



Investigation on the removal performances of heavy metal ions with the layer-by-layer assembled forward osmosis membranes



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HIGHLIGHTS

- Removal of heavy metal ions by LbL assembled FO membranes was investigated.
- The five heavy metal ion rejection during the FO process exceeded 99.31%.
- Heavy metal ion adsorption on FO membranes played an important role in the high rejection.

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ABSTRACT

The removal performances of heavy metal ions with the layer-by-layer (LbL) assembled forward osmosis (FO) membranes were investigated in this study. The prepared FO membrane with the multi-layer polymer network was fabricated by assembling multiple polyethylenimine (PEI) and sodium alginate (SA) bilayers on a polydopamine-functionalized polyvinylidene fluoride (PVDF) supporting membrane. The prepared FO membrane possessed high rejection of five heavy metal ions, i.e., Cu^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} . The influences of different osmosis modes, number of bilayers, pH, time, temperature, regeneration as well as the concentration of feed and draw solutions on the heavy metal ion removal performances of the FO membrane were studied. Results showed that all the heavy metal ion rejections with the 3-layer assembled FO membranes exceeded 99.31% in AL-FS (the active layer facing the feed solution) mode when 1 M MgCl_2 was employed as the draw solution, and the rejection in AL-FS mode was higher than that in AL-DS (active layer facing the draw solution) mode. The experimental results revealed that the number of bilayers of the polyelectrolyte pairs, the hydrated radii of metal ions and the heavy metal ion adsorption all contributed to the high rejection of the heavy metal ions.

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1. Introduction

Many of the fresh water resources are severely polluted, especially by heavy metal ions in recent years along with the development of the industry [1]. Heavy metal pollution is easy to cause severe health problems such as minamata and itai-itai diseases [2]. In order to effectively remove the heavy metal ions from water, a variety of methods have been applied, including reverse osmosis (RO), nanofiltration (NF), floating, chemical precipitation, ion exchange, reduction and adsorption [3–5]. By comparison, the emerging forward osmosis (FO) technique have lots of superiority, including high salt rejection, low fouling propensity and environ-

mental friendliness [6–12]. This makes the FO technique a potential application prospect in treating waters and wastewaters containing heavy metal ions.

The properties of the FO membranes, as well as the compositions of feed and draw solutions affect the rejection efficiency of pollutants. The rejection of heavy metal ions in wastewater by means of the FO process has been reported. For instance, Cui et al. reported a thin film composite (TFC)-type FO membrane for treating heavy metal wastewater, with the water flux of 16.5 LMH and the heavy metal ion rejection of 99.7% [11]. Zhao et al. achieved the heavy metal ion rejection of more than 93% using both the cellulose triacetate (CTA) FO membrane and a TFC-type FO membrane, for the treatment of Ni^{2+} ions in wastewater with high salinity [12]. Therefore, the FO membranes can achieve both the high rejection of heavy metal ions and the moderate water flux in treating heavy metal wastewaters.

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The LbL polyelectrolyte assembled membrane is a promising candidate material for the removal of heavy metal ions. Various polyelectrolyte membranes have recently been fabricated as FO membranes using the simple LbL technology, which is able to fabricate ultrathin films with adjustable surface morphology and precise controllable thickness [13–18]. In addition, the internal structure of the LbL assembled layers owning dense charges has size and charge repulsion functions towards the heavy metal ions. Many reports showed that the rejection of Mg^{2+} was higher than that of Na^+ using the LbL assembled FO membranes [13–18]. However, heavy metal ions are usually multivalent ions that feature large hydrated radii and hence are possible to be rejected by the LbL assembled FO membranes.

Recently, polydopamine (PDA) has drawn much research interest due to its wide application as the surface modification agent and its multiple functional groups for further functionalization [19–22]. PDA-modified porous PVDF ultrafiltration membranes enhance the hydrophilicity and surface charge features on the membrane surface [23,24], which also provide the immobilization sites for the deposition of polyelectrolytes. Therefore, PDA-modified PVDF membranes provide a good basis for the fabrication of LbL assembled FO membranes. To our best knowledge, no reports have been published so far regarding the removal of heavy metal ions using the LbL assembled PVDF-based FO membranes. The investigation on the heavy metal ion removal performances with the LbL assembled PVDF-based FO membranes would expand the application of the PVDF-based membranes, and provide more insight into the FO performances with the LbL assembled FO membranes.

In this study, the LbL assembled FO membrane was fabricated by assembling multiple polyethylenimine (PEI) and sodium alginate (SA) bilayers on a PDA-functionalized PVDF support. The influences of the number of bilayers of the polyelectrolyte pairs, different FO modes, the pH of the feed solution, time, temperature, regeneration as well as the concentration of draw and feed solutions were investigated on the removal of heavy metal ions.

2. Experimental

2.1. Materials

Polyvinylidene fluoride (PVDF, MG15) was purchased from Arkema. Poly(ethylene glycol) (PEG, Mn = 11 kDa), dopamine hydrochloride (DA, AR, 98%), tris (hydroxymethyl) aminomethane (Tris, AR, $\geq 99.8\%$), hyperbranched polyethyleneimine (PEI, Mn = 600 Da, 99%), copper sulfate ($CuSO_4$), zinc nitrate ($Zn(NO_3)_2$), nickel nitrate ($Ni(NO_3)_2$), lead nitrate ($Pb(NO_3)_2$) and cadmium nitrate ($Cd(NO_3)_2$) were purchased from Aladdin Reagent Co. Ltd. Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, AR, 98%), acrylic acid (AA, AR, $>99\%$), sodium alginate (SA, with the viscosity of 200 ± 20 mPa·s), and *N,N*-dimethyl acetamide (DMAc, AR, 99%) were purchased from Macklin Reagent Co. Ltd. The deionized (DI) water was produced by an ULUPURE ultrapure water system (ULUPURE, China).

2.2. Preparation of PDA modified PVDF membranes

PVDF substrate was prepared using the phase inversion technique [25–27]. A membrane casting solution containing 15% PVDF, 76% DMAc and 9% PEG was prepared, which was subsequently poured onto a clean glass plate and spread using a 100 μm stainless steel scraper. The plate with the cast polymer membrane was then immediately put into a water bath (25 °C) for phase inversion and immersed for 48 h in DI water for eliminating the residual solvent and pore-forming agent.

In order to introduce the positive charges and increase the hydrophilicity of the PVDF membrane substrate, the upper side of the PVDF membrane was saturated in 2 g/L DA Tris-AA buffer solution (200 mM, pH = 8.5) and reacted for 5 h in a shaker with the shaking speed of 120 r/min at the temperature of 60 °C for the preparation of the PDA-modified PVDF membrane (PDA-PVDF). After the reaction, DI water was used to clean the membrane surface and remove the physically-attached PDA.

2.3. Preparation of the LbL assembled FO membrane

In this study, SA and PEI were used as the polyelectrolytes for the formation of the LbL assembled FO membrane through the manual dip-coating method at room temperature of 25 °C. 5 mg/mL SA and 5 mg/mL PEI aqueous solutions were both prepared. The positively charged PDA-PVDF was first fixed in a laboratory-prepared mold, with only the upper surface allowed to be in contact with the reaction solution. Then, the polyanion SA solution was poured onto the upper surface of the PDA-PVDF in the mold and allowed to stay for 5 min, and the excess of the SA solution was removed afterwards, followed by three times of DI water rinsing. After that, the polycation PEI solution was poured in the mold and allowed to stay for 5 min. The excess PEI solution was then removed, and the prepared membrane surface was rinsed again by water for three times. As a result, one pair of the SA/PEI polyelectrolytes was deposited onto the membrane surface. In this paper, one layer of polyelectrolytes is defined as the deposition of one pair of the SA/PEI polyelectrolytes, and thus n-layer LbL assembled FO membrane refers to the FO membrane with the deposition of n pairs of SA/PEI polyelectrolytes.

2.4. Membrane characterizations

Field emission scanning electron microscope and an energy-dispersive X-ray spectroscopy unit (FESEM & EDX, JSM-7800F & TEAM Octane Plus, JEOL, Japan) were used to observe the surface morphologies and the element compositions, respectively, of the prepared membranes. The hydrophilicity property of the membrane samples was measured using the water contact angle (WCA) testing equipment (SDC-70, Shengding, China). The WCA measurement was conducted at six different places of the membrane sample surface and the average value was used for the hydrophilicity analyses. Attenuated total reflectance fourier transform infrared spectroscopy (ATR-FIR, Bruker V70, Germany) was used to analyze the surface functional group compositions of the prepared membranes. Each sample was scanned for 128 times in the range of 600–4000 cm^{-1} at the resolution of 4 cm^{-1} . X-ray photoelectron spectrometer (XPS, Thermo Fisher Scientific ESCALAB 250Xi) was used to examine the oxidation state of the surface elements of the prepared membranes.

The water permeability (A , $L m^{-2} h^{-1} bar^{-1}$, denoted as $LMH bar^{-1}$), salt permeability B ($L m^{-2} h^{-1}$, denote as LMH) and salt rejection (R , %) of the LbL assembled FO membranes were determined by testing the prepared membranes under pressure in a lab-scale RO unit and pre-compacted for 0.5 h under 1 bar, with DI water and 10 mM $MgCl_2$ solution as feed solutions, respectively.

The water permeability, A ($LMH bar^{-1}$), is calculated according to Eq. (1).

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

where ΔQ (L/h) is the permeation volume of the pure water flow during the permeation time (h), A_m is the effective area of the membrane (m^2) which is fixed at 9 cm^2 , and ΔP (bar) is the pressure difference across the membrane.

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