Journal of Membrane Science 361 (2010) 113–119

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Study on phosphorylated Zr-doped hybrid silicas/PSF composite membranes for treatment of wastewater containing oil

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ARTICLE INFO

Article history:
Received 7 March 2010
Received in revised form 29 April 2010
Accepted 1 June 2010
Available online 10 June 2010

Keywords:
Phosphorylated
Hybrid silica
Zr-doped
Composite membrane
Wastewater containing oil

ABSTRACT

Polysulfone (PSF) membranes are broadly applied in the field of the treatment for wastewater containing oil owing to their good physicochemical stability, resistance to oxidation and chlorine. But they are easy to be contaminated by oil for its hydrophobic property, which limits their application in large scale. To enhance the capability of PSF membrane, such as hydrophilic property, anti-fouling ability and tensile strength, phosphorylated Zr-doped hybrid silica particles (SZP particles) were added to the porous matrix of PSF and a novel composite membrane (SZP/PSF) was prepared through a sol–gel process under optimum preparation conditions. The results of tensile strength and contact angle measurements show that the mechanical strength and hydrophilic property of composite membrane have been enhanced to a large extent respectively. SEM micrographs indicate that composite membrane with the asymmetry structure has both layers of compact layer and porous layer with SZP particles uniformly dispersed in PSF. The result shows that the oil concentration of 0.84 mg/L in permeation meets the standard for wastewater reuse (less than 10 mg/L). It can be concluded that the anti-fouling ability and hydrophilic property of composite membrane are significantly enhanced, and therefore, the novel composite membrane is desirable in the treatment of wastewater containing oil.

1. Introduction

Wastewater containing oil produced from industry pollutes the environment and is difficult to be treated. Many conventional methods including gravity settling, dewatering and incineration perform cannot efficiently treat emulsified and soluble oil in wastewater. Membrane technology is currently utilized in treating wastewater containing oil; this is because wastewater containing oil may be effectively treated using membrane technology [1]. However, membranes are easy to be contaminated by oil, which forms an oil-layer on membrane surface [2]. Hence, the enhancement of the hydrophilic and anti-fouling property of PSF membranes has become a focus of many researchers.

The method of doping inorganic oxide particles to polymer to prepare organic–inorganic composite membranes is attractive, owing to its simple operating process and preparation technology. Bottino et al. [3] improved membrane's thermodynamic property, mechanical strength, tenacity and so on by adding nanosilica to poly(vinyl alcohol) membrane. Nunes et al. [4] prepared composite membrane with SiO_2 nano-dispersed in polyetherimides (PEI) and the resistance of the membrane to compactability has increased to some extent. Zhang and Ding [5] doped $A1_2O_3$ to PSF membrane to enhance the hydrophilic property and anti-fouling ability of the membrane.

Though the capability of polymer membranes can be enhanced by adding inorganic oxide particles, further enhancement is limited because there are few Lewis acid sites and hydroxide radicals on the surface of stoichiometric monocomponent inorganic oxide particles [6]. Nonstoichiometric inorganic oxide nanoparticles have many point defects inside and lots of exposed hydroxide radicals on the surface, so these nanoparticles show stronger activity in the course of chemical bonding than stoichiometric monocomponent inorganic oxide particles [7,8]; especially when nonstoichiometric inorganic oxide nanoparticles are filled in polymer membranes, the capability of membranes is evidently improved. Recently, Zhang et al. doped small-sized particles such as Ce-doped nonstoichiometric nanosilica, Y-doped nonstoichiometric zirconnia to PSF membrane to prepare composite membranes for enhancing its hydrophilic property and anti-fouling ability [9,10].In this paper, a novel composite membrane (SZP/PSF) was prepared by adding SZP particles to the porous matrix of PSF to enhance the capability of PSF membrane, such as hydrophilic property, anti-fouling ability and tensile strength. The properties of membranes were evaluated by permeability, tensile strength, hydrophilic property and so on. Further

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doi:10.1016/j.memsci.2010.06.002

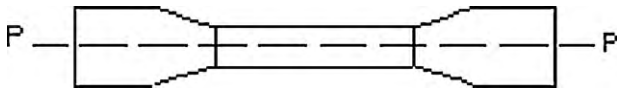

Fig. 1. Shape of specimen for tensile test.

more, these composite membranes could be used to treat wastewater containing oil.

2. Experimental

2.1. Materials and reagents

PSF was purchased from Dalian Polysulfone Co., Ltd. and its MW and polydispersity were 84,400 Da and 1.37, respectively. SZP particles with the diameter from 1 to 3 μm were prepared in our laboratory. Bovine serum albumin (BSA), bought from Beijing Aobo Star Biotechnology GmbH. Polyethylene glycol with average MW 400 Da (PEG400) was supplied by Tianjin Jinyu Fine Chemical Factory. N,N-dimethylacetamide (DMAC) was obtained from Tianjin Damao Service of Chemical Instruments. The last two kinds of reagents were analytical grade and used as received.

2.2. Preparation and characterization of membranes

2.2.1. Preparation of SZP particles

Preparation process of SZP particles is similar to literature [11].

2.2.2. Preparation of membranes with different casting solutions

Preparation process of SZP/PSF membranes is similar to literature; the details are as follows [12].

Firstly, DMAC in a 500 mL flask was heated to 40–50 °C in a water bath. PSF was then added and dissolved with stirring. And then, PEG 400 with a mass ratio of 10% to PSF was added as porogen to promote the yield of pores in the gelation process. After that, SZP particles with a mass ratio of 10% to PSF were added into the mixture. They were mixed with vigorous stirring under the condition of ultrasounds until a homogenous solution was obtained. And then the solution was stilly kept for 24–48 h. Then the solution was poured onto a dense glass plate and cast to form thin films (thickness ca. 0.3 mm) that after a 10 s exposure period in air (20 °C and 60% relatively humidity) were immersed into a water bath at 20 °C. Membranes were leached under running water for at least 2 d prior to being soaked in 30 wt.% glycerin aqueous solution. Finally membranes were stored in de-ionized water containing 1 wt.% formaldehyde to avoid bacteria growth.

PSF membranes and nanosilica/PSF membranes were prepared by using the same procedure mentioned above, except for inorganic oxide nanoparticles were doped to casting solutions. Nothing was added to the former casting solution and nanosilica particles instead of SZP particles were added to the latter casting solution.

2.2.3. Measurement of tensile strength

Specimen was cut out from a membrane sample which should be level led off. Dogbone-shaped specimen is shown in Fig. 1. The specimen was tested with a M350 almighty material extensometer supplied by Testometric Corporation, England.

Operating parameters were: the length of the specimen in gauge section, 25 mm; the width, 4 mm; the thickness, 0.30 mm; applied stroke speed, 15 mm/min; measuring range, 0–3 MPa; test temperature, 21 °C.

2.2.4. Measurement of hydrophilic property

Contact angles of membrane samples cast from different casting solutions were measured with a 1501 dynamic contact angle measuring instrument supplied by Micromeritics Corporation, America. The accuracy of measurements is ±0.1 °C.

2.2.5. Measurement of porosity and pore diameter

Round membrane piece with its diameter of 6 cm was weighed accurately with vacuum drying for 8 h at 50 °C. After being immersed in water for 48 h, the same piece was wiped with filter paper and weighed again.

Porosity (Pr) was calculated as a function of the membrane weight, which can be described by the following equation:

$$P_r = \frac{W_w - W_d}{\rho A l} \times 100\% \quad (1)$$

$$A = \frac{1}{4}\pi d^2 \quad (2)$$

where W_w represents weights of membrane containing water at equilibrium swelling; W_d the weights of membrane at dry state; A the area of the membrane; l the thickness of the membrane; d the average diameter of the membrane; ρ the density of water.

Membrane pore diameter was measured by thermoporometry. Thermal effect of water's liquid–solid transition in membrane was measured by DSC. Assumes that the pore channels in membrane are cylindrical, pore diameter can be calculated by the following formula:

$$r_p = 0.68 - \frac{32.33}{\Delta T} \quad (3)$$

$$w = -0.155\Delta T^2 - 11.39\Delta T - 332 \quad (4)$$

where r_p is the pole radius (nm); ΔT the subcooled temperature (°C); w is the thermal effects of liquid–solid transformation (J/g).

2.2.6. SEM studies of membrane

The composite membrane pieces were thoroughly rinsed by de-ionized water, immersed in 30% glycerin aqueous solution and then dried in air for the SEM analysis. Cross-section samples were obtained by being freeze-fractured in liquid nitrogen to obtain a tidy cross-section and then sputtered with gold. Membrane surfaces and cross-section were observed under a JEOL JSM-6400F scanning electron microscope (SEM).

2.3. Oil–water separation studies

The model waste water containing oil (oil-in-water emulsion) was created by machine oil and de-ionized water with vigorous stirring at 3000 rpm speed over 30 min until a homogenous solution was obtained, whereupon the emulsion was prepared with an oil concentration of 80 mg/L. The stability of the emulsion was observed visually over 24 h period and the mixture maintained cloudy, turbid, indicating that oil was in emulsified and soluble condition. Diameter of the used membrane sample was 50 mm, hole diameter of the used membrane sample between 0.1 and 0.2 μm, thickness of the used membrane sample 0.2 mm. Membrane evaluation device was made in our laboratory. The conditions for the long term run of the separation experiments was intermittent mode.

2.4. Cleaning and operation studies of membrane

In general, the permeation flux of membrane would decline owing to fouling and block, even under optimum operating condition. So it is necessary to clean membrane to remove pollutant and resume the permeate flux as much as possible. To regenerate membranes and resume the permeation flux of membranes, combination of backflushing and chemical cleaning method are adopted in this paper. PSF membrane and SZP/PSF composite membrane (the amount of adding SZP particles 10 wt.%) are compared, and