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Separation of acidic HCl/glyphosate liquor through diffusion dialysis and electrodialysis

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A B S T R A C T

Acidic HCl/glyphosate (Gly) liquor is the intermediate product during the production of glyphosate herbicide. Here the acidic liquor contains about 2.8 mol L^{-1} (*M*) HCl, 1.0 *M* Gly, 34 wt% other organic components and 40 wt% water. The HCl component is recovered by diffusion dialysis (DD) and subsequent electrodialysis (ED) processes, and the Gly product is precipitated at low acid concentrations. The DD process shows significant water osmosis, which can obtain the recovered HCl concentration ($C_{d\text{-}H}$) of 0.54–0.98 mol/L (*M*), HCl recovery ratio (R_H) of 29.2–35.9% and Gly rejection (η_{Gly}) of 96.8–98.6%. The obtained residual liquors are further separated by the ED process. The ED process shows water reverse osmosis, which can obtain $C_{d\text{-}H}$ of 0.65–1.30 *M*, R_H of 23.8–57.2%, η_{Gly} of 74.9–97.2% and energy consumption of 1.14–10.03 kWh kg^{-1}. Besides, 51–59% Gly product can be precipitated in the residual solution without previous neutralization and concentration. Hence, the combination of DD and ED processes can balance the water osmosis, recover most of HCl from the acidic liquor, save energy greatly, and precipitate Gly directly. The combination of DD and ED processes may become the foundation for practical separation of the acidic liquor.

Keywords: Diffusion dialysis; Electrodialysis; Glyphosate; Acid recovery; Energy consumption

1. Introduction

Glyphosate (Gly) is a widely used herbicide [1], which is mainly produced by the process of glycine-dimethylphosphite (DMP) [2]. The DMP process generates a type of acidic liquor containing about 2.4–2.8 mol L^{-1} (*M*) HCl, 1.0 *M* Gly, 34 wt% other organic components and 40 wt% water as shown in Fig. 1. The Gly is highly dissolvable in the acidic liquor but can be precipitated at low acid concentration due to its isoelectric point at pH 1.5. Hence, the HCl component needs to be removed by various methods as shown in Fig. 2. The acidic liquor is traditionally neutralized by 50 wt% NaOH solution to obtain maximum Gly precipitation. The traditional neutralization not only wastes useful component of HCl and consumes excessive NaOH, but also produces waste water containing 13–17 wt% NaCl and other components [3]. The waste water needs further treatment such as bipolar membrane electrodialysis [3,4]. Though the bipolar membrane electrodialysis can remove most of the NaCl from the waste water, the cost of bipolar membrane and energy consumption increases significantly. Hence, the acidic liquor is then separated by a membrane process of diffusion dialysis (DD).

The DD process, driven by concentration gradient, has no obvious energy consumption [5]. The DD dialyzer contains two compartments separated by a sheet of a membrane. One compartment is fed with the acidic liquor to collect residual liquor. The other compartment is fed with water to collect recovered solution. Hence, the acidic liquor is separated by both batch and continuous DD pro-

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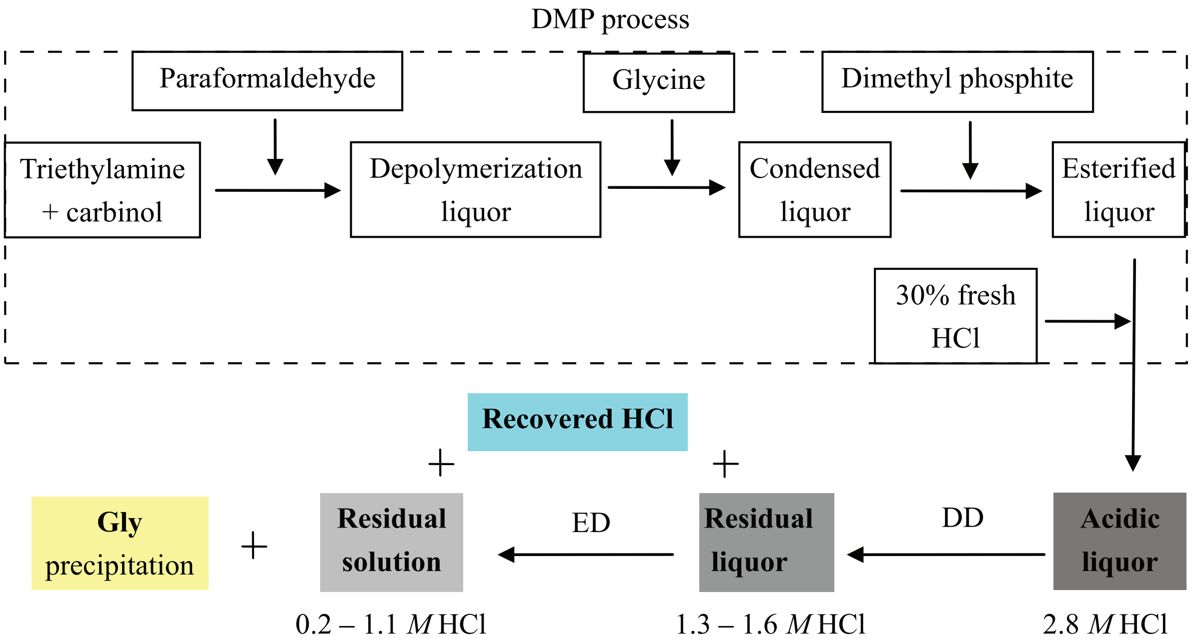

Fig. 1. The DMP process is used to generate the acidic liquor, which is separated by DD and ED processes to recover HCl and precipitate Gly product.

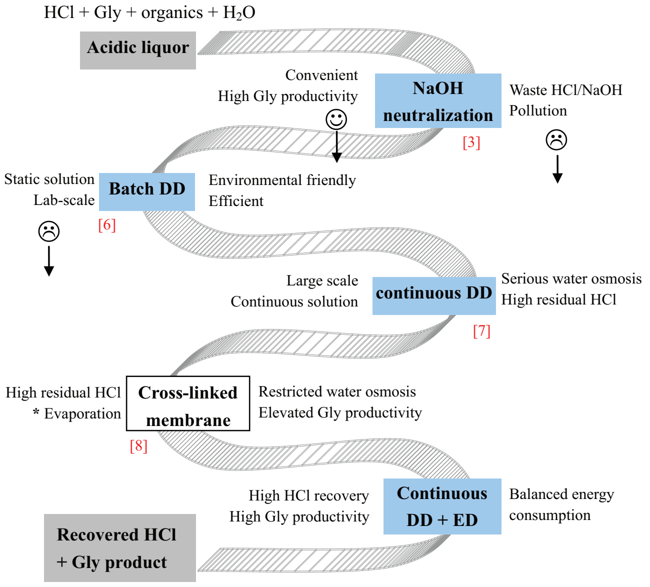

Fig. 2. Developing process of various methods to treat the acidic liquor. Note: (1) Symbols of "☺" and "☹" represent the advantage and shortcoming correspondingly. (2) * "Evaporation" means that the residual liquor needs to be evaporated to precipitate Gly product.

cesses (Fig. 2). The batch DD process was running with only a sheet of a membrane and static solutions, and thus was only used in lab-scale simulation [6]. The continuous DD dialyzer, equipped with dozens sheets of membranes with continuous flowing solutions [7], could recover most of HCl and retain most of Gly in the residual liquor. However, water osmosis was serious for the commercial membrane TWDD-III ($2.2–3.4 \times 10^{-4}$ m h^{-1}) and for the self-prepared QPPO/PVA membrane ($1.9–2.9 \times 10^{-4}$ m h^{-1}). The water osmosis was obvious due to the high concentration of organic components in the acidic liquor and therefore Gly concentration was reduced in the residual liquor. The Gly concentration in the residual liquor was 109.8 g L^{-1} (after water osmosis). The residual liquor needed to be highly concentrated to remove 40–80% solvent and then to precipitate Gly product.

The water osmosis was then restricted by cross-linked membranes. The water osmosis was reduced to 0.71–1.44 $\times 10^{-4}$ m h^{-1} [8], and the Gly concentration was elevated to 132.1 g L^{-1} in the residual liquor. However, the residual liquor still contained 1.32 *M* HCl, which was much higher than the ideal concentration of pH 1.5 (0.27–0.29 *M* HCl). The Gly could not be precipitated directly due to the high solubility of Gly in the residual liquor. The residual liquor was still evaporated to remove 10–50% solvent and then to precipitate Gly product. The evaporation would consume large amounts of energy and thus was difficult to be used on a large scale production.

The high HCl concentration in residual liquor is attributed to the inherent limitation of DD process. The HCl concentration decreases in the feed compartment and increases in the recovery compartment, which means the concentration gradient decreases as the time prolongs. The decreasing driven force reduces the transport rate of HCl, and thus large amount of HCl is still kept in the residual solution. The limitation of DD process reminds us of another membrane separation process of electrodialysis (ED).

The ED is driven by electric field, whose driven force can be adjusted by a direct current supplier [9]. The electric field is always much stronger than the concentration gradient. Hence, the ions can be transported from the low concentration side to the high concentration side, and thus the recovered concentration can be higher than the residual concentration [4]. The ED process can also be used to separate hydrochloric acid, sulfuric acid and organic acids [10–16]. The process may recover high concentration of HCl, and water osmosis may be further restricted due to the driven force of electric field. The residual solution is expected to contain high concentration of Gly but low concentration of HCl, which would precipitate more amount of Gly product.

Hence in this work, the DD and ED processes will be combined to separate the acidic liquor (Fig. 1). The acidic liquor is firstly separated by a continuous DD dialyzer, which uses the cross-linked PVA membrane to restrict the water osmosis. The DD process recovers a part of HCl component to obtain residual liquors. The residual liquors are then separated by the ED process, which further recovers the other part of HCl component to obtain the residual solutions. The residual solutions, due to the reduced water osmosis and HCl concentration, are anticipated to directly precipitate the Gly product. The effect of current density is fully investigated on the ED performances, including the recovered HCl concentration, recovery ratio, voltage drop, current efficiency, energy consumption, Gly rejection and Gly productivity.

2. Experimentals

2.1. Acidic liquor and membrane materials

All reagents were purchased from the company of China. Polyvinyl alcohol (PVA), with the average degree of polymerization 1750 ± 50, was supplied by Shanghai Sinopham Chemical Reagent Co., Ltd. Tetramethoxysilane (TMOS) was purchased from Nanjing Jingtianwei Chemical Co., LTD. Purified water was used throughout, which was supplied by Tidynet purified Water company. The acidic liquor was synthesized through the DMP method [17], which included depolymerization, condensation, esterification and hydrolysis (Fig. 1). The acidic liquor contained 2.60–2.83 *M* HCl, 1.0 *M* (168.3–180.4 g L^{-1}) Gly, 35 wt% other organic components and 40 wt% water. The concentrations of various components were fluctuated somehow due to the different production batches.

Anion exchange membrane Neosepta AMX and cation exchange membrane Neosepta CMX (ASTOM Crop, Japan) were used in ED process, whose properties were cited from previous work [18] and listed in Table 1. Membrane G-T was used in DD process, which was prepared according to previous method [8] and briefly introduced as following. TMOS (21.3 mL) was dropped into 500 mL PVA solution at 60°C within 1 h. The mixture was stirred at 60°C for 24 h to obtain a casting solution. The casting solution was cast onto glass plates. The casting solution was dried at room temperature under adequate aeration to form a film. The film was peeled off, then heated from 60°C to 130°C at the rate of 10°C h^{-1}, and kept at 130°C for 2.5 h. The obtained membrane was immersed in the glutaradehyde solution at 40°C for 2.5 h, and then washed by water. The membrane thickness is 0.18 mm. The water uptake is 53.2%, and the swelling degree is 86.3% in the acidic liquor for 8 d [8].

Table 1
Properties of the commercial membranes applied in ED process [18]

Membrane	AMX	CMX
Thickness, µm	134	164
Water uptake, %	16	18
IEC, meq g^{-1}	1.25	1.62
Area resistance, Ω cm^2	2.35	2.91
Transport number, %	91	98

2.2. Continuous DD for the acidic liquor to obtain residual liquor

Membrane G-T was firstly immersed in water for one day, and then four sheets of membrane sample were equipped in the continuous dialyzer. Each sheet of membrane had an effective area of 0.0082 m^2, and thus the total membrane area was 0.0328 m^2. The acidic liquor was fed into one compartment and then collected as residual liquor after continuous running, while water was fed into another compartment and then collected as recovered solution. The flows of entering streams (acidic liquor and water) were controlled by two peristaltic pumps [7]. The DD was running for 2–3 h to reach a dynamic equilibrium state before timekeeping [19], and then running continuously to obtain two types of residual liquors.

Residual liquor 1 was obtained under the feed flow rate of 0.34 L m^{-2} h^{-1} and water flow rate of 0.34 L m^{-2} h^{-1}. Residual liquor 2 was obtained under the feed flow rate of 0.34 L m^{-2} h^{-1} and water flow rate of 0.68 L m^{-2} h^{-1}. The obtained residual liquors were used as the feed solution for the following ED process.

2.3. Electrodialysis (ED) for the residual liquors

The laboratory-scale setup of ED was composed of (1) two electrodes which were made of titanium coated with ruthenium; (2) tanks (three 500 mL beakers) to store the solutions; (3) the direct current power supply (WYJ-0) which was supplied by Shanghai Quanli Electronic Equipment Co., Ltd., China; (4) the peristaltic pump (BT300-2J) which was supplied by Baoding Longer Pump Co., Ltd., China; and (5) the membrane stack as illustrated in Fig. 3. The stack was comprised of membranes and several Plexiglas spacers. The effective area of each membrane sample was 20 cm^2. Two sheets of anion exchange membrane and three sheets of cation exchange membrane were used, and thus the total effective membrane area was 100 cm^2. The plexiglas spacers, with thickness of 10 mm, contained a round hole in the middle using silicon rubber as the seals. Each chamber was circulated for several minutes before the experiment to eliminate the visible bubbles [20].

Three kinds of solutions were used in ED process. The residual liquors from DD process (250 mL) were used as the feed; H_2SO_4 (250 mL, 0.2 *M*) was used as the electrode rins-

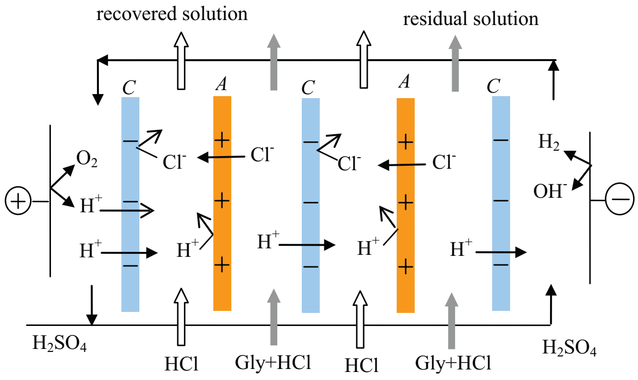

Fig. 3. Schematic configuration of the ED membrane stack (“*A*” and “*C*” are anion and cation exchange membranes correspondingly).

ing solution, and HCl (250 mL, 0.1 *M*) was used as the initial solution for the acid tank.

2.4. Date analyses and calculations

The Gly concentration was determined by UV spectrophotometer at 242 nm [21]. 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 concentration of NaOH was 0.10 *M*, and methyl orange was used as the titration indicator.

The DD and ED performances are evaluated by HCl recovery ratio (R_H) and Gly rejection (η_{Gly}). Besides, the DD performance is also evaluated by water osmosis coefficient (U_{H2O}).

$$U_{H2O}(m/h) = (Q_{res} - Q_{feed})/A \tag{1}$$

where Q_{res} is the out flow of residual solution (L h^{-1}), Q_{feed} is the inlet flow of acidic liquor (L h^{-1}), A is the total effective membrane area (m^2).

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

where Q_d is the out flow of recovered acid (L h^{-1}), C_{d-H} is the HCl concentration in the recovered solution (*M*), and C_{f-H} is the HCl concentration in the acidic liquor (*M*).

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

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

The ED performance can be further evaluated by current efficiency η (%) [22] and energy consumption *E* (kW h kg^{-1}) [9]:

$$\eta = \frac{n \cdot (C_t - C_0) \cdot V \cdot F}{N \cdot I \cdot t} \tag{4}$$

Here C_0 and C_t (*M*) are the recovered HCl concentration at time 0 and *t*, respectively. *n*, *V*, *F*, *N*, *I* and *t* are the ion's absolute valence (*n* = 1), the solution volume in acid cell (L), the Faraday constant (96500 C mol^{-1}), number of repeating units of the stack, the current used in the stack (*A*) and the test time (*s*), respectively.

$$E = \int_0^t \frac{U \cdot I \cdot dt}{(C_t - C_0) \cdot V \cdot M} \tag{5}$$

Here *U* is the total voltage drop across the entire stack (*V*); *M* is the HCl molar mass.

3. Results and discussions

3.1. Continuous DD for separating the acidic liquor

The DD performance was compared among different membranes in our previous work [8], which showed membrane G-T had optimized stability and acid recovery ability. Hence, membrane G-T is used at different feed conditions for the recovery of two type residual liquors as shown in Table 2.

The DD running at 0.34 L m^{-2} h^{-1} for both feed and water shows the HCl recovery ratio (R_H) of 29.2% and Gly rejection of 98.6%. The obtained residual liquor 1 contains 1.66 *M* HCl and 153.9 g L^{-1} Gly. The DD running at 0.34 L m^{-2} h^{-1} for feed and 0.68 L m^{-2} h^{-1} for water shows higher water osmosis of 1.16 × 10^{-4} m h^{-1}, higher R_H of 35.9% and similar Gly rejection of 96.8%. The obtained residual liquor 2 contains 1.32 *M* HCl and 127.8 g L^{-1} Gly. Hence, a part of HCl component can be recovered, and most of Gly can be retained in the residual liquor. However, the Gly concentration in the residual liquor (127.8–153.9 g L^{-1}) is still significantly lower than that in the acidic liquor (168–180 g L^{-1}) due to the Gly leakage and water osmosis. Moreover, the HCl concentration in the residual liquor is still in a high range (1.32–1.66 *M*), which restricts the precipitation of Gly in the residual liquor. Though the Gly can be precipitated after the concentration of residual liquors [7,8], the energy consumption is too high to be suitable for large scale production.

The water osmosis and high residual HCl concentration are attributed to the limits of DD process, which uses the concentration gradient as the driving force. Hence in this work, ED is applied to further recover the HCl component in residual liquors (1 and 2). Besides, the acidic liquor is also directly separated by ED process as comparison. The current density is adjusted to optimize the ED performance. The obtained residual solution will be directly precipitated to obtain Gly product.

3.2. Water reverse osmosis during ED process

The ED process shows water reverse osmosis from the feed chamber to the recovery chamber. The volume of recovered solution increases from initial 250 mL to 256–285 mL at 20–50 mA cm^{-2}, while the volume of feed solution decreases. The reverse osmosis is contrary to the water osmosis in DD process, which is a good news for the combination of DD and ED processes. Continuous DD process shows that the water osmosis is in the range of 0.67–1.16 ×

Table 2
Continuous DD performances for separating the acidic liquor

Flow rate/ L m^{-2} h^{-1}	0.34 for both feed and water		0.34 for feed and 0.68 for water	
Solution type	Residual liquor 1	Recovered acid 1	Residual liquor 2	Recovered acid 2
HCl/mol L^{-1}	1.66	0.98	1.32	0.54
Gly/g L^{-1}	153.9	3.01	127.8	3.11
R_H/ %	29.2	–	35.9	–
Gly rejection/ %	98.6	–	96.8	–
Water osmosis/ m h^{-1}	0.67 × 10^{-4}	–	1.16 × 10^{-4}	–

10^{-4} m h^{-1} (Table 2). The DD process increases the volume of residual liquor, while the ED process decreases the volume of residual solution. The balanced volume is beneficial to precipitate the Gly product.

The contrary osmosis of DD and ED processes should be attributed to their different driven force and thus different transport mechanisms. Here only a tentative explanation is given. The DD process, driven by concentration gradient, can transport water from water side to feed side [7]. The ED process, driven by electric field, can transport H$^+$ and Cl$^-$ ions from the feed chamber to recovery chamber. The ions are hydrated and thus the ions are transported along with the water.

3.3. Recovered HCl concentration by ED process

Three types of liquors including acidic liquor, residual liquors 1 and 2 are separated by the ED process. The recovered HCl concentration as shown in Fig. 4, increases linearly with the current density and the time. The linear increasing concentration is one of the advantages of ED process with respect to the DD process. The ED is driven by electric field, which is adjustable to fix the voltage drop or current density. The fixed current density can obtain the fixed ion transport rate and thus high recovery ratio (46%–57% for 10h at 40 mA cm^{-2}). On the contrary, the driven force of DD process decreases with the increasing ions concentration in the recovered solution, which restricts the ion transport rate and recovery ratio (29.2–35.9%).

The ED process is always accompanied with the acid leakage due to the concentration gradient among different chambers [23]. For example, the recovered HCl concentrations are also affected by the feed concentrations. The acidic liquor, due to its high HCl concentration and thus high concentration gradient, is more likely to permeate HCl component from the feed chamber to the acid chamber. Hence, the acidic liquor has the highest recovered HCl concentrations, while the residual liquor 2 has the lowest concentrations under the same current density and time.

The HCl concentrations in residual solutions at 50 mA cm^{-2} after 10 h are 1.57 *M*, 0.38 *M* and 0.19 *M* for the acidic liquor, feed liquor 1 and 2, respectively. The high residual concentration for the acidic liquor means that longer time is needed to further recover the HCl component, which indicates that more energy would be consumed for single ED process. The low concentrations for residual liquors are attributed to the combination of DD and ED processes,

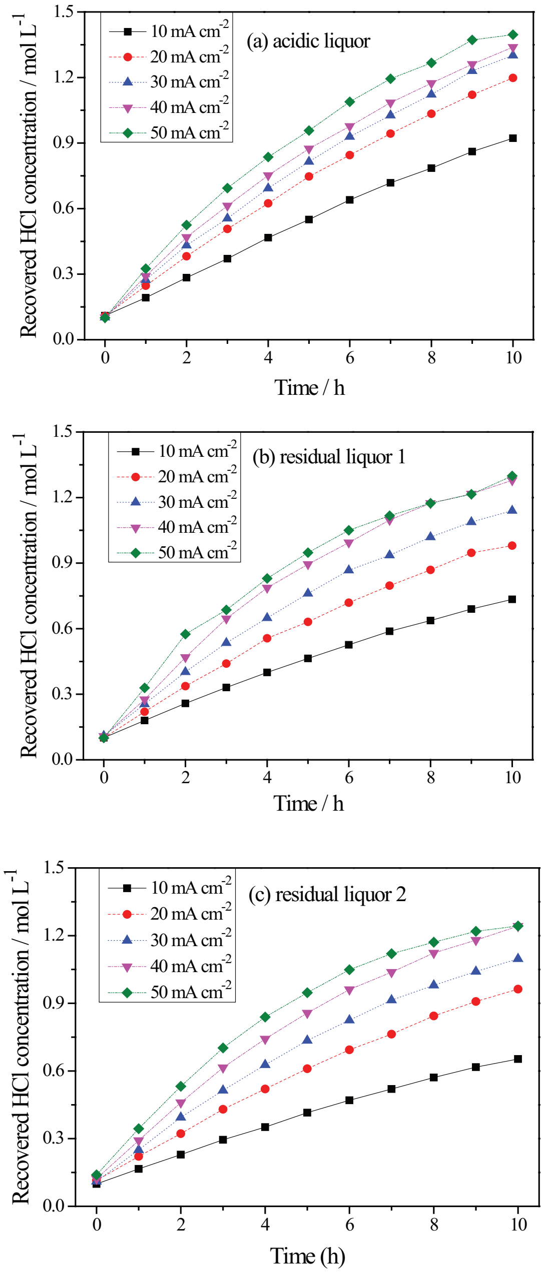

Fig. 4 Recovered HCl concentration after ED process for (a) the acidic liquor, (b) residual liquor 1 and (c) residual liquor 2.

which recover most of HCl component and thus save the energy.

3.4. HCl recovery ratio and Gly rejection

The ED separation performances after running 10 h are evaluated by the HCl recovery ratio and Gly rejection as shown in Fig. 5. The HCl recovery ratio increases with the current density, for more H^+ and Cl^- ions are transported at high current density. However, the increasing rate becomes slow due to the restriction of recovered HCl concentration. Besides, the recovery ratio of residual liquor 2 is higher than that of residual liquor 1, which may be attributed to their different water content. Residual liquor 2 has higher water content (53%) that residual liquor 1 (48%) due to its higher water osmosis during DD process. The higher water content should be beneficial to the ions transport [6].

The Gly rejection decreases from 96.3–97.2% to 74.9–77.0% as the current density increases, for high current density brings high driven force to the Gly component. However, the Gly rejection is still at a high level, indicating that most of Gly component can be retained in the residual solution. Besides, the decreasing rate increases as the current density increases, indicating that low current density is more suitable to elevate Gly concentration in the residual solution.

3.5. Voltage drop during ED process

The voltage drop as shown in Fig. 6, decreases in the initial 1 h, which is attributed to the increasing concentration in the recovered solution. The voltage is then stable at 10–20 mA cm^{-2} during subsequent operation, for the HCl concentration increases in the recovery chamber while decreases in the feed chamber smoothly.

The voltage goes up in the latter stage at high current densities such as 40–50 mA cm^{-2}. The HCl concentration decreases more rapidly in the feed chamber at high current densities, whose resistance would increase significantly as the HCl component depletes. For example, as the HCl concentration in residual liquor 2 is much lower than that in the acidic liquor, the voltage increases more significantly for residual liquor 2 than that for the acidic liquor at latter stage.

The voltage drop at 40–50 mA cm^{-2} is in the range of 8.1–11.6 V in the initial 5 h for the acidic liquor, while the

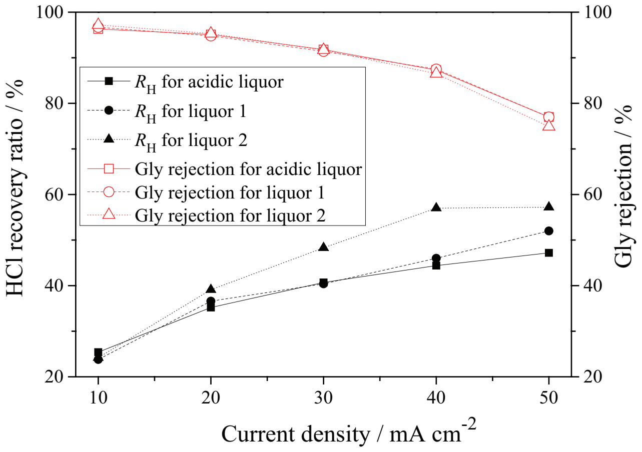

Fig. 5 HCl recovery ratio (R_H) and Gly rejection after ED running 10 h. Note: the standard error is only in the range of 0.1–1.2 (for the acidic liquor).

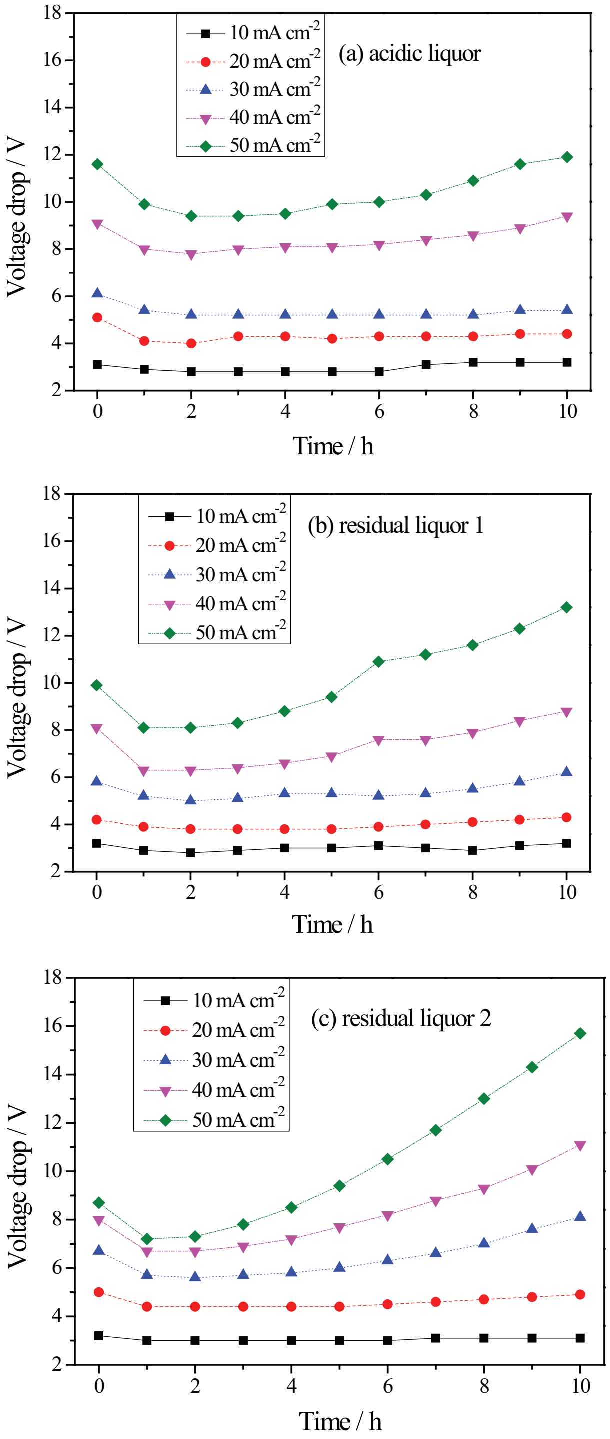

Fig. 6 Voltage drops during ED process for (a) the acidic liquor, (b) residual liquor 1 and (c) residual liquor 2.

values are in the range of 6.3–9.9 V for the residual liquors. The higher voltage drop for the acidic liquor is attributed to its low water content (~40%). The low water content may restrict the ions transport [6] especially at high current densities. The residual liquors, due to their water osmosis during DD process, have higher water content of about 48.1–52.8%. The increased water content is beneficial to the ions transport and thus may reduce the resistance.

3.6. Current efficiency

The current efficiency decreases as the current density increases, as shown in Fig. 7. The values at 10 mA cm^{-2} are not listed in the figure, for the values can even be higher than 100%. The abnormal values are examined again, and then checked by the HCl leakage at no current density. The leakage at no current density can be reflected from the dialysis coefficient of HCl, which is measured here according to previous method [6]. The dialysis coefficient of HCl is 0.0013–0.0024 m h^{-1} for membrane AMX at 15–25ºC, indicating the HCl component can easily transport through the membrane under concentration gradient. Though the leakage of HCl should be different after application of electric field, the leakage under concentration gradient may still be significant during ED process.

The significant leakage should be attributed to the low size and valence of H^{+} ions, which have much higher activity than the other ions. Hence, the HCl component is transported by the driven forces of both concentration gradient and electric field. The transport of HCl under concentration gradient enhances the current efficiency especially at low current density.

The current efficiency decreases linearly with the time, which should be also correlated with the acid transport under concentration gradient. The concentration gradient decreases due to the decreasing concentration in the feed chamber and the increasing concentration in the recovery solution. As the time further prolongs, the concentration in the feed can be lower than that in the recovery solution, and thus the concentration gradient is contrary with that in the initial stage. The decreasing or contrary concentration gradient reduces the current efficiency. For example, the residual liquor 2, due to its lower initial acid concentration (1.32 mol/L), has lower concentration gradient and thus lower current efficiency than the other feed liquors. Besides, the leakage of other components such as Gly becomes more serious as the feed concentration decreases (Fig. 5), which also reduces the current efficiency.

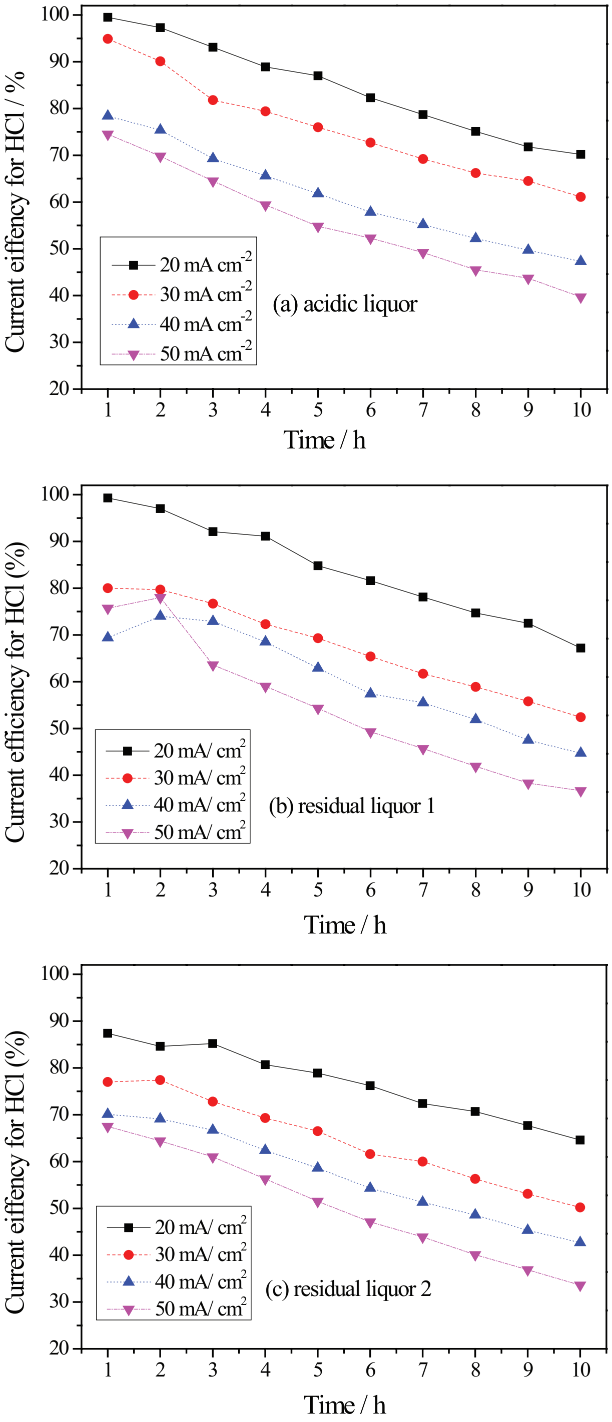

Fig. 7 Current efficiency during ED process for (a) the acidic liquor, (b) residual liquor 1 and (c) residual liquor 2.

3.7. Energy consumption

Fig. 8 shows the energy consumption increases with the current density, which is in accordance with previous reports [24]. The energy must be consumed in ED process due to the driven force of electric field, which is used to transport ions and to overcome the resistance. The resistance would increase with the ion transport rate. The DD process, on the other hand, consumes no obvious energy due to no electric field. The energy only is required in running the solutions, which can be neglected when compared to the high energy consumption in ED process. For example, energy of 1 kWh can elevate 1000 kg solution to a height of 367 m theoretically, while the energy consumption is in the range of 0.8–10 kWh kg^{-1} in our ED process. Hence, the combination of DD and ED processes is essential to balance the energy consumption.

The energy consumption of residual liquors is in the range of 1.14–4.66 kWh kg^{-1} at low current densities (10–30 mA cm^{-2}). The energy consumption increases rapidly at high current density (40–50 mA cm^{-2}), which is more significant for the acidic liquor. The rapid increase of energy consumption should be mainly attributed to the increased resistance, decreased current efficiency and the low water content in the liquors. Firstly, high current density means that the ions are transported more rapidly, which is accompanied by high friction among ions and solvent. Secondly, the current efficiency decreases as the current density increases, which means that more energy is wasted. Finally, the low water content in the liquors restricts the ions transport rate, for the ions need to be transported in hydrated state and in aqueous media [25].

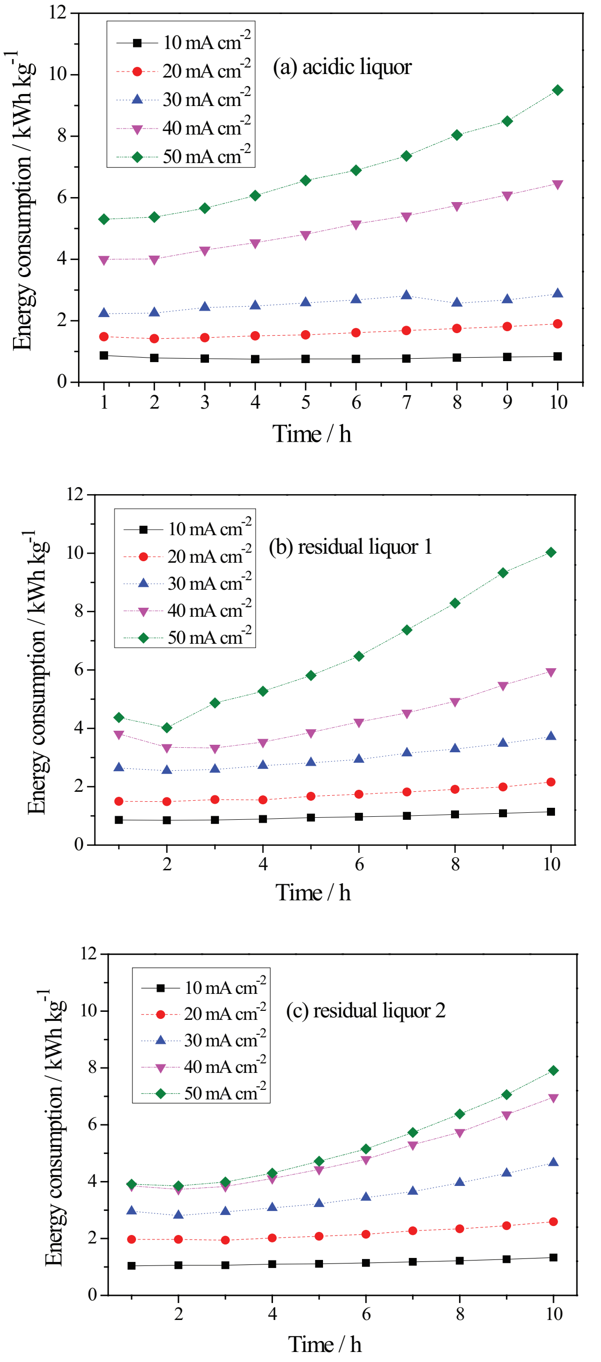

Fig. 8. Energy consumption during ED process for (a) the acidic liquor, (b) residual liquor 1 and (c) residual liquor 2.

The acidic liquor has the lowest water content (40 wt%), and thus more energy is consumed at high current density. For example, the energy consumption is in the range of 4.0–6.46 kWh kg^{-1} at 40 mA cm^{-2}, and 5.3–6.89 kWh kg^{-1} at 50 mA cm^{-2} in the initial 6 h, which are all higher than those of residual liquor 1 (3.81–5.95 and 4.37–6.47 kWh kg^{-1} correspondingly). However, the HCl component in residual liquor 1 is more likely to be depleted due to its lower concentration, and thus its energy consumption increases more rapidly at 50 mA cm^{2} in the latter 4 h.

3.8. Gly productivity and purity

The acidic liquor and residual liquors are separated by the ED process to obtain recovered HCl and residual solutions. The residual solution from the acidic liquor still contains 1.6 *M* HCl, which is much higher than the concentration of pH 1.5. The Gly can not be precipitated directly due to the high HCl concentration. The residual solutions 1 and 2 contain 0.38–1.10 *M* HCl and 0.19–0.71 *M* HCl correspondingly. Though the concentrations are still higher than the ideal concentration of pH 1.5, the Gly can be precipitated directly after standing for 10 h. The direct precipitation overcomes the defects of previous neutralization and concentration methods [2–4,6–8], which waste plenty of NaOH resource and energy, and also induce secondary pollution. Hence, the combination of DD and ED may become the foundation for the practical separation of the acidic liquor.

The Gly productivity and purity are shown in Table 3. The productivity increases with the current density, for high current density can recover more amount of HCl and thus obtain lower HCl concentration in residual solution. The highest Gly productivity is 59.0% and 32.6% for residual liquors 1 and 2, with the purity of 84.2% and 89.9% correspondingly. The purity is higher than previous values obtained from single continuous DD process (71.3–89.6% [7], and 71–82% [8]). Previous single continuous DD process, if used QPPO/PVA membrane, obtained residual liquor containing 0.71 *M* HCl and 109.8 g/L Gly [7]. The residual liquor was neutralized by NaOH and then concentrated to obtain 58.3% Gly product. The single DD process, if used membrane G-T, obtained residual liquor containing 1.32 *M* HCl amd 132.1 g/L Gly [8]. The

Table 3
Gly productivity and purity from the residual solutions

	Current density/ mA cm^{-2}	10	20	30	40	50
Residual liquor (solution) 1	Productivity/%	19.7	23.4	34.4	49.5	59.0
	Purity/%	84.2	86.9	91.0	85.1	84.2
Residual liquor (solution) 2	Productivity/%	–	13.8	25.5	28.0	32.6
	Purity/ %	–	83.1	82.9	94.0	89.9

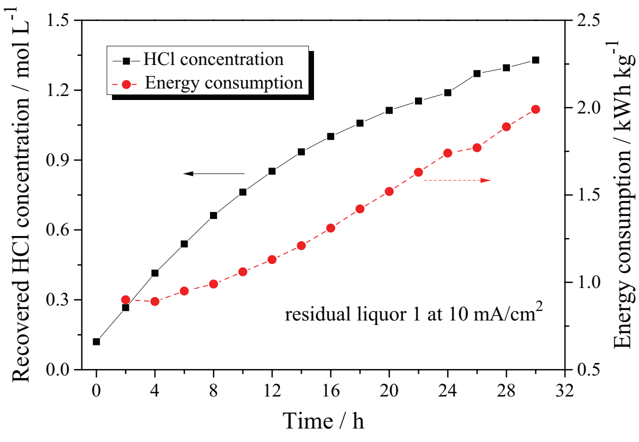

Fig. 9. ED performances for residual liquor1 by extending time at 10 mA cm^{-2}.

high HCl concentration restricted the precipitation of Gly. Hence, the residual liquor had to be evaporated to remove 10–50% solvent, and then was precipitated to obtain 20.9–83.3% Gly productivity.

3.9. Prolonged running time at low current density

The above investigation shows that as the ED running time is fixed at 10 h, the recovered HCl concentration, Gly productivity and energy consumption all increase with the current density. The increasing concentration and Gly productivity are attributed to the decreasing HCl concentration in residual solution. Hence, low current density may be selected with prolonged running time to reduce the energy consumption. Residual liquor 1 is selected for running 30 h at 10 mA cm^{-2}, as shown in Fig. 9.

The recovered HCl concentration increases from 0.12 to 1.33 *M*, which recovers 48.0% HCl component after running 30 h. As the previous DD process recovers 29.2% HCl component, total 77.2% HCl component is recovered after the combination of DD and ED process. The energy consumption increases from 0.90 to 1.99 kWh kg^{-1}, which is much lower than the values at high current densities (5.95–10.03 kWh kg^{-1} after 10 h). Hence, low current is more suitable to save energy.

Besides, the volume of recovered solution increases from 250 mL to ~280 mL after running 30 h, indicating the water reverse osmosis of ED process. The residual solution can be precipitated directly to obtain Gly product. The Gly productivity is 51.0% with the purity of 87.4%.

4. Conclusions

Continuous DD and ED processes are combined to recover HCl component and precipitate Gly product. The DD process can recover 29.2–35.9% HCl component and obtain residual liquors. The residual liquors are further separated by ED process, which can recover 23.8–57.2% HCl component. The ED running after 10h shows that as the current density increases, the recovered HCl concentration increases from 0.65 to 1.30 *M*, the current efficiency decreases, and the energy consumption increases from 1.14 to 10.03 kWh kg^{-1}. The residual HCl concentration can be only 0.19–0.38 *M*, which is beneficial to precipitate the Gly product. The Gly can be directly precipitated with the productivity of 13.8–59.0% and the purity of 83.1–94.0%. The ED running after 30 h shows that the low current density (10 mA cm^{-2}) can save energy to 1.99 kWh kg^{-1}, and precipitate 51.0% Gly product with the purity of 87.4%.

The DD process consumes insignificant energy, but has significant water osmosis and high residual HCl concentration. The ED process, on the contrary, has the advantages of water reverse osmosis and low residual HCl concentration, but consumes high energy. Hence, the combination of DD and ED processes can not only balance the water osmosis and energy consumption, but also recover most of HCl component and precipitate Gly directly. The combination may become the foundation for practical separation of the acidic liquor.

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Symbols

Gly — Glyphosate (g L^{-1})
DD — Diffusion dialysis
ED — Electrodialysis
M — mol L^{-1}
PVA — Polyvinyl alcohol
DMP — Glycine-dimethylphosphite
$C_{f\text{-}H}$ — HCl concentration in the acidic liquor (mol L^{-1})
$C_{d\text{-}H}$ — Recovered HCl concentration (mol L^{-1})
$C_{f\text{-}Gly}$ — Glyphosate concentration in the feed solution (acidic liquor) (g L^{-1})
$C_{d\text{-}Gly}$ — Glyphosate concentration in the recovered acid (g L^{-1})
η_{Gly} — Glyphosate rejection (%)
Q_{res} — Out flow of the residual solution (L h^{-1})
Q_d — Out flow of recovered HCl solution (L h^{-1})
Q_{feed} — Inlet flow of the acidic liquor (L h^{-1})
U_{H2O} — Water osmosis coefficient (m h^{-1})
R_H — HCl recovery ratio (%)
E — Energy consumption (kWh kg^{-1})
η — Current efficiency (%)

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