a 25% decline of water permeability was observed probably due to the fact that a higher monomer concentration leads to more intense IP reaction and results in a denser thin film structure [14, 31, 32]. A further increment of total amine concentration in the aqueous phase solution resulted in elevated PWP and reduction in salt rejection. This is in agreement with the trend observed for PEI only as the aqueous phase monomer in our previous study [21]. Since the macromolecular PEI was cross-linked by the TMC molecules during the polymerization reaction, a high PEI concentration gave a deficit in TMC, resulting in a thin-film layer with lower cross-linking density, higher water permeability and lower salt rejection as a consequence.

3.2.3 Effect of amine solution pH

When the pH of mixed PEI/PIP aqueous solution increased from 9 to 11.5, the resultant composite hollow fiber experienced a drop in water permeability but an enhancement in $MgSO_4$ rejection, as revealed in Fig. 9. By increasing the pH, the capability for the amine solution to neutralize the hydrochloric acid produced during the reaction between amine and acyl chloride was enhanced, so that the polymerization was promoted toward a higher extent and a tighter thin-film layer with lower permeation to both water and solutes was produced [19]. In addition, the drop in membrane rejection was observed with a jump in water

permeation when the amine solution pH was further increased to 12, which was owing to the hydrolysis of TMC acyl chloride under strong alkanine environment [14, 33].

Based on the results shown in Figs. 7 to 9, the PIP amount of 5% in total amine or the PEI/PIP mixing ratio of 95/5 (w/v) with 0.25% (w/v) total amine concentration at solution pH 11 yielded the mixed PEI/PIP-based membranes with the best combination of PWP and solute rejection. This batch of hollow fibers was utilized for subsequent characterization and separation performance evaluation, and compared with single aqueous phase monomer (PEI only or PIP only) membranes made using the identical conditions of amine concentration, solution pH and all other preparation parameters.

3.3 Separation properties of mixed PEI/PIP–based membrane

3.3.1   Neutral solute rejection

The rejection behavior of the newly developed composite hollow fiber membranes to neutral solutes was examined using 200 ppm single solute feed solutions containing glucose, sucrose or raffinose, respectively, under 2 bar operating pressure. The Stokes radii of the hree neutral solutes as well as their corresponding rejections are listed in Table 2. It can be seen that the PEI/PIP membrane possessed higher rejection to neutral solutes than the PEI only membrane. Since the rejection of NF membranes to neutral solutes is solely based on size exclusion, it suggests that the mixed PEI/PIP monomer yielded a tighter IP thin-film layer comparing to the situation where only PEI involved in the polymerization process.

The MWCO and pore size of the three composite membranes were determined based on the data listed in Table 2 and calculated according to the solute transport method described previously [21, 34, 35]. The MWCO of the PEI only, PEI/PIP and PIP only membranes were

found to be 530, 380 and 270 Da, while the effective pore diameter for the three membranes were around 1.34, 1.27 and 1.09 nm, respectively. All three membranes exhibited MWCO and pore size within the range of NF membranes [9]. It was also discovered from the above data that the PEI/PIP membrane had a small pore size than the PEI only membrane, whereas the PIP membrane possessed the tightest IP thin-film layer. Referring to the discussion regarding the FTIR spectra, the introduction of PIP into the PEI aqueous phase provided additional cross-linking to the original PEI-TMC network, and resulted in a denser pore structure. Likewise, the PIP only membrane exhibited the highest degree of polymerization as interpreted from the FTIR analysis, so its smallest MWCO and pore size were deemed plausible.

3.3.2   Separation of electrolyte solutions

A series of electrolyte feed solutions with 1000 ppm of $MgCl_2$, $MgSO_4$, NaCl or Na_2SO_4 as the single solute were employed for filtration under an operating pressure of 2 bar, and the respective rejections for the three membranes are illustrated in Fig. 10. As shown in the figure, the salt rejections for both PEI only and PEI/PIP membranes decreased in the order of $R(MgCl_2) > R(MgSO_4) > R(Na_2SO_4) > R(NaCl)$, while PIP membrane possessed salt rejections in the order of $R(Na_2SO_4) > R(MgSO_4) > R(MgCl_2) > R(NaCl)$. According to the Donnan exclusion principle, cationic membranes exhibit higher $MgCl_2$ rejection than Na_2SO_4, which is opposite to the rejection behavior of anionic membranes [20]. Therefore, the PEI only and PEI/PIP membranes were both positively charged, and the PIP only membrane possessed negative surface charges. The interpretation about the membrane surface charge character is in agreement with the zeta potential data of these membranes provided in Section 3.1.3. Moreover, the NaCl rejection was found to be lower than Na_2SO_4 for both PEI only and PEI/PIP membranes, and lower than $MgCl_2$ rejection for the PIP only membrane. The

above rejection behavior is opposing the Donnan exclusion principle, so that the effect of steric hindrance must have been involved during the NF separation. Briefly, the Na^+ and Cl^- ions are smaller in hydrated radii, and receive less hindrance by the membrane pores comparing to the larger Mg^{2+} and SO_4^{2-} ions in the aqueous feed solution [21]. Furthermore, for all three membranes, the $MgSO_4$ rejection appeared to be in between of $MgCl_2$ and Na_2SO_4 rejections. For cationic PEI only and PEI/PIP membranes, the positive electric field was greatly affected by SO_4^{2-}, the divalent counter-ion, and the Donnan effect was weakened. The $MgSO_4$ rejection was thus lowered comparing to the case of $MgCl_2$. The higher $MgSO_4$ rejection comparing to Na_2SO_4 is however attributed to the larger size of hydrated Mg^{2+}, the divalent co-ion [36]. For the PIP only membrane, similar rationale could explain the $MgSO_4$ rejection except that the co-ion and counter-ion switched, as the membrane is negatively charged. In summary, for all three currently developed membranes, both surface charge and pore size influenced the salt rejection behavior of the membrane, and neither the effect of Donnan exclusion nor steric hindrance could fully determine the rejection.

Meanwhile, by comparing the rejection data between PEI only and mixed PEI/PIP membranes, it was found that the addition of PIP resulted in improvement of rejection to all four salts, especially $MgSO_4$ and Na_2SO_4 rejections. As the introduction of PIP into the PEI-TMC network made the resultant IP thin film structure denser, the SO_4^{2-} ions could be better retained by the tightened membrane pores through size exclusion. It is therefore expected that the mixed PEI/PIP-based composite NF hollow fiber membrane could be more capable for water softening applications especially when abundant SO_4^{2-} or other divalent anions present in the hard water feed stream.

Pure water permeability and salt rejections of the three composite NF hollow fibers are compared in Table 3 and benchmarked with several NF membranes available in the commercial market. All the commercial membranes listed in Table 3 are flat-sheet membranes in the configuration of spiral wound modules, and are interfacially polymerized membranes designed for low-pressure operations, as claimed by the manufacturer [36-40]. According to the table, the mixed PEI/PIP-based membrane possesses the highest water permeability among the three currently developed membranes, and is superior to all the commercial NF membranes in terms of PWP. Its $MgCl_2$ rejection is also higher than most of the listed membranes except UTC20 membrane from Toray. However, it should be noted that the high rejections for UTC20 were achieved with 5 times higher operating pressure at 10 bar, and that all the other membranes operates under higher operating pressures than the current study does, even though lower than 10 bar pressure has already been commonly considered as low-pressure NF operation [9]. Regarding the water permeability, NF270 from Dow-Filmtec and TFC-SR2 from Koch, the two commercial NF membranes with higher water permeation, have similar PWP to the current PEI only membrane. However, their rejection behavior and zeta potential data revealed that the membranes are negatively charged at neutral pH [37], so that they might not be suitable for low-pressure water softening applications duo to the ineffectiveness in removing divalent cations. In fact, the rejection profile of the current PIP only membrane is comparable to most of the negatively charged commercial NF membranes.

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

Water softening performance of the NF membrane is greatly influenced by the quality of feed water with a variety of ionic species. Other than a single electrolyte feed solution, interactions

among different ion charges affect the solute transport through the membrane. The rejection of a typical hard water metal ion, i.e. the hardness removal efficiency of the membrane is affected by the presence of other co-ions, concentration and valence of the counter-ions, and total ionic concentration within the feed water [41]. Hence it is necessary to apply feed solutions with a mixture of ionic species in addition to single salt feed solutions in order to better evaluate the membrane water softening performance. Three types of simulated hard water with total dissolved salt (TDS) ranging from 1000 to 5000 ppm and hardness from about 500 to 2000 mg/l as $CaCO_3$ were employed as the feed solutions, and their detailed ionic compositions and other properties are listed in Table 4. It is worthy to note that Feed 1 was composed of 500 ppm of $CaCl_2$ and 500 ppm of NaCl, whereas Feed 2 and Feed 3 were prepared according to the ionic concentration of one source of well water in Florida [42] and RO concentrate from an inland desalination plant in Oman [43], respectively.

Water softening performance of the mixed PEI/PIP-based composite hollow fibers when dealing with the three types of simulated hard water feed solutions under 2 bar operating pressure is listed in Table 5, and compared with the performance of the other two membranes made with PEI or PIP alone as the aqueous phase IP monomer. As shown in the table, the PEI/PIP membrane exhibited greater water softening capability than the other two membranes in term of higher water permeability as well as better hardness removal for all the three types of feed water. Specifically, both PEI only and PEI/PIP showed over 90% hardness removal for Feed 1, while the PEI/PIP membrane possessed better water permeation. Comparing to the other two, the PIP only membrane had poorer rejection to Ca^{2+} due to its anionic membrane surface charges. As for the case of Feed 2, the hardness removal for PEI only membrane decreased to about 82%, while PEI/PIP membrane remained the hardness removal at around 90%. Comparing to Feed 1, an additional divalent counter-ion (SO_4^{2-}) was

introduced in Feed 2. The presence of SO_4^{2-} ions neutralized the positive charge of the PEI only membrane so that the rejections of Mg^{2+} and Ca^{2+} ions via Donnan effect were greatly affected. The water softening performance of the PEI only membrane was thus dropped significantly. Whereas the PEI/PIP membrane possesses smaller pore size and the rejection of divalent cations are less dependent on the positive membrane charge but rely more on size exclusion. The hardness removal of PEI/PIP membrane was therefore less interfered by the presence of SO_4^{2-} ions. When the membranes were further challenged by Feed 3, the water permeability for all three membranes declined substantially. The hardness removal for both PEI only and PIP only membranes dropped to less than 80%. The only capable membrane for the effective softening of Feed 3 remained the mixed PEI/PIP-based membrane, with hardness removal kept at about 87%. The reduction in both water permeation and hard water metal ion rejection were mainly attributed to the elevated osmotic pressure difference. According to Table 4, the concentration of both co-ions and counter-ions in Feed 3 were higher than the first two types of hard water feed solution, which resulted in higher osmotic pressure difference during NF operations. When operating pressure was kept as low as 2 bar for the current study, the effective driving force across the membrane reduced significantly, and led to decrease in water permeation as well as the overall ionic rejection.

Table 5 also presented one set of water softening data reported in the literature using commercial NF90 and NF 270 membranes with 10 bar operating pressure [44]. The hard water adopted for the study was from one groundwater source in Morocco. The feed water exhibited TDS of about 2300 ppm, hardness of 1100 mg/l as $CaCO_3$, and the ionic species presented were similar to the Feed 2 in the current study. The result showed that NF270 is ineffective in water softening with only 40% removal of total hardness. NF90 possessed high rejection to hard water metal ions, but the water permeation was lower than the currently

developed mixed PEI/PIP-based composite membrane. Moreover, as revealed in the table, NF90 presented high rejection to monovalent ions like Na^+ and Cl^-, whereas the 3 membranes developed in the current work exhibited much lower rejection to monovalent ions. High rejection to monovalent ions is unfavorable for low-pressure water softening, because it further increases the osmotic pressure difference, which produces an extra energy barrier and affect the water permeation as well as the permeate water quality. The high monovalent ionic rejection also produces highly concentrated brine, and the membrane could thus subject to the problems of severe membrane fouling.

4. Conclusions

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

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

As revealed by zeta potential and contact angle measurements, the mixed PEI/PIP-based thin-film selective layer exhibited positive surface charges with a highly hydrophilic nature. The optimized NF membrane possessed MWCO of 380 Da, an effective pore diameter of 1.27 nm, and pure water permeability (PWP) of 18.2 l/m^2 h bar. Under the operating pressure of 2 bar, the membrane exhibited rejection of 96.3% and 93.8% to 1000 ppm $MgCl_2$ and $MgSO_4$ feed solutions, respectively. The capability of the newly developed membrane for low-pressure water softening were evaluated by employing simulated hard water feed solutions with different ionic compositions and total hardness. By the combining effect of electrostatic repulsion and size exclusion, the mixed PEI/PIP-based composite hollow fiber offers better water softening performance compared with the membranes made with PEI or PIP alone as the aqueous phase IP monomer.

Acknowledgements

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