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The preparation and application of a low-cost multi-channel tubular inorganic–organic composite microfiltration membrane

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ABSTRACT

Low-cost multi-channel tubular inorganic–organic composite microfiltration membranes were prepared by a convenient compression coating approach employing 19-channel ceramic support (pore sizes ranging from 5 to 20 μm) as substrate, and PVDF/CA blend as separation layer. The membranes were characterized in terms of water permeability, selectivity, as well as the performance of purifying rice bran fermentation. Obtained results show that the pure water flux of composite membranes with PVDF/CA skin layer increases from 200 to 2000 L/m^2 h as the PVDF/CA concentration in coating solution decreases from 18 to 8 wt%, and the retention rate to polyethylene oxide (Mw = 1,000,000) is much higher than that of ceramic membrane with an average pore diameter of 50 nm, and the ratio of turbidity removal is up to 99% when the composite membranes were applied to treat rice bran fermentation broth. More significantly, the composite membranes showed a high recovery rate of pure water flux after a simple physical cleaning process. It is found that the concentration of PVDF/CA coating solution appeared to be the key factor on the separation performance of composite membrane, and higher concentration would result in a higher rejection rate. To understand the relationship between the preparation condition and membrane performance, the viscosity of coating solution and morphology of composite membranes were characterized by arotational viscometer and scanning electron microscope (SEM), respectively. Finally, the result of cost analysis shows that the composite membranes have an advantage over the commercial ceramic membranes and could be recognized as a promising a candidate for industrial applications.

1. Introduction

Due to their remarkable advantages, such as high temperature and pressure resistance, high stability in organic media, stable over a wide pH range, easy regeneration after fouling and long reliable lifetime [1–3], inorganic ceramic microfiltration (MF) membranes are widely applied for oily wastewater treatment in petrochemical industry [4–6], bacteria removing in pharmaceutical industry [7,8], and fermentation broth purification in food and biological industries [9–11]. For these applications, ceramic MF membranes have been prepared by coating inorganic powder layer onto ceramic substrate through either particle sintering method [12–14] or sol–gel process [15–17]. The complicated preparation procedure especially the high temperature sintering process often leads to a high manufacture cost and restricts the application of ceramic membranes. Against that, organic polymeric membranes can be easily prepared through solution casting [18] or hot press methods [19], and the membranes structure can easily be fine-tuned through controlling the parameters such as concentration, evaporation and gelation processes. The production cost is very low and the obtained membranes possess all the desired advantages, such as high selectivity, diverse variety, and manageable pore structure [20]. Nevertheless, polymer membranes are difficult to clean and unstable in high temperature and organic media [21]. This inspired us that the membranes composited from inorganic ceramic and organic polymer materials can combine together the merits of two materials and of low cost with high separation performance.

Directly coating polymer solution onto a ceramic substrate is an easy method to fabricate inorganic–organic composite membranes. Ji et al. [22] developed tubular ceramic-based multilayer composite nanofiltration (NF) membranes via layer-by-layer method, and the ceramic substrates have average pore sizes of 0.1–0.2 μm. Xing et al. [23] fabricated highly fouling-resistant composite membranes by grafting polyacrylic acid (PAA) brushes onto ZrO_2 ceramic membranes with an average pore diameter of 0.2 μm. Nandi et al. [24] prepared the composite MF membranes

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by coating 2–4 wt% cellulose acetate (CA) on ceramic plate, where the average pore size of ceramic substrate is 0.56 μm. Somen et al. [25] prepared ceramic-chitosan composite membranes for both microfiltration (MF) and ultrafiltration (UF) applications using ceramic supports with an average pore size of 1.1 μm. Nataraj et al. [26] fabricated ceramic-CA composite membranes by coating 17 wt% CA on ceramic tube with different configurations, in which the mean pore size of ceramic support was 1.2 μm. However, in these preparations, the pore sizes of ceramic supports were required to be around 0.1–1.2 μm, i.e. ceramic MF membrane (not raw substrate) should be used, which inevitably leads to a high cost of ceramic-polymer composite membranes.

In this research, 19-channel ceramic tube with pore sizes of 5–20 μm was chosen as the support for the composite membranes to further reduce the cost. Poly(vinylidene fluoride) (PVDF) was selected as the main coating material. As PVDF is widely used to fabricate MF membrane due to its outstanding solvent resistance, good thermal stability and mechanical strength [27]. However, microporous PVDF membrane has low permeability and poor antifouling ability because of its highly hydrophobic property [28,29]. Thus, another hydrophilic material CA was selected as an additive to improve the permeability and antifouling properties [30,31]. The composite membranes were prepared via coating method followed by conventional dry-wet phase inversion, and the effect of solution viscosity on the membranes morphologies was discussed. The pure water flux and the retention for polyethylene oxide (Mw = 1,000,000) were investigated and compared with standard ceramic MF membrane (50 nm). To investigate the application feasibility, the obtained composite membranes were applied to treat rice bran fermentation broth.

2. Experimental

2.1. Materials

α-Alumina ceramic supports and standard ceramic membrane were obtained from Shanghai Corun Membrane Technology (Shanghai, PR China). The configuration of the support is a 19-channel array (channel diameter: 4 mm, outer diameter: 30 mm, length: 240 mm, porosity: 35% pore sizes: 5–20 μm), and the effective filtration area is 0.057 m^2. The standard ceramic membrane has a zirconia separation layer with an average pore size of 50 nm and the thickness of 20 μm, and the porosity is 45%. The configuration of the ceramic membrane is the same as the support, and is designated as CM-50. Poly(vinylidene) fluoride (PVDF) was purchased from Inner Mongolia 3F-Wanhao Fluorine Chemical Co., Ltd. (Mongolia, PR China). Cellulose acetate (CA, acetyl content 54.5–56.0%, viscosity 300.0–500.0 mPa s) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, PR China). Polyethylene oxide (PEO, molecular weight 1,000,000) was acquired from Alfa Aesar (Tianjin, PR China). Rice bran fermentation broth (mean particle size: 8 μm, sugar content: 3.0%) was provided by Hefei Chemjoy Polymer Materials Co., Ltd. (Hefei, PR China). Dimethylacetamide (DMAC) with analytical grade was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, PR China). All chemicals were used as obtained without any further purification. Deionized water was used throughout.

2.2. Experimental set up

Fig. 1 shows the flow sheet and experimental set-up of rejection test in apparatus. The device consists of a feed tank, a centrifugal pump, a membrane module and other parts such as pressure gauges and valves. Raw solution is circulated by centrifugal pump on the upstream side of membrane cell. The membrane module contains a stainless steel housing holding one ceramic-polymer composite membrane tube. A valve installed on the inlet of pipe is used to regulate the pressure, which is monitored by a pressure gauge.

2.3. Preparation of composite membranes

After being rinsed with deionized water for 30 min, the supports were dried in oven at 60 °C for 12 h, and then coated with PVDF/CA solution via air compressor with an exerted pressure (c.f. Fig. 2). When the PVDF/CA concentration is 8 wt%, the pressure is 0.05 MPa, and for the other concentrations, the pressure is 0.3 MPa. The solution was maintained inside the tube for 5 min and then drained out. Subsequently, the prepared membranes were kept at 40 °C with 100% humidity for 4 h. The composite membranes were immersed in deionized water for further use. The codes of composite membranes and corresponding composition of PVDF/CA casting solution were given in Table 1.

2.4. Characterization of coating solution and membranes

2.4.1. Viscosity of coating solution

The viscosity of PVDF/CA blend solution was measured using arotational viscometer (NDJ-5S, Weide Co., Ltd, China) at a constant temperature of 14 °C. The value was averaged from three independent measurements.

2.4.2. Morphology of membranes

The ceramic support and composite membranes were destroyed into pieces for the inner surface and cross-section characterization using Scanning electron microscopy (TM-3000, Hitachi company, Japan).

2.4.3. Porosity and average pore size of membranes

The composite membrane porosity was characterized by determining the porosity of the organic polymer, which was peeled off from the ceramic support. The water on the surface of polymer was carefully wiped off, and then the weight, length, width and thickness of the polymer layer in wet state were measured. After that, the wet samples were dried in an oven at 60 °C for 24 h. Then, the dry weight was weighed. The membrane porosity was calculated using the following equation: [32]

$$\varepsilon = \frac{W_w - W_d}{\rho_w A l} \tag{1}$$

where W_w and W_d are the wet and dry weight of the organic polymer, respectively. ρ_w is the density of water at room temperature. A and l are the area and thickness of the polymer layer in wet state, respectively.

The mean pore size of the composite membranes was characterized by measuring the average pore size of the separation layer through the filtration velocity method. Mean pore radius (r_m) was calculated according to the Guerout–Elford–Ferry equation: [33]

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon)8\eta l Q}{\varepsilon A \Delta P}} \tag{2}$$

where η is the viscosity of water at room temperature. l is the membrane thickness. Q is the volume of the permeate water per unit time. A is the effective area of the membrane, and ΔP is the operation pressure.

2.4.4. Permeability and retention rate of membranes

Pure water flux (PWF) was measured at room temperature through the setup shown in Fig. 1, where the feed tank was filled with 9 L deionized water. The operation pressure was kept at 0.1 MPa and the feed is kept recycling throughout the experiment.