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Using ammonia as an additive to fabricate a high performance PVDF hollow membrane for distillation

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ABSTRACT

Highly hydrophobic polyvinylidene fluoride (PVDF) hollow fiber membrane with high porosity is specially desired to meet the requirements of distillation. Here, a novel approach was proposed to fabricate a hydrophobic PVDF hollow fiber membrane by using aqueous ammonia ($NH_3{\cdot}H_2O$) as an additive. Adding $NH_3{\cdot}H_2O$ to the PVDF spinning solution increased the porosity, enhanced the thermal stability, improved the water contact angle, and reduced the vapor transport resistance of the fabricated membranes. The membranes achieved nearly 99% salt rejection when they were used to desalinate a 3.5 wt% sodium chloride solution, and the maximum transmembrane permeate flux was ~32 kg/($m^2{\cdot}h$) when the hot feed solution and cold distillate were 80°C and 20°C, respectively. In addition, the PVDF hollow fiber membrane exhibited good stability in desalination. The method of utilization $NH_3{\cdot}H_2O$ described here provides an operable route to the production of highly hydrophobic PVDF hollow fiber membrane with high porosity.

Keywords: PVDF; $NH_3{\cdot}H_2O$; Membrane; Desalination

1. Introduction

Membrane distillation is a promising membrane separation technology based on using the temperature gradient created on membrane surfaces as a driving force. It is usually applied where water is the major component of the feed solution to be treated [1]. In membrane distillation, a porous, non-selective, hydrophobic membrane acts as a physical support separating a warm solution from a cooler chamber containing either a liquid or a gas [2]. Compared with conventional separation processes such as evaporation and reverse osmosis, membrane distillation can be operated under relatively low temperature or low pressure with low energy consumption [3–5]. However, membrane distillation has not yet gained industrial-scale application owing to several technical issues including the availability of suitable membrane materials, membrane fouling, membrane module design, and uncertain energy recovery [6], so the development of a high-flux membrane for membrane distillation is still a key issue.

Membrane performance is affected by various factors including membrane hydrophobicity and morphology-related characteristics including pore size, porosity, and pore tortuosity. As an important interfacial property, hydrophobicity is an essential requirement for implementing membrane distillation, which is directly related to the membrane performance. Meanwhile, membrane distillation is strongly affected by the membrane pore structure. An ideal distillation membrane should exhibit a well-designed pore structure to enhance water flux [1,7–12].

Distillation membranes are conventionally made mainly of hydrophobic materials such as polypropylene (PP),

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polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF) [13]. PP-based membranes can be prepared by thermally induced phase separation or melt spinning and cold stretching [14]. PTFE-based membranes are prepared by stretching and heating [15]. PVDF-based membranes can be fabricated by non-solvent-induced phase separation and can show asymmetric membrane morphology, which is important for achieving high permeability [16,17]. PVDF membranes have recently been prepared by treating the surface of perfluorodecyltriethoxysilane [18], by TiO_2 nanoparticle deposition [19], and by plasma polymerization of fluoropolymers [20]. However, most of the reported membranes have shown significant flux reduction attributed to a compact layer of high mass transfer resistance to water vapor, resulting from the surface modification.

Here, a high water flux, superhydrophobic PVDF hollow fiber membrane was fabricated. $NH_3{\cdot}H_2O$ was added to the PVDF spinning solutions for the first time to improve the surface hydrophobicity and internal structure of the membrane. The optimal proportion of $NH_3{\cdot}H_2O$ was determined, and the performance of the obtained membrane was tested by desalinating a 3.5 wt% sodium chloride solution.

2. Experimental setup

2.1. Materials

PVDF (FR-904, molecular weight = 534,000) was obtained from Shanghai 3F New Materials Co., Ltd., China. *N*-Methyl kelopyrrolidide (NMP, >99%) purchased from Tianjin Fuyu Fine Chemical Co., Ltd., China, was employed as the solvent. Aqueous ammonia ($NH_3{\cdot}H_2O$, 25%–28%), ethanol (C_2H_5OH, 95%), and sodium chloride (NaCl, ≥99.5%) were supplied by Tianjin Fuyu Fine Chemical Co., Ltd., China. Ultrapure water whose resistivity was 18 MΩ·cm was produced by a Milli-Q unit (Millipore, USA) and was used in all the experiments.

2.2. Preparation of PVDF hollow fiber membrane

The PVDF spinning solution was prepared by dissolving 1 g of the PVDF powder in 10 mL of the NMP solution and continuously stirring the mixture at 50°C for about 2 h, until a homogenous solution was formed. The as-prepared solution was degassed under vacuum using a water circulation pump at 50°C for about 6 h, and the solution was then deposited for about 24 h. Subsequently, 0.1, 0.2, 0.3, 0.4, or 0.5 mL of $NH_3{\cdot}H_2O$ was added to different samples of the as-prepared PVDF spinning solution, denoted as PMN-1, PMN-2, PMN-3, PMN-4, and PMN-5, respectively. A control sample of the PVDF spinning solution without $NH_3{\cdot}H_2O$ is denoted as PMN-0. The PVDF hollow fiber membranes were fabricated using dry-jet wet-phase inversion and spinning equipment. The spinning solution was then extruded using a tube-in-orifice spinneret (outer diameter (OD) = 1.70 mm and inner diameter (ID) = 0.68 mm) to form a hollow fiber. The spinning solution was extruded from the spinneret, was passed through 20 mm of air gap, and was then immersed into a water coagulation bath. The spinning dope and ultrapure water were both setup as the bore fluid, flowing at 20 and 10 mL/min, respectively [21]. In order to remove the NMP, the as-prepared PVDF hollow fiber membrane was dipped in ultrapure water for 2 d. The PVDF hollow fiber membrane was then immersed in ethanol to replace the water molecules and air dried at room temperature.

2.3. Membrane characterization

The morphology of the as-prepared PVDF hollow fiber membrane was investigated using a scanning electron microscope (SEM; Quanta 200 FEG). The porosity of the PVDF hollow fiber membrane was calculated based on the following equation [22]:

$$\varepsilon = \frac{\dfrac{(m_1 - m_2)}{\rho_\omega}}{\dfrac{(m_1 - m_2)}{\rho_\omega} + \dfrac{m_2}{\rho_\mu}} \times 100 \tag{1}$$

here, ε is the porosity of the PVDF hollow fiber membrane (%), m_1 is the mass of the wet PVDF hollow fiber membrane (g), m_2 is the mass of the dry PVDF hollow fiber membrane (g), ρ_μ is the density of the PVDF hollow fiber membrane (g/cm^3), and ρ_ω is the density of pure water (g/cm^3).

The mechanical properties of the PVDF hollow fiber membrane were measured using a Zwick/Roell Z 2.5 test unit. The as-prepared samples were stretched at 1 mm/min to obtain the Young's modulus, breakage tensile force, and elongation percentage of the PVDF hollow fiber membrane [23]. The water contact angle of the PVDF hollow fiber membrane was tested using a contact angle and surface tension measurement system (Physics Instruments Ltd., Germany) to characterize the hydrophobicity of the PVDF hollow fiber membrane.

2.4. PVDF hollow fiber membrane performance

The performance of the as-prepared PVDF hollow fiber membrane was explored by desalinating a 3.5 wt% NaCl solution. A schematic of the membrane distillation equipment is shown in Fig. 1. The length of the PVDF hollow fiber membrane in the membrane module was ~5 cm. The hot NaCl feed solution flowed through the inside of the fiber membranes, and the cold distillate water flowed through the outside. The temperature of hot NaCl feed solution and cold distillate water was at 80°C and 20°C, respectively. Two peristaltic pumps (Shanghai Seisun Pumps, China) were employed to provide driving force, and the revolving speed was 10 and 30 rpm for the NaCl solution and cold water, respectively. The transmembrane water vapor flux was calculated based on the following equation:

$$J = \frac{\Delta M}{A \times t} \tag{2}$$

where J is the water vapor flux (kg/(m^2·h)); ΔM is the amount of permeate collected at the end of each test (kg); t is the run time (h); and A is the active membrane surface area (m^2) calculated based on the number, inner diameter, and length of the fibers. In order to determine the salt rejection of the PVDF hollow fiber membrane, the electrical conductivity of the desalinated water was measured [24].

3. Results and discussion

3.1. Morphology

The cross-sectional morphologies of the as-prepared PVDF hollow membrane are shown in Fig. 2. Adding $NH_3{\cdot}H_2O$ to the PVDF spinning solution significantly affected the morphology of the PVDF hollow fiber membrane. Compared with the PMN-0 sample, the PMN-1 to PMN-5 samples showed more finger- and sponge-like structures.

Fig. 3 presents SEM images showing the surface morphologies of the as-prepared PVDF hollow fiber membrane. Adding $NH_3{\cdot}H_2O$ to the PVDF spinning solution caused

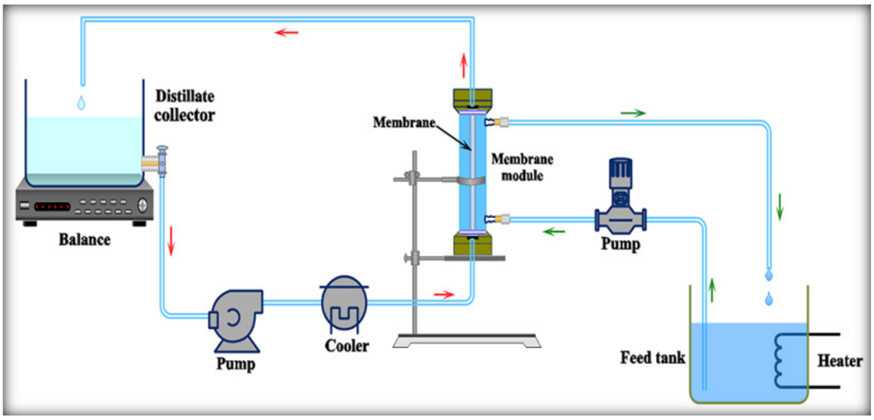

Fig. 1. Schematic of the equipment used for membrane distillation.

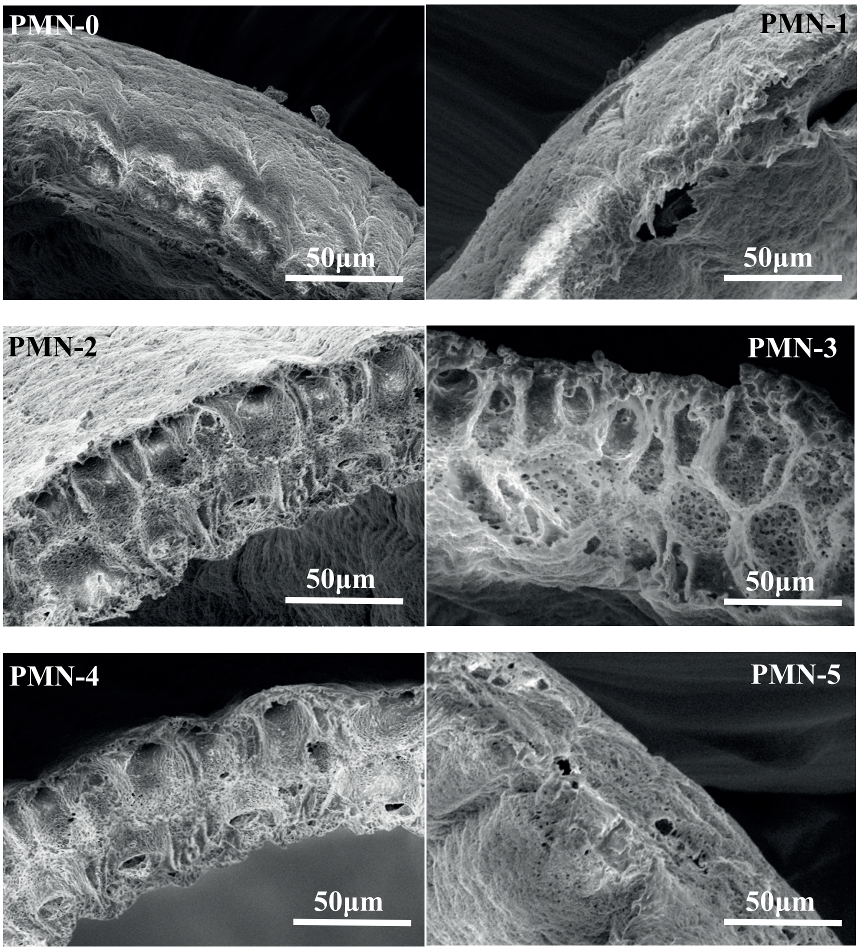

Fig. 2. Cross-sectional SEM images of the PVDF hollow fiber membrane.

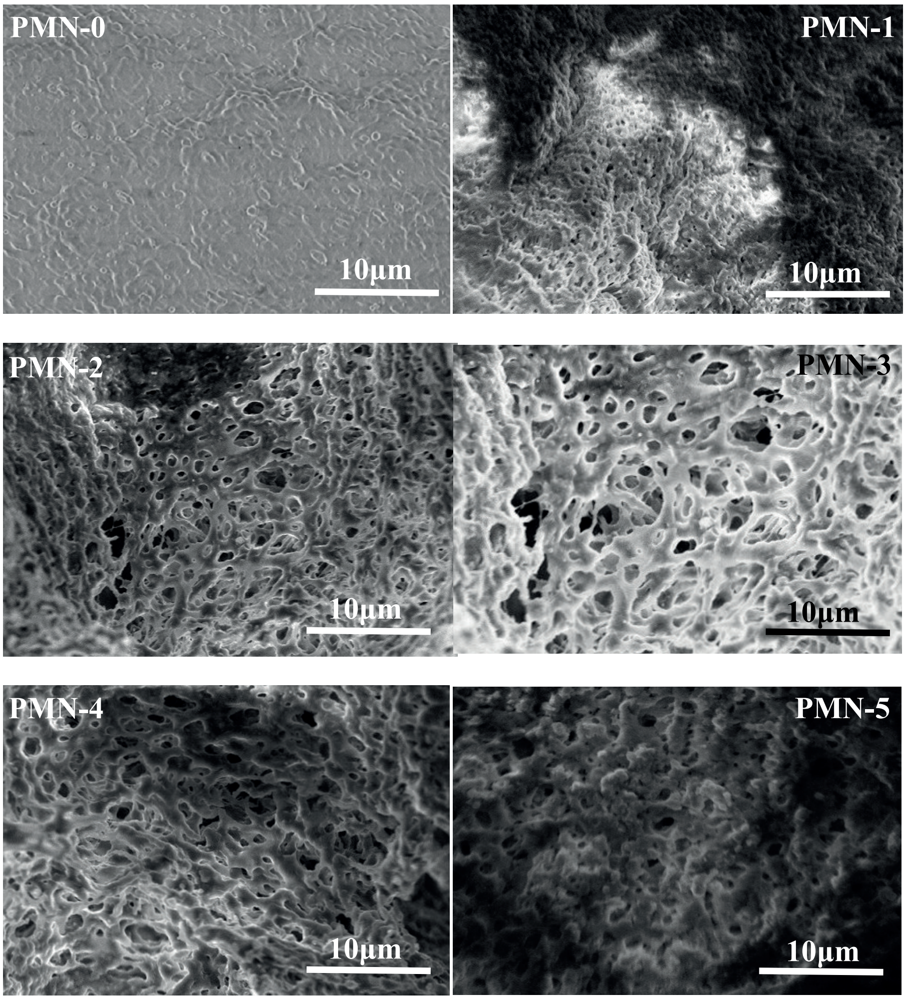

Fig. 3. Surface SEM images of the PVDF hollow fiber membrane.

macropores to form in the PVDF hollow fiber membrane. Clearly, the amount of $NH_3 \cdot H_2O$ added to the spinning solution significantly influenced the morphology of the PVDF hollow fiber membrane.

3.2. Porosity

Membrane porosity plays a key role in permeation flux; hence, the porosities of the as-prepared PVDF hollow fiber membrane were characterized. As shown in Fig. 4, the prepared PVDF hollow fiber membrane exhibited high porosities in the range 88%–95%, higher than that of the pure PVDF hollow fiber membrane, principally attributed to the $NH_3 \cdot H_2O$ additive. Since the $NH_3 \cdot H_2O$ was dissolved in the NMP, the PVDF in the spinning solution could be modified by the $NH_3 \cdot H_2O$. As a result, the PVDF hollow fiber membranes prepared in this study were endued with a good porous texture. Fig. 4 also shows that the porosities of the PVDF hollow fiber membrane prepared using PMN-1 to PMN-3 gradually increased with increasing $NH_3 \cdot H_2O$ content in the spinning solution but then slowly decreased with further increasing $NH_3 \cdot H_2O$ for the membranes prepared using PMN-4 and PMN-5, indicating that the PVDF hollow fiber membrane prepared using PMN-3 showed the optimal porosity.

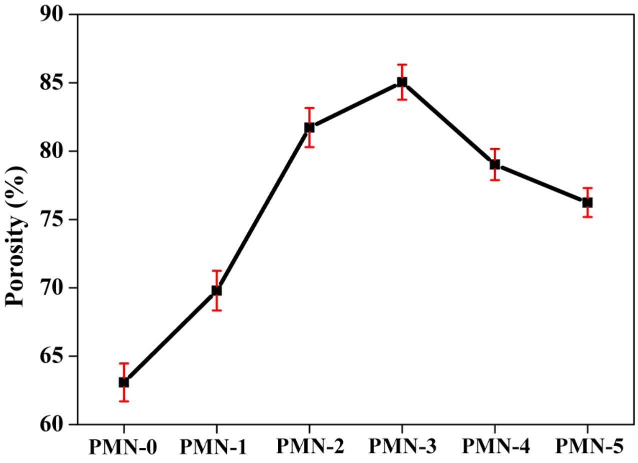

Fig. 4. The porosity of the PVDF hollow fiber membrane.

3.3. Mechanical properties

In order to investigate the mechanical properties of the prepared PVDF hollow fiber membranes, the Young's modulus and stress of unit displacement were measured. Fig. 5 shows that the stretching strengths of the PMN-1- to PMN-5-based membranes were significantly lower than that of the pure PVDF-fiber-based one and that the PMN-3-based membrane showed the lowest stretching strength, indicating that the formation of the finger-like structures and the increased porosity in the PVDF hollow fiber membrane decreased the mechanical strength of the membranes.

3.4. Water contact angle

To further elucidate how the $NH_3{\cdot}H_2O$ contributed to the fabrication of the PVDF hollow fiber membrane, the membrane hydrophobicity was evaluated by measuring their water contact angles. As shown in Fig. 6, the water contact angle of the PMN-0-based membrane was about 81°, whereas that of the PMN-1-based membrane increased to 121°. The PMN-3-based membrane showed the largest water contact angle, 152°. Since the water contact angle is closely related to the membrane hydrophobicity, a PVDF hollow fiber membrane showing a large water contact angle would be beneficial for water permeation.

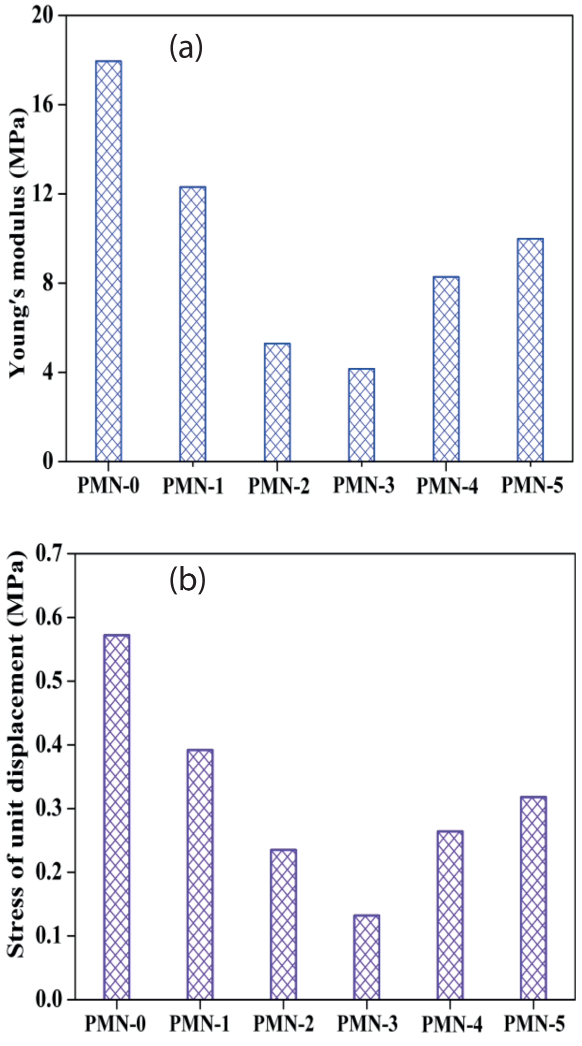

Fig. 5. (a) Young's modulus and (b) unit displacement stress of the PVDF hollow fiber membrane.

3.5. Water vapor flux

The water vapor flux of the PVDF hollow fiber membrane, where 3.5 wt% sodium chloride at 80°C was used as the feed solution, is displayed in Fig. 7. The water vapor flux increased from the PMN-0 to PMN-3, and then decreased from PMN-3 to PMN-5. The water vapor flux of PMN-3 reached 32 kg/($m^2{\cdot}h$), approximately eight times higher than that of the PMN-0, which attribute to the high porosity and the hydrophobicity of the PMN-3 membrane.

3.6. Conductivity of permeate water

Fig. 8 shows the conductivity of the desalinated water. It can be seen from Fig. 8 that the conductivity of the water are nearly unchanged from PMN-0 to PMN-5, and the corresponding conductivities range from 130 to 170 μS/cm. Considering the conductivity of 3.5 wt% sodium chloride solution is about 47,000 μS/cm, >99% salt rejection was obtained using the PVDF hollow fiber membrane.

3.7. Stability

To investigate the stability of the PVDF hollow fiber membrane, the PMN-3-based membrane was used to

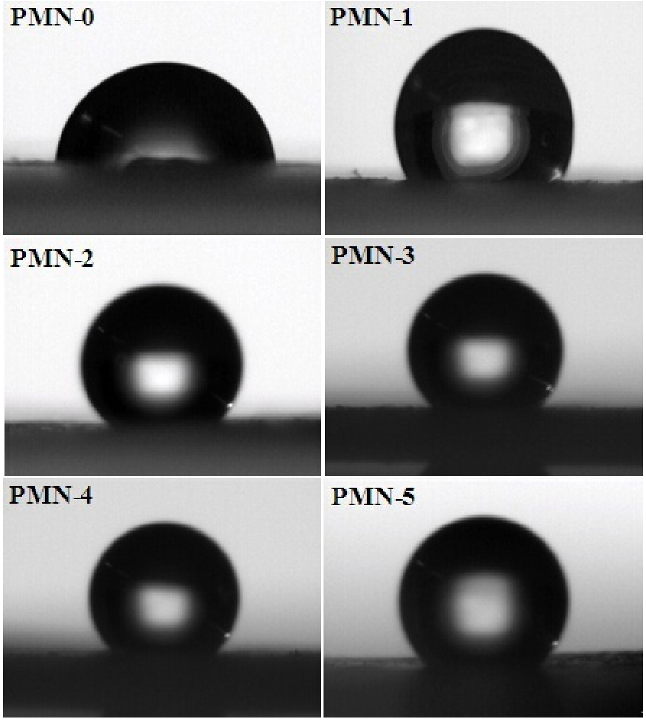

Fig. 6. The water contact angles of the PVDF hollow fiber membrane.

desalinate a 3.5 wt% sodium chloride solution for 192 h. The desalination performance is presented in Fig. 9. The salt rejection stabilized at ~99%, and the permeate flux remained at ~32 kg/(m^2·h), indicating that the PVDF hollow fiber membrane exhibited satisfactory stability.

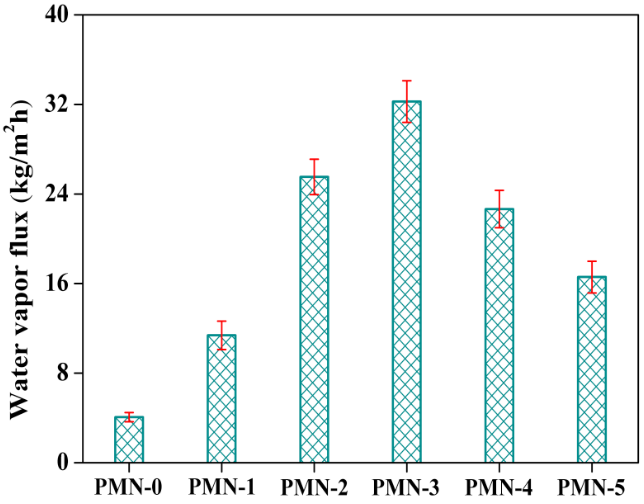

Fig. 7. The water vapor flux of the PVDF hollow fiber membrane (80°C).

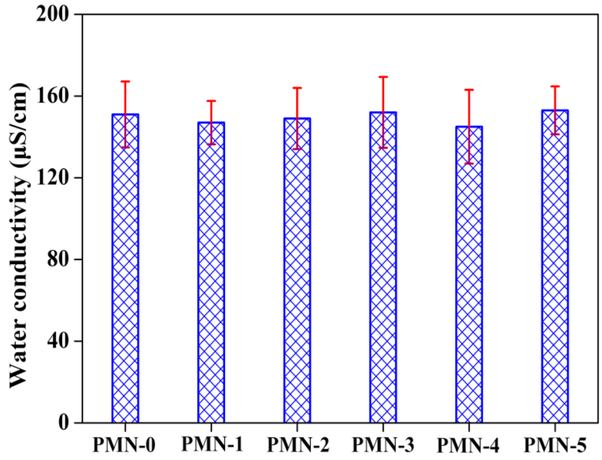

Fig. 8. The conductivity of the desalinated water.

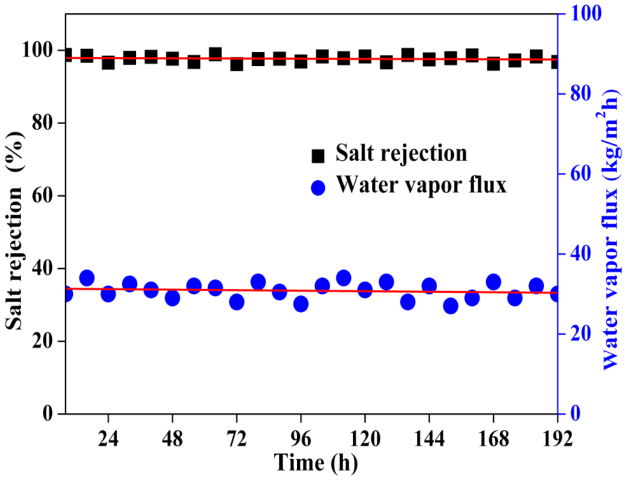

Fig. 9. The stability of PMN-3-based membrane.

4. Conclusions

In this work, PVDF hollow fiber membrane was prepared by adding $NH_3·H_2O$ as the additive, which not only optimized the finger-like membrane morphology and the membrane porosity but also improved the membrane water vapor flux. It is worth noting that the permeate flux of 32 kg/(m^2·h) was reached and >99% salt rejection was obtained. Hence, the method of adding $NH_3·H_2O$ is very significant from the view of PVDF hollow fiber membrane fabrication.

Acknowledgments

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