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Efficient removal of heavy metal ions based on the optimized dissolution-diffusion-flow forward osmosis process

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ABSTRACT

In order to efficiently remove the heavy metal ions in wastewater, a novel thin film composite (TFC)-type forward osmosis (FO) membrane was prepared specifically with the glass nanofiber supporting layer and the bovine serum albumin (BSA)-embedded polyamide (PA) swellable active layer, and used for the removal of heavy metal ions from water by enhanced dissolution-diffusion-flow FO process. The separation results indicated that the appropriate addition of BSA in the PA active layer improved the dissolution-diffusion process of the traditional PA layer by providing the swellable sites as water channels in aqueous solutions and enhanced the rejection effect on heavy metal ions. In addition, the ultra large porosity and pore size of the glass nanofiber supporting layer provided smooth flow channels, accelerating the flow process and alleviating the concentration polarization problem, with the structural parameter (S) value decreasing to 172 μm. This paper proved that the specific structural construction of the functional membranes was a convenient method to prepare applicable membranes with tunable FO performances.

1. Introduction

Heavy metal pollution is a serious environmental issue, which has a great harm to human health. The efficient removal of heavy metal ions in water has been a hot research topic in the field of wastewater treatment. In recent years, forward osmosis (FO) technology has shown broad application prospect in seawater desalination, water treatment and energy conversion [1–3]. It is well known that FO membranes show the considerable removal effect on the monovalent salt ions, which provides an excellent basis for the removal of multivalent metal ions from aqueous solutions. However, there are several drawbacks in the FO application process, such as low separation efficiency and serious concentration polarization. Therefore, the efficient preparation of the FO membrane with a high separation performance is the focus of the current research field in FO processes [4,5]. A large number of studies have shown that thin film composite (TFC)-type FO membranes have the expected separation performance, and both HTI and Oasys Water companies have realized the commercialization of the TFC-type FO membranes. At present, much research work is mainly focused on the modification of the active layer and the porous supporting layer of the TFC-type FO membranes to improve the separation efficiency [6–10].

Based on the double layer structure of the TFC-type FO membranes, the active layer and the supporting layer play different roles in the FO separation process. Therefore, it is necessary to analyze the separation functions and defects of the dense active layer and the porous supporting layer separately to optimize the separation performance [4,6]. For the active skin layer, it is the functional region for the separation of water molecules by means of the dissolution-diffusion process, as well as the speed-limiting step of the whole separation process. Therefore, the efficiency of the active layer determines the separation efficiency of the FO membrane. In order to ensure a good separation performance, the active layer should have a certain density to ensure the accurate rejection to salt ions, and a certain free volume for the swelling effect to accelerate the diffusion and permeation of water molecules. The existing active layers of the commercial membranes and experimental FO membranes are mainly made of polyamide (PA) and PA-based derivatives [2]. The highly cross-linked structure greatly limits the dissolution-diffusion process of water molecules in the PA layer, forming great diffusion resistance which reduces the separation efficiency of the FO membrane. It is well known that there are efficient water channels in nature, such as aquaporins, which can be used as efficient and selective channels for water molecules [11–14]. It can be deduced that if the water molecule channel is constructed in the active layer, the water permeation efficiency of the FO membrane would be improved. Therefore, we propose to construct a local swelling channel in the active layer to reduce the permeation resistance of water molecules

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through the active layer, while retaining the rejection ability to salt ions. The functional medium is added into the active layer to construct the local swelling region providing free spaces and channels, which would accelerate the separation process in both the dissolution and diffusion processes [15]. As far as we know, bovine serum albumin (BSA) has a large number of amino acid residues with the reported sizes of 4–8 nm, and is a partially swellable amphiphilic macromolecule, which is suitable for the construction of the nano-scale swellable water channels [16–20]. In addition, there are strong interactions between BSA and the organic macromolecules, heavy metal ions and other solutes in the feed solution, showing the rejection capacity.

For the porous supporting layer, it provides the supporting effect and the flow channels for the FO process [3]. The existing studies have proved that the porous supporting layer of the FO membrane requires large porosity, low tortuosity factor and excellent hydrophilicity. The nanofiber membrane is considered to be one of the most excellent supporting layers ever reported, including the PVDF and PVA nanofiber membranes [21–24]. However, such polymer-based nanofiber membranes are generally produced by electro-spinning technique, which may be a costly and time-consuming process. In contrast, the commercialized glass nanofiber membrane has a better application prospect, due to the advantages of strong heat resistance, good corrosion resistance, excellent hydrophilicity, low cost, high porosity and good mechanical strength, which can be used as an ideal supporting material for the TFC-type FO membranes [25].

In this paper, a novel TFC-type FO membrane was prepared by the interfacial polymerization method, with the porous glass nanofiber as the supporting layer and the BSA-modified PA as the swellable active layer. The physical and chemical structures of the prepared FO membrane were characterized and the separation performances under different conditions (e.g., the feed solutions containing pure water and heavy metal ions) were investigated. The purpose of this paper is to provide a convenient preparation method to improve the application separation performance of the FO membranes based on the improved dissolution-diffusion-flow mechanism.

2. Experimental

2.1. Materials

Trimesoyl chloride (TMC, 98%), m-phenylenediamine (MPD, 99%), n−hexane (> 98%) and sodium chloride (NaCl, > 99.5%) were all purchased from Aladdin (China). Bovine serum albumin (BSA, Mw ~ 67000 Da) was purchased from Sinopharm Group (China). The glass nanofiber membranes with the thickness of 300 μm, pore size of 0.8 μm and porosity of 95% were purchased from Taoyuan Chemical Company (Haining, China), and the surface morphology of the glass nanofiber membrane was shown in Fig. 1. The polyvinylidene fluoride (PVDF, 0.03 μm and 0.22 μm) and polyether sulfone (PES, 0.8 μm) porous membranes used as the reference samples were also purchased from Taoyuan Chemical Company (Haining, China). Copper sulfate ($CuSO_4$), lead nitrate ($Pb(NO_3)_2$) and cadmium chloride ($CdCl_2$) were all purchased from Aladdin (China). The deionized water (18.25 MΩ*cm) used in the experiments was produced by an ultrapure water system.

Table 1
The aqueous and organic phase solutions for the fabrication of the FO membranes.

Membrane	MPD in aqueous (water) phase (wt%)	BSA in aqueous (water) phase (wt%)	TMC in organic (hexane) phase (wt%)
MB-0	4	0	0.6
MB-1	3.9	0.1	0.6
MB-2	3.8	0.2	0.6
MB-3	3.6	0.4	0.6

2.2. Membrane preparation

The FO membranes were prepared by the conventional interfacial polymerization method. The glass nanofiber membrane was placed in a mold in which a single-sided interfacial polymerization was performed. The aqueous phase solution was poured onto the membrane surface, and the excess solution was removed after 1 min with the adsorptive paper. The organic phase solution containing TMC was then poured onto the membrane surface and reacted for 30 s, followed by the removal of the excess organic phase solution. Finally, the prepared FO membranes were dried in an oven at 80 °C for 1 h, and stored in a vacuum oven for the subsequent characterization and performance tests. The specific compositions of the above-mentioned organic phase and aqueous phase solutions were shown in Table 1. The preparation conditions of the reference samples (PVDF-0.03, PVDF-0.22, PES-0.80) were consistent with those of the MB-0 membrane shown in Table 1.

2.3. Membrane characterization

2.3.1. Physical and chemical properties

The surface and cross-section morphologies of all the prepared membranes were observed using a Field Emission Scanning Electron Microscope (FESEM, JSM-7800F, JEOL, Japan). The samples were pretreated for 60 s for the sputter-coating of a gold layer before the FESEM observation. The surface chemical compositions of the membrane samples were measured using the X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi), with an incidence angle of 90 degrees. The surface wetting properties of all the prepared FO membranes were tested with the water contact angle (WCA) measuring system (SDC-70, Shengding, China). The WCA was tested on six different positions of the membrane surface, and the average value of the measured WCAs was used for the analyses.

2.3.2. Swelling property evaluation of the active layer

The swelling behavior of the active layer was achieved by

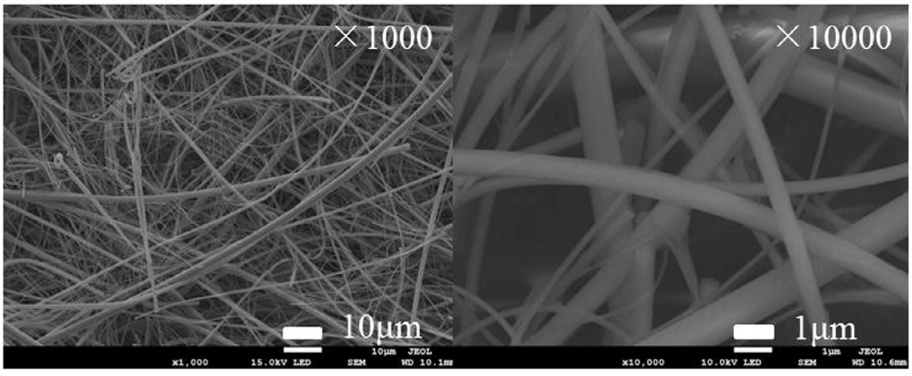

Fig. 1. SEM images of the glass nanofiber membrane.