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High efficient water/ethanol separation by a mixed matrix membrane incorporating MOF filler with high water adsorption capacity
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Abstract

In order to promote the selective water permeation through porous filler, hydrophilic MOF-801 crystals with superior water adsorption ability were incorporated into chitosan (CS) matrix to fabricate MOF-801/CS mixed matrix membranes (MMMs) for pervaporation dehydration of ethanol. Both the experimental and molecular simulation results confirm the selective adsorption of water molecules in MOF-801 crystals, while the free volume and the lowest energy sorption sites analyses demonstrate the subdued diffusion of ethanol molecules through MOF-801. As a result, the porous structure in MOF-801 provides additional transport pathways for water molecules, and meanwhile makes the transport pathways of ethanol molecules more tortuous, thus achieving simultaneously enhanced flux and separation factor. The optimized membrane with MOF-801 loading of 4.8 wt% exhibits the total flux of 1937 g/m² h and separation factor of 2156.

Keywords: MOF-801, Mixed matrix membrane, Pervaporation, Water adsorption

1. Introduction

Polymeric membranes have been extensively investigated and used in pervaporation dehydration processes of water/alcohol mixtures for their diversity, low cost, facile preparation, and good film-forming property and so on. In order to further improve the selectivity and stability of polymeric membranes, the cross-linking method is usually adopted, which inevitably reduces the permeation flux due to the decreased polymer chain mobility and chain spacing. Alternatively, the incorporation of rationally designed porous fillers into polymer matrix to prepare mixed matrix membranes (MMMs) has been identified to be an effective strategy to address this issue [1-10]. It was proved that the pervaporation performance can be enhanced by improving the selective sorption and/or selective diffusion of water molecules via incorporating appropriate fillers [11-16]. Among various porous materials, the emerging metal organic frameworks (MOFs) formed through bridging of metal ions with organic ligands, exhibit high potential as fillers for molecular separation [17-25]. The existence of organic moieties and the attendant rich functionalization approaches confer MOFs with higher interfacial compatibility with polymer matrix compared with conventional inorganic porous fillers.
To date, diverse MOFs-based MMMs have been employed in pervaporation dehydration process [26-29], which mainly focused on zeolitic imidazolate frameworks (ZIFs) materials such as ZIF-7 (0.29 nm) [9], ZIF-8 (0.34 nm) [30], ZIF-71 (0.48 nm) [31] et al. For instance, Chung and Amirilargani et al. incorporated ZIF-8 into polybenzimidazole or PVA matrix to fabricate MMMs, which achieve significantly enhanced permeation flux for alcohol dehydration [30, 32]. In these works, the porous structure provides additional transport pathways to increase permeation flux, while the proper pore size smaller than alcohol molecules confers size-sieving effect. However, ZIFs are intrinsically hydrophobic, which is disadvantageous for water adsorption and interfacial compatibility between filler and polymer matrix. Therefore, it is believed to be effective to promote pervaporation dehydration performance via incorporating a new type of MOFs with high water affinity and especially high water adsorption capacity into polymer matrix [19, 33-38].

In this study, hydrophilic MOF-801 with superior water adsorption ability was incorporated into chitosan (CS) matrix to fabricate MOF-801/CS MMMs for pervaporation dehydration of ethanol. MOF-801 is composed of $\text{Zr}_6\text{O}_4(\text{OH})_4(-\text{CO}_2)$ secondary building units, which exhibits stable water adsorption capacity after multiple adsorption/desorption cycles [33]. Herein the effects of incorporating MOF-801 on the morphologies, physical/chemical properties, and PV performance of CS membrane were systematically investigated. Furthermore the adsorption behaviors of MOF-801 crystals towards water and ethanol were intensively studied via experimental and molecular simulation strategies to analyze the impacts of MOF-801 on water/ethanol separation performance.

2. Experimental

2.1 Materials

Fumaric acid was obtained from Alfa Aesar, $\text{ZrOCl}_2\cdot8\text{H}_2\text{O}$ was purchased from Sigma Aldrich. CS (>90% N-deacetylation degree) was obtained from Sinopharm Chemical Reagent Co., Ltd., China. Ethanol was purchased from Wuxi City Yasheng Chemical Co. Ltd. N,N-Dimethylformamide (DMF) was obtained from Sinopharm Chemical Reagent Co. Ltd. Formic acid was purchased from Xilong Chemical Co., Ltd. Sulfuric acid and acetic acid (glacial) were obtained from Shanghai Chemical Reagent Co., Ltd., China. All the above regents are of analytical purity. The flat-sheet polyacrylonitrile (PAN) ultrafiltration membrane with a molecular weight cut-off of
100,000 was received from Shanghai Mega Vision Membrane Engineering & Technology Co. Ltd. (Shanghai, China). Deionized water was used in all experiments.

2.2 Synthesis of MOF-801

MOF-801 particles were synthesized according to previous report [33]. Fumaric acid (5.8 g, 50 mmol) and ZrOCl$_2$·8H$_2$O (16 g, 50 mmol) were dissolved in a solvent mixture of DMF/formic acid (200 mL/70 mL) in a Teflon-lined stainless steel autoclave and stirred at 303 K for 30 min to form a homogeneous solution, which was heated at 130 °C for 6 h. White precipitate was formed and then washed with fresh DMF and methanol for three times. As-synthesized MOF-801 particles were immersed in 100 mL of methanol for 3 days, and rinsed with 50 mL of anhydrous DMF three times per day, during which time the methanol was also replaced three times per day. Then the solid was dried at 150 °C under vacuum overnight to yield activated MOF-801 sample.

2.3 Preparation of MOF-801/CS MMMs

PAN ultrafiltration membranes were used as supports. A certain amount of MOF-801 was dispersed in 20 mL of deionized water containing 2 wt% of acetic acid and stirred for about 1 h at room temperature. Then chitosan (0.5 g) was dissolved in the mixture solution and stirred constantly for 12 h. The solution was filtered to remove the undissolved residues and kept still for several minutes to remove air bubbles in the solution. The mixed matrix membranes were prepared via spin-coating. Before the membrane casting solution was spin-coated, the PAN ultrafiltration membranes (6 cm×6 cm) were soaked in deionized water for 2 days to remove glycerin from the surfaces, and then fully dried. The as-prepared MMMs were dried at room temperature and then immersed into sulfuric acid solution (2 mmol/L) for cross-linking. After 24 h, the membranes were cleaned with deionized water and dried at room temperature. A pristine CS membrane was also prepared using the similar process for comparison. The MOF-801 loading in the membrane was calculated as following formula:

$$w_{MOF} = \frac{m_{MOF}}{m_{MOF}+m_{CS}} \times 100\%$$ (1)

The mixed matrix membranes with the MOF-801 loadings of 0, 2.4, 4.8, 7.0 and 9.1 wt% were named as CS, CM-2.4, CM-4.8, CM-7.0 and CM-9.1, respectively.
2.4 Characterization

The crystal phases of samples and mixed matrix membranes were determined by X-ray diffraction (XRD) (Rigaku, Miniflex 600, Japan). Diffraction patterns were collected at room temperature in the angle range of $5^\circ \leq 2\theta \leq 50^\circ$ with a step width of 0.05$^\circ$ and a scan rate of 0.2 s step$^{-1}$. The functional groups of synthesized MOF-801 MOFs were characterized by Fourier transform infrared (FTIR, AVATAR-FT-IR-360, Thermo Ncolet, USA) spectra with range of 600-4000 cm$^{-1}$. Thermogravimetric analyzer (TGA, STA 209 F1, NETZSCH, Germany) was used to determine the thermal stabilizers of the MOF-801 crystals and mixed matrix membranes in the temperature range of 30-800 °C with a heating rate of 10 °C min$^{-1}$ in a nitrogen atmosphere. The equilibrium adsorption and desorption isotherms for ethanol and water vapor with MOF-801 crystals were measured by adsorption instrument (Belsorp-Max, Bel Inc., Japan). The surface area, micropore volume and pore size distribution of MOF-801 were calculated from N$_2$ sorption isotherms using Brunauer-Emmet-Teller (BET), t-plot and NL-DFT methods (Microtrac BELSORP-mini II, Bel Inc., Japan). The morphology of composite membrane matrix and topography of membrane surfaces were observed by field emission scanning electron microscopy (FESEM) (Hitachi Limited, S-4800, Japan). Energy dispersive spectrometry (EDS) elemental mapping was taken using an energy dispersion of X-ray system equipped with a window connected to a FESEMS4800 operating at 30 kV. The morphology of the crystals was chartered by transmission electron microscope (TEM) (Tecnai G2 20 S-TWIN). X-ray photoelectron spectroscopy (XPS) (ESCALAB250Xi, ThermoFisher Scientific, USA) was used to analyze the element composition of the membrane.

2.5 Swelling studies

The homogeneous membranes with different MOF contents were dried in a vacuum oven. Subsequently, the membranes were immersed into 90 wt% ethanol aqueous solution at 343 K for 48 h. The membrane surfaces were wiped with tissue paper and then weighed quickly to obtain the mass of the swollen membranes. All the experiments were repeated three times. The mass swelling degree ($D_s$, %) could be calculated by

$$D_s = \frac{W_s - W_d}{W_d} \times 100\%$$

(2)

where $W_s$ and $W_d$ are the mass of the swollen and dry membranes (g).
2.6 Pervaporation experiment

The pervaporation experiments were conducted with a homemade apparatus [41]. The flat membranes were stationed in stainless steel-made PV cell. The feed solution was maintained at preset concentration and temperature, circulated between the feed tank and the membrane cell with a flow rate of 12 L/h by a circulation pump. The permeate vapor was collected in liquid nitrogen trap. The pressure at permeate side was below 300 Pa during collections by a vacuum pump. The concentration of feed and result were determined by gas chromatography (SP-6890, Shandong Lunan, China). The type of packed column is GDX-102. The detector type is thermal conductivity detector (TCD), and the detection limit is $10^{-5}$ mg/mL. The temperatures of column, detector and injector are 383 K, 423 K and 423 K, respectively. The PV performance of a membrane is usually expressed on the basis of the total flux $J$ and separation factor $\beta$. The PSI (Pervaporation separation index) can be integrated to represent the pervaporation performance, which is equal to the product of the separation factor $\alpha$ minus one and the permeate flux $J$. For each MOF-801 loading, three samples were fabricated and tested with the average data as the final results.

The total flux ($J$, g/m$^2$h) and separation factor ($\alpha$) at steady state were calculated by the following equations:

$$J = \frac{W}{At}$$

$$\alpha = \frac{Y_w/(1-Y_w)}{X_w/(1-X_w)}$$

$$\text{PSI} = J(\beta - 1)$$

where $W$ (g) represents the mass of permeate over a period of $t$ (h); $A$ (m$^2$) is the effective area of flat membrane; $l$ (µm) is the membrane thickness; $X_w$ and $Y_w$ are the mass fractions of water in feed and permeate side, respectively.

In addition, the permeance of individual components ($P/l_i$, GPU) (1 GPU=7.501×10$^{-12}$ m$^3$(STP)/m$^2$·s·pa) and selectivity ($\beta$) were calculated by the following equations:

$$\frac{(P/l_i)}{P_{io}-P_{it}} = \frac{J_i}{Y_{io}X_{io}P_{io}-P_{it}}$$

$$\beta = \frac{(P/l)_W}{(P/l)_E}$$

where $X_{io}$ and $Y_{io}$ are the mass fractions of water in feed and permeate side, respectively.
where $J_i$ is the permeation flux of component $i$ (g/(m²·h)), $l$ is the thickness of membrane (m), $p_{i0}$, $p_{i\text{il}}$ are the partial pressures of component $i$ in the feed side and permeate side (Pa), and $p_i$ can be calculated approximately as 0 for the high vacuum degree in the permeate side. $\gamma_{i0}$ is the activity coefficient of component $i$ in the feed liquid, $x_{i0}$ is the mole fraction of the component $i$ in the feed liquid, $p_i^{\text{sat}}$ is the saturated vapor pressure of pure component $i$ (Pa). The permeation flux of water and ethanol should be transformed into the volumes under standard temperature and pressure (STP): 1 kg of water vapor at STP=1.245 m³ (STP), 1 kg of ethanol vapor at STP=0.487 m³ (STP).

2.7 Simulation model and method

The simulations were carried out in Materials Studio 6.0. First, the structure file of MOF-801 was downloaded from the CCDC databases. The fugacity of water and ethanol with different concentration was obtained by the Wilson calculation [39]. The fixed pressure sorption and sorption isotherms were performed by the Monte Carlo (MC) [40] simulation at the above fugacity and temperature. First, the geometric structure was optimized after energy minimization with 50000 iterations. Then the sorption simulation was calculated with $10^6$ equilibration and production steps. The interatomic interaction was described by COMPASS [41] force field, which is widely used in MOF materials’ simulation. The electrostatic interaction and van der Walls interaction were predicted by Ewald [42] calculation with the accuracy of $10^{-5}$ kcal/mol and atom-based method with 12.5 Å cut-off distance, respectively.

3. Results and discussion

3.1 MOF-801 crystal characterization

According to TEM image (Fig. 1a), MOF-801 crystals have regular and uniform particle size about 400 nm. The diffraction peaks from the XRD pattern of the as-prepared MOF-801 crystals (Fig. 1b) are in good agreement with the simulated results [38], indicating the high phase purity. In addition, to identify that the crystal structure was not destroyed in the prepared process of MMMs, MOF-801 crystals were soaked in acid solution for 12 h. XRD of acid treated MOF-801 crystals exhibits same diffraction peaks as that of its fresh phase. For the FTIR of the MOF-801
crystals, the peaks at 1404 cm\(^{-1}\), 1586 cm\(^{-1}\) and 1660 cm\(^{-1}\) are identified as -C=O-O-bonds, the peaks at 1200 cm\(^{-1}\) and 1100 cm\(^{-1}\) belong to the -C=O-OH and -C-O- arising from the functional groups of the fumaric acid in the MOF-801 particles (as shown in Fig. 1c). Fig. 1d shows the TGA curve of synthesized MOF-801 crystals. A 19.5% weight loss occurred at approximately 110 °C, owing to the adsorbed water in atmosphere. Another weight loss was at 220 °C, which arised from the evaporation of the DMF solvent from the particle cages. Furthermore, MOF-801 crystals were thermally stable up to 400 °C.

![Image](95x75 to 501x789)

**Fig. 1.** (a) TEM image of MOF-801 crystals; (b) XRD patterns of simulated MOF-801 crystals, as-prepared MOF-801 crystals and acetic acid soaking MOF-801; (c) FT-IR spectra of MOF-801 crystals; (d) The TGA and DTG curves of MOF-801 crystals.

N\(_2\) physisorption measurement of MOF-801 shows type I isotherm, characteristic for micro-porosity (Fig. 2a). The specific BET surface area, Langmuir surface area, micropore volume, and pore size are 986.1 m\(^2\)/g, 1165.3 m\(^2\)/g, 0.4751 cm\(^3\)/g and ~6 Å, respectively. As shown in Fig. 2b, the water uptake is as high as 350 cm\(^3\)/g, while sharply in contrast, the ethanol uptake reaches to 30 cm\(^3\)/g. The distinctly different sorption capacities of MOF-801 for water and ethanol demonstrates its hydrophilic pore surface, reflecting the potential in solvent dehydration.
To better understand those performance, we used the hard-spherical particles with given probe radius to formulate the free volume morphologies of MOF-801-single crystal (MOF-81-SC). MOF-81-SC has a hollow skeleton and highly interconnected intrinsic microporosity. The available free volume for water molecules (0.45103) to diffuse is nearly 1.4 times higher than that for ethanol (0.32711) via fractional accessible volume (FAV) analysis, especially the windows available for water connected between two cages. So it can be predicted that water molecules will permeate faster than ethanol molecules due to the more free transport space inside MOF-801. In order to verify the reliability of the simulation, the adsorption performance of the pure component in MOF-801 was simulated after obtaining the fugacity of pure water and ethanol at 313.15 K and 1 bar using Wilson method. The results are shown in Table 1. Both simulated and experimental results showed preferential adsorption capacity for water molecules. The simulated water sorption amount presented in Table 1 are in high agreement with the experimental value, which indicates that the simulation models and methods used in this work are quite reasonable. The amount of ethanol adsorption and the experimental value are of some difference, because the tunnel structure of MOF-801 crystal is rigid while the actual structure is flexible [43, 44]

Free volume can be estimated using the following equations:

$$FAV_{sim.} = \frac{V - V_0}{V}$$

(8)

where $V$ is the cell volume, $V_0$ is the occupied volume.
Table 1 The sorption amounts of simulation and experimental values

<table>
<thead>
<tr>
<th>Component</th>
<th>Sorption amount (cm³/g)</th>
<th>Experimental values</th>
<th>Simulation values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>330</td>
<td>382.4495</td>
<td></td>
</tr>
<tr>
<td>Pure ethanol</td>
<td>20</td>
<td>107.644</td>
<td></td>
</tr>
</tbody>
</table>

3.2 Membrane characterization

3.2.1 Chemical and physical structure of mixed matrix membranes

Fig. 3a shows the effect of the MOF-801 loading on the membrane structure as investigated via XRD characterization. Compared to the XRD pattern of pristine CS, the characteristic peaks of MOF-801 at 2θ=8.5° become stronger with the increasing loading of MOF-801. Therefore, it can be concluded that the crystal structure of MOF-801 is not broken during membrane fabrication process, which is consistent with the result of the stability in acetum solution (Fig. 1b). Fig. 3c shows the TGA curves of CS control membrane and MMMs. The homogeneous membranes with different loadings of MOF-801 were dried in a vacuum oven before measured. The entire thermal degradation process includes three major weight loss stages. The first stage arises from the evaporation of the residual water in membranes (40-200 °C). The pristine CS membrane shows less weight loss in the first stage compared with the MMMs, indicating the water adsorption ability of the evacuated MOF-801 crystals. The second stage is attributed to the deacetylation and depolymerization of CS (200-300 °C), which is the foremost to evaluate the thermal stability of membranes. From the TGA and DTG curves in Fig. 3b and c, both the initial degradation temperatures and the maximum weight loss temperatures of MMMs are slightly higher than CS. After incorporating MOF-801 crystals into CS matrix, the hydrogen bonds between polymeric and inorganic phases inhibit the mobility of CS polymer chains, exhibiting a little increased thermal stability. The third stage belongs to the residual decomposition of CS (300-800 °C). In summary, all the mixed matrix membranes possess desirable thermal stability. The XPS spectrum of the CM-4.8 membrane is shown in Fig. 3d. Zr3d peak appears on the spectrum, confirming the incorporation of MOF-801 crystals.
Fig. 3. (a) XRD spectra of different MOF-801/CS MMMs; (b) DTG curves of different MOF-801/CS MMMs; (c) TGA curves of different MOF-801/CS MMMs; (d) XPS spectrum of CM-4.8 membrane

3.2.2 Morphology of mixed matrix membranes

Fig. 4a-e shows the surface morphologies of pure CS membrane and MMMs with different MOF-801 loadings. The surface of pure CS membrane is smooth and defect-free. After embedding the MOF-801 filler into CS matrix with the loading varying from 2.4 wt% to 9.1 wt%, the membrane surfaces exhibit granular protuberances without visible interfacial voids, owing to the good compatibility between MOF-801 and CS matrix. However, with excess MOF-801 crystals (more than 7.0 wt%), agglomeration can be observed in the SEM images of membrane surface.

The cross section of the mixed matrix membrane with MOF-801 loading of 4.8 wt% was characterized by FESEM (Fig. 4f). The thickness of the membrane is about 1 μm. The elemental maps of the CM-4.8 membrane are shown in Fig. 5. The green-colored, red-colored and white-colored dots represent nitrogen, zinc and carbon, respectively. Zn element (red) uniformly disperses in membrane, which indicates the homogeneous distribution of the MOF-801 nanoparticles.
3.2.3 Swelling study
Swelling is a common phenomenon for hydrophilic membrane in aqueous solution, which exerts serious influence on membrane structure and separation performance. Therefore, the mass swelling degrees of membranes, after being immersed in 90 wt% ethanol aqueous solution at 343 K for 48 h, were evaluated to characterize the membrane structure stability (Fig. 6). From the result, the swelling degree of MMMs slightly fluctuates when the MOF-801 loading is lower than 4.8 wt%, reflecting the negligible influence of incorporating MOF-801. Although the introduction of MOF-801 crystals in CS matrix may generate the additional solvent adsorption inside porous filler during swelling test, the interfacial hydrogen bonds between MOF-801 and CS restricts the mobility of polymer chains and decreases the adsorption quantity in polymer matrix, thus offsetting the increased adsorption in MOF-801. When the MOF-801 loading is higher than 7.0 wt%, the occurrence of filler agglomeration generates interfacial microdefects and lowers the interfacial interaction, leading to increased swelling degree.

3.3 Pervaporation experiment

To investigate the effect of incorporating MOF-801 on selective water-permeation, the pervaporation performance of pristine CS membrane and MMMs were evaluated with 90 wt% ethanol aqueous solution at 323 K as shown in Fig. 7. With the increase of MOF-801 loading, the separation factor of MMMs significantly increases at the beginning and then declines, while the flux exhibits the tendency of continuous increase (Fig. 7a). When the MOF-801 loading reaches 4.8 wt%, the MMM obtains the optimal performance with the flux of 1113 g/m²·h and separation factor of 2098, which are 11.5% and 160% higher than those of pristine CS membrane, successfully overcoming the trade-off effect. After incorporating MOF-801 crystals into CS matrix, the porous filler with high water adsorption...
Capacity provides additional transport pathways for water molecules, and meanwhile makes the transport pathways of ethanol molecules more tortuous. As a result, water flux increases from 987 g/m²·h to 1110 g/m²·h, while ethanol flux decreases from 11 g/m²·h to 4 g/m²·h (Fig. 7b). With the further increase of MOF-801 loading higher than 4.8 wt%, excess MOF-801 crystals may reunite and then lead to microdefects at the interface between MOF crystals as well as between MOF-801 and CS matrix, which decrease the diffusion selectivity of membrane towards water, resulting in the significantly increased ethanol flux and the subsequently decreased separation factor.

Due to the optimal comprehensive performance, the MMM with MOF-801 loading of 4.8 wt% was selected for the following pervaporation experiments.

![Fig. 7. The pervaporation performance of different MMMs.](image)

![Fig. 8. (a) Effect of temperature on the separation performance of the CM-4.8 membrane with water concentration in feed of 10 wt%; (b) Arrhenius plots of permeation flux for separating water/ethanol mixture by CM-4.8 membrane.](image)

Pervaporation experiments under different temperatures ranging from 313 K to 343 K were carried out employing CM-4.8 membrane with water concentration in feed of 10 wt% (Fig. 8). It can be seen that increasing the temperature leads to the continuous increase of flux and separation factor. The high pervaporation performance with the permeation flux of 1937 g/m²·h and the separation factor of 2156 could be obtained when the temperature reaches 343 K. The impacts of operation temperature on the PV process can be ascribed to the driving force, the membrane structure and the interactions between permeate molecules and membrane. The continuous increase of water and ethanol fluxes confirms that the positive impacts on flux arising from the
promoted driving force and the loosen membrane structure (i.e. the increased polymer chain mobility) transcend the negative impacts of weakened interaction between permeate molecules and membrane and the subsequently reduced molecule adsorption on membrane surface.

The relationship between operation temperature and flux usually conforms to the Arrhenius law:

\[ J_p = J_{p0}\exp\left(\frac{-E_P}{RT}\right) \]  \( (9) \)

where \( J_p, J_{p0}, E_P, R \) and \( T \) represent the permeation flux, pre-exponential factor, apparent activation energy, gas constant and feed temperature, respectively. From the slopes of fitted lines in the range of 313-343 K, we can get the activation energies for the permeation of water (39.19 kJ/mol) and ethanol (17.99 kJ/mol). The much higher water activation energy indicates the higher temperature sensitivity of water permeation over ethanol permeation.

The impacts of operation temperature on the PV process can be ascribed to the driving force, the membrane structure and the interactions between permeate molecules and membrane. In order to achieve in-depth analysis, the driving force-normalized permeation flux (permeance) and selectivity were calculated and listed in Table 2. The continuously decreased ethanol permeance with temperature confirms that the positive impact arising from the membrane swelling (the increased polymer chain mobility) is inferior to the negative impacts of the weakened interaction between water and ethanol (the prohibited concomitant diffusion of ethanol molecules with water molecules) as well as the weakened interaction between ethanol and membrane (the reduced molecule adsorption on membrane surface). On the other hand, the accelerated water adsorption-desorption process in MOF at a higher temperature promotes the permeation of water molecules, thus leading to enhanced water permeance and selectivity.
Table 2 Permeance and selectivity of MOF-801/CS membrane under different temperatures and feed water contents

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Water content in feed (wt%)</th>
<th>$(P/l)_W$ (GPU)</th>
<th>$(P/l)_E$ (GPU)</th>
<th>Selectivity</th>
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<tr>
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<td>10</td>
<td>12781</td>
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</table>

Fig. 9. Effect of feed concentration on the separation performance of the CM-4.8 membrane at temperature of 343 K.

The effect of feed concentration on the flux and separation factor of the CM-4.8 membrane at 343 K was also investigated (Fig. 9). It is shown that when the feed water concentration increases from approximately 5 wt% to 20 wt%, the permeation flux increases while the separation factor declines. The increase in the feed water concentration, normally results in an increasing activity and partial pressure, which will enhance the driving force for the permeation of water. Besides that, the aggravated membrane swelling and the consequent larger free volume cavities arising from higher water concentration also contribute, which can be confirmed by the increase of water permeance. The ethanol permeance shows more significant increase than water permeance, partly because of the severer influence of membrane swelling on ethanol diffusion, imparting the membrane with higher ethanol permeability and lower diffusion selectivity at higher water concentration. Furthermore, the interaction between water and ethanol molecules increases with the water concentration.
increasing from 5 wt% to 20 wt%, thus promoting the concomitant diffusion of ethanol molecules with water molecules. As a result, the selectivity and separation factor decline with feed water concentration.

3.4 Sorption isotherms in ethanol/water mixture

In order to investigate the actual adsorption performance of MOF-801 in the pervaporation process, the adsorption isotherms of MOF-801 in the water/ethanol mixture solution with water content of 10 wt% at 343 K were calculated by the same simulation method. Via fitting Langmuir type, we obtained the maximal sorption amount ($Q_{\text{max}}$) and sorption equilibrium constant ($K_{\text{e}}$) of MOF-801 for water and ethanol molecules ($Q_{\text{H}_2\text{O, max}} = 332 \text{ cm}^3/\text{g}$, $K_{\text{H}_2\text{O, e}} = 22.051 \text{ kPa}^{-1}$; $Q_{\text{EtOH, max}} = 144 \text{ cm}^3/\text{g}$, $K_{\text{EtOH, e}} = 8.954 \text{ kPa}^{-1}$). The sorption amount of water is approximately 2.6 times of ethanol’s even though water has a very low concentration in feed solution.

The solubility coefficient of permeating molecules is defined as following [45]:

$$S_0 = \lim_{p \to 0} \frac{q}{p}$$  \hspace{1cm} (10)

From the limiting slope of the sorption isotherm at zero pressure, the solubility coefficients of water and ethanol can be obtained. Then, the solubility selectivity of MOF-801-SC for water can be calculated to be nearly 6.0.

![Fig. 10](image-url)  
(a) The density distribution of water and ethanol and free volume distribution in MOF-801-SC. (b) Magnification of circular area. Green balls (and dots) and red ellipse balls (and dots) represent water and ethanol molecules, respectively. Blue and gray areas denote the inside and outside surface of cage voids.

During simulating the realistic sorption process in pervaporation, the lowest energy sorption sites for water and ethanol are studied and presented in Fig. 10. In combination with free volume distribution, we can clearly find that water molecules will preferentially occupy the cages and open windows area, and then exclude the ethanol, while ethanol molecules will tend to become clusters in cage’s interior (seeing the magnification area), thus being hindered from jumping out the windows.

In order to quantitatively explain the higher affinity of MOF-801-SC to water molecules, we calculate the hydrogen bond in the last frame of pure water and ethanol
sorption in MOF models. Two geometrical criteria were used to examine hydrogen bonding: (1) the angle of hydrogen-donor–acceptor $\leq 150^\circ$; (2) the distance between a donor and an acceptor $\leq 3.5$ Å [46]. On average, per water molecule generates 1.43 hydrogen bonds in this MOF skeleton, which is lower than that in bulk water (3.5)[47] due to the confinement effect occurring in pores of MOF-801[48]. While one ethanol molecule forms 0.62 hydrogen bonds, which indicates that the affinity of MOF-801-SC to ethanol is much lower than that to water.

3.5 The Long-term operation stability

The long-term durability of the pervaporation performance of the CM-4.8 membrane was tested for 100 h with 90 wt% ethanol aqueous solution at 323 K. As shown in Fig. 11, the flux fluctuate in a narrow range while the water concentration in permeate decreases at the first 60 h and then reaches steady state. Similar phenomena were also observed in previous literatures [49, 50], which arises from the plasticization and relaxation process of CS membrane structure under the atmosphere of high temperature and solvents and needs to be addressed in the following research works. After 100 h operation, the stable membrane performance is still high enough to achieve efficient separation of water/ethanol mixture, indicating the potential application prospect of MOF-801/CS MMMs.

![Image of Fig. 11](image)

**Fig. 11.** The long-time pervaporation performance of the CM-9.1 membrane.

3.6 Comparison of PV performance with literatures

Chitosan (CS) is one of the most studied materials for pervaporation dehydration due to its high water affinity for selective sorption, as well as the structural rigidity and regularity for selective diffusion. Table 2 lists the PV dehydration performance of CS-based MMMs with different fillers for ethanol/water mixtures. The thinner
thickness of the composite membrane is favorable in obtaining a higher permeate flux, owing to the decrease of the transport resistance. In order to comprehensively compare membrane performance from permeation flux and separation factor, the PSI values of membranes in literatures and in this work were calculated. Comparatively, the MOF-801 filled CS membrane prepared in this work exhibits the highest PSI value and could be a promising candidate for pervaporation dehydration of water/ethanol mixtures.

Table 3 Summary of CS-based MMMs for pervaporation dehydration of water/ethanol mixtures

<table>
<thead>
<tr>
<th>Membrane</th>
<th>T (°C)</th>
<th>Thickness (µm)</th>
<th>Water content in feed (wt%)</th>
<th>Flux (g/m² h)</th>
<th>Separation factor</th>
<th>PSI (×10⁵ g/m² h)</th>
<th>Reference</th>
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<tr>
<td>CS</td>
<td>25</td>
<td>25</td>
<td>10</td>
<td>602</td>
<td>148</td>
<td>0.89</td>
<td>[9]</td>
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<tr>
<td>CS-OAPS</td>
<td>30</td>
<td>30-40</td>
<td>10</td>
<td>30</td>
<td>373</td>
<td>1.12</td>
<td>[51]</td>
</tr>
<tr>
<td>CS-OAPS</td>
<td>60</td>
<td>30-40</td>
<td>10</td>
<td>270</td>
<td>30</td>
<td>0.81</td>
<td>[51]</td>
</tr>
<tr>
<td>ZIF-7/CS</td>
<td>25</td>
<td>25</td>
<td>10</td>
<td>322</td>
<td>2812</td>
<td>9.05</td>
<td>[9]</td>
</tr>
<tr>
<td>CS-Ti-DHPPA</td>
<td>77</td>
<td>0.25</td>
<td>10</td>
<td>1403</td>
<td>730</td>
<td>10.24</td>
<td>[10]</td>
</tr>
<tr>
<td>CS-graphene</td>
<td>30</td>
<td>84</td>
<td>10</td>
<td>10</td>
<td>1093</td>
<td>0.11</td>
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<tr>
<td>CS-graphene</td>
<td>30</td>
<td>84</td>
<td>10</td>
<td>13</td>
<td>584</td>
<td>0.077</td>
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<tr>
<td>CS-APTEOS</td>
<td>50</td>
<td>18</td>
<td>15</td>
<td>900</td>
<td>600</td>
<td>5.39</td>
<td>[52]</td>
</tr>
<tr>
<td>CS-S-silica</td>
<td>70</td>
<td>30</td>
<td>10</td>
<td>410</td>
<td>1102</td>
<td>4.51</td>
<td>[15]</td>
</tr>
<tr>
<td>Prussian blue/CS</td>
<td>25</td>
<td>-</td>
<td>10</td>
<td>614</td>
<td>1472</td>
<td>9.04</td>
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</tr>
<tr>
<td>CS-Fe₃O₄(10)</td>
<td>77</td>
<td>0.6</td>
<td>10</td>
<td>1024</td>
<td>1500</td>
<td>15.36</td>
<td>[13]</td>
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<tr>
<td>ETS-10/CS</td>
<td>50</td>
<td>53</td>
<td>15</td>
<td>550</td>
<td>30</td>
<td>0.17</td>
<td>[53]</td>
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<tr>
<td>CS-MWNT</td>
<td>60</td>
<td>3.27</td>
<td>10</td>
<td>340</td>
<td>573</td>
<td>1.94</td>
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<td>CS-HY zeolite</td>
<td>25</td>
<td>-</td>
<td>10</td>
<td>253</td>
<td>102</td>
<td>0.26</td>
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<tr>
<td>CS-TiO₂</td>
<td>70</td>
<td>-</td>
<td>10</td>
<td>287</td>
<td>207</td>
<td>0.59</td>
<td>[54]</td>
</tr>
<tr>
<td>MOF-801/CS</td>
<td>70</td>
<td>1</td>
<td>10</td>
<td>1937</td>
<td>2156</td>
<td>41.76</td>
<td>This work</td>
</tr>
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</table>

4. Conclusions

In summary, MOF-801 nanoparticles with exceptional water adsorption capacity were synthesized, and then incorporated into CS matrix to fabricate MMMs for pervaporation dehydration of ethanol. Both the experiment and simulation results confirm the preferential adsorption of MOF-801 for water molecules arising from its higher affinity towards water. On the other hand, the free volume and the lowest
energy sorption sites analyses reveal that ethanol molecules tend to form clusters in the interior of MOF-801 cages, thus the diffusion of ethanol molecules can be hindered by the water molecules in window area. Consequently, the introduction of MOF-801 achieves the remarkably elevated separation factor and flux via simultaneously improving the selective sorption and selective diffusion of water molecules, overcoming the trade-off effect of CS membrane. The membrane with MOF-801 loading of 4.8 wt% exhibits the highest separation performance with the total flux of 1937 g/m²·h and separation factor of 2156 for water/ethanol mixture with 10 wt% water at 343 K. The excellent separation performance and easy fabrication process demonstrate the potential of MOF-801/CS MMMs for pervaporation dehydration of organic solvents.

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Nomenclature
Symbols
A membrane area (m²)
Ds mass swelling degree (wt%)
E apparent activation energy (kJ/mol)
FAV free volume
J permeation flux (g/m²·h)
K sorption equilibrium constant (kPa⁻¹)
l membrane thickness(m)
m mass of MOF-801 or polymer (g)
p pressure (kPa)
P/l permeance (GPU)
q equilibrium sorption amount per g of MOF-801 (cm³/g)
\( Q \) sorption amount (cm\(^3\)/g)
\( S_o \) solubility coefficient of permeating molecules
\( T \) feed temperature (K)
\( t \) time interval (h)
\( V \) cell volume (Å\(^3\))
\( V_o \) occupied volume (Å\(^3\))
\( W \) mass of permeate (g)
\( w \) mass ratio of MOF-801 to CS (wt%)
\( W_S \) mass of swollen membrane (g)
\( W_D \) mass of dry membrane (g)
\( X \) mass fractions in feed solution (wt%)
\( Y \) mass fractions in permeate solution (wt%)

**Greek letters**
\( \alpha \) separation factor
\( \beta \) selectivity
\( \gamma \) activity coefficient
\( \theta \) diffraction angle (deg)

**Abbreviations**
E ethanol
PSI pervaporation separation index
W water

**References:**


[38] Y. Chen, J. Xiao, D. Lv, T. Huang, F. Xu, X. Sun, H. Xi, Q. Xia, Z. Li, Highly efficient mechanochemical


Highlights

1. MMMs containing hydrophilic MOF-801 were prepared for pervaporation dehydration.
2. MOF-801 based MMMs show extraordinary high water/ethanol separation performance.
3. Molecular simulation was conducted to study the separation mechanism of MOF-801.