



Highly chlorine-resistant multilayer reverse osmosis membranes based on sulfonated poly(arylene ether sulfone) and poly(vinyl alcohol)

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HIGHLIGHTS

- Novel TFC RO membranes were obtained by coating SPAES-C on a microporous polysulfone support.
- A secondary cross-linked PVA layer was coated on the top of SPAES-C layer to improve the NaCl rejection.
- After cross-linking, the NaCl rejection increased from 91.2% to 96.8%.
- The multilayer RO membranes showed good chlorine-tolerance.

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ABSTRACT

Sulfonated cardo poly(arylene ether sulfone) copolymers (SPAES-C) were synthesized via post-sulfonation of the parent polymer. A series of reverse osmosis composite membranes were obtained by coating SPAES-C on porous polysulfone support membranes, with varying the concentration of coating solutions. The SEM results indicated that the obtained reverse osmosis membranes had smooth surface, and no defect was observed. Meanwhile, the functional layer thickness obtained from the SEM results was in the range from 300 to 400 nm. All the resulting membranes showed good water flux and appropriate NaCl rejection. In order to improve the NaCl rejection, a secondary layer of formaldehyde-cross-linked polyvinyl alcohol was coated on the surface of SPAES-C membrane, and this layer could improve NaCl rejection from 91.2% to 96.8% without a serious loss of water permeability. Compared with commercial PA reverse osmosis membrane, the composite membranes based on SPAES-C showed excellent chlorine-tolerance in reverse osmosis operation.

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1. Introduction

Membrane filtration processes such as nanofiltration (NF) or reverse osmosis (RO) are receiving tremendous attention as energy-efficient and environmentally-friendly routes to produce clean water for a variety of applications [1–3]. Most commercially available RO membranes are typically made of polymeric materials such as cellulose acetate (CA) and polyamide (PA) [4,5]. However, CA membranes have a narrow optimum pH range of 5–6 as the ester groups in cellulose acetate are subject to hydrolysis in acidic (pH < 4) and basic (pH > 8) conditions. They also suffer from compaction at higher temperatures and pressures, and are amenable to microbial attack [6]. Comparing with the CA membrane, PA membranes can operate over a wider pH range (4 to 11) and withstand higher temperatures. Currently, they dominate the desalination market due to their high water flux and salt rejection [7]. Currently, PA RO membranes are also available in composite form mostly as

thin-film composite (TFC) membranes. The thin film is formed from interfacial polymerization and deposited on a microporous polysulfone support [8,9]. The resulting membranes have very high water permeability and excellent salt rejection characteristics even at very low driving pressures. Unfortunately, practical application of PA membranes is often limited by continuous exposure to chlorine and other oxidizing environment [10,11]. It is believed that the amide group is vulnerable to chlorine attack unless the feed-water chlorine concentrations are lower than 0.1 ppm. Thus, an additional de-chlorination step of chlorine-treated water is required to prevent chemical degradation of the PA membrane, resulting in the increase of water purification cost [12].

Poly(arylene ether) copolymers, especially poly(arylene ether sulfone), as the engineer plastic, show much better chlorine resistance than PA membranes because no susceptible amide linkages are present in the polymer structure. After sulfonation, the hydrophilicity of the copolymers could enhance water permeation [13,14]. As a result, several research groups are focusing on the development of sulfonated copolymers as candidates for RO membrane materials, such as sulfonated poly(arylene ether sulfone) (SPAES), sulfonated poly(arylene ether) (SPA) and so on. Kim and coworkers fabricated end-group cross-

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linked SPAE RO membranes, and the resulting membranes exhibited much more improved chlorine tolerance properties even under 4000 ppm NaOCl solution for 30 days compared with commercial PA membranes [15]. Paul et al. reported a novel RO membrane based on cross-linked SPAES with epoxy, exhibiting high NaCl rejection and chlorine tolerance ability [16]. Although these sulfonated RO membranes showed good separating properties as well as chlorine tolerance, low water flux rendered them unsuitable for practical applications in RO systems. This is because that the sulfonated RO membranes must possess a certain thickness to keep mechanical strength, which restricts the water molecule passing through. Currently, in order to improve the water flux of the membranes, several research groups prepared RO membranes by coating sulfonated copolymers on a porous polysulfone support-layer. The resulting TFC membranes that were fabricated using sulfonated copolymers as the selective coating layer could enable high rates of water transport while maintaining good salt rejection, especially exhibiting high tolerance to aqueous chlorine and other strong oxidants [17,18]. Park et al. developed a biphenol-based SPAES TFC RO membrane, remaining good water flux and salt rejection properties in a wide pH range from 4 to 10 for 40 h, even at the NaOCl concentration up to 500 ppm [19].

In this study, sulfonated poly(arylene ether sulfone) containing cardo groups (SPAES-C) with excellent thermal and mechanical stability was synthesized. Then, it was coated onto the supporting polysulfone ultrafiltration membrane to fabricate the TFC RO membranes. To further enhance the rejection properties of the primary SPAES-C layer, we coated a secondary polymer layer, which was deposited from aqueous solution on the surface of the SPAES-C layer. Poly(vinyl alcohol) (PVA) is a hydrophilic and electric neutral polymer that has been reported as a selective coating layer to the RO membrane for improving antifouling properties and enhancing chlorine resistance [20]. Considering the long-term stability in the chlorine-rich environment, cross-linked structure of these coated layers is desirable. The final multilayer RO membranes consisting of SPAES-C and formaldehyde-crosslinked PVA were expected to improve the salt rejection without a serious loss of water permeability, and have an excellent chlorine tolerance in reverse-osmosis operation.

2. Experimental

2.1. Materials

PAES-C was synthesized by the direct copolymerization of 4,4'-dichlorodiphenylsulfone and phenolphthalein. Then, SPAES-C was prepared by a post-sulfonation method using concentrated sulfuric acid as the sulfonated reagent [21,22]. Bisphenol-A polysulfone (Udel-3500) and "Awa-10" non-woven polyester paper were obtained from Solvay and Awa Paper Ltd (Japan), respectively. Other solvents and reagents were obtained from Beijing Chemical Company and used without further purification.

2.2. Multilayer membrane fabrication

The microporous polysulfone ultrafiltration membrane as the support-layer in RO membrane was prepared by coating 17% w/v solution of Bisphenol-A polysulfone (Udel-3500) in dimethylformamide on Awa-10 non-woven polyester paper, and the primary membrane was gelled in water at ambient temperature [23].

Various amounts of SPAES-C were firstly dissolved in formic acid to make solutions with different concentrations (0.5, 0.75, and 1.0% w/v). The TFC RO membranes (SPAES-C-xx: xx refers to the concentration of sulfonated copolymers in the coating solutions) were prepared by brush coating these SPAES-C solutions onto the obtained microporous polysulfone ultrafiltration membranes, and subsequently dried at 60 °C for 10 min. The resulting TFC membrane formed from a 1%

(w/v) SPAES-C solution was over-coated with an aqueous solution of polyvinyl alcohol (1% w/v), formaldehyde (4% w/v) and sulfuric acid (0.5% w/v). The resulting secondary coating layer was cross-linked and dried at 60 °C for 30 min to remove the resident solvent.

2.3. Performance testing

The separation performance tests of the SPAES-C RO membranes were conducted at 2.0 MPa using a 2000 ppm NaCl solution at room temperature in dead-end cells (HP4750, Sterlitech). The membranes were initially subjected to a pure water pressure of 2.0 MPa for 2 h prior to performing the RO test experiments, and the effective membrane area (for each cell) was around 13.85 cm².

The water flux was determined by direct measurement of permeate volume, which was calculated by the following equation:

$$J = V/At \quad (1)$$

where $V(L)$ is the volume of permeated water, $A(m^2)$ is the effective membrane area and $t(h)$ refers to the permeation time.

The NaCl rejection was measured by the salt concentration in the permeate obtained through measurements of the permeate and the feed using a conductivity meter (DDS-11A, China). The NaCl rejection was calculated according to the following equation:

$$R(\%) = (1 - C_p/C_f) \times 100 \quad (2)$$

where $C_p(mg/L)$ and $C_f(mg/L)$ are the permeate and feed concentration, respectively. All membrane samples were tested in at least three measurements until it had reached to a constant value. In this case, good data reproducibility can be ensured.

In order to investigate the chlorine-tolerance properties of the SPAES-C RO membranes, the samples were exposed to 2000 ppm chlorine as NaOCl solution at pH 7.5 for a desired time. The separation performance of the SPAES-C RO membrane after continuous exposure to NaOCl solution was evaluated by measuring the change of water flux and salt rejection under a constant pressure of 2.0 MPa using a 2.0 g/L NaCl solution.

2.4. Membrane characterizations

The structure of SPAES-C was confirmed by ¹H NMR spectrum, which was carried out on a 500 MHz Bruker 510 spectrometer with deuterated dimethyl sulfoxide (DMSO-d₆) as the solvent and tetramethylsilane as an internal reference. Attenuated Total Reflectance Infrared (ATR-IR) spectra were acquired using a Nicolet 6700 spectrophotometer. The multilayer coating thickness and surface morphology were visually examined using a scanning electron microscope (SEM, Hitachi S-4800, Japan). The cross-sectional SEM measurement was performed by fracturing the membrane in liquid nitrogen and the fractured surface was sputter-coated with Au prior to measurement. The element composition on the surface of RO membranes was evaluated by Energy dispersive spectroscopy (EDS, Hitachi S-4800, Japan).

3. Results and discussion

3.1. SPAES-C synthesis and characterization

Poly(arylene ether sulfone) with cardo groups derived from phenolphthalein is a novel kind of engineering thermoplastics. In the PAES-C structure, there is a carbon atom involved in a five-member lactone ring of a phenolphthalein moiety, which could give the improvement on the mechanical strength, thermal, chemical and dimensional stabilities of the polymer membranes [24]. Herein, sulfonated PAES-C can be achieved by dissolving the parent PAES-C polymer in concentrated sulfuric acid at 60 °C for 10 h.

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