Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.24903

175 (2020) 49–59
January

Graphene oxide modified porous anion exchange membranes for acid recovery through diffusion dialysis

Wenya Liu[a], Meng Li[a], Mengjie Sun[a], Xu Zhang[a], Cuiming Wu[a,*], Yonghui Wu[b,*]

[a]*Anhui Key Lab of Controllable Chemical Reaction & Material Chemical Engineering, School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei 230009, China, Tel. +86-0551-62901450; email: cmwu@ustc.edu.cn (C. M. Wu), Tel. +86-13635657292; email: 1371253779@qq.com (W. Liu), Tel. +86-15077922386; email: 1510388117@qq.com (M. Li), Tel. +86-18756933962; email: 841936089@qq.com (M. Sun), Tel. +86-0551-62901450; email: xzhang@hfut.edu.cn (X. Zhang)*
[b]*School of Chemistry and Environmental Engineering, Yancheng Teachers University, Yancheng 224002, China, Tel. +86-15895198337; email: wuyonghui1000@126.com*

Received 29 April 2019; Accepted 13 September 2019

ABSTRACT

Graphene oxide (GO) - P84 co-polyimide composite membranes are prepared through vacuum filtrating of GO on the porous P84 anion exchange supports, followed by crosslinking with ethylenediamine. The cross-linking provides the stacked GO nanosheets with the necessary stability to overcome their inherent dispersibility in water environment. The membranes are first applied to the diffusion dialysis process to separate H_2SO_4 from the H_2SO_4/$FeSO_4$ mixed feed. The dialysis coefficient (U_{H2SO4}) for the H_2SO_4 is 0.0083–0.011 m/h, and the H^+/Fe^{2+} separation factor (S_{H2SO4}) is 8.0–10.8, both of which are higher than the values of the commercial membrane S203 (~0.0018 m/h, ~8). The S_{H2SO4} value is also higher than that of the P84 support membrane (~5.4), showing that the selectivity of the GO-P84 composite membranes is obviously improved. Besides, the membranes are used to separate HCl from the organic acidic liquor containing HCl/glyphosate, which is produced largely from the preparation process of glyphosate pesticide. Results show that the dialysis coefficient of the HCl (U_{HCl}) is ranging from 0.0065 to 0.0081 m/h, and the HCl/glyphosate separation factor ($S_{HCl/Gly}$) is 8.5–11.4. In contrast, the U_{HCl} and $S_{HCl/Gly}$ values of the P84 porous support membrane are 0.0097 m/h and 4.8, respectively. What's more, the composite membranes show less water osmosis. The results further indicate that the GO-P84 composite membranes have good separation ability for the acidic solutions.

Keywords: Graphene oxide; Porous; Ion exchange membrane; Diffusion dialysis; Acid recovery

---

1. Introduction

At present, a large amount of waste acidic solution is generated in the industrial processes [1,2]. For instance, as an important industrial chemical, sulfuric acid (H_2SO_4) is widely produced and utilized in the metallurgical and chemical processes, resulting in the generation of waste solutions containing free H_2SO_4 and metallic ions. Taking the production process of titanium dioxide with the H_2SO_4 method as an example, for producing every ton of titanium dioxide, it will produce 200–400 tons of acid waste liquid, which contains free H_2SO_4 (10%–20%), $FeSO_4$ (15%–20%) and other metal ions [3]. Another example of the generated organic acidic liquor is during the production process of glyphosate, which is used widely for weeding the agricultural crops because of its low toxicity and high efficiency. The total production quantity of glyphosate in China has grown rapidly, from 318,200 tons in 2010 to 504,800 tons in 2017 [4]. More than 70% of China's total glyphosate is produced by glycine-dimethyl phosphite (DMP) process [5].

---

* Corresponding authors.

The DMP process produces an organic acidic liquor containing HCl (2.5–3.0 mol/L), glyphosate (1.1–1.5 mol/L), other organic ingredients (34–35 wt%) and water (38–40 wt%) [6]. The glyphosate is highly dissolvable in the organic acidic liquor but can be precipitated at low acid concentration due to its isoelectric point at pH 1.5. Hence, the organic acidic liquor is traditionally neutralized by NaOH to precipitate and recover the glyphosate product [5]. The neutralization not only consumes a great deal of chemical reagents but also produces much wastewater and causes secondary pollution. Therefore, new techniques are needed to treat the organic acidic liquor. Diffusion dialysis (DD), as a typical example of ion exchange membrane separation technology, has been widely used for the recovery of inorganic or organic acids from waste liquid due to the unique advantages such as environmental friendliness and low energy consumption [7]. However, traditional commercial membranes face severe technical limitations for DD application. The acid permeability is low because of the dense membrane structure. What's more, the polymer materials are relatively hydrophobic such as poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), polyphenylene ether (PPE), polystyrene (PS) or polysulfone (PSf) [8], which is also disadvantageous for the acid permeation. For example, the commercial membrane DF-120 based on PPO shows a dialysis coefficient of 0.009 m/h for HCl at 25°C [9], while the commercial membrane S203 based on PSf exhibits a dialysis coefficient of ~0.0018 m/h for H_2SO_4 [3].

Novel ion exchange membranes have been prepared by different trials for improving the acid permeability. One of the trials is to adopt the phase inversion process to produce membranes with porous structure. For instance, porous anion exchange membranes (AEMs) based on PPO were prepared and tried for the $HCl/FeCl_2$ separation [9]. The porous structure and high ion exchange capacities of the AEMs lead to the high acid permeability. Unfortunately, the membranes also show significant swelling (water uptake: 449%), and hence modification by cross-linking [10] or coating of multisilicon copolymer [11] has to be undertaken for improvement. P84 co-polyimide has a high glass transition temperature of 315°C, shows excellent heat and chemical resistance, possess sufficient mechanical strength, and can react with amine for further modifications [12]. Accordingly, porous P84 AEMs have been prepared and then applied for the recovery of H_2SO_4 from $H_2SO_4/FeSO_4$ mixture. It is revealed that the category of non-solvent during the phase separation process influences significantly the membrane morphology and DD performances. Using of water as the non-solvent produces P84 membranes with large finger-like voids, which show low selectivity (U_{H2SO4}: 0.00771 m/h; separation factor: 3.0 at 25°C) [13]. Using of isopropanol (IPA) as the non-solvent, on the other hand, results into membranes with sponge-like porous structure, which show higher selectivity (U_{H2SO4}: 0.0068 m/h and S_{H2SO4}: 51.3 at 25°C). Nevertheless, the preparation of membranes in IPA coagulation bath is difficult for industrial scale up. Accordingly, it is feasible to modify the P84 porous membranes, so that water as a clean non-solvent can be used, while selectivity can still be achieved.

Graphene oxide (GO) has been demonstrated to be one type of promising nanomaterial and can be reassembled into large-area membranes with interlocked structure and controlled thickness through multiple ways [14–16]. Sheets of GO possess numerous oxygen-containing functional groups: hydroxyl and carboxyl groups are located around the edges, whereas carbonyl and epoxide groups are in the center [17]. These groups can be used to induce chemical reactions and provide additional functional groups, thereby increasing the flexibility and diversity of GO applications. Meanwhile, the existence of these various types of hydrophilic groups allows GO to be easily exfoliated when it is in the wet state. Chemical crosslinking of GO sheets using divalent metal ions, amino acid or dopamine produces stable and mechanically improved membranes [18–21]. The application of GO membranes in various areas, including gas separation, seawater desalination and recovery of organic solvents has been reported [22,23]. What is more, GO free-standing membranes have been tried for separation of $HCl/FeCl_3$ mixture [24]. High selectivity was achieved since the mutual coordination between GO and Fe^{3+} ions hinders the diffusion of $FeCl_3$. However, the free-standing GO membranes are brittle and cannot be easily enlarged.

Therefore, porous P84 AEMs from phase inversion in water are used as the supports in this work; then GO-P84 composite membranes are prepared via vacuum filtration. Compared with the unsupported GO membrane, the GO-P84 composite membranes can have higher toughness and strength, easiness for scale-up production and application. Furthermore, for avoiding the exfoliation of GO in wet state, ethylenediamine (EDA) is chosen for crosslinking the GO nanosheets. The obtained GO-P84 composite membranes are characterized by various ways and then applied to DD process for recovering acid from $H_2SO_4/FeSO_4$ or HCl/glyphosate mixture. The separation performances are discussed, which can provide meaningful guidance for the practical application of porous membranes.

2. Experimental section

2.1. Materials

P84 co-polyimide with a molecular weight (M_w) of 153 kDa was obtained from HP polymer GmbH (Austria). Natural graphite powder, sodium nitrate ($NaNO_3$), sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30%), hydrochloric acid (HCl), ferrous sulfate ($FeSO_4$), ethylenediamine (EDA), isopropanol (IPA), methanol and 1-methyl-2-pyrrolidone (NMP) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All the chemicals were of analytical grade and used as received. Deionized water was used throughout the experiments.

Glyphosate was prepared using the (DMP) process, which included depolymerization, condensation, esterification and hydrolysis [5]. The DMP process generated an organic acidic liquor containing 2.5–3.0 mol/L HCl, 180–250 g/L glyphosate, 34–35 wt% organics and 38–40 wt% H_2O [6].

2.2. Preparation of graphene oxide (GO)

The modified Hummers' method was employed for the preparation of GO powder [25]. H_2SO_4 (23 mL) was added to a mixture of graphite (1.0 g) and $NaNO_3$ (0.5 g), and maintained below 5°C using ice bath. Subsequently, $KMnO_4$ (3.0 g) was added slowly under stirring and ice bath. The mixture was then warmed to 35°C and stirred for 2 h, and added with water (46 mL) slowly. The addition of water released a large amount of heat to maintain the solution at 98°C for 0.5 h. Then the mixture was cooled to about 50°C using a water bath, followed by addition of water (140 mL at 50°C–60°C) and 30% H_2O_2 (3–6 mL). The resulting mixture became bright yellow. It was cooled to room temperature and washed with 5 wt% HCl solution for several times to remove SO_4^{2-} ions, and then was washed with water until the pH was close to 7. Finally, the obtained GO was dried under vacuum at 50°C for about 48 h.

2.3. Preparation of the GO-P84 composite membranes

The GO-P84 composite membranes consisted of porous P84 AEM (signified as M0) as the supports and modified GO component as the top layers.

M0 was prepared through procedures similar to our previous work [26]. First, P84 co-polyimide was dissolved in NMP to form 23 wt% solution. The solution was cast with a casing knife (slit of 250 μm) and then underwent the phase inversion process in water at around 20°C for 4 h. Subsequently, the formed non-charged P84 base membrane was subject to amination reaction in a 5/5/90 (v/v/v) ethylenediamine/1, 4-butanediamine/methanol mixture for 0.5 h. Finally, it was quaternized by immersion in a 30% (wt%) bromine/methanol solution for 12 h at 56°C. The obtained M0 membrane was soaked in 0.5 mol/L HCl solution for 12 h, fully washed with water, and then stored in 0.5 mol/L NaCl solution.

The GO was modified by dispersing in water under ultrasonication for 0.5 h to form a 0.02 mg/mL suspension, followed by addition of EDA and ultrasonicating for 0.5 h. The concentration of EDA in the mixed solution was 0.1 mol/L. Subsequently, the mixed solution containing 1, 2, 3, 4, 5 or 6 mg GO was filtrated onto M0 with area of 12.44 cm^2 using vacuum filtration setup. Then it was fixed on a glass plate, inverted downward on a beaker and heated using water vapour for 4 h at 80°C. The GO-P84 composite membranes thus obtained were named M1, M2, M3, M4, M5 and M6 with increasing GO content. The membrane preparation process is shown in Fig. 1. Besides, M2-N was prepared by coating of 2 mg GO powder onto M0, but with no EDA crosslinking. M2-N, together with M0 and the non-charged P84 base membrane were used as comparisons with the composite membranes.

2.4. Membrane characterizations

2.4.1. Fourier transform infrared spectra, scanning electron microscopy and X-ray diffraction analysis

Fourier transform infrared (FTIR) spectroscopy was recorded using FTIR spectrometer (Nicolet 67, Thermo Fisher Scientific, USA) with a resolution of 0.09 cm^{-1} and a spectral range of 4,000–400 cm^{-1}. The membrane samples, including non-charged base P84 membrane, M0 and the GO-P84 composite membranes were taken and dried at 50°C under vacuum for 4 h before FTIR investigations. Since it is the GO layer that mainly determines the performances of the composite membranes, the side of the GO layer was exposed to the interferometer of the FTIR spectrometer during the test. As a comparison, GO powder without coating onto M0 support was also taken for the FTIR observation.

Membrane morphologies were observed through field emission scanning electron microscopy (FESEM; SU8020 Hitachi, Japan). The membranes were first cryogenically fractured in liquid nitrogen to obtain fresh cross-sections. Then the cross-sections were coated with gold and observed through FESEM.

The GO layer of the composite membrane was further studied by X-ray diffraction (XRD; X'Pert PRO MPD, Panalytical Co., Ltd., Netherlands). Before the measurement, the GO layer in a GO-P84 composite membrane (M4) was taken as completely as possible from M0 support, then dried at 50°C. As a comparison, the GO powder without coating onto M0 support was also measured.

2.4.2. Water uptake

Water uptake (W_R) was measured to investigate the membrane hydrophilicity. The membrane sample was dried in an oven to a constant weight M_1, and then immersed in water for 2 d. The water on the membrane surface was wiped out by the filter paper and the membrane was weighed as M_2. The process of wiping and weighing was generally finished within 5 min. The value of W_R was calculated according to the following equation [13]:

$$W_R = \frac{M_2 - M_1}{M_1} \times 100\% \tag{1}$$

2.4.3. Ion exchange capacity

Ion exchange capacities (IEC) were determined with the Mohr method [27]. Dry membrane samples were accurately weighed and transformed into the Cl$^-$ form in 1.0 mol/L NaCl solution for 2 d at room temperature. Subsequently, they were washed thoroughly with water in order to remove the presence of excess NaCl and then immersed in 0.5 mol/L Na_2SO_4 for 48 h. The Cl$^-$ ions released from the membranes were titrated with aqueous $AgNO_3$ solution (0.1 mol/L). The IEC values were calculated from the released Cl$^-$ ions and expressed as mmol/g of dry membrane (in Cl$^-$ form).

$$\text{IEC} = \frac{V_{\text{AgNO}_3} \times C_{\text{AgNO}_3}}{w_{\text{dry}}} \tag{2}$$

where W_{dry}, V_{AgNO3} and C_{AgNO3} represent the dry weight of the membrane, the volume of $AgNO_3$ consumed during titration and the concentration of the $AgNO_3$ solution, respectively.

2.4.4. Diffusion dialysis

DD operation was carried out using a two-compartment cell separated by the membrane [9]. The two compartments were equal and the volume of each compartment was 100 mL. The dialysate compartment of the cell was filled with organic acidic liquor containing HCl/glyphosate or the

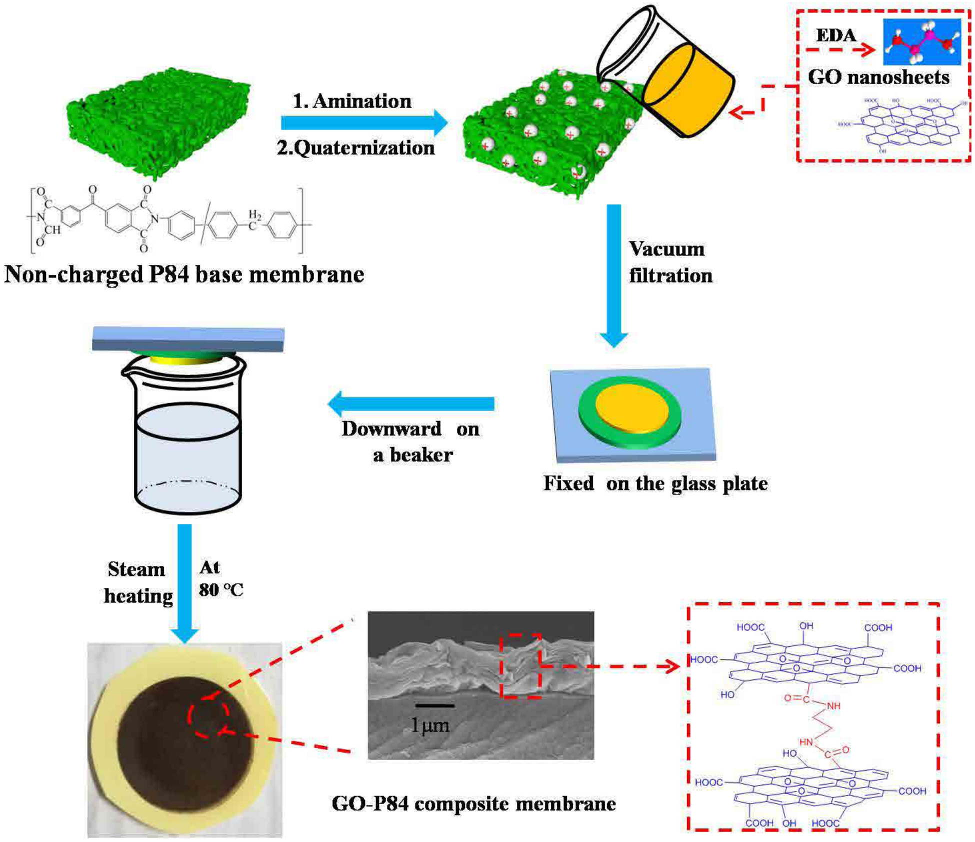

Fig. 1. Preparation procedures for the GO-P84 composite membranes.

mixture solution of H_2SO_4 (0.5 mol/L) + $FeSO_4$ (0.25 mol/L), while the diffusate compartment was filled with water [3]. The membranes were conditioned for 2 h in the feed solution prior to the test. Diffusion was allowed for 1, 3 or 5 h and then the solutions were removed from both sides of the cell. The concentration of H_2SO_4 or HCl was determined by titration with a standard Na_2CO_3 solution, while Fe^{2+} or glyphosate concentration was determined by UV spectrophotometer at 512 nm [28] or 242 nm [29] (UV-2401PC, Shimadzu Co., Ltd., Japan), respectively. All experiments were performed at room temperature.

The separation factor (S) with respect to one species over another is given as the ratio of dialysis coefficients (U) of the two species present in the solution. U can be calculated by the following formula [9]:

$$U = \frac{M}{At\Delta C} \tag{3}$$

where M is the amount of component transported in moles, A is the effective area in square meters, t is the time in h, and ΔC is the logarithm average concentration between the two chambers in mole/m^3 and defined as below [9]:

$$\Delta C = \frac{C_f^0 - \left(C_f - C_d\right)}{\ln\left(\dfrac{C_f^0}{C_f - C_d}\right)} \tag{4}$$

where C_f^0 and C_f are the dialysate concentrations at time 0 and t, respectively, and C_d is the diffusate concentration at time t.

The water osmosis value (J_{H2O}) is calculated by the following formula [23]:

$$J_{H_2O} = \frac{\overline{V_{H_2O}}}{18At} \tag{5}$$

where A is the effective membrane area, t is the running time, $\overline{V_{H_2O}}$ is the volume of water passing through the membrane:

$$\overline{V_{H_2O}} = \frac{(V_f^t - V_f^0) + (V_d^0 - V_d^t)}{2},\ V_f^0 = V_d^0 \tag{6}$$

where V_f^0 and V_f^t are the volume of dialysate compartment at time 0 and t; V_d^0 and V_d^t are the volume of diffusate compartment at time 0 and t.

3. Results and discussion

3.1. Membrane composition by FTIR and XRD

The GO-P84 composite membranes are composed of the GO surface layers and the M0 support layers. The FTIR spectrum of M0 is shown in Fig. 2a, with that of non-charged P84 base membrane as a comparison. M0 was obtained by amination and quaternization of the base

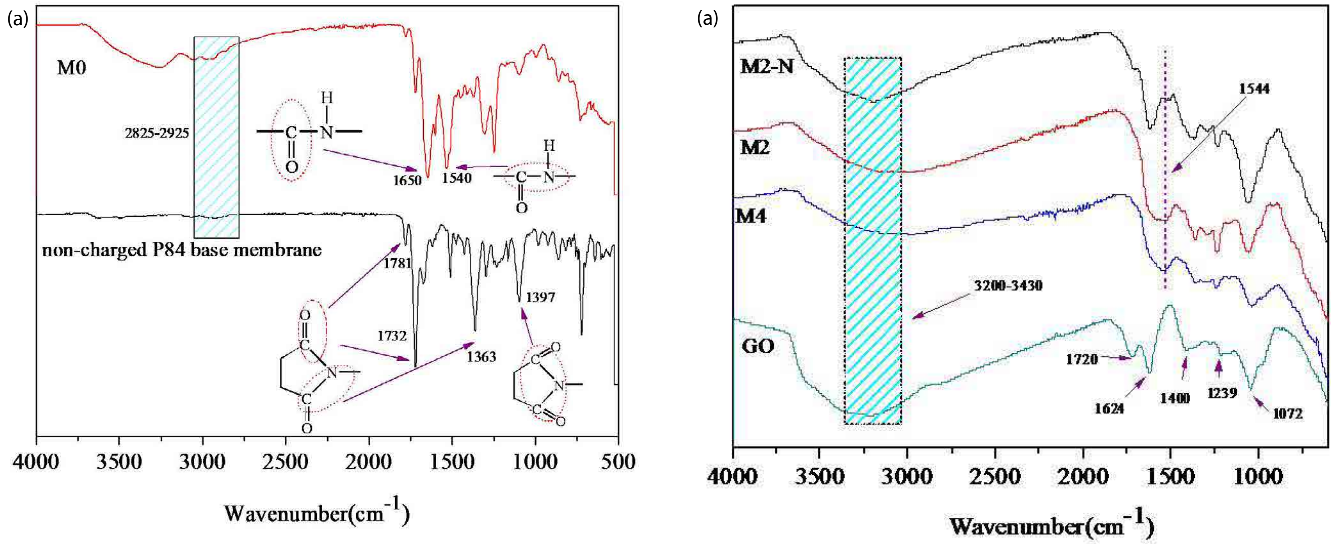

Fig. 2. FTIR spectra of the different membranes and materials, including (a) M0 and non-charged P84 base membrane; and (b) GO-P84 composite membranes (M2, M4, M2-N) and GO powder material.

membrane. The amide groups-related absorption peaks of M0 at 1,097; 1,363; 1,732 and 1,781 cm^{-1} become significantly weakened as compared with the non-charged P84 base membrane, while the characteristic peaks attributed to –C=O stretching and –C–N– stretching of the amide group appear at 1,650 and 1,540 cm^{-1} [12], respectively. Moreover, –C–H stretching absorption in the range of 2,825–2,925 cm^{-1} appears, which is associated with the $–CH_2–CH_3$ groups in $–N^+(CH_2CH_3)_3Br^-$ [30].

The FTIR spectra of the GO layers in composite membranes M2, M4 and M2-N are shown in Fig. 2b, with the GO powder as comparison. In the spectrum of GO powder, the absorption peaks at 3,200–3,430; 1,720; 1,624; 1,400; 1,239 and 1,072 cm^{-1} are due to the stretching of hydroxyl (O–H), carboxyl (C=O), aromatic (C=C), carboxy (C(=O)–OH), epoxy (C–O) and alkoxy (C–O), respectively [20,23]. Therefore, different functional groups are present, which can lead to the hydrophilic nature of GO. Compared with the spectrum of GO powder, the peak of the hydroxyl bond at 3,200–3,430 cm^{-1} is significantly weakened for the GO layer in the composite membranes M2 and M4, while the –C=O stretching at 1,720 cm^{-1} disappears, and a new peak at 1,544 cm^{-1} from –CO–NH– indicates that EDA has reacted with the hydroxyl group on the surface of the GO layer [19]. For further confirmation, M2-N which was prepared without EDA does not have the absorption peak at 1,544 cm^{-1}.

Comparison of the different spectra in Fig. 2b also shows that M2-N has slightly stronger 3,200–3,430 cm^{-1} absorption band than M2 and M4, indicating the presence of higher amount of –OH groups since M2-N has not undergone EDA crosslinking. Nevertheless, M4, which has the highest dosage of GO, shows no stronger bands of –OH and epoxy functional groups than M2 in the regions of 3,200–3,430 cm^{-1} and 1,239 cm^{-1}. This may seem abnormal at first glance, but can be reasonably explained as following: The GO layer of M4 has higher thickness (as confirmed later by FESEM observation), but the same composition as compared with that of M2. Besides, different amount of water may be absorbed into the membrane samples during the preservation period, which also influences the absorption area of 3,200–3,430 cm^{-1}.

The XRD patterns of the GO powder and the GO layer of the composite membrane (M4) are given in Fig. 3.The diffraction peak of the GO powder is located at $2\theta = 10.29°$, corresponding to the interlayer spacing of 8.58 Å [31]. When EDA is used as the crosslinking agent, the diffraction peak shifts to a lower position at $2\theta = 8.00°$, and the interlayer spacing rises to 11.05° due to the intercalation effect. Considering the thickness of the single-layer graphene oxide of 3.40 Å [32], the interlayer spacing of adjacent GO sheets can be obtained as 5.18 Å (8.58–3.40) and 7.65 Å (11.05–3.40) for the GO powder and the GO layer of the composite membrane, respectively. This result confirms that the surface of GO has been successfully modified by EDA with an increase in the interlayer distance between GO sheets.

3.2. Ion exchange capacity (IEC), water uptake (W_R) and morphologies

The IEC and W_R values of M0–M6 are shown in Fig. 4. As the GO content increases, the IEC values decrease from 0.90 to 0.44 mmol/g. GO contains plenty of –OH, –COOH groups, but no anion exchange groups. As the amount of GO increases, the total weight of the membrane increases, and hence the content of $–N^+(CH_2CH_3)_3Br^-$ groups from P84 support decreases, leading to gradually lower IEC [33,34].

The W_R value of M1 is increased by around 20% as compared with M0 membrane. The reason is that GO has the functional groups with high hydrophilicity, such as hydroxyl and epoxy groups. The W_R values of M1–M6 are similar, ranging from 180% to 191%. Although there are a number of hydrophilic groups on GO, the surface layer of the composite membrane may become denser as the amount of GO increases, which restricts the adsorption of water and leads to relatively stable W_R values.

Fig. 5 shows the FESEM images of the GO-P84 composite membranes. All the composite membranes contain porous

P84 AEM (M0) as the support layers, which is around 150 μm thick and has an asymmetric structure including a thin top layer, a porous middle layer with finger-like voids and a thin bottom layer. The liquid–liquid demixing between water and NMP occurs fast due to the high polarity of water, and accordingly large finger-like pores are formed in M0 [26]. The GO layer in M2-N possesses a wrinkled and well-layered lamellar structure, and there is obvious gap between the GO layer and the M0 support. As comparison, M2 and M4 become more smooth and compact, confirming the effectiveness of crosslinking with EDA [19]. The GO thickness on M2 and M4 is 2 and 4 μm, respectively, indicating that the thickness of the GO layer of the composite membranes can be easily tuned by adjusting GO content.

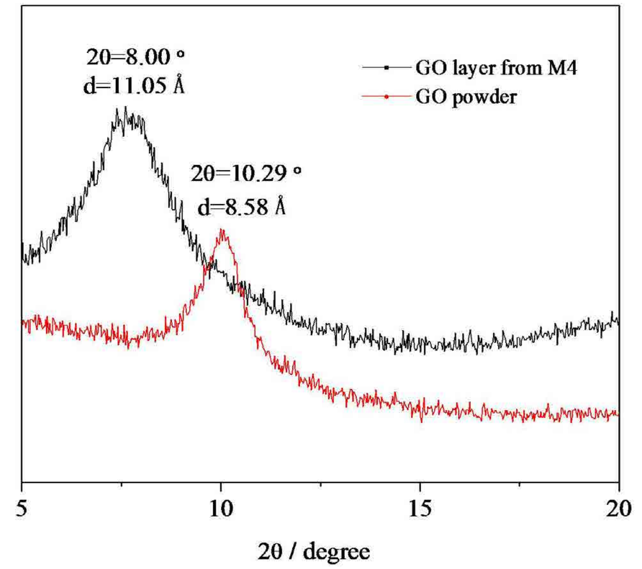

Fig. 3. XRD patterns of the GO powder and the GO layer from the composite membrane M4.

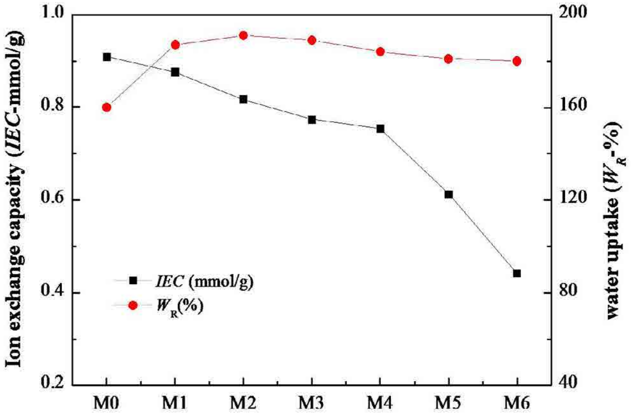

Fig. 4. Ion exchange capacity (IEC) and water uptake (W_R) of the composite membranes.

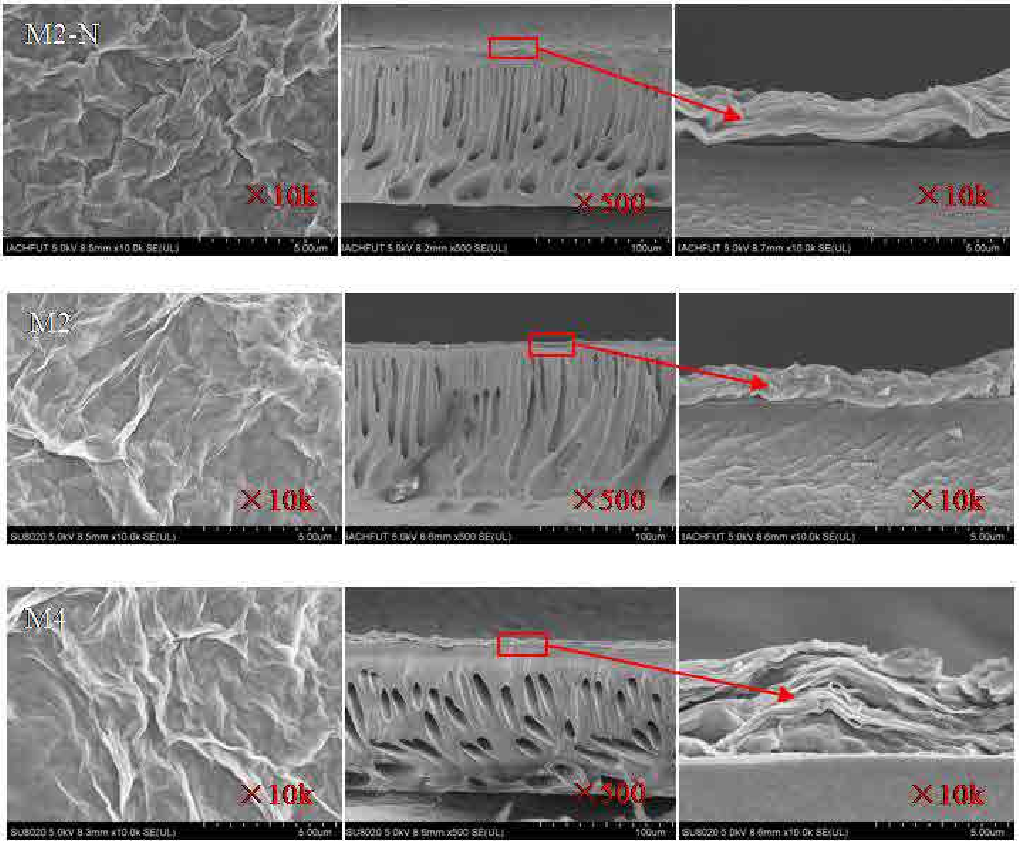

Fig. 5. FESEM graphs of the membranes' top surfaces (left) and cross-sections (middle and right).

3.3. Diffusion dialysis performances for $H_2SO_4/FeSO_4$ mixture

The DD performances of M0–M6 after running 1 h are illustrated in Fig. 6. Membrane M0 without GO layer shows high dialysis coefficient of H_2SO_4 (U_{H2SO4}) value of 0.013 m/h, but quite low S_{H2SO4} value of 5.4. M0 has a large finger-shaped pore channel structure (Fig. 5), and hence different ions can easily diffuse through the membrane to reach the diffusate compartment, leading to a high permeability but low selectivity. Previous U_{H2O4} and S_{H2SO4} values are only ~0.0018 m/h and ~8 correspondingly by commercial membrane S203 [3], and 0.00223 m/h and 47.92 by commercial membrane DF-120 [35]. The results indicate that the porous structure facilitates the transport of acids significantly, but is not favorable for hindering the transport of salts.

The GO-P84 composite membranes can have significantly improved DD performances. For instance, M1 with coating of 1.0 mg GO shows U_{H2SO4} and S_{H2SO4} value of 0.011 m/h and 8.0, which are higher than the commercial membrane S203. The U_{H2SO4} value is also higher than that of the commercial membrane DF-120 (0.00223 m/h). The S_{H2SO4} value continuously increases, while the U_{H2SO4} value generally decreases with the increase of GO dosage. The GO has layered structure and the spacing between the layers provides the channel for the ion transport. XRD results have confirmed that the layer spacing of GO layers crosslinked by EDA is 7.65 Å. Previous researches also reveal that the GO membranes with layer spacing of 9–10 Å can act as molecular sieves to block the solutes with hydrated radii larger than 4.5 Å in an aqueous environment [36], since ion permeation through the GO laminate is limited by a nanocapillary network containing two layers of water. Meanwhile, the GO surface is attached to various oxygen-containing functional groups including –COOH and –OH, as well as –NH– from EDA crosslinking. These groups, though have no strong ion exchange ability, can play important role for the transport of acid or alkali through hydrogen bonding [37,38].

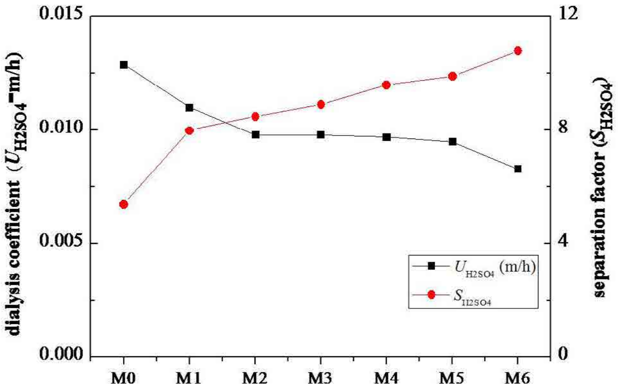

Fig. 6. Dialysis coefficients (U_{H2SO4}) and separation factors (S_{H2SO4}) for the $H_2SO_4/FeSO_4$ mixture after running 1 h.

During the DD process of $H_2SO_4/FeSO_4$ mixture, the H^+ ions with hydrated radium of 2.82 Å [39] receive less hindrance. Instead they can rapidly propagate along the hydrogen bond network formed by the functional groups in the inter layer spacing of GO [40]. Therefore, the transport of H^+ ions is selectively facilitated and the U_{H+} can remain high for M2–M5. As for Fe^{2+} ions, their hydrated radii are 4.28 Å, less than the limiting size for blocking in the interlayer spacing of GO. Nevertheless, there are chemical interactions between the metal ions and the surface functional groups of GO [41], leading to adsorption rather than permeability of the heavy metal ions. Therefore, Fe^{2+} ions transport is hindered, and high selectivity can be achieved for M2–M5 (S = 8.5–9.9), while relatively high acid permeability (0.0095–0.0098 m/h) can still be maintained. However, excessive GO deposition induces a much thicker layer and higher mass transfer resistance, decreasing the U_{H2SO4} of M6. The transport process of the different ions through the GO layer can be illustrated in Fig. 7.

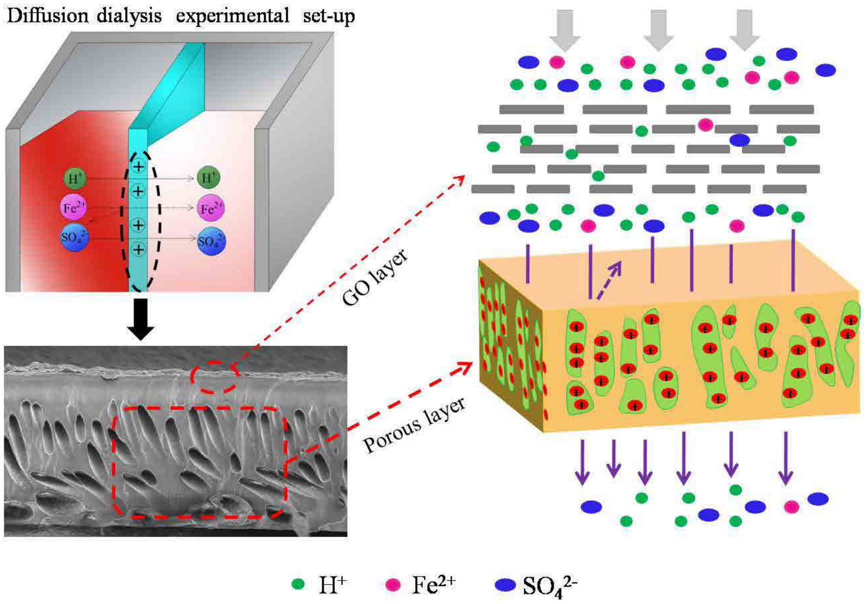

Fig. 7. Plausible physical model of ions transferred through GO-P84 composite membranes.

For investigating the DD running stability, M4 is also selected for a 3-h testing and the results are shown in Fig. 8. It can be seen that the U_{H2SO4} values vary in the range of 0.0095–0.01 m/h, and the S_{H2SO4} values are in the range of 8.7–9.7. The above data indicate that the composite membranes have good stability in running longer-time DD experiment. Previous studies also show that DD performances are generally stable with the time [42].

3.4. DD of organic acidic liquor containing HCl/glyphosate

3.4.1. Acid permeability and selectivity

The membranes are used to separate organic acidic liquor containing HCl and glyphosate. The HCl component can transport through the membrane from the organic acidic liquor side to water side due to its high activity and low resistance. Other components such as glyphosate and organic solvents are less likely to transport due to their weak acidity, high molecular size or non-electrolyte properties. The obtained values of dialysis coefficients of HCl, U_{HCl} and $S_{HCl/Gly,}$ after running for 1 h are shown in Fig. 9. The U_{HCl} values are in the range of 0.0065–0.0081 m/h for GO-P84 composite membranes, and 0.0097 m/h for membrane M0. The values are higher than that of commercial AEMs (the DF-120 membrane of 0.0040 m/h; and the 9010 membrane of 0.0062 m/h [43]), indicating the excellent acid permeability of the composite membranes, which is essential to separate the organic acidic liquor. The $S_{HCl/Gly}$ values are in the range of 8.47–11.31 for the composite membranes, while the value of membrane M0 is only 4.85. The $S_{HCl/Gly}$ values seem to be relatively low when compared with the commercial membrane (*S* value for the organic acidic liquor is not provided in the reference, but the value for aqueous HCl/$FeCl_2$ mixture is 18.5 for DF-120 membrane). The lower selectivity indicates that some glyphosate can also be transported along with the HCl component through the porous structure. However, as the recovered acid can be reused to produce the organic acidic liquor [6], some leakage of glyphosate should cause no serious harmful influence.

The changing trend of the U_{HCl} and $S_{HCl/Gly}$ values is similar as that for H_2SO_4/$FeSO_4$ system: U_{HCl} values decrease as the dosage of GO increases from M0 to M6, while the $S_{HCl/Gly}$ values increase. As already described in the FESEM section, the thickness of GO gradually increases from M1 to M6, which can induce higher hindrance for ions transport. On the other hand, the oxygen-containing functional groups along the spacing of GO layers can provide transport channels for H^+ through hydrogen bonding. Accordingly, the U_{HCl} values remain relatively stable, while the $S_{HCl/Gly}$ remains increasing for M2–M5. Excessive GO dosage for M6 causes a sharp increase of $S_{HCl/Gly}$ value, but obvious decrease of U_{HCl}. Overall, proper dosage of GO layer (2–5 mg) can yield composite membranes with excellent acid permeability and selectivity, which is advantageous for DD application.

Membranes M2 and M4, due to their balanced permeability and selectivity, are selected to run 5 h. The longer running time can further reduce the HCl concentration in the dialysis compartment, and thus some glyphosate may be precipitated and recovered. Membrane M0 is also used as comparison, and the results are exhibited in Fig. 10. The U_{HCl} decreases slightly, while $S_{HCl/Gly}$ increases slightly as the time increases. Theoretically, the values should be stable with respect to the time, and previous research reveals that the values are relatively stable as the time prolongs from 1 to 3 h [42]. The unstable values in Fig. 10 may be caused by other factor, such as the adsorption and permeation of the other organic components. The organic components in the organic acidic liquor may be adsorbed on or transported through the membranes. The adsorption would induce membrane fouling, and the transportation would introduce organic components in the diffusate solution, both of which increase the transport resistance, leading to lower U_{HCl} but higher $S_{HCl/Gly}$ values.

3.4.2. Water osmosis during DD process and glyphosate recovery after DD process

Water osmosis is a natural phenomenon in which water molecules enter a high concentration from a low concentration solution through the membranes under the osmotic pressure [6]. The J_{H2O} value of M0 is 57.7 mmol/m^2 s after running 1 h, and the values of M1–M6 are 37.6–40.1 mmol/m^2 s as shown in Fig. 11. The water osmosis increases to a greater

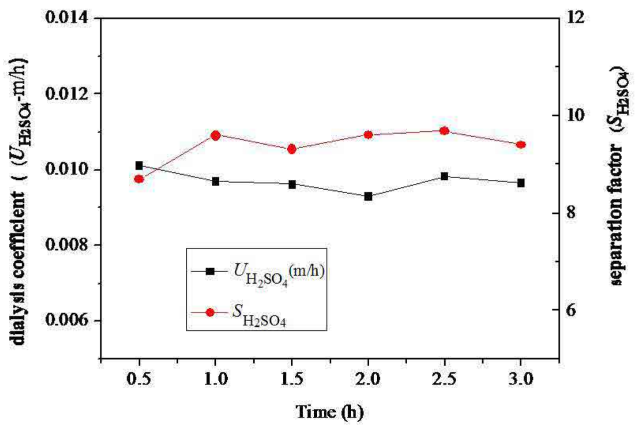

Fig. 8. DD performance of membrane M4 with respect to the time.

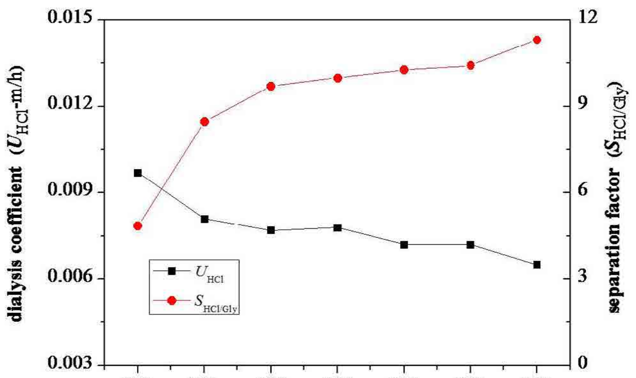

Fig. 9. Dialysis coefficients of HCl (U_{HCl}) and separation factors ($S_{HCl/Gly}$) for the organic acidic liquor containing HCl/glyphosate after running 1 h.

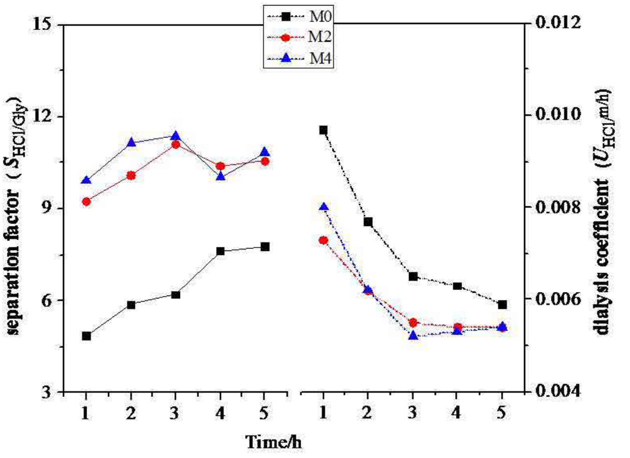

Fig. 10. Dialysis coefficients (U_{HCl}) and separation factors ($S_{HCl/Gly}$) of the M0/M2/M4 with the HCl/glyphosate system.

extent as the time prolongs, which is disadvantageous for the recovery of acid and glyphosate [44]. Using of M0 yields the highest water osmosis value of 72.7 mmol/m^2 s after 5 h running, because of the large amount of quaternary ammonium groups and finger-shaped pore structure. The GO-P84 composite membranes have a denser GO surface layer, so the J_{H2O} value is decreased to 62.7 mmol/m^2 s and 52.7 mmol/m^2 s for M2 and M4 as shown in Fig. 12. Nevertheless, compared with the data of commercial dense membrane 9010 (13.9 mmol/m^2 s after 36 h running [6]), the composite membranes may still have more obvious water osmosis. The layer spacing of GO provides a channel for ion and water migration, and hence water molecules are relatively easy to pass as compared with dense membrane.

The glyphosate maybe precipitated as the HCl concentration in the dialysate solution decreases, for the glyphosate can be crystallized to maximum extent at its isoelectric point (pH = 1.5) [43]. The H$^+$ concentration of the dialysate compartment decreases from 3.5 mol/L to 2.5–2.8 mol/L after running for 5 h. Membrane M0 recovers about 5.4 g of glyphosate, and membranes M2 and M4 recover 6.2–6.9 g of glyphosate through standing of the dialysate compartment for 5 d at 7°C. The recovery ratio of glyphosate is ~29.5% for M0, and 33.9%–37.7% for M2 and M4. Comparison of the above data indicates that membrane M0 can recover less glyphosate than the composite membranes, even though it shows the highest acid permeability. This is because the porous membrane structure of M0 leads to more obvious leakage of glyphosate and higher water osmosis, both of which can result in lower concentration of glyphosate in the dialysate solution.

The glyphosate recovered after DD process has a purity of 95.7% after repeated washing and drying. Therefore, relatively high purity of glyphosate product can be obtained by treating of the HCl/glyphosate acidification solution through DD process.

4. Conclusion

Graphene oxide (GO)-P84 polyimide composite membranes are prepared by filtering of different amount of GO and ethylenediamine (EDA) mixed solution to the surface of P84 porous AEMs. The GO nanosheets are crosslinked by EDA, which leads to stable membrane structure. The cross-sections of the P84 supports have finger-shaped pores and GO lays have a well-layered lamellar structure. The GO dosage influences the thickness and surface charge of the composite membranes, and thus the membrane performances in DD.

The composite membranes are used in DD to separate the $H_2SO_4/FeSO_4$ system. The H$^+$/Fe^{2+} separation factors (S_{H2SO4}) are 8.0–10.8, higher than the value of P84 porous support (5.4). The dosage of GO can also influence the DD performances significantly. Composite membranes with proper dosages of GO can have both excellent selectivity and acid permeability, since H$^+$ ions can rapidly propagate along the hydrogen bond network formed by the functional groups in the inter layer spacing of GO.

The composite membranes are then used in DD for separation of organic acidic liquor (HCl/glyphosate). The dialysis coefficient (U_{HCl}) for HCl is 0.0065–0.0081 m/h, and the HCl/glyphosate separation factors ($S_{HCl/Gly}$) are 8.5–11.4 after 1 h of DD running. In contrast, the U_{HCl} and $S_{HCl/Gly}$ values of the P84 porous support are 0.0097 m/h

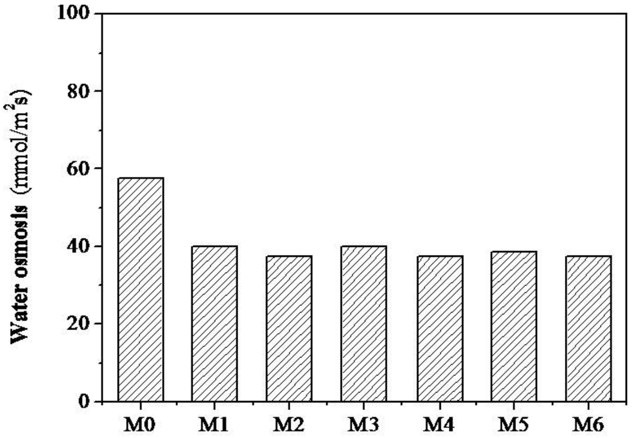

Fig. 11. Water osmosis after running for 1 h.

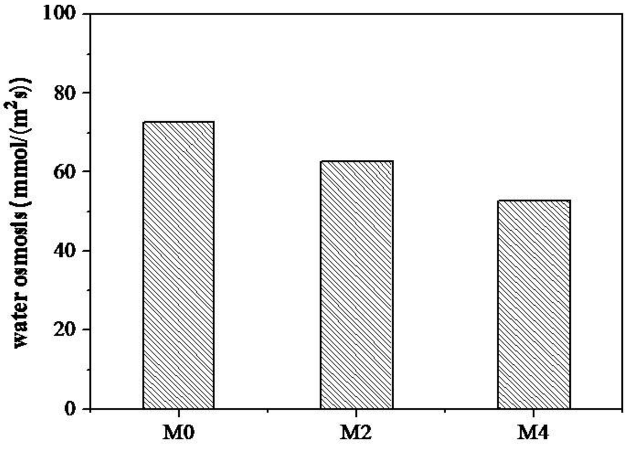

Fig. 12. Water osmosis after running for 5 h.

and 4.8. After running by 5 h, the recovery of glyphosate is in the range of 33.9%–37.7%, which is higher than that of P84 porous support membrane (~29.5%). These results demonstrate that the GO-P84 composite membranes exhibit remarkable potential and can be promising candidates for using in acid recovery.

Acknowledgments

This project was supported by National Science Foundation of China (No 21476056 and 21606063).

References

[1] M.Q. Xue, A. Kendall, Z.M. Xu, J.L.M. Schoenung, Waste management of printed wiring boards: a life cycle assessment of the metals recycling chain from liberation through refining, Environ. Sci. Technol., 49 (2015) 940–947.

[2] J.Y. Lin, W.Y. Ye, J. Huang, B. Ricard, M.C. Baltaru, B. Greydanus, S. Balta, J.N. Shen, M. Vlad, A. Sotto, P. Luis, B. Van der Bruggen, Toward resource recovery from textile wastewater: dye extraction, water and base/acid regeneration using a hybrid NF-BMED process, ACS Sustain. Chem. Eng., 3 (2015) 1993–2001.

[3] T.W. Xu, W.H. Yang, Sulfuric acid recovery from titanium white (pigment) waste liquor using diffusion dialysis with a new series of anion exchange membranes-static runs, J. Membr. Sci., 183 (2001) 193–200.

[4] The Report on Development of Glyphosate Market, Southern pesticide, 2018 (in Chinese).

[5] J.N. Shen, J. Huang, H.M. Ruan, J.D. Wang, B. Van der Bruggen, Techno-economic analysis of resource recovery of glyphosate liquor by membrane technology, Desalination, 342 (2014) 118–125.

[6] P.F. Wang, G.C. Zhang, Y.H. Wu, Diffusion dialysis for separating acidic HCl/glyphosate liquor, Sep. Purif. Technol., 141 (2015) 387–393.

[7] A. Zheleznov, D. WindmOller, S. Korner, K.W. Boddeker, Dialytic transport of carboxylic acids through an anion exchange membrane, J. Membr. Sci., 139 (1998) 137–143.

[8] J.Y. Luo, C.M. Wu, T.W. Xu, Y.H. Wu, Diffusion dialysis-concept, principle and applications, J. Membr. Sci., 366 (2011) 1–16.

[9] L. Ge, A.N. Mondal, X.H. Liu, B. Wu, D.G. Yu, Q.H. Li, J.B. Miao, Q.Q. Ge, T.W. Xu, Advanced charged porous membranes with ultrahigh selectivity and permeability for acid recovery, J. Membr. Sci., 536 (2017) 11–18.

[10] X.C. Lin, E. Shamsaei, B. Kong, J.Z. Liu, Y.X. Hu, T.W. Xu, H.T. Wang, Porous diffusion dialysis membranes for rapid acid recovery, J. Membr. Sci., 502 (2016) 76–83.

[11] F.J. Sun, C.M. Wu, Y.H. Wu, T.W. Xu, Porous BPPO-based membranes modified by multisilicon copolymer for application in diffusion dialysis, J. Membr. Sci., 450 (2014) 103–110.

[12] C.Y. Ba, J. Langer, J. Economy, Chemical modification of P84 copolyimide membranes by polyethylenimine for nanofiltration, J. Membr. Sci., 327 (2009) 49–58.

[13] P. Wang, C.M. Wu, M.J. Sun, X. Zhang, Y.H. Wu, Porous P84 co-polyimide anion exchange membranes for diffusion dialysis application to recover acids, Desal. Wat. Treat., 108 (2018) 40–48.

[14] N. Meng, W. Zhao, E. Shamsaei, G. Wang, X.K. Zeng, X.C. Lin, T.W. Xu, H.T. Wang, X.W. Zhang, A low-pressure GO nanofiltration membrane crosslinked via ethylenediamine, J. Membr. Sci., 548 (2018) 363–371.

[15] C.M. Chen, Q.H. Yang, Y.G. Yang, W. Lv, Y.F. Wen, P.X. Hou, M.Z. Wang, H.-M. Cheng, Self-Assembled Free-Standing Graphite Oxide Membrane, Adv. Mater., 21 (2009) 3007–3011.

[16] Z.Q. Jia, W.X. Shi, Tailoring permeation channels of graphene oxide membranes for precise ion separation, Carbon, 101 (2016) 290–295.

[17] G. Eda, G. Fanchini, M. Chhowalla, Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material, Letters, 3 (2008) 270–274.

[18] M. Hu, B.X. Mi, Enabling graphene oxide nanosheets as water separation membranes, Environ. Sci. Technol., 47 (2013) 3715–3723.

[19] W.S. Hung, C.H. Tsou, M. De Guzman, Q.F. An, Y.L. Liu, Y.M. Zhang, C.C. Hu, K.R. Lee, J.Y. Lai, Cross-Linking with diamine monomers to prepare composite graphene oxide-framework membranes with varying d-spacing, Chem. Mater., 26 (2014) 2983–2990.

[20] J.H. Li, L.F. Li, B.W. Zhang, M. Yu, H.J. Ma, J.Y. Zhang, C. Zhang, J.G. Li, Synthesis of few-layer reduced graphene oxide for lithium-ion battery electrode materials, Ind. Eng. Chem. Res., 53 (2014) 13348–13355.

[21] Y.Q. Zhan, X.Y. Wan, S.J. He, Q.B. Yang, Y. He, Design of durable and efficient poly(arylene ether nitrile)/bioinspired polydopamine coated graphene oxide nanofibrous composite membrane for anionic dyes separation, Chem. Eng. J., 333 (2018) 132–145.

[22] S. Kim, J. Hou, Y.Q. Wang, R.W. Ou, G.P. Simon, J.G. Seong, Y.M. Lee, H.T. Wang, Highly permeable thermally rearranged polymer composite membranes with a graphene oxide scaffold for gas separation, J. Mater. Chem. A, 6 (2018) 7668–7674.

[23] M.Y. Wu, J.Q. Yuan, H. Wu, Y.L. Su, H. Yang, X.D. You, R.N. Zhang, X.Y. He, N.A. Khan, R. Kasher, Z.Y. Jiang, Ultrathin nanofiltration membrane with polydopamine-covalent organic framework interlayer for enhanced permeability and structural stability, J. Membr. Sci., 576 (2019) 131–141.

[24] P.Z. Sun, K.L. Wang, J.Q. Wei, M.L. Zhong, D.H. Wu, H.W. Zhu, Effective recovery of acids from iron-based electrolytes using graphene oxide membrane filters, J. Mater. Chem. A, 2 (2014) 7734–7737.

[25] D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z.S. Zhong, Tour, Improved Synthesis of Graphene Oxide, ACS Nano, 4 (2010) 4806–4814.

[26] C.Y. Zhang, S. Xue, G.S. Wang, C.M. Wu, Y.H. Wu, Production of lactobionic acid by BMED process using porous P84 co-polyimide anion exchange membranes, Sep. Purif. Technol., 173 (2017) 174–182.

[27] Y. Li, T.W. Xu, M. Gong, Fundamental studies of a new series of anion exchange membranes: membranes prepared from bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) and pyridine, J. Membr. Sci., 279 (2006) 200–208.

[28] W. Li, Y.M. Zhang, J. Huang, X.B. Zhu, Y. Wang, Separation and recovery of sulfuric acid from acidic vanadium leaching solution by diffusion dialysis, Sep. Purif. Technol., 96 (2012) 44–49.

[29] Glyphosate Aqueous Solution (GB 20684–2007), National Standard of the Peoples Republic of China, 2017.

[30] D.W. Mangindaan, N.M. Woon, G.M. Shi, T.S. Chung, P84 polyimide membranes modified by a tripodal amine for enhanced pervaporation dehydration of acetone, Chem. Eng. Sci., 122 (2015) 14–23.

[31] K.M. Jeong, Y.H. Li, D.G. Yoo, N.K. Lee, H.G. Lee, S.J. Ando, C.S. Ha, Effects of crosslinking agents on the physical properties of polyimide/amino-functionalized graphene oxide hybrid films, Polym. Int., 67 (2018) 588–597.

[32] R.R. Nair, H.A. Wu, P.N. Jayaram, I.V. Grigorieva, A.K. Geim, Unimpeded permeation of water through helium-leak-tight graphene-based membranes, Science, 335 (2012) 442–444.

[33] Y.H. Wu, M.M. Jiang, J. Cao, T.W. Xu, F.L. Mao, Combination of OH^- ions and –OH groups within QPPO/PVA hybrid membranes for acid recovery, Desal. Wat. Treat., 57 (2016) 21023–21033.

[34] Y.H. Wu, J.Y. Luo, L.L. Zhao, G.C. Zhang, C.M. Wu, T.W. Xu, QPPO/PVA anion exchange hybrid membranes from double crosslinking agents for acid recovery, J. Membr. Sci., 428 (2013) 95–103.

[35] K. Wang, Y.M. Zhang, J. Huang, T. Liu, J.P. Wang, Recovery of sulfuric acid from a stone coal acid leaching solution by diffusion dialysis, Hydrometallurgy, 173 (2017) 9–14.

[36] R.K. Joshi, P. Carbone, F.C. Wang, V.G. Kravets, I.V. Wu, A.K. Geim, R.R. Nair, Precise and ultrafast molecular sieving through graphene oxide membranes, Science, 343 (2014) 752–754.

[37] J.J. Gu, C.M. Wu, Y.H. Wu, J.Y. Luo, T.W. Xu, PVA-based hybrid membranes from cation exchange multisilicon copolymer for alkali recovery, Desalination, 304 (2012) 25–32.

[38] C.M. Wu, J.J. Gu, Y.H. Wu, J.Y. Luo, T.W. Xu, Y.P. Zhang, Carboxylic acid type PVA-based hybrid membranes for alkali recovery using diffusion dialysis, Sep. Purif. Technol., 92 (2012) 21–29.

[39] ER Nightingale Jr, Phenomenological theory of ion salvation. Effective radii of hydrated ions, J. Phys. Chem., 63 (1959) 1381–1387.

[40] M.R. Karim, K. Hatakeyama, T. Matsui, H. Takehira, T. Taniguchi, M. Koinuma, Y. Matsumoto, T. Akutagawa, T. Nakamura, S. Noro, T. Yamada, H. Kitagawa, S. Hayami, Graphene oxide nanosheet with high proton conductivity, J. Am. Chem. Soc., 135 (2013) 8097–8100.

[41] G.Q. Rao, C. Lu, F.S. Su, Sorption of divalent metal ions from aqueous solution by carbon nanotubes: a review, Sep. Purif. Technol., 58 (2007) 224–231.

[42] Y.H. Wu, J.J. Gu, C.M. Wu, T.W. Xu, PVA-based cation exchange hybrid membranes with multifunctional groups prepared from ternary multisilicon copolymer, Sep. Purif. Technol., 104 (2013) 45–54.

[43] F.L. Mao, G.Z. Zhang, J.J. Tong, T.W. Xu, Y.H. Wu, Anion exchange membranes used in diffusion dialysis for acid recovery from erosive and organic solutions, Sep. Purif. Technol., 122 (2014) 376–383.

[44] Y.H. Wu, P.F. Wang, G.C. Zhang, C.M. Wu, Water osmosis in separating acidic HCl/glyphosate liquor by continuous diffusion dialysis, Sep. Purif. Technol., 179 (2017) 86–93.