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Surface modification of commercial aromatic polyamide reverse osmosis membranes by graft polymerization of 3-allyl-5,5-dimethylhydantoin

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ABSTRACT

A commercially available aromatic polyamide reverse osmosis (RO) membrane was chemically modified to improve its chlorine resistance and anti-biofouling property. The raw RO membranes were modified by free-radical graft polymerization of 3-allyl-5,5-dimethylhydantoin (ADMH) using 2,2′-azobis(isobutyramidine) dihydrochloride as an initiator. Attenuated total reflective Fourier transform infrared spectra (ATR-FTIR) verified the successful graft of ADMH on the raw membrane surfaces. It was shown that two new FTIR adsorption bands at 1770 and 1714 cm^{-1} corresponding to two carbonyl groups in hydantoin ring appeared after graft polymerization, and the intensities of these two bands increased with increasing grafting time. Based on X-ray photoelectron spectroscopy (XPS), contact angle, and streaming potential measurements, graft polymerization increased the nitrogen and oxygen atom contents, improved surface hydrophilicity, and reduced surface charges of the raw membranes. The water fluxes of the ADMH-grafted membranes were higher than that of the raw membranes; however, the salt rejections decreased slightly. The chlorine resistances of the ADMH-grafted membranes were significantly improved by showing slight changes in water fluxes and salt rejections after chlorine treatments as compared with those of the raw membranes. Furthermore, the chlorinated ADMH-grafted membranes demonstrated obvious sterilization effects on *Escherchia coli* and substantial preventions against microbial fouling.

1. Introduction

Thin film composite (TFC) aromatic polyamide reverse osmosis (RO) membranes with high selectivity and permeability and capability of working at low pressures have become tremendously important in desalination of brackish and sea water, wastewater filtration, and separation and purification of chemical and biological products [1]. However, the aromatic polyamide RO membranes are vulnerable to biofouling due to their relatively hydrophobic and rough surfaces [2–4]. Biofouling can cause obvious increases in hydraulic resistances and substantial decreases in membrane permeate fluxes [4–6]. It has been standard practice to control biofouling by pretreatment of feed solution with free chlorine [6,7]. However, the aromatic polyamide RO membranes are also susceptible to free chlorine damage. The free chlorine in feed solution can cause degradation of aromatic polyamides and ultimately result in membrane failure as measured by enhanced passages of solutes [8–11]. Improving membrane chlorine resistances and anti-biofouling properties are the main challenges for the aromatic polyamide RO membranes to realize high performance over a long period of operation.

Surface modifications such as physical adsorption and chemical bond formation are potential methods to improve membrane chlorine resistances and anti-biofouling properties. It has been reported that the chlorine resistances of the aromatic polyamide RO membranes can be improved by coating with high chlorine-resistance polymers (such as poly(N,N-dimethylaminoethyl methacrylate) [12] and poly(vinyl alcohol) [13,14]) which cover the active sites of aromatic polyamides and protect them from chlorine scouring. An anti-biofouling aromatic polyamide RO membrane with photocatalytic destructive capability on microorganisms was designed by self-assembly of TiO_2 nanoparticles onto membrane surface [15,16]. To the best of our knowledge, however, no information has been reported on improving both chlorine resistances and anti-biofouling properties of the aromatic polyamide RO membranes by surface modifications, besides our previous work [17,18]. In our previous work, hydantoin derivative 3-monomethylol-5,5-dimethylhydantoin (MDMH) was successfully grafted onto

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the nascent aromatic polyamide RO membrane surfaces mainly through reaction with active acyl chloride groups. The grafted MDMH with high reaction activity with free chlorine could play as sacrificial pendant groups when membranes suffered from chlorine attacks; and the chlorination products N-halamines with strong antimicrobial function could sterilize microorganisms on membrane surfaces and regenerate to MDMH. These two effects endowed the MDMH-modified RO membranes with durable high chlorine resistances and anti-biofouling properties. However, at present, significant challenges still remain in surface modifications for existing RO membranes (which do not contain active acyl chloride groups) to improve both the properties at the same time. In addition, there is a great potential to further improve membrane chlorine resistances and anti-biofouling properties by developing other high-performance hydantoin derivatives for surface modifications besides MDMH.

Hence, in this work, the purpose was to develop a novel method suitable for surface modification of a commercially available aromatic polyamide RO membrane to improve its chlorine resistance and anti-biofouling property. The primary modification involved free-radical graft polymerization [19,20]. The grafting monomer 3-allyl-5,5-dimethylhydantoin (ADMH) with a hydantoin ring in chemical structure similar to MDMH was prepared according to the method developed by Sun [21–23]. The membrane physicochemical properties such as surface functional groups, element contents, hydrophilicity, and charges were analyzed after graft polymerization of ADMH. Permeability and selectivity of the raw and ADMH-grafted membranes were evaluated by filtration of 2000 ppm NaCl aqueous solution at 25 °C under 1.5 MPa. Exposures of the membranes to 100 ppm free chlorine solutions for different times were carried out to evaluate membrane chlorine resistances. A preliminary study on membrane antimicrobial and anti-biofouling properties was also performed.

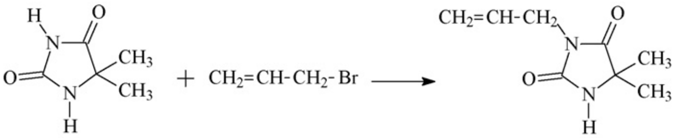
2. Experiments

2.1. Materials

A commercially available TFC aromatic polyamide RO membrane (RE2521-TL, Woongjin Chemical Co., Ltd., Korea) made of trimesoyl chloride and m-phenylene diamine was used for grafting, and the membrane was denoted as “raw membrane” in this work. The initiator 2,2′-azobis(isobutyramidine) dihydrochloride (AIBA) was purchased from Aldrich (USA) and used without further purification. Chemicals used in synthesis of the grafting monomer ADMH including 5,5-dimethylhydantoin (DMH) and allyl bromide were purchased from Jingchun Chemical Reagent Co. Ltd. (Shanghai, China). Sodium hypochlorite solution (NaClO, 10 wt.% free chlorine) used in membrane chlorine exposure experiments was purchased from Kewei Chemical Reagent Co. Ltd. (Tianjin, China). Other reagents such as sodium chloride (NaCl), potassium chloride (KCl), potassium hydroxide (KOH), hydrochloric acid (HCl), and methanol were of analytical grade and used without further purification. Pure water with conductivity less than 5 μs/cm was produced by a two-stage reverse osmosis system.

2.2. Synthesis and characterization of ADMH

The grafting monomer ADMH was synthesized according to Scheme 1 [21–23]. A solution of 6.4 g (0.05 mol) of DMH in 25 mL H_2O containing 2.8 g (0.05 mol) of KOH was combined with a solution of 4.4 mL (0.05 mol) allyl bromide in 10 mL of methanol. The solution was stirred at 60 °C for 2 h, cooled, and dried under reduced pressure at room temperature of approximately 25 °C. The resulting solid was recrystallized from petroleum ether, yielding 5.6 g (67%).



Scheme 1. Reaction between DMH and allyl bromide to produce ADMH.

The Fourier transform infrared (FTIR) spectra of DMH and ADMH in range of 500–4000 cm^{-1} were obtained using a Nicolet MAGNA-560 spectrometer (Thermo Nicolet Corp., USA) collected at 4 cm^{-1} resolution. The proton nuclear magnetic resonance (^1H NMR) spectra of DMH and ADMH were obtained with a Varian INOVA 500 spectrometer (Varian, Palo Alto, CA) at 500 MHz using DMSO-d_6 as solvent.

2.3. Preparation of ADMH-grafted RO membranes

The graft polymerizations of ADMH onto the aromatic polyamide RO membrane surfaces were performed as follows. The raw membrane pieces (13 cm × 11 cm) were fixed in polyfluortetraethylene frames to ensure contacts of the reactant solutions solely with the membrane barrier layers. The aqueous solutions of the initiator AIBA (0.02 wt.%) and the grafting monomer ADMH (5.0 wt.%) were first prepared. The raw membranes were covered by the AIBA solutions for 15 min, followed by removing excess solutions and drying by nitrogen gas at about 30 kPa. The AIBA saturated membranes were then coated by ADMH solutions for 15 min, before removing excess solutions and drying by nitrogen. Then the membranes filled with AIBA and ADMH were placed in an oven, and the graft polymerizations were performed at 70 °C for 10, 20, 40, 60, and 100 min, respectively. Every 20 min or so, the membranes were taken out from oven, and refilling of the membrane surfaces with AIBA and ADMH was performed so as to ensure sufficient reactants for graft polymerizations. The resulting membranes were removed from the frames, thoroughly washed, and stored in pure water. The raw membrane and the membranes after 10, 20, 40, 60, and 100 min graft polymerizations shall herein after be referred to as M_0, M_{10}, M_{20}, M_{40}, M_{60}, and M_{100}, respectively.

It needs to be pointed out that in the above grafting process, after every delivery of an aqueous solution containing initiator or monomer onto the membrane surface, the solvent was removed before initiating the graft polymerization to ensure a solvent-free graft reaction. Such conditions can minimize formation of homopolymerization of the monomers and increase graft efficiency [24].

2.4. Characterization of ADMH-grafted RO membranes

2.4.1. Spectral analysis

The membrane samples including raw membranes and ADMH-grafted membranes were dried at 40 °C before the following analyses. Attenuated total reflectance mode Fourier transform infrared spectroscopy (ATR-FTIR, MAGNA-560, Thermo Nicolet Corp., USA) was used to study the surface chemical composition. Each ATR-FTIR spectrum was averaged from 48 scans collected at 4 cm^{-1} resolution. The elemental compositions of the membrane top surfaces (2–5 nm) were analyzed by an X-ray photoelectron spectroscopy (XPS, PHI-1600, Physical Electronics Inc., USA) using Mg Kα as the radiation source. Survey spectra were collected over a range of 0–1100 eV and the takeoff angle of photoelectron was set at 45°. PHI-MATLAB software was used to analyze the XPS spectra.

2.4.2. Contact angle measurement

In order to characterize surface hydrophilicity, contact angles of the membrane surfaces were measured using a sessile drop method