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Improving fouling resistance of thin-film composite polyamide reverse osmosis membrane by coating natural hydrophilic polymer sericin

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ABSTRACT

In this study, a commercial thin-film composite aromatic polyamide reverse osmosis membrane was modified through coating a surface layer of natural polymer sericin for improved antifouling property. The deposition of sericin on the membrane was carried out through dip-coating followed by in situ cross-linking and was confirmed by ATR-FTIR spectroscopy. The changes of surface charge, hydrophilicity and roughness that resulted from the sericin application were analyzed using zeta-potential analysis, contact angle measurement and atomic force microscopy, respectively. The separation performance was evaluated through cross-flow permeation tests. It was found that the sericin-coated membrane showed improved surface hydrophilicity, enhanced surface negative charge, smoothed surface morphology, and decreased pure water permeability and salt permeability coefficient. The results of fouling experiments with bovine serum albumin aqueous solution revealed that the fouling resistance of the reveres osmosis membrane could be effectively improved by coating sericin surface layer. Although the initial flux of the modified membrane was lower than that of the unmodified membrane under the same operating pressure due to the additional hydraulic resistance, the rate of flux decline slowed after modification due to the mitigation of foulant deposition on the membrane surface and compensated for the initial flux decline within 40 h.

1. Introduction

During the past two decades, reverse osmosis (RO) process, which uses polymeric semi-permeable membranes to achieve molecular separation, has become the main technology for the desalination of saltwater, the production of drinking and ultra-pure water and the reclamation of wastewater [1,2]. The dominated reverse osmosis membrane in current use is thin-film composite (TFC) aromatic polyamide membrane, which is usually fabricated by forming a dense aromatic polyamide barrier layer on a porous polysulphone support through interfacial polarization of an aromatic polyamine with one or more aromatic polyacyl halides [3]. Despite its advantages such as high water permeability and ion rejection, resistance to pressure compaction, wide operation temperature and pH ranges, and high stability to biological attack, the TFC polyamide RO membrane faces a major challenge of fouling, which is mainly due to the buildup of the material being rejected and manifests itself as a decline in flux with operation time [4,5].

It is known from literatures that foulants can adsorb to the membrane surface through hydrophobic interaction, hydrogen bonding, van der Waals attraction, Lewis acid–base interaction and electrostatic interaction [6,7], and the surface characteristics of the TFC polyamide reverse osmosis membrane such as hydrophilicity, roughness and charge are known to be strongly related to fouling [8,9]. Membranes with a smooth hydrophilic surface of similar charge to the foulant seem to possess good antifouling property [10–13]. Therefore, many research efforts have been devoted to modify the surface characteristics of the TFC polyamide RO membrane through coating hydrophilic materials so as to improve the antifouling property.

For example, neutral polymer polyvinyl alcohol (PVA) was coated on the surface of TFC polyamide reverse osmosis membrane by Kim et al. [14]. It was found that the modified membrane had a smooth surface with decreased surface negative charge and exhibited improved fouling resistance in treating dyeing wastewater. The coating of synthetic polyether–polyamide block copolymer

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on the surface of TFC polyamide reverse osmosis membrane was conducted by Louie et al. [15]. It was reported that the protective coating layer resulted in a smooth, neutral and hydrophilic surface with improved fouling resistance, but a declined flux. In consideration of the fact that most of the thin-film composite polyamide membrane surfaces are negatively charged, polyethyleneimine (PEI) was coated on the surface of TFC polyamide reverse osmosis membrane by electrostatic self deposition [16]. The surface charge was effectively reversed from negative to positive after modification and the modified membrane exhibited good fouling resistance to cationic foulants as the result of the electrostatic repulsion. In our previous studies [17,18], hydrophilic thermo-responsive copolymers poly(N-isopropylacrylamide-co-acrylic acid) and poly (N-isopropylacrylamide-co-acrylamide) were used to modify commercial TFC polyamide RO membrane through surface coating technique. It was found that the modified membrane had a more hydrophilic surface of thermo-responsive property and showed not only improved antifouling property but also enhanced physical cleaning efficiency. More recently, the deposition of polyelectrolytes on the surface of TFC polyamide reverse osmosis membrane was performed by Ishigami et al through layer-by-layer assembly [19]. The membrane surface became more hydrophilic and smoother after modification and showed reduced fouling when filtrated with bovine serum albumin (BSA) aqueous solution.

In summary, the surface characteristics of the commercial TFC polyamide reverse osmosis membrane could be effectively modified for improved fouling resistance through coating a thin surface layer of hydrophilic material. However, the coating layer tended to offer additional resistance to water permeation and/or to decrease the membrane surface negative charge, and thereby decreasing water permeability and/or salt rejection. Therefore, research interest still remains in the modification of commercial thin-film composite polyamide reverse osmosis membranes for improved antifouling and separation properties through coating a surface layer of functional material.

Accordingly, in this study, the natural hydrophilic polymer sericin, a water-soluble globular protein having polar side groups of hydroxyl, carboxyl and amino groups [20], was used to modify the commercial thin-film composite polyamide reveres osmosis membrane for improved antifouling property through surface coating followed by cross-linking with glutaraldehyde (GA). Membrane surface chemical structure, morphological structure, hydrophilicity and charge were characterized to analyze the changes that resulted from the deposition of sericin layer. The permeation properties of the unmodified and sericin-coated TFC polyamide reverse osmosis membranes were evaluated through cross-flow permeation tests by investigating the pure water permeability and salt permeability coefficient. Additionally, cross-flow fouling experiments with bovine serum albumin (BSA) aqueous solution were also carried out to investigate the antifouling properties of the membranes in terms of the time-dependant flux, cumulative volume of the permeate produced and hydraulic resistance to water permeation.

2. Materials and methods

2.1. Materials

A commercial flat-sheet thin-film composite polyamide reverse osmosis membrane was obtained from the Development Center of Water Treatment Technology (Hangzhou, China). It was manufactured through interfacial polymerization of m-pheylenediamine with trimesoyl chloride on a reinforced polysulfone porous substrate. The membrane had a cross-linked polyamide barrier layer, as shown schematically in Fig. 1.

Natural polymer sericin (average Mw = 10,000 g/mol, chemical structure schematically shown in Fig. 2) was supplied by Aotesi Biotechnology (China). Glutaraldehyde (GA) and bovine serum albumin (BSA) were sourced from Tianjin Kemiou Chemical Reagent Co., Ltd. (China) and Aldrich Chemical, respectively, and used without further purification. De-ionized water was used as the solvent for preparing the aqueous coating solutions as well as for soaking and rinsing the membrane samples during membrane modification. It was also used to prepare the feed solutions for membrane testing and to flush the fouled membranes for physical cleaning. All other chemicals of analytic grade were used as received.

2.2. Membrane modification

Prior to modification, the commercial TFC RO membrane samples were soaked in de-ionized water for a minimum of 4.0 h, replacing the water every hour, and then rinsed thoroughly with de-ionized water to remove all preservative materials in the membranes. Surface modification was then carried out in an assembly clean room by soaking the membrane samples into the aqueous solution of 25.0 °C containing predetermined content of sericin (50–200 mg/l). After soaking for 5 min, the membrane samples were removed from the coating solution and air-dried at room temperature until no liquid remained. Then, an aqueous solution of 25.0 °C containing 0.2% (w/w) GA and 0.1% (w/w) sulfuric acid was poured on the surfaces of the sericin-saturated membrane samples and remained for 5 min before draining off the excess solution from the surface. The resulting membranes were heat cured at 40.0 °C for 5.0 min, washed thoroughly with de-ionized water and stored in de-ionized water before being characterized and tested.

2.3. Membrane characterization

Attenuated total reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was adopted to determine the surface chemistry of the composite membrane. Spectra were obtained using a Nicolet Aratar 370 FTIR spectrometer with a ZnSe crystal as the internal refection element with an angle of incidence of 45°. All the membrane samples for ATR-FTIR analysis were dried at 25.0 °C under vacuum for at least 10.0 h.

Contact angle measurements were performed with a DSA10-MK2 contact angle analyzer (KRUSS BmbH Co, Germany) to evaluate the membrane surface hydrophlicity. The sessile drop method was used to measure the contact angles of de-ionized water (about 3 μl) on the dried surfaces of the membranes at 25.0 °C. Images were captured 5 s after introducing the drop and the contact angles were calculated. At least ten measurements on different locations of the membrane were performed and averaged. All the results presented were an average data from five membrane samples with standard deviation of the measured values.

Surface roughness of the membrane was determined quantitatively using an atomic force microscope (AFM) (Park Systems XEI-100E, Korea). Dry membrane sample was mounted on a specimen holder and 10 μm × 10 μm area was scanned using a tapping mode in air. Surface roughness was reported in terms of root mean square roughness (RMS) [21].

Scanning electron microscopy (SEM) of the cross-section of the composite membrane was carried out with a field emission scanning electron microscopy (FE-SEM) (Hitachi S-4800, Japan).

An electrokinetic analyzer (EKA) from Anton Paar GmbH, Austria was employed to conduct the measurement of the streaming potential of the membrane surface. Measurements were carried out with 0.001 mol/l KCl aqueous solutions at 25 ± 1.0 °C and pH ranging from 3.0 to 9.0. Surface zeta potentials were determined