Nanoparticles filled PVA/PVDF hollow fiber membrane towards enhanced performance for air dehumidification

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Abstract. Membrane-based technology for gas separation has great potential in HVAC (Heating, Ventilating, and Air Conditioning) industry. In this research, the nanoparticle filled poly(vinyl alcohol)/poly(vinylidene fluoride) (PVA/PVDF) hollow fiber membrane was fabricated for indoor air dehumidification. The Poly(vinyl alcohol) thin film incorporated with nanoparticles was coated in the cavity of the Poly(vinylidene fluoride) substrate membranes. The enhanced performance of three types of nanoparticles [Zeolite, Titanium Dioxide (TiO\textsubscript{2}) and Graphene Oxide (GO)] was investigated experimentally for evaluating the water vapor permeability. The effects of nanoparticle types and nanoparticle loading concentration on the permeability enhancement of the nanoparticles filled PVA/PVDF membrane were compared and analyzed. The results indicate that the nanoparticles additives of great benefit to the performance improvement of water vapor permeability. The enhancement performance of three nanoparticles is as follows: Zeolite > GO > TiO\textsubscript{2}. The addition of 0.05 wt\% Zeolite nanoparticles lead to twice enhancement on the water vapor permeance than the original PVA/PVDF membranes. The GO nanoparticle additive enhances the water vapor permeance to around 1500 GPU (gas permeation unit) with the nanoparticle concentration from 0.1 wt\% to 0.2 wt\%. However, the addition of TiO\textsubscript{2} nanoparticle has no obvious enhancement due to its large particle size. This work provides a new perspective for strengthening the air dehumidification performance of composite membrane.

1. Introduction
The application of membrane-based technology for gas separation has drawn extensive attentions and showed great potential due to its low energy consumption, simple configuration, less maintenance components and friendly to the environment [1-2]. Among the various applications of membrane technique, indoor air dehumidification attracts increasing interest in HVAC (Heating, Ventilating, and Air Conditioning) industry. However, the development of the conventional polymeric membranes has
to seek a compromise between permeability and selectivity [3-5]. The membrane surface modification for the sake of enhancing its properties, together with the addition of nanoparticles into the membrane layer has attracted various researchers [6-7]. Especially, addition of nanoparticles in membrane material drastically increases the hydrophilicity and separability of the membrane. Ingle et al. synthesized the hydroxylated TiO₂ nanoparticles and fabricated nanocomposite polysulfone membranes. The results reflected that the addition concentration of modified hydroxylated TiO₂, 0.2 wt%, showed the best increase effect in the permeate flux of the water vapor [8]. The nanocomposite hollow fiber membranes incorporated with sulfated b-cyclodextrin (sb-CD) were fabricated for water vapor separation by An et al. [9]. The increase of sb-CD loading leads to the improvement of membrane permeability and selectivity.

It is noted that there are few reports about the influence of nanoparticle additives types and their incorporation conditions on the dehumidification performance of composite membranes. In this study, three different types of nanoparticles are incorporated into the selective layer material of PVA/PVDF membrane. The membrane performance is assessed in the light of enhancement ratio and water vapor permeance. Influence of nanoparticle types and nanoparticle loading concentration in the permeance of nanoparticles filled PVA/PVDF membrane are studied experimentally. The outcomes from the present work provide useful insights for the incorporation of nanoparticles on enhancing water vapor permeability of the dehumidification membranes.

2. Experiments and methods

2.1. Materials

Poly(vinylidene fluoride) (PVDF) was purchased from Arkema to fabricate the porous membrane substrate. Poly(vinyl alcohol) (PVA) (89000-98000, 99+%) and Glutaraldehyde (GA) was produced by Sigma. The physical drawings of the three nanoparticle additives are shown in the Figure 1. Zeolite was provided by Aldrich Chemical Company Inc. Titanium Oxide (TiO₂) was provided from Sinopharm Chemical Reagent Co., Ltd Highly concentrated Graphene Oxide was obtained from Graphenea SA.

![Nanoparticle additives: (a) Zeolite powder, (b) TiO₂ powder, (c) Highly concentrated GO.](image)

Figure 1. Nanoparticle additives: (a) Zeolite powder, (b) TiO₂ powder, (c) Highly concentrated GO.

2.2. Nanoparticle filled membrane preparation

The PVDF support membranes were shaped with the approach of dry-wet spinning. The inner and outer diameter of the hollow fibers are 0.58 and 0.86 nm, respectively. The effective length of the membrane used for the permeance experiment is 17.0 cm. The PVA aqueous solution is kept at the concentration of 5.0 wt%. The addition concentration of nanoparticle in the PVA solution (0.01 ~ 0.2 wt%) is an
experimental variable. The 1.0 vol% Glutaraldehyde (GA) is used for the crosslinking reaction of the selective layers.

2.3. Measurement of permeance

The dehumidification experiment is conducted as described elsewhere [10]. The water vapor permeance can be obtained by the following two equations:

\[
J_w = \frac{Q_w}{A(P_{fa} - P_{pa})}
\]

\[
Q_w = F(C_1 - C_2)
\]

\(J_w\) [GPU (10^-6 cm^3 STP)/(cm^2 s cmHg)] is the water vapor permeance, and \(Q_w\) (g h^-1) is the water vapor flow rate. \(A\) (m^2) is the membrane effective area, \((P_{fa} - P_{pa})\) (bar) is the pressure difference on both sides of membrane, and \(F\) (m^3 h^-1) is the feed air flow rate, \((C_1 - C_2)\) (g m^-3) is the concentration difference between import and export.

3. Results and discussion

3.1. Effects of nanoparticle types

The change of water vapor permeance and enhancement ratio with the coating time for three types of nanoparticles (Zeolite, TiO2, GO) is presented in Figure 2 and Figure 3. The differences in water vapor permeability among the three nanoparticles filled PVA/PVDF membranes are compared and analyzed at the nanoparticle loading of 0.05 wt% and 0.1 wt%. As shown in Figure 2, the water vapor permeance of the original PVA/PVDF membrane increases firstly and then decreases with the increase of coating duration. The maximum water vapor permeance of 1096 GPU is obtained at the coating duration of 90 min. The mean value of water vapor permeance is stable at around 1000 GPU.

When the nanoparticle loading is fixed at 0.05 wt%, the change of water vapor permeance for Zeolite filled PVA/PVDF membrane is similar with that of original PVA/PVDF membrane. At the coating duration of 90 min, the peak value of 2298 GPU is achieved. Compared with the original PVA/PVDF, the addition of Zeolite nanoparticle into the selective layer leads to an approximately doubling of water vapor permeance under all four coating time. The water vapor permeance of TiO2 filled PVA/PVDF membrane first increases and then stabilizes at around 1150 GPU. Except for 1.3 times enhancement of water vapor permeance at the coating duration of 60 min, the enhancement is weak at the rest of the coating duration. Regarding GO filled PVA/PVDF membrane, the water vapor permeance is enhanced by about 1.5 times than that of original PVA/PVDF membrane at the shortest coating time. Then, the permeance is lower than that of the original PVA/PVDF membrane with further increase in the coating duration. This is because that the size of GO nanoparticles is relatively small, which is not beneficial to optimize the mass transfer channels at low concentration. Increasing film thickness deteriorates the enhancement of nanoparticles at low GO nanoparticle loadings. And the nanoparticle embedding increases the mass transfer resistance of water vapor though the selective layer.

When the nanoparticle loading increases to 0.1 wt%, both Zeolite and GO filled PVA/PVDF membrane present a great enhancement on the water vapor permeance. The permeance of GO filled membrane fluctuates around 1500 GPU according to the coating time from 30 min to 120 min. The
average enhancement of permeability is about 1.44 times. On the contrary, the agglomeration of TiO$_2$ nanoparticle occurred at high loadings due to the larger size of particles, which blocks the water vapor diffusion channels. So the water vapor permeance decreases in comparison with that of original PVA/PVDF membrane.

Generally, the addition of Zeolite nanoparticles presents the best effect on enhancing water vapor permeance of PVA/PVDF membrane. And the GO nanoparticle possesses tremendous potential for enhancing mass transfer of water vapor at the suitable nanoparticle loading. By contrast, TiO$_2$ nanoparticle has no obvious effect on water vapor permeance due to its large particle size.

![Figure 2](image1.png)  ![Figure 3](image2.png)

**Figure 2.** Change of water vapor permeance with coating time for three types of nanoparticle: (a) the nanoparticle concentration of 0.05 wt%, (b) the nanoparticle concentration of 0.1 wt%.

**Figure 3.** Change of enhancement ratio with coating time for three types of nanoparticle: (a) the nanoparticle concentration of 0.05 wt%, (b) the nanoparticle concentration of 0.1 wt%.

### 3.2. Effects of nanoparticle loading concentration

Figure 4(a) and Figure 5(a) illustrate the permeance performance of Zeolite filled membrane based on the different nanoparticle loading concentration. At the nanoparticle loading of 0.01 wt%, the water vapor permeance first displays a fluctuation around 1000 GPU and then rises sharply to 2165 GPU at the coating duration of 120 minute. Further increasing Zeolite loading to 0.05 wt% has positive impacts on the water vapor permeance and leads to an great enhancement of twice. However, the enhancement...
of water vapor permeance is obviously weakened as the Zeolite loading concentration increases to 0.1 wt%. The enhancement ratio is only 1.8 even high at the peak value of water vapor permeance. This is because that the agglomeration of Zeolite nanoparticle at high loading concentration is not conducive to the formation of water vapor diffusion channels. Thus it can be seen that the Zeolite loading concentration of 0.05 wt% is optimal to enhancing the performance of PVA/PVDF membrane within the tested concentration range of Zeolite nanoparticle.

![Figure 4](image1.png)

**Figure 4.** Change of water vapor permeance with coating time for various nanoparticle loading concentration: (a) Zeolite nanoparticle, (b) GO nanoparticle.

![Figure 5](image2.png)

**Figure 5.** Change of enhancement ratio with coating time for various nanoparticle loading concentration: (a) Zeolite nanoparticle, (b) GO nanoparticle.

The results shown in Figure 4(b) and Figure 5(b) are the change of water vapor permeance and enhancement ratio for various GO nanoparticle loading concentration, respectively. When the GO loading concentration is 0.05 wt%, the water vapor permeance of GO filled PVA/PVDF membrane shows a certain degree of decline in comparison with that of original PVA/PVDF membrane. Nevertheless, the water vapor permeance demonstrates a fluctuation around 1500 GPU with the further increase in the nanoparticle loading to 0.1 wt% even 0.2 wt%, associated with an average enhancement ratio of 1.5. This indicates that the GO loading concentration from 0.1 wt% to 0.2 wt% may help to form effective water vapor transport channels without causing a serious nanoparticle agglomeration. It is
extremely beneficial to improve the water vapor permeability of the GO filled PVA/PVDF membrane.

4. Conclusion

Three types of nanoparticles were adopted to fabricated nanoparticles filled PVA/PVDF composite membranes towards the enhanced performance of air dehumidification. The water vapor permeability of the nanoparticle filled membranes was tested experimentally to study the effects of nanoparticle types and nanoparticle loading concentration on the water vapor permeance. In summary, the nanoparticle filled PVA/PVDF membranes show some beneficial value in enhancing the permeance of water vapor. The addition of Zeolite nanoparticles presents the best enhancement among the three types of nanoparticles. The Zeolite loading concentration of 0.05 wt% leads to an great enhancement of twice nearly on the water vapor permeance than the original PVA/PVDF membranes. The addition of GO nanoparticle enhances the water vapor permeance to around 1500 GPU with the nanoparticle loading from 0.1 wt% to 0.2 wt%. On the contrary, the addition of TiO₂ nanoparticles has no obvious effect on enhancing the water vapor permeance due to its large particle size. It is expected that the findings from this work may offer a new perspective for the development of nanoparticles filled composite membrane in the air dehumidification.

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