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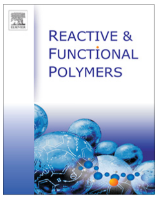

Enhanced hollow fiber membrane performance via semi-dynamic layer-by-layer polyelectrolyte inner surface deposition for nanofiltration and forward osmosis applications

Chang Liu, Lei Shi, Rong Wang *

School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798, Singapore
Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, Singapore 637141, Singapore

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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 fiber 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 L/m^2 h using 0.5 M $MgCl_2$ as draw solution in active layer facing draw solution configuration) and reduced salt leakage (around 0.5 g/m^2 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.

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].

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 Cl^-/SO_4^{2-} or Na^+/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 $Cl^-/H_2PO_4^-$ selectivity of 310 and a flux of 13.53 m^3/m^2-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

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* Corresponding author.
E-mail address: rwang@ntu.edu.sg (R. Wang).

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Table 1
Characteristics of PES hollow fiber substrate.

Dimension			Porosity ε (%)	MWCO outer/inner surface (kDa)	Mean pore size D^* (nm)	Standard deviation σ	Pure water permeability (LMH/bar)	Tensile modulus (MPa)	Stress at break (MPa)	Strain at break (%)
OD (μm)	ID (μm)	Thickness (μm)								
1480	1080	200	84	39 56	10.9	1.04	350	70.4	3.64	66

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.

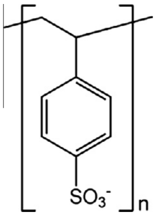
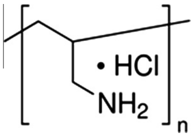
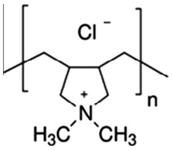
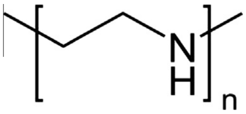
Based on our groups' past experience of interfacial polymerization on the inner surface of various hollow fiber UF membrane substrates [21,22], it is believed that the inner surface modification may possess several advantages over the shell side: (1) the lumen surface of the hollow fiber substrate is 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 = 120 k–200 k 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 ($CaCl_2$) and magnesium chloride ($MgCl_2$) (Merck) were used for NF and FO performance

Table 2
Polyelectrolyte structure and functional groups.

Name	Molecular structure	Functional groups
Poly(styrene sulfonate) **PSS**		SO_3^-
Poly(allylamine hydrochloride) **PAH**		NH_3^+
Poly(diallyl-dimethylammonium chloride) **PDADMAC**		NR_4^+
Poly(ethyleneimine) **PEI**		NH_3^+ NRH^{2+} NR_2H^+