



Surface mineralization of commercial thin-film composite polyamide membrane by depositing barium sulfate for improved reverse osmosis performance and antifouling property



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HIGHLIGHTS

- Surface mineralization was adopted to modify the TFC PA-RO membrane.
- BaSO₄-based mineral coating was deposited by alternate soaking process.
- Membranes became more hydrophilic and negatively charged after mineralization.
- Surface mineralization could enhance water flux and salt rejection simultaneously.
- The mineralized membrane possessed improved fouling resistance to BSA.

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ABSTRACT

In this study, a novel approach, namely surface mineralization, was adopted to modify the commercial thin-film composite (TFC) polyamide (PA) reverse osmosis (RO) membrane for improved membrane properties. BaSO₄-based mineral coating was deposited on the surface of the PA-RO membrane by alternate soaking process (ASP) using aqueous solutions containing barium chloride (BaCl₂) and sodium sulfate (Na₂SO₄), respectively. Membranes with different mineralization degrees were prepared by varying the number of ASP cycles. The mineralized TFC PA-RO membranes were characterized through FESEM microscopy, AFM analysis, EDX analysis, zeta-potential analysis, contact angle measurement and cross-flow permeation test. It was found that the mineral coating composed of BaSO₄ particles distributed evenly on membrane surface. The surface of the membrane became more hydrophilic and negatively charged after mineralization and the membranes modified under certain conditions exhibited both increased water flux and salt rejection. Fouling experiments with bovine serum albumin (BSA) aqueous solution also demonstrated that the BaSO₄-based surface coating layer could effectively alleviate the adsorption and deposition of foulant molecules on the membrane surface through enhancing electrostatic repulsion and lowering hydrophobic interaction between BSA molecules and membrane surface, and that the mineralized membrane possessed improved fouling resistance to BSA aqueous solution.

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1. Introduction

Reverse osmosis (RO) process, which uses polymeric semi-permeable membranes to achieve molecular separation, has become a well-developed and the most promising technology for water desalination process during the past two decades [1–3]. Thin-film composite (TFC) polyamide (PA) membrane, which was invented by Cadotte in 1981 through the interfacial polymerization between *m*-phenylenediamine

and trimesoyl chloride on a porous polysulfone support membrane [4], has become the dominated type of reverse osmosis membrane for its advantages such as high water permeability, high salt rejection, resistance to pressure compaction, wide operation temperature and pH ranges, and high stability to biological attack [5,6]. However, the major problem facing with the commercial thin-film composite polyamide reverse osmosis membranes is fouling, which usually leads to degraded separation performance, increased operating cost, as well as shortened using life [7]. Therefore, it is of great importance and interest to improve the antifouling property of the TFC PA-RO membrane.

It is known from literatures that foulants can adsorb to the membrane surface through hydrophobic interaction, hydrogen bonding,

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van der Waals attraction and electrostatic interaction, and membrane surface properties such as hydrophilicity, roughness and charge are known to be strongly related to fouling [8,9]. Therefore, an effective method to reduce membrane fouling is to alleviate these adsorptive interactions and enhance the repulsive interaction between the foulant molecules and membrane surfaces by modulating the membrane surface properties [10,11]. Membranes with a smooth and hydrophilic surface of similar charge to the foulant seem to possess good anti-fouling property [12–14]. Therefore, many research efforts have been devoted to improve the antifouling property of the commercial thin-film composite polyamide RO membrane through surface coating, which has been proved to be an effective approach to modulate membrane surface properties.

For example, Kim et al. [15] coated a neutral layer of polyvinyl alcohol (PVA) on the surface of the commercial TFC polyamide reverse osmosis membrane. Compared with the unmodified membrane, the PVA-coated membrane had a smoother surface with lower negative charge density and exhibited improved fouling resistance in treating dyeing wastewater. Louie et al. [16] applied a protective coating layer of polyether–polyamide block copolymer on the surfaces of the polyamide thin-film composite membranes. It was reported that the protective coating layer resulted in a neutral, smoother and more hydrophilic surface. The modified membrane exhibited improved fouling resistance, but a declined permeate flux. Choi et al. [17] coated a layer of methyl methacrylate–hydroxy poly(oxyethylene) methacrylate (MMA–HPOEM) comb-polymer on the surface of the TFC polyamide seawater reverse osmosis (SWRO) membrane. The membrane surface became more hydrophilic after modification and exhibited reduced fouling when filtrated with bovine serum albumin (BSA) aqueous solution. On the other hand, polydopamine was deposited on the surface of the commercial thin-film composite polyamide reverse osmosis membrane by Kasemset et al. [18]. Compared with the unmodified membrane, membranes with polydopamine depositing layer were significantly more resistant to fouling in filtration oil/water emulsions. More recently, Matin et al. [19] deposited a copolymer film of hydroxyethyl methacrylate (HEMA) and perfluorodecyl acrylate (PFDA) on the surface of the commercial TFC PA-RO membranes through in-situ direct copolymerization. It was found that the surfaces of the PA-RO membranes became amphiphilic after modification and the deposited copolymer coating had negligible effect on permeate water flux and salt rejection.

The aforementioned examples reveal that the surface properties of the commercial TFC polyamide reverse osmosis membrane could be effectively modulated through surface coating for improved fouling resistance.

Accordingly, a novel approach, namely surface mineralization, was adopted to modify the commercial thin-film composite polyamide reverse osmosis membrane in this study. BaSO₄-based mineral coating was deposited on the surface of the TFC PA-RO membrane by an alternate soaking process (ASP) using aqueous solutions containing barium chloride (BaCl₂) and sodium sulfate (Na₂SO₄), respectively. The degree of surface mineralization was changed by varying the numbers of ASP cycles. Membrane morphological structure, surface hydrophilicity and charge were characterized to analyze the changes that resulted from the deposition of BaSO₄-based mineral surface coating layer. The permeation properties of the 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 and hydraulic resistance to water permeation.

2. Materials and methods

2.1. Materials

A commercial flat-sheet thin-film composite polyamide reverse osmosis membrane used as the base membrane for surface

mineralization was provided by Hangzhou Tianchuang Environmental Technology Co., LTD. (Hangzhou, China). It is an ultra-low pressure RO membrane and manufactured through the interfacial polymerization of m-phenylenediamine with trimesoyl chloride on a reinforced polysulfone porous substrate. The chemical structure of the aromatic polyamide selective layer is shown schematically in Fig. 1.

Barium chloride (BaCl₂) and sodium sulfate (Na₂SO₄) of analytical grade were used to prepare the aqueous solutions for surface mineralization. Bovine serum albumin (BSA), as the model foulant to estimate the antifouling property of the membranes, was purchased from Shisheng Cell Biotechnology Co., Ltd. (China) 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 surface mineralization

Membrane surface mineralization was carried out in an assembly clean room. Prior to mineralization, samples of the base thin-film composite polyamide reverse osmosis membrane were soaked in de-ionized water for a minimum of 10.0 h, replacing the water every hour, and then rinsed thoroughly with de-ionized water to remove all preservative materials in the membrane samples. Neutral aqueous solutions of BaCl₂ and Na₂SO₄ with the concentration of 0.05 M were prepared, respectively.

Surface mineralization was then conducted through an alternate soaking process (ASP) as described in [20]. The membrane sample was sequentially immersed in BaCl₂ aqueous solution of 25.0 °C for 60 s, rinsed with de-ionized water for 60 s, immersed in Na₂SO₄ aqueous solution of 25.0 °C for 60 s, and rinsed again with de-ionized water for 60 s. The above four steps were considered as one cycle. The mineralization degree was changed by varying the cycle number. The base membrane and membranes mineralized with ASP cycles of 1, 2, 4 and 6 were designated as M0, M1, M2, M4 and M6, respectively. The mineralization degree was determined gravimetrically from the weight of each membrane sample before and after mineralization according to the method described in [21]. The samples were rinsed thoroughly with de-ionized water and dried at 40 °C under vacuum until constant weight was obtained. The mineralization degree (MD) was calculated through the following Eq. (1):

$$MD \left(\text{g/m}^2 \right) = \frac{w_1 - w_0}{A} \quad (1)$$

where w_0 and w_1 are the constant dry weights of each membrane sample before and after mineralization, and A is the surface area of the membrane sample.

2.3. Membrane characterization

Surface and cross-sectional morphologies of the composite membranes were characterized through scanning electron microscopy (SEM), which was carried out with a field emission scanning electron microscopy (FE-SEM) (Hitachi S-4800, Japan). The membrane samples were sputtered with gold before SEM observation. The element compositions of the surface of the membrane before and after mineralization were determined by energy dispersion X-ray (EDX) analysis employing the FESEM with a 20 keV energy beam.

Quantitative surface roughness analysis of the composite membrane was measured using AFM imaging and analysis (Park Instrument Auto Probe CT). Air-dried membrane samples were fixed on a specimen holder and 5.0 μm × 5.0 μm areas were scanned by tapping mode in

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