Journal of Membrane Science 457 (2014) 88–94

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Surface modification of APA-TFC membrane with quaternary ammonium cation and salicylaldehyde to improve performance

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ARTICLE INFO

Article history:
Received 18 September 2013
Received in revised form
9 January 2014
Accepted 11 January 2014
Available online 21 January 2014

Keywords:
Polyamide membrane
Modification
Quaternary ammonium cation
Salicylaldehyde
Anti-biofouling
Chlorine resistance

ABSTRACT

The chlorine resistance and the anti-biofouling properties are the main characteristics of an aromatic polyamide (APA) thin film composite (TFC) membrane in the reverse osmosis (RO) desalination technology. In this work, quaternary ammonium cation (QAC) and salicylaldehyde (SA) were used to modify the membrane surface. QAC and SA can endow the membrane with the durable anti-biofouling properties by acting as the antimicrobial agents and bacteria contact-killers together, while QAC can endow the membrane with the high hydrophilicity by acting as the hydrophilic material, and SA endows the membrane with the high chlorine resistance by acting as the chlorine-consumer. The modified membranes were characterized by the Fourier transform infrared spectroscopy, the zeta potential analyzer, the contact angle analyzer and the scanning electron microscopy. The experimental results showed that the higher density of QAC and SA on the membrane surface led to the higher hydrophilicity, the stronger chlorine resistance and the more powerful anti-biofouling properties of the membrane.

1. Introduction

Fresh water shortage has become a global problem, which has an important influence on social stability and economic development. To solve the current situation, reverse osmosis (RO) membranes as one of the technologies for producing fresh water from saline water and other waste waters has been widely used so far [1]. Commercial RO membranes are generally thin film composite (TFC) composed of a support membrane and an aromatic polyamide (APA) skin layer, which are easily fabricated by the interfacial polymerization of aromatic amines and acyl chlorides as monomers [2]. However, the widespread application of APA-TFC membranes has also brought the challenge of biofouling and chlorination degradation [3], which resulted in deteriorating water permeate quality and shortening membrane lifespan. Earlier much attention had been focused on the chlorine pretreatment during the water feed to kill microorganism and to overcome the microbial adhesion and filter clogging [4]. Dealing with the influence of the residual chlorine, the chlorination degradation of the APA-TFC membrane was found later. Therefore, the current approaches are to create the novel functional monomers and the new modifications and fabrications to improve the chlorine resistance and the anti-biofouling properties.

It was reported that an effective way to reduce chlorine degradation was using piperazine and aromatic secondary amines during the membrane fabrication instead of aromatic primary amines monomers in order to eliminate chlorine-sensitive sites of the APA-TFC membrane and to improve the chlorine resistance [5,6]. However, this approach was at the expense of reduced salt rejection for the membrane. Relatively membrane surface modification was considered as a potential route to prepare the anti-biofouling membrane by binding the hydrophilic compounds included with amino polyol [7], poly(ethylene glycol) [8] or polyepoxide [9], by tethering antimicrobial moieties [10], by grafting betaine monomers for achieving biocide leaching and bacteria contact killing as well as bacteria adhesion resistance [11,12]. However, there was still a risk of the chlorine degradation for the above modified membranes, because they had only high anti-biofouling properties without any high chlorine resistance [13].

As a part of our program, here we report a novel APA-TFC membrane modified with the quaternary ammonium cation (QAC) and salicylaldehyde (SA), in which QAC and SA were used as the hydrophilic material, the chlorine-consumer and the fungicide with the purpose of improving the hydrophilicity, the chlorine resistance and the anti-biofouling properties of the membrane. As is well known, quaternary ammonium salts have been widely used as a bactericide and a surfactant [14]. SA has not only been

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http://dx.doi.org/10.1016/j.memsci.2014.01.024

used as an antibacterial or a preservative, but also it can react with the chlorine like as an aromatic amines or amides to be used as a chlorine-consumer [15].

According to the reports, the residual acyl chloride groups on the APA-TFC membrane surface could react with water or substituted amines, which are the inherent functional groups of the membrane attributed to incomplete reactions of aromatic acyl chlorides monomers with amines during the APA-TFC membrane fabrication by interfacial polymerization [7,16]. To the best of our knowledge, these residual acyl chloride groups can be converted into ester with tertiary amino alcohol. Therefore the tertiary amino groups is first introduced onto the APA-TFC membrane surface based on the above esterification of the residual acyl chloride groups. Secondly, the tertiary amino groups on the APA-TFC membrane surface will be further converted into the quaternary ammonium salt through the quaternarization with 5-chloromethylsalicylaldehyde. The results are that QAC and SA are simultaneously linked on the surface of the APA-THC membrane. Ultimately surface modification of APA-TFC membrane with QAC and SA was completed.

2. Experimental section

2.1. Materials

The polysulfone support membrane was supplied by Vortron Technology Co. Ltd. (Beijing, China). Trimesoyl chloride (TMC), m-phenylenediamine (MPD) and triethyl amine (TEA) were purchased from Jingchun Chemical Reagent Co. Ltd. (Shanghai, China). Dimethylaminoethanol (DMAE) used as a tertiary amino alcohol was purchased from Fuchen Chemical Reagent Co. Ltd. (Tianjin, China). 5-Chloromethylsalicylaldehyde (CSA) was prepared according to the literature [17]. Sodium hypochlorite solution (NaOCl, 4.6 wt%) used in membrane chlorination experiments was purchased from Times Supermarket (Lianyungang, China). Other reagents such as n-hexane and sodium chloride were of analytical grade and used without further purification.

2.2. Fabrication of APA-TFC membrane

The APA-TFC membrane containing the residual acyl chloride groups was prepared by the interfacial polymerization of TMC (0.1 wt% in organic solution) and MPD (2.0 wt% in aqueous solution) [18,19]. The MPD solution was coated over the support membrane for 60 s, then dried. And the MPD saturated support membrane was immersed into the TMC solution for 60 s, then heat cured at 35 °C for 1 min and at 80 °C for 5 min, followed by rinsing with TEA and acetonitrile. This process was resulted in the formation of “nascent” APA-TFC membrane containing the residual acyl chloride groups (referred to as the nascent membrane).

2.3. Preparation of modified APA-TFC membranes

The nascent membrane was immersed into DMAE (0.1–10.0 wt%) aqueous solution or the acetone solution containing DMAE (1.0–50.0 wt%) at 25 °C or 60 °C for 4–20 h. After the esterification, the tertiary aminated APA-TFC membranes (referred to as the TA-membranes) were formed, then rinsed with 2 wt% sodium carbonate solution and dried. At last, the TA-membranes were covered with CSA solution for 2 h at room temperature followed by rinsing with acetone. The results showed that tertiary amino groups had been converted into the quaternary ammonium salt and salicylaldehydes on the surfaces of APA-TFC membranes (referred to as the modified membranes) at the same time.

2.4. Characterization of modified membranes

2.4.1. Membrane chemical composition and morphology analysis

The membrane samples including the nascent membrane, the TA-membrane and the modified membrane were dried at 40 °C before the following analyses. To investigate the surface chemical structure and morphology before and after the modification, attenuated total reflectance 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 100 scans collected at 4 cm^{-1} resolution. The morphologies of the membrane samples were observed by a scanning electron microscope (JEOL J5M-6700F, Electronics Corp., Japan).

2.4.2. Contact angle measurements

The contact angles of the TA-membrane and the modified membrane surfaces were measured in order to characterize the hydrophilicity using a sessile drop method with Dropmeter A-200 equipment (Jiangdong testing instruments Co. Ltd., Ningbo, China). Pure water was used as the probe liquid. Before the measurements, the TA-membrane and the modified membrane samples were conditioned overnight at 40 °C with a relative humidity of 50%. The point data of each membrane was given with an average value based on three contact angle measurements at three random locations on the membrane specimens.

2.4.3. Zeta-potential determinations

The zeta-potential values of the TA-membrane and the modified membrane were determined from electrophoretic mobility measurements using a commercially available electrophoresis measurement apparatus (ELS-8000, Otsuka Electronics, Japan) in a background electrolyte solution containing 10 mmol L^{-1} KCl over a pH range of 3–10 at room temperature. First, the initial pH of the background electrolyte solution was adjusted to pH 3 using HCl solution (1 mol L^{-1}). Then, solution pH was increased in small steps by adding KOH solution (0.2 mol L^{-1}). The streaming potential (ΔE) at each pH was obtained after stabilization. ΔE at five different pressures (ΔP) ranging from 0.1 to 0.5 bar were measured, and the zeta potential (ξ) was determined with the streaming potential slope versus pressure plots based on the Helmholtz-Smoluchowski equation (1) [20]:

$$\xi = \frac{\Delta E \mu \eta}{\Delta P \varepsilon} \tag{1}$$

where ε is the dielectric constant, and μ and η are the viscosity and conductivity of the solution, respectively.

2.4.4. Chlorination experiments of membranes

Short-time exposures of the TA-membrane and the modified membrane to high free chlorine concentrations were professionally accepted [21] to evaluate the membranes' chlorine resistance in this paper. The chlorine solutions with concentrations of 1000, 3000, 5000 and 7000 ppm were prepared by diluting a commercial sodium hypochlorite solution with pure water. The pH value of the free chlorine solutions was adjusted by HCl solution (1 mol L^{-1}). Membrane chlorination experiments were carried out by soaking tests under various chlorine concentrations at pH 4.0 for 4 h at room temperature. The performance of the chlorinated membranes was tested after being thoroughly rinsed with pure water and immersed in pure water for 48 h. The water flux and the salt rejection were tested under 1.6 MPa using 2000 ppm NaCl solution at 25 °C and a pH of 7.0 for 2 h. The water flux was determined by the direct measurement of permeate flow in terms of liter per square meter per hour ($\mathrm{L\,m^{-2}\,h^{-1}}$). The salt rejection