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Formation and characterization of polytetrafluoroethylene nanofiber membranes for vacuum membrane distillation

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ABSTRACT

The polytetrafluoroethylene nanofiber membranes for membrane distillation were prepared by sintering the precursor electrospun polytetrafluoroethylene/polyvinyl alcohol composite membranes. The effects of sintering temperature and time on the morphology and properties of the prepared membranes were investigated. The prepared membranes were characterized by contact angles, IR and SEM to observe the structure evolution of the fibers during the sintering process. A unique moniliform structure was formed in proper conditions. The relationship between fiber morphology and membrane hydrophobicity, mechanical strength and porosity were discussed. The effect of membrane thickness on the liquid entry pressure was also studied to make sure the membrane was available in vacuum conditions. Moreover, membrane was tested in vacuum membrane distillation configuration. The pure water flux and salt rejection were tested to evaluate the membrane permeability and separation property.

1. Introduction

Membrane distillation (MD) as a thermally driven process has received a lot of attention in both academic areas and industry. MD has many potential applications, including seawater desalination [1,2], solution concentration [3,4] and wastewater purification [5] due to a low cost, energy-saving alternative to conventional separation processes such as distillation and reverse osmosis (RO). As a thermally driven process, MD is usually applied under the lower operating temperature (40–80 °C) and ambient pressure or vacuum pressure which can be easily achieved. The possibility of totally using industrial heat waste in MD operation is widely believed [6–9]. Furthermore, the rejection of ions, molecules, cells and other nonvolatile constituents is theoretically 100% [10,11] as MD operates on the principles of vapor–liquid equilibrium.

Since only vapor molecules are allowed to pass through a porous hydrophobic membrane, this membrane plays a major role during the MD process. The membrane must not be wetted, and non-condensable gases are present within its pore. Besides, other membrane characteristics, such as thickness, porosity and pore size distribution can also influence membrane performance. Currently, most membranes applied in MD process are commercial hydrophobic microporous membranes that are usually used in microfilter processes. These porous hydrophobic membranes with pores ranging from 0.2 to 1.0 um are often made from the hydrophobic materials such as polypropylene (PP), polyethylene (PE), polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) [7,12]. But for higher efficiency distillation, better hydrophobicity, higher porosity and narrower pore size distribution are the main focuses to improve performance of the membranes. Among all four MD configurations, direct contact membrane distillation (DCMD) is the most studied in literature due to its conventional operation [7]. Considering the industrial potential, vacuum membrane distillation (VMD) provided the highest permeate fluxes compactable to RO [8,11,13]. Decreasing downstream pressure will highly increase the fluxes [14,15]. However, in VMD, to prevent the membrane wetting, the relative high trans-membranous hydrostatic pressure was unsuitable for some membrane systems with low feed liquid entry pressure (LEP). This may be another restriction of VMD application.

Nano-fibers have been widely assembled into membranes applied as filters [16]. Electrospinning technology has been recognized as effective in fabricating polymer nanofibers [17]. Recently, electrospun nanofiber membranes used in MD process were also studied [2,5,18]. Electrospinning process can facilely produce nanofiber membranes with controllable membrane parameters, including pore size, porosity and thickness [8], which is attractive for MD. However, most researchers believe the limitation of nanofiber membrane represented by the low LEP value [19]. According to the limitations above, most studies on nanofiber membrane in MD process take the DCMD or air-gap membrane distillation (AGMD) configuration [2,5,18,19]. However, research in VMD process has hardly been carried out.

In this paper, PTFE nanofiber membranes were prepared by sintering PTFE/polyvinyl alcohol (PVA) electrospun membranes.

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The effect of sintering conditions on the morphology and properties of PTFE nanofiber membranes were investigated. By morphology research, we found the fibers melted and bonded to form nanofiber networks in proper conditions. Further studies show this membrane still has high porosity and applicable strength. The complex pore geometries and high contact angle formed in the melting fluxion gave these membranes relatively high LEP value. This electrospun membrane was successfully applied in VMD process, and the pure water fluxes and salt rejection were observed.

2. Experimental

2.1. Materials

PTFE emulsion (FR301B) was supplied by 3F Co. Ltd. China. This contains 60 wt% of PTFE fine particles dispersing in water. These particles are short rod-like in appearance. PVA 1799 was purchased from Sichuan Vinylon Factory (China).

2.2. Membrane preparation

2.2.1. Precursor nanofiber membrane preparation

The nanofiber PTFE precursor membrane was prepared by the electrospinning method. The electrospinning solution was prepared with a mass ratio of PVA to PTFE of 3:7 and a concentration of 26%. A direct current voltage of 15 kV was applied at a distance of 15 cm between the needle and the collector screen which was made by an aluminum foil [20]. After more than 6 h of steadily spinning, the membrane was carefully separated from the aluminum foil.

2.2.2. PTFE membrane preparation

The separated precursor electrospun membrane was then twisted around a glass tube with a diameter of about 3 cm to form a tape-in-tube of this membrane. The tape-in-tube membrane was directly placed in an atmosphere tube furnace (JGL1200, Shanghai Jiugong Electric Co. LTD, China). The thickness of the membranes was controlled by the layers of electrospun membranes. The sintering process was carried out in a high-pure nitrogen atmosphere with a gas flow rate of 200 ul/min. The furnace was first heated to 150 °C with a heating rate of 10 °C/min and held for 1 h to remove moisture, and then directly heated to 300 °C with a heating rate of 5 °C/min, and 3 °C/min from 300 °C to the target temperature for a certain time. Since the melting point of PTFE is above 320 °C, in this paper 330 °C, 350 °C, 370 °C, 380 °C and 390 °C were chosen to be researched. The sintering time was held for 5 min, 10 min, 20 min and 30 min at each temperature. During the sintering process nitrogen atmosphere was maintained until the temperature was back to room temperature.

2.3. Membrane properties and characterization

2.3.1. Morphologies observation

Scanning electron microscopy (SEM) images were obtained to investigate the morphology of the sample surface using a JEOL JSM-7500F SEM. The SEM images were analyzed using the Image-Pro Plus image analysis program.

2.3.2. Contact angle

The water contact angle (WCA) measurements were made at room temperature using a DataPhysics OCAH200 goniometer. A distilled water drop of about 4 μl was deposited on the flat sample surface by a syringe, the corresponding picture was saved and the WCA was determined by the equipment internal program.

2.3.3. IR examination

Infrared spectrums (IR) were obtained by a Nicolet 6700 FT-IR spectrometer to determine the residual extent of PVA in each sample before or after sintering treated.

2.3.4. Mechanical strength

The mechanical strength of the original or sintered membranes was tested using an electronic fabric strength tester (YG065C, Laizhou Electron Instrument Co. Ltd., China) with a crosshead speed of 10 mm/min at room temperature.

The specimens were cut into 5 mm(wide) × 50 mm (length) test strips. The thickness of the specimens was determined by a pointer type pachymeter (CH-10-AT, Liuling Instrument Factory, Shanghai, China), whose measurement precision is 0.001 mm. Five specimens from each sample were tested.

2.3.5. Porosity

The porosity was determined by a gravimetric method [21], the volume of the membrane pores was replaced by immerse liquid. In this experiment ethanol was used as the wetting liquid. Eq. (1) was used to calculate the membrane porosity of the membrane.

$$\text{Porosity} = \frac{w_1 - w_2/\rho_l}{w_1 - w_2/\rho_l + w_2/\rho_p} \quad (1)$$

where w_1 is the weight of wet membrane, w_2 is the weight of the dry membrane. ρ_l is the density of ethanol, which equals 0.816 g/ml, and ρ_p is the polymer density, ρ_p(PTFE)=2.20 g/ml.

2.4. Applications of membrane distillation

2.4.1. LEP measurements

According to the characterization of the membrane properties, optimal sintering condition was determined. Membranes prepared in this condition were further used in VMD application. As LEP is the threshold value of pressure to assure the long-term stable operation of the membrane system, the LEP of water was measured in static mode described in literature [22]. Furthermore, the membrane thickness was also measured since the LEP value was strongly related to the membrane thickness.

2.4.2. Pure water VMD tests and salt rejection estimation

Pure water permeation flux by VMD was tested to determine the membrane permeability. The VMD device was assembled according to the literature [9]. A schematic diagram of the VMD set-up used in our experiment was illustrated in Fig. 1. The condensated water was collected and measured in volume to calculate the flux in different feed temperatures and vacuum pressures. To estimate the membrane distillation for desalination, NaCl solutions with a concentration of 3.5% (approximately to the salinity of seawater) was used as feed. NaCl concentrations both in feed and collected solutions were determined through conductivity measurement by a conductivity meter (DDS-307A, INESA Scientific Instrument Co. Ltd., Shanghai, China).

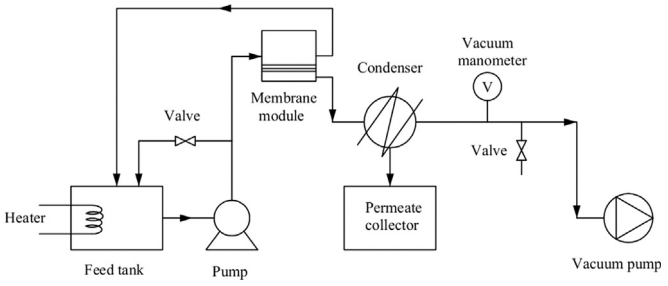

Fig. 1. Schematic of the experimental VMD set-up.