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Mixed matrix membrane containing ZIF-7 exhibits the excellent performance in the recovery of acetone from fermentation broths.
1. Introduction

As one of important petrochemical products and commonly used organic solvents, acetone can be acquired by chemical synthesis and fermentation production of agricultural products such as acetone-butanol-ethanol (ABE) fermentation broth. Up to now, a great deal of research efforts were devoted to recovering butanol or ethanol, whereas those for acetone are very scare, which is also of significant importance from both economic and environmental points of view. In general, the concentration of acetone in fermentation broth is very low (below 2 wt. %), indicating that the operation cost should be high if the conventional recovering methods are used, such as distillation and liquid-liquid extraction. In contrast, pervaporation (PV) is attracting more and more widespread concern due to its high efficiency and low energy consumption, especially for low concentration liquid separation. PV process has been widely used in the dehydration process of organic solvent-water mixtures, the removal/recovery of organics from aqueous solution and the separation of organic mixtures. Based on solution-diffusion mechanism, the PV membrane technology was developed, where the functional membrane is the key for a certain purpose of separation. Thus, great efforts are being made in the development of such membranes with excellent performance. Mixed matrix membranes (MMMs), originally constructed from filler and polymer matrix, were considered as the most promising ones. These membranes combine the easy processibility and low cost of polymer as well as the high intrinsic permeability or selectivity of the fillers. Despite the advantages of MMMs in liquid PV, the separation performance of such membranes still needs to be further improved to meet the practical demands. In this respect, MMMs based on metal-organic frameworks (MOFs) provide a good platform thanks to the highly designable structure and chemical diversity of MOFs. These kinds of MMMs have actually displayed good performance in gas separations. However, for liquid separation, only very limited works were reported up to now. These works have suggested that MMMs are very promising in the recovery of organic compounds, while the investigations on acetone are very scare.

Therefore, in this work MMMs with ZIF-7 and polydimethylsiloxane (PDMS) were prepared for the recovery of acetone from aqueous solution. As a typical one of zeolitic imidazolate frameworks (ZIFs), a subclass of MOFs, ZIF-7 is constructed by connecting zinc cluster to benzimidazolate (bIM) ligand in sodalite (SOD) topology structure. More importantly, ZIF-7 has the hexagonal window size of 0.29 nm in the cage with superhydrophobicity, which makes it ideal candidate filler in polymers for recovering organics, such as acetone. Polydimethylsiloxane (PDMS) was selected as the polymer matrix because of its superior structure and properties. It is a kind of organic permselective membrane material with perfect comprehensive performance, with high selectivity and good biocompatibility for volatile organic compounds (VOCs) in solution.
synthesized MMMs may efficiently separate acetone from aqueous solution.

2. Experimental

2.1 Materials

Zinc nitrate hexahydrate (Zn (NO₃)₂·6H₂O, >99%) and bIM (>99%) were purchased from Aladdin. PDMS (A.R., $M_w = 10,000$) was supplied by Shandong Zhaoyang Chemical Company. Polyvinylidene-fluoride film supports (PVDF, pore size = 0.22 μm) were purchased from Beihua Liming Membrane Separation Technology Co. Ltd. N, N'-dimethylformamide (DMF, >99%), n-heptane (A.R.), methanol (A.R.), acetone (A.R.) were purchased from Beijing Chemical Works. Tetraethyl-orthosilicate (TEOS, A.R.) as the cross-linker was purchased from Xilong Chemical Co., Ltd. Dibutyltin dilaurate (DBTDL, A.R.) as the catalyst was purchased from Tianjin FuChen Chemical Reagents Factory. All the chemicals were used as received without further purification.

2.2 Synthesis of ZIF-7

ZIF-7 was synthesized by a modified recipe reported by Li et al. at 298.15 K. 300 mL DMF was added to a solid mixture of 0.906 g Zn (NO₃)₂·6H₂O and 2.307 g bIM with stirring (molar composition of the synthesis solution of Zn²⁺/bIM/DMF = 0.154/1/200) for 48 h, followed by the separation of product using a centrifuge. Then the solid was washed with MeOH for five times (100 mL×5) to remove unreacted reagents and DMF within ZIF-7 pores by stirring overnight. After centrifugation, the particles are directly dispersed into the H₂O/EtOH (weight ratio is 30/70) mixture. The particle agglomeration can be avoided using such kind of solvent mixture, as suggested in literatures.

The sample was kept in vacuum oven at 333 K overnight for the following study.

2.3 Membranes preparation

The n-heptane solution of ZIF-7 was prepared by adding a certain weight of ground ZIF-7 (about 80 nm in size as shown in Fig. 3(a)) to n-heptane (1.0 g). The solution was stirred for 6 hours, accompanying with sonication for 15 min every hour. Then, PDMS was added into the mixture with the total weight of ZIF-7 and PDMS was 1.5 g (the concentration of ZIF-7/PDMS in n-heptane is 0.6 g g⁻¹). Subsequently, the solutions of different weight ratio were stirred for 4 h accompanying with sonication for 15 min every hour. TEOS and DBTDL were then added and the weight ratio of PDMS: TEOS: DBTDL was kept as 10:1:0.1. PDMS homogeneous casting solution contained 0, 5, 10, 15, 20, 25, 30, 35, 40 wt. % ZIF-7 nanocrystals were prepared. PVDF film was used as the support with an easy processing procedure. The PVDF support was immersed into a 10 wt. % ethanol aqueous solution and then into deionized water for 10 min successively. Subsequently, the wet PVDF support was fixed on the glass plate with adhesive tape. To remove the excess deionized water, the PVDF support was simply wiped by filter paper. The solution was dropped on the pre-treated wet PVDF support and casted with the casting machine. The solvent was evaporated for 4 h at 298 K and then transferred into vacuum oven for 8 h at 353 K. In this way, PV experiments were conducted using these membranes. The samples prepared on plastic petri dish were used in uptake experiment and XRD characterization of membranes.

2.4 Characterization

X-ray diffractometry (XRD) analysis of ZIF-7 nanocrystals and MMMs was conducted on a SHIMADZU XRD-6000 X-ray diffractometer in reflection mode using Cu Kα radiation ($\lambda = 1.5406$ Å) at 298 K. The 2θ range from 5° to 50° was scanned with a step size of 0.05°. The morphologies of ZIF-7 and the membranes were characterized by scanning electron microscopy (SEM) (FEI, JEOL JSM-7800F microscope). To get sharp clear cross-sectional images of the membranes, the samples were fractured under liquid nitrogen. All samples were mounted on tape and coated with a 1.5–2 nm Au layer to increase the conductivity and the measurements were operated under 10-20 kV acceleration voltage.

The ATR-FTIR (attenuated total reflection Fourier transform infrared spectroscopy) characterization was performed on Nicolet 6700 FTIR spectrophotometer. Spectra were recorded in the 4000-650 cm⁻¹ wave number range. The contact angle of the membranes was measured using a DSA 100 system. CO₂ adsorption isotherm of ZIF-7 powder at 298K was measured on an Autosorb-iQ-MP (Quantachrome Instruments) automated gas sorption analyser. Before measurements, the samples were degassed at 423 K overnight.

2.5 Uptake experiment

Uptake experiments of PDMS membrane and MMMs were performed at 303 K. Before the uptake experiment, the membrane sample was dried at 353 K for 3 h and weighed (denoted by $W_D$, g). Then, the membrane was immersed in 1 wt. % acetone solution for 22 h, and after that it was wiped with tissue paper and weighed again (denoted by $W_W$, g). The uptake (wt. %) was calculated according to

$$\text{Uptake} = \frac{W_W - W_D}{W_D} \times 100\%$$
where \( W_D \) and \( W_W \) are masses (g) of a dry and a swollen membrane, respectively.

2.6 Pervaporation

\[
Uptake(\text{wt.}%)=\frac{W_D-W_W}{W_D}\times100\% \quad (1)
\]

The flux was calculated by condensing and freezing the permeate vapor in the condenser pipe. Moreover, at least three identical membranes were tested for each of the PV condition to ensure the reliability of the results. The frozen permeate was heated up to 298 K and then weighted to calculate the flux. The concentration was analyzed by using a gas chromatography (GC, Agilent Technologies Inc.). Total flux and separation factor were calculated through the following equations:

\[
J = \frac{m}{A \cdot t} \quad (2)
\]

and

\[
\alpha = \frac{Y_{\text{Acetone}}/(1-Y_{\text{Acetone}})}{X_{\text{Acetone}}/(1-X_{\text{Acetone}})} \quad (3)
\]

3. Results and Discussion

3.1 Characterization

The morphology of ZIF-7 nanocrystals prepared in DMF at 298 K is shown in Fig. 3(a). According to the SEM image, ZIF-7 has a uniform particle size distribution of 80 nm. It should be noted that the agglomeration of nanoparticles can be avoided to a certain extent if the samples are dried after being washed in EtOH/H\(_2\)O mixture. Cross sectional SEM images of the prepared PDMS membrane and MMMs with different ZIF-7 loadings are shown in Fig. 3(b-f). It can be seen that all of the membranes are dense and defect-free. As illustrated in Figs. 3(c-f), ZIF-7 was homogeneously dispersed and closely embedded in the PDMS phase, with few voids around them observed, indicating that the polymer matrix and ZIF-7 are compatible well. The sizes of ZIF-7 are still about 80 nm similar to that of ground ZIF-7 (Fig. 3a), indicating that they did not separate during membrane fabrication. However, when the ZIF-7 loading was above 25\%, the dispersion of ZIF-7 is not good compared to those in MMMs with 10~25 wt. % filler loading, and there are obvious aggregations of particle surrounded by voids in polymer matrix (Fig. S1 in ESI†).

In order to determine the structure of the prepared ZIF-7, the experimental XRD pattern (denoted as ZIF-7-Exp) was conducted to be compared with the simulated XRD pattern (denoted as ZIF-7-Sim). As shown in Fig. 4, they are in good agreement with each other. The PXRD peaks of ZIF-7 can also
be found in the XRD patterns of MMMs, demonstrating that the structure of ZIF-7 remains intact in the polymer matrix. The porous structure of ZIF-7 nanoparticles was investigated through measuring the CO$_2$ adsorption isotherm as shown in Fig. S2 in the ESI†, since there is no adsorption of N$_2$ at 77 K due to the small pore diameter$^{47-49}$.

![Fig. 4 XRD patterns of ZIF-7 and MMMs with different ZIF-7 loadings.](image)

The FTIR spectra of ZIF-7 and MMMs are shown in Fig. 5. Among these MMMs, two obvious peaks at approximately 1455 and 750 cm$^{-1}$ were observed, which are corresponding to those in ZIF-7 particles identified as C=C and C-H bonds in the benzene functional group of benzimidazole$^{30}$. These results also confirmed that ZIF-7 was successfully incorporated into the MMMs and no chemical reaction was found between ZIF-7 and PDMS.

![Fig. 5 FTIR spectra of ZIF-7 and MMMs with different ZIF-7 loadings.](image)

3.2 Pervaporation

3.2.1 EFFECT OF ZIF-7 LOADING  The effect of the ZIF-7 loading in MMMs on the PV performance at 333K is shown in Fig. 6. It can be observed that the total PV flux increases with the increase of ZIF-7 loading, from 732.6 g·m$^{-2}$·h$^{-1}$ for pure PDMS membrane up to 1542.6 g·m$^{-2}$·h$^{-1}$ for MMMs with 40 wt. % filler. This is attributed to high specific interactions between acetone and the super-hydrophobic ZIF-7 nanocrystals. Besides the super-hydrophobic pores of ZIF-7 providing preferential diffusion paths for acetone, the aggregation at high loadings may form voids that could also contribute to the increase of flux. Moreover, a great enhancement in separation factor is achieved with the help of such super-hydrophobic filler. In fact, the hydrophobicity of MMM also increases with increasing the filler content, as illustrated by the increase of contact angle as shown in Fig. 7. It is attributed to the fact that the amount of ZIF-7 nanocrystals as well as their super-hydrophobic pores exposed to the membrane surface increases with the increase of ZIF-7 loading. The increasing hydrophobicity of MMMs could also play a positive role in the improvement of separation performance. However, separation factor decreases on the condition that the ZIF-7 loading is above 25 wt. %. This may be due to the formation of voids between nanoparticles, which become low selective transport paths$^{34}$ (Fig. S1 in ESI†).

![Fig. 6 The effect of ZIF-7 loading on PV performance of MMMs with feed solution of 1 wt. % acetone at 333K.](image)

![Fig. 7 The contact angle of MMMs with different ZIF-7 loadings.](image)

It is known that PV process follows solution-diffusion transport mechanism, which contains three steps: adsorption,
diffusion, desorption. The PV performance is the comprehensive result of these three steps. Thus, the uptake characteristic of a membrane plays an important role in PV performance since it indirectly reflects the affinity between permeating molecules and membrane. The uptake of MMMs increases with increasing filler content, because the presence of super-hydrophobic ZIF-7 nanoparticles can enhance the acetone uptake into the membranes. Since the addition of ZIF-7 changes membrane characteristics of solvent-induced swelling, it will also affect the PV performance. As shown in Fig. 8, the dependence of uptake on ZIF-7 loading is similar to that of the total PV flux (Fig. 6).

3.2.2 Effect of Temperature To investigate the effect of temperature, we further conducted PV experiments of PDMS membrane and the MMM with 25 wt. % ZIF-7 loading at different temperatures, including 303 K, 313 K, 323 K and 333 K. As shown in Fig. 9, both the total flux and the separation factor increase as temperature increases. High temperature promotes the pass of both acetone and water through the membrane. However, acetone has lower boiling point (329.4 K) than water, inducing that acetone molecules can pass the membrane easier. Thus, the PV separation performance can be enhanced with the increase of feed temperature. Moreover, according to the solution-diffusion mechanism, the effect of temperature on the total flux can be described by Arrhenius equation:

\[ J = J_0 \exp\left(\frac{-E_a}{RT}\right) \]  (4)

where \( J \) is flux, \( J_0 \) is pre-exponential factor, \( R \) is universal gas constant, \( T \) is the operating temperature, and \( E_a \) is the apparent activation energy of flux. Fig. 10 presents the plots of ln (J) versus operation temperature for pristine PDMS and the MMM with 25 wt. % ZIF-7. According to equation (4), \( E_a \) of total flux across the MMM is 27.5 kJ mol\(^{-1}\), showing a 28.7% decrease in energy barrier compared with the pristine PDMS membrane (38.6 kJ mol\(^{-1}\)). Such low energy barrier leads to the less resistance for acetone molecules and water molecules passing the membranes. On the other hand, increasing the feed temperature will lead to the increase of the energy consumption, which is not suitable from the practical point of view. Therefore, the operating temperature should be optimized balancing the separation performance and energy consumption, for example, slightly above the acetone boiling point, 333 K.

3.2.3 Effect of Feed Concentration PV performance of MMMs is also influenced by feed concentration, as shown in Fig. 11. The PV experiments of MMM with 25 wt. % loading were conducted with different feed solutions at 333 K. There is a “trade-off” relationship between total flux and separation factor with the increase of feed concentration. The MMM exhibits higher separation efficiency towards low concentration of acetone aqueous solution, which is ascribed to the fact that the decreased uptake caused by low concentration solution can reduce the free volume. As a result, acetone molecules can pass the membrane more easily than water molecules to induce the increase of separation factor. In addition, with increasing concentration, associated effect between water and acetone becomes more and more significant, resulting in the easy pass of water molecules through membranes. Correspondingly, the separation factor decreased from 39.1 to 28.3 with the
concentration of feed solution increases from 1 to 5 wt. %, a decrease of 27.6 %.

3.3 Comparison with other membranes

Table 1 shows a comparison of PV performance of the ZIF-7/PDMS membranes with various membranes previously reported in literatures. To the best of our knowledge, both the total flux and the separation factor of MMM with 25 wt. % ZIF-7 loading at 333 K are higher than all of the reported values. The excellent separation performance of these MMMs for acetone/water mixture is mainly attributed to the super hydrophobicity of the filler ZIF-7 crystals, as well as their well dispersion in the hydrophobic polymer matrix. This superior performance not only demonstrates the potential of incorporating ZIF-7 into PDMS matrix for recovering acetone from low concentration of aqueous solution, such as fermentation broth, but also opens a new way for the fabrication and application of ZIF-7 based MMMs.

Table 1 Comparison with other membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Temperature (K)</th>
<th>Total flux (g m⁻² h⁻¹)</th>
<th>Separation factor</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS/ceramic</td>
<td>310.15</td>
<td>-</td>
<td>20.6</td>
<td>6</td>
</tr>
<tr>
<td>Pervap-1060</td>
<td>313.15</td>
<td>340</td>
<td>14.5</td>
<td>56</td>
</tr>
<tr>
<td>Pervap-1070</td>
<td>313.15</td>
<td>100</td>
<td>16.7</td>
<td>56</td>
</tr>
<tr>
<td>Silicalite-PDMS</td>
<td>343.15</td>
<td>907</td>
<td>13.7</td>
<td>57</td>
</tr>
<tr>
<td>PEBA 2533</td>
<td>296.15</td>
<td>140.1</td>
<td>3.3</td>
<td>58</td>
</tr>
<tr>
<td>ZIF-7/PDMS</td>
<td>333.15</td>
<td>1236.8</td>
<td>39.1</td>
<td>This work</td>
</tr>
</tbody>
</table>

More importantly, this work demonstrates that the addition of MOFs to polymers is a promising way to prepare MMMs that may find industrial applications for recovering organic solvents from aqueous solutions.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Cross sectional SEM of MMM with 30 wt. % ZIF-7 loading, CO₂ adsorption isotherm of ZIF-7 powder at 298 K. See DOI: 10.1039/b000000x/


