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Green Modification of Outer Selective P84 Nanofiltration (NF) Hollow Fiber

Membranes for Cadmium Removal

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Abstract

Outer-selective thin-film composite (TFC) hollow fiber membranes are normally made from interfacial polymerization of m-phenylenediamine (MPD) and trimesoyl chloride (TMC). However, the removal of excess MPD solution and the large consumption of alkane solvents are their technical bottlenecks. In this study, green methods to prepare the outer selective TFC hollow fiber membranes were explored by firstly modifying the membrane substrate with polyethyleneimine (PEI) and then by water soluble small molecules such as glutaraldehyde (GA) and epichlorohydrin (ECH). Using P84 polyimide as the substrate, not only do these modifications decrease substrate's pore size, but also vary surface charge by making the membranes less positively charged. As a result, the resultant membranes have higher rejections against salts such as Na_2SO_4 , NaCl and MgSO_4 . The PEI and then GA modified membrane has the best separation performance with a NaCl rejection over 90 % and a pure water permeability (PWP) of $1.74 \pm 0.01 \text{ Lm}^{-2}\text{bar}^{-1}\text{h}^{-1}$. It also shows an impressive rejection to CdCl_2 (94 %) during long-term stability tests. The CdCl_2 rejection remains higher than 90% at operating temperatures from 5 to 60 °C. This study may provide useful insights for green manufacturing of outer-selective nanofiltration (NF) hollow fiber membranes.

Key words:

Nanofiltration (NF); cadmium; P84 polyimide; thin film composite (TFC); hollow fiber membrane

1. Introduction

Cadmium is a common heavy metal presents in industrial effluents from pesticide, smelting, dye manufacturing and electroplating industries [1, 2]. Like other heavy metals, cadmium is non-biodegradable. Accumulation of cadmium can occur in living systems through food chain and drinking water. Side effects, such as nausea, bone lesions, renal disturbances and cancer, may happen if cadmium is accumulated in human beings [3, 4]. Thus, the removal of cadmium from wastewater before discharge has important meanings to the human society.

Comparing to other methods, membrane technology offers a unique solution to treat heavy metal contaminated wastewater with advantages of cost effective, high removal efficiency, small footprint and environmental friendly [5-7]. Nanofiltration (NF) is a membrane filtration process with a membrane pore size in the sub-nano scale [8-10]. Due to its special rejection mechanisms: size exclusion and charge repulsion [5, 6, 8], NF is able to offer good rejections to multi-valent heavy metal ions without much compromising water flux as compared to those of reverse osmosis (RO) membranes [11, 12]. So far, NF membranes have found growing applications to remove heavy metals, for instance lead, chromate, cadmium, zinc, etc [13-15].

Most NF membranes are thin-film composite (TFC) membranes consisting of a thin selective layer and a porous substrate. Interfacial polymerization is frequently used to form the thin selective layer [6, 13, 16-19]. In this process, membrane substrates are contacted with an aqueous amine solution such as m-phenylenediamine (MPD) solution and then an acid chloride solution such as trimesoyl chloride (TMC) in alkane solution so that a thin dense layer can be synthesized at the interface between the two phases. By changing the reaction conditions, interfacial polymerization can create membranes with high permeability and salt rejection [20-25]. Thus, it has been widely adopted in commercialized membranes, most of which are in flat sheet configurations.

There is a growing interest in TFC hollow fiber membranes. Comparing to flat sheet membranes, hollow fiber membranes have a higher surface to volume ratio, require no spacer, and can be self-supported [26]. The TFC layer can be formed on both inner and outer surfaces of hollow fiber membranes [16, 27, 28]. The outer selective TFC hollow fiber membranes may have less mass transfer resistance and lower chances being blocked by foulants compared to the inner ones. Thus, the outer selective TFC fibers can be fabricated into smaller fiber dimensions with a higher package density in modules [16]. Despite these advantages, the molecular design of an ideal TFC layer on the outer surface of hollow fiber membranes remains a challenge, making the mass production difficult [29]. Since most TFC

layers are made from interfacial polymerization of MPD and TMC, removing excess solution after the MPD coating is the major obstacle in the process [21]. Vacuum assist interfacial polymerization or wipe drying are required to make a defect free polyamide layer [16, 30]. Another obstacle is that a large amount of alkane solvents has to be used during interfacial polymerization, which brings extra costs and environmental issues [31, 32]. Eliminating alkane solvents is critical to lower manufacture costs and yield a green production process.

Since the cross-linking reaction between polyethyleneimine (PEI) and polyimide substrates is simple and easy to be conducted with a ring opening reaction on the backbone of polyimide [33], this approach has been recently used to form the outer selective layer of polyimide based NF hollow fibers [34, 35]. The PEI cross-linking not only decreases membrane pore size, but also brings in a plenty of amine groups on membrane surface. These amine groups are able to increase the surface charge of the PEI cross-linked membranes, making the membranes highly positively charged against cations [36]. Most importantly, they may also provide sites for further surface modifications so that the membrane properties can be further tuned according to users' needs [37-42]. Thus, the aims of the study are to: (1) chemically modify the PEI cross-linked membrane to develop outer selective hollow fiber membranes; (2) investigate the effects of different cross-linkers on NF performance of the modified membranes; (3) develop a green method by avoiding using the alkane solvent that is currently

compulsory during interfacial polymerization. As a result, the study may open up an alternative to the traditional interfacial polymerization to fabricate outer selective NF hollow fiber membranes.

To conceptually demonstrate the new approach, P84 (co-polyimide of 3,3',4,4'-benzophenone tetracarboxylic dianhydride with 80 % toluenediisocyanate and 20 % methylphenylenediisocyanate (BTDA-TDI/MDI)) was used to develop the hollow fiber substrate. Hyperbranched PEI (MW: 60K gmol^{-1}) was employed to enhance the rejection and bring in more amine groups onto the surface of the P84 substrate [43, 44]. Small molecules such as TMC, glutaraldehyde (GA) and epichlorohydrin (ECH), with molecular structures shown in Figure 1, were used to further cross-link the unreacted amine groups on the membrane surface after the PEI cross-linking. NaCl, Na_2SO_4 , MgCl_2 and MgSO_4 , were then utilized to investigate the NF performance of the resultant membrane. The rejection against CdCl_2 was subsequently tested to explore the potential application of the newly developed membranes for heavy metal removal. This study may provide a greener method to produce outer selective hollow fiber membranes for heavy metal ion removal.

2. Experimental

2.1 Materials

The hollow fiber substrates were made from P84 powder (MW 153,000 g mol^{-1} ; HP Polymer GmbH, Austria). P84 was chosen because of its good chemical resistance and thermal stability [45, 46]. To prepare the dope solution for the substrate, methanol (99.8 %, Fisher Chemical) and N-methyl-2-pyrrolidone (NMP, 99.5 %, Merck, Germany) were used as non-solvent and solvent, respectively. Hyperbranched PEI (MW 60,000 g mol^{-1} , Acros Organics, USA) was employed as a cross-linking agent to the substrate and was dissolved in a mixture of isopropanol (99.98 %, Fisher Chemical) and deionized water (50:50 wt%) to form a 1 wt% solution. To further cross-link the unreacted amine groups on the membrane surface after the PEI cross-linking, GA (50 %, Alfa Aesar), TMC (98 %, Aldrich) and ECH (≥ 99 %, Fluka Analytical) were studied. Organic solutes, including ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), glucose and sucrose from Alfa Aesar and Sigma-Aldrich, were used to form 200 ppm aqueous solutions for pore size and pore size distribution analyses. NaCl (99.5 %, Sigma), NaSO₄ (99 %, Riedel_de Haen), MgCl₂ · 6H₂O (99 %, Merck) and MgSO₄ (≥ 99.5 %, Sigma-Aldrich) were acquired to test the NF performance of the membranes. After that, the heavy metal salt, for instance, CdCl₂ (>99 %, Acros Organics), was utilized to test the heavy metal rejection and long term stability of the membranes. All salts were tested in the form of 1000 ppm aqueous solutions.

2.2 Fabrication of outer selective hollow fiber substrates

The detailed spinning procedures were similar to those in our previous work [34], while Table 1 shows the spinning conditions. The dope and bore fluid solutions were degassed overnight in two different ISCO pumps prior to spinning. The two solutions with different flow rates were pumped into a spinneret with the inner and outer diameters of 1.05 mm and 1.6 mm, respectively. Nascent fibers were subsequently formed in a coagulation tank after the two solutions passing through a certain air gap and then the fibers were collected by a take-up unit. The as-spun hollow fiber substrates were transferred to a water tank for two days to remove residual solvents. The resultant fibers were immersed in a 50 wt% glycerol aqueous solution for another two days and air dried subsequently. The air-dried hollow fibers were cut and assembled to make hollow fiber modules. The P84 hollow fiber substrate had an outer diameter of $473.68 \pm 7.46 \mu\text{m}$ and an inner diameter of $263.23 \pm 12.32 \mu\text{m}$. Each module comprised 20 pieces of fibers with an effective length of 14 cm. To remove the glycerol residual in hollow fibers, all hollow fiber modules were rinsed before tests.

2.3 Chemical modifications of hollow fiber substrates

The cross-linking of hollow fiber substrates were carried out in a cross-flow set-up as described in our previous work [44]. As elucidated in Figure 2, PEI was firstly dissolved in a 50 wt% isopropanol/water mixture to form a 1 wt% solution. The solution was then heated to 50 °C and circulated around the shell side of the hollow fiber substrates in a module with a flow rate of 400 ml/min for 1 h. For additional GA and ECH modifications, the modules were rinsed by DI water to wash away the unreacted PEI after the first PEI cross-linking modification. Then the modules were circulated by either a 0.5 wt% GA aqueous solution or a 6 wt% ECH aqueous solution around the shell side for certain durations at 50 °C. For the TMC modification, the PEI cross-linked membrane was air-dried for 10 min immediately after the cross-linking. A 0.25 wt% TMC in hexane solution was then flowed around the shell side of the membrane for 3 min to induce additional cross-linking. After that, the TMC modified membrane was heat treated for 15 min in an oven before stored in DI water for performance tests. For easy identification, M-PEI, M-PEI&GA, M-PEI&TMC and M-PEI&ECH were used to refer the PEI cross-linked only, GA, ECH and TMC modified membranes, respectively.

2.4 Characterizations of the membranes

2.4.1 Morphology

The morphologies of the membranes were observed with a field emission scanning electron microscope (FESEM, JEOL, JSM-6700F) and a scanning electron microscope (SEM, JEOL, JSM-5600LV). To prepare the FESEM and SEM samples, all hollow fibers were freeze dried first. The fibers were then fractured in liquid nitrogen and stuck onto sample holders with carbon tapes. A thin layer of platinum was then coated on each sample surface with a platinum ion sputtering device (JEOL, JFC-1300E) before observation.

2.4.2 Surface charge

A SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria) was used to measure the surface charge of the membranes. The experiments were conducted through streaming potential measurements using flat sheet membranes because of the better reproducibility of flat sheet membranes than hollow fiber membranes. To mimic the surface properties of the hollow fiber membranes, the flat sheet membranes were prepared using the same dope formulation and post-treatment conditions. During the measurement, the zeta-potential of the membrane was taken initially in a 0.01M NaCl solution. After that, the pH of the solution decreased gradually to pH 2.6, and then increased to pH 11 by auto-titrating of 0.1 M HCl and 0.1 M NaOH solutions, respectively. Zeta-potential values of the membranes were then recorded accordingly at various pH values between these ranges.

2.4.3 Mechanical strength

An Instron 5542 tensile equipment was used to test the mechanical properties of P84 hollow fiber substrates, PEI cross-linked membranes and GA/ECH/TMC modified membranes. All hollow fiber membranes were tested at the wet state. To prepare the samples, the targeted membranes were cut into fragments with a length of 80 mm. After that, the two ends of a fragment were clamped by the tensile testing equipment so that the fiber with an effective length of 50 mm between the two clamps was measured. The fiber was then elongated at a fixed rate of 10 mm/min till fiber breakage. The tensile stress, extension at break and Young's modulus of the fiber were obtained. To ensure experimental accuracy, at least 10 fibers of each condition were measured and an average value was reported.

2.4.4 Pure water permeability, pore size, pore size distribution and salt rejection

Pure water permeability (PWP) and salt rejection of the membranes were tested as follows using different feed solutions. DI water was the feed solution to test the PWP of the membranes. It was flowed against the shell side of the hollow fiber membranes at 5 bar. After the membranes were stabilized for 1 h, the permeate was collected. Three permeate samples

were taken successively to ensure the PWP was stabilized. The following equation was used to obtain the PWP ($\text{Lm}^{-2}\text{bar}^{-1}\text{h}^{-1}$) of the membranes:

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

where Q is the net water permeability across the membrane (L/h), A is the effective filtration area (m^2) and ΔP is the transmembrane pressure (bar).

Pore size and pore size distribution were determined as described elsewhere [47]. In short, organic solutes were dissolved in water to form 200 ppm solutions individually. The solutions were then circulated in the shell side of the membranes at 5 bar. After stabilizing for 1 h, permeate solutions from the lumen side were collected. The organic solute concentrations in both feed and permeate were then determined by a total carbon analyzer (TOC ASI-5000A, Shimadze, Japan). The organic solute rejection R (%) of each molecule was calculated by the following equation:

$$R = \left(1 - \frac{c_p}{c_f}\right) \times 100\% \quad (2)$$

where c_p and c_f are the concentrations of the permeate and the feed solutions, respectively. A relationship between solute radius and its rejection was then found. The molecular weight cut-off (MWCO) of a membrane is assumed to be equivalent to the molecular weight of a solute when the rejection of the solute is exactly 90 %. The geometric mean diameter of solutes (μ_s) is defined to be the Stoke diameter of a solute when the solute rejection is 50 %.

The geometric standard deviation of μ_s (σ_g) can be calculated from the ratio of Stoke diameter when the solute rejection is 84.13 % over that when rejection is 50 %. The mean effective pore diameter (μ_p) and the geometric standard deviation (σ_p) of a membrane are assumed to be the same as μ_s and σ_g , respectively. The probability density function curve of membrane pore size is then determined with the following equation [48-50]:

$$\frac{dR(d_p)}{dd_p} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp\left[-\frac{(\ln d_p - \ln \mu_p)^2}{2(\ln \sigma_p)^2}\right] \quad (3)$$

where d_p is the pore size of the membrane.

To test the salt rejection, membranes were washed thoroughly with DI water at 5 bars to ensure the conductivities of the permeates below 1 $\mu\text{S/cm}$. 1000 ppm NaCl, MgCl_2 , Na_2SO_4 and MgCl_2 solutions were prepared. They were then circulated sequentially against the shell sides of the membranes at 5 bar. To ensure the rejection was stabilized, three samples with a time interval of 1 h were taken consecutively. A conductivity meter was employed to determine the conductivities of the feed and permeate solutions. As conductivities of these salt solutions are proportional to their concentrations, these conductivities were used to calculate the salt rejection. After that, the heavy metal rejection of these membranes was tested using a 1000 ppm CdCl_2 solution. Concentrations of Cd ions in both feed and permeate solutions were measured by an ICP-OES (Optima 7300DV, Perkin Elmer, USA). All salt

rejections were then calculated similarly by changing organic solute concentrations to salt concentrations accordingly in Equation (2).

3. Results and discussion

3.1 Morphology of the membrane

Figure 3 shows the morphologies of the M-PEI&GA hollow fiber membrane including its 84 substrate and PEI cross-linked surface. Since a high content of NMP, i.e., 90 wt%, was employed as the bore fluid and tap water was used as the external coagulant, the resultant hollow fiber substrate is outer selective. The outer surface is a bit dense but the inner surface is fully porous. A few large outward pointed macrovoids can be found on the substrate cross-section because of water intrusion from the shell side of the membrane during phase inversion [51]. These macrovoids may be eliminated by increasing polymer concentration, air gap or take-up speed [51, 52]. Except the few macrovoids, the fiber cross-section is spongy-like, as observed in the enlarged images (Figure 3(a-b)) with a magnification of 10,000. The pore structure is fully inter-connected, indicating the membrane may have low resistance to water transport and have a high water flux. Many large pores can be found on the inner surface of the membrane as shown in Figure 3(c) due to the high NMP content in the bore fluid. No large pores can be observed on the outer surface of the P84 substrate (Figure 3(e)),

implying its suitability for the PEI cross-linking [34]. After the PEI cross-linking, small nodules can be observed on the membrane surface as shown in Figure 3(f). More nodules can be observed after the GA modification (Figure 3(g)). The surface roughness indirectly signifies the success of cross-linking on the membrane surface.

3.2 Surface charge of the membranes

Figure 4 illustrates the surface charge profiles of the four membranes between pH 2 to pH 11. The isoelectric point of the PEI cross-linked membrane is pH 10, implying the membrane is positively charged below pH 10 and negatively charged above pH 10. A critical point of pH 9 can be found in the positively charged portion. At $\text{pH} > 9$, the membrane is highly positively charged but the zeta-potential decreases rapidly with an increase in pH. The zeta-potential drops to negative values at pH higher than 10. Compared to the PEI cross-linked membrane, the zeta-potential curves of the GA, TMC and ECH modified membranes move down, implying these modifications lower the surface charge and make the surface more negatively charged. The isoelectric points of GA, TMC and ECH modified membranes are pH 6.1, pH 5.2 and pH 6.7, respectively, which are much lower than that of the PEI cross-linked membrane. Interestingly, the three curves intercept at pH 4.1. Compared to GA and TMC modifications, a more flattened curve is found for the ECH modified membrane, indicating

the ECH modification decreases the surface charge of the membrane both positively and negatively. As a result, a less surface charge may be found on the membrane surface of M-PEI&ECH at all pH range. Since ECH does not bring in new functional groups such as –COOH and –CHO as compared to TMC and GA, the less charged membrane may have a better anti-fouling property [53].

3.3 Influence of different modifications on the performance of the PEI cross-linked membranes

The influence of GA, TMC and ECH modifications on the separation performance of the PEI cross-linked membranes is displayed in Figure 5. Four salts such as MgCl_2 , Na_2SO_4 , NaCl and MgSO_4 were used in NF tests. The PEI cross-linked membrane has the highest rejection to MgCl_2 while the lowest rejection to Na_2SO_4 due to the Donnan effect of typical positively charged membranes. The PEI cross-linked membrane has comparable low rejections to NaCl and MgSO_4 . Since hexane was used as the solvent to dissolve TMC, the TMC modification is used as a reference in this study to mimic the traditional interfacial polymerization. Among the three modifications, the TMC modification has the lowest enhancement in separation performance compared to the PEI cross-linked membrane. The TMC modified membrane has higher rejections to Na_2SO_4 and MgSO_4 than the PEI cross-linked membrane due to the

decreased surface charge of the former membrane as shown in Figure 4. However, the TMC modification could not guarantee a significant improvement in rejection because of its inability to decrease membrane's pore size, as discussed in the late section. The GA and ECH modified membranes have much higher rejections to Na_2SO_4 because they are less positively charged as compared to the PEI cross-linked membrane, as shown in Figure 4. In addition to Na_2SO_4 , both membranes show higher salt rejections against MgCl_2 , NaCl and MgSO_4 . These results indicate that the GA and ECH modifications not only change membrane's surface charge but also decrease membrane's pore sizes. Comparing to ECH, GA is more effective to modify the PEI cross-linked membrane with a higher rejection because the GA modified membrane has rejections above 90% to the four salts.

Since part of our objectives is (1) to replace MPD in interfacial polymerization by the PEI cross-linking so that the removing process of the excess MPD solution can be eliminated and (2) to avoid the use of hexane for TMC so that the polymerization reaction is more environmental friendly than the traditional one, the PEI cross-linking fulfils the 1st objective and makes the coating process easy to be conducted and scaled up, while the GA and ECH modifications meets the 2nd objective because no alkane solution is involved. In addition, since both modifications take place in aqueous conditions, it makes the process relatively simple. Comparing to other studies, the newly developed process is also time-saving because

no air drying is required after the amine coating [40, 54]. A defect free NF layer with enhanced rejection can be formed almost immediately after the GA and ECH modifications of the PEI cross-linked membranes.

Apart from the aforementioned advantages, the mechanism of forming the selective layer by the GA and ECH modifications is different from the conventional interfacial polymerization. In the conventional interfacial polymerization, MPD diffuses from the substrate pores, reacts with TMC at the interface of the two phases and results in a rough ridge-valley morphology [21, 22, 55]. In this study, amine groups are grafted and fixed on the membrane surface after the PEI cross-linking and then react with GA, ECH or TMC which diffuses from its aqueous or organic phase to the membrane surface. As a result, the formed selective layer is smoother.

Figure 6 presents the PWP and rejection values to DEG and CdCl_2 of the four membranes. The GA, ECH and TMC modifications reduce the PWP of the PEI cross-linked membrane but enhance its rejection, indicating the successful formation of the selective layer. If the rejection to DEG is directly proportional to the reciprocal of pore size [56], the membrane's pore size may follow the order of $\text{M-PEI} > \text{M-PEI\&TMC} > \text{M-PEI\&ECH} > \text{M-PEI\&GA}$. In other words, GA, TMC and ECH modifications result in a decrease in pore size. Among them, the GA modification is the most effective. Figure 6 also compares their rejections to CdCl_2 .

Consistent with their rejections to DEG, M-PEI&GA and M-PEI&ECH have higher rejections than the rest two because of the decreased pore sizes. However, the enhancements are lower than the expected due to the decreased surface charge. Because the M-PEI&GA membrane possesses enhanced rejections to DEG and CdCl_2 with a reasonable good flux, it is used for subsequent studies.

3.4 Pore size distribution and mechanical strength of the hollow fiber

Figure 7 shows the cumulative pore size distribution and probability density function curves of the PEI cross-linked and M-PEI&GA membranes, while Table 2 summaries their pore properties. Generally, M-PEI&GA has smaller pores than those of M-PEI. The former also has a narrower pore size distribution than the latter. Specifically, most of M-PEI's pore sizes fall below 0.65 nm with a mean effective pore radius of 0.303 nm and a MWCO of 318 Da. After the GA modification, most of M-PEI&GA's pore sizes are smaller than 0.45 nm with a mean effective pore radius of 0.254 nm and a MWCO of 154 Da. Clearly, the GA modification can decrease the pore sizes of the PEI cross-linked membrane efficiently.

The mechanical strength of the substrate, PEI cross-linked and GA modified membranes are tabulated in Table 3. The Young's moduli of these three membranes have an increasing trend

in the order of M-PEI&GA > M-PEI > substrate, indicating the proposed surface modifications help to improve Young's modulus. The PEI cross-linked membrane shows a decreased tensile strength and elongation at break because the ring opening reaction during the PEI cross-linking modification may weaken the polyimide backbone. However, after the GA modification, both tensile strength and elongation at break are enhanced because the GA modification further cross-links the outer surface of the PEI cross-linked membrane with higher mechanical properties.

3.5 Influence of GA coating time and concentration on NF performance

Figure 8 displays the effects of GA modification conditions in terms of GA coating time and concentration on NF performance against Cd ions. For easy comparison, all water permeability in this section is normalized by the water permeability of the membrane modified by a 0.5 wt% GA solution for 40 min. As show in Figure 8(a) where the GA coating time varies but the GA concentration is constant (i.e., 0.5 wt%), the rejection increases slightly with an increase in coating time while the water permeability drops because a thicker selective layer may be formed on top of the substrate.

Figure 8(b) illustrates the effects of GA concentration on rejection against Cd ions where a

constant GA coating time (40 min) is employed. A similar trend is found. The rejection against CdCl_2 increases with a sharp decrease in water permeability. Comparing to Figure 8(a), Figure 8(b) implies that an increase in GA concentration has a greater effect on the modified membrane with an enhanced rejection to CdCl_2 than manipulating the coating time.

3.6 Stability of the membranes

Figure 9 shows the long term stability and thermal stability of the M-PEI&GA hollow fiber membrane. Similar to the Section 3.5, the membranes tested in this section were modified by a 0.5 wt% GA solution for 40 min. The membrane displays stable separation performance during the 72h continuous run. Its rejection remains a straight line. However, the water permeability fluctuates a bit. The slightly decreasing trend in water permeability can be restored every 24 h when replenishing the feed solution with the collected permeate solution. In other words, since the feed concentration is kept increasing due to the release of the diluted permeate during the test, it results in a decrease in water permeability because of the increase in osmotic pressure [57]. Thus, to maintain the feed concentration, the feed solution needs dilution every 24 h with the collected permeate solution. Since the water permeability can be almost fully restored, this suggests that fouling on the membrane is low.

Figure 9(b) illustrates the influence of operating temperature from 5 to 60°C on separation performance. The water permeability increases significantly with an elevated operating temperature, reaching almost 2.5 times of the control sample (25°C) at 60°C. However, the salt rejection reaches the highest at 15 °C and then drops slightly at either higher or lower operating temperatures. The lowest rejection occurs at 60 °C. Nevertheless, the rejections at all testing temperatures are above 90 % with a difference of 3.3 % between the highest and the lowest values. Clearly, the M-PEI&GA membrane has a good stability under a wide range of temperature potentially suitable for various separation applications.

4. Conclusions

In this study, a greener method to prepare outer-selective TFC hollow fiber membranes was developed. Unlike the traditional interfacial polymerization, the polyimide substrate was initially cross-linked with PEI. Then, three molecules, i.e., GA, TMC and ECH, were employed to further modify the PEI cross-linked membrane. Following conclusions can be drawn from this study:

- (1) The PEI cross-linking can be used as an alternative to overcome the difficulties in removing the excess MPD solution during interfacial polymerization. The PEI cross-

linking modification can induce sites for further GA and ECH modifications, in which no alkane solution is needed as those traditional TFC membranes made from MPD and TMC. The process may decrease the fabrication cost and is also environmental friendly.

- (2) GA, TMC and ECH modifications decrease the surface charge of the PEI cross-linked membrane, making the membranes less positively charged. In addition, the three modifications also decrease the pore sizes of the PEI cross-linked membranes and improve salt rejections.
- (3) GA and ECH modifications significantly enhance the salt rejection of the formed membranes, especially against Na_2SO_4 . The rejection of the GA modified membrane to NaCl can reach 90 % with a PWP of $1.74 \pm 0.01 \text{ Lm}^{-2}\text{bar}^{-1}\text{h}^{-1}$.
- (4) Increasing GA cross-linking time or GA concentration during the modification enhances salt rejection but decreases water permeability.
- (5) The newly developed M-PEI&GA membrane has good long term stability up to 72 h with impressive thermal stability. It can be used for a wide range of operation temperature from 5 to 60°C.

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List of Figures:

Figure 1. The chemical structures of (a) trimesoyl chloride (TMC), (b) glutaraldehyde, (GA) and (c) epichlorohydrin (ECH).

Figure 2. The modification procedures of the membranes.

Figure 3. The FESEM images of the M-PEI&GA hollow fiber membranes: (a) outer edge; (b) middle cross-section; (c) inner surface; (d) whole cross-section; (e) outer surface of the P84 substrate; (f) outer surface of the PEI cross-linked membrane and (g) outer surface of the GA modified membrane.

Figure 4. The surface charge profiles of the membranes with different modifications as a function of pH.

Figure 5. The rejection of the membranes to MgCl_2 , Na_2SO_4 , NaCl and MgSO_4 .

Figure 6. PWP and rejection to CdCl_2 and diethylene glycol (DEG) of the four membranes.

Figure 7. Cumulative pore size distribution curves (left) and probability density function curves (right) of M-PEI and M-PEI&GA.

Figure 8. Influence of GA coating time (left) and concentration (right) on cadmium rejection and water permeability of the M-PEI&GA membrane.

Figure 9. Long term stability (left) and thermal stability (right) of the M-PEI&GA membrane for cadmium removal.

List of Tables:

Table 1. The spinning conditions of the hollow fiber substrate.

Table 2. Summary of mean effective pore radius (r_p), geometric standard deviation σ_p and MWCO of M-PEI and M-PEI&GA.

Table 3. Young's modulus, tensile strength and elongation at break of the fibers

Highlights:

- A green method was developed to form outer selective hollow fiber membranes.
- Membranes with NaCl rejection above 90 % can be fabricated.
- CdCl_2 can be removed efficiently with a rejection above 94 %.
- The membranes are stable in a continuous running of at least 72 h.
- The membranes can be operated in a wide range of temperature from 5 to 60°C.

Table 1. The spinning conditions of the hollow fiber substrate.

Spinning condition	Parameter
P84 dope solution (wt.%)	P84/ methanol/ NMP (24:12:64)
Dope flow rate (ml/min)	3
Bore fluid composition (wt.%)	NMP/ DI water (90:10)
Bore fluid flow rate (ml/min)	1
Air gap (cm)	4
Take-up speed (m/min)	16.4
External coagulant (-)	Tap water
Dope temperature (°C)	26±1
Bore fluid temperature (°C)	26±1
External coagulant temperature (°C)	26±1
Room humidity (%)	65~70
Dimension of spinneret (mm)	i.d. /o.d. (1.05/1.6)
Die length of spinneret (mm)	6.5

Table 2. Summary of mean effective pore radius (μ_p), geometric standard deviation σ_p and MWCO of M-PEI and M-PEI&GA.

	μ_p (nm)	σ_p	MWCO (Da)
M-PEI	0.606	1.38	318
M-PEI&GA	0.508	1.26	154

Table 3. Young's modulus, tensile strength and elongation at break of the fibers.

	Young's modulus (Mpa)	Tensile strength (Mpa)	Elongation at break (%)
Substrate	267.74±21.34	7.26±0.36	17.62±0.01
M-PEI	285.38±11.26	6.47 ±0.44	11.68±1.85
M-PEI&GA	352.48±17.07	8.90±0.38	16.64±2.93

Graphic Abstract

Green Modification of Outer Selective P84 Nanofiltration (NF) Hollow Fiber Membranes for Cadmium Removal

Figures and Tables

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