



# Preparation of low-pressure water softening hollow fiber membranes by polyelectrolyte deposition with two bilayers



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## HIGHLIGHTS

- Low-pressure NF hollow fibers were prepared by polyelectrolyte deposition.
- Performance of the membranes prepared using different poly-cations was evaluated.
- Deposition condition was optimized to obtain high performance for water softening.
- High  $Mg^{2+}/Ca^{2+}$  rejections were obtained by two bilayers of polyelectrolyte deposition.

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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 (SWF) of 12 LMH/bar and 94%  $Mg^{2+}$  rejection was 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.

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## 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 the 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 the UV-initiated graft polymerization of methacrylateethyl trimethyl ammonium chloride (DMC) onto polysulfone membranes. The resultant membranes demonstrated a 94.8%  $MgCl_2$  (1000 ppm) rejection accompanied with a flux of

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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%  $\text{MgCl}_2$  (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 the preparation of NF membranes is the 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 becomes 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 are 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 the size-selective passage of uncharged solutes [35], for the 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 bilayer deposition, the LBL membrane performance on separating  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  was 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 (Mw) = 500 kDa) was purchased from Alfa Aesar. Poly(sodium 4-styrenesulfonate) (PSS, Mw = 70 kDa), Poly(diallyldimethylammonium chloride) (PDADMAC Mw = 120–200 kDa, 20 wt.% in water), Poly(ethylenimine) (PEI, branched, average Mw  $\approx$  250 kDa) and Poly (allylamine hydrochloride) (PAH, Mw = 56 kDa) were purchased from Sigma-Aldrich. Poly (allylamine hydrochloride) (PAH, Mw = 120000–200 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 ( $\text{NaCl}$ ,  $\geq 99\%$ ), magnesium chloride ( $\text{MgCl}_2$ , hexahydrate), and calcium chloride ( $\text{CaCl}_2$ , dehydrate) were purchased from Merck. Deionized water (Milli-Q, 18.2 M $\Omega$  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 0.5 kN 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 analyzed by gel permeation chromatography (GPC) on a Polymer Laboratories-GPC 50 plus system (double PL aquagel-OH Mixed-M 8  $\mu$  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].

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