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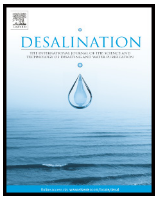

A homogeneous polysulfone nanofiltration membrane with excellent chlorine resistance for removal of Na_2SO_4 from brine in chloralkali process

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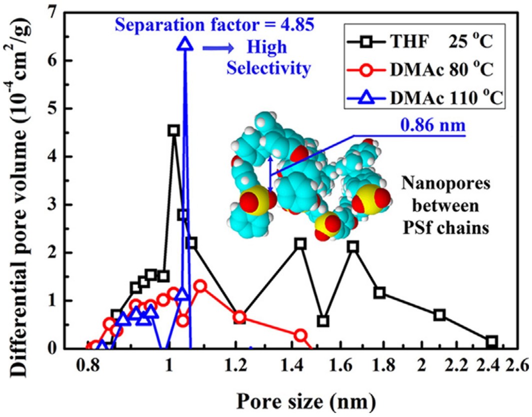
HIGHLIGHTS

- A homogeneous PSf NF membrane was fabricated by solvent evaporation method.
- The nanopores of the membrane were tunable around 1.0 nm.
- High rejection to Na_2SO_4 (>80%) and low rejection to NaCl (<15%) were observed.
- The membrane showed excellent chlorine resistance and tensile strength over 66 MPa.

GRAPHICAL ABSTRACT



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ABSTRACT

A homogeneous polysulfone nanofiltration membrane with a dense structure was fabricated by solvent evaporation method. Two solvents, tetrahydrofuran (THF) and dimethylacetamide (DMAc), were utilized to prepare the membranes with tunable pores around 1.0 nm. The pore size was affected by the solvent species, and it decreased when THF was replaced by DMAc. Correspondingly, the rejections to Na_2SO_4 of the membranes fabricated with DMAc (80–82%) were higher than those of the membranes fabricated with THF (65–67%). To further improve the performance, by applying a higher membrane formation temperature (110 °C), the pore size became even smaller and the rejection to Na_2SO_4 was improved to 87%. The feasibility of removing sulfate ions from brine by the membrane was proved by rejection to Na_2SO_4 of 80% and rejection to NaCl of almost zero in the mixed salt solution. The structure of the membrane was independent of the thickness, and thus the flux could be gradually improved by reducing the thickness while maintaining a high rejection. Moreover, the membrane had high mechanical strength larger than 66 MPa and excellent chlorine resistance. It kept good separation performance even after exposed to the 50,000 ppm sodium hypochlorite solution for 24 h.

Abbreviations: C_f, solute concentration of feed; C_p, solute concentration of permeate; D, solvent self-diffusion coefficient; DMAc, dimethylacetamide; d, membrane thickness; E, tensile modulus; FESEM, field emission scanning electron microscope; IC, ion chromatography; J_v, water volume flux; MF, microfiltration; NF, nanofiltration; NIPS, nonsolvent induced phase separation; P, water permeability; Δp, pressure difference; P_c, critical pressure for reliable water flux measurement; PA, polyamide; PSf, polysulfone; R, rejection; r_1, solvent loss rate; r_2, solvent diffusion rate; RO, reverse osmosis; S, separation factor; T, tensile strength; T_g, glass transition temperature; TGA, thermogravimetric analysis; THF, tetrahydrofuran; UF, ultrafiltration; w, solvent weight fraction; w^*, critical solvent weight fraction; ε, tensile strain; σ, tensile stress.

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1. Introduction

Chloralkali process is an important chemical industry process to produce sodium hydroxide, chlorine and hydrogen based on the electrolysis of saturated brine [1]. The brine contains various impurities including a significant amount of sodium sulfate (Na_2SO_4) [2]. The sulfate ions (SO_4^{2-}) can accumulate and adversely effect on the electrolyzer [3]. Chemical precipitation, crystallization, ion exchange and brine purging have been proposed for the removal of sulfate [4], but these methods suffer from either high capital/operation costs or environmental constraints [5]. Nanofiltration (NF) becomes a promising approach to effectively remove sulfate due to its high rejection to multivalent anion salts, low cost and environmental friendliness [6,7]. Commercial NF membranes developed for this process to date are mainly polyamide (PA) composite membranes [5,8,9]. However, PA networks are vulnerable to sodium hypochlorite (NaClO), which are used for oxidizing the organics such as algae and humic acid in primary brine purification. The degradation of PA occurs even at very low chlorine concentrations on the order of 1–10 ppb [10]. Costly additional de-chlorination steps are needed to prevent the chemical oxidation of PA membranes [11]. Therefore, it's highly desired to develop novel NF membranes from chlorine-resistant materials for removing Na_2SO_4 from brine in the chloralkali process.

Polysulfone (PSf) is one of the most important membrane materials owing to its good mechanical, thermal and chemical stabilities. It has been widely used to fabricate porous membranes from microfiltration (MF) to NF because of its excellent film-forming properties [12]. In order to obtain good NF performance for separating multivalent and monovalent salts, it is crucial to control the size of the nanopores of PSf membranes. Grafting polymerization on PSf UF membranes has provided an access to NF membranes [13–16], but the complex chemical reactions and multiple preparation steps restrict their industrial production. Alternatively, a one-step method, nonsolvent induced phase separation (NIPS) method has been used to prepare PSf NF membranes with asymmetric structures [17]. However, due to the rapid exchange between the solvent and nonsolvent, the skin layer formed on the surface can't be dense enough to efficiently reject multivalent ions in common cases [18–20]. Some attempts have been adopted to slow down the solvent/nonsolvent exchange, such as increasing the concentration of casing solutions or incorporating some additives. As a result, the skin layer becomes thicker and the mass transfer resistance becomes larger, resulting in a dramatic decrease of the permeability [21–25]. Thus, there is a trade-off relationship between flux and rejection in PSf membranes fabricated by NIPS.

Solvent evaporation is a simple method which provides direct access to dense membranes applicable in NF or reverse osmosis (RO) processes [10,26–29]. The nanopores are formed between the polymer chains after the solvent is evaporated from the polymer solution. Thus the pore size are determined by the interspace of polymer chains and large pore formation in the membrane can be prevented [26,30]. Moreover, the resultant membrane is symmetric and homogenous, so the reduction of thickness will not result in the change of membrane structure [29–31]. In this way, the permeability can be gradually improved, on the basis of guaranteeing a high level of rejection. Different polymer materials such as disulfonated poly(arylene ether sulfone) and cellulose acetate have been used to prepare uniform and dense membranes by solvent evaporation method [10,26–29]. The membranes showed good separation performance and tunable flux by reducing the thickness. However, studies on preparation and characterization of PSf NF membranes by the solvent evaporation method have not been reported yet.

In this work, a novel PSf NF membrane was fabricated by solvent evaporation method. The solvent species, casting solution thickness, polymer concentration, and membrane formation temperature were adjusted to control the pore size and performance of the membrane. The membrane was then applied to separate Na_2SO_4 from sodium chloride (NaCl) in different mixed salt solutions. Furthermore, the chlorine resistance, thermal durability and mechanical strength of the membrane were also characterized.

2. Experimental

2.1. Materials

The membrane material PSf (Udel®P-3500) was purchased from Solvay Co., Ltd., Belgium. Tetrahydrofuran (THF), dimethylacetamide (DMAc), NaCl, Na_2SO_4 and NaClO were provided by Sinopharm Chemical Reagent China Co., Ltd., China.

2.2. Membrane preparation

Dense, homogeneous, and freestanding PSf membranes were fabricated via solvent evaporation method. Briefly, A certain amount of PSf was dissolved in THF or DMAc at room temperature and stirred for 24 h to form a homogenous casting solution. After being degassed, the solution was cast on a clean glass plate by a doctor blade (Elcometer Co., Ltd., UK). The cast membrane was dried in an oven at different temperatures for 24 h. The relative humidity of ambient air was controlled below 10% during the casting and the evaporation process. Afterward, the membrane was peeled off from the glass plate and stored in deionized water until use. The solvent species, polymer concentration, casting solution thickness, and membrane formation temperature are shown in Table 1.

2.3. Membrane characterization and performance evaluation

2.3.1. Membrane morphology

The morphologies of the membranes were characterized by a field emission scanning electron microscope (FESEM, 6301F, JEOL) at an accelerating voltage of 3 kV. In order to obtain the cross-sectional structures, the membranes were immersed in liquid nitrogen and fractured quickly. Prior to imaging, the samples were sputtered with platinum of about 10 nm at 5 mA for 1 min.

Nitrogen adsorptions onto the membranes were carried out on an accelerated surface area and porosimetry system (ASAP 2020, Micromeritics Co., Ltd., USA) at 77 K. The pore size distributions were calculated by the Horvath–Kawazoe method [32].

2.3.2. Separation performance

Water permeabilities and salt rejections of the membranes were evaluated with a self-made dead-end filtration equipment. Each PSf NF membrane has an effective area of 36.3 cm^2. The separation performances of the membranes were characterized by single salt solutions of Na_2SO_4 and NaCl with a fixed concentration of 1000 ppm. The electrolyte concentrations of the feeds as well as the permeates were measured by a conductivity meter (DDSJ-308A; INESA, China). The rejection to the solute R (%) can be expressed by

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{1}$$

where C_p (g/L) is the solute concentration of permeate, and C_f (g/L) is the solute concentration of feed.

The feasibility of removing Na_2SO_4 from brine by the membrane was investigated by filtering mixed salt solutions of NaCl and Na_2SO_4 with different compositions. The compositions of the feeds and permeates of the mixed salt solutions were measured by ion chromatography (IC, LC-20A, Shimadzu Co., Ltd., Japan).

The pressure applied to the membranes was increased step by step until reliable fluxes can be measured. This pressure was termed as P_c. Each membrane was pre-compressed at a pressure that was 4 bar higher than P_c for 24 h. For most membranes, the pre-compression