Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21284

87 (2017) 109–119
August

Membrane cross-linking to restrict water osmosis in continuous diffusion dialysis

Lingfei Zou[a], Pengfei Wang[b], Yonghui Wu[b,*], Gencheng Zhang[b,*]

[a]*College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing, Jiangsu 210009, China, Tel. +86-515-88233188, email: 603411257@qq.com*

[b]*School of Chemistry and Environmental Engineering, Yancheng Teachers University, Yancheng, Jiangsu 224051, China, Tel. +86-515-88233188, email: 937111748@qq.com (P. Wang), Tel. +86-515-88233188, email: wuyonghui1000@126.com (Y. Wu), Tel. +86-515-88233080, email: zgchx406@163.com (G. Zhang)*

Received 21 February 2017; Accepted 3 August 2017

ABSTRACT

Acidic HCl/glyphosate (Gly) liquor is produced largely during the production of Gly herbicide. The HCl component can be recovered by continuous diffusion dialysis (DD), while the Gly is precipitated maximumly at the pH ~1.5. Previous DD process showed that the Gly productivity is only 28.0% due to the serious water osmosis ($2.0–2.9 \times 10^{-4}$ m/h), which reduced the Gly concentration. Hence in this work, the water osmosis is restricted by membrane cross-linking. Polyvinyl alcohol (PVA) is cross-linked with glutaraldehyde (GA) together with tetra-methoxysilane (TMOS) or 3-aminopropyl-triethoxysilane (APTEOS) to prepare non-charged membranes. Continuous DD process shows that the water osmosis is reduced to $0.71–1.44 \times 10^{-4}$ m/h. The optimized flow rate of acidic liquor is 0.34 L/(m^2 h) and the flow ratio between water and acidic liquor is 2:1. The membrane cross-linked with GA can have the recovered HCl concentration ($C_{d\text{-}H}$) of 0.93 mol/L, HCl recovery ratio (R_H) of 63.9% and Gly rejection (η_{Gly}) of 99.5%. The membrane cross-linked with GA and TMOS can have the $C_{d\text{-}H}$ of 1.00 mol/L, R_H of 78.6% and η_{Gly} of 96.8%. Besides, 83.3% Gly productivity can be obtained from the residual solution after concentration. Hence, the water osmosis is reduced and the Gly productivity is elevated by using the cross-linked membranes.

Keywords: Acid recovery; Diffusion dialysis; Glyphosate; PVA; Water osmosis

1. Introduction

Glyphosate (Gly), as a widely used herbicide [1], is mainly produced by the process of glycine-dimethylphospite (DMP) [2]. The DMP process generates a type of acidic liquor containing about 2.4 mol/L (*M*) HCl, 1.0 *M* Gly, 40 wt% water and 34 wt% other organic components such as trimethylamine and methanol. The acidic liquor is traditionally neutralized by 50 wt% NaOH to obtain maximum Gly precipitation due to its isoelectric point at pH 1.5. The neutralization not only wastes useful component of HCl and consumes excessive NaOH, but also produces wastewater containing 13–17 wt% NaCl and other components [3]. The NaCl component needs further treatment such as bipolar membrane electrodialysis (BMED) [4]. Though the BMED can remove most of the NaCl from the neutralized liquor, the cost and energy consumption increase significantly.

The acidic liquor can be separated by batch and continuous diffusion dialysis (DD) process. The batch dialyzer is generally used in lab-scale simulation, which contains a piece of membrane and two compartments. One compartment is used as the dialysate (feed) side and filled with the acidic liquor, while the other compartment is used as the diffusate side and filled with water. The HCl component, due to its high mobility and activity, can transport through the membrane from the dialysate side to diffusate side. Hence, 0.29–0.78 *M* HCl and 53.2% Gly can be recovered, and 62% NaOH is saved after running 24 h [5]. The batch dialyzer proves the feasibility of DD process in separating the acidic liquor. The continuous dialyzer contains dozens pieces of membranes with two inlets and two outlets. The

---

*Corresponding author.

acidic liquor (feed) and water are continuously flowed into the two inlets and then residual solution and recovered solution are obtained from the two outlets correspondingly. The continuous dialyzer can be practically applied in separating aqueous HCl, H_2SO_4 or HNO_3 solution [6–9].

The acidic liquor was also attempted to be separated by the continuous dialyzer in our recent research [10], which was equipped with commercial membrane TWDD-III or self-prepared membrane QPPO/PVA. The flow rate and flow ratio between water and acidic liquor were optimized (0.63 L/(m^2 h), 3:1) to obtain the HCl recovery ratio (R_H) of 80.9% and Gly rejection (η_{Gly}) of 83.2% for the commercial membrane. However, the commercial membrane showed high water osmosis of 2.2–5.9 × 10^{-4} m/h due to the high content (>34 wt%) of organic components in the acidic liquor. The high water osmosis reduced Gly concentration in the residual solution, which contained only 0.43 *M* Gly and thus needed to be highly concentrated to remove 80% solvent and to obtain 60.7% Gly productivity. Though the self-prepared membrane had lower water osmosis of 1.9–2.9 × 10^{-4} m/h, the residual solution contained only 0.65 *M* Gly and still needed to be greatly concentrated to precipitate Gly [10].

The water osmosis means that water molecules transport through the membrane from the diffusate side to dialysate side. The water transport rate should be mainly determined by the membrane thickness and structure [10]. Theoretically, high thickness should be able to reduce the water transport rate, but it also reduces the transport rate of HCl and thus the DD efficiency. The membrane cross-linking has great effects on membrane hydrophilicity and ion transport rate [11], and thus may restrict the water osmosis. Glutaraldehyde (GA) has strong cross-linking ability through the cross-linking among –CHO and –OH groups [12], while alkoxysilane can improve the membrane amorphous region through the formation of silica network [13]. Both GA and alkoxysilane can cross-link with polyvinyl alcohol (PVA) to form network structure. Besides, the -OH groups of PVA may accelerate the transport of HCl [14].

Hence in this work, polyvinyl alcohol (PVA) will be cross-linked with GA together with tetra-methoxysilane (TMOS) or 3-aminopropyl-triethoxysilane (APTEOS) to prepare non-charged membranes. The cross-linking is essential to enhance membrane compactness and reduce membrane hydrophilicity due to the highly hydrophilic PVA matrix. Hence, the water osmosis is expected to be reduced. Besides, though the membranes have no ion exchange groups, they contain plenty of –OH groups, which may be used to separate the acidic liquor. Hence, the non-charged membranes are firstly attempted to recover acid through continuous DD process. The flow rates of acidic liquor and water are adjusted to optimize the DD performances, including the water osmosis, recovered HCl concentration, HCl recovery ratio, and Gly rejection and productivity.

2. Experimental

2.1. Materials and the acidic liquor

All reagents were purchased from domestic company (China). Polyvinyl alcohol (PVA), with the average degree of polymerization 1750 ± 50, was supplied by Shanghai Sinopharm Chemical Reagent Co., Ltd. γ-aminopropyl-triethoxysilane (APTEOS) was bought from Hangzhou Jessica Chemical Reagents Co. Ltd. Tetramethoxysilane (TMOS) was purchased from Nanjing Jingtianwei Chemical Co. Ltd. Purified water was used throughout the experiments, which was supplied by Tidynet purified Water Company. The water conductivity was lower than 6 μS/cm at 25ºC.

Solution of 5 wt% PVA was obtained by immersing the PVA material in water at room temperature for one day. Then the mixture was heated to 102ºC at the rate of 8ºC/h and kept at 102ºC for around 2.5 h. The glutaraldehyde (GA) solution contained 0.96 mol/L (*M*) Na_2SO_4, 0.2 *M* H_2SO_4 and 0.03 *M* GA, which were supplied by Shanghai Sinopharm Chemical Reagent Co. Ltd. The acidic liquor was synthesized through the DMP method [15]. The acidic liquor contained about 2.4 *M* HCl, 1.0 *M* (170 g/L) Gly, 35 wt% other organic components and 40 wt% water.

2.2. Membrane cross-linking

Three types of membranes were prepared by cross-linking with GA together with TMOS or APTEOS as shown in Fig. 1. PVA solution was cast onto glass plates (80 mL per each plate). The size of each glass plate was 20 × 30 cm^2, while the size of cast area was only about 246 cm^2 to ensure no leakage of casing solution out of the plate. The casting solution was dried at room temperature under adequate aeration to form a film. The film was peeled off, then heated from 60ºC to 130ºC at the rate of 10ºC/h, and kept at 130ºC for 2.5 h. The obtained base membrane was designated as PVA. The base membrane was immersed in the GA solution at 40ºC for 2.5 h, and then washed by water. The immersed membrane was designated as G.

The TMOS or APTEOS (21.3 mL) was dropped into 500 mL PVA solution at 60ºC within 1 h. The mixture was stirred at 60ºC for 24 h to obtain a casting solution. The casting solution was cast onto glass plates, and then followed the same steps as those of membrane G. The obtained membranes were designated as G-T for TMOS or G-A for APTEOS. The membrane was examined to select seven sheets with proper thickness (0.16–0.18 mm) and no bubbles. The seven sheets of membrane would be equipped in the continuous dialyzer for DD separation.

Two other membranes were also prepared to further prove the effect of APTEOS on the dialysis coefficient of HCl. The dialysis coefficient was used to evaluate the transport rate of HCl, which was measured in a batch DD dialyzer [11]. The membranes were prepared by following procedures similar to our previous work [10]. Quaternized poly (2,6-dimethyl-1,4-phenylene oxide) (QPPO, 2 g) was mixed with 2 g PVA (40mL) to prepare QPPO/PVA membrane, while QPPO (4 g), PVA (2 g) and APTEOS (2.55 g) were mixed to prepare QPPO/PVA/APTEOS membrane. The mixtures were stirred, casted and heated by following the same procedures as membranes G, G-T and G-A.

2.3. Membrane swelling in water and acids

Fourier transform infrared spectroscopy (FTIR) was recorded using FTIR spectrometer (Nicolet 67, Therom Nicolet) with a resolution of 0.09 cm^{-1} and a spectral range of 4000–400 cm^{-1}. Membrane morphology was observed with a SEM (field emission scanning electron microscopy,

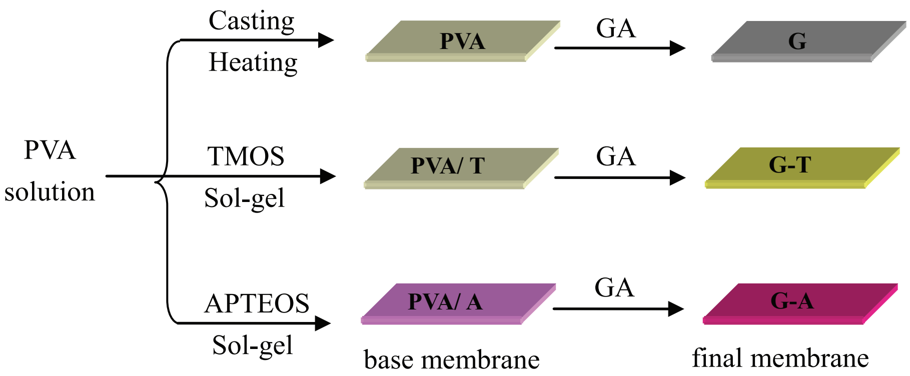

Fig. 1. Preparation procedures for membranes G, G-T and G-A.

SU8020 Hitachi). Membrane sample was fractured in liquid nitrogen, dried under vacuum at room temperature and then coated with platinum before SEM observation.

Water uptake (W_R) was measured to investigate the membrane hydrophilicity. The dried membrane sample was weighed and immersed in water at 25ºC for 2 d. Surface of the wet sample was then carefully dried and the sample was weighed. W_R was calculated as the relative weight gain per gram of the dry membrane sample.

Swelling resistance was measured by membrane swelling behavior in 65ºC water [11]. Pre-weighed membrane sample was immersed in 65ºC water, and then taken out at different time. The surface was quickly wiped dry with filter paper and the wet sample was weighed. Swelling degree, calculated as weight gain per gram of dry sample, was recorded over the time. Finally, the wet sample was dried till constant weight. The weight loss percent was calculated as the relative weight loss per gram of the original dry membrane sample.

Acidic resistance was measured by immersing membrane sample in HCl solution or the acidic liquor, for membrane stability in acidic solution was a serious concern during long-term continuous DD running. The sample was weighed, followed by immersion in HCl (1-3.5 *M*) solution or acidic liquor for two days, and then taken out and wiped with filter paper to remove residual solution on the surface and the wet sample weighed. Finally, the wet sample was dried till constant weight. The swelling degree and weight loss percent were calculated as weight gain and weight loss per gram of dry sample correspondingly. Besides, the membranes were also immersed in the acidic liquor for 8 days to investigate the long-term stability.

2.4. Continuous DD running for the acidic liquor

The membrane was firstly immersed in water for one day and then equipped in the continuous dialyzer. The dialyzer was equipped with 7 sheets of membrane. Each sheet had an effective area of 0.0082 m², and thus the total membrane area was 0.0574 m². The dialyzer had two inlets and two outlets, which formed two channels. One channel, used as the dialysate, was imported with the acidic liquor and exported with the residual solution. The other channel, used as the diffusate, was imported with water and exported with the recovered HCl, as shown in Fig. 2. The flow rates of acidic liquor and water were controlled by peristaltic pumps. The DD was running for 2–3 h to reach a dynamic equilibrium state before time keeping [16]. However, some bubbles still emerged after running long time (6–8 h), which may affect the DD performance.

The acidic liquor was separated by DD process to obtain recovered acid and residual solution. The residual solution contained residual HCl (~0.7 *M*) and diluted Gly (~130 g/L) due to water osmosis. Hence, the residual solution was evaporated to remove 10–50% solvent and then precipitated to obtain the Gly product (Fig. 2). The precipitated Gly was dried and weighed, and then examined by UV spectrophotometer to obtain its purity.

2.5. Date analyses and calculations

The Gly concentration was determined by UV spectrophotometer at 242 nm [17]. As both HCl and Gly were acidic in the solution, the solution was sampled and titrated with NaOH to determine the total acidity, from which the HCl concentration was calculated.

The DD performance can be evaluated by six parameters. The parameters include the flow rate of water or acidic liquor (υ), recovered HCl concentration ($C_{d\text{-}H}$), Gly concentration in residual solution ($C_{res\text{-}Gly}$), HCl recovery ratio (R_H), Gly rejection (η_{Gly}), and water osmosis coefficient (U_{H_2O}).

$$\upsilon\ (\mathrm{L/(m^2\ h)}) = Q/A \tag{1}$$

where Q is the flow of water or acidic liquor (L/h), A is the total effective membrane area (m²).

$$R_H(\%) = \frac{Q_d C_{d-H}}{Q_{feed} C_{f-H}} \times 100 \tag{2}$$

where Q_d is the out flow of recovered acid (L/h), Q_{feed} is the inlet flow of acidic liquor (L/h), and $C_{f\text{-}H}$ is the HCl concentration in the acidic liquor (*M*).

$$\eta_{\mathrm{Gly}}(\%) = (1 - \frac{Q_d C_{d-Gly}}{Q_{feed} C_{f-Gly}}) \times 100 \tag{3}$$

where $C_{d\text{-}Gly}$ is the Gly concentration in the recovered solution, and $C_{f\text{-}Gly}$ is the Gly concentration in the acidic liquor.

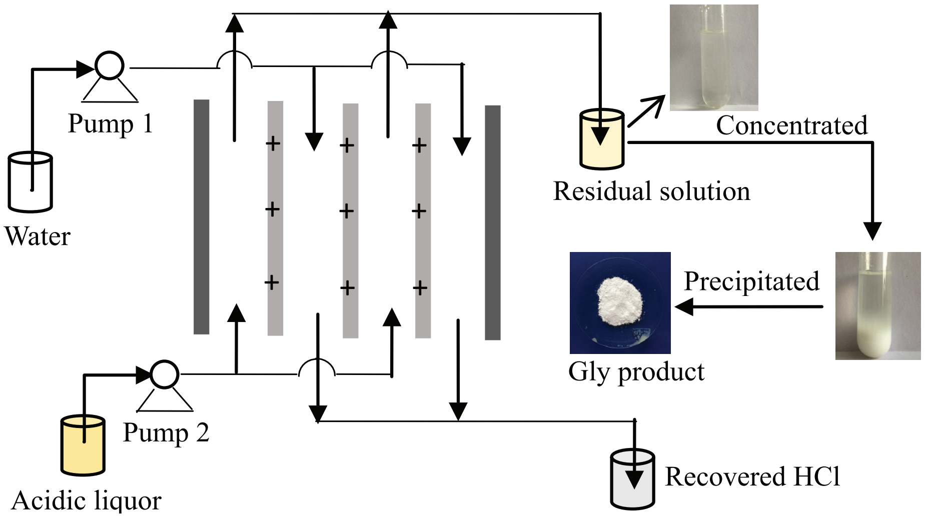

Fig. 2. Continuous diffusion dialysis (DD) for separating the acidic liquor to obtain recovery HCl and Gly product.

$$U_{H_2O}(\mathrm{m}/h) = (Q_{res} - Q_{feed})/\mathrm{A} \tag{4}$$

where Q_{res} is the out flow of residual solution. The residual solution is collected by a fixed cylinder to measure its volume every 1 h. The Q_{res} value is calculated as the ratio of solution volume to the time.

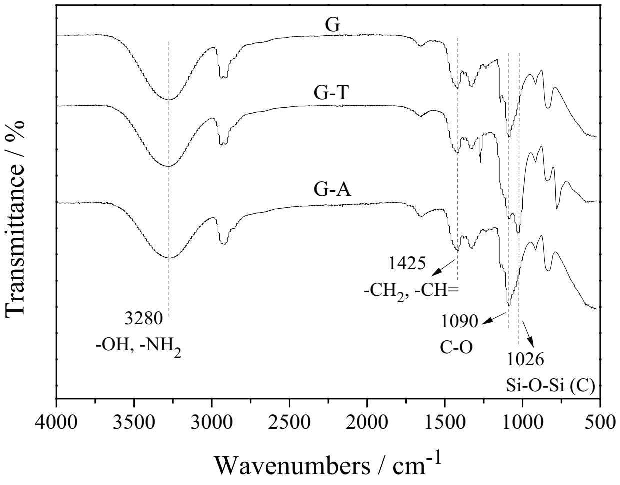

Fig. 3. FTIR spectra of the cross-linked membranes.

3. Results and discussions

3.1. FTIR spectra and SEM

Membrane structure is characterized by FTIR and SEM. The FTIR is shown in Fig. 3. The wide band around 3280 cm^{-1} is from the stretch vibration of –OH groups including C–OH and Si–OH and maybe some absorbed water. Besides, –NH_2 groups should also induce the stretch vibration for membrane G-A. The band at 1425 cm^{-1} is from the stretching of CH_2– and CH– groups (δ) [18]. The band at 1090 cm^{-1} is ascribed to the stretching vibration of C–O– groups [19], which may include the –C–O–H and –C–O–C groups. The band at 1026 cm^{-1} is due to the stretching vibration of Si-O-Si and Si-O-C groups [18]. The band is more significant for membrane G-T, for the TMOS contains four –Si(OR) groups.

Membrane cross-section is observed by SEM, as shown in Fig. 4. Membrane G is homogeneous due to its pure organic phase of PVA. Membrane G-T contains plenty of particles with the diameter of 30–100 nm. The particles should be composed of silica due to the self-crosslinking of Si-OCH_3 groups [18]. Membrane G-A is more homogeneous than membrane G-T, which is mainly attributed to the effect of –NH_2 groups. The –NH_2 groups have high polarity and can form weak interactions such as hydrogen bonds with PVA-OH groups [13], which can elevate the compatibility between PVA and APTEOS.

3.2. Membrane stability in water and acids

The continuous DD is running with the import of water and acidic liquor. The water and acidic liquor flow around the membrane two sides. Hence, membrane stability needs to be investigated in water and acids, which can be reflected from their swelling degrees and weight loss percent.

The water uptake (W_R) is in the range of 53.2–130.4% as shown in Table 1. The swelling degrees in 65ºC water are in the range of 94.3–203.3% as shown in Fig. 5. The values can be compared with those of other reported PVA based membranes (W_R of 84–157%, and swelling degrees of 153–347% [20]), which are cross-linked with the alkoxysilane of methacryloxypropyl trimethoxy silane. Firstly, the present values are much lower than the reported values, indicating the effective cross-linking of alkoxysilane and GA. The GA contains double –CHO groups and thus is favorable to cross-link with PVA [21]. Secondly, though the values at 65ºC are higher than the values at room temperature (W_R), the increasing extent is less significant than those of the previous membranes [20]. The lower extent indicates the more effective cross-linking among PVA, GA and alkoxysilane.

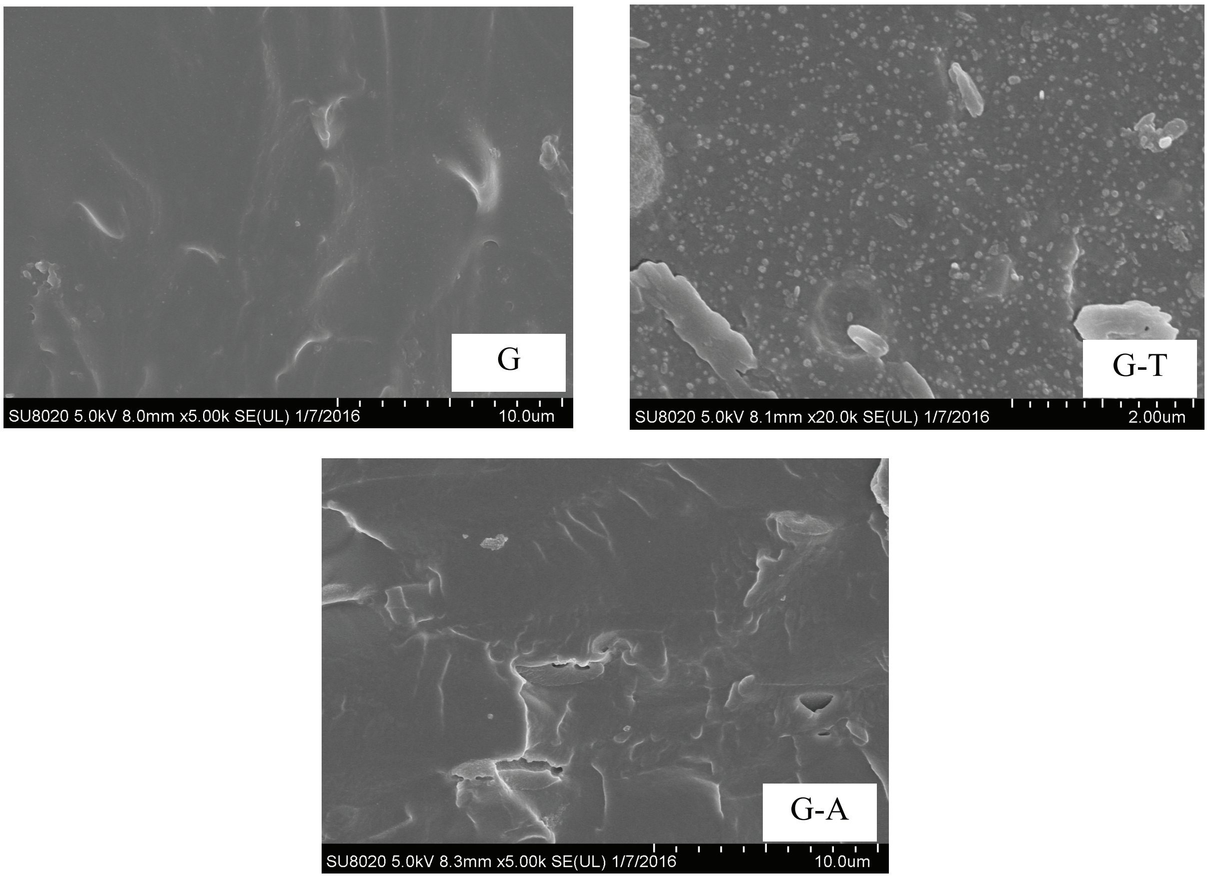

Fig. 4. The SEM images of membrane cross-sections.

Table 1
Composition and properties of membranes G, G-T and G-A

Membrane	G	G-T	G-A
Crosslinking agents	GA	GA/ TMOS	GA/ APTEOS
Thickness (mm)	0.16	0.18	0.17
W_R (%)	78.0	53.2	130.4
Weight loss percent in 65°C water (%)	4.4	7.6	5.4
Weight loss percent in 3.3 *M* HCl (%)	17.9	7.6	15.2
Swelling degree in the acidic liquor for 2 days (%)	92.9	68.9	112.7
Swelling degree in the acidic liquor for 8 days (%)	104.6	86.3	130.6

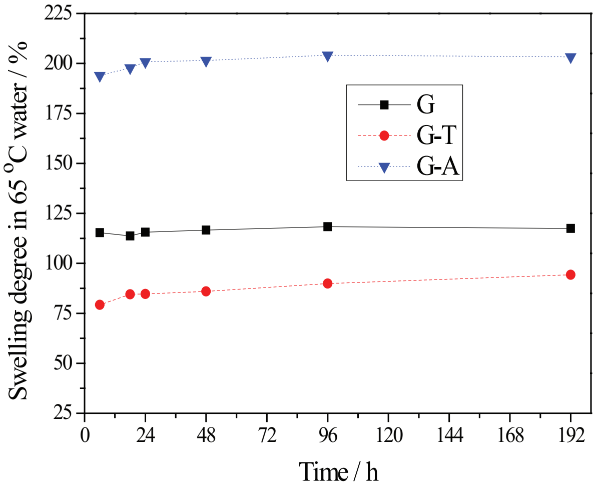

Fig. 5. Swelling degrees in 65 °C water for 192 h.

Finally, membrane G-T has the lowest values than the other membranes, indicating the effective combination of TMOS and GA. The GA can cross-link with PVA through the formation of acetal bonds [12], while alkoxysilane can form silica network through sol-gel reaction. Membrane G-A has higher values due to the $–NH_2$ groups. The $–NH_2$ group is hydrophilic, which can combine with water through hydrogen bonds. Besides, the $–NH_2$ group reduces the number of –Si(OR) groups within APETEOS. The APTEOS has only three –Si(OR) groups while the TMOS has four –Si(OR) groups. The lower number of –Si(OR) groups reduces the cross-linking ability of APTEOS.

The swelling degrees in acidic liquor are in the range of 68.9–112.7% for two days immersion, while in the range of 86.3–130.6% for 8 d immersion (Table 1). Membrane G-T still has the lowest value than the other membranes. The values of 8 days immersion are higher than the values of two days immersion, indicating that the membrane swelling degrees increase after long-term immersion. The membrane swelling is further investigated through the immersion in HCl solution, as shown in Fig. 6. The swelling degrees are relatively stable as the HCl concentration increases from 1.06 to 2.62 *M*, while increase and then jump when the concentration increases to 3.14–3.30 *M*. The swelling degrees in 3.3 *M* HCl solution are in the range of 422.6–648.1%, which are about 5–8 times higher than the W_R values. The higher swelling in HCl solution indicates that the PVA matrix is sensitive to HCl concentration. For example, the base membrane PVA without cross-linking is almost dissolved in 3.3 *M* HCl.

Besides, the weight loss percents in 65°C water are in the range of 4.4–7.6%, which are lower than the previous values of membrane QPPO/PVA (13.7–16.4% [22]), indicating the effective cross-linking of GA and alkoxysilane.

3.3. Water osmosis

The water osmosis coefficients (U_{H_2O}) are investigated for the fixed flow rate ratio (water/feed = 1:1) and the fixed flow rate of acidic liquor (0.34 L/(m^2 h)), as shown in Fig. 7a,b correspondingly. Fig. 7a shows that the U_{H_2O} values are in the range of 0.71–1.44 × 10^{-4} m/h, which are only 1/2-1/3 values of the previous commercial membrane (2.2–3.4 × 10^{-4} m/h) and self-prepared QPPO/PVA membrane (1.9–2.9 × 10^{-4} m/h) [10]. The lower U_{H_2O} values indicate that the cross-linked PVA membranes can effectively restrict water osmosis. The cross-linking can reduce the membrane hydrophilicity and thus water permeation. Besides, the membrane should become compact after the cross-linking [23], which also impedes the water transport.

The U_{H_2O} values increase as the water and feed flow rate increase from 0.24 to 0.54 L/(m^2 h), which should be attributed to the reduced retention time of the water and feed. The reduced retention time would enhance the concentration gradient between dialysate and diffusate sides, and thus the osmosis pressure increases. As the flow rate increases further, some bubbles are emerged in the dialysate side in some cases after running long time, and thus the U_{H2O} values at 0.64 L/(m^2 h) are not provided in Fig. 7a.

Fig. 7b shows the U_{H2O} values are in the range of 0.77–1.2 × 10^{-4} m/h as the flow rate ratio of water/feed increases. The U_{H2O} values are lower and more stable than those of the previous commercial membrane (4.4–5.9 × 10^{-4} m/h) and self-prepared QPPO/PVA membrane (2.1–2.9 × 10^{-4} m/h). The lower U_{H2O} values indicate that the cross-linked PVA membranes can effectively restrict water osmosis. Hence, the Gly concentration is diluted less seriously in the dialysate solution, which may be beneficial to precipitate Gly and thus elevate Gly productivity.

The U_{H2O} values of membrane G are lower than those of membrane G-T and T-A, indicating the different cross-linking effects of GA and alkoxysilanes. The GA cross-linking can enhance membrane compact and thus impede

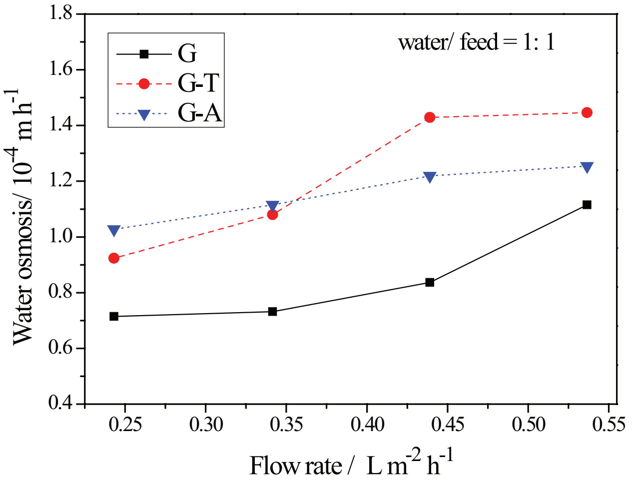

Fig. 7. (a) Water osmosis coefficients (U_{H2O}) with respect to the flow rate of water or acidic liquor.

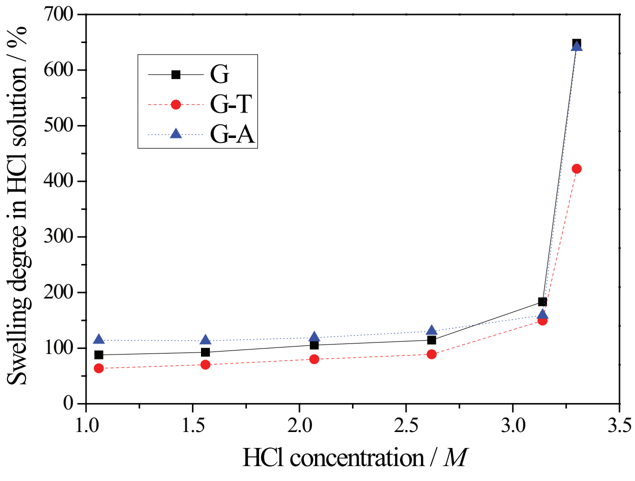

Fig. 6. Swelling degrees in HCl solutions (1.1–3.3 *M*) for 48 h.

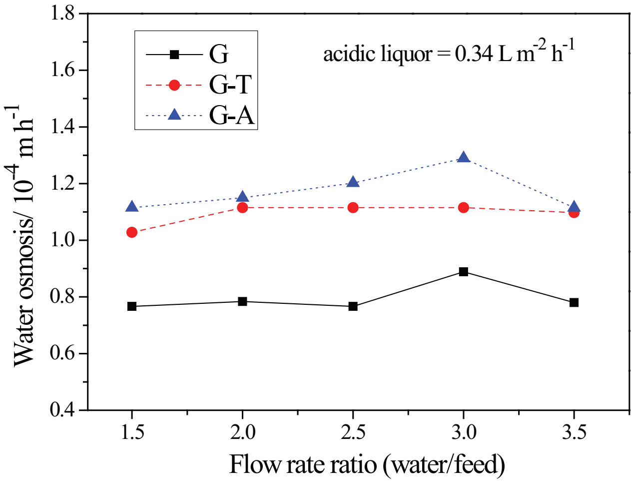

Fig. 7. (b) U_{H2O} with respect to the flow rate ratio of water/feed.

the water transport. However, the cross-linking of alkoxysilanes can form silica structure and thus enhance the amorphous region of hybrid membranes [13], which may provide some chances for water permeation. Besides, the amorphous region may weaken the following cross-linking effect of GA. Hence, the hybrid membranes show higher water osmosis than the pure organic membrane.

Membrane G-T has higher water osmosis than membrane G-A when the flow rate is higher than 0.34 L/(m^2 h) in Fig. 7a; while membrane G-T has lower water osmosis than membrane G-A as the flow rate ratio increases in Fig. 7b. This phenomenon indicates that membrane G-A is more sensitive to the flow rate of water, which is attributed to its higher hydrophilicity (W_R of 130.4%). Membrane G-T is more sensitive to the flow rate of acidic liquor, which is due to its silica particles (SEM in Fig. 4) and thus more obvious interfaces between organic and inorganic phases. The interfaces may provide some chances to transport small organics such as methanol in the acidic liquor. Hence, the concentration gradient of the organics increases with the flow rate of acidic liquor due to the decreasing retention time. The increasing concentration gradient of the organics may induce more significant water osmosis.

3.4. Concentrations with the increasing flow rate

The concentration of recovered HCl ($C_{d\text{-}H}$) determines its economic value for reuse, while the Gly concentration in residual solution ($C_{res\text{-}Gly}$) determines its precipitation amount and thus the Gly productivity. The $C_{\text{d-H}}$ values decrease from 2.3 to 0.9 *M* with the increasing flow rate, as shown in Fig. 8a. The decreasing $C_{\text{d-H}}$ values should be mainly attributed to the enhanced flow rate of water, for higher water flow rate would dilute the HCl concentration in the diffusate side.

The $C_{\text{d-H}}$ values are lower than the previous values of self-prepared QPPO/PVA membrane (from 3.1 to 1.9 *M*). The lower values are attributed to the different membrane structures. The present membranes are non-charged with only –OH groups, which can not accelerate the transport of Cl^- ions. Besides, some –OH groups are cross-linked to enhance the membrane compactness, which may be disadvantage to the transport of H^+ ions [22]. However, here PVA based membranes, though non-charged without any ion exchange groups, are firstly used in DD process for acid recovery. The results prove that non-charged membranes can also have acceptable DD performances in acid recovery, which gives a new clue to develop DD membranes.

The $C_{res\text{-}Gly}$ values are in the range of 125.1–148.4 g/L, as shown in Fig. 8b, which can give three inspirations. Firstly, the $C_{res\text{-}Gly}$ values in residual solution are lower than that in acidic liquor (170 g/L), for 0.84-12.41 g/L Gly leaks from the dialysate side into the diffusate side. Moreover, water permeates through the membrane from the diffusate side into the dialysate side, which dilutes the residual solution and thus the Gly concentration. Secondly, the values are higher than those of the commercial membrane (91.5–119.7 g/L) and self-prepared QPPO/PVA membrane (106.9–136.9 g/L) [10]. The higher values are attributed to the lower U_{H2O}. For example, membrane G has the highest $C_{res\text{-}Gly}$ values due to its lowest U_{H2O}. Thirdly, the $C_{res\text{-}Gly}$ values of membranes G-T and G-A are lower than those of membrane G, which is attributed to the amorphous region induced by the silica network. The interfaces between organic and inorganic phases may provide more chances for the ions permeation [20] and thus Gly leakage. Finally, the $C_{res\text{-}Gly}$ values increase rapidly as the flow rate increases from 0.24 to 0.44 L/(m^2 h), which is attributed to the decreasing retention time of the feed solution in the continuous dialyzer. The values can reach up to 143–148 g/L at the flow rate of 0.63 L/(m^2 h), which is close to the feed concentration (170 g/L). The stable and high Gly concentration is beneficial for Gly precipitation and productivity.

3.5. HCl recovery and Gly rejection with the increasing flow rate

The HCl recovery ratios (R_H) are in the range of 29.8–66.4%, as shown in Fig. 9a. The R_H values increase initially

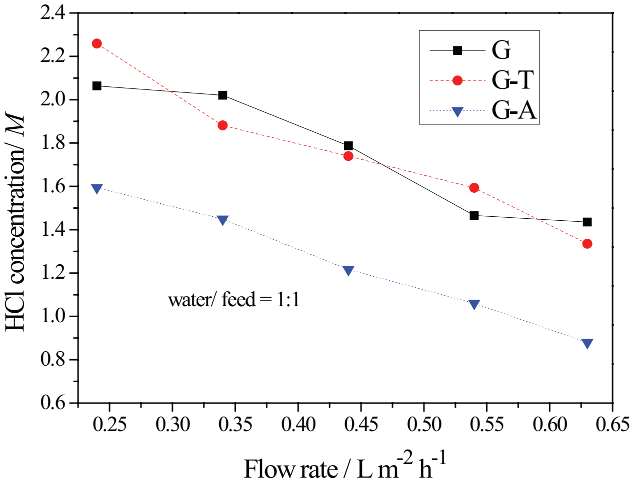

Fig. 8. (a) Recovered HCl concentrations with respect to the flow rate of water or acidic liquor.

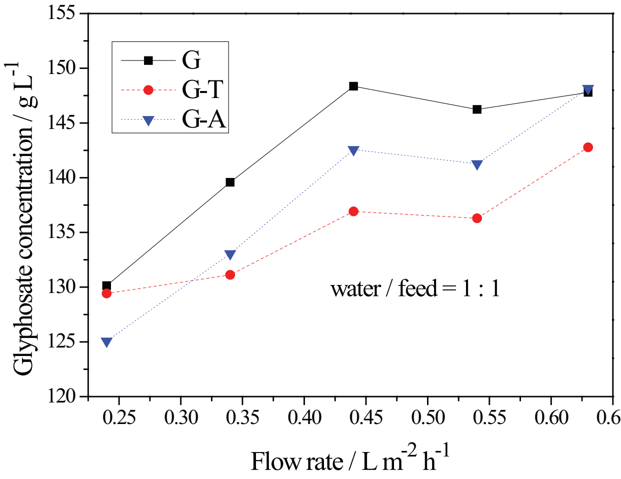

Fig. 8. (b) Residual Gly concentrations with respect to the flow rate of water or acidic liquor.

as the flow rate increases from 0.24 to 0.34 L/(m² h), and then decrease all along as the flow rate increases further.

The optimized flow rate is 0.34 L/(m² h) under the comprehensive consideration. The U_{H2O} values are at a low level (0.73–1.11 × 10^{-4} m/h) and the C_{d-H} values are relatively high (1.45–2.02 mol/L) at the flow rate of 0.34 L/(m² h). Here the R_H values are 66.4%, 52.0% and 44.8% for membranes G-T, G and G-A, respectively. The values of 52.0–66.4% are similar to the values of previous membrane QPPO/PVA (55% under optimized flow rate of 0.63 L/(m² h)) [10]. The similar R_H values may be mainly attributed to the lower membrane thickness and the high density of –OH groups. The present membranes have lower thickness (0.16–0.18 mm) than previous QPPO/PVA membrane (0.18–0.24 mm). The lower thickness reduces the transport resistance of HCl and thus elevates the recovery ratio. Besides, though the present membranes are non-charged and thus contain no ion exchange groups, they contain abundant –OH groups. The density of –OH groups, calculated from the structural formula of PVA, is theoretically 22.7 mmol/g for pure PVA (1000/44 = 22.7). The value is much higher than the density of anion exchange groups (1.43 mmol/g). The –OH groups can elevate the transport rate of H^+ ions through hydrogen bonds [14] and thus elevate the recovery ratio.

Membrane G-A has the lowest R_H value, which may be partly attributed to the $–NH_2$ groups. The $–NH_2$ groups, though can absorb the HCl component, may not be easily desorbed in the diffusate side. The effect of $–NH_2$ groups is further examined by the addition of APTEOS (42 wt%) to QPPO/PVA casting solution during membrane preparation. The dialysis coefficient of HCl, measured by the batch diffusion dialysis process [11], decreases from 0.0162 m/h for QPPO/PVA membrane to 0.0139 m/h for the membrane added with APTEOS.

The Gly rejection (η_{Gly}) values are in the range of 95.8-99.7%, as shown in Fig. 9b, which are higher than previous values (94.8–98.4%) [10]. The high values indicate that the Gly molecule, due to its high molecular weight (169 g/mol) and weak acidity, is less likely to transport through the cross-linked membrane. The values increase with the flow rate, which is attributed to the reduced retention time of dialysate solution. Membrane G has higher rejection values than membranes G-T and G-A, for membranes G-T and G-A contain silica component. The silica component enhances the amorphous region of hybrid membranes [13] and thus may provide more chances for Gly transport.

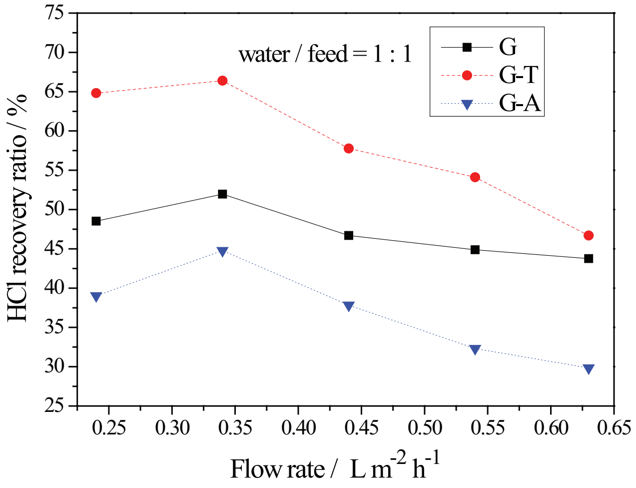

Fig. 9. (a) HCl recovery ratio (R_H) with respect to the flow rate of water or acidic liquor.

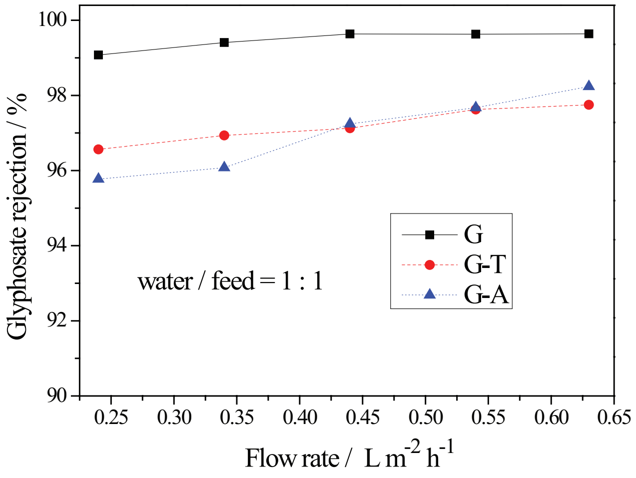

Fig. 9. (b) Gly rejection (η_{Gly}) with respect to the flow rate of water or acidic liquor.

3.6. Concentrations with the increasing flow rate ratio

The feed of acidic liquor is fixed at the optimized flow rate of 0.34 L/(m² h), while the water flow rate increases to enhance the flow rate ratio of feed/water. The C_{d-H} values decrease from 1.2 to 0.34 *M* as shown in Fig. 10a. The reduced concentration is attributed to the shortened retention time of diffusate solution and the limited transport rate of HCl. The shortened retention time permits less amount of HCl to be transported through the membrane. Hence, the flow rate of water needs to be restricted to obtain an acceptable acid concentration. Membrane G-T has higher C_{d-H} values, which is attributed to its silica network and thus amorphous structure. The higher concentration is beneficial for the reuse of recovered HCl.

The $C_{res-Gly}$ values are relatively stable in the range of 123.2–144.2 g/L as shown in Fig. 10b. The $C_{res-Gly}$ values of membrane G (137.4–144.2 g/L) are higher than previous values of commercial and QPPO/PVA membranes (124.1–139.7 g/L) [10]. The $C_{res-Gly}$ values are relatively stable as the flow rate ratio increases, which is attributed to the high Gly rejection of cross-linked membranes and the stable U_{H2O} values.

3.7. HCl recovery and Gly rejection with the increasing flow rate ratio

The HCl recovery ratios (R_H) increase initially and then balance or even decrease as the flow rate ratio increases, as shown in Fig. 11a. The R_H values at the ratio of 2.0 are 78.6%, 63.9% and 49.8% for membranes G-T, G and G-A, respectively. The value of 78.6% is higher than that of previous

QPPO/PVA membrane (68.1%) or close to that of commercial membrane (83.4%) [10]. Hence, the non-charged hybrid membranes can have similar recovery ability with the anion exchange membranes. The R_H values decrease as the flow rate ratio increases further, which may be attributed to the emerged bubbles in the dialyzer as the running time prolongs.

The Gly rejection (η_{Gly}) is almost not affected by the increasing flow rate ratio, as shown in Fig. 11b. The high η_{Gly} values (96.9–99.6%) indicate the membrane can effectively hinder the Gly transport. The η_{Gly} values of membrane G-T and G-A are lower than those of membrane G, indicating that the silica network would slightly enhance the Gly transport due to the amorphous structure.

Overall, as the flow rate ratio increases, the $C_{d\text{-}H}$ values decrease sharply, the R_H values increases in the initial stage, the $C_{res\text{-}Gly}$ and η_{Gly} values are relatively stable. Hence, the optimized flow rate ratio is selected as 2.0. Membrane G and G-T can obtain 0.93–1.00 *M* recovered HCl, 63.9%–78.6% recovery ratio, 131.6–140.2 g/L residual Gly and 97.0–99.5% rejection ratio.

3.8. Gly productivity and purity

The continuous DD is running at the optimized condition, which selects membrane G-T with the Q_{feed} of 0.34 L/(m^2 h) and flow ratio of 2. The residual solution contains 1.32 *M* HCl and 132.1 g/L Gly, which is evaporated to remove 10–50% solvent and then precipitated. The Gly productivity and purity are shown in Fig. 12.

The Gly productivity increases from 20.9% to 83.3% as the concentrated degree increases from 10% to 50%, while Gly purity decreases from 82.4% to 71.1%. The impurities within Gly product should be the other components in acidic liquor such as trimethylamine hydrochloride [5], for the DD process introduces no additional chemical reagents. In previous work, the residual solution without

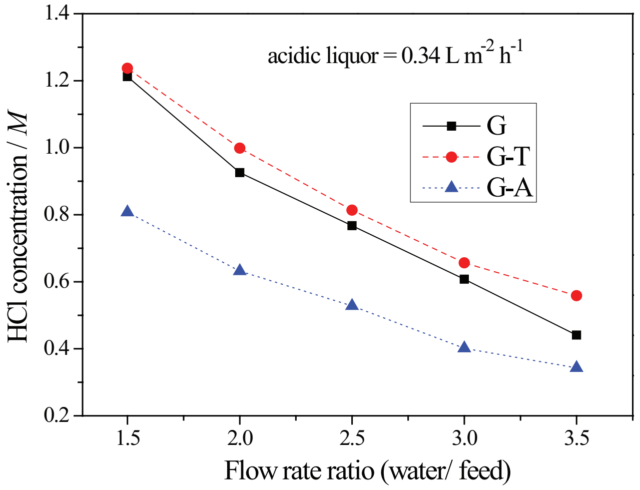

Fig. 10. (a) Recovered HCl concentrations ($C_{d\text{-}H}$) with respect to the flow rate ratio.

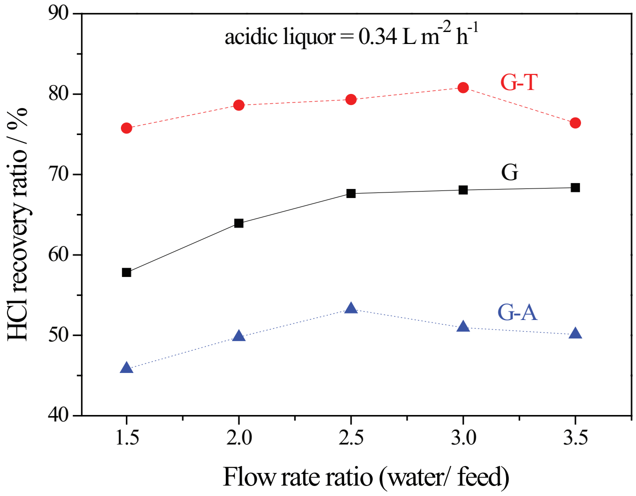

Fig. 11. (a) HCl recovery ratio (η_H) with respect to the flow rate ratio.

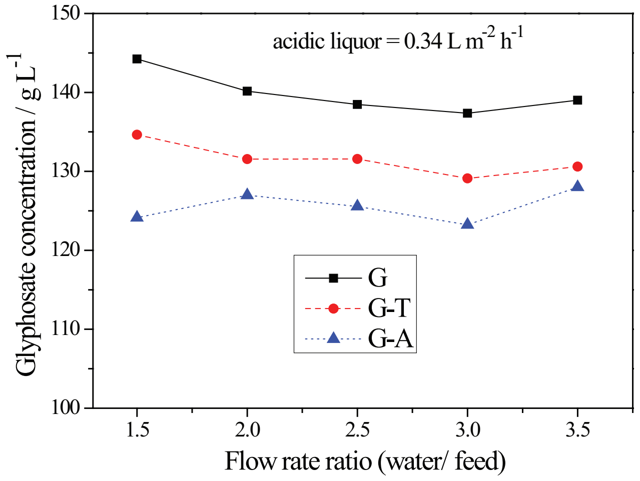

Fig. 10. (b) Residual Gly concentrations ($C_{res\text{-}Gly}$) with respect to the flow rate ratio.

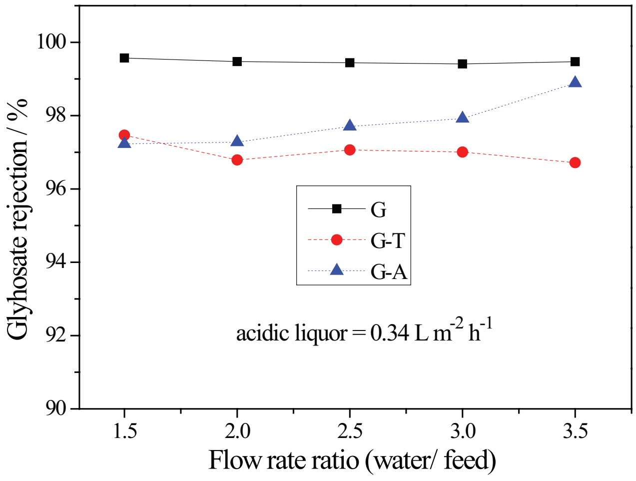

Fig. 11. (b) Gly rejection (η_{Gly}) with respect to the flow rate ratio.

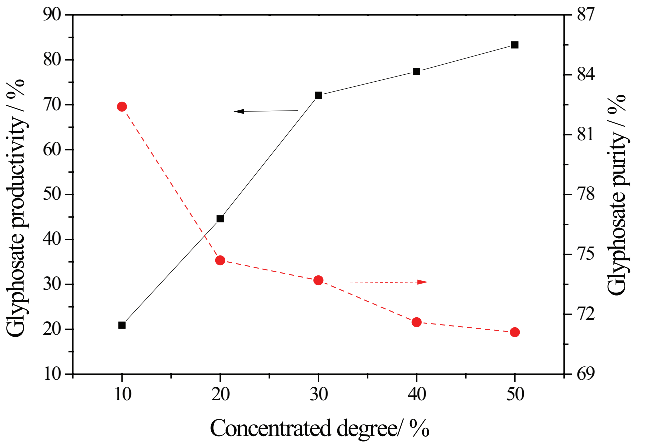

Fig. 12. Gly productivity and purity with respect to the concentrated degree of the residual solution.

neutralization can only obtain 21.1–28% productivity with the purity of 81.6–89.7% at the concentrated degree of 50% [10]. The present Gly productivity is higher than the previous values, which is attributed to the higher Gly concentration in the residual solution. The Gly concentration is enhanced by the cross-linking membranes. The membranes, on one hand, can effectively hinder the Gly leakage; on the other hand, can restrain water osmosis.

4. Conclusions

Acidic liquor containing HCl and glyphosate is separated by continuous DD process to obtain recovered HCl and residual solution. The DD dialyzer is equipped with PVA based membrane, which is prepared from the cross-linking between PVA and glutaraldehyde together with TMOS or APTEOS. The membranes show that the water osmosis coefficients are in the range of 0.71–1.44 × 10^{-4} m/h, which are only 1/2–1/4 values of the previous commercial membrane (2.2–3.4 × 10^{-4} m/h) and self-prepared QPPO/PVA membrane (1.9–2.9 × 10^{-4} m/h).

The running conditions are optimized to be the Q_{feed} of 0.34 L/(m^2 h) with the flow rate ratio (water/feed) of 2. The HCl recovery ratios of membranes G-T, G-A and G are 78.6%, 63.9% and 49.8%, respectively, indicating that the non-charged membranes can also be used for acid recovery. The Gly rejection is in the range of 97.0–99.5%, indicating that the membranes can effectively hinder the Gly leakage. The reduced water osmosis elevates the Gly concentration in the residual solution, which is in the range of 127.0–140.2 g/L. The residual solution is concentrated to precipitate 20.9%–83.3% Gly.

Acknowledgements

This project was supported in part by the National Natural Science Foundation of China (Nos. 21376204 and 21476056), and A Project Funded by the Flagship Major Development of Jiangsu Higher Education Institutions (PPZY2015B113).

Symbols

Gly — Glyphosate
DD — Diffusion dialysis
M — mol/L
QPPO — Quaternized poly(2,6-dimethyl-1,4-phenylene oxide), which is a type of anion exchange material.
PVA — Polyvinyl alcohol
DMP — Glycine-dimethylphospite
FTIR — Fourier transform infrared spectroscopy
SEM — Scanning electron microscopy
$C_{f\text{-}H}$ — HCl concentration in the acidic liquor mol/L
$C_{d\text{-}H}$ — Recovered HCl concentration mol/L
$C_{f\text{-}Gly}$ — Glyphosate concentration in the feed solution (acidic liquor) g/L
$C_{d\text{-}Gly}$ — Glyphosate concentration in the recovered acid g/L
$C_{res\text{-}Gly}$ — Glyphosate concentration in the residual solution g/L
R_H — HCl recovery ratio %
η_{Gly} — Glyphosate rejection %
Q_{res} — Flow of the residual solution L/h
Q_d — Flow of the recovered HCl solution L/h
Q_{feed} — Flow of the acidic liquor L/h
υ — Flow rate of water or acidic liquor L/(m^2 h)
W_R — Water uptake %

References

[1] A.D. Baylis, Why glyphosate is a global herbicide: strengths, weaknesses and prospects, Pest. Manage. Sci., 56 (2000) 299–308.
[2] M. Xie, Z.Y. Liu, Y.H. Xu, Removal of glyphosate in neutralization liquor from the Glycine-dimethylphosphit process by nanofiltration, J. Hazard. Mater., 181 (2010) 975–980.
[3] 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.
[4] X.X. Wang, M. Wang, Y.X. Jia, T.T. Yao, The feasible study on the reclamation of the glyphosate neutralization liquor by bipolar membrane electrodialysis, Desalination, 300 (2012) 58–63.
[5] P.F. Wang, G.C. Zhang, Y.H. Wu, Diffusion dialysis for separating acidic HCl/glyphosate liquor, Sep. Purif. Technol., 141 (2015) 387–393.
[6] J.X. Zhuang, Q. Chen, S. Wang, W.M. Zhang, W.G. Song, L.J. Wan, K.S. Ma, C.N. Zhang, Zero discharge process for foil industry waste acid reclamation: Coupling of diffusion dialysis and electrodialysis with bipolar membranes, J. Membr. Sci., 432 (2013) 90–96.
[7] X. Zhang, C.R. Li, H.C. Wang, T.W. Xu, Recovery of hydrochloric acid from simulated chemosynthesis aluminum foil wastewater by spiral wound diffusion dialysis (SWDD) membrane module, J. Membr. Sci., 384 (2011) 219–225.
[8] Z. Palaty, H. Bendová, Continuous dialysis of mixture of inorganic acids, Sep. Purif. Technol., 172 (2017) 277–284.
[9] F.B. Luo, X. Zhang, J.F. Pan, A.N. Mondal, H.Y. Feng, T.W. Xu, Diffusion dialysis of sulfuric acid in spiral wound membrane modules: Effect of module number and connection mode, Sep. Purif. Technol., 148 (2015) 25–31.
[10] 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.
[11] 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. Water. Treat., 57 (2016) 21023–21033.

[12] A.L. Ahmad, N.M. Yusuf, B.S. Ooi, Preparation and modification of poly (vinyl) alcohol membrane: Effect of crosslinking time towards its morphology, Desalination, 287 (2012) 35–40.

[13] Q.G. Zhang, Q.L. Liu, Z.Y. Jiang, Y. Chen, Anti-trade-off in dehydration of ethanol by novel PVA/APTEOS hybrid membranes, J. Membr. Sci., 287 (2007) 237–245.

[14] C.L. Cheng, Z.J. Yang, J.F. Pan, B. Tong, T.W. Xu, Facile and cost effective PVA based hybrid membrane fabrication for acid recovery, Sep. Purif. Technol., 136 (2014) 250–257.

[15] L.R. Gao, J.H. Hu, F.X. Li, Glycine-dimethyl phosphate synthesis of glyphosate (in Chinese), Shanxi Chemical Industry, 31 (2011) 15–18.

[16] 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.

[17] Glyphosate technical (GB 12686-2004), National Standard of the People's Republic of China, 1990.

[18] B. Tong, C.L. Cheng, M.I. Khan, Y.H. Wu, T.W. Xu, Double cross-linking PVA-SiO_2 hybrid membranes for alkali recovery, Sep. Purif. Technol., 174 (2017) 203–211.

[19] S. Razavi, A. Sabetghadam, T. Mohammadi, Dehydration of isopropanol by PVA-APTEOS/TEOS nanocomposite membrane, Chem. Eng. Res. Design, 89 (2011) 148–155.

[20] Y.H. Wu, H.Y. Lin, G.C. Zhang, T.W. Xu, C.M. Wu, Non-charged PVA-SiO_2 hybrid membranes for potential application in diffusion dialysis, Sep. Purif. Technol., 118 (2013) 359–368.

[21] M. Amirilargani, A. Ghadimi, M.A. Tofighy, T. Mohammadi, Effects of poly(allylamine hydrochloride) as a new functionalization agent for preparation of polyvinyl alcohol/multiwalled carbon nanotubes membranes, J. Membr. Sci., 447 (2013) 315–324.

[22] 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.

[23] H.Y. Chang, C.W. Lin, Proton conducting membranes based on PEG/SiO_2 nanocomposites for direct methanol fuel cells, J. Membr. Sci., 218 (2003) 295–206.