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High-performance polyamide thin-film composite nanofiltration membrane: Role of thermal treatment

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ABSTRACT

Nanofiltration (NF) membranes have many excellent applications (e.g., removing multivalent ions and pretreating water before reverse osmosis, RO), but their relatively high cost limits their application. Especially in recent years, researchers have paid substantial attention to reducing the cost of NF membranes. In this paper, high-performance NF membranes were fabricated using interfacial polymerization (IP) methods. The polymer concentration, IP solution concentration, and thermal treatment conditions were varied. The synthesized membranes were characterized using scanning electron microscopy (SEM), atomic force microscopy (AFM), a contact angle goniometer, X-ray photoelectron spectroscopy (XPS), attenuated total reflectance fourier transform infrared (ATR-FTIR) spectroscopy, and performance tests. The results show that water flux was significantly improved using a hot-water thermal treatment method. Our fabricated thermal-treated NF membrane had an approximately 15% higher water permeability with a value of 13.6 L/(m^2 h bar) than that of the commercially available GE HL membrane with a value of 11.8 L/(m^2 h bar). Our membranes had the same $MgSO_4$ rejection as that of the GE HL membrane. We found that the thermal treatment causes the NF membrane surface to be smoother and have a high crosslinking degree.

1. Introduction

Global water resources have been declining and are becoming more polluted [1–4]. The estimated worldwide water demand will increase from 4500 billion m^3/year to at least 6900 billion m^3/year by 2030 [5]. It is estimated that 3.5 million people will die due to fresh water depletion and water-borne diseases [6,7]. Accordingly, the development of novel and low-cost water treatment technologies and access to clean and sanitized water are imperative [5,8–10]. Nanofiltration (NF) can be incorporated into a treatment plant to treat and reuse wastewater and to increase the drinking water supply [8,11–17]. NF membranes have been increasingly used in recent years [3,18–20]. NF is the latest membrane technology applied to drinking water purification [9,21], and the transmembrane pressure [13,22] is between that of reverse osmosis (RO) and ultrafiltration (UF) [11,23]. NF has excellent separation capabilities, selective performance and a lower operation pressure than RO, resulting in a lower cost [11]. NF can efficiently remove many of the pollutants in reclaimed water, such as ionic compounds [24], organic compounds, bacteria, and viruses [25–27]. NF can be easily used or combined with other treatment technology to remove some specific components of water and wastewater [28–32].

One of the limitations of NF is increased membrane fouling compared with that of microfiltration (MF) and ultrafiltration (UF) due to the smaller pores of the NF membrane than those of MF and UF membranes [33]. More specifically, polyamide NF membranes have hydrophobic aromatic groups and a high cross-linking degree, which lower the water flux and increase desalination costs [5,10]. Many studies have reported the use of various reactant materials to form the active layer of the polyamide NF membrane [34–36]. The studies used chemical reactions between the amine groups on a diamine monomer and acyl chloride groups on the membrane surfaces to achieve a high permeate flux, pol-

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Table 1
The composition of the casting solution and IP solutions and the treatment methods.

Membrane ID	PSf (g)	NMP (g)	IP Solution A			IP Solution B			Thermal treatment
			Piperazine	NaOH	DI Water	TMC (μL)	Isophthaloyl Chloride (g)	Solvent 500 mL	
M1	15	85	1 wt.%	0.7 wt.%	1 L	835	2.4817	Isopar-G	NO
M2	15	85	1 wt.%	0.7 wt.%	1 L	835	2.4817	Hexane	NO
M3	18	82	2 wt.%	0.1 wt.%	1 L	835	–	Isopar-G	95 °C Water Bath
M4	18	82	2 wt.%	0.1 wt.%	1 L	835	–	Isopar-G	NO
M5	15	85	2 wt.%	0.1 wt.%	1 L	835	2.4817	Isopar-G	95 °C Water Bath

lutant rejection, and good antifouling performance [37]. Choumou Zhou et al. investigated the natural material, sericin, as an aqueous phase reactant and 1,3,5-benzenetricarbonyl trichloride or trimesoyl chloride (TMC) as the organic phase solution to prepare the thin active layer of a novel thin-film composite NF membrane. Through interfacial polymerization (IP) on the porous polysulfone (PSf) substrate layer, the newly formed membrane had a better antifouling property to bovine serum albumin (BSA) and sodium alginate (SA) than that of the commercial membrane NF270 [38]. Yong-Jian Tang et al. fabricated a novel NF membrane with good chlorine resistance and desalination performance via the IP method applied to the porous PSf UF membrane using diamine monomers of piperazine (PIP) and 2,2'-bis(1-hydroxyl-1-trifluoromethyl-2,2,2-triflutoethyl)-4,4'-methylenedianiline (BHTTM) [39]. Recently, some novel low-pressure NF membranes have been successfully fabricated by using layer-by-layer deposition method, and these membranes can work under 2 bar low-pressures [40,41]. This kind of membrane has excellent potential for application and prospects, but there are still many research works that need to be done before large-scale applications. Based on a previous study [27], polyamide membranes have been fabricated commercially using interfacial polymerization with *m*-phenylenediamine (MPD) in the aqueous phase and TMC in the organic phase. Commercial NF membranes, such as HL, DK, DL (GE Osmonics, Minnetonka, MN, USA), NF90, NF270, NF245 (Dow, Minneapolis, MN, USA), VNF1, VNF2 (Vontron, Guiyang, China), NE 70, and NE 90 (Saehan, South Korea), are available for use. Some of these NF membranes were systematically characterized in previous studies [42,43]. Considering the potential for commercial applications, we focused on creating an improved NF membrane composed of an active polyamide layer with a PSf support.

The above-mentioned commercial membranes are proprietary products, and very little information about their fabrication is available. To better understand how to fundamentally improve the NF membrane performance, the polymer concentration, IP solution concentration, and the influence of thermal treatment on the membrane performance were investigated. The experimental design of these parameters was developed using the orthogonal experimental method to obtain high-performance nanofiltration membranes. In this study, we developed a high flux and high $MgSO_4$ rejection NF membrane via the IP method applied to PIP and TMC and used thermal treatment to improve the resulting membrane performances.

2. Materials and methods

2.1. Materials and chemicals

Ultrapure water with a resistivity of 18.2 MΩ cm was supplied by an ULUPURE ultrapure water purification system (Chengdu, China). Polysulfone (PSf) (CAS No. 25135-51-7, average Mn ~22,000 Da), 1-methyl-2-pyrrolidinone (NMP, CAS No. 872-50-4, anhydrous, 99.5%), hexane (CAS No. 110-54-3, anhydrous, 95.0%), piperazine (PIP, CAS No. 110-85-0, ReagentPlus®, 99%), 1,3,5-benzenetricarbonyl trichloride or trimesoyl chloride (TMC, CAS No. 4422-95-1, 98.0%), isophthaloyl chloride (CAS No. 99-63-8, ≥99.0%), sodium chloride (CAS No. 7647-14-5, ACS reagent, ≥99%), magnesium sulfate (CAS No. 7487-88-9, anhydrous, ReagentPlus®, ≥99.5%), and sodium hydroxide (NaOH, CAS No. 1310-73-2, reagent grade, ≥98.0%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Magnesium chloride (CAS No. 7791-18-6, AR), sodium sulfate (CAS No. 7757-82-6, AR) were purchased from Kelong Chemical (Chengdu, China). TMC was dispersed in Isopar-G, a proprietary nonpolar organic solvent (Univar, Redmond, WA, USA). All chemicals were used as received. A commercial polyester non-woven fabric (polyethylene terephthalate (PET), Grade 3249, Ahlstrom, Helsinki, Finland) was used as a backing layer for the PSf supports.

2.2. Fabrication of the TFC NF membrane

The supporting membrane was prepared by casting solutions containing PSf and NMP according to the compositions listed in Table 1. The casting solution of PSf and the NMP were prepared in 125-mL conical flasks and heated to approximately 60 °C under stirring at 500 rpm using Super-Nuova™ multi-position digital stirring hotplates (Thermo Fisher Scientific Inc., Waltham, MA, USA). After the polymers were dissolved completely and stirred for at least 24 h,

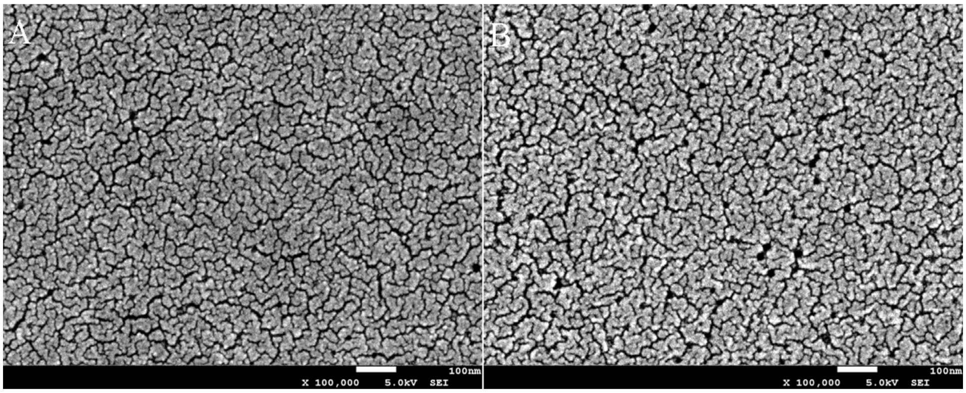

Fig. 1. Substrate layer of PSf with the different polymer concentrations of (a) 15 wt.% and (b) 18 wt.%.