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Rapid communication

Preparation of polysulfone–Fe_3O_4 composite ultrafiltration membrane and its behavior in magnetic field

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Abstract

In this paper, polysulfone (PSF)–Fe_3O_4 composite ultrafiltration membrane was made by phase-inversion process and its structure of surface and cross-section was examined by scanning electron microscopy. Especially its ultrafiltration performance in magnetic field was studied by determining the variation of rejection to lysozyme. As a result, the addition of nano-sized Fe_3O_4 particles had an important influence on membrane performance in magnetic field. The rejection to lysozyme declined obviously in magnetic field, however, when the magnetic field was moved away, the rejection made a comeback quickly. While the rejection of the PSF membrane remained invariable in magnetic field. Furthermore, with the increase of the magnetic intensity, the rejection declined more obviously. Hence, the result indicated that it was possible to separate different substances with a composite membrane in turn by altering the magnetic intensity.

Keywords: Polysulfone–Fe_3O_4 composite ultrafiltration membrane; Phase-inversion; Nano-sized; Magnetic field; Rejection to lysozyme

1. Introduction

Ultrafiltration (UF) has been widely used in many fields, such as wastewater treatment [1], protein recovery and concentration [2–5] and so on. In recent years, different techniques have been developed to improve the performance of membrane. Among which organic polymer membrane mixed with inorganic particles aroused great interest especially [6–13].

However, once the membrane has been formed, it would be difficult to change its molecular weight cut-off (MWCO). That is to say, the substances cannot be separated with a membrane if there is no remarkable difference between their molecular weights. In order to gain the single object, it will cost much and need complex operations, which limit their large-scale application. If the MWCO of the membrane can change with the condition of the operation as expected, objectives can be separated by it in turn. Then it will contribute to the development of UF membrane.

The objective of this work was to prove the novel idea feasible. PSF–Fe_3O_4 composite membrane was prepared using the phase-inversion method by adding nano-sized Fe_3O_4 particles to casting solution. The composite membrane has magnetism and is performed in a magnetic field.

Fe_3O_4 nanoparticles have been used in the magnetic liquid, magnetic memorizing material, magnetic polymer microspheres and so on for its superparamagnetism [14–19]. They will be magnetized and arrange along the magnetic line of force in magnetic field, and when the field is moved away, they can come back quickly. Furthermore Fe_3O_4 have magnetic striction and the magnetostriction coefficient of which is 39×10^{-6}. Magnetic striction means the size of matter will change along its axes in a magnetic field [20].

Because the nano-sized Fe_3O_4 particles were enwrapped by oleic acid, they were expected to be able to distribute homogeneously in the membrane [21]. On the one hand, when the composite membrane was in magnetic field, the nano-sized Fe_3O_4 particles would bring deformation to the skin layer and pore structure. On the other hand matters have their peculiar sensitivity in the magnetic field [22], so matter will permeate through the PSF–Fe_3O_4 composite membrane more easily or difficultly in the magnetic field. By adjusting the magnetic field,

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different substances will probably pass through the composite membrane in turn.

The effects of the addition of the nano-sized Fe_3O_4 particles on the membrane morphology, contact angle, porosity and thermal analysis were examined, especially the composite membrane performances in magnetic field were examined by pure water flux and variation of the rejection to lysozyme. The results of the work indicate the novel idea doable.

2. Experimental process

2.1. Materials

The PSF ($[\eta] = 0.62$) was purchased from ShuGuang chemical plant in Shanghai. Fe_3O_4 nanoparticles enwrapped in the oleic acid (8–12 nm in size) were purchased from Anhui Jinke Magnetic Liquid Co. Ltd. Polyethylene glycol (PEG) with average molecular weight of 400 and dimethylformamide (DMF) were supplied by Shanghai Chemical Regents Company.

2.2. Preparation of membranes

PSF–Fe_3O_4 composite membrane was prepared by the phase-inversion method. Polymer dope consisting of PSF (15%, by weight of the solution), PEG (2%, by weight of the solution) and DMF (83%, by weight of the solution) was dissolved at about 60 °C for 3 h with vigorous stirring. After the uniform polymer dope was formed, nano-sized Fe_3O_4 particles were added to the dope with vigorous stirring for 3 h. Fe_3O_4/PSF ratio (w/w) of casting solution was 0.27. Then the casting solution were kept in the dark for at least 12 h to remove air bubbles. Casting solutions were casted with 100 μm casting knife onto the polyester non-woven fabric. The membrane evaporated at 20 ± 1 °C, 60 ± 5% relative humidity for 1 min before it was immersed in 15 ± 1 °C deionized water coagulation bath. The preparation of PSF membrane was the same with that of PSF–Fe_3O_4 composite membrane.

2.3. Characterization

2.3.1. Characterization of the PSF membrane and the PSF–Fe_3O_4 composite membrane

The morphology of the surface and cross-section of the membranes were observed by scanning electron microscope (TSM-6700F). Cross-sections of membranes were prepared by being fractured in the liquid nitrogen. Samples were coated with a thin layer of gold before analysis.

Differential thermal analysis and thermal gravitational analysis were carried out using differential scanning calorimeter (DSC-60, Japan Shimadzu) and thermal gravitational analysis-different thermal analyser (DTG-60H, Japan Shimadzu) to observe the effect of Fe_3O_4 particles on the polysulfone membrane.

Static contact angles of the PSF membrane and PSF–Fe_3O_4 composite membrane were measured using the captive air bubble technique. Membranes were inverted in deionized water and air bubbles were placed in contact with the surface. The static angles were measured using an Eromag-I contact angle testing apparatus. All data were measured 10 times and averaged.

Porosity was calculated as follows:

$$\theta = 1 - \frac{m_1 + m_2 - m_3}{V_t \rho_w} \quad (1)$$

where m_1, m_2 and m_3 are the mass of the dried sample, the mass of a pycnometer leveled with pure water and the mass of the same pycnometer when it contains the sample, respectively. V_t is its geometrical or total volume ($V_t = S\Delta\chi$) and ρ_w is the water density. This method is called pycnometric [23].

2.3.2. The effect of magnetic field on performances of the membranes

The effect of external magnetic field (B_e) on performances was examined with a device as shown in Fig. 1. The effective membrane area fixed in membrane cell was 0.0201 m^2. The upstream pressure and the feed flow rate were adjusted with a throttle valve. The asymmetric magnetic field is produced

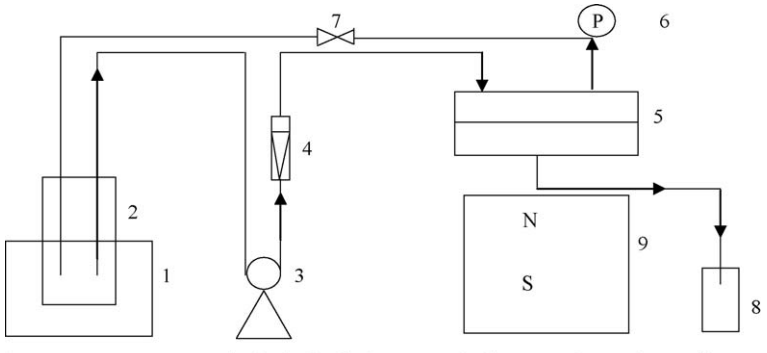

Fig. 1. Schematic diagram of the crossflow lysozyme filtration system.