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Enhanced hollow fiber membrane performance via semi-dynamic
layer-by-layer polyelectrolyte inner surface deposition
for nanofiltration and forward osmosis applications

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Abstract

The layer-by-layer (LBL) polyelectrolyte deposited membranes have drawn increasing attention in various applications due to the ease of selective layer formation and their stability and versatility. In this study, the LBL deposition was performed at the inner surface of the Polyethersulfone (PES) hollow fibre substrate to form composite nanofiltration (NF) membrane. The semi-dynamic deposition procedure was adopted with the aid of syringes. The newly developed inner deposited (id-LBL) membranes were then tested in NF and forward osmosis (FO) applications and the performance were compared with outer surface deposition as well as some literature data. The id-LBL membranes could not only withstand higher operating pressure but also possess superior hardness rejection especially in high concentration mixed salt solutions (more than 95% rejection to Mg^{2+} and Ca^{2+} in a 5000 ppm total dissolved salt (TDS) mixture under 4.8 bar). As for the FO process, with only two layer deposition, the id-LBL membranes also demonstrated significant performance improvement with increased water flux (up to $70 \text{ L/m}^2\cdot\text{h}$ using 0.5 M MgCl_2 as draw solution in active layer facing draw solution configuration) and reduced salt leakage (around $0.5 \text{ g/m}^2\cdot\text{h}$ using 1 M MgCl_2 draw solution in active layer facing feed water configuration). This study suggests that for hollow fiber substrate, the inner surface is more suitable for the formation of the selective layer via LBL deposition than the outer surface.

Keywords: layer-by-layer polyelectrolyte assembly; hollow fiber membrane; inner surface deposition; nanofiltration; forward osmosis.

1. Introduction

The layer-by-layer (LBL) assembly technique has been applied on the porous membrane substrates to form thin film composite (TFC) membranes since the late 1990s. Compared with the traditional Langmuir-Blodgett thin-film deposition method, the ease of film formation and film stability and versatility are the main advantages of this new technique [1]. Based on the combination of various polyelectrolyte pairs and substrates, the LBL assembled membranes have been studied for a wide range of applications such as pervaporation [2, 3], fuel cell [4], nanofiltration (NF) [5, 6] and wastewater treatment [7], etc.

Due to their charged nature, the TFC polyelectrolyte membranes are capable in selective removal of multivalent ions from monovalent ions by Donnan exclusion effect. In a series of studies conducted by Bruening's group [5, 8-10], the polyelectrolyte multilayer films were successfully deposited on both porous alumina and commercial flat sheet polyethersulfone (PES) membranes. Upon carefully control of deposition conditions, relatively high selectivity of $\text{Cl}^-/\text{SO}_4^{2-}$ or $\text{Na}^+/\text{Mg}^{2+}$ with considerable water flux were achieved under NF operation. Besides, the LBL membranes can also be used to separate some other species in water treatment based on either electrostatic repulsion or size exclusion. Aravind *et al.* [11] used chitosan/poly(styrenesulfonic acid) (PSS) multilayered membranes to treat paper mills and textile effluents with a substantial reduction in colour and chemical oxygen demand. In a recent study, phosphate recovery was reported in the form of H_2PO_4^- with $\text{Cl}^-/\text{H}_2\text{PO}_4^-$ selectivity of 310 and a flux of $13.53 \text{ m}^3/\text{m}^2\text{-day}$ at a very low pressure (0.28 bar) by the deposition of Poly(ethyleneimine) (PEI)/PSS films on a nylon substrate [12].

The most traditional LBL deposition procedure is the alternately dip coating method which involves the immersion of a substrate into polyelectrolyte solutions with opposite charges alternatively with rising steps in between. This is a straightforward method which was also automated at the later stage [13]. However, it is time consuming since each deposition step needs few minutes to complete. To speed up the process, alternated spray deposition [14] and spin-coating methods [15] were invented which require only a few second deposition time. Yet, most of those studies were focused on the inorganic substrate or flat sheet membranes only. As for the hollow fiber membrane substrate, we have successfully demonstrated the outer surface LBL

deposition by immersion method which is similar to the traditional dip-coating process and explored their applications in NF [16] and forward osmosis (FO) process [17]. Meanwhile, some research groups have also investigated the possibility of applying LBL deposition on the inner surface of hollow fiber substrate. The common practice involves running the polyelectrolyte solution through the substrate lumen with [7, 18] or without [19] applied pressure or even with negative pressure [20] at the shell side.

Based on our groups' past experience of interfacial polymerization on the inner surface of various hollow fiber UF membrane substrates [21, 22], it is believed that the inner surface modification may possess several advantages over the shell side: (1) the lumen surface of the hollow fiber substrate is better protected during the membrane spinning, handling and storage process; (2) the confined space inside the substrate lumen enhances the homogeneity and controllability of the chemical modification and significantly reduces the chemical requirement; (3) it can minimize the experimental uncertainty caused by air bubbles, membrane overlapping, etc., that are often encountered during outer surface deposition; and (4) the **thin-wall structured** membrane can withstand much higher operating pressure from the lumen surface which is more preferable in the pressure driven process. Therefore, in this study the inner skin deposited LBL membrane was fabricated using a semi-dynamic process which involves the dynamic introduction/replacement of solutions into the fiber lumen by syringes followed by the static contact for a desired time. In contrast with other inner deposition methods mentioned earlier on, no peristaltic or vacuum pumps were required in the process **with simpler procedure and much less chemical consumption**. The developed membranes were characterized by a series of standard protocols, and then tested in NF and FO applications. Their performances were also compared with previous studies to confirm the superiority of the inner deposition LBL method.

2. Materials and experiments

2.1. Materials

The polyethersulfone (PES) hollow fiber substrates were produced in-house. Their properties **and characterization methods** have been reported elsewhere [23, 24] and

are summarized in Table 1. Poly(allylamine hydrochloride) (PAH, PolyScience, Mw =120k-200k Da), Poly(ethyleneimine) (PEI, Sigma Aldrich, Mw=750 kDa), Poly(diallyldimethylammonium chloride) (PDADMAC, Sigma Aldrich, Mw=100-200 kDa) and poly(styrenesulfonic acid) sodium salt (PSS, Alfa Aesar, Mw = 500 kDa) were used to make polyelectrolyte solutions with sodium chloride (NaCl, Merck) as the supporting electrolyte. The molecular structures and functional groups of the above mentioned polyelectrolytes can be found in Table 2. NaCl, calcium chloride (CaCl₂) and magnesium chloride (MgCl₂) (Merck) were used for NF and FO performance tests. Neutral organic solutes such as glucose, sucrose and raffinose were purchased from Merck and used to determine LBL membrane molecular weight cut-off (MWCO). Hydrochloric acid (HCl fuming 37%) and sodium hydroxide (NaOH) obtained from Merck were used to adjust membrane storage water for acid/ alkaline stability test. DI water was produced by a Mili-Q system (Milipore, USA).

2.2. Inner surface Layer-by-layer deposition

The dried hollow fibers were sealed into plastic membrane modules with an effective length of 24 cm. The LBL deposition at the lumen surface of the substrate was performed by introducing the polyelectrolyte solution throughout the fiber lumen with a syringe and maintained for a desired contact time. The schematic drawing of the deposition process is shown in Fig. 1. The poly-anion PSS (0.02 M with 0.5 M NaCl without pH adjustment) and poly-cation PAH, PDADMAC, PEI (0.02 M with 2.5 M NaCl each without pH adjustment) solutions were applied alternately to achieve the desired number of layers. The contact times for the hollow fiber with PSS and different poly-cation solutions were 3 and 5 min, respectively, with 3 min DI water rinse in between. Membrane modules were then stored in DI water for NF and FO performance evaluation. For a comparison purpose, the outer deposited LBL membrane were also fabricated following the same protocol as our previous work [16] and tested in NF application. Throughout the paper, the id-LBL and od-LBL refer to inner surface deposited and outer surface deposited LBL membranes respectively; one pair of poly-anion (PSS)/poly-cation (PAH) deposition is considered as one layer of polyelectrolytes and thus LBL-xI(O) refers to the membrane with x pairs of (PSS/PAH) inner(outer) deposition.

2.3. Membrane characterization and performance evaluation

2.3.1. Characterization of membrane substrates and LBL membranes

The morphology of the substrate and LBL membranes were examined by a Field Emission Scanning Electron Microscope (FE-SEM JSM-7600F, JEOL, Japan). The surface charge properties of these membranes were determined by streaming potential method using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria) with an electrolyte solution of 0.01M potassium chloride (KCl). **The zeta potential results were then calculated by its built-in software using Helmholtz-Smoluchowski equation.** The molecular weight cut-off (MWCO), i.e., the molecular weight of the solute with 90% rejection, of the LBL membranes were measured on a bench scale cross-flow filtration unit at 1 bar using a 200 ppm solution of glucose, sucrose and raffinose respectively. The rejection of neutral organic solutes was obtained from the concentration of the feed and permeate solutions based on the total organic carbon measurements using a TOC analyzer (TOC-VCSH, Shimadzu, Japan).

2.3.2 NF and FO performance tests

The salt water permeability and salt rejection of the LBL hollow fiber membranes were determined by the same cross-flow filtration unit under 2 bars pressure. A relatively high cross flow velocity (0.5m/s) was maintained for the salt solution flow to minimize the concentration polarization effect. The salt solutions were always facing the membrane active layer where the inside-out filtration was performed for id-LBL membranes and vice versa. The single salt rejection tests were conducted using a 1000 ppm $MgCl_2$ solution, based on the conductivity measurements (Ultrameter II, Myron L Company, Canada) of the permeate and feed water. For the 3000 and 5000 ppm mixed salt tests, cation concentrations in the feed and permeate solutions were determined by an inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8000, Perkin Elmer, USA). In addition, various membrane stability tests including acid/alkaline, high shear flow and back wash tests were also performed using the same filtration unit.

Two FO orientations, the active layer facing draw solution (AL-facing-DS) and active layer facing feed water (AL-facing-FW), were tested using a lab-scale FO unit which is similar to the unit reported previously [25]. The Reynolds numbers of the fluids

flowing in the lumen and shell side of the modules were kept at around 2000 to minimize external concentration polarization (ECP). MgCl_2 solutions with different concentrations were used as the draw solutions while DI water was used as the feed. The volumetric water flux, J_v , and salt flux, J_s , were measured by the weight and conductivity changes in the feed tank using a digital mass balance and a conductivity meter connected to a computer logging system. The operation was performed at room temperature of $\sim 23^\circ\text{C}$.

3. Results and discussion

3.1 Characteristics of LBL hollow fibers

The characteristics of the PES membrane substrate and both outer and inner surface deposited LBL hollow fibers are studied and compared in this section including surface morphology, charge properties as well as the MWCO of the membranes.

The FE-SEM images of membrane surface before and after LBL deposition are shown in Fig. 1. Visible pores exist on both outer (Fig.1 (a)) and inner surface (Fig.1 (c)) of PES substrates. The smooth surface with patterned structure which may be related to the vertical stretching force during the spinning process were observed on the fiber lumen. In contrast, the outer surface seems to be rougher with irregular topography which may cause an uneven distribution of the deposited layer. Nevertheless, upon two layer LBL deposition, the surface pores were fully covered by the polyelectrolyte multilayer on both surfaces (Fig.1 (b, d)) with some possible polymer aggregates.

The surface charge properties of the substrate and the LBL membranes are presented in Fig. 2. The PES substrate possesses slightly negative surface charge throughout the tested pH range (auto-titrated from pH 10 to 4). On the other hand, the isoelectric points for both the od-LBL and id-LBL membranes are around pH 8 which suggests that these membranes are positively charged below this pH value since the poly-cation PAH were used as the capping layer. Moreover, the higher zeta potential readings of the id-LBL membrane indicate its higher surface charge density than the outer deposited one.

The rejection of the NF membranes towards the neutral solute is exclusively depended on the size-based selectivity by eliminating the Donnan effect and often used to estimate the MWCO and the effective pore size of the NF membrane [26, 27]. The

properties of the three neutral solutes, glucose, sucrose and raffinose, are listed in Table 3 together with their rejections by both the od-LBL and id-LBL membranes. The Stokes radius of the solutes were calculated using the empirical equation **based on their molecular weights** [26]. It can be seen that the MWCO of the od-LBL and id-LBL membranes were around 855 Da and 296 Da, respectively, by plotting their rejections against solute molecular weights. The mean value of the effective pore radius for those membranes were about 0.95 nm and 0.6 nm, respectively, estimated by the Donnan-steric-Pore (DSPM) model [26]. It seems that both membranes' pore sizes are within the range of NF membrane, but the inner deposition could achieve a much tightened pore structure than the outer deposition.

3.2 Nanofiltration performance

3.2.1. Single salt rejection tests

Three poly-cations, Poly(allylamine hydrochloride) (PAH), Poly(ethyleneimine) (PEI) and Poly (diallyldimethylammonium chloride) (PDADMAC), were used to form id-LBL membranes and tested with a 1000 ppm MgCl_2 solution under 2 bar pressure. The results are plotted and compared with outer deposited membranes in Fig. 4. It is clearly shown that the rejection for all inner deposited membranes were improved with a noticeable 100% increment of PDADMAC membrane, which was considered to be not capable for multivalent cation rejection in previous studies [10, 16]. Since the NF rejection is governed by both Donnan effect and size hindrance, the better rejection could probably due to a more effective selective layer with higher surface charge density and smaller pore sizes produced by the inner deposition, evidenced by the characterization results in Section 3.1. Among all, the PAH id-LBL membrane had the best rejection performance with a salt water permeability (SWP) of 9.8 LMH/bar and an over 98% Mg^{2+} rejection. Therefore, only PAH deposited membranes were used for further study.

The membranes were then challenged with an elevated salt concentration (4000 ppm MgCl_2 solution) at a higher operating pressure (4.8 bar). The od-LBL membrane **was squashed** quickly in the outside-in filtration configuration under this pressure. However, the id-LBL membrane could still maintain excellent performance (SWP of 8 LMH/bar and rejection of 97%) up to 8 hours of testing time. It suggests that the id-

LBL membrane can withstand higher operating pressures and thus is more suitable for the NF application.

In Table 4, the NF performance of the id-LBL membrane is compared with commercial NF membranes [10, 28], the best LBL membrane for cation separation reported previously [10] and some other chemically modified positively charged NF membranes [29-31]. Among all, the id-LBL membrane shows superior performance in terms of both water flux and MgCl_2 rejection. Only the positively charged commercial UTC-20 membrane has the comparable performance but it requires a considerably higher operating pressure of 10 bar.

3.2.2. Mixed salt rejection tests

The performance enhancement of the id-LBL membrane was more pronounced over the outer deposited ones in the mixed salt solution tests. In Table 5, the cation compositions of the 3000 and 5000 ppm TDS feed solutions are listed with the rejection performance of both membranes. It is known that rejection ability of the NF membranes is greatly influenced by the ionic strength of the feed solution. With increased counter-ion concentration, the membrane rejection based on the Donnan exclusion is weakened due to the screening effect while the steric hindrance gradually plays a more important role. In our experiments, it is obvious that the od-LBL membranes cannot effectively reject Mg^{2+} and Ca^{2+} when tested with a 5000 ppm TDS solution, while the id-LBL membranes can still maintain more than 90% rejection for both of them. This is probably also due to the higher surface charges carried by the id-LBL membrane in combination with smaller surface pores shown earlier on. Nevertheless, in all the cases, Na^+ rejection was much lower than that of Mg^{2+} and Ca^{2+} due to the co-ions competition where Na^+ with less charges and higher mobility was easier to pass through the membrane [32]. This is one of the crucial features for good NF membranes that the selective passage of monovalent co-ions could effectively reduce the osmotic pressure difference in the water softening process. However, the operating pressure still needs to be adjusted accordingly to overcome the elevated osmotic pressure caused by the feed solution. Otherwise, as shown in the last two rows (operated at 2 and 4.8 bar) of Table 5, both water permeability and ion rejection of the membrane would decline due to the lack of sufficient driving force.

3.2.3. Membrane stability tests

The id-LBL membranes were stored in either pH 2 or pH 12 solutions for 14 days to test their chemical stability. The pH value of the solutions was adjusted after each filtration test and the membrane lumen was refilled with the solution by a syringe. From the repeated test results shown in Fig. 5, only slightly flux drop with no rejection deterioration was observed during the testing period.

In addition, the mechanical strength (selective layer binding stability) of the id-LBL membrane were tested by 8 hours of high shear flow (6 times higher than the normal operation at 3.2 m/s) and 8 hours of back flush by DI water at 2 bar subsequently. Similarly, no noticeable flux and rejection drop of the tested membranes were obtained upon stability tests. Therefore, we can conclude that the id-LBL membrane possess superior chemical and mechanical stability with great potential in future practical application.

3.3 Forward osmosis performance

In our previous study, the six-layer od-LBL membrane was studied in FO process with considerable high water flux and low salt leakage by using low concentration $MgCl_2$ draw solutions [23]. Encouraged by the remarkable NF performance improvement by switching to inner surface deposition, the id-LBL membranes were also tested in FO experiments for both AL-facing-DS and AL-facing-FW orientations. As expected, with only two layer deposition, the id-LBL membrane demonstrated greater competency in terms of both improved water flux and reduced salt leakage.

In the AL-facing-DS configuration, a remarkable flux (J_v) increment (about 80% increase from ■ to □ data sets) could be achieved for the id-LBL membranes in all tested draw solution concentrations as shown in Fig. 6 (A). By comparing the same pair of salt flux over water flux (J_s/J_v) data in Fig. 6(B), it can be seen that because of the better $MgCl_2$ rejection, the id-LBL membrane is able to utilize the osmotic driving force from the draw solution more efficiently and thus can achieve higher flux than the od-LBL membranes.

However, the flux increment was not so obvious in the AL-facing-FW configuration with only about 20% increase from ● to ○ data sets. This is due to the dilutive internal concentration polarization which greatly reduces the effective osmotic

pressure in this configuration. Similar observation had been discussed in details in our previous study [23]. Nevertheless, the id-LBL membrane still produced the lowest J_s/J_v value with only around 0.03 g/L using 1 M $MgCl_2$ draw solution, as compared with reported data in the literature.

In Table 6, the FO performance of the id-LBL membrane using 0.5M $MgCl_2$ draw solution with DI water as feed solution is compared with other polyelectrolyte LBL FO membranes [33, 34] with glutaraldehyde [35] and UV crosslinking [36]. Despite the fewest modification steps involved, the id-LBL membrane is able to achieve the highest water flux with lowest reverse salt flux among all.

4. Conclusions

The LBL polyelectrolyte deposition was successfully applied on the inner surface of the PES hollow fiber substrate to form composite NF membrane. The deposition was carried out in a semi-dynamic process with the aid of syringes. The developed membranes were then characterized and tested in NF and FO applications and the performance were compared with our previous studies using outer surface deposition and literature data.

It is found that the id-LBL membranes were more suitable for NF application than the outer deposited ones not only because they could withstand higher operating pressure but also possess superior hardness rejection especially in high concentration mixed salt solutions. As for the FO process, with only two layer deposition, the id-LBL membranes also demonstrated significant performance improvement with increased water flux and reduced salt leakage. Therefore, it can be concluded that for the hollow fiber substrate, the inner surface is more suitable for LBL deposition than the outer surface. In further experiments, the deposition formula will be further optimized to enhance the water permeability. The feasibility for the pilot scale study will also be explored.

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