Hydrophobic Two-Dimensional MoS$_2$ Nanosheets Embedded in a Polyether Copolymer Block Amide (PEBA) Membrane for Recovering Pyridine from a Dilute Solution

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ABSTRACT: A two-dimensional molybdenum disulfide (MoS$_2$) nanosheet, as a new type of inorganic material with high hydrophobicity and excellent physicochemical stability, holds great application potential in the preparation of a high separation performance organic–inorganic hybrid membrane. In this work, high hydrophobic MoS$_2$ was embedded in hydrophobic polyether copolymer block amide (PEBA) to prepare PEBA/MoS$_2$ organic–inorganic hybrid membranes. The structure, morphology, and hydrophobicity of the hybrid membrane were characterized by scanning electron microscopy, thermogravimetric analysis, contact angle goniometry, X-ray diffraction, infrared spectroscopy analysis, and atomic force microscopy. The effect of embedding of MoS$_2$ on the swelling degree and pervaporation separation performance of the PEBA/MoS$_2$ hybrid membrane was studied with a 1.0 wt % pyridine dilute solution. The results indicated that with increasing the MoS$_2$ content, the separation factor of PEBA/MoS$_2$ increased first and then decreased, while it showed a downward trend in the permeation flux. When the MoS$_2$ content in the PEBA/MoS$_2$ hybrid membrane was 10.0 wt %, the permeation flux was 83.4 g m$^{-2}$ h$^{-1}$ (decreased by 21.5% compared with the pure PEBA membrane), and the separation factor reached a maximum value of 11.11 (increased by 37.6% compared with the pure PEBA membrane). Meanwhile, the effects of feed temperature on the pervaporation separation performance of PEBA/MoS$_2$ hybrid membranes were also studied. In addition, as the PEBA/MoS$_2$ hybrid membrane has excellent thermal stability, it is expected to be a promising material for recovering pyridine from wastewater.

1. INTRODUCTION

Pyridine, one of the most widely used heterocyclic compounds, is an important fine chemical raw material. Pyridine is toxic and, at the same time, has an unpleasant odor, is volatile, and soluble in water. It mainly originates in low content during industrial activities such as dye production, insecticide production, research and development of drugs, and food processing. Pyridine is one of volatile organic pollutants (VOCs) and is not easily degraded. The US Environmental Protection Agency pointed out that pyridine is a dangerous organic substance with very high toxicity and carcinogenicity. Even if the content is low, it poses a certain threat to human beings. Therefore, removal of pyridine from a low-concentration pyridine solution is critical.

In general, these pyridine-containing industrial wastewaters or pyridine-contaminated soils are treated by different physicochemical methods, such as adsorption, electrochemical degradation, liquid membrane method, solvent extraction, or biological methods, etc. Nowadays, because of its outstanding advantages that new substances are not introduced during the separation process with no secondary pollution, the pervaporation technology has become one of the most preferable separation processes. Because of its energy saving nature, easy operation, and requires simple equipment, pervaporation is a promising method for the recovery of pyridine from a low-concentration pyridine solution. Singh et al. used carbon black (N330 grade) to fill the styrene–butadiene rubber membrane that was used to remove pyridine, and the membrane exhibits better selectivity and mechanical strength. Ray et al. studied the combination of sulfur-sulfurized RSS4 natural rubber and carbon black (N330 grade) to make a cross-linked membrane for pervaporation. The cross-linked membrane shows good pyridine recovery performance.

Polyether copolymer block amide (PEBA) is a very flexible thermoplastic block polymer. The ratio of $-$PE$-$ and $-$PA$-$ segments can be adjusted, and hence the properties of the PEBA can be changed thereby improving the separation properties of the PEBA-based membrane material. PEBA has...
been widely used in membranes for recovering organic compounds in water,\(^2\) and has a good separation factor. At present, adding appropriate nanoparticles is a good way to promote pervaporation performance. Porous nanoparticles can provide another transport channel for the PEBA membrane. Ding et al.\(^2\) pointed out that the introduction of hydrophobic ZIF-8 enhances the hydrophobicity of the PEBA membranes, thereby promoting the delivery of aromatic compounds. Liu et al.\(^2\) mentioned that under the load of ZIF-71, the chain accumulation of MMM is looser than the PEBA membrane. Due to the flexible frame and the hole effect of ZIF-71, butanol molecules can diffuse freely through the holes of the ZIF-71 cage. Rychlewskas et al.\(^2\) used a hydrophobic PEBAbased and PDMS-based composite membrane to separate organosulfur compounds from gasoline. The results show that the separation factor of the former is higher than that of the latter. Choudhari et al.\(^2\) filled two-dimensional layered materials such as graphene oxide and graphene into a PEBAbased matrix to prepare a composite membrane for recovering butyric acid in water, which showed improved performance. Mandal et al.\(^2\) prepared a hydrophobic PEBA pervaporation membrane for the enrichment of pyridine from a pyridine/water solution. The results show that the PEBA membrane has high selectivity to pyridine. Chen et al.\(^2\) studied the application of PEBACuO MMMs for the recovery of pyridine from the pyridine/water solution. The result indicates that PEBACuO MMMs are expected to be the candidate materials for the actual recovery of pyridine.

MoS\(_2\) is one of the most studied transition metal dichalcogenides\(^2\) with a hexagonal crystal structure. Each crystal is composed of multiple MoS\(_2\) molecular layers, and the distance between the layers is 0.69 nm. Each MoS\(_2\) molecular layer is composed of two sulfur atom layers and one molybdenum atom. It is a layered compound with a graphenelike structure, and the layer forms a sandwichlike structure in the form of S−Mo−S.\(^2\) Therefore, MoS\(_2\) has many excellent properties, such as hydrophobicity, solid lubricants, energy storage, and photovoltaic properties. It is highly favored by the scientific community and widely used in membrane field, biosensors, and other fields.\(^1\) Two-dimensional nanomaterials are generally stacked in parallel with the surface of the hybrid membrane to form a brick-layering structure.\(^3\) Interlayer channels and marginal spaces provide a tortuous path for molecule transport, while the hydrophobicity of MoS\(_2\) also maximizes the rejection of water passage. The two-dimensional channel of MoS\(_2\) can be used for molecular screening of organic vapor molecules.\(^4\)

Therefore, in this work, strong hydrophobic MoS\(_2\) was filled into a PEBAbased matrix for preparing a MoS\(_2\)/PEBAorganically inorganic hybrid membrane, which was used for the enrichment of trace pyridine from wastewater. To the best of our knowledge, MoS\(_2\) was the first to be used for the enrichment of trace pyridine by pervaporation. The physicochemical properties of the MoS\(_2\)/PEBA membrane were studied by X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, and water contact angle measurements. The effects of MoS\(_2\) loading, feed concentration, and temperature on the pervaporation separation performance were also studied.

2. EXPERIMENTAL SECTION

2.1. Materials. Polyether block amide (PEBA-2533) was purchased from French Arkema Co., Ltd. Molybdenum disulfide (MoS\(_2\)) (99.5% metals basis, <2 μm) was supplied by Aladdin Reagent Co. Pyridine (C\(_5\)H\(_4\)N, AR) and N-methylpyrrolidone (NMP, AR) were purchased from Xiqiao Chemical Co., Ltd. PEBA-2533 was dried at 80 °C for 8 h before use, and other chemicals were used as is throughout the study.

2.2. Preparation of the Membrane. 2.2.1. Preparation of the PEBA-2533 Membrane. The preparation process of the homogenized membrane was as follows. The PEBA-2533 homogeneous membranes were prepared by the solution casting method. A clean conical flask was charged with PEBA-2533 (5.6 g) and N-methylpyrrolidone (65.4 g), and stirred at 343 K until PEBA-2533 was completely dissolved. A certain amount of MoS\(_2\) was added to the solution, and the whole solution was sonicated for 30 min, and stirred again for 1 h. The solution was allowed to stand for 1 day to remove air bubbles. Then, the solution was poured onto a glass plate and cast into a membrane. Finally, the membrane was dried in an oven at 343 K for 24 h until the solvent was evaporated completely, and further dried in a vacuum oven at 323 K for 24 h. The loading amount of MoS\(_2\) was 0, 5.0, 10.0, 15.0, and 20.0 wt % of PEBA-2533 mass, respectively; the obtained membranes were named as PEBA/MoS\(_2\)-0, PEBA/MoS\(_2\)-5, PEBA/MoS\(_2\)-10, PEBA/MoS\(_2\)-15, and PEBA/MoS\(_2\)-20.

2.2.2. Characterization of MoS\(_2\) and the PEBA-2533 Membrane. The surface and the cross section of the PEBA-2533 membrane were observed by a scanning electron microscope (SEM, JSM-6010LA, Japan). The MoS\(_2\) filler dispersion was shown by energy-dispersive spectrometry (EDS) elemental mapping. The structures of the PEBA-2533 membrane and MoS\(_2\) were analyzed by an X-ray diffractometer (XRD, D/MAXTRIII). The morphologies of MoS\(_2\) were observed by a transmission electron microscope (TEM, JEM-2100, Japan). Fourier transform infrared (FT-IR) analysis was carried out using the Thermo Scientific Nicolet 8700 FTIR spectrophotometer in the wavenumber range of 500−4000 cm\(^{-1}\). A thermogravimetric analyzer (TGA 209 F1, Netzsch) was used to analyze the thermal stability of membrane materials and MoS\(_2\). The water contact angle of the hybrid membrane was measured by the SL200B static drop contact angle measuring instrument (SL200B, SOLON TECH, Shanghai, China). The surface characteristics of the membranes were investigated using an atomic force microscope (AFM, CSPM5500).

2.3. Membrane Swelling Adsorption Experiment. First, the dry membrane to be tested was weighed and then immersed in a 1.0 wt % pyridine solution at 305 K for 24 h. After that, the membrane was taken out at regular intervals, and the solution on the membrane surface was quickly wiped off with a filter paper and then weighed quickly. For all experiments, the operation was repeated at least three times and the average was obtained.

Then, the swelled membrane was put into a desorption device. The adsorbed liquid was extracted from the membrane, and the composition of the analytical solution was analyzed. The swelling degree (DS) of the membrane is calculated as

\[
DS (%) = \left(\frac{W_s - W_d}{W_d}\right) \times 100\%
\]

where \(W_d\) is the weight of the dry membrane and \(W_s\) is the weight of the swollen membrane.

The adsorption selectivity (\(\alpha_i\)) of the membrane is evaluated as
where $M_w$ and $M_p$ are the mass fractions of water and pyridine adsorbed in the membrane, respectively, and $F_w$ and $F_p$ are the mass fractions of water and pyridine in the raw material liquid, respectively.

### 2.4. Pervaporation Experiments

The pervaporation system is as described in other literature. The downstream of the membrane was evacuated by a vacuum pump with a vacuum of 1 mbar and a feed flow rate of 0.025 m$^3$ h$^{-1}$. The permeate was collected through a liquid nitrogen cold trap. The compositions of the pyridine/water mixtures were analyzed by a GC-4000A gas chromatograph (Beijing Puxi General Instrument Co., Ltd. China), equipped with a TCD detector and a 30 -m capillary column MXT-5 made by Restek. The effect of MoS$_2$ loading on the pervaporation separation performance was studied in the range of 0 - 20.0 wt %. The effect of feed temperature and pyridine concentration on the pervaporation separation performance was also investigated.

The performance of membranes can be usually expressed by flux ($J$), separation factor ($\beta$), and diffusion selectivity ($\alpha_s$).

$$J = \frac{Q}{A t}$$  \hspace{1cm} \text{(3)}

$$\beta = \frac{Y_A / Y_B}{X_A / X_B}$$  \hspace{1cm} \text{(4)}

where $X_A$ and $X_B$ are the mass fractions of the two components in the feed liquid, respectively, and $Y_A$ and $Y_B$ are the mass fraction of the infiltrated components, respectively. The separation factor ($\beta$) indicates the degree of separation of the two substances. When the separation factor is greater than 1, the A component preferentially permeates the membrane than the B component, and the larger the separation factor, the better the separation performance of the membrane and more complete is the separation. The pervaporation process of pyridine/water separation is mainly carried out according to the solution diffusion mechanism; the diffusion selectivity ($\alpha_s$) of the membrane was evaluated by

$$\alpha_s = \beta / \alpha$$  \hspace{1cm} \text{(5)}

The value of $\beta$ depends on the operating condition, while $\alpha_s$ reveals the effect of membrane material performance on pervaporation.
the crystalline phase. The PEBA/MoS₂-0 membrane has only a broad peak between 12 and 35°, indicating that the PEBA membrane is an amorphous crystal. In the XRD pattern of the PEBA/MoS₂-10 hybrid membrane, no new peak was found.

Figure 3. SEM images of PEBA/MoS₂ hybrid membranes with various MoS₂ loadings: (a) 0 wt %, (b) 5.0 wt %, (c) 10.0 wt %, (d) 15.0 wt %, and (e) 20.0 wt %.

Figure 4. SEM images of the cross sections of the PEBA/MoS₂ hybrid membrane: (a) PEBA/MoS₂-0 and (b) PEBA/MoS₂-10.
and only the characteristic peaks of PEBA and MoS2 were found, indicating that the PEBA/MoS2-10 hybrid membrane has good compatibility. The synergistic effect of the hydrophobicity crystalline MoS2 and the noncrystalline PEBA can reduce the swelling degree of the PEBA/MoS2-10 hybrid membrane, thereby reducing the flux of water and improving the selectivity for pyridine.

3.1.2. Infrared Spectroscopy Analysis (FT-IR). FT-IR spectra of MoS2, PEBA/MoS2-0, and PEBA/MoS2-10 are shown in Figure 2. The bands around 3500−3300 and 1646 cm−1 are attributed to the N−H stretching vibration of polyamide and the stretching vibration of the H−N−C═O group, respectively, as shown by PEBA/MoS2-0. It is noteworthy that an obvious band at 3436 cm−1 attributed to the O−H stretching, was observed for MoS2 and the PEBA/MoS2-10 membrane. It indicates that there may be coordination between MoS2 and PEBA. On comparing FT-IR spectra of PEBA/MoS2-0 and PEBA/MoS2-10, one can find that a new peak appeared at 682.44 cm−1 for PEBA/MoS2-10, which can be assigned to the C−S bond stretching vibration. 3.1.3. Scanning Electron Microscopy (SEM) Analysis and Transmission Electron Microscopy (TEM) Analysis. Figure 3 shows the surface morphology of PEBA/MoS2-0, PEBA/MoS2-5, PEBA/MoS2-10, PEBA/MoS2-15, and PEBA/MoS2-20 hybrid membranes. It can be clearly observed from Figure 3a that the pristine PEBA membrane surface is uniformly smooth and dense. Figure 3b,c indicates that the MoS2 particles are uniformly distributed in the PEBA/MoS2 hybrid membrane when the MoS2 content does not exceed 10%. However, when the loading mass fraction is more than 10.0 wt %, as indicated in Figure 3d,e, the particles are partially agglomerated in the PEBA matrix.

Cross-sectional morphologies of PEBA/MoS2-0 and PEBA/MoS2-10 hybrid membranes are shown in Figure 4. One can observe that the pristine PEBA membrane surface is relatively flat, and the PEBA/MoS2-10 membrane surface is relatively rough. Meanwhile, one also can clearly find that MoS2 is evenly distributed in the membrane, which benefits for rejecting the passage of water and allowing the passage of organic matter, attributing to the hydrophobic property of MoS2.

It was also proved by EDS elemental mapping that MoS2 (green and red dots represent Mo and S elements, respectively) was uniformly dispersed in the PEBA polymer matrix, as shown in Figure 5.

The morphology of MoS2 nanosheets was characterized by TEM. Figure 6 displays that the MoS2 is a two-dimensional layered structure. The two-dimensional channel of MoS2 can promote organic vapor molecules,34 and its hydrophobicity can hinder the passage of water, which is conducive to the transmission of pyridine to a certain extent.

3.1.4. Atomic Force Microscopy (AFM) Analysis. The surface morphologies of PEBA/MoS2-0, PEBA/MoS2-5, PEBA/MoS2-10, PEBA/MoS2-15, and PEBA/MoS2-20 hybrid membranes were analyzed by AFM and are shown in Figure 7. It is pointed out that as the MoS2 loading gradually increases, the surface of the membrane becomes rougher (average roughness (Ra) are 26.3, 57.9, 82.5, 87.6, and 89.3 nm, respectively). The greater the Ra, the rougher the surface roughness of the membrane. The rougher the membrane surface, the larger the contact area between pyridine and MoS2, which is beneficial to the transfer of pyridine and improves the performance of the membrane. It is consistent with the results of SEM characterization.

3.1.5. Thermal Performance Analysis (TGA). The thermal stabilities of PEBA/MoS2-0 and PEBA/MoS2-10 hybrid membranes were assessed by TGA, as exhibited in Figure 8. It can be seen from Figure 8 that the mass fraction of the two membranes is substantially constant from 298 to 573 K, which indicates that the membranes have good thermal stability. In the interval of 573−753 K, the membranes began to decompose gradually. The weight loss ratio of PEBA/MoS2-0 was faster than that of PEBA/MoS2-10. In summary, the embedding of MoS2 helps improve the thermal stability of the PEBA/MoS2-10 membrane.

3.1.6. Membrane Contact Angle Testing. The membrane used to recover pyridine from wastewater must be hydrophobic. The higher the hydrophobicity of the membrane, the more favorable it is for the diffusion of pyridine molecules.
through the PEBA/MoS₂ hybrid membranes but not for the water molecules. The hydrophobic property of the membrane can be determined using water as a test solvent.⁴⁰−⁴² As shown in Figure 9, the higher the MoS₂ loading, the stronger hydrophobic is the PEBA/MoS₂ hybrid membrane. This can be attributed to the hydrophobicity of the MoS₂ nanosheets³⁸ and their low surface energy,⁴³ which improves the hydrophobicity of the PEBA/MoS₂ hybrid membranes, which facilitates the adsorption and diffusion of pyridine molecules through the PEBA/MoS₂ hybrid membranes.

3.2. Membrane Swelling Adsorption Experiment. The effect of MoS₂ loading on the swelling behavior of the PEBA/MoS₂ hybrid membrane is exhibited in Figure 10. One can find that as the loading amount of MoS₂ increases, the swelling degree of the PEBA/MoS₂ hybrid membrane tends to decrease. This is mainly due to the following two factors: first, the filling of MoS₂ reduces the softness of the PEBA
segment and enhances the rigidity of the polymer, which reduces the swelling degree of the PEBA/MoS$_2$ hybrid membrane; second, the hydrophobicity of the PEBA/MoS$_2$ hybrid membrane is also enhanced with increasing the MoS$_2$ loading. The swelling features of the MoS$_2$-filled hybrid membrane are similar to that of the Tanaka et al. study. According to the solubility parameter theory, the solubility parameters of PEBA is 19.5 J$^{1/2}$ cm$^{-3/2}$, and the solubility parameters of pyridine and water are 17 and 31.29 J$^{1/2}$ cm$^{-3/2}$, respectively, where PEBA and pyridine are very close to each other, indicating that PEBA membrane has a preferential adsorption property for pyridine.

Membrane adsorption selectivity ($a_s$) and diffusion selectivity ($a_d$) are affected by MoS$_2$ loadings. From Figure 11, one can observe that with an increasing MoS$_2$ loading
amount, \( a_i \) of the membrane increases first and then decreases, and \( a_w \) decreases throughout. The main reason is that the hydrophobic MoS\(_2\) in the membrane can enhance adsorption of pyridine molecules and reduce the adsorption of water molecules. However, the agglomeration of MoS\(_2\) in the membrane results in a large nonselective region between the MoS\(_2\) particles and the membrane polymer matrix for pyridine and water molecules, which reduces \( a_i \) of the membrane. Therefore, when the MoS\(_2\) loading is 10.0 wt %, \( a_i \) of the hybrid membrane reaches a maximum value. With increasing MoS\(_2\) loading, the molecule diffusion resistance of the permeate in the membrane also increases. Because the molecular dynamics diameter of water is smaller than that of pyridine, the diffusion resistance of water molecules in the membrane is smaller than that of pyridine molecules, which causes a decrease of the diffusion selectivity of the hybrid membrane.

3.3. Pervaporation Performance Experiment. 3.3.1. Effects of MoS\(_2\) Loadings on Pervaporation Separation Performance. The effect of MoS\(_2\) loadings on the pervaporation separation performance of the PEBA/MoS\(_2\) hybrid membrane is demonstrated in Figure 12. It indicates that as the MoS\(_2\) loading increases, the total permeate flux decreases; however, the separation factor shows a trend of increasing first and then decreasing, reaching a maximum value at a loading of 10.0 wt %. In the loading of MoS\(_2\), the main diffusion route of pyridine molecules and water molecules is diffusion through the PEBA/MoS\(_2\) matrix, which depends on the expansion and deformation of the polymer chain segment. A main physical interaction between MoS\(_2\) and PEBA is observed and it may be the coordination between Mo atoms and oxygen-containing functional groups on the PEBA chain.\(^{38}\) Due to the large contact area of MoS\(_2\) nanosheets with the polymer matrix and good polymer–filler compatibility, the hydrophobicity of the membrane is enhanced and the adsorption of pyridine is promoted. When the permeate diffuses forward, it can only bypass MoS\(_2\), which reduces the flux to some extent.\(^{38,47}\) The improvement of separation performance may be attributed to the solution/adsorption process based on the solution diffusion mechanism.\(^{47,48}\) The organophilicity of PEBA and MoS\(_2\) nanosheets preferentially attracts pyridine molecules, so it is beneficial to the solution/adsorption process of pyridine molecules by the PEBA/MoS\(_2\) hybrid membrane.

When the loading amount of MoS\(_2\) is less than 10.0 wt %, it can be uniformly and separately scattered in the PEBA polymer matrix to maintain the continuous phase of the membrane as a whole. At the same time, because of the strong hydrophobicity of MoS\(_2\), the more the loading amount, the stronger is the hydrophobicity of the PEBA/MoS\(_2\) membrane (as observed by the water contact angle in Figure 9), and the water molecules passing through the membrane surface also decrease. Therefore, the water flux decreases with increasing MoS\(_2\) loadings.

In the whole process of pervaporation, the content of pyridine in the liquid is relatively low, and the change in the flux mainly comes from the change in the water flux, that is, the separation factor increases with the decrease of water flux. When the MoS\(_2\) loading amount is more than 10.0 wt %, the agglomeration phenomenon of MoS\(_2\) particles appears to some extent, which destroys the continuous phase structure of the membrane, creates the interface gap between the filler and the polymer, and provides a nonselective area for the permeability components. As a result, the selectivity of the membrane decreases and the permeability flux decreases slowly.

When the MoS\(_2\) loading amount is 10.0 wt %, the separation factor reaches a maximum value. Figure 13 shows the effect of MoS\(_2\) loading on the permeate flux of water and pyridine recovery. It can be seen that as the MoS\(_2\) loading amount increases, the permeate flux of pyridine first increases and then
adsorption and the diffusion component, which affects the permeate component. The temperature of the feed affects the pervaporation separation performance. The PSI values of hybrid membranes with different MoS$_2$ loadings reported in Figure 14 show that the PEBA/MoS$_2$-10 hybrid membrane exhibits significantly higher PSI values (855.4 g m$^{-2}$ h$^{-1}$) than the pure PEBA membrane (739.32 g m$^{-2}$ h$^{-1}$) in a 1.0 wt % pyridine solution at 303 K. 

3.3.2. Effects of Feed Temperature on Pervaporation Separation Performance. The pervaporation is a process of different component molecules adsorbing and diffusing in the membrane. According to Figure 15, as the feed temperature increases, the total permeate flux and the separation factor both show an upward trend. The organic solute molecules have a strong interaction with the hydrophobic polymer membrane. According to the principle of adsorption and diffusion, the diffusion rate is related to the microscopic motion of the polymer segment. The temperature of the feed affects the adsorption and the diffusion coefficient of the permeate component, which affects the mass transfer process of the permeate component.

The effect of feed temperature on the permeate flux can be expressed by the following Arrhenius equation

$$ J = J_0 \exp(-E_a/RT) $$

where $J_i$ (g m$^{-2}$ h$^{-1}$) is the flux of component $i$ and $J_0$ (g m$^{-2}$ h$^{-1}$), $E_a$ (J mol$^{-1}$ K$^{-1}$), and $R$ (J mol$^{-1}$ K$^{-1}$) are the pre-exponential factor, activation energy, molar gas constant, and absolute temperature, respectively. Under other constant conditions, an increase in temperature favors the increase in permeate flux. Because the temperature increases, the thermal motion of the polymer segment is also intensified, and therefore, the free volume space in the membrane increases. The relationship between $\ln J$ and $1/T$ is shown in Figure 16, and it is clear that the plots of $\ln J$ versus $1/T$ for the PEBA/MoS$_2$-10 hybrid membrane are linear. The activation energies of pyridine molecules and water molecules are 28.9 and 18.9 kJ mol$^{-1}$, respectively. The activation energy of pyridine molecules is greater than that of water molecules, which means its sensitivity to temperature is higher than that of water molecules. Therefore, with increasing feed temperature, the change in the pyridine flux is greater than that of water, and the permeation concentration of pyridine increases with increasing feed temperature. In addition, due to the increase of feed temperature, the free volume of the hybrid membrane increases, that is, the channel through which the molecules diffuse becomes larger, which makes passage of large-sized pyridine molecules easier. In summary, the separation factor increases with the increase of feed temperature.

3.3.3. Effects of the Feed Pyridine Concentration on Pervaporation Separation Performance. The effects of the feed pyridine concentration on the pervaporation separation performance of the PEBA/MoS$_2$-10 hybrid membrane are demonstrated in Figure 17. It indicates that the total flux increases with increasing feed pyridine concentration; however, the separation factor shows the opposite trend. With increasing feed pyridine concentration, the concentration of pyridine adsorption in the membrane becomes higher, so does the swelling degree of the membrane. The swelling of the membrane weakens the interaction between the chain segments of PEBA, increases the free volume of the polymer, and reduces the mass transfer resistance of the molecule through the membrane, thus increasing the permeation flux of the membrane. The molecular dynamics diameter of pyridine is much larger than that of water, which makes it easier for small-molecule water to penetrate the membrane. The rate of the water permeation flux increases faster than that of pyridine molecules. In summary, an increase in the feed pyridine concentration is beneficial to the permeation flux of pyridine and water but not to the separation factor.

Table 1 describes the comparison of the pervaporation performance of the PEBA/MoS$_2$ hybrid membrane with other membranes reported in the literature. It can be found that the PEBA/MoS$_2$ hybrid membrane exhibits encouraging pervaporation performance.

### 4. CONCLUSIONS

In this work, PEBA/MoS$_2$ organic–inorganic hybrid membranes were prepared by filling hydrophobic MoS$_2$ into a PEBA matrix. It was characterized by XRD, FT-IR, SEM, AFM, and TGA. It was shown that MoS$_2$ particles and the PEBA matrix can maintain good compatibility, and MoS$_2$ particles are uniformly dispersed in the PEBA matrix membrane, as shown by SEM and AFM. A main physical interaction is observed between MoS$_2$ and PEBA. The transfer process of the membranes to pyridine was promoted with the filling of MoS$_2$. It was observed that MoS$_2$ successfully embedded in the PEBA polymer, as shown by FT-IR. The TGA displayed that the thermal stability of the PEBA/MoS$_2$ hybrid membrane was improved by the loading of MoS$_2$. It was revealed that the surface hydrophobicity of the membrane increased with the increase of MoS$_2$ content by contact angle testing. Adding hydrophobic MoS$_2$ makes it harder for water molecules to pass through the membrane. The pervaporation separation for the pyridine/water mixture demonstrated the decrease in the permeation flux of the membrane with the increase of MoS$_2$ loading, while the separation factor increases first and then decreases. When the MoS$_2$ loading reaches 10.0 wt %, the enrichment of pyridine by pervaporation through the PEBA/MoS$_2$ hybrid membrane from a 1.0 wt % pyridine solution at 303 K reaches a maximum with a highest separation factor of
11.11 and pyridine flux of 83.4 g m\(^{-2}\) h\(^{-1}\). According to the pervaporation test, permeate flux and the separation factor both are influenced positively by the feed temperature and feed concentration. In conclusion, PEBA/MoS\(_2\) hybrid membranes facilitate the recovery of pyridine from a dilute pyridine solution.

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Notes

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