Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22993

133 (2018) 37–44
November

Combination of continuous diffusion dialysis and electrodialysis for separating $NaOH/NaAlO_2$ solution

Yonghui Wu*, Yan Li, Xue Du, Lingfei Zou

School of Chemistry and Environmental Engineering, Yancheng Teachers University, Yancheng, Jiangsu 224051, China, Tel. +86-515-88233188, emails: wuyonghui1000@126.com (Y. Wu), 2361918594@qq.com (Y. Li), 1569439319@qq.com (X. Du), 603411257@qq.com (L. Zou)

Received 20 February 2018; Accepted 18 August 2018

ABSTRACT

Diffusion dialysis (DD), driven by concentration gradient, has inherent defects such as significant water osmosis, low transport rate, and recovery ratio. Meanwhile, electrodialysis (ED) is driven by electric field, which has high transport rate but consumes significant energy. Hence, the DD and ED processes are combined here to separate $NaOH/NaAlO_2$ solution. The continuous DD process is first used to separate the alkaline solution, which is equipped with self-prepared polyvinyl alcohol (PVA)-based cation exchange membrane. The running condition is optimized at feed flow rate of 0.83 L m^{-1} h^{-1} and water flow rate of 1.0 L m^{-1} h^{-1}, which can obtain recovered NaOH of 0.66 mol L^{-1} (M), recovery ratio of 44.4%, and rejection ratio of 91.2%. The residual liquor is further separated by ED process. The ED process running at 20 mA cm^{-2} for 2 h can recover 0.40 M NaOH. The current efficiency is 79.4% and the energy consumption is 2.2 kWh kg^{-1}. The combination of DD and ED processes can remove 97.9% NaOH with the AlO_2^- rejection ratio of 85.4%. The energy is greatly saved due to insignificant energy consumption in DD process. Hence, the combination can elevate separation efficiency and save energy.

Keywords: Diffusion dialysis (DD); Electrodialysis (ED); Polyvinyl alcohol (PVA) membrane; Alkaline recovery; Energy consumption

1. Introduction

Diffusion dialysis (DD), driven by concentration gradient, is a natural separation process. The process is characterized by low energy consumption and environmental friendliness, which is running in a batch or continuous dialyzer. The batch dialyzer generally uses a membrane of a small area (e.g., 5.7 cm^2 [1] or 4 × 4 cm^2 [2]) to separate two compartments. The acid or base component can be transported from one compartment with the other compartments and thus it is recovered. The batch dialyzer is suitable for lab-scale research but cannot be used in industrial separation due to its low membrane area and static solution. The continuous dialyzer contains dozens sheets of membranes, which are imported with the feed and water and then exported as the residual and recovery solutions correspondingly. The continuous dialyzer has been widely used in separating HCl, H_2SO_4, and HNO_3 [3–5]. Over 84% H_2SO_4 was recovered and 85%–93% metal ions are rejected for the acid leaching solution generated in vanadium producing process [4].

However, as the DD process is driven by concentration gradient, it has some inherent defects including low transport rate [6] and significant water osmosis in some cases [7]. More precisely, the ions transport rate decreases with the time due to the decreasing concentration gradient. Hence, the acid or base cannot be completely recovered. For example, a batch dialyzer was used to separate an alkaline aluminum solution of $NaOH/NaAlO_2$, which was the intermediate product during the production of aluminum. Theoretically, the NaOH component needed to be separated and then the $Al(OH)_3$ could be more easily precipitated. However, the OH^- recovery ratio was only 6.3% after 4 h in the batch dialyzer [6], which was too low to precipitate the $Al(OH)_3$.

---

* Corresponding author.

1944-3994/1944-3986

The water osmosis reduces the flow rate of recovery solution and enlarges the flow rate of residual solution. The reduced flow rate of recovery solution decreases the recovery ratio, while the enlarged flow rate of residual solution decreases its concentration. For example, a type of acidic liquor containing HCl, glyphosate, and other organic components was separated by continuous DD process [8]. The water osmosis was in the range of 1.95–5.98 × 10^{-4} m h^{-1}, which reduced 1/2–1/3 flow rate of the recovery solution. The recovery ratio was only 42% at the flow ratio of 1: 1 (water/feed), and the glyphosate could not be precipitated directly due to its low concentration

Hence, the DD process needs to be combined with other separation processes, such as vacuum distillation [9] and electrodialysis (ED) [10–13]. The ED process is driven by electric field, which shows some advantages when compared with the concentration gradient. Firstly, the force of electric field is stronger than that of concentration gradient. Hence, the ions transport rate is accelerated, and the flux is significantly elevated in ED process [13]. Secondly, the electric field is adjustable through a direct current power supply, which can fix the current density and the ion transport rate. The concentration in recovery solution can be higher than that in the residual solution [12]. Finally, the water osmosis may be less significant [13] due to the fast transport rate of hydrated ions. The transported ions also bring water molecules from the feed solution to the recovery solution, which is contrary to the water osmosis induced by the concentration gradient.

Though the combination of DD and ED processes shows those advantages in acid recovery [10–13], the combination has not been reported in alkali recovery, which should be mainly attributed to the high corrosive alkaline solution and the low transport rate of OH^- ions when compared with H^+ ions. For example, the dialysis coefficient of OH^- ions (U_{OH}) is only 0.003 m h^{-1} for commercial cation exchange membrane FSB [6], which is much lower than the HCl dialysis coefficient of commercial anion exchange membrane DF-120 (0.009 m h^{-1} at 25°C [14]). Hence, on one hand, single ED process was used to separate the $NaOH/NaAlO_2$ solution, which was high efficient but it consumed much energy (7.29–7.65 kWh kg^{-1} [15]). On the other hand, high stable and permeable membranes were developed, which contained –OH groups to accelerate the transport rate of OH^- ions in DD process [16,17]. The membrane had been used in batch dialyzer to evaluate its permeability, but it still not been used in continuous dialyzer for practical separation.

Hence in this work, the continuous DD will be combined with ED process to separate $NaOH/NaAlO_2$ solution. The DD process consumes insignificant energy, which uses polyvinyl alcohol (PVA)-based cation exchange membrane due to its favorable alkali permeability. The ED process consumes high energy, which uses commercial membranes due to their high stability. The feed solution will be firstly separated by the continuous DD process to recover a part of the NaOH component and to obtain residual liquor. The residual liquor is standing for about 1 week to precipitate some gibbsite ($Al(OH)_3$ and its complex), and then is separated by the ED process to further recover the NaOH component. The effect of current density is fully investigated on the ED performances, including the recovered NaOH concentration, recovery ratio, voltage drop, current efficiency, and energy consumption.

2. Experimentals

2.1. Membrane materials

All reagents were purchased from the company of China. PVA, with the average degree of polymerization 1,750 ± 50, was supplied by Shanghai Sinopham Chemical Reagent Co., Ltd (Shanghai, China). Purified water was supplied by Tidynet purified Water Company (Yancheng). Anion exchange membrane Neosepta AMX and cation exchange membrane Neosepta CMX (ASTOM Corp, Japan) were used in the ED process, whose properties were cited in the previous work [18] and listed in Table 1.

Membrane SP was used in the continuous dialyzer, which was prepared from PVA and multisilicon copolymer. The preparation process was similar to previous work [16] but with higher dosage of PVA component, for high content of PVA could enhance membrane flexibility and thus the membrane was more suitable to be mounted in the continuous dialyzer. The multisilicon copolymer was prepared from the copolymerization of sodium styrene sulfonate and γ-methacryloxypropyl trimethoxy silane. The copolymer solution (10 g) was added into 5 wt% PVA solution (30 g) and then stirred at 60°C for 18 h. Subsequently, the mixture was cast onto glass plates, and dried at room temperature for 2 d. The formed film was peeled off from the glass plates, heated from 60°C to 120°C at the rate of 10°C h^{-1}, and kept at 120°C for 4 h to get the hybrid membrane. The membrane had the thickness of ~150 μm.

2.2. Properties of membrane SP

Membrane SP was characterized by water uptake, ion exchange capacity (IEC), and batch DD process according to previous methods [6,14]. The batch DD process was used to separate $NaOH/NaAlO_2$ solution at room temperate, from which the dialysis coefficients of OH^- and AlO_2^- ions (U_{OH} and U_{AlO_2}), together with separation factor, were calculated [6].

The water swelling resistance was measured by immersing membrane sample in 65°C water for 192 h [16], after which the swelling degree and weight loss percent were calculated. The alkaline resistance was measured by immersing the dried membrane sample (m_1) in 65°C NaOH solution (0.1–2 M) for 60 h. Then the sample was washed with water for four times. The sample surface was wiped with filter paper and weighed as m_2. Finally, the sample was dried at

Table 1
Properties of the anion exchange membrane (AEM) and cation exchange membrane (CEM) used in ED process [18]

Manufacturer	Tokuyama Co., Japan	Tokuyama Co., Japan
Membrane name	Neosepta AMX	Neosepta CMX
Membrane type	AEM	CEM
Thickness, μm	134	164
IEC, meq g^{-1}	1.25	1.62
Water uptake, %	16	18
Area resistance, Ω cm^2	2.35	2.91
Transport number, %	91	98

65°C till constant weight and weighed as m_3. The swelling degree was calculated as $(m_2–m_3) \times 100\%/ m_3$. The weight loss percentage was calculated as $(m_1–m_3) \times 100\%/ m_1$.

2.3. Continuous DD for the feed solution to obtain residual liquor

The feed solution containing NaOH and $NaAlO_2$ was prepared by a chemosynthesis method as described previously [6]. The concentrations of NaOH and $NaAlO_2$ were 1.22–1.56 and 0.39–0.41 M, correspondingly. The AlO_2^- concentration was determined by addition of excess disodium ethylenediamine tetraacetic acid (EDTA-Na) and then back-titration with $CuSO_4$, and the OH^- concentration was determined by addition of excess HCl and then back-titration with Na_2CO_3, using methyl orange as an indicator [15].

Membrane SP was firstly immersed in water for 1 d, and then 11 sheets of the membranes were mounted in the continuous dialyzer. Each sheet had the area of 0.02 m² with an effective area of 0.0082 m². The dialyzer had two channels, as shown in Fig. 1(a). One channel, used as the feed side, was imported with the feed solution and exported with the residual liquor. The other channel, used as the water side, was imported with water and exported with the recovered NaOH. The flows of entering streams (feed and water) were controlled by two peristaltic pumps, while the outlet flow rates were measured by collecting the recovered solution and residual liquor every 0.5 h. The DD was running for 2–3 h to reach a dynamic equilibrium state before timekeeping [4], and then running continuously to obtain the residual liquor. The running condition was optimized by firstly fixed the feed flow rate at 0.4 L m^{-2} h^{-1} and increasing the flow ratio (water/feed) from 1.2, 1.4, 1.6, to 1.8. Then the flow ratio was fixed, and the water flow rate increases from 0.4, 0.6, 1.0, to 1.6 L m^{-2} h^{-1}. The obtained residual liquor at optimized running condition was used as the feed for the following ED process.

2.4. Electrodialysis for the residual liquor

The laboratory-scale setup of ED, similar to previous reports [15] but with enlarged membrane area, was composed of (1) two electrodes which were made of titanium coated with ruthenium; (2) tanks to store the 250 mL 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 was composed of three repeating units, as illustrated in Fig. 1(b). The effective area of each membrane sample was 20 cm². 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 about 0.25 h before the experiment to eliminate the visible bubbles [19].

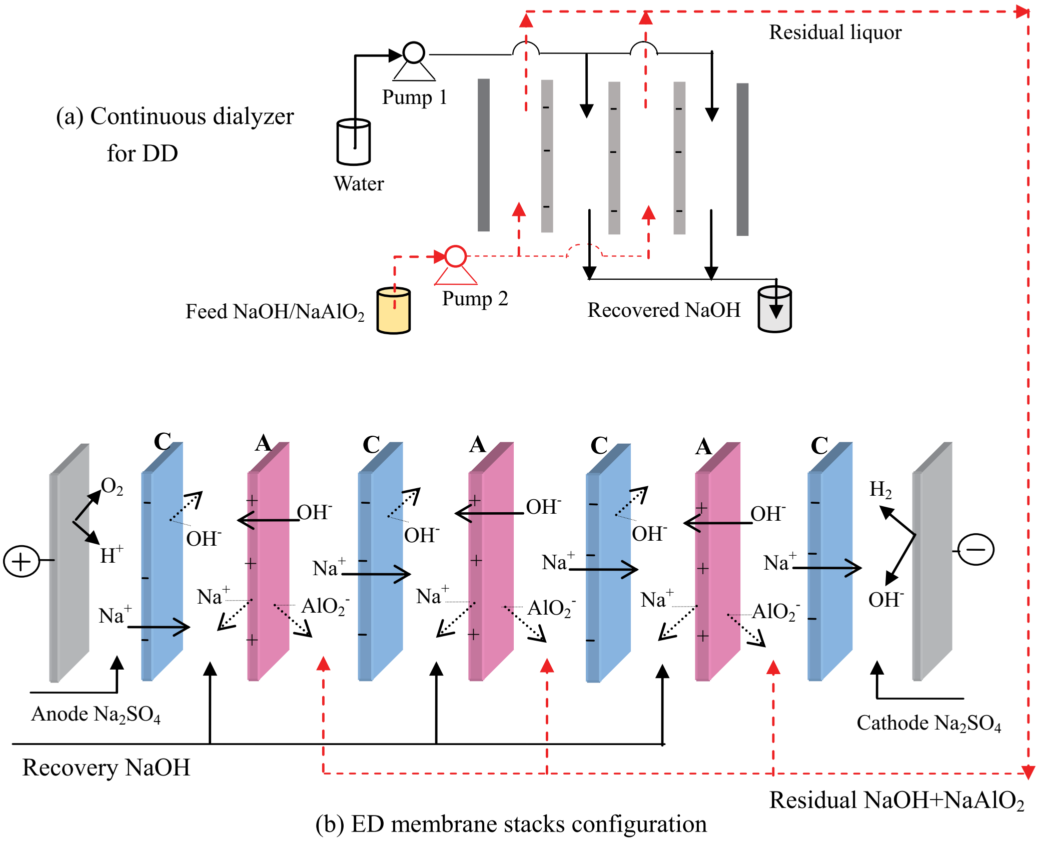

Fig. 1. (a) Continuous dialyzer for diffusion dialysis (DD); and (b) ED membrane stacks configuration containing three cell pairs. *C* is the cation-exchange membrane CMX; *A* is the anion-exchange membrane AMX.

Three kinds of solutions were used in ED running. The residual liquor from DD process was used as the feed; Na_2SO_4 (0.5 M) was used as the electrode rinsing solution, and NaOH (0.1 M) was used as the initial solution for the base tank.

2.5. Date analyses and calculations

The DD and ED performances are evaluated by NaOH recovery ratio (R_{OH}) and AlO_2^- rejection ratio (η_{AlO_2}). Besides, the DD performance is also evaluated by water osmosis coefficient (U_{H_2O}).

$$U_{H_2O}\left(\frac{m}{h}\right)=\frac{\left(Q_{res}-Q_{feed}\right)}{A} \tag{1}$$

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

$$R_{OH}\left(\%\right)=\frac{Q_d Q_{d-OH}}{Q_{feed} C_{f-OH}}\times 100 \tag{2}$$

where Q_d is the outflow of recovery solution (L h^{-1}), $C_{d\text{–}OH}$ is the NaOH concentration in the recovery solution (M), and $C_{f\text{–}OH}$ is the NaOH concentration in the feed (M).

$$\eta_{AlO_2}\left(\%\right)=\left(1-\frac{Q_d C_{d-AlO_2}}{Q_{feed} C_{f-AlO_2}}\right)\times 100 \tag{3}$$

where $C_{d\text{–}AlO_2}$ is the leaked AlO_2^- concentration in the recovery solution, and $C_{f\text{–}AlO2}$ is the AlO_2^- concentration in the feed.

The ED performance is further evaluated by current efficiency η (%) and energy consumption E (kW h kg^{-1}) [20]:

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

where C_0 and C_t (M) are the recovered NaOH 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 base cell (L), the Faraday constant (96,500 C mol^{-1}), number of the repeating units of the stack ($N = 3$), the current used in the stack (A), and the test time (s), respectively.

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

where U is the total voltage drop across the entire stack (V) and M is the NaOH molar mass. Besides, as the DD consumes insignificant energy, the combined energy consumption of DD and ED (E') can be calculated from Eq. (6):

$$E'=\int_0^t\frac{U\times I\times dt}{\left(C_t-C_0\right)\times V\times M+C_{d-OH}\times V'\times M} \tag{6}$$

where V' is the volume of recovery solution.

3. Results and discussion

3.1. Properties of membrane SP

Membrane SP has the water uptake of 63.3% and IEC of 0.33 mmol g^{-1}. The membrane is also tested in batch DD dialyzer to separate $NaOH/NaAlO_2$ solution. The batch DD process shows the membrane has the dialysis coefficient of OH^- ions (U_{OH}) of 0.0074 m h^{-1} with the separation factor of 10.8, as shown in Table 2.

Membrane sample SP is immersed in 65°C water for 192 h to investigate swelling resistance. The swelling degree is 197.8%, with the weight loss percent of 16.6%. The swelling degree is higher than that of previous membrane (74.4% after 216 h, [16]), which should be attributed to the lower dosage of multisilicon copolymer and thus lower cross-linking degree.

Membrane sample SP is also immersed in 65°C NaOH solution to investigate alkaline resistance. As the NaOH concentration increases, the swelling degrees decreases (243%), the percent weight loss increases (26.5%) and then it is balanced, as shown in Fig. 2. The decreasing swelling degrees may be partly attributed to the loss of functional groups. The OH^- ions may damage the functional groups (–OH and/or $–SO_3Na$) especially at high NaOH concentration and elevated temperature (65°C), which decreases the membrane hydrophilicity. The weight loss percent increases initially due to the increasing NaOH concentration and

Table 2
Properties of self-prepared membrane PS

Water uptake, %	63.3
IEC, meq g^{-1}	0.33
[1]Transport number, %	81 – 84
U_{OH}, m h^{-1}	0.0074
U_{AlO_2}, m h^{-1}	0.00068
Separation factor	10.8

[1]The transport number is cited from Ref. [21], which uses PVA-II membrane. The PVA-II membrane has the similar composition with membrane PS but it contains fiber support.

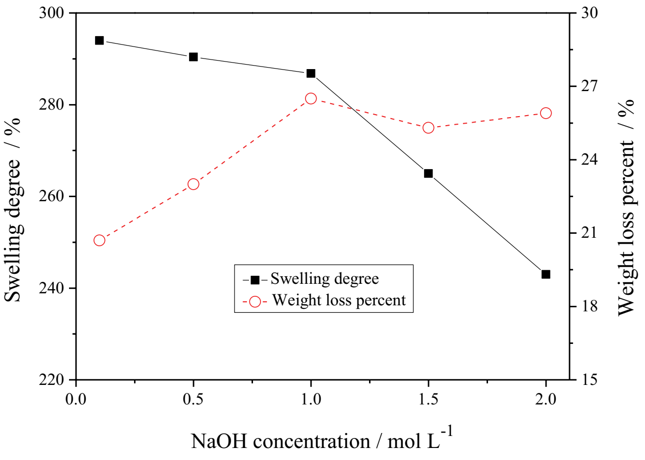

Fig. 2. Swelling degrees and weight loss percents of membrane PS in 65ºC NaOH solution.

thus increasing erosion. However, the decreasing swelling restricts the further erosion, which induces the balanced weight loss percents.

Membrane SP instead of commercial membrane is used in the continuous DD process due to its favorable hydrophilicity and plenty of PVA-OH groups. The –OH groups can accelerate the transport of OH^- ions [16,17]. The DD process consumes insignificant energy due to no electric field. The energy only is required in running the solutions, which can be neglected when compared with the high energy consumption in ED process.

3.2. Water osmosis in continuous DD process

Water osmosis, due to osmotic pressure across the membrane [22], decreases the flow rate of recovery solution. The flow rate of recovery solution can be elevated by increasing the water flow rate, which can increase the NaOH recovery ratio according to Eq. (2) in Section 2.5. Hence, here the water flow rates are all higher than the feed flow rate. The feed flow rate is firstly fixed at 0.4 L m^{-2} h^{-1}, while the flow ratio (water/feed) increases from 1.2 to 1.8. Then the flow ratio is fixed, and the flow rates of both water and feed increase.

The water osmosis (U_{H_2O}), flow rate of residual liquor and flow rate of recovery solution all increase with the increasing flow ratio or water flow rate, as shown in Fig. 3. The U_{H2O} increases from 3.6 to 7.7 × 10^{-5} m h^{-1} as the flow ratio increases from 1.2 to 1.8, while the values increase from 5.5 to 16.1 × 10^{-5} m h^{-1} as the flow rate increases. The U_{H_2O} values are lower than those of other feed (1.95–5.98 × 10^{-4} m h^{-1} for the acidic liquor [8]), and are only about 1/10 of the water flow rate, indicating that the water osmosis may not seriously reduce the DD performance. The water osmosis increases with the water flow rate, for the concentration of recovery solution decreases, and thus the concentration gradient across membrane increases. The concentration gradient should increase more significantly as the flow rates of both feed and recovery solutions increases. Hence, the water osmosis is more significant for the increasing flow rate.

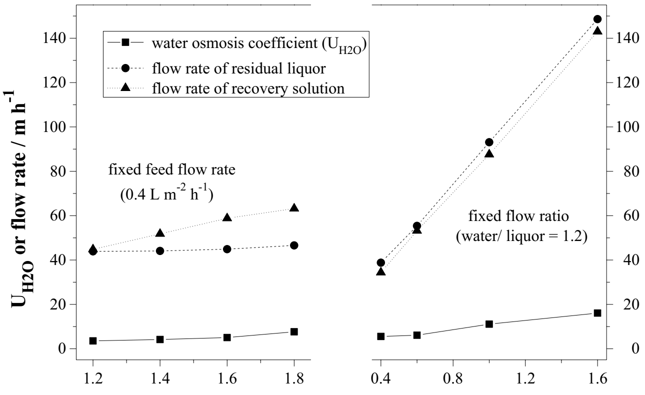

Fig. 3. Water osmosis coefficient (U_{H_2O}), flow rate of residual liquor and flow rate of recovery solution during the continuous DD process for the fixed feed flow rate (0.4 L m^{-2} h^{-1}) and the fixed flow ratio (water: feed = 1.2: 1).

3.3. Continuous DD with the increasing flow ratio

As the flow ratio increases, the ions concentrations generally decrease in both residual liquor and recovery solution, as shown in Fig. 4(a). For example, the OH^- concentration in the residual liquor decreases from 0.72 to 0.48 M, and the OH^- concentration in the recovery solution decreases from 0.48 to 0.37 M. The decreasing concentration in the residual liquor is partly attributed to the increasing water osmosis, and the decreasing concentration in the recovery solution is attributed to the increasing flow rate. The concentration of AlO_2^- ions is relatively stable within 0.27–0.29 M in the residual liquor, which is attributed to the low permeability of AlO_2^- ions for membrane SP. The AlO_2^- ion has larger size and is less likely to be transported through the PVA-OH groups when compared with the OH^- ion. Hence, the leakage of AlO_2^- ions is relatively low and its concentration is lower than 0.08 *M* in the recovery solution.

The NaOH recovery and AlO_2^- rejection ratios are shown in Fig. 4(b). The AlO_2^- rejection ratio decreases from

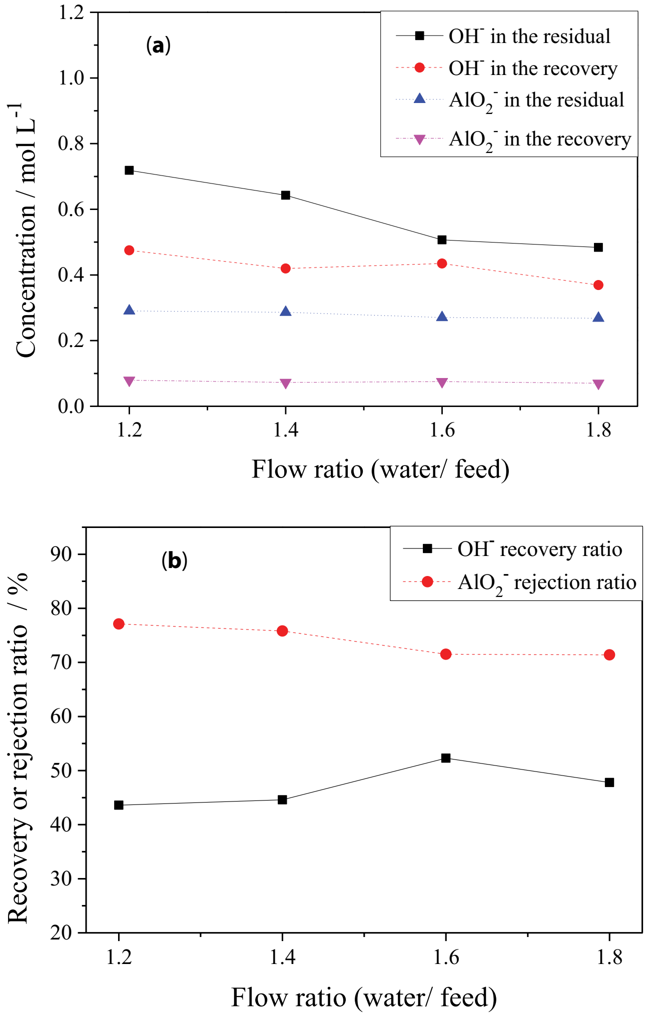

Fig. 4. (a) Anions (OH^- and AlO_2^-) concentrations in the recovery and residual solutions during DD process at fixed feed flow rate (0.4 L m^{-2} h^{-1}). (b) NaOH recovery and AlO_2^- rejection ratios during DD process at fixed feed flow rate (0.4 L m^{-2} h^{-1}).

77.4% to 71.4%, and the recovery ratio increases from 43.6% to 52.3%, which are attributed to the increasing concentration gradient as the water flow rate increases. The relatively low recovery ratio at flow ratio 1.8 may be attributed to the emerged bubbles after longtime running [8]. The recovery ratios are much lower than those of the acids (84% for H_2SO_4 [4], and 88% for HCl [23]), which should be mainly attributed to the lower activity of OH^- ions when compared with the H^+ ions [24,25]. The lower recovery ratios mean that the NaOH component needs to be further recovered from the residual liquor.

Flow ratio at 1.2 or 1.6 may be the optimized ratio after comprehensive consideration. Flow ratio at 1.6 can have lower residual OH^- concentration and higher recovery ratio, while flow ratio at 1.2 can have lower water osmosis and higher recovered NaOH concentration. As the NaOH component in the residual liquor will be further recovered by the ED process, the flow ratio at 1.2 is selected.

3.4. Continuous DD with the increasing flow rates

The flow rates of both feed and water increase to elevate the handling capacity of one dialyzer. The OH^- concentration in the residual liquor increases from 0.86 to 1.05 M, as shown in Fig. 5(a). The OH^- concentration in the recovery solution increases initially and then decreases, with the highest value of 0.66 M at water flow rate of 1.0 $L\ m^{-1}\ h^{-1}$. The initial increase should be attributed to the increased concentration gradient between feed and recovery solutions, while the latter decrease is attributed to the increasing flow rate of recovery solution.

The water flow rate at 1.0 $L\ m^{-1}\ h^{-1}$ can also obtain the highest NaOH recovery ratio (44.4%) and AlO_2^- rejection ratio (91.2%), as shown in Fig. 5(b). Hence, the flow rate at 1.0 $L\ m^{-1}\ h^{-1}$ is used to collect the residual liquor. The residual liquor is standing for about 1 week to precipitate the gibbsite ($Al(OH)_3$ and its complex [15]). Then the residual liquor, containing ~0.29 M AlO_2^- and ~0.48 M NaOH, is used for the following ED process.

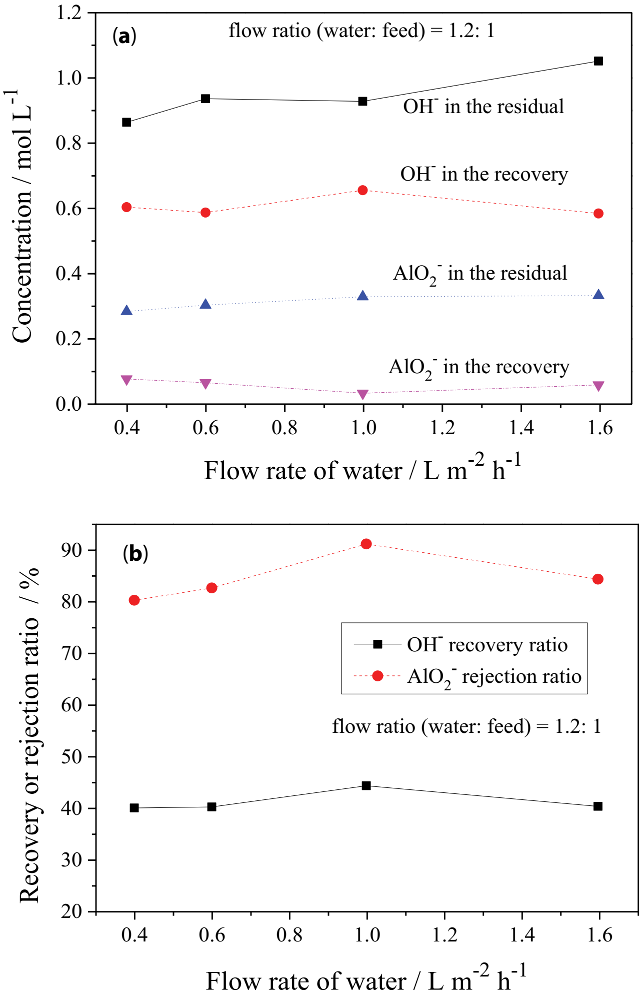

Fig. 5. (a) Anions (OH^- and AlO_2^-) concentrations in the recovery and residual solutions during DD process at fixed flow ratio (water: feed = 1.2: 1). (b) NaOH recovery and AlO_2^- rejection ratios during DD process at fixed flow ratio (water: feed = 1.2: 1).

3.5. NaOH concentration during ED process

The recovered NaOH concentration, as shown in Fig. 6, increases linearly with the time at the current density of 20 $mA\ cm^{-2}$. The linear increasing concentration is due to the driving force of electric field. The electric field is stronger than the concentration gradient in DD process, and thus the recovered NaOH concentration is mainly controlled by the electric field.

In the second phase of the process, the recovered NaOH concentration increases slower at higher current density (30 $mA\ cm^{-2}$), which may be attributed to the depleted NaOH component in the feed. The depleted OH^- ions at the latter running stage would induce significant leakage of AlO_2^- (Fig. 6). The leakage is more serious at higher current density. Hence, low current density (20 $mA\ cm^2$) may be more suitable to separate the residual liquor.

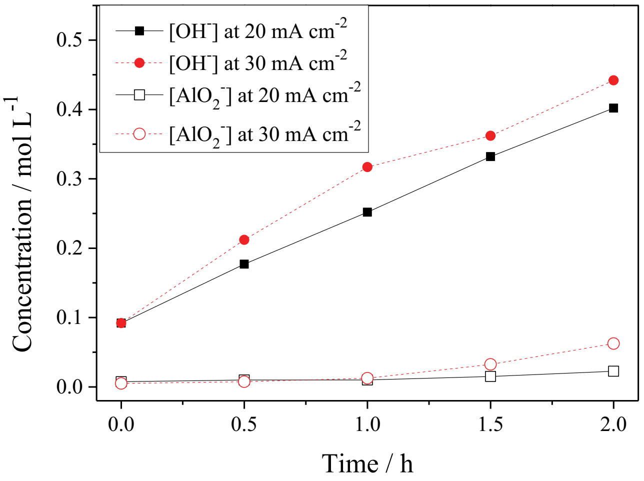

Fig. 6. Recovered NaOH and leaked AlO_2^- concentrations with respect to the running time during ED process.

3.6. Voltage drop and energy consumption

The voltage drop, as shown in Fig. 7, decreases in the initial 0.5–1 h due to the increasing concentration in the

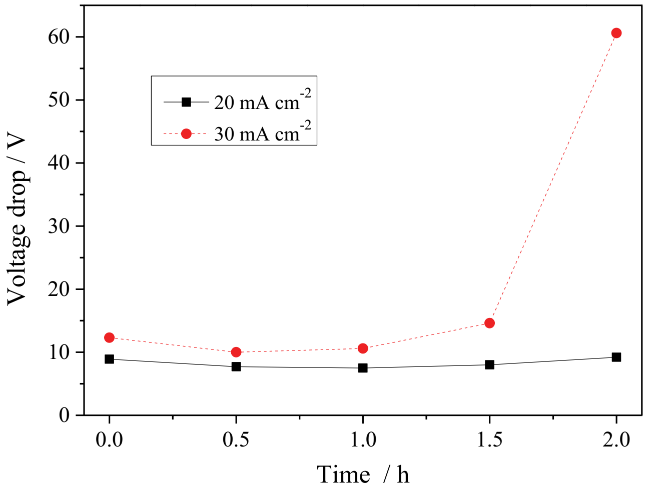

Fig. 7. Voltage drop with respect to the time during ED process.

recovery solution. The voltage then increases at the latter stage of running, which is attributed to the decreasing concentration in the residual solution. The voltage drop jumps to a high value at 30 mA cm^{-2} after 2 h due to the depleting of NaOH component. On the contrary, the voltage at 20 mA cm^{-2} is much lower and more stable than the values at higher current density.

3.7. Current efficiency and energy consumption

The current efficiency generally decreases with the time, as shown in Fig. 8, which is attributed to the decreasing NaOH concentration in the residual liquor and the increasing leakage of AlO_2^-. Current efficiency at 20 mA cm^{-2} is in the range of 79.4%–91.8%, which are higher than previous values (53.7%–71.1%) [15], indicating the superiority of present ED running conditions. Firstly, the present running uses membrane AMX instead of previous membrane FQB. Secondly, the present effective membrane area is 20 cm^2, which is larger than previous 5.73 cm^2. Finally, the present current density is 20–30 mA cm^{-2}, which is lower than previous 350 mA cm^{-2}. Hence, though the present feed concentration is much lower than previous concentration (1.50–1.57 M [15]), the current efficiency can still be higher.

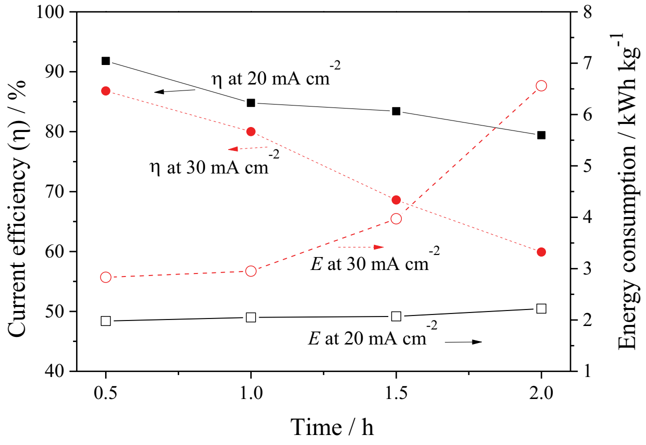

Fig. 8. Current efficiency (η) and energy consumption (*E*) for NaOH in ED process.

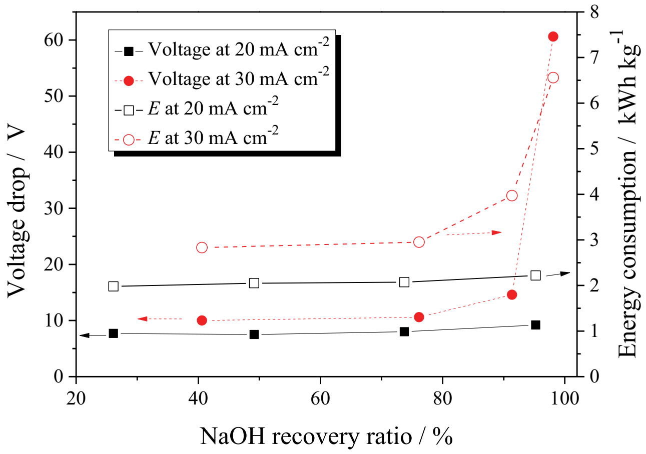

Fig. 9. Voltage drop and energy consumption with respect to the NaOH recovery ratio in ED process.

The energy consumption is only 2.0–2.2 kWh kg^{-1} at 20 mA cm^{-2}, which is much lower than previous values (7.29–7.65 kWh kg^{-1} [15]). The energy consumption increases rapidly at high current density due to the high voltage drop, which jumps from 14.6 to 60.6 V at the latter stage of ED running at 30 mA cm^{-2} (Fig. 7). Hence, the energy consumption also jumps at the latter stage of running.

As the NaOH feed is depleted faster at high current density, the voltage drop and energy consumption can also be compared on basis of the NaOH recovery ratio, as shown in Fig. 9. The values of voltage drop and energy consumption at 20 mA cm^{-2} are lower than those at 30 mA cm^{-2}. As the NaOH recovery ratio increases, the values are generally stable at 20 mA cm^{-2}. However, the values increase after 76% recovery ratio and then jump after 91% recovery ratio at 30 mA cm^{-2}. Hence, current density at 20 mA cm^{-2} for running 2 h should be the optimized running condition.

The ED and DD processes can be combined at their optimized running conditions to evaluate the total recovery and rejection ratios, together with the combined energy consumption. About 97.9% NaOH is removed, and 85.4% AlO_2^- ions are rejected. Besides, as the DD consumes insignificant energy, the combined energy consumption is reduced to only 0.71 kW h kg^{-1} for the NaOH component.

4. Conclusions

Continuous DD and ED processes are combined to separate the NaOH/$NaAlO_2$ solution, whose NaOH component is recovered and AlO_2^- component is precipitated. The DD process shows that the water osmosis is in the range of 3.6–16.1 × 10^{-5} m h^{-1}. The running condition is optimized at the flow ratio of 1.2 (water/feed) and the water flow rate of 1.0 L m^{-2} h^{-1}. The running condition can recover 0.66 *M* NaOH with the recovery ratio of 44.4% and the rejection ratio of 91.2%. The residual liquor is initially precipitated and then further separated by the ED process.

The ED process running at 20 mA cm^{-2} for 2 h can recover 0.40 M NaOH. The current efficiency is 79.4% with the energy consumption of 2.2 kWh kg^{-1}. The combination of DD and ED processes can totally recover 97.9% NaOH with the AlO_2^- rejection ratio of 85.4%. The combined energy consumption is only 0.71 kWh kg^{-1} due to insignificant energy consumption in DD process. Hence, the combination of DD and ED processes is a feasible method to elevate separation efficiency and save energy, which should be also applicable to other liquor solutions.

Acknowledgments

This project was supported in part by the Natural Science Foundation of China (Nos. 21376204 and 21476056).

Symbols

DD — diffusion dialysis
ED — electrodialysis
PVA — polyvinyl alcohol
M — mol L^{-1}
IEC — ion exchange capacity
U_{OH} — dialysis coefficient of OH$^-$ ions
U_{AlO_2} — dialysis coefficient of AlO_2^- ions
R_{OH} — NaOH recovery ratio, %
η_{AlO_2} — AlO_2^- rejection ratio, %
U_{H_2O} — Water osmosis coefficient, m h^{-1}
Q_{res} — outflow of the residual solution, L h^{-1}
Q_{feed} — inlet flow of the feed solution, L h^{-1}
Q_d — outflow of recovered NaOH solution, L h^{-1}
A — total effective membrane area, m^2
$C_{d\text{–OH}}$ — NaOH concentration in the recovery solution, mol L^{-1}
$C_{f\text{–OH}}$ — NaOH concentration in the feed, mol L^{-1}
$C_{d\text{–AlO}_2}$ — Leaked AlO_2^- concentration in the recovery solution, mol L^{-1}
$C_{f\text{–AlO}_2}$ — AlO_2^- concentration in the feed, mol L^{-1}
η — current efficiency, %
E — energy consumption of electrodialysis, kWh kg^{-1}
E' — combined energy consumption of diffusion dialysis and electrodialysis, kWh kg^{-1}

References

[1] M. Irfan, N. Ul Afsar, E. Bakangura, A.N. Mondal, M.I. Khan, K. Emmanuel, Z.J. Yang, L. Wu, T.W. Xu, Development of novel PVA-QUDAP based anion exchange membranes for diffusion dialysis and theoretical analysis therein, Sep. Purif. Technol., 178 (2017) 269–278.

[2] D.H. Kim, J.H. Park, S.J. Seo, J.S. Park, J.S. Park, S. Jung, Y.S. Kang, J.H. Choi, M.S. Kang, Development of thin anion-exchange pore-filled membranes for high diffusion dialysis performance, J. Membr. Sci., 447 (2013) 80–86.

[3] 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.

[4] 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.

[5] S.J. Lan, X.M. Wen, Z.H. Zhu, F. Shao, C.L. Zhu, Recycling of spent nitric acid solution from electrodialysis by diffusion dialysis, Desalination, 278 (2011) 227–230.

[6] H.Y. Yan, S. Xue, C.M. Wu, Y.H. Wu, T.W. Xu, Separation of NaOH and $NaAl(OH)_4$ in alumina alkaline solution through diffusion dialysis and electrodialysis, J. Membr. Sci., 469 (2014) 436–446.

[7] 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.

[8] 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.

[9] J.Y. Kim, C.H. Shin, H. Choi, W. Bae, Recovery of phosphoric acid from mixed waste acids of semiconductor industry by diffusion dialysis and vacuum distillation, Sep. Purif. Technol., 90 (2012) 64–68.

[10] J.N. Mathur, M.S. Murali, M.V.B. Krishna, V. Ramachandhran, M.S. Hanra, B.M. Misra, Diffusion dialysis aided electrodialysis process for concentration of radionuclides in acid medium, J. Radioanal. Nucl. Ch., 232 (1998) 237–240.

[11] E.G. Akgemci, M. Ersoz, T. Atalay, Transport of formic acid through anion exchange membranes by diffusion dialysis and electro-electro dialysis, Sep. Sci. Technol., 39 (2004) 165–184.

[12] X. Zhang, C.R. Li, X.L. Wang, Y.M. Wang, T.W. Xu, Recovery of hydrochloric acid from simulated chemosynthesis aluminum foils wastewater: an integration of diffusion dialysis and conventional electrodialysis, J. Membr. Sci., 409–410 (2012) 257–263.

[13] L.F. Zou, Y.H. Wu, G.C. Zhang, Separation of acidic HCl/glyphosate liquor through diffusion dialysis and electrodialysis, Desal. Wat. Treat., 105 (2018) 199–208.

[14] J.Y. Luo, C.M. Wu, Y.H. Wu, T.W. Xu, Diffusion dialysis of hydrochloride acid at different temperatures using PPO-SiO_2 hybrid anion exchange membranes, J. Membr. Sci., 347 (2010) 240–249.

[15] H.Y. Yan, C.M. Wu, Y.H. Wu, Separation of alumina alkaline solution by electrodialysis: membrane stack configuration optimization and repeated batch experiments, Sep. Purif. Technol., 139 (2015) 78–87.

[16] 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.

[17] N.U. Afsar, J.B. Miao, A.N. Mondal, Z.J. Yang, D.B. Yu, W. Bin, K. Emmanuel, L. Ge, T.W. Xu, Development of PVA/MIDA based hybrid cation exchange membranes for alkali recovery via diffusion dialysis, Sep. Purif. Technol., 164 (2016) 63–69.

[18] C.X. Jiang, Y.M. Wang, Z.H. Zhang, T.W. Xu, Electrodialysis of concentrated brine from RO plant to produce coarse salt and fresh water, J. Membr. Sci., 450 (2014) 323–330.

[19] C.X. Jiang, Y.M. Wang, T.W. Xu, An excellent method to produce morpholine by bipolar membrane electrodialysis, Sep. Purif. Technol., 115 (2013) 100–106.

[20] L. Cui, G.P. Li, Y.Z. Li, B. Yang, L.Q. Zhang, Y. Dong, C.Y. Ma, Electrolysis-electrodialysis process for removing chloride ion in wet flue gas desulfurization wastewater (DW): influencing factors and energy consumption analysis, Chem. Eng. Res. Des., 123 (2017) 240–247.

[21] H.Y. Yan, C.Y. Xu, Y.H. Wu, A.N. Mondal, Y.M. Wang, T.W. Xu, Integrating diffusion dialysis with membrane electrolysis for recovering sodium hydroxide from alkaline sodium metavanadate Solution, ACS Sustain. Chem. Eng., 5 (2017) 5382–5393.

[22] K. Lutchmiah, A.R.D. Verliefde, K. Roest, L.C. Rietveld, E.R. Cornelissen, Forward osmosis for application in wastewater treatment: a review, Water Res., 58 (2014) 179–197.

[23] J. Xu, S.G. Lu, D. Fu, Recovery of hydrochloric acid from the waste acid solution by diffusion dialysis, J. Hazard. Mater., 165 (2009) 832–837.

[24] D. Asthagiri, L.R. Pratt, J.D. Kress, M.A. Gomez, Hydration and mobility of HO-(aq), P. Natl. Acad. Sci. USA, 101 (2004) 7229–7233.

[25] C. Knight, G.A. Voth, The curious case of the hydrated proton, Acc. Chem. Res., 45 (2012) 101–109.