Journal of Membrane Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Fabrication of phenolic resin based desalting membrane with ordered mesostructure and excellent chlorine resistance

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ARTICLE INFO

Keywords:
Phenolic resin
Chlorine resistance
Mesostructure
Desalting membrane
Selectivity

ABSTRACT

A novel ordered cubic mesostructured phenolic resin (PR)/F127 desalting membrane was fabricated by a spin-coating approach *via* the self-assembly of PR oligomer and Pluronic F127 triblock copolymer template on a polyacrylonitrile (PAN) ultrafiltration substrate. It has a thin PR/F127 desalting active layer (30 nm) and negatively charged membrane surface, and It can reject 83.7% potassium sulphate under 2 g/L feed solution and 2.4 MPa operating pressure. The rejection to potassium citrate can be elevated to 95.6%, and corresponding permeate flux is 11.0 L/m^2 h, suggesting good separation capability to multivalent-anion salts. Moreover, it was found that this membrane has a good selective passage for non-charged organic species. Additionally, after the membrane was partially carbonized by adding sulphuric acid, the permeate flux can be dramatically improved to 35.9 L/m^{2}h with a slight potassium citrate rejection decrease (85.4%). Furthermore, the potassium citrate rejection of the membrane can be still kept at a high level (91.7%) after being treated for 6 h in NaClO aqueous solution (pH 4), indicating excellent chlorine resistance performance. This membrane also shows good resistance to acid and alkaline solutions (pH 3–9). The negatively charged membrane surface and F127 templated dense mesostructure play a key role for improving the separation capability of the PR/F127 membrane. This membrane material should have a good application prospect in multi-component separation and reclamation of oxidative waste water.

1. Introduction

Membrane technology has been extensively employed in desalination, water softening, waste water treatment, food manufacture, pharmaceutical and biotechnology in the past few decades [1,2]. It attracts a wide variety of interests of worldwide researchers, because of its advantages in practical application including low operating cost, low energy consumption, operability and good separation performance [3]. Nowadays, the main-stream commercial pressure-driven desalting membranes, are polyamide (PA) based polymer materials, due to their high salt rejection, permeate flux, and good resistance to microbial attack and pressure compression [4,5].

Furthermore, active chlorine is usually added into the feed solution in practical water treatment process [6,7], acting as a good biocide to mitigate fouling, elongate membrane life span and regenerate membrane due to its low cost and high efficiency [8–10]. However, these traditional PA membranes usually possess poor resistance to active chlorine. The hydrogen bonds formed between the amide groups of PA material can be severely destroyed [11,12], which decreases the densification of PA polymer network and lowers its rejection to salts and organic species. Although the concentration of active chlorine can be decreased by adding reductant ($Na_2S_2O_3$) for avoiding destroying the membrane structure, the operating cost will be dramatically increased. Therefore, this limits the practical application of PA membrane in desalting field.

Developing new membrane materials using novel raw materials by interfacial polymerization (IP) reaction, layer-by-layer assembly, and other fabrication approaches has been extensively employed for improving the chlorine resistance [13–15]. For example, Cho et al. [15] fabricated a glutaraldehyde crosslinked polyelectrolyte membrane with sulfonated polysulfone by spraying assisted layer-by-layer assembly approach, which has around 96% $MgCl_2$ rejection and can withstand the 3500 ppm of chlorine attack for more than 6 h at pH 8.0. To date, chlorine resistance is usually evaluated under neutral and/or basic conditions with relatively weak oxidation [13–21], although stronger chlorine resistance membrane is also required in practical application. Only few reports are involved with the fabrication of desalting membrane possessing strong chlorine resistance under low pH-value solution ($pH < 5$) [22–24]. Developing novel desalting membrane with excellent resistance to acidic active chlorine solution currently still faces

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http://dx.doi.org/10.1016/j.memsci.2017.10.058
Received 1 September 2017; Received in revised form 27 October 2017; Accepted 29 October 2017

Please cite this article as: Li, Q., Journal of Membrane Science (2017), http://dx.doi.org/10.1016/j.memsci.2017.10.058

great challenge.

Additionally, selective separation for a multi-component solution is very crucial to applications in chemical processes, food and beverage process, and waste-water reclamation process. Traditionally, selection separation is accomplished by combining two or three different membrane processes (such as nanofiltration, reverse osmosis, and electrodialysis) and/or by adjusting the pH value, concentration, operating pressure of the feed solution [25,26]. However, these approaches are usually complex, costly, and time consuming. Phenolic resin (PR), as an important polymeric precursor and industrial raw material, has been extensively employed to fabricate microporous and/or mesoporous carbon membranes supported by inorganic substrates, because of the heat resistance, thermosetting, high carbon yield properties, and low cost [27,28]. These membranes are usually used for gas separation, and ultrafiltration [27–29]. Moreover, PR has many hydroxyl groups, which can form strong hydrogen-bond interaction with polyether surfactants, such as Pluronic F127, P123, and F108. Zhao group prepared a series of highly ordered mesoporous polymer and carbon materials, using PR oligomer as the raw material, triblock copolymer surfactant as the template, and silicon wafer as the substrate by evaporation induced self-assembly (EISA) and removing the template in high temperature (> 350 °C) [30–33]. These works promoted the development of PR based mesoporous materials, and many new water-treatment materials soon appeared. For example, Chua et al. [34] synthesized a hexagonal mesostructured mesoporous silica-carbon nanocomposite membrane supported by a porous alumina substrate using PR oligomer and tetraethyl orthosilicate as the raw materials and Pluronic F127 as the template, which exhibited good separation performance in vacuum membrane distillation. Furthermore, the formed hydrogen bonds between these hydroxyl groups of PR and ethylene oxide (EO) chain of the polyether surfactant can decrease the reduction activity of PR polymer and improve their resistance to oxidants. Therefore, fabrication of mesostructured PR/polyether surfactant composite membrane may be an effective solution for improving chlorine resistance of desalting membranes.

To the best of our knowledge, there is not yet any report involved with the fabrication of PR based polymer desalting membrane. Herein, we report a mesostructured PR based desalting membrane fabricated using F127 as the template by spin-coating method. This membrane shows high rejection to multivalent-anion salts and good selective passage for non-charged organic species. This PR/F127 membrane exhibits excellent chlorine resistance after being exposed to 3500 ppm active chlorine solution (pH 4) for 6 h. It has great application prospect in multicomponent separation and reclamation of oxidative wastewater.

2. Experimental

2.1. Chemicals and materials

Pluronic F127 (PEO_{106}–PPO_{70}–PEO_{106}, $M_w = 12{,}600$) was purchased from Sigma Aldrich. Phenol, formaldehyde, sodium hydroxide, ethanol, sucrose, potassium sulphate, potassium citrate, hydrochloric acid, and sodium hypochlorite were obtained from Chem Supply. Polyacrylonitrile (PAN) ultrafiltration membrane (MWCO = 20 kDa) was bought from AMI®, USA. TW30 polyamide membrane was obtained by cutting a TW30-2521 membrane element produced by Dow, USA. According to the data provided by the company, this element possesses 99.5% salt rejection and 0.76 m^3/d permeate flow rate under 2 g/L of sodium chloride feed solution, 1.55 MPa operation pressure, and 8% recovery rate.

2.2. Fabrication of phenolic resin/F127 (PRF) composite desalting membranes

The PR oligomer was synthesized by the polymerization of phenol and formaldehyde using a base catalyst [35]. The mesostructured PRF desalting membrane was fabricated using PR oligomer as the raw material, Pluronic F127 as the template, and PAN ultrafiltration membrane as the substrate by spin-coating method. The precursor solution was prepared based on the report of mesoporous FDU-16 polymer [33,35]. Typically, 0.5 g F127 was dissolved in 15.5 g ethanol by stirring under room temperature. Then, 3.34 g of 30% PR oligomer ethanol solution was added into the above solution to form a homogeneous precursor solution. 2 g precursor solution was then dropwisely spin-coated on the surface of the circular PAN substrate with 6 cm diameter within 2 min with a rotating rate of 4000 rpm. After this, the coated PAN membrane was kept in room temperature for 5 h to allow the precursor to self assembly. Finally, the PRF membrane (named as PRF0) was obtained by thermal crosslinking the precursor coated membrane in oven at 100 °C for 20 h. It was stored in dry state at room temperature.

To improve the permeate flux of the PRF desalting membrane, a series of PRF membranes carbonized partially by sulphuric acid were prepared using the aforementioned procedure by respectively introducing 0.06 g, 0.12 g, and 0.25 g of 44 w/w% sulphuric acid into the precursor solution for carbonizing the membrane during the thermal crosslinking process. The carbonized membranes are correspondingly designated as PRF1, PRF2 and PRF3.

Additionally, for confirming the role of F127 template in PRF-membrane separation performance, pure PR membrane without F127 (named as PPR) as a control sample was also fabricated using the same procedure as PRF0 membrane. The PR oligomer concentration used was about 2.3 times of that in the PRF0 precursor solution.

2.3. Surface and microstructure analysis

The membrane surface functional groups were characterized using FTS 7000 Fourier transform infrared (IR) spectrometer (Varian, USA) equipped with an attenuated total reflectance (ATR) accessory. The surface elements and compositions were analysed using Kratos Axis Ultra X-photon spectroscopy (XPS, Thermo Scientific, UK). Surpass solid surface zeta potential instrument (Anton Paar, Austria) was employed to measure the surface charge properties. Small angle X-ray diffraction patterns (SAXRD) were collected with D8 Advance (Bruker, Germany) powder X-ray diffractometer by using Cu Kα radiation (40 kV, 40 mA). The *d*-spacing value was calculated using the formula $d = \lambda/2(\sin\theta)$, and the unit cell parameter was calculated using the formula $a = (\sqrt{2})d_{110}$. To prepare the SAXRD samples, the PR precursor solution mentioned above was poured on a petri dish, and treated with the same procedure as the PRF membrane fabrication. After thermal crosslinking, the sample was scratched off and ground into powder with an agate mortar. The membrane surface morphologies were investigated using Quanta 200F (FEI, USA) scan electronic microscopy (SEM).

2.4. Separation performance test

2 g/L of sodium chloride, potassium sulphate, potassium citrate, and sucrose aqueous solutions were respectively used as feed solutions to evaluate the rejection and permeate flux of the membranes using a dead-end filtration cell (Sterlitech HP4750) with an active membrane area of *ca.* 11.34 cm^2 under 2.4 MPa test pressure at room temperature. The test pressure was generated and controlled by connecting a nitrogen cylinder. To decrease concentration polarization on the membrane surface, the solution was constantly stirred using a magnetic stirrer. Prior to the evaluation, all membranes were compacted at 2.4 MPa for 2 h using Milli-Q water. The rejections of potassium sulphate and potassium citrate were calculated by conductivity measurement. The sucrose rejection was calculated by measuring the concentrations of feed solution and permeate using high performance liquid chromatography (HPLC). The permeate flux was calculated based on the mass of permeate collected over time recorded by an Ohaus