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Preparation of Low-Pressure Water Softening Hollow Fiber Membranes by Polyelectrolyte Deposition with Two Bilayers

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Abstract

The layer-by-layer (LBL) polyelectrolyte deposition was applied on polyethersulfone (PES) hollow fiber ultrafiltration membrane to prepare nanofiltration (NF) membrane for low pressure water softening application for the first time. The effects of polyelectrolyte type and molecular weight (MW), deposited bilayer number, polyelectrolyte solution pH and supporting electrolyte concentration on the performance of resultant membranes were studied thoroughly.

Experiments revealed that the pH of the polyelectrolyte solution and supporting electrolyte concentration presented the most notable effects. For weak poly-cations, Poly(ethylenimine) (PEI) and Poly (allylamine hydrochloride) (PAH), the solution pH affected the membrane performance significantly, and high water permeability and divalent cation rejection were obtained at optimum pH values. Using a low concentration of supporting electrolyte at underneath layers was proved to be an effective way to increase water permeability while maintaining high salt rejection. A salt water flux (SWP) of 12 LMH/bar and 94% Mg^{2+} rejection were obtained by depositing only two bilayers of PSS/PAH polyelectrolytes on the PES substrate, while for the 3000 ppm mixed salt solution, the water permeability was 11 LMH/bar with Mg^{2+} and Ca^{2+} rejection as high as 90%. These promising results demonstrate that LBL technique is potentially applicable for preparing low-pressure water softening hollow fiber membranes.

Key words:

layer-by-layer deposition; polyelectrolytes; nanofiltration; hollow fiber membrane; low operating pressure of 2 bar.

1. Introduction

Water hardness, which refers to the presence of high concentrations of Ca^{2+} and Mg^{2+} in water, is one of the major problems for producing potable water from sea, brackish and ground water. Compared with traditional water softening methods such as ion-exchange or lime-soda ash treatment, membrane technology is a promising approach due to its lower energy cost and no chemicals involved [1]. Among all kinds of membranes, nanofiltration (NF) membranes are the most suitable candidate for water softening. Monovalent ions such as Na^+ , which are not necessary to be separated for water softening purpose, pass through the membrane, resulting in lower osmotic pressure and higher water permeability than that of Reverse Osmosis (RO) membranes [2].

NF membranes can be prepared from a variety of methods including integrally skinned membranes, dip coating, interfacial polymerization, mixed matrix, polymer grafting and surface modification [3]. In some recent studies, Yu et al. [4] fabricated a thin-film composited NF membrane by interfacial polymerization of polymeric polyamine polyvinylamine (PVAm) with isophthaloyl chloride (IPC) on a polysulfone support to achieve a rejection of 96.7% using a 1000 ppm MgCl_2 solution under 6 bar with the pure water permeability of 4.15 LMH/bar; Deng and co-workers [5] produced a NF membrane by UV-initiated graft polymerization of methacryloethyl trimethyl ammonium chloride (DMC)

onto polysulfone membranes. The resultant membranes demonstrated a 94.8% MgCl_2 (1000 ppm) rejection accompanied with a flux of 20.3 LMH at 2 bar; Ji et al. [6] introduced zwitterionic terpolymers P(DMC-HEA-DMAPS) (PDHD) composed of 2-methacryloyloxy ethyl trimethylammonium chloride (DMC), 2-hydroxyethyl acrylate (HEA) and 3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate (DMAPS) into NF membranes via the combination of surface coating and chemical cross-linking with glutaraldehyde (GA). By optimizing the reaction conditions, they could achieve a 96.5% MgCl_2 (1000 ppm) rejection and a flux of 47.8 LMH at 6 bar. Very recently, dual layer composite nanofiltration hollow fiber membranes [7] and interfacially polymerized composite nanofiltration hollow fiber membranes [8] for low-pressure water softening were also reported.

An alternative method for preparation of NF membranes is layer-by-layer (LBL) deposition of polyelectrolytes which was developed in the early 1990s [9]. The LBL method, which typically involves the alternating adsorption of poly-cations and poly-anions, with water rinsing between each adsorption, can be simply carried out essentially on any substrate that will support the adsorption of an initial layer of polymer [10]. Since the substrate, which is usually a porous MF or UF membrane, does not exhibit any selectivity by itself, the separation function for the composite membrane can be exclusively ascribed to the deposited polyelectrolyte multilayer [11].

The properties of the deposited layer such as film thickness, charge polarity and density, roughness and swelling can be easily controlled by varying polyelectrolyte types or/and other deposition conditions [10-24]. Some of these parameters are briefly explained here. With the increased number of deposit polyelectrolyte layers, the selective layer become thicker and consequently water permeability decreases and separation capability increases [12, 25]. Using a polyelectrolyte with lower molecular weight resulted in membrane with low water permeability. It was assumed that the short polymer chains are able to enter and block the pores of the supporting membranes so that the flux is decreased [26]. As another important parameter, the structure of the polyelectrolyte affects the charge density of the deposited film. The higher the charge density, the smaller the nanopores, the lower the water permeability and the higher the separation capability [27]. The conformation of polyelectrolyte polymers in a solution is known to be highly dependent on the pH (for weak polyelectrolyte only) and the ionic strength of the solution. Consequently, the ionization of polar groups and chain conformation of the adsorbed polymer on the substrate is also affected, so that the thickness, surface roughness and charge density of the polyelectrolyte multilayers become a function of pH and ionic strength of the polyelectrolyte solutions [14-16, 28, 29].

Over the last decade, the LBL deposition has been widely studied for membrane preparation used in many areas such as water treatment [30], pervaporation [31, 32] and gas

separation [33, 34]. Stanton et al. [17] were the first group who showed that alternating polyelectrolyte deposition on porous alumina supports can yield nanofiltration membranes that allow high water flux along with selective ion transport. They found that by using different kinds of polyelectrolytes and changing deposition conditions, it is possible to tailor the permeation properties of the multilayer film for specific applications [18, 35]. Depending on the polyelectrolytes employed, prepared membranes can be used as size-selective passage of uncharged solutes[35], for separation of proteins, size selective passage of specific sugars [18], removal of salts from sugar, amino acid and dye solution [36], amino acid separation [37], or ion separation [22, 23, 38]. Although in a number of studies, the separation of anions by using negatively charged membranes prepared via LBL deposition was investigated [13, 17, 20, 22, 38-40], few studies were reported for cation separation using positively charged membranes. Ouyang *et al.* [23] and Stanton et al. [17] reported that, divalent cation rejection increased when the polyelectrolyte deposited film was capped with a poly-cation; and by increasing the concentration of the supporting electrolyte during the deposition of the terminating layer, a higher surface charge could be attained and hence a higher ion rejection as well as the divalent/monovalent selectivity of the prepared membrane.

However, most of the LBL studies in the literature are mainly focused on the inorganic substrate or flat sheet membranes. In contrast, hollow fiber substrates possess several practical advantages in the membrane applications such as high packing density, self-

support structure and ease of scale up. Therefore, in this study, the LBL deposition of the polyelectrolytes on a home-made polyethersulfone (PES) hollow fiber membrane was employed to prepare positively charged NF hollow fiber membrane for the first time. Three different poly-cations were studied to identify the most preferable poly-cation to obtain a high divalent cation rejection. Meanwhile, by changing supporting electrolyte concentration and the solution pH, the properties of the prepared membrane was tailored in order to achieve high water permeability and high rejection. With only two bilayers deposition, the LBL membrane performance on separating Mg^{2+} and Ca^{2+} were investigated using both single and mixed salt solutions. The relatively low operating pressure of 2 bar not only is more suitable for hollow fiber membrane configuration but also can effectively reduce the energy requirement for the water softening.

2. Experimental

2.1. Materials

The polyethersulfone (PES) hollow fiber substrate was acquired from Singapore Membrane Technology Centre. Poly(styrene sulfonic acid) sodium salt (PSS, molecular weight (M_w) = 500 kDa) was purchased from Alfa Aesar. Poly(sodium 4-styrenesulfonate) (PSS, M_w = 70 kDa), Poly(diallyldimethylammonium chloride) (PDADMAC M_w = 120-200 kDa, 20 wt.% in water), Poly(ethylenimine) (PEI, branched, average $M_w \approx 250$ kDa) and

Poly (allylamine hydrochloride) (PAH, Mw =56 kDa) were purchased from Sigma-Aldrich.

Poly (allylamine hydrochloride) (PAH, Mw =120 000-200 kDa) was supplied by Polyscience

Inc. The chemical structures of PSS, PAH, PEI and PDADMAC are shown in Fig. 1.

For filtration experiments, sodium chloride (NaCl , $\geq 99\%$), magnesium chloride (MgCl_2 , hexahydrate), and calcium chloride (CaCl_2 , dehydrate) were purchased from Merck.

Deionized water (Milli-Q, 18.2M Ω cm) was employed for rinsing membranes and preparing polyelectrolyte and feed solutions. The pH of polyelectrolyte solutions was adjusted using hydrochloric acid (HCl fuming 37%) and sodium hydroxide (NaOH) obtained from Merck.

All the reagents were used as received without any further purification.

2.2. PES substrate characterization

A series of standard protocols for substrate characterization can be found elsewhere [41] in details. The morphology of the PES hollow fiber membranes were examined by a JSM-7600F Field Emission Scanning Electron Microscope (FE-SEM). Tensile strength test of the hollow fiber membranes was performed using a Zwick 0.5kN Universal Testing Machine at room temperature. To measure pure water permeability (PWP) and molecular weight cut-off (MWCO), hollow fiber modules were made by plotting 3 pieces of hollow fibers into a plastic tube with an effective length of 17 cm. Compaction was carried out at 2 bar for 1 h prior to measurement. PWP of the prepared membranes was evaluated using a

bench scale cross-flow filtration unit. The hydraulic pressure up to 1 bar was applied on the shell side of hollow fiber membranes and permeated water was collected from the tube side of the modules. MWCO of the PES hollow fiber substrate was determined by the filtration method using a 2000 ppm dextran solution and analysed by gel permeation chromatography (GPC) on a Polymer Laboratories-GPC 50 plus system (double PL aquagel-OH Mixed-M 8 μ columns). The dextran solution was made by mixing several different molecular weights of dextran from 6000 Da to 500,000 Da. The detailed procedure was described elsewhere [42].

2.3. Layer-by-Layer deposition

The similar membrane modules were used for LBL deposition. Each deposition started by immersing the prepared module in a 0.02 M PSS solution (polyelectrolyte concentrations are always given with respect to the repeating unit of the polymer) with pre-decided supporting electrolyte concentration for 2 minutes. PSS deposition takes place on PES substrate based on the hydrophobic interaction [20]. Then, the substrate was rinsed with deionized water for 1 min before immersing in the poly-cation solution (PAH, PEI or PDADMAC) for 5 minutes followed by another 1 min rinse [17, 23]. Additional layers were deposited similarly to give the desired number of bilayers. In this study, the composition of the deposited layers is shown inside a parenthesis by the name of the poly-anion with the supporting polyelectrolyte concentration and type, followed the poly-cation and the supporting polyelectrolyte

concentration and type. Two of them are separated by a slash. In the case that the bilayer deposition was repeated, the number of deposited bilayers, n, is shown after the parenthesis with a cross mark, x. (PSS 0.5 M NaCl / Poly-cation 2.5 M NaCl) x n is an example. The membrane modules were then stored in DI water for NF performance evaluation.

2.4. Filtration performance for single and mixed salts

The salt rejection of the prepared membranes was evaluated using the same module used for PWP test. The hydraulic pressure up to 2 bar was applied on the shell side of hollow fiber membrane and permeated water was collected from tube side of the modules. The single salt rejection experiment was carried out using a 1000 ppm MgCl_2 solution based on conductivity measurements (Ultrameter II, Myron L Company, Carlsbad, CA) of permeate and feed water. For mixed salt rejection experiments, a 3000 ppm salt solution including 500 ppm MgCl_2 , 900 ppm CaCl_2 and 1600 ppm NaCl were used. The cation concentrations in the mixed salt feed solution and the permeate solution were determined by using an inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8000, Perkin Elmer). Single salt filtration was conducted first followed by the mixed salt filtration for the selected prepared membranes.

3. Results and discussion

3.1. Substrate characterization

The home-made PES hollow fiber membranes, designated as membrane #A and #B, with the characterizations summarized in Table 1 were used as the substrate. While the substrates #A and #B have similar pure water permeability and mechanical strength, the MWCO for substrate #B was more than three times larger than that of substrate #A. Figs.2(a) and (b) show the enlarged cross section, and Figs.2(c) and (d) show the FE-SEM images of the outer surface of the PES substrates, respectively. It can be seen that tightly compacted needle-like pores were developed from the outer and inner surfaces for both substrates #A and #B. There was no large macro-void formation for the substrate #A but some large macro-voids could be found at the middle part of the substrate #B. These structures provided membranes with high porosity and pure water permeability. A larger MWCO at the outer surface of the substrate #B can be clearly observed by comparing the visible pore structures under high magnification in Figs. 2 (c) and (d).

3.2. Counter effects of substrate MWCO and deposited polyelectrolyte molecular weight

Two bilayers of polyelectrolyte (PSS/PAH) with different molecular weights were deposited on the outer surface of substrates #A and #B. The salt water permeability (SWP) and Mg^{2+} rejection are summarized in Table 2. It shows that when the substrate #A with a

small MWCO (around 70k) was used as a substrate, the effect of polyelectrolyte molecular weight was negligible. As for the substrate #B with a MWCO of 200k, similar results were obtained using a polyelectrolyte with large molecular weight as previous cases. The FESEM images of the outer surface of the membranes #A and #B after two bilayer depositions of polyelectrolytes with larger molecular weights are shown in Fig.3 (a) and (b), respectively. By comparing images before (Fig. 2 (c) and (d)) and after polyelectrolyte deposition (Fig.3 (a) and (b)), it can be clearly observed that the pores on the substrates were covered effectively, which was also confirmed by high Mg^{2+} rejection of the resultant membranes.

However, when the molecular weight of polyelectrolytes (56k for PAH and 70k for PSS) was much smaller than the MWCO of the membrane substrate (200 kDa), the water permeability and Mg^{2+} rejection decreased sharply to 7 LMH/bar and 81%, respectively. This was probably due to the penetration of the polyelectrolytes into the substrate pores [20], which increased the mass transfer resistance and also resulted in the non-uniform multilayer distribution. Therefore, for the subsequent part of this study, substrate #A was used with larger molecular weight polyelectrolytes to prevent the penetration of the polyelectrolytes into the substrate pores.

3.3. Effects of deposited bilayer number and poly-cation type

Water permeability and Mg^{2+} rejection for LBL membranes using three types of poly-cations (PAH, PEI and PDADMAC) and different bilayer numbers are shown in Figs.4 (a) and (b), respectively. As expected, while Mg^{2+} rejection increased by increasing deposited bilayer numbers, water permeability decreased sharply due to the formation of the polyelectrolyte multilayer which covered the substrate pores. Considering both water permeability and Mg^{2+} rejection, it can be concluded that the deposition of two bilayers of polyelectrolytes was sufficient to obtain a NF membrane with water permeability as high as 12 LMH/bar and Mg^{2+} rejection higher than 90%. There was no significant rejection improvement with further increasing bilayer number. To our best knowledge, this is the lowest bilayer number ever reported to fabricate NF membrane by LBL deposition. While in the literature [13, 17, 18, 20-23, 35, 38, 40, 43], depositing more than three bilayers on any substrate is necessary to obtain NF membranes with acceptable divalent ion rejections (>90%). Using a substrate with high initial water permeability and small pore size on the deposition surface, and applying polyelectrolytes with large molecular weights enable us to reach high divalent ion rejection by only two bilayers deposition in this study.

As for the choice of poly-cations, despite the relatively high water permeability, PDADMAC deposited membrane was firstly excluded from further assessments due its low Mg^{2+} rejection. This is because PDADMAC swelled more severely in water than PAH and PEI due to its relatively low charge density and the accompanied lower ionic cross-links

density [21, 39]. Using PEI as poly-cation resulted in a NF membrane with slightly higher water permeability and lower Mg^{2+} rejection than that of PAH. In the same way, it could be explained by the slightly lower charge density of PEI compared to PAH [27, 44]. The solution pH and the supporting electrolyte concentration of these two poly-cations, which greatly affect the thickness, surface roughness and charge density of the polyelectrolyte multilayers [14-16, 19, 28, 29], were further studied in order to achieve best membrane performance.

3.4. Effect of poly-cation solution pH

Although the effect of pH on weak polyelectrolyte solutions was investigated in several published papers [14-16, 19, 28, 29], the use of different substrates, supporting electrolyte type and concentration makes it difficult to compare and decide an appropriate pH value for each type of polyelectrolyte solutions [19]. Therefore, for current study, the desirable pH value for PAH and PEI solutions were evaluated experimentally by single salt filtration, while no pH adjustment was needed for PSS as it is a strong polyelectrolyte [19, 27]. The effect of PAH and PEI solution pH on the water permeability and rejection of the NF membranes were shown in Fig.5 and Fig.6, respectively.

As shown in Fig.5, by increasing pH of the PAH solution from 1.7 to 4.5, a slight increase in water permeability was observed, while Mg^{2+} rejection increased from 80% to

94%. However, by further increasing the pH value of the PAH solution from 4.5 to 7, Mg^{2+} rejection decreased sharply to 60%. At a low pH, although most of the amine groups of PAH were fully protonated, the excessive H^+ in the solution suppressed the negative charges on the PSS layer. Hence, the electrostatic interaction between PSS and PAH became weaker, leading to a lower Mg^{2+} rejection. By increasing solution pH to 4.5, the protonation percentage of PAH molecules did not change so much [19], but on the other hand, the suppression of negative charges on the PSS layer by H^+ in the solution was greatly reduced. Therefore, a highly electrostatic crosslinked multilayer was expected to be formed, leading to improved Mg^{2+} rejection. However, a further increase in the pH of the PAH solution, i.e., $\text{pH} > 4.5$, the amine groups of PAH deprotonated significantly [19]. Thus, a loose layer was formed with considerably lower positive charge density, which resulted in a NF membrane with low Mg^{2+} rejection and high water permeability. It can be concluded from Fig.5 that pH of 4.5 is an optimum value within the evaluated pH range in this study to obtain a NF membrane with 12 LMH/bar water permeability and 94% Mg^{2+} rejection.

Since PEI is less environmentally harmful than PAH, we considered PEI as another alternative poly-cation, and the results are shown in Fig.6. The optimal point was observed at pH 11 with the highest Mg^{2+} rejection of 79% and 14 LMH/bar water permeability. The lower rejection of the membrane made by PEI was probably attributed to the lower charge density [27, 44]. On the other hand, the trend of performance variation was different from

that of the membrane made by PAH showed earlier on. From Fig.6 it can be observed that, at a low pH, water permeability was high with a very low Mg^{2+} rejection. It could be explained as, in addition to the charge suppression of PSS layer mentioned earlier, a much looser multilayer structure was formed due to the steric hindrance effect of the branched PEI. By increasing pH from 2 to around 6, water permeability decreased and Mg^{2+} rejection increased sharply as a result of tighter electrostatic crosslinking between the PEI and PSS layers. By further increasing its pH up to 11, the amine groups of PEI deprotonated accordingly. Since PEI consists of primary, secondary and tertiary amine groups in variable ratios and the deprotonation of each group took place at different pH levels [45], there was no clear trend observed in this range but the optimal pH was confirmed at 11 after multiple trials. Further experiments were conducted for better understanding PEI deprotonation behavior. Although not shown here, it was found that when 500 ppm MgCl_2 was used as the feed solution, water permeability around 18 LMH/bar with 90% Mg^{2+} rejection could be attained for PEI deposited LBL membrane. However, by increasing the feed solution concentration to 1000 ppm, the membrane performance decreased dramatically. It can be concluded that the PEI deposited LBL membrane is appropriate for water softening application only at low salt concentrations in the feed solutions.

3.5. Effects of supporting electrolyte concentration and deposited film composition

The addition of salt (supporting electrolyte) changes the ionic strength of deposition solution and reduces the electrostatic repulsion of the polymer chains. Therefore, the polymer chain will be adsorbed as coil conformation rather than in flat conformation [13, 26]. Consequently, the thickness of the individual layer will increase and hence, the flux will decrease with improved rejection.

In this study, the effects of supporting electrolyte concentration and deposited film composition on water permeability and Mg^{2+} rejection of the NF membrane were evaluated and results are tabulated in Table 3. By comparing the performance of membrane I with II, and membrane III with IV, it can be seen that by decreasing supporting electrolyte concentration from 2.5 M to 0.5 M in the poly-cation solution used for the first layer, water permeability increased around 20%. On the other hand, when the supporting electrolyte concentration in the poly-anion solution decreased from 0.5 M to 0.1 M (comparing membrane I with V, and III with VI), water permeability also increased slightly. Meanwhile, no notable change in the divalent cation rejection was observed for each modification since the charge density at the terminating layer was not altered. It seems the rejection was mainly controlled by the charge density of the capping layer [17, 23], and thinner deposited layers with higher water permeability could be formed by decreasing the supporting electrolyte concentration at the underlying layers.

3.6. Filtration of mixed salt solutions

After evaluating the performance of resultant NF membranes using single salt filtration, mixed salt filtrations were performed for the selected membranes (membrane I and III in Table 3) and results are shown in Table 4. It shows that the membrane I (prepared by using PAH as poly-cation) kept high divalent-cation rejection with slightly decreased water permeability due to the elevated osmotic pressure of the mixed salt solution. On the other hand, the divalent cation rejection of the membrane III (prepared by using PEI as poly-cation) decreased sharply. This was probably because of the relatively low charge density of PEI, that was considerably suppressed by the high concentration feed solution. As for the rejection of different cations, it is believed the Donan exclusion was the major mechanism while the size exclusion also played certain rule [3]. For both membranes, Na^+ rejection (11% and 2%, respectively) was much lower than divalent cations due to the weaker electrostatic repulsion of the monovalent co-ions ; Mg^{2+} rejection (91% and 45% respectively) was higher than Ca^{2+} (87% and 40%, respectively) because of the larger hydrated diameter of Mg^{2+} . From these results it can be concluded that the PAH deposited LBL membranes can effectively separate water hardness at a low operating pressure of 2 bar.

4. Conclusions

Positively charged nanofiltration hollow fibre membrane was successfully prepared by using LbL deposition of polyelectrolytes. From the single salt filtration experiment results, the performance of the resultant membranes was affected significantly by the pH value of the PEI and PAH solutions, and the optimum pH values were identified for both polyelectrolyte solutions. It was also found that using a low concentration of supporting polyelectrolyte at underlying layers and a high concentration at the capping layer, water permeability could be improved while maintaining the same divalent cation rejection. By depositing only two bilayers of PSS/PAH polyelectrolytes at optimum pH and supporting electrolyte concentration, water permeability around 12 LMH/bar and 94% Mg^{2+} rejection were obtained using a single salt solution. While for the mixed salt solution with 3000 ppm salt concentration, the water permeability was 11 LMH/bar with Mg^{2+} and Ca^{2+} rejection as high as 90%. These promising results demonstrated that LbL technique is potentially applicable to prepare positively charged hollow fiber membranes for water softening at 2 bar low operating pressure.

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