Full Length Article

Surface modification of polyamide reverse osmosis membrane with sulfonated polyvinyl alcohol for antifouling

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A B S T R A C T

Sulfonated polyvinyl alcohol (SPVA) was synthesized by esterification reaction of PVA and sulfuric acid, and the structure was characterized by FTIR spectrum. Then a series of TFC membranes modified with cross-linked SPVA layer were fabricated by coating method, with glutaraldehyde as the cross-linker. The resulting TFC membranes were characterized by SEM, AFM, ATR-FTIR, XPS, streaming potential as well as static contact angle. The TFC membranes modified with SPVA exhibit decreased water flux and increased NaCl rejection with SPVA content increasing in the coating aqueous solution. The optimal PA-SPVA-0.5 sample exhibits a NaCl rejection of 99.18%, which is higher than the 98.32% of the virgin PA membrane. More importantly, the PA-SPVA-0.5 membrane shows much more improved fouling resistance to BSA and CTAB than virgin PA membrane and the TFC sample modified with PVA (PA-PVA-0.5). PA-SPVA-0.5 membrane loses about 8% of the initial flux after BSA fouling for 12 h, which is much lower than those of virgin PA and PA-PVA-0.5 membranes (28% and 15%, respectively). Furthermore, the flux recovery of the PA-SPVA-0.5 membrane reaches above 95% after cleaning. Thus, the PA-SPVA-0.5 membrane shows potential applications as antifouling RO membrane for desalination and purification.

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1. Introduction

Reverse osmosis technology is the most advanced and energy-saving effectively membrane separation technology [1,2]. Up to now, the most widely used RO membranes are thin-film-composite (TFC) polyamide (PA) types, which are fabricated through interfacial polymerization of *m*-phenylenediamine (MPD) in the aqueous phase and trimesoyl chloride (TMC) in the organic phase [3]. The TFC RO membranes based on PA have dominated the desalination market, due to their improved permeation property. However, it must be pointed out that although recent advances in RO technology have widen its application, further improvement of the membrane properties related to antifouling, chlorine-tolerance, solvent-tolerance, as well as acid/alkali-tolerance, is still very challenging [4–10].

It has been previously reported that the membrane fouling is the main cause of drop in water flux of RO membrane [11,12]. When fouling occurs on the membrane surface, the performance of

membrane separation process, such as efficiency (e.g. flux, membrane permeability, permeate recovery, as well as permeate quality) and effectiveness (e.g. rejection of selectivity) are typically reduced, leading to an increase in production cost due to the increased energy demand and chemical cleaning, reduced membrane life and addition labor for maintenance [13,14]. In order to mitigate the membrane fouling and improve the application of RO technology, strategies including pretreatment, design of special modules and devices, and development of antifouling RO membranes have been examined [15–18]. Compared to other preventive strategies, developing antifouling RO membrane can fundamentally mitigate membrane fouling and maintain the permeation property of the membrane. Thus more and more researchers have focused their attention on the development of novel RO membranes for antifouling.

According to the previous report, foulants can adsorb to the membrane surface by the hydrophobic interactions, hydrogen bonding, van der Waals attractions and electrostatic interactions [19,20]. Therefore, antifouling property can be improved by reducing these adsorptive interactions between foulants and membrane surface [21,22]. Due to the excellent permeation property of the TFC RO membrane based on PA, a great effort has been devoted

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to changing the surface properties (roughness, hydrophilicity, and surface charge) of the PA layer without impairing their transport characteristics by surface modification for antifouling [23–25]. Surface modification techniques such as surface absorption, surface coating, surface grafting and surface hydrolysis have been widely adopted to modify or tailor the surface properties of the TFC RO membranes based on PA [26–29]. It has been illustrated that surface coating or surface grafting is an efficient and simple technique for membrane surface modification. The modified TFC membranes with smooth and hydrophilic polymer materials, such as polyvinyl alcohol (PVA), polyether-polyamide block copolymers, poly(ethylene glycol), polyvinyl amine, zwitterionic and so on, have created a fouling resistance layer on PA [30–36]. Among of all the hydrophilic polymers used for surface modification, PVA is the most widely used due to its inexpensiveness and easy locking on TFC membrane by crosslinking. Hachisuka and Ikeda coated hydrophilic PVA onto PA RO membrane to improve the antifouling [37]. In order to increase the stability of the PVA layer for long-term operation, some researchers further crosslinked the PVA layer with glutaraldehyde [38,39]. The resulting membranes exhibited a better antifouling property in industrial wastewater and cation/anion surfactant feeding solution than the virgin PA membrane. However, the PVA layer can provide an additional hindrance to water molecular for permeating, resulting in a much decrease of water flux of the modified TFC RO membrane. Gao et al. fabricated a series of TFC membranes by surface modification via covalent attachment of PVA. The resulting TFC membranes show much more improved antifouling property than the virgin PA membrane, without water flux decreasing seriously [40,41].

Herein, in order to enhance the water permeability of PVA layer, sulfonated polyvinyl alcohol (SPVA) with improved hydrophilicity was synthesized by esterification reaction. Then a series of TFC membranes modified with SPVA were prepared by coating the aqueous solution containing SPVA and cross-linker on the membrane surface. After thermal treatment, the TFC membranes with cross-linked SPVA modifying layer on the surface have been fabricated, and the crosslinking structure could avoid the leaching out of SPVA during long-term operation. The SPVA modified TFC membranes were well characterized by ATR-FTIR, SEM, XPS and AFM. Furthermore, the properties related to permeation and antifouling were also evaluated thoroughly.

2. Experimental

2.1. Materials

RO membrane was fabricated by interfacial polymerization of m-phenylenediamine (MPD) in the aqueous phase and trimesoyl chloride (TMC) in the organic phase, as reported previously [42]. MPD, TMC and PVA (95% hydrolysed, M_W: 95000) were purchased from Aldrich. Bovine serum albumin (BSA, 96%), dodecyltrimethylammonium bromide (DTAB, 99%) and glutaraldehyde (GD) were purchased from Sinopharm Chemical Reagent Co.,Ltd. Isopar E was obtained from Exxonmobil Chemical. Other reagents and solvent were used as received without further purification.

2.2. Synthesis of SPVA

A typical synthetic procedure to prepare SPVA is described as follows: 2 g PVA and 30 mL deionized H_2O were added into a 100 mL three-necked flask equipped with a mechanical stirrer, a condenser and a dropping funnel. After PVA was dissolved completely, the solution was cooled down to 0 °C (ice bath) and 5 g H_2SO_4 was added dropwise. Then the reaction solution was stirred at 40 °C for 6 h. Finally, the reaction solution was poured into methanol, and the

resulting precipitate was washed with methanol for several times. The obtained white solid was dried at 60 °C in the vacuum oven for 24 h.

2.3. Preparation of TFC membrane modified with SPVA or PVA

The RO membrane fabricated by interfacial polymerization was placed between a poly(vinyl chloride) plate and poly(vinylidene fluoride) frame (inner hole size: 8 cm × 15 cm) designed to hold the solutions on the active layer side of the membrane. SPVA aqueous solution (30 mL) containing glutaraldehyde with a pH between 2 and 3 was poured into the frame to cover the active layer of the membrane for 1 min. Subsequently, the SPVA solution was discarded, followed by heating the membrane for crosslinking. Finally, the obtained membrane designated as PA-SPVA-xx, where xx refers to the concentration percentage of SPVA in the coating solution, was rinsed with deionized water for several times and stored in deionized water for further testing. By the same fabrication process, the sample modified with PVA was also prepared for comparison.

2.4. Instrumentation and testing

Attenuated Total Reflectance Infrared (ATR-FTIR) spectra were acquired using a Nicolet 6700 spectrophotometer. The surface morphology of the TFC membrane modified with SPVA was visually examined using a scanning electron microscope (SEM, Hitachi S-4800, Japan). Static water contact angle measurements were performed using a DSA100 contact angle analyzer (KRUSS, Germany). All membrane samples were dried at 60 °C for 12 h to remove the water in the TFC membranes and tested in at least three measurements, results of which had been averaged. Quantitative surface roughness analysis of the TFC sample was measured using atomic force microscopy (AFM) imaging and analysis (Park Instrument Auto Probe CT). X-ray photoelectron spectroscopy (XPS) measurements were employed to analyze the surface element of the membranes using Surface Science Instruments model ESCALAB250 with monochromatized Al-Kα X-ray source (1486.4 eV). Surface zeta potential of the TFC membranes was measured by a streaming potential analyzer (Aaton Paar zeta potential analysis meter, Austria). Streaming potential measurements were carried out with 0.001 mol/L KCl aqueous solution at 25 °C and pH 7.0.

The permeation performance tests of the TFC membranes were conducted at 1.55 MPa using a 2000 ppm NaCl aqueous solution, at 25 °C in cross-flow cells (CF042SS, Sterlitech Corp.) The membranes were initially subjected to a pure water pressure of 1.55 MPa for 2 h prior to performing the RO test experiments, and the effective membrane area (for each cell) was 42.2 cm². The water flux was determined by direct measurement of permeate flow and calculated through the following equation: $J = \frac{Q}{A \Delta t}$, where J is the permeate water flux (L/m²h), A is the effective area of the membrane for permeation (m²), and Q is the volume of permeation over a time interval Δt. The rejection was measured by the salt concentration in the permeate obtained through measurements of the permeate and the feed using a conductance meter (DDS-11A, China). The salt rejection was calculated according to the following equation: $R\ (\%) = (1 - C_p/C_f) \times 100$, where C_p (mg L^{-1}) and C_f (mg L^{-1}) are the permeate and feed concentration, respectively. All membrane samples were prepared and tested in at least three measurements, results of which had been averaged.

Membrane fouling experiments were performed via cross-flow filtration of an aqueous solution containing 2000 ppm foulant (BSA or CTAB) and 2000 ppm NaCl. The antifouling property of the membrane was evaluated by monitoring the permeation flux as a function of time. For the experimental protocol, the membrane was first stabilized by filtrating a 2000 ppm NaCl solution at 1.55 MPa