Development of robust energy-efficient membrane dehumidifier for indoor air humidity control

Y L Liu1,2, Y Y Wei2, Y Cao3, X Cui1, L W Jin1, L Y Zhang1* and J C Su2*

1 School of Human Settlements and Civil Engineering, Xi’an Jiaotong University, No. 28 Xianning West Road, Xi’an, 710049, China
2 School of Life Sciences & Chemical Technology, Ngee Ann Polytechnic, 535 Clementi Road, 599489, Singapore
3 China Architecture Design & Research Group, Beijing, Xicheng District, 100044, China
E-mail: zhangly@xjtu.edu.cn; sji2@np.edu.sg

Abstract. The membrane-based dehumidification technology is greatly energy-efficient for the humidity control. The poly (vinyl alcohol)/poly (vinylidene fluoride) hollow fiber composite membrane for dehumidification has been developed and evaluated in this study. The Poly (vinylidene fluoride) (PVDF) membrane substrates were prepared by the dry-wet spinning. The Poly (vinyl alcohol) (PVA) selective layer was formed through the dynamic cross-flow coating in the lumen side of the PVDF substrate membranes. The effects of the PVA concentration and the coating time on the water vapor performance and the heat removal ratio of the PVA/PVDF composite membrane were investigated experimentally. The results indicated that the PVA concentration of 5.0 wt% and the coating time of 60 min are the optimal conditions for the fabrication of PVA/PVDF hollow fiber composite membrane. With the composite membrane prepared under optimal conditions, a water vapor permeance of 6084 GPU and a heat removal ratio of 10.94% were obtained at 25°C. This work offers a new sight for the development of a novel high-performance composite membrane for the indoor air dehumidifiers.

1. Introduction
Humidity is a key element of indoor air quality. The warm weather and high precipitation contribute to high air humidity, e.g., >80% in tropical areas such as Singapore. In recent years, membrane-based dehumidification technology has gained increasing attention due to its distinct technical and economic advantages such as simple structure, uncomplicated operation, low process cost, and environment-friendly [1,2]. Roy et al. fabricated the porous poly (acrylamide-co-acrylic acid)
hydrophilic composite membrane, which has a great water vapor permeance of \(2 \times 10^9\) mol \(\cdot\) cm\(^2\) \(\cdot\) min\(^{-1}\) \(\cdot\) cmHg\(^{-1}\) and a water removal of 37\% [3]. A small-scale air dehumidification system with nine PAN/PDMS hollow fiber membrane modules embedded in it was constructed by Zhao et al. [4]. The membrane module shows good water vapor permeation under the pressure difference of only 0.78 bar pressure difference. Liang et al. previously proposed a new method for preparing the PDMS/PAN membrane through post crosslinking for the efficient separations of various gases [5]. Recently, the high-performance polyamide-imide hollow fiber membranes were manufactured and tested to remove the water vapor and decrease the energy consumption in the process of the water gas shift reaction [6]. By updating the coating conditions, Liang et al. produced poly(dimethylsiloxane)/poly(acrylonitrile) composite membranes, which have a 260-nm ultrathin and dense PDMS layer [7]. Under the different operation conditions, the optimum permeance of water vapor is as high as 3700 GPU based on the novel membranes. For dehumidification membranes, the polymerization and functionalization of the micro-porous substrate and the ultrathin selective layer are the crucial directions to not only reduce the resistance of water vapor transport and energy consumption but also improve the water vapor permeability. However, the current methods still face the challenges to fabricate the defect-free dehumidification membrane with high performance by means of low energy consumption and high efficiency, which need to be improved through extensive investigation.

In this study, the high efficiency membrane dehumidifier has been developed for indoor air humidity control. Single-bore hollow fiber composite membranes are fabricated using poly(vinylidene fluoride) (PVDF) as the substrate and cross-linked poly(vinyl alcohol) (PVA) as the separation layer. The dehumidification performance has been evaluated in terms of the water vapor permeance and the heat removal ratio. Effects of the PVA concentration and the coating time on the dehumidification performance of PVA/PVDF hollow fiber composite membrane have been studied. It is believed that this work provides useful insights for the development of robust hollow fiber composite membranes and their application for indoor air humidity control.

2. **Experiments and methods**

2.1. **Materials**

Poly(vinylidene fluoride) (PVDF) was supplied by Arkema (Singapore). Poly(vinyl alcohol) (PVA) with molecular weight of 89000-98000 and hydrolysis grades of 99+\% was purchased from Sigma-Aldrich (Singapore) as the materials of dense film. Glutaraldehyde (GA) was provided by Sigma-Aldrich(Singapore) as a 25\% aqueous solution.

2.2. **Fabrication of PVA/PVDF membrane**

To explore the optimal fabrication conditions of selective layer, several concentrations of PVA aqueous solution (2.5 wt%, 5.0 wt%, 7.5 wt% and 10.0 wt%) and the coating time (30 min, 60 min, 90 min, 120 min) were tested in this study. The PVA aqueous solutions were prepared by being dissolved in deionized water under mechanical stirring at 90 °C for 2 h. The 1.0 vol\% Glutaraldehyde (GA) containing the catalyst of 0.15 vol\% HCl was adopted for the crosslinking of PVA layers.

The PVDF membrane substrates were spun through the method of dry wet spinning as described elsewhere [8]. The inner diameter of the formed hollow fibers was 0.58 mm. Then the PVA solutions were driven by a peristaltic pump and flowed along the inner cavity of the PVDF membrane to form the
ultrathin and dense selective layer. After the coating, the GA solution was brought to crosslink with the surface of the PVA layer. The membrane modules formed were then dried over 24 h at 50°C in an oven.

2.3. Determination of permeances

The water vapor flux and the heat removal ratio were determined with a setup schematically shown in Figure 1. High purity compressed air fed to the test apparatus was divided into two streams, one directly flowing to the mixing tank while another being humidified through a bubbler. The two streams of air were mixed in the mixing tank and the mixture was then introduced into the inner cavity of the module. The shell side of the membrane was connected to a dry vacuum pump which continuously removed the moisture-rich air. The real-time measurements were conducted for the humidity, temperature and flow rate of both the feed air and retentate air.

Based on the readings of humidity and temperature, the water vapor concentration was calculated in the psychrometric chart. Through the following two equations, the water vapor flux can be obtained:

\[ J_w = \frac{Q_w}{A(P_{fw} - P_{pw})} \]  \hspace{1cm} (1)

\[ Q_w = F(C_1 - C_2) \]  \hspace{1cm} (2)

\( J_w \) is the water vapor flux; \( Q_w \) is the flow rate of the permeated water vapor; \( A \) is the effective membrane area; \( (P_{fw} - P_{pw}) \) is the water vapor pressure difference between the two sides of membrane; \( F \) is the flow rate of the humid air; \( (C_1 - C_2) \) is the concentration difference of water vapor between the inlet and the outlet.

Furthermore, the permeance with a unit of GPU \((10^{-6} \text{ cm}^3 \text{ (STP)}/(\text{cm}^2 \text{ s cmHg}))\) and the permeability with a unit of Barrer \((10^{-10} \text{ cm}^3 \text{ (STP) cm}/(\text{cm}^2 \text{ s cmHg}))\) can be calculated according to the water vapor flux.

Heat removal ratio is the performance parameter used to characterize the total heat removed from the humidity air through the membrane. It can be defined using the following equation:

\[ \varepsilon = \frac{h_1 - h_2}{h_1} \]  \hspace{1cm} (3)

\( \varepsilon \) is the heat removal ratio; \( h_1 \) is the inlet enthalpy of air; \( h_2 \) is the outlet enthalpy of air.

Figure 1. The test rig for the permeation of water vapor.
3. Results and discussion

3.1. Effects of PVA concentration

Figure 2 depicts the water vapor performance of PVA/PVDF membranes based on different PVA concentration but same coating time of 60 min. The water vapor permeance and permeability increases when the PVA concentration varies from 2.5 wt% to 5.0 wt% and then decreases when the PVA concentration further increases to 10.0 wt%. It is suspected that the low PVA concentration of 2.5 wt% leads to more intrusion due to its low volume viscosity. However, due to the relatively low PVA concentration, the formed PVA layer on the inner surface is thin and not defect-free, leading to a good water vapor permeance. At higher concentrations, the viscosity of PVA solutions increases and intrusion into the membrane substrate becomes less serious. Thus, a thicker and uniform PVA selective layer is formed. The very different influences of these factors on water vapor permeation result in a maximum water permeation at a certain point, i.e., 5.0 wt% PVA. Further increase in the PVA concentration to 10.0 wt%, the PVA layer formed is too thick to allow fast permeation of water vapor. When the water vapor is removed from the humidity air, the temperature of the air stream slightly changes. Analogous to the results presented in Figure 2, Figure 3 shows that the heat removal ratio increases initially, reaching a maximum value when the PVA concentration is 5.0 wt% and then decreases with the increment in the PVA concentration. Using the composite membrane coated with 5.0 wt% PVA, about 10.94% of total heat can be effectively removed from the humidity air. It can be concluded that the 5.0 wt% is the optimal PVA concentration for the formation of composite membranes for dehumidification.

![Figure 2. Effects of PVA concentration on water vapor permeance of PVA/PVDF membrane (coating time 60 min).](image1)

![Figure 3. Effects of PVA concentration on heat removal ratio of PVA/PVDF membrane (coating time 60 min).](image2)
3.2. Effects of coating time

The influence of coating time on the water permeance and permeability is shown in Figure 4. It should be noted that the PVA concentration for this batch of membrane is fixed at 5.0 wt%. The permeance and permeability increases with increasing the coating time from 30 to 60 min. Subsequently, water vapor permeance and permeability decrease with further increase in the coating time. The reason for the phenomena is that too short coating time (e.g., 30 min) led to a thin selection layer with defects. Longer coating time not only significantly reduces the number of defects but also increases the thickness of the selective PVA layer. A coating time of 60 min obviously results in the PVA layer with good integrity and reasonable thickness. Further increase in the coating time might have formed very thick PVA layer, for which the resistance for water vapor to permeate through is apparently increased. When the coating time is 120 min, the permeance and permeability drop to 1139 GPU and 319 Barrer, which are even lower than those corresponding to 30 min coating. Figure 5 exhibits the effects of the coating time on the heat removal ratio and the trend is similar to that of the permeance and permeability. Obviously, the 60-minute duration is optimal for the PVA coating. The PVA/PVDF composite membrane based on the coating condition of 5.0 wt% PVA concentration and 60 min coating time show 6084 GPU water vapor permeance and 1704 Barrer permeability, respectively.

4. Conclusion

PVA/PVDF hollow fiber composite membranes have been successfully developed in this study for air dehumidification. The PVDF membrane substrates have the mean pore size of 9.72 nm and the porosity of 70.3%. The separation layer of the composite membrane was formed by coating and crosslinking PVA on PVDF hollow fiber inner surface. The effects of the PVA concentration and the coating time on the dehumidification performance of PVA/PVDF composite membrane were studied. The PVA/PVDF composite membranes coated with 5.0 wt.% PVA solution subject to a 60-minute duration have the optimal performance for dehumidification as seen from a water vapor permeance of 6084 GPU and permeability of 1704 Barrer, respectively. With the membrane, about 10.94% of total heat can be effectively removed from the humid air. Obviously, PVA/PVDF composite membranes possess a great potential for indoor air humidity control. It is expected that the findings from this work may offer a new site for the development of a novel high-performance composite membrane as the material of the
membrane dehumidifiers. Based on the obtained optimal coating conditions, PVA/PVDF composite membranes can be further optimized through adding new elements into the coating materials to improve their performance in the indoor air humidity control.

Acknowledgments
The authors are grateful for the support by the Scientific and Technological Innovation Project in Shaanxi Province (2015KTCQ01-99), the Key Scientific Research Innovation Team Project of Shaanxi Province (2016KCT-16).

References
[1] Zhang L Z 2012 Energy Convers. Manage. 63(6) 173-195
[2] Woods J 2014 Renew. Sust. Energ. Rev. 33(33) 290-304
[3] Roy S, Hussain C M and Mitra S 2013 Sep. Purif. Technol. 107(107) 54-60
[4] Zhao B W, Na P, Liang C Z, Yong W F and Chung T S 2015 Membr. 5(4) 722-738
[5] Liang C Z, Yong W F and Chung T S 2017 J. Membr. Sci. 541 367-377
[6] Kim K H, Ingole P G and Lee H K 2017 Int. J. Hydrogen Energy 42(38) 24205-12
[7] Liang C Z and Chung T S 2018 Sep. Purif. Technol. 202 345-356
[8] Su J C and Wei Y Y 2018 J. Water Proc. Eng. S2214714418300898