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Mixed polyamide-based composite nanofiltration hollow fiber membranes with improved low-pressure water softening capability

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ABSTRACT

Mixed polyamide-based composite nanofiltraiton (NF) hollow fiber membranes with suitable characteristics for water softening under ultrafiltration (UF)-range low operating pressure were successfully developed. The thin-film selective layer of the composite membrane was formed via interfacial polymerization on the inner surface of a microporous polyethersulfone (PES) hollow fiber substrate with trymesoyl chloride (TMC) being the organic phase monomer, and a mixture of branched polyethyleneimine (PEI) and piperazine (PIP) being the monomers in the aqueous phase.

In was found that there was a synergetic effect of PEI and PIP on the formation of the selective layer. The water permeability and salt rejection of the resultant membrane were both enhanced with a small amount of PIP added into the PEI aqueous phase, but dropped quickly with a higher PIP to PEI ratio. The optimized NF membrane possessed a molecular weight cut-off (MWCO) of 380 Da, an effective pore diameter of 1.27 nm, and pure water permeability (PWP) of 18.2 l/m^2 h bar. Under an operating pressure of 2 bar, the membrane exhibited rejection of 96.3% and 93.8% to 1000 ppm $MgCl_2$ and $MgSO_4$ feed solutions, respectively. The capability of the newly developed membrane for low-pressure water softening was evaluated by employing simulated hard water feed solutions with different ionic compositions and total hardness. By the combining effect of electrostatic repulsion and size exclusion, the mixed PEI/PIP-based composite hollow fiber offered superior water softening performance compared with the membranes made with PEI or PIP alone as the aqueous phase IP monomer.

1. Introduction

Water softening, a process to remove abundant calcium and magnesium cations as well as other water hardening minerals from raw water stream, is not only indispensable to the domestic and industrial water supply, but also important as a pre-treatment process for brackish water and seawater desalination to improve water recovery by minimizing membrane scaling [1]. Different from conventional water softening methods involving ion-exchange resin, zeolite or lime-soda ash treatments, water softening via membrane is a one-stage process that serves the role of hardness removal and the rejection of bacteria, virus, natural organic compounds and other undesirable chemical compounds simultaneously [2]. With the rapid development of nanofiltration (NF) technology in recent years, it becomes possible to selectively remove divalent cations from monovalent ions under an operating pressure much lower than typically applied pressure in reverse osmosis (RO). Thus membrane softening has great potential to supersede traditional water softening methods in terms of effectiveness and operating costs, especially for the effective removal of major hardness contributing ions from raw water with high salt concentration such as brackish water [3,4], seawater [5,6] and desalination concentrate [7].

Most commercial NF membranes with water softening capability such as NF series manufactured by Filmtec, Desal series by GE-Osmonics, and ESNA series by Hydranautics, are thin-film composite flat sheet membranes with an interfacially polymerized polyamide selective layer [8,9]. The water softening performance of the composite NF membrane is mainly determined by the hydrophilicity, charge and structure of the thin-film active layer, which is basically controlled by the interfacial polymerization (IP) monomers that formed the layer. As a result, the effect of different IP monomers on the polymerization process and the characteristics of the resulted thin film were thoroughly investigated in the past decade. Although piperazine (PIP) and trymesoyl chloride (TMC) were accepted as the most established monomer pair for commercial NF membrane fabrication, various types of amine

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[10–12], acyl chloride [13,14], alcohol [15] and isocyanate [16] were also studied as the IP monomers to develop novel composite NF membranes with improved permeation flux and divalent ion rejection at lower operating pressure, better chemical tolerance and fouling resistance.

As an alternative to PIP and other monomeric amine monomers, polymeric amines such as polyethyleneimine (PEI) [17], polyamidoamine [18] and polyvinylamine [19] were used as the aqueous phase monomers for the thin film synthesis. Due to the excess amine groups in the polymer chain, polymeric amines usually yield polyamide thin-film active layer with a lower cross-linking degree. NF membranes with higher permeation flux could therefore be obtained, which are able to reduce the required operating pressure for water production and reduce energy consumption. Moreover, unlike conventional negatively charged polyamide thin film made from monomeric IP monomers, the excess amine groups also result in positively charged membrane surfaces. This unique feature makes the membrane more favorable for water softening applications, as divalent metal cations could be better rejected by the positively charged membrane through electrostatic interaction (Donnan exclusion) in addition to the normal steric (size exclusion) effect [20].

In our previous work [21], a type of positively charged NF membrane was prepared with suitable characteristics for water softening under ultrafiltration (UF)-range low operating pressure. The polyamide thin-film selective layer was formed through IP technique on the inner surface of a polyethersulfone (PES) UF hollow fiber membrane substrate with branched PEI and TMC employed as the monomers in aqueous and organic phases, respectively. As an extension of our previous work, the fabrication of mixed polyamide-based composite NF hollow fiber membranes were reported in current study. The resultant hollow fiber membrane was found to exhibit improved low-pressure water softening performance comparing to NF hollow fibers prepared with PEI or PIP alone as the aqueous IP monomer in the IP process. The synergetic effect of PEI and PIP on the formation of the selective layer was investigated thoroughly.

2. Experimental

2.1. Membrane material and chemicals

The PES UF hollow fiber substrate was fabricated by the phase inversion method through a dry-jet wet spinning process, which has been reported elsewhere [22,23]. The inner and outer diameters of the hollow fiber substrate are 1.01 and 1.37 mm, whereas the pure water permeability and molecular weight cut-off (MWCO) of the substrate fibers are around 270 l/m^2 h bar and 45 kDa, respectively.

Branched polyethyleneimine (PEI) with molecular weights of 50,000–100,000 (MP Biomedicals), piperazine (PIP, Merck), trimesoyl chloride (TMC, Sigma-Aldrich), sodium dodecyl sulfate (SDS, Reagents), and cyclohexane (Merck) were used for the synthesis of thin-film selective skin layer. A series of neutral solutes including glucose, sucrose, and raffinose, and different analytical grade salts including $MgCl_2$, $MgSO_4$, NaCl, Na_2SO_4 and $CaCl_2$ (Merck) were involved in the preparation of various single and mixed solute feed solutions with pH of around 6.5. Deionized water (Milli-Q, 18 MΩ cm) was employed for the aqueous solution preparation, and all chemicals were used as received.

2.2. Preparation of composite NF hollow fibers by interfacial polymerization

The detailed procedure for the preparation of interfacially polymerized composite NF hollow fiber membranes was reported in our previous work [21]. In the current study, an aqueous solution was prepared to contain a mixture of PEI and PIP with total amine concentration ranging from 0.05% to 1% (w/v) by varying their mixing ratio, and SDS (0.1% (w/v)) at a solution pH ranging from 9 to 12 adjusted by adding sodium hydroxide and hydrochloric acid. This solution was firstly brought into the lumen of the substrate fibers and in contact with the fiber inner surface for 30 min. After purging the excess aqueous amine solution with pure cyclohexane, a TMC organic solution (0.1% (w/v) in cyclohexane) was slowly pumped through the fiber lumen (30 ml/min) for 2 min to allow the IP reaction to take place. The fibers with an IP thin-film layer formed on the fiber inner surface were rinsed with and stored in DI water afterwards for further uses.

2.3. Hollow fiber characterization

The physiochemical properties of the composite NF hollow fiber membranes made from mixed PEI/PIP were examined thoroughly via a series of standard characterization techniques as described previously [21,24], and compared with composite fibers made using PEI or PIP alone as the aqueous phase monomer. Briefly, the morphology of hollow fiber membranes was observed by a field emission scanning electron microscope (FESEM, JEOL, Japan), while the membrane surface topology and roughness were examined using an atomic force microscope (AFM, Park system, Korea) via the noncontact mode. Besides, the chemical composition of the thin-film selective layer was analyzed using a Fourier transform infrared spectrometer (FTIR, Shimadzu, Japan) via the attenuated total reflection (ATR) method, whereas membrane surface charge characteristics were measured by the streaming potential method using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria). Furthermore, the wettability of the membrane was determined by dynamic contact angle measurements using a tensiometer (Data Physics, Germany), and the fiber mechanical properties were characterized by the tensile strength test using a universal testing machine (Zwick, United Kingdom).

2.4. Nanofiltration experiments

The lab-scaled membrane module was made by potting 4 pieces of hollow fibers into a PTFE tube with an effective length of 18 cm. NF experiments were initiated by circulating DI water through the lumen of the membrane module under a trans-membrane pressure of 2 bar, while the permeate was collected from the shell of the module. After the membrane went through compaction with DI water for about 1 h, the membrane pure water permeability, PWP (l/m^2 h bar), was measured under consistent operating pressure (2 bar) and calculated as follows:

$$PWP = \frac{F}{\Delta P} = \frac{Q}{A\Delta P} \tag{1}$$

where F is the permeation flux (l/m^2 h), ΔP is the trans-membrane pressure (bar), Q is the volumetric permeation flow rate (l/h), and A is the effective membrane filtration area (m^2).

Afterwards, the newly developed composite NF hollow fiber membranes were further tested by applying various single solute feed solutions successively. Membrane pore size and molecular weight cut-off (MWCO) were estimated by the rejection to neutral organic solutes, whereas membrane charge properties were characterized by inorganic salt feed solutions. Finally, the water softening performance of the membrane was evaluated via a series of simulated hard water feed solutions with a mixture of ionic species. All solute separation experiments were conducted under the same low operating pressure (2 bar), and the solute rejection,