Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2018.22419

120 (2018) 119–132
July

Wastewater recovery by ultrafiltration and electrodialysis in the integrated citric acid-methane production process

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Received 19 September 2017; Accepted 22 April 2018

ABSTRACT

The integrated citric acid-methane production process was developed in previous study to recycle wastewater in citric acid industry. This paper investigated the technical feasibility of wastewater recovery by ultra filtration and electro dialysis in the integrated process. Treated with coagulation, flocculation and ultra filtration (200 kD), the turbidity of anaerobic digestion effluent was below 1 NTU. The optimized conditions of electro dialysis operations were applied voltage of 10 V, flow velocity of 2.16 cm/s and concentrate to diluate stream of volume ratio of 1:4. The concentration of Na^+ and ammonium in diluate of electro dialysis were 46 mg/L and 36 mg/L, respectively. The pH of concentration in electro dialysis was adjusted to 6.5 by HCl and the scale of $CaCO_3$ was eliminated. Citric acid production with treated anaerobic digestion effluent was comparable to production with deionized water. The experiment further improved the technical feasibility of cleaner production with integrated citric acid-methane production process.

Keywords: Citric acid; Anaerobic digestion; Ultrafiltration; Electrodialysis

1. Introduction

Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) is one of most important intermediate compounds produced by fermentation, widely applied in the food, medicine, chemical, and other industries [1,2]. It has been reported that 50–60 tons of wastewater arise from each ton of citric acid produced [3]. Extraction wastewater has high levels of chemical oxygen demand (COD) (15,000–20,000 mg/L) and low pH (4.5–4.8). In 2010, approximately 1.3 million tons of citric acid wastewater were produced in China, and it is conventionally treated by an anaerobic-aerobic process [4,5]. Anaerobic digestion effluent can produce valuable methane, but aerobic digestion requires high investment, operational charges, and large spaces. Additionally, anaerobic digestion effluent still needs to be treated further for it to meet national discharge standards.

Many scholars had tried various methods to deal with citric acid wastewater [3,6], but the methods could not keep up with its application in industry scale. Thus, our laboratory proposed an integrated process to deal with the citric acid wastewater [7] (Fig. 1a). High concentrations of metal ions, especially Na^+, and ammonium in anaerobic digestion effluent are inhibitors for citric acid fermentation. After anaerobic digestion effluent was treated by the air stripping and electro dialysis, citric acid production was comparable to production with deionized water [8].

However, the integrated process is still restricted by some factors. Firstly, ammonium ions can be also removed by the electric field force in the electro dialysis process. Electro dialysis has been confirmed as an efficient method, and has been widely used for removing ammonia from wastewater. Gain et al. investigated the use of membrane electrolysis and electro dialysis for treating ammonium nitrate wastewater [9]. Electro dialysis and reverse osmosis was used to recycle and concentrate ammonia from swine manure [10]. Without air stripping, electro dialysis is fully

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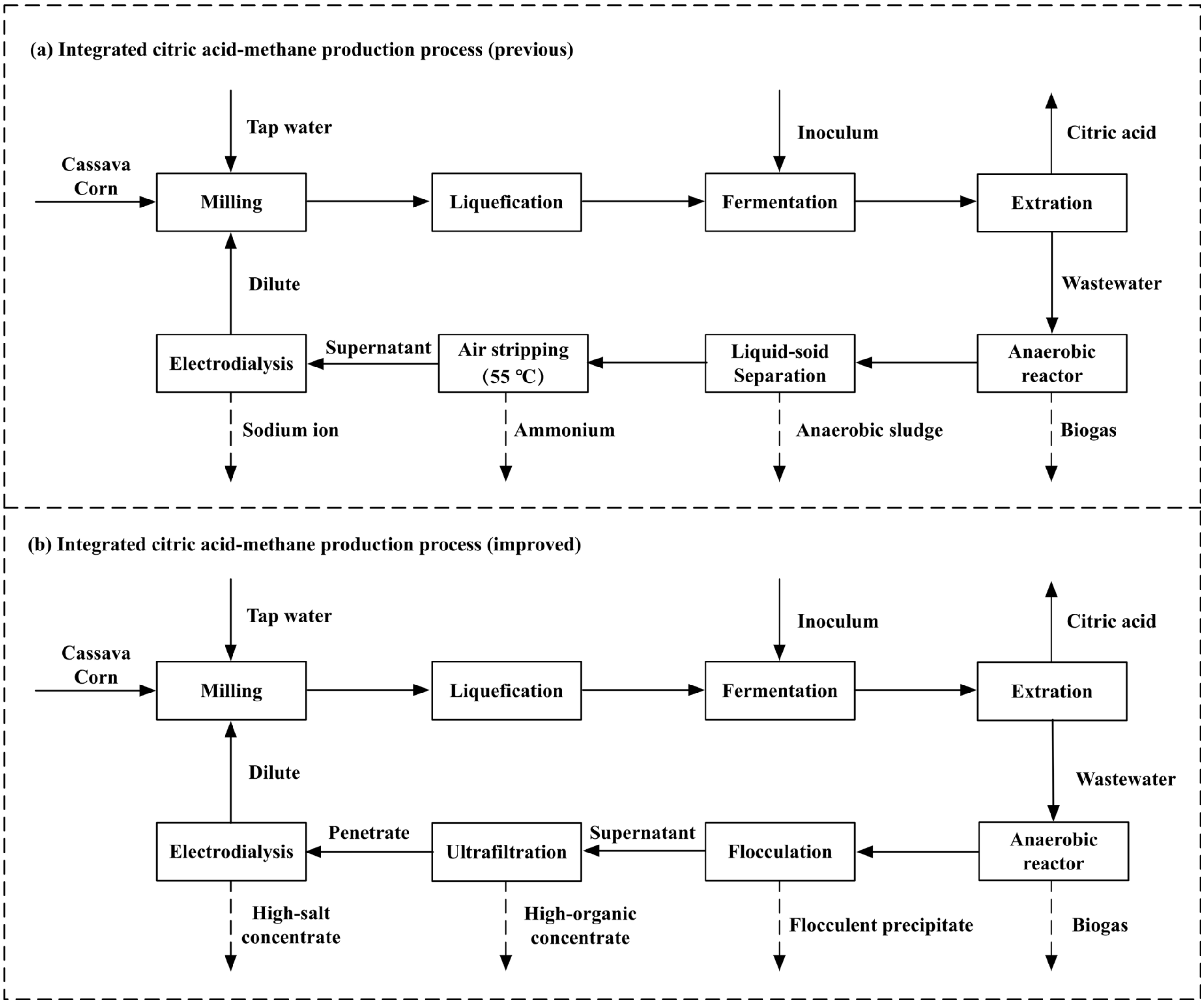

Fig. 1. Flow chart of the integrated citric acid-methane production process.

capable of removing either metal ions or ammonium ions from anaerobic digestion effluent. In addition, the temperature of anaerobic digestion and the air stripping treatment was respectively 35°C and 55°C. It meant the temperature rise would cost a lot of heat energy to improve the effectivity in previous process. Secondly, the electro dialysis design in a previous study [8] was different from the conventional electro dialysis design, despite it being useful in previous integrated citric acid-methane production process. The electro dialysis process conducted in the previous study only used one tank, which meant that the diluate solution, concentrate solution, and electrode solution shared one tank. The conductivity of the diluate solution increased with time, as the concentrate solution was recycled in the shared tank. The increase in conductivity of the diluate solution was not beneficial for desalination. Finally, the turbidity of feed water was not determined and controlled, which could lead to membrane fouling in the electro dialysis process. When handling high-salt organic wastewater, ion exchange membrane of electro dialysis was usually polluted by organic matter and inorganic scale. Negatively charged organic matter in anaerobic digestion effluent migrated though the anion exchange membrane under electric field forces [11]. Organic-fouling substances absorbed on the membrane's surface and in the membrane's pores, which result in ion exchange membrane organic pollution [12]. When the polarization took place or the solution was supersaturated, cation ions, such as Ca^{2+}, Mg^{2+} or high valance ions, can scale on the surface or inner of ion exchange membrane. A fluidized pellet reactor removed efficiently 74% of Ca^{2+} and 73% of Ni^{+} [13], and reduced scaling in bipolar membrane electro dialysis [14]. Calcium carbonate dissolves in acid, so the addition of acid was an appropriate method for converting calcium carbonate into calcium bicarbonate and carbon dioxide [15,16]. Adequate pretreatment for the electro dialysis process must be conducted to produce high-quality feed water. The ion exchange membranes are easily polluted by suspended matter, colloids, and organic macromolecules, particularly negatively charged organic macromolecules [12,17]. Ultra filtration has been widely used as an efficient pretreatment for electro dialysis. Lemaire et al. used ultra filtration to remove macromolecules from hemi cellulosic hydrolysates before purifying pentose using electro dialysis [18]. Yen et al. investigated the effects of different types of ultra filtration on reversal electro dialysis and reverse osmosis in a pilot-scale study [19]. It was very necessary to introduce ultra filtration in integrated process.

In this study, a combination of ultra filtration and electro dialysis was proposed to replace air stripping and electro dialysis to manage anaerobic digestion effluent (Fig. 1b) in the integrated process. Ultra filtration was investigated as pretreatment for electro dialysis to reduce organic matter and the turbidity of the anaerobic digestion process. In this study, electro dialysis was conducted in three separate compartments and was equipped with homogeneous ion exchange membranes. The electro dialysis performance was evaluated by conductivity and ammonium removal rates, energy consumption, and efficiency. The operating parameters of electro dialysis were optimized for efficiently managing anaerobic digestion effluent. Additionally, the method was expanded to eliminate $CaCO_3$ in the desalination process. The purpose of this study is to further improve the technical feasibility of the integrated citric acid-methane production process in industry.

2. Materials and methods

2.1. Strain and seed culture conditions

A. niger was obtained from our laboratory for citric acid production. Potato dextrose agar slants were used and the

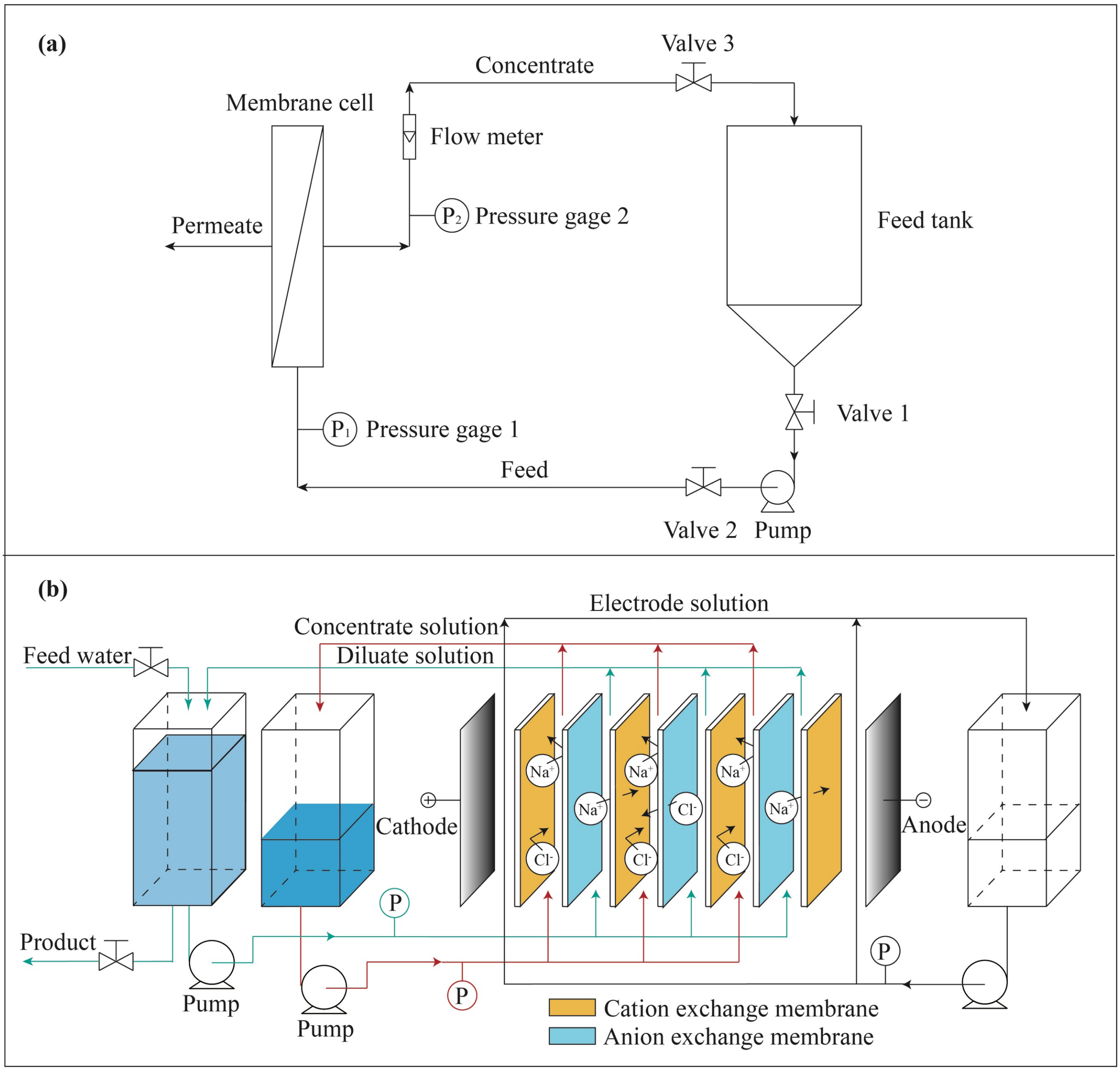

Fig. 2. Flow diagram of the experimental setup (a) ultra filtration and (b) electro dialysis.

culture was maintained at 4°C for preservation. Cassava powder (approximately 0.45 mm) and deionized water were thoroughly mixed (1:4, w/v). The pH of slurry was adjusted to 6.0 with either 30% (w/w) H_2SO_4 or 10% (w/v) NaOH. High-temperature amylase (provided by Genencor China Co., Ltd.) was added to 10 U/g of cassava power and kept for 2 h at 100°C. The seed medium contained liquefaction slurry and 0.1% (w/v) ammonium sulfate as the nitrogen source, and its pH was adjusted to 5.5. The seed medium was autoclaved at 115°C for 20 min. A spore suspension (10 mL) in sterile water, containing approximately 6×10^6/mL of conidia from a 7-day-old PDA plant, was added to 70 mL of seed medium in a 1000-mL shake flask. The seed culture was used as the inoculum for citric acid fermentation after incubated on a rotating shaker (200 rpm) at 36 ± 1°C for 20 h.

2.2. Citric acid fermentation

Cassava powder (80 g) and corn powder (20 g) were mixed with 450 mL of either deionized water or anaerobic digestion effluent. The initial total sugar content of the liquefaction slurry was adjusted to about 155 g/L, and the slurry was autoclaved under the same conditions as the seed medium. In a 500-mL shake flask, 40 mL of a fermentation medium was inoculated with 6 mL of the seed medium. Fermentation was performed on a rotating shaker at 260 rpm, 37.5 ± 1°C for 92 h.

2.3. Methane production conditions

A 5-L working volume up flow anaerobic sludge blanket (UASB) reactor (provided by Shanghai Daming, China) was used for methane fermentation. A circulator bath was used to maintain the temperature of UASB at 35 ± 1°C. The reactor was inoculated with anaerobic granular sludge (provided by Yixing Xielian Biological Chemical Co., Ltd, China). One liter of citric acid wastewater was fed into the reactor by a peristaltic pump every day. The samples of anaerobic digestion effluent was stored at 4°C for follow-up experiments.

2.4. Ultra filtration device

To assess the influence of molecular cut off on the removal of organic matter, two types of membranes were used: 100 kD and 200 kD. The ultra filtration device and the membranes were purchased from Anhui Pulang Membrane Technology Co. Ltd., China (Fig. 3a). The membrane material was polyvinylidene fluoride (PVDF), and the membrane area was 0.24 m². The ultra filtration device was capable of performing cross-flow filtration through different types of membrane. The operating pressure could be controlled between 0.15 and 0.45 MPa, and cross-flow flow could be controlled from 0–150 L/h. The temperature of the feed solution was controlled between 15 °C and 65°C by the condensing device. The volume of the ultra filtration feed tank was 15 L, and the dead volume was approximately 2 L. The experiment was stopped when the volume concentration factor (VCF) reached 5.

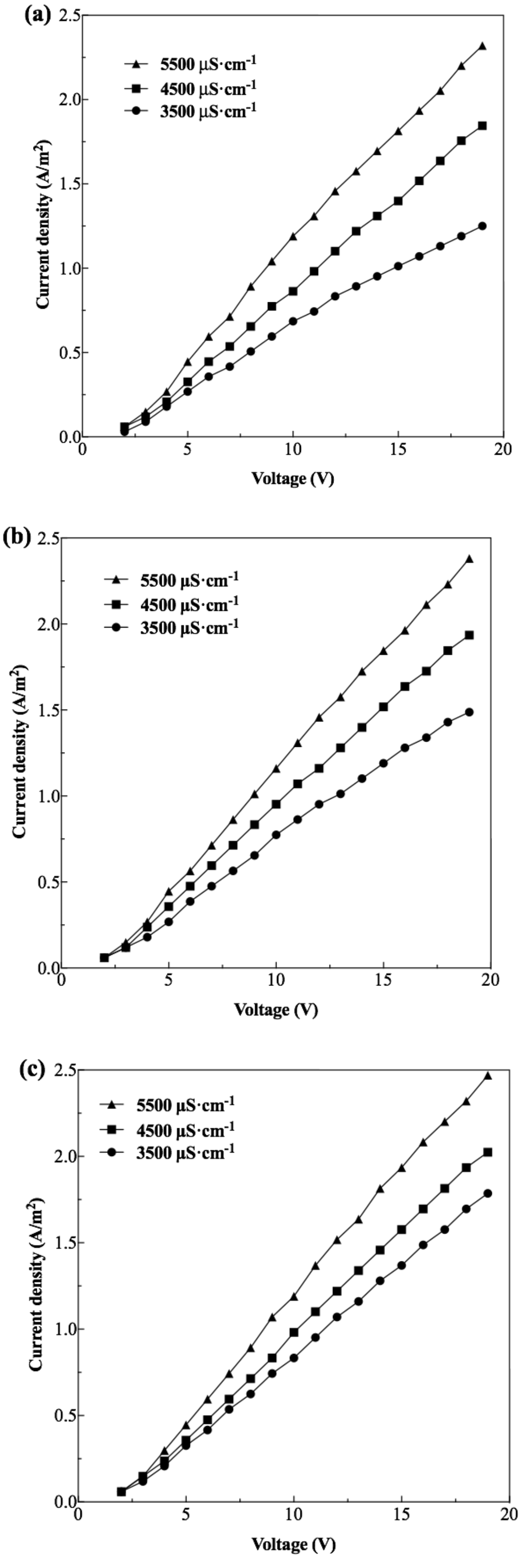

Fig. 3. Voltage-current curves under different sodium bicarbonate conductivities at different flow velocities. (a) 1.44 cm/s, (b) 2.16 cm/s, (c) 2.89 cm/s.

2.5. Electro dialysis unit

The laboratory-scale electro dialysis (Shandong Tianwei Membrane Technology Co. Ltd., China) was composed of three centrifugal pumps, three rotameters (0–100 L/h), and three 2 L tanks (Fig. 3b). The electro dialysis stack contained two electrodes, 20 homogeneous anion exchange membranes (AEMs), and 21 homogeneous cation exchange membranes (CEMs). The electro dialysis unit had a total effective area of 0.336 m^2. The direct current was supplied by a CV regulated power supply, and the range of voltage applied was 0–19 V. All the desalination experiments were operated at room temperature (20 ± 1°C). The total volume of diluate solution and concentrate solution was 2 L during testing of the effects of electro dialysis operation conditions.

2.6. Analysis methods

The samples were centrifuged at 10,000´g for 20 min, and the supernatant was filtered through a 0.45 mm membrane for analysis. Citric acid and residual glucose content were determined by a Dionex U3000 high-performance liquid chromatographer (HPLC) using an ultraviolet and refraction index detector (UV/RID) and the C18 column, maintained at 65°C. A sulfuric acid solution (0.005 mol/L) was used as the mobile phase at a flow rate of 0.6 mL/min. Total sugar content was determined by a biosensor (SBA-40B, Shandong Academy of Sciences, China) after the samples collected during citric acid fermentation were subjected to acid hydrolysis (20 g/L hydrochloric acid, 100°C, 2 h). Metal ions were detected by flame atomic absorption spectrometry. The COD, ammonium (NH_3-N), alkalinity, hardness, and color (410 nm) of anaerobic digestion effluent were measured following standard methods. Total dissolved solids (TDS) and conductivity were measured with a conductivity meter.

2.7. Data analysis

Conductivity removal rate (κ,%) is calculated from Eq. (1):

$$\eta = \frac{\kappa_0 - \kappa_t}{\kappa_0} \tag{1}$$

here κ_t and κ_o are the conductivities of the diluate solution at t (s) and 0 (s), respectively.

Current efficiency (ce,%) is given by Eq. (2) [20]:

$$\text{ce} = \frac{ZVF\left(C_t - C_0\right)}{NIt} \tag{2}$$

where C_t and C_o are the concentrations of free HCO_3^- in the diluate compartment at t (s) and 0 (s), respectively; Z is the absolute valence of ion ($Z = 1$); V (L) is the circulated volume of solution in the diluate compartment; F is the Faraday constant (96,500 C mol^{-1}); I (A) is the current; and N is the number of repeating units ($N = 20$); t is the operation time (s). As volume change in each tank was negligible during operation, V is equal to the initial volume of the diluate solution.

Energy consumption (E, kWh·m^{-3}) (not including pumping energy consumption) in the electro dialysis process is given by Eq. (3):

$$E = \int_0^t \frac{UI}{V} dt \tag{3}$$

where U is the potential (V), I is the current (A), V is the circulated volume in the diluate compartment, and t is the operation time (h).

At pH 6.5–9.5, the Langelier saturation index (LSI) [21] is used to indicate the scaling potential of water containing carbonates, and is calculated by Eq. (4):

$$\text{LSI} = \text{pH} - \text{pH}_s \tag{4}$$

where pH_s is the pH at which the water was saturated with calcium carbonate. pH_s is:

$$\text{pH}_s = (9.3 + \text{A} + \text{B}) - (\text{C} + \text{D}) \tag{5}$$

where A = ($\log_{10}[\text{TDS}]^{-1}$)/10, [TDS] is the concentration of total dissolved solids (mg L^{-1}); B = –13.12 × $\log_{10}$(T) + 34.55, T is temperature (K); C = $\log_{10}[C^*_{Ca^{2+}}] - 0.4$, $[C^*_{Ca^{2+}}]$ is the concentration of Ca^{2+} as $CaCO_3$ (mg/L); and D = $\log_{10}$[Alk], [Alk] is the concentration of alkalinity as $CaCO_3$ (mg/L).

3. Results and discussion

3.1. Removal of macromolecules by ultra filtration

Before anaerobic digestion effluent was used as the feed water for electro dialysis, suspended matter, colloids, and organic macromolecules were removed. Negatively charged organic matter in anaerobic digestion effluent can migrate to the anion exchange membrane under electric field forces. Organic-fouling substances can absorb on the membrane's surface and in the membrane's pores, which result in ion exchange membrane pollution [12]. Two different molecular cut offs of ultra filtration membrane were used to assess the influence of molecular cut off on organic matter removal. The temperature was maintained at 20°C and the operating pressure at 0.15 MPa. The pH of anaerobic digestion was not adjusted in this experiment.

Table 1 shows that after treatment through the 100 kD membrane the removal rate of COD and turbidity were 43.1% and 98.5%, respectively. After treatment through the 200 kD membrane, the removal rate of COD and turbidity of anaerobic digestion effluent were 39.2% and 94.7%, respectively. The performance of the 100 kD membrane was superior to that of the 200 kD. This could be due to the smaller pore sizes of the 100 kD membrane than those of the 200 kD, and more organic matter could be retained in the concentrate solution in the feed tank. The turbidity of both filtered solutions were higher than 1 NTU, indicating ultra filtration this alone did not meet the requirements of the electro dialysis process [22]. Coagulation and flocculation were used to reduce the turbidity of ultra filtration feed water and reduce organic load on the ultra filtration membrane [23,24]. The optimal added concentrations of polytonal-ism chloride (PAC) and anionic polyacrylamide (APAM) in anaerobic digestion effluent were 300 ppm and 2 ppm, respectively (Table SM-3). After treatment by PAC and APAM, the supernatant of the anaerobic digestion effluent was filtered through the 200 kD membrane. The turbidity of

Table 1
Chemical parameters of anaerobic digestion effluent (ADE) treated with different ultra filtration membranes

Parameters	ADE	ADE[a]	ADE[b]	ADE[c]
pH	7.07	8.36	8.27	8.31
COD (mg/L)	602	342	366	331
Turbidity (NTU)	230.20	3.42	12.09	0.05
NH_3-N (mg/L)	270	158	150	138

[a] ADE treatment with 100 kD membrane.
[b] ADE treatment with 200 kD membrane.
[c] ADE treatment with coagulation and 200 kD membrane.

the treated solution was 0.05 NTU, which met the requirements of electro dialysis [22]. The pH of the penetrate was higher than that of anaerobic digestion effluent. This could be due to the recycling of the concentrate solution to the feed tank by a pump, where the solution was then shocked. The shock was strong when the liquid level in the tank was lower than the reflux outlet of the concentrate solution. This process was similar to air stripping, and allowed ammonium in the solution to escape. As a result, the ammonium of the treated solution had decreased when the experiment ended.

3.2. Voltage-current curves

In the electro dialysis process, polarization should be avoided, because a large amount of H^+ and OH^- form at the surface of the ion exchange membrane [25]. In this situation, $Ca(OH)_2$ or $Mg(OH)_2$ precipitates can form. When polarization takes place in a bicarbonate solution, $CaCO_3$ precipitates may form due to reactions between OH^- and HCO_3^-. Therefore, current density in experiments should be lower than the limiting current density. When the pH of anaerobic digestion effluent was 7–8, the major anion in anaerobic digestion effluent is HCO_3^- [26]. $NaHCO_3$ was used as the simulated solution in the experiment measuring limiting current. Fig. 3 shows the effects of voltage on the current; the conductivity of the $NaHCO_3$ solution increased from 3500 mS/cm to 5500 mS/cm at different flow velocities. Conductivity and flow velocity had important effects on current density,and current density was almost proportional to voltage, which increased from 2 V to 19 V. It was indicated that there was no alteration of the voltage-current curves, and the limiting current region did not exist [27]. To conclude, polarization did not occur when the electro dialysis system treated anaerobic digestion effluent within a voltage range of 2–19 V [25].

3.3. The effects of electro dialysis operation conditions

3.3.1. Effects of applied voltage

The inhibition concentration of Na^+ on citric acid fermentation is 200 mg/L [28]. According to the calibration curve, the Na^+ concentration in the diluate solution could be determined by measuring its conductivity. When the conductivity of the diluate solution was lower than 800 mS/cm, the Na^+ concentration was lower than 200 mg/L (Fig. SM1). Considering the complex composition of anaerobic digestion effluent, the conductivity of the diluate solution was maintained at 700 mS/cm here. Applied voltage is an important parameter for removal efficiency in the potentiostatic mode [29]. Fig. 4a describes the removal rate of conductivity under different applied voltages, at a flow velocity of 2.16 cm/sand a volume ratio of 1:1. Because ions moved from the diluate solution to the concentrate solution by the electric field force, the conductivity of the diluate solution decreased with operation time. The resistance of the electro dialysis unit increased with the reduction of ions in the diluate solution, so the conductivity removal rate of the diluate solution decreased through the desalination process. Under a higher voltage, the ions move faster across the ion-exchange membranes, leading to shorter operation times [30,31]. A voltage of 14 V resulted in the shortest operation time.

Current efficiency of HCO_3^- rapidly increased from 59.74% to 82.1%, as the applied voltage increased from 8 V to 14 V. The current efficiency at 10 V (73.7%) was close to that of 12 V (73.2%; Fig. 4d). This result could be attributed to fluctuations in the removal rate and current density over time. Energy consumption increased sharply from 0.60 kWh/m^3 at 8 V to 0.91 kWh/m^3 at 14 V. This could be due to higher voltages requiring more energy to overcome electro dialysis resistance [32]. The removal rates of ammonium in anaerobic digestion effluent were all over 80%. The concentration of residual ammonium at 8 V was 23 mg/L, which is below the inhibition concentration (50 mg/L) [28]. Considering conductivity and ammonium removal rates, current efficiency, and energy consumption, 10 V was determined to be the optimal applied voltage for the electro dialysis process in anaerobic digestion effluent treatment.

3.3.2. Effect of flow velocity

The flow velocity of the solution in a compartment is an important parameter in the treatment of anaerobic digestion effluent during the electro dialysis process [30]. The conductivity removal rate increased more rapidly, and operation time decreased under higher flow velocities (Fig. 4b) at an applied voltage of 10 V and a volume ratio of 1:1. This could be due to solutions in compartments obtaining higher electrical densities under higher flow velocity, and higher currents strengthening the electric field force driving ions across ion-exchange membranes [33]. Additionally, a higher flow velocity contributed to shorter operation times. A flow velocity of 3.61 cm/s resulted in the lowest operation time.

Fig. 4e shows the energy consumption and current efficiencies of HCO_3^- at different flow velocities. Energy consumption decreased slightly from 0.71 kWh/m^3 at 1.44 cm/s to 0.68 kWh/m^3 at 3.61 cm/s. Higher electrical densities under high flow velocity decreased electro dialysis resistance and then decreased energy consumption with increasing flow velocity. The current efficiency HCO_3^- of increased from 69.9% at 1.44 cm/s to 72.8% at 3.61 cm/s, and the current efficiency at 2.16 cm/s (72.54%) was close to that at 1.44 cm/s (72.1%) in Fig. 4e. A higher current density strengthens the electric field force for driving ions across ion exchange membranes and increases the ion removal rate [33]. However,

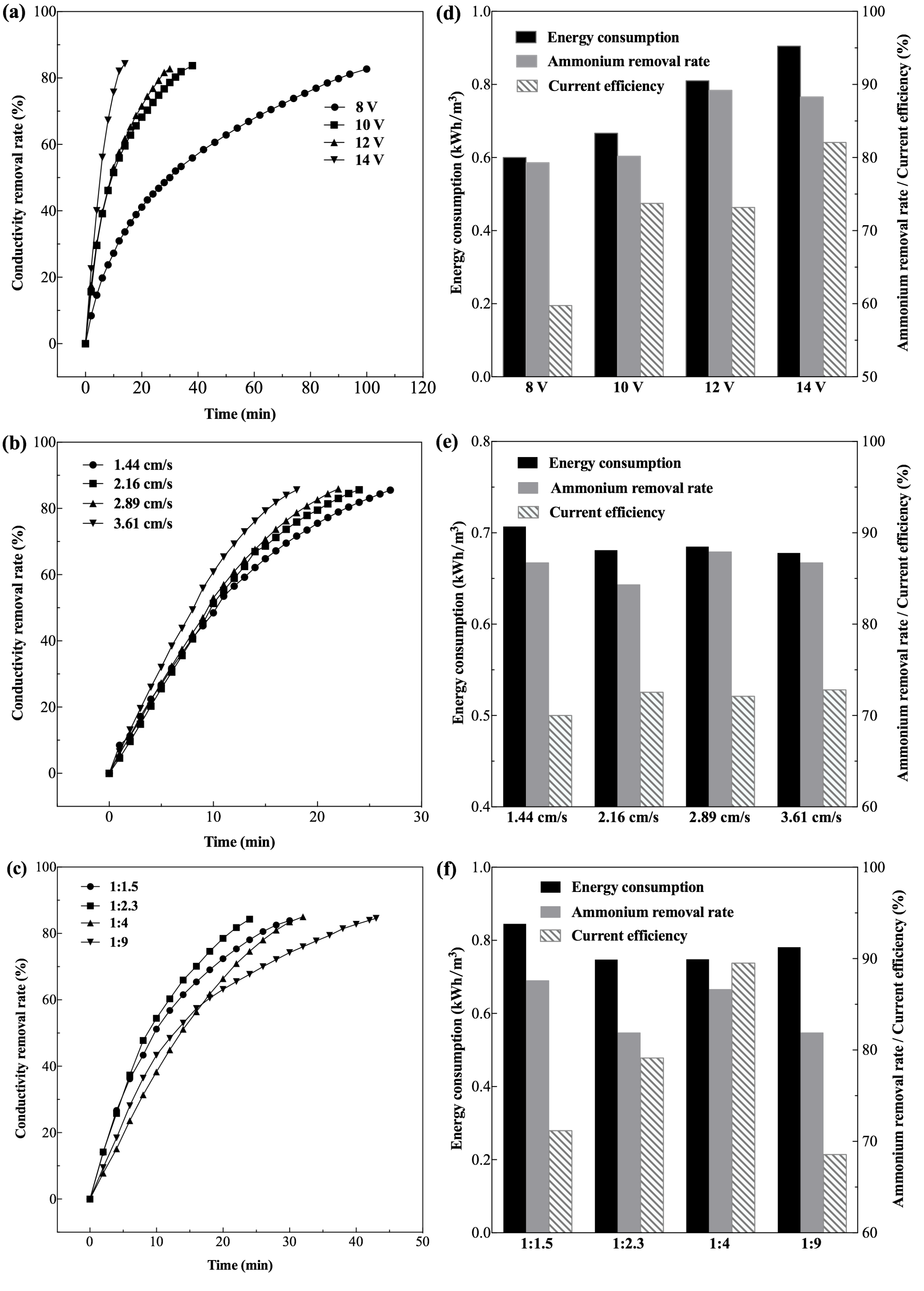

Fig. 4. The effects of operational electro dialysis conditions in the circulation experiment. (a) and (d) at a flow velocity of 2.16 cm/s and a volume ratio of 1:1, (b) and (e) at an applied voltage of 10V and volume ratio of 1:1, (c) and (f) at a flow velocity of 2.16 cm/s and applied voltage of 10 V.

the increase of flow rate could damage the membranes and shorten its life [30]. The removal rates of ammonium from anaerobic digestion effluent were all above 80%. The concentration of residual ammonium at 2.16 cm/s was 26 mg/L, which is below the inhibition concentration. As mentioned above, considering conductivity and ammonium removal rates, current efficiency, and energy consumption, 2.16 cm/s was determined to be the optimal applied flow velocity for the electro dialysis process in anaerobic digestion effluent treatment.

3.3.3. Effect of stream volume ratio

The concentrate to diluate solution stream volume ratio is an important parameter for the treatment of anaerobic digestion effluent by an electro dialysis process, and represents the water recovery of the diluate solution [31]. Owing to the low water recovery of diluate solutions at a volume ratio of 1:1, the concentrate to diluate solution stream volume ratios investigated were 1:1.5, 1:2.3, 1:4, and 1:9. The effects of different volume ratios were tested at an applied voltage of 10 V and flow velocity of 2.16 cm/s.

The removal rate of conductivity decreased slowly and operation time increased under a higher volume ratio (Fig. 4c). When the total volume of the diluate and concentrate solutions were constant, a higher volume ratio indicated that more of the diluate solution needed to be desalinated, i.e., more ions in the diluate solution were transported from the diluate to the concentrate solution. Therefore, the conductivity of the diluate solution decreased slowly and more of the operation time was spent on transporting ions at a higher volume ratio.

The energy consumption and current efficiencies of at different concentrate to diluate stream volume ratios are shown in Fig. 4f. Energy consumption decreased from 0.85 kWh/m^3 at 1:1.5 to 0.74 kWh/m^3 at 1:4, and then increased to 0.78 kWh/m^3 at 1:9. This could be due to variations in energy consumption, which was related to an increase in stream volume ratios, decrease in current density, and increase in operation time at a constant applied voltage, according to Eq. (2). Increasing volume ratios increased the current efficiency of HCO_3^- from 71.16% at 1:1.5 to 89.51% at 2:8, and decreased it to 68.55% at 1:9 (Fig. 4f). Under higher concentrate to diluate stream volume ratios, the current efficiency of HCO_3^- increased, which was due to increases in volume ratio and current with operation time, according to Eq. (2). When the volume ratio was 1:9, however, the expected increase of HCO_3^- current efficiency was eliminated by increasing current with operation time. The removal rates of ammonium from anaerobic digestion effluent were all over 80%. The concentrations of residual ammonium of 1:2.3 and 1:9 were 38 mg/L, which is below the inhibition concentration. Considering conductivity and ammonium removal rates, energy consumption, and current efficiency, 1:4 was adopted as the optimal concentrate to diluate stream volume ratio for the electro dialysis process during anaerobic digestion effluent treatment.

3.4. Results obtained by the electro dialysis process under optimized conditions

Table 1 shows the results obtained from electro dialysis under optimized conditions. The removal rates of COD and NH_3-N from the diluate solution were 20% and 84%, respectively. In the electro dialysis process, negatively charged soluble organic matter can migrate through anion exchange membranes to the concentrate solutions by the electric field force. It was shown (Table 1) that the increase of COD in the diluate solution was slightly higher than the increase in the concentrate solution, because part of the negatively charged soluble organic matter was detained on the surface of or inside the anion exchange membrane. Ammonium, which is positively charged in anaerobic digestion effluent, can migrate through a cation exchange membrane to the concentrate solution, which caused the decrease of ammonium in the diluate solution.

The removal rates of alkalinity, and calcium hardness and total hardness of the diluate solution were 91%, 92%, and 89%, respectively. Alkalinity mainly resulted from, which was driven from the diluate solution to the concentrate solution by the electric field force. Ca^{2+} and Mg^{2+} were efficiently removed so the calcium and total hardness decreased throughout the electro dialysis process. The Langelier saturation index (LSI) of each sample were calculated by Eqs. (4) and (5).The LSI of anaerobic effluent was already higher than 0, indicating that the anaerobic effluent quality was easy to scale [34]. With increases of alkalinity, and calcium hardness and total hardness, scale was strengthened in the concentrate solution. However, at the end of the experiment, the LSI of the concentrate solution was slightly lower than that of anaerobic effluent. This could be due to the white powder at the bottom of the concentrate solution tank in the experiment, which indicated that a large amount of calcium had precipitated [21]. In contrast to the concentrate solution, the LSI of the diluate solution decreased below 0, due to the migration of calcium and magnesium ions, and bicarbonate to the concentrate solution.

Fig. 6a describes the evolution of cations in the diluate solution. The migration rates of different cations were different, which could be due to their characteristics (Table 3) such as their hydrated radius and hydration free energy [35]. The ions migrated in the form of hydrated ions in the solution, so the smaller the hydrated ion radius, the faster the migration rate. Additionally, the migration rate was related to the polarization free energy, and the smaller the free radical energy, the faster the migration rate. The migration rates of cations decreased in the sequence of: $K^+> Na^+>Mg^{2+}>Ca^{2+}$ (Fig. 6a). This is not consistent with other reports [15,36], because the migration rate of Mg^{2+} was faster than that of Ca^{2+}. This could be due to the HCO_3^- in the diluate solution. The migration rate of Mg^{2+} could have been limited by the precipitation of $Mg(OH)_2$at a concentration of 38 g/L, when the anion was chloride and the solution was at a specific pH (6.5–7.5) [36]. In this experiment, the abnormal performance of Ca^{2+} could have been due to the precipitation of $CaCO_3$. The LSI of the diluate solution was larger than the critical fouling point (LSI = 1) at the beginning of desalination, and the migration rate of Ca^{2+} was inhibited by the precipitation of $CaCO_3$. When the LSI of the diluate solution decreased over time, inhibition by the precipitation of $CaCO_3$ gradually decreased until it disappeared. Therefore, it was shown in Fig. 6a that the migration rate of Ca^{2+} was slower than that of Mg^{2+} within the first 15 min, and then gradually reached that of Mg^{2+}.

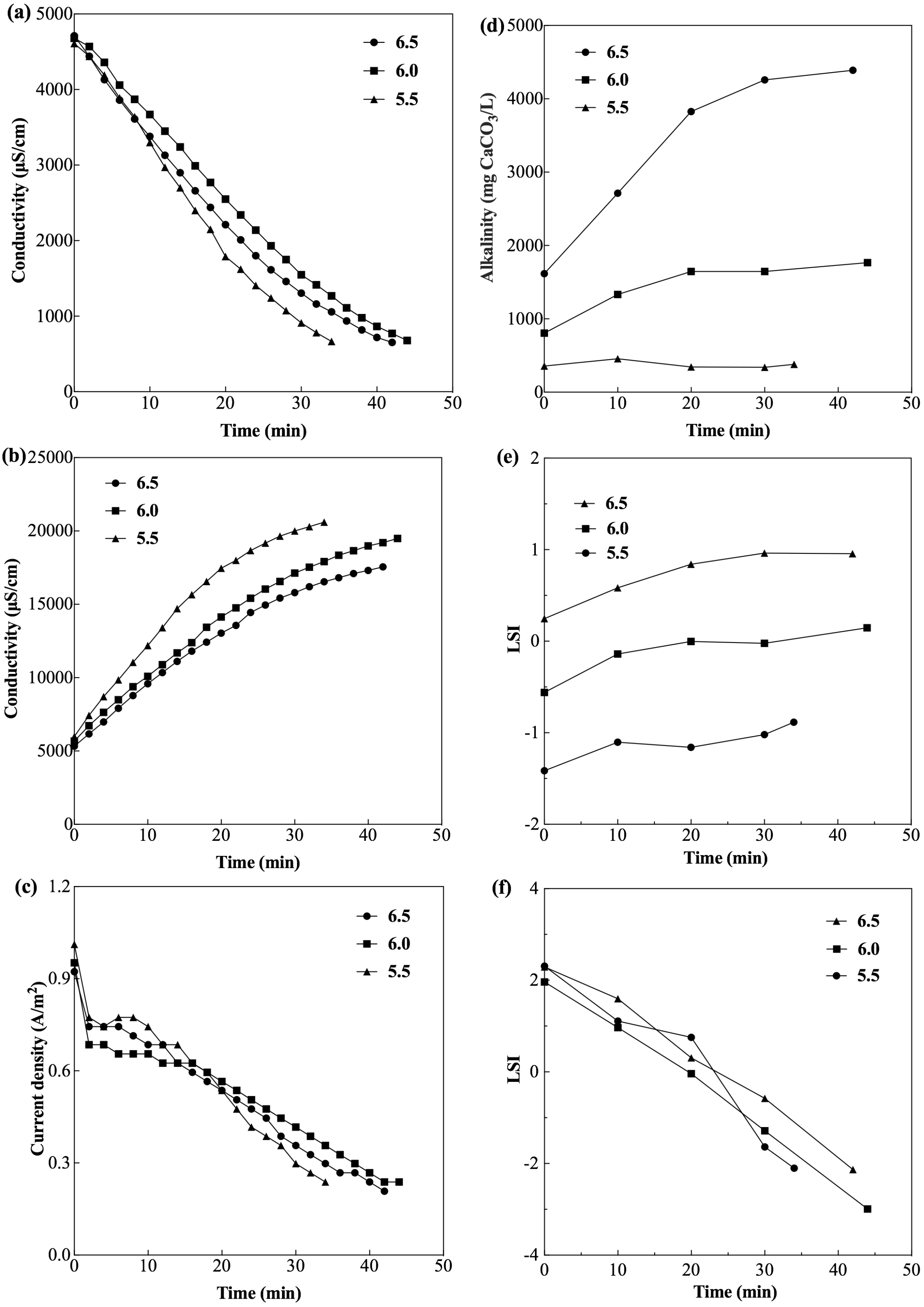

Fig. 5. The decarbonation of the eletro dialysis concentrate solution at different pH levels. (a) conductivity of diluate solution, (b) conductivity of concentrate solution, (c) current density, (d) alkalinity of concentrate solution, (e) LSI of concentrate solution, (f) LSI of diluate solution.

3.5. The decarbonation of electro dialysis concentrate solution

The previous experiment confirmed that calcium carbonate precipitation occurred during the desalination of anaerobic digestion effluent. Precipitation enhanced membrane resistance and reduced process efficiency [15]. To ensure the stability of the desalination process, decarbonation of the concentrate solution in the electro dialysis process was necessary. Calcium carbonate dissolves in acid, so the addition of acid was an appropriate method for converting calcium carbonate into calcium bicarbonate and carbon dioxide [15,16]. Adding hydrochloric acid into the concentrate solution is superior to adding sulfuric acid when there is a large number of calcium and magnesium ions. When the LSI was below the critical scaling concentration (CSC) (LSI = 1.00), the scale did not happen in short period [16]. The concentrate solution's pH was adjusted by adding hydrochloric acid to pH of 5.5, 6.0 and 6.5. All of the experiments were carried out under the previously obtained optimal conditions, i.e., an operating voltage of 10 V, a volume ratio of 1:4, and a flow velocity of 2.16 cm/s.

In Fig. 5a, the desalination rate of the concentrate solution at pH 6.5 was almost equal to that at pH 6.0. However, the desalination rate was the fastest at pH 5.5. This is because the initial conductivity of the concentrate solution was higher at the beginning of the experiment to adjust the pH of concentration solution to 5.5 (Fig. 5b). The resistance of the electro dialysis unit was the smallest and the current density was largest at pH 5.5 than those at pH 6.0 and 6.5 within the first 15 min. A stronger electric field force was created for driving ions through ion exchange membranes. It was shown in Fig. 5d that, when the pH of the concentrate solution was 6.5 and 6.0, alkalinity increased with time, and eventually stabilized. At pH 6.5, more hydrochloric acid was added into the concentrate solution than at pH 6.0, so more bicarbonate was converted into carbon dioxide. When the pH of the concentrate solution was 5.5, the alkalinity was maintained at a low level and did not increase with time. It was attributed to the amount of hydrochloric acid being equal to the increase in alkalinity when the pH of the concentrate solution was maintained at 5.5. Fig. 5e shows that the LSI of the concentrate solution increased with time. The LSI of the concentrate solution was maintained below the critical scaling concentration (LSI = 1.00) at different pH throughout the experiments, indicating that adding HCl to the concentrate solution to adjust pH was useful. According to Eqs. (4) and (5), the LSI of the concentrate solution increased with increases of TDS, calcium hardness, and alkalinity at pH 6.5 and 6.0. For pH 5.5, although the alkalinity of concentration solution was unchanged, the LSI still increased with increases of TDS and calcium hardness. Fig. 5 f shows the that LSI of the diluate solution decreased with time, due to reductions of alkalinity and calcium hardness.

3.6. Citric acid fermentation of anaerobic digestion effluent treated by electro dialysis

Fig. 6b shows the results of the fermentation of anaerobic digestion effluent treated by electro dialysis. When anaerobic digestion effluent was directly recycled, citric acid production was 125.4 ± 1.2 g/L, which was 12% lower than that of deionized water (142.5 ± 0.8 g/L). Meanwhile, residual total sugar and isomaltose increased to 29.2 ± 0.7 g/L and 18.0 ±1.4 /L, respectively. It indicated that the degradation and use of dextrin was restricted by inhibitors in anaerobic digestion effluent, i.e., Na^+ and ammonium. When anaerobic digestion effluent was treated with ultra filtration and electro dialysis, the concentrations of ammonium and Na^+ were 36 mg/L (Table 2) and 46.2 mg/L (Fig. 6a), respectively, which were lower than their inhibition concentrations [28]. Therefore, the citric acid production (140.7 ± 0.3 g/L) of the diluate solution in electro dialysis was comparable to that of fermentation with deionized water (142.5 ± 0.8 g/L). The residual total sugar and isomaltose decreased to 18.0 ±1.4 g/L and 1.1 ± 0.2 g/L, respectively. This indicates that the inhibitors, i.e., Na^+ and ammonium, transported from the diluate to the concentrate solution in electro dialysis. The slight difference in performance between anaerobic digestion effluent treated by ultra filtration and electro dialysis and deionized water was due to the inhibitors of anaerobic digestion effluent that could be removed by adding glucoamylase in fermentation [37]. Qi investigated the inhibition concentrations of PAC and APAM in citric acid fermentation by *A. niger* [38]. They found that the concentrations of polyacrylamide and polytonalism chloride in the diluate solution did not affect citric acid production. In summary, anaerobic digestion effluent treated with flocculation, ultra filtration, and electro dialysis did not inhibit citric acid fermentation when it was reused as fermentation water.

4. Conclusion

The integrated citric acid-methane production process was improved by applying ultra filtration and electro dialysis. Treatment with coagulation, flocculation, and ultra filtration, meant that the turbidity of anaerobic digestion effluent met the requirements of electro dialysis. Under optimized conditions, electro dialysis could effectively remove metal ions and ammonium. $CaCO_3$ could be eliminated by

Table 2
Chemical parameters of anaerobic digestion effluent treated by electro dialysis under optimized conditions

Chemical parameters	Raw water	Dilute	Concentrate	Removal rate (%)
pH	8.43	7.15	7.72	–
Conductivity (μS/cm)	4,830	655	15,510	86
TDS (mg/L)	2,425	328	7,720	86
Alkalinity (mg $CaCO_3$/L)	2,620	238	11,389	91
Calcium hardness (mg $CaCO_3$/L)	352	29	380	92
Total hardness (mg $CaCO_3$/L)	693	78	1,315	89
COD (mg/L)	296	237	488	20
NH_3-N (mg/L)	120	36	272	84
LSI	1.97	–1.35	1.88	–

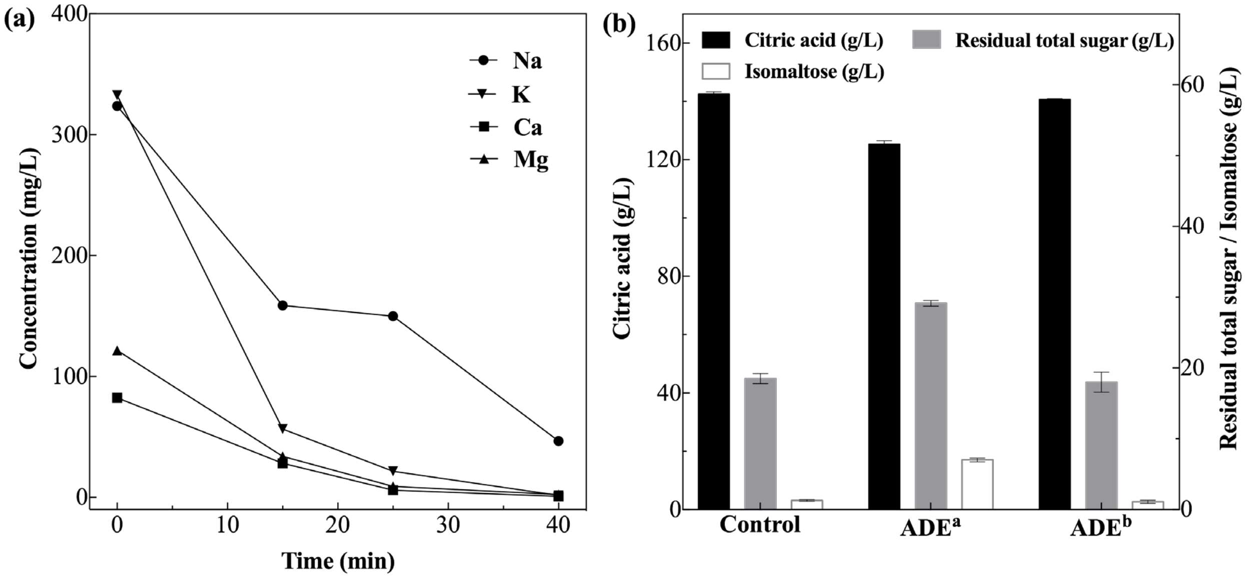

Fig. 6. (a) Evolution of cation concentration variations with time in electro dialysis, (b) the citric acid fermentation of anaerobic digestion effluent(ADE) with different treatments. [a]ADE with no treatment, [b]ADE treated with coagulation, flocculation, and ultra filtration. ($p < 0.05$).

Table 3
Bare ion radius, hydrated radius, and hydration free energy for cations

Ion	Bare ion radius (nm)	Hydrated radius (nm)	Hydration free energy (kJ/mol)
K^+	0.149	0.331	295
Na^+	0.117	0.358	364
Ca^{2+}	0.100	0.412	1,504
Mg^{2+}	0.072	0.428	1,828

adding hydrochloric acid to the concentrate solution. Citric acid production with treated anaerobic digestion effluent was comparable to production with deionized water. This novel study further improved the technical feasibility of the integrated citric acid-methane production process in industrial applications, and provided new insight into cleaner production of other submerged fermentation industries.

Acknowledgements

This work was supported by the Jiangsu province "Collaborative Innovation Center for Advanced Industrial Fermentation" industry development program, and the Priority Academic Program Development of Jiangsu Higher Education Institutions, and the 111 Project (111-2-06).

Symbols

ADE — Anaerobic digestion effluent
APAM — Anionic polyacrylamide
C_e — Current efficiency, %
C_o — Concentrations of free HCO_3^- in the diluate compartment at t (0), mol/L
C_t — Concentrations of free HCO_3^- in the diluate compartment at t (s), mol/L
COD — Chemical oxygen demand
E — Energy consumption, kWh/m^3
F — Faraday constant (96,500 C/mol)
I — Current, A
LSI — Langelier saturation index
N — Number of repeating units
NTU — Nephelometric turbidity unit
PAC — Polytonalism chloride
PDA — Potato dextrose agar
pH$_s$ — pH at which the water was saturated with calcium carbonate
T — Temperature, K
t — Operation time, s
TDS — Total dissolved solids, mg/L
U — Potential, V
V — Circulated volume of solution in the diluate compartment, L
VCF — Volume concentration factor
Z — Absolute valence of ion

Greek

η — Conductivity removal rate, %
κ_o — Conductivities of the diluate solution at t (0), µS/cm
κ_t — Conductivities of the diluate solution at t (s), µS/cm

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Supplementary

Table SM-1
Characteristic of ultra filtration organic membranes

Parameters	100 kD	200 kD
Material	Polyvinylidene difluoride	Polyvinylidene difluoride
Surface (m^2)	0.079	0.077
Diameter (mm)	8	8
Filtrate diameter (nm)	20	30
pH	2–11	2–11
Pressure (MPa)	0.1–0.45	0.1–0.45
Temperature (°C)	< 65	< 65

Table SM-2
Characteristic of ion exchange membranes

Parameters	Cation exchange membrane (CEM)	Anion exchange membrane (AEM)
Product name	TWEDAI Standard membrane	TWEDAI Standard membrane
Type	homogeneous	homogeneous
Exchange capacity (mmol/g)	0.90–1.10	0.90–1.10
Electrical resistance (Ω/cm^2)	≤ 4.50	≤ 5.00
Transport number	≥ 0.98	≥ 0.99
Thickness (μm)	40–50	40–50
Wet water content (%)	15–20	15–20
pH	1–12	1–12

Table SM-3
The turbidity of anaerobic digestion effluenttreated by PAC and APAM

Dosage (mg/L)		Turbidity (NTU)	Removal rate (%)
PAC	APAM		
0	0	197.10	¾
100	1	139.50	29.22
100	2	77.19	60.84
100	3	76.75	61.06
100	4	74.21	62.35
100	5	74.86	62.02
200	1	48.73	75.28
200	2	34.87	82.31
200	3	45.21	77.06
200	4	46.50	76.41
200	5	46.70	76.31
300	1	29.29	85.14
300	2	26.97	86.32
300	3	25.57	87.03
300	4	26.90	86.35
300	5	27.97	85.81
400	1	22.97	88.35
400	2	22.78	88.44
400	3	19.99	89.86
400	4	19.92	89.89
400	5	19.53	90.09
500	1	15.34	92.22
500	2	14.41	92.69
500	3	14.55	92.62
500	4	14.58	92.60
500	5	14.34	92.72

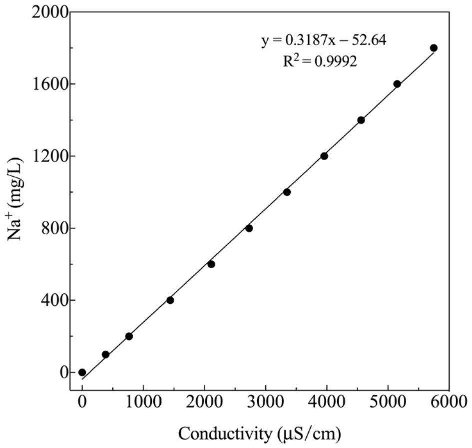

Fig. SM-1. The calibration curve of $NaHCO_3$.

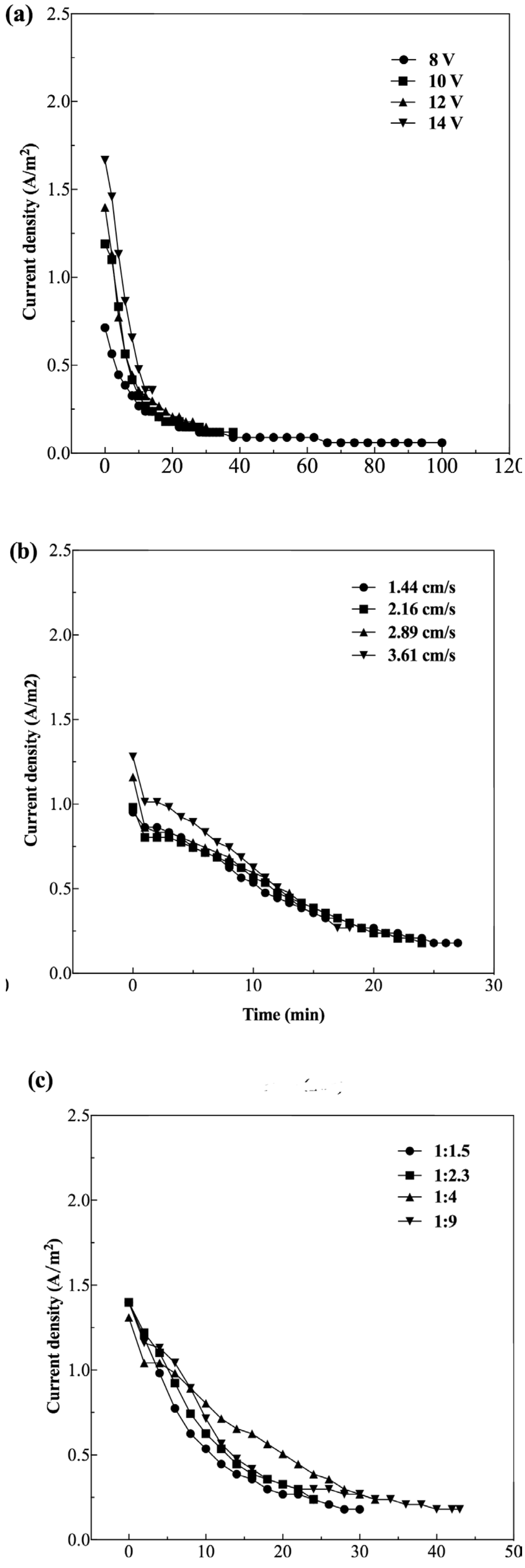

Fig. SM-2. Evolution of current density variations with time in electrodialysis.

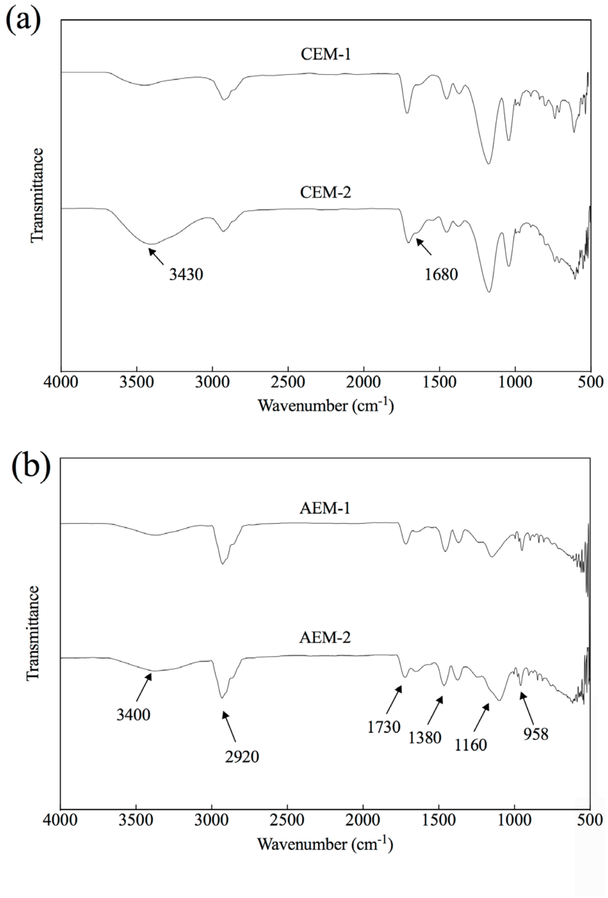

Fig. SM-3. The ATR-FTIR spectra of the original CEM ((a)-1) and AEM ((b)-1), the fouled CEM ((a)-2) and AEM ((b)-2).