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A novel approach to fabricate interconnected sponge-like and highly permeable polyvinylidene fluoride hollow fiber membranes for direct contact membrane distillation

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ABSTRACT

A novel, environmental friendly approach was introduced to fabricate polyvinylidene fluoride hollow fiber membranes with interconnected sponge-like structure and high permeability for membrane distillation. The effect of different parameters on the morphologies and properties of the membranes were investigated. The pore size and porosity were in the range of 0.20–0.40 μm and 61.07–79.36% respectively. The maximum tensile strength was 6.941 MPa. The nitrogen flux under 0.2 MPa and pure water flux were as high as 44 L/(m^2 s) and 4290 L/(m^2 atm h) respectively. The direct contact membrane distillation flux reached 77.6 kg/(m^2 h). The membranes prepared by this method meet the requirements of direct contact membrane distillation.

1. Introduction

Membrane distillation (MD) [1,2] technique is a kind of membrane separation technology combined with traditional distillation technology, which has been widely used in chemical separation and enrichment, seawater desalination and industrial waste water treatment. Among the membrane materials applied in MD, semi-crystalline polyvinylidene fluoride (PVDF) has attracted much attention owing to its notable chemical stability, stain resistance, mechanical properties, wide processing temperature, and pliability [3–11]. Varieties of methods are available for membrane preparation [12–14]. Among them, thermally induced phase separation (TIPS) method is a promising approach for preparing porous membrane due to several accepted advantages: (1) fewer influence factors and easy operation; (2) homogeneous pore size distribution and high porosity; (3) excellent mechanical property. In the TIPS process, the homogeneous casting solution is obtained by dissolving the polymer in the solvent with high boiling point and low molecular weight at an elevated temperature. Then the casting solution is shaped into flat or hollow fiber and cooled in the coagulation bath to induce phase separation and solidify the membrane. Finally, the residual diluents are extracted by extractant which is further evaporated to yield the micro-porous structure. The structure of membranes prepared by the TIPS process can be controlled by modifying the compatibility between polymer and diluents, the polymer concentration, the composition of the mixed diluent, the coagulation bath temperature and other factors [15–18]. Several papers have reported that both cellular and spherulitic structures of PVDF membranes prepared by TIPS method were obtained by adjusting the composition of mixed diluent, such as dibutyl phthalate

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(DBP)/di-(2-ethylhexyl) phthalate (DEHP) [19], DBP/dioctyl phthalate (DOP) [20], triacetin/glycerol [21], dimethyl phthalate (DMP)/dioctyl adipate (DOA) and DMP/dioctyl sebacate (DOP) [22]. However, most of them focused on the preparation of the flat membranes [23–30]. Few of studies discussed the preparation of specialized porous PVDF hollow fiber membranes for direct contact membrane distillation (DCMD). In this work, the mixture of DOP/γ-butyrolactone (γ-BL) was adopted as a novel mixed diluent, nitrogen and water were introduced as bore fluid and coagulation bath respectively to fabricate unique interconnected sponge-like and highly permeable PVDF hollow fiber membranes especially for DCMD. The effects of PVDF concentration, DOP/mixed diluent ratio and coagulation bath temperature on formation mechanism, morphology and performance of the hollow fiber membranes in this environmentally friendly TIPS process were investigated. The permeabilities of the hollow fiber membranes in DCMD were tested.

2. Material and methods

2.1. Materials

The PVDF ($M_w = 2.55 \times 10^5$, $M_w/M_n = 1.9$, m.p. 174 °C) used in the study was provided by Solvay Solexis (Solef 6008). γ-BL (b.p. 204 °C), DOP (b.p. 248 °C), ethanol were analytical reagents (AR grade) and purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). All chemicals used in this study were not purified further.

2.2. Preparation of hollow fiber membranes

Hollow fiber membranes were prepared by an extrusion apparatus as shown in Fig. 1. The casting solution of PVDF, γ-BL and DOP were fed to the vessel, heated to 180 °C and has been stirring for several hours under the nitrogen atmosphere. After released the air bubbles, the homogeneous casting solution was fed to a spinneret under the nitrogen pressure. The spinneret consisted of an outer tube and an inner tube with diameters was 3.1 and 1.1 mm respectively. Another stream of nitrogen was blown into the spinneret to make a lumen at the center of the fiber.

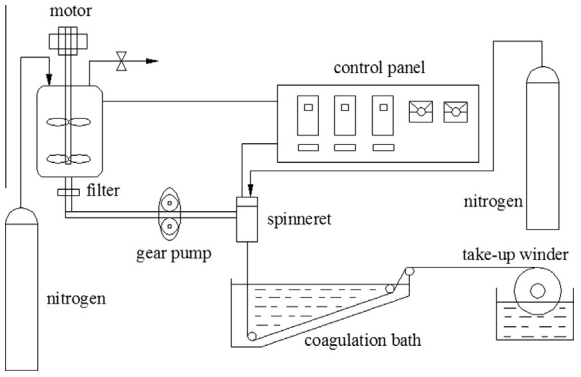

Fig. 1. Schematic diagram of the TIPS process for the preparation of the hollow fiber membranes.

The solution was partly cooled in the air, and then entered into the coagulation bath to induce the phase separation and solidify the membrane. The solidified hollow fiber membranes were collected by a take-up machine and further extracted by immersion in ethanol for 24 h to remove the residual solvents. At last, the wet fibers were dried in the air at room temperature until yield porous membranes.

Nitrogen, water and ethanol are employed as bore fluid, coagulation bath and extractant respectively to lower costs, reduce post-processing difficulties and form an environmentally friendly TIPS process. The velocity of nitrogen and casting solution were fixed at 15 ml/min and 10 ml/min respectively to make the spinning process went smoothly. The take up speed was adjusted to 0.5 m/s and the air gap between the spinneret and coagulation bath was fixed at 10 cm. PVDF concentration, DOP/mixed diluent ratio and coagulation bath temperature are key parameters in the spinning process. When the PVDF concentration is lower than 20%, the poor mechanical property, even broken hollow fibers were obtained. However, when the PVDF concentration is more than 30%, the casting solution is too concentrated to be extruded. Moreover, inhomogeneous casting solution was caused when DOP/mixed diluent ratio was more than 50%. The instability of viscosity induced the nonuniform thickness, even broken hollow fibers. Furthermore, high coagulation bath temperature was disadvantageous to the solidification and shaping of hollow fibers. Casting solution cannot be solidified quickly after entered into the coagulation bath. The structure of the hollow fibers was easily changed in the traction process. Based on the above analysis, other parameters being equal, different spinning processes were performed according to the change of key parameters as shown in Table 1.

2.3. Morphological study of hollow fiber membranes

The dry hollow fiber membranes were freeze-fractured in liquid nitrogen and then sputter coated with gold (Hitachi, E1020). The cross sections and the surfaces of the membranes were observed by a field-emitting Scanning Electron Microscope (SEM) (Hitachi, S-4800).

2.4. Porosity and pore size distribution of hollow fiber membranes

The apparatus for measuring the pore size distribution of the hollow fiber membranes is shown in Fig. 2. Ethanol was added into the butter tank. The membranes were immersed in i-butanol for 24 h and taken out to be weighted immediately after removing i-butanol on the surface. The overall porosity was determined by gravimetric method. The porosity of the hollow fiber was calculated by the following equation [31]

$$\varepsilon = \frac{(m_2 - m_1)\rho_1}{\rho_1 m_2 + (\rho_2 - \rho_1)m_1} \times 100\% \quad (1)$$

where m_1 is the weight of dry membrane, m_2 is the weight of wet membrane, ρ_1 is the density of PVDF and ρ_2 is the density of wetting solution.