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Preparation and characterization of phosphorylated Zr-doped hybrid silica/PSF composite membrane

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ABSTRACT

Polysulfone (PSF) membranes are broadly applied in many fields owing to good physicochemical stability, resistance to oxidation and chlorine. But when treated with wastewater containing oil, PSF membranes are easy to be contaminated for its hydrophobicity, which can result in the declining of flux and lifespan of the membrane and limit their application in large scale. To enhance the capability of PSF membrane in the above circumstances, phosphorylated Zr-doped hybrid silica particles (SZP particles) were firstly prepared. SZP particles have various point defects inside their structure and lots of hydroxide radicals on their surface. SZP particles were added to the porous matrix of PSF to prepare a novel composite membrane (SZP/PSF) through a phase inversion process. Finally, the optimum preparation conditions of SZP/PSF composite membranes were determined. The optimum conditions are: the mass ratio of PSF, PEG400 and SZP is 12:10:10; ultrasound 10 min inside each 30 min; the pre-evaporating time is 10 s. Optimized SZP/PSF composite membrane was characterized by scanning electron microscope (SEM) and ultrafiltration experiment. The results indicate that SZP particles can be uniformly dispersed in SZP/PSF composite membranes with excellent hydrophilic property, antifouling capability and tensile strength. Therefore, it can be concluded that the optimized SZP/PSF composite membrane is desirable in the treatment of wastewater containing oil and wastewater.

1. Introduction

Wastewater containing oil produced from industry not only pollutes the environment but also wastes crude oil and water resource. Moreover, emulsified and soluble oil in wastewater is difficult to be treated by traditional methods. Membrane technology has been widely used in water treatment, especially utilized in the treatment of wastewater containing oil [1]. This is because membrane separation technology is one of the most potential operation units of chemical engineering, for it has a lot of advantages such as easy operation, low cost, no phase transition, high efficiency and capability of reducing contaminants. But large-scale applications of the membrane separation technology (especially PSF membrane) for wastewater containing oil are limited because polymer membranes are easy to be contaminated by oil. Hence, the enhancement of the hydrophilic and anti-fouling property of PSF membranes captured a lot of attention of many researchers [2].

In recent years, lots of methods have been developed to enhance the properties (such as hydrophilic property, tensile strength and anti-fouling ability) of polymer membrane. 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. By adding ZrO_2 particles to PSF, Genné et al. [3] prepared a novel porous ZrO_2/PSF composite membrane to increase the permeability and reduce the resistance of composite membrane. By adding nanosilica to poly-4-methyl-2-pentine membrane, Merkel et al. [4] prepared a sort of composite membrane which had high permeability and selectivity. Yang et al. [5] added TiO_2 to PSF membrane to prepare a sort of composite membrane which had excellent water permeability, hydrophilic property, mechanical strength and good anti-fouling ability.

Though the capability of polymer membranes can be enhanced by adding inorganic oxide particles (ZrO_2, TiO_2, SiO_2, etc.), further enhancement of polymer membranes' properties is limited due to few Lewis acid sites and hydroxide radicals on the surface of stoichiometric monocomponent inorganic oxide particles [6]. Many researches [7,8] have been demonstrated that nonstoichiometric inorganic oxide particles have many point defects inside them and lots of exposed hydroxide radicals on their surface, which show stronger activity in the course of chemical bonding than stoichiometric monocomponent inorganic oxide particles. So when

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nonstoichiometric inorganic oxide particles are dispersed in polymer membranes, the capability of polymer membranes is evidently improved. Recently, we have been committing to study on high active inorganic oxide particles for the membrane modification. In our previous works, we prepared Ce-doped nonstoichiometric nano-silica particles and sulfated Y-doped nonstoichiometric zirconia particles which were doped into PSF membranes to prepare composite membranes to enhance their hydrophilic property, tensile strength and anti-fouling ability [9–12]. In this paper, in order to enhance the capability of PSF membrane, phosphorylated Zr-doped hybrid silica particles (SZP particles) were firstly prepared. SZP particles have various point defects inside their structure and lots of hydroxide radicals on their surface. Then, SZP particles were then added to the porous matrix of PSF to prepare a novel composite membrane (SZP/PSF) through a phase inversion process. Finally, the optimum preparation conditions of SZP/PSF composite membranes were determined, and the properties of SZP/PSF as-prepared composite membrane were investigated.

2. Experimental

2.1. Materials and instruments

PSF was provided by 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. The SZP particles were characterized with SEM (X-650, Hitachi, Japan) and X-ray diffraction (XRD) with a PANalytical X'Pert HighScore (produced in Netherlands) using Co Kα radiation under 40 kV 40 mA. *N*,*N*-dimethylacetamide (DMAC) was purchased from Tianjin Damao Service of Chemical Instruments. Polyethylene glycol with average MW 400 Da (PEG400) was supplied by Tianjin Jinyu Fine Chemical Factory. The last two kinds of reagents were analytical grade and used as received.

2.2. SZP particles preparation

SZP particles with the diameter from 1 to 3 μm were prepared in our laboratory as an additive of composite membrane. The preparation process of SZP particles is similar to the literature [13], and the detailed procedure is as follows:

$ZrOCl_2{\cdot}8H_2O$ and TEOS were grinded fully in a mortar, and APTES (aminopropyltriethoxysilane) was then added to the mortar for mixing. Then the whole mixture was put in an ice water bath and stirred to form the gelatin form, and followed by being settled in room temperature for 24 h, then dried for 24 h in 100 °C. Then spread in the mixed solution of H_3PO_3 and HCHO, refluxed under the temperature of 80 °C for 6 h, then cooled down to room temperature, repeated centrifugal and washed. And then dried in 100 °C to constant weight, and finally samples of different diameters of SZP particles were obtained.

2.3. Composite membrane preparation

Dried PSF was firstly added to *N*,*N*-dimethylacetamide (DMAC), then stirred at 40–50 °C in a water bath to completely dissolve PSF. Then PEG400 was added as porogen to promote the yield of pores in a gelation process. After SZP particles were added to the mixture, vigorous stirring was needed until a homogenous solution was obtained. Finally, the solution was stilly kept for 24–48 h. The membranes (thickness ca. 0.3 mm) were cast and formed on a horizontal glass plate using a glass blade. After evaporated 10 s in the air, the membranes were leached by running water for 2 days. Finally, membranes were soaked in 30 wt.% glycerin aqueous solution for 5–12 h. To comparison, the pure PSF membranes were obtained by using the same procedure mentioned above. Finally membranes were stored in de-ionized water containing 1 wt.% formaldehyde to avoid the growth of bacteria. The influence of the concentration of PSF, content of SZP particles and content of PEG400 on the performance and morphology structure of the membranes were studied.

2.4. SEM studies

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

2.5. Measurement of permeation flux

The flux (water permeation flux) was measured under pressure of 0.10 MPa at the temperature of 20 °C. The flux (F) is calculated as follows:

$$F = \frac{V}{At} \tag{1}$$

$$A = \frac{1}{4}\pi d^2 \tag{2}$$

where V is the volume of permeation (L), A is the effective membrane area (m^2), t is the operating time (s) and d is the diameter of membrane (m).

2.6. Measurement of retention

The retention of membrane can be measured by the solvent of Bovine Serum Albumin (BSA). Azocarmine and H_2SO_4 were used as color agent in this performance. The retention (R) of the membrane can be calculated by the following:

$$R = \left(1 - \frac{C}{C_0}\right) \times 100\% \tag{3}$$

where C is the concentration of BSA in the permeation (mg/L), C_0 is concentration of BSA in the feed (mg/L).

2.7. 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.

3. Results and discussion

3.1. Characterization of SZP particles

It can be seen from Fig. 1 that SZP particles with the diameter from 1 to 3 μm are spherical shape. The schematic of structure of SZP particle is shown in Fig. 2. The phosphorus hydroxyls are grafted to the surface of hybrid silica [14]. At the same time, Si–Zr composite oxide also has lots of strong Lewis acid sites and Brönsted acid sites. Thus, SZP particles theoretically perform the good hydrophilic property.

3.2. Effect of concentration of PSF on performance of composite membrane

At first, the content of PEG400 and SZP particles were both fixed at 10 wt.% [11]. As could be seen in Fig. 3, when the concentration of PSF changes from 10 to 18 wt.%, the flux (water permeation flux) of