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Superhydrophobic PVDF–PTFE electrospun nanofibrous membranes for desalination by vacuum membrane distillation

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HIGHLIGHTS

- PVDF–PTFE electrospun nanofibrous membranes (ENMs) were fabricated by electrospining.
- The ENMs with different PTFE micro-powder contents were prepared and characterized.
- The PVDF–PTFE electrospun nanofibrous membranes were superhydrophobic.
- The ENMs were used for desalination via vacuum membrane distillation.
- The ENMs presented a high permeate flux with stable performance.

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ABSTRACT

In this study, a superhydrophobic nanofibrous membrane was prepared on the basis of an electrospun polyvinylidene fluoride (PVDF)–polytetrafluoroethylene (PTFE) nanofibrous scaffold coupled with a microporous PTFE substrate. The PVDF–PTFE nanofibrous scaffold was fabricated by electrospining of PVDF–PTFE blend solutions, it was observed that by changing the PTFE micro-powder content in the dope solutions from 0 wt.% to 12 wt.%, the water contact angle (WCA) and the liquid entry pressure (LEPw) of the membrane vary from 130.4° and 84 kPa to 152.2° and 137 kPa, respectively. The superhydrophobic PVDF–PTFE nanofibrous membrane was then tested for desalination by vacuum membrane distillation (VMD), a stable flux of 18.5 kg/m^2 h and salt rejection higher than 99.9% was presented throughout the entire testing period of 15 h, indicating the great potential of the PVDF–PTFE nanofibrous membranes in VMD. For further application of the PVDF–PTFE nanofibrous membranes in VMD, a mathematical model was presented to predict the vapor flux of the novel membrane under various operation conditions. A good agreement between the experimental and theoretical values for vapor fluxes was obtained; the results indicated that the VMD flux increased with the increase of feed temperature and flow rate and decreased with the increase of permeate pressure.

1. Introduction

Membrane distillation (MD) is a non-isothermal separation process which is driven by a vapor pressure difference through a porous hydrophobic membrane. There are generally four different MD configurations including direct contact membrane distillation (DCMD), sweeping gas membrane distillation (SGMD), vacuum membrane distillation (VMD) and air gap membrane distillation (AGMD). Compared with other separation process, MD has a great potential in desalination for possessing the advantages of lower operating temperature, less energy consumption as well as 100% theoretical rejection of non-volatile solute [1–4].

Although the membrane only acts as a physical barrier in membrane distillation, the performance of MD is strongly affected by the membrane surface morphology and pore structure. An ideal membrane for MD should exhibit a superhydrophobic surface to avoid pore wetting and a well-designed pore structure to enhance water flux [5–11]. These properties mainly depend on the polymer or additives that are used for preparing the membrane and also on the method of synthesis of membrane.

Most of the materials employed in the preparation of membranes for MD applications are hydrophobic, such as polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF). However, the commercial membranes fabricated out of these polymers are commonly made through a melting process or phase inversion process, the surface of these membranes is not highly hydrophobic and the porosity is low, which is the major barrier impeding MD industry applications [12,13].

Electrospinning is an attractive approach for the fabrication of nanometer or submicrometer-sized fibers which received an increasing attention in recent years [14–17]. Compared with commercial membranes

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made through conventional process, the electropsun nanofiber membranes (ENMs) have showed great potential in membrane distillation due to their high void volume fraction and interconnected open structure [18–21]. Feng et al. firstly attempted to use ENM in MD [18], up to 22% of saline water was treated with the membrane. The salt rejection was about 99%, and the fluxes were as high as or higher than those of commercial PVDF membrane, which shows the great potential of PVDF ENM in MD. Essalhi and Khayet [19] investigated the effect of eletrospinning time on ENMs; a considerable increase of both the thickness and the liquid entry pressure of water with the electrospinning time was observed, while only a slight enhancement was detected for the void volume fraction. Yuan Liao et al. [20] optimized the pore sizes of PVDF ENMs by varying polymer dope compositions, electrospinning process parameters and heat-press treatment. The DCMD test for the post-treated PVDF ENMs was much better than the commercial PVDF membranes, suggesting the competency of PVDF ENMs for MD applications. However, the uniform electropsun nanofiber membranes fabricated by pure polymer dopes without hydrophobic additives are usually not superhydrophobic [18–20]. Preparation and characterization of superhydrophobic ENMs for MD were reported by Prince et al. [21]. The superhydrophobic membrane with a water contact angle of 154.2° was obtained by electrospining of PVDF blended with clay nanocomposites, but the PVDF–clay membrane presented quite a low flux (<5.5 kg/m^2 h) in direct contact membrane distillation, which limits its application.

The goal of this study was to fabricate a superhydrophobic nanofibrous membrane with high water flux for membrane distillation. The PTFE micro-powders were added in the electrospining of PVDF dope solutions to improve the surface hydrophobicity of the nanofibrous membrane, as previous studies showed that the PVDF–PTFE composite membranes fabricated by phase inversion method or coxial-electrospining method exhibited enhanced hydrophobicity [22–25]. In this work, PVDF–PTFE nanofibrous membranes with different properties were prepared by electrospining of PVDF–PTFE blend solutions on a PTFE microporous substrate, which acts as a support layer to improve the mechanical properties. The schematic diagrams for the assembly of the PVDF–PTFE nanofibrous membranes were shown in Fig. 1. The prepared membranes were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), water contact angle (WCA) and liquid entry pressure of water (LEPw) to investigate their surface and structure. Subsequently, these nanofibrous membranes were tested in vacuum membrane distillation to compare with a commercial MD membrane.

2. Experimental

2.1. Materials

Polyvinylidene fluoride (PVDF, Solef® 6010) was purchased from Solvay Advanced Polymers, L.L.C. (Alpharetta GA, USA) and polytetrafluoroethylene (PTFE) micro-powders (Dyneon TF9207) were purchased from Shanghai Xianglan chemicals CO. LTD (China). For PTFE micro-powders, the primary particles are 120 nm in diameter, and the average aggregate length is 4 μm. All other solvents and reagents were analytical grade and purchased from Shanghai Sinopharm Chemical Reagent CO. LTD (China). The PTFE microporous substrate was purchased from Shanghai Nuozhen New Chemical Materials CO. LTD (China), the thickness of the substrate was 65 μm, with a mean pore size of 1 μm and porosity of 75%. Commercial PTFE membrane manufactured by Sumitomo Electric Industries, Ltd was used to compare with the nanofibrous membranes in vacuum membrane distillation.

2.2. Preparation of PVDF–PTFE nanofibrous membranes

The dope solutions were first prepared by dissolving 15 wt.% PVDF in the solvent mixture of N, N-dimethylacetamide (DMAC) and acetone (50/50 wt.%), different amounts of PTFE micro-powders at 0, 3, 6 and 12 wt.% were added into the dope solutions to enhance the hydrophobicity of the membrane. The compositions of the dope solutions for electrospinning corresponding to the membrane samples S1–S4 are presented in Table 1. The PVDF–PTFE solutions were allowed to stir at 50 °C for about 24 h before electrospinning.

The electrospinning setup used in the present work was the same in our previous study [25–28]. It consisted of a 20 mL plastic syringe to hold the polymer solution connected to a syringe pump (WC50C6, Zhejiang) to control the injection rate of the polymer solution, two electrodes (a metallic needle and a grounded metallic collector kept in horizontal position), and a high-voltage power supply (DWP3031ACD8, Tianjin) which could generate positive direct current voltage up to 30 kV. The polymer drop from the tip of the needle (0.4 mm inner diameter) connected to the syringe by a Teflon tube is drawn into a fiber due to the high voltage. The whole setup was placed in a temperature controlled room.

The PVDF–PTFE nanofibrous membranes were fabricated by electrospinning the dope solutions on a PTFE microporous substrate, as shown in Fig. 1. A positive voltage of 18 kV was applied across a distance of 15 cm; the polymer was electrospun at a rate of 0.5 mL/h to get

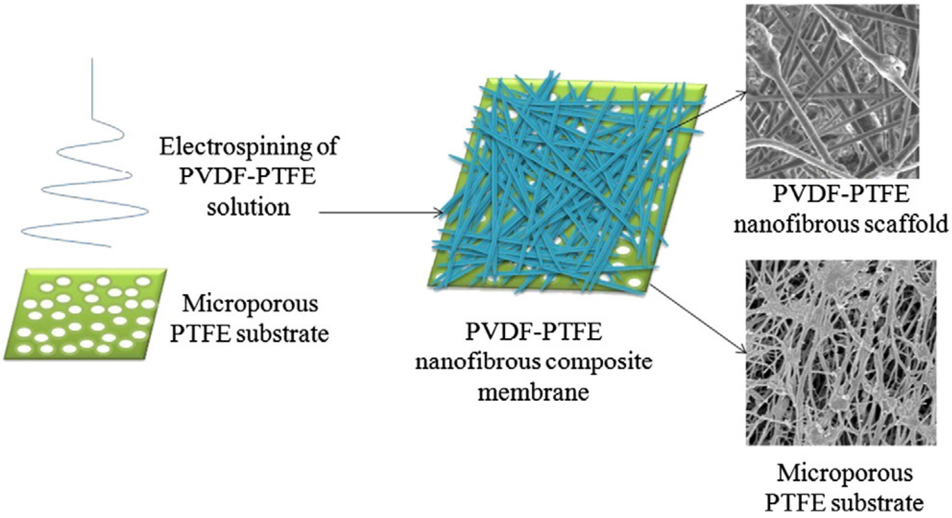

Fig. 1. Fabrication schematics of PVDF–PTFE nanofibrous composite membrane.