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Desalination of l-threonine (THR) fermentation broth by electrodialysis

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ABSTRACT

l-Threonine (THR) is widely used in the areas of pharmaceutical industry, medicine and food, which can be extracted from THR fermentation broth. The fermentation broth is pretreated by microfiltration and active carbon for decolorization, and then desalted by electrodialysis (ED) to remove salt ions such as Cl^-, NH_4^+, Mg^{2+} and Fe^{x+}. The ED performances are adjusted by the operation voltage, membrane type and initial feed pH, which are optimized to be 30 V, polyvinyl alcohol-based hybrid membranes and isoelectric point of 6.16, respectively. The end of desalination can be reached in the shortest time (106 min) when initial feed pH is at the isoelectric point. The highest THR recovery ratio is 86.1% with desalination ratio of 96.9%. The process energy consumption is 4.36 kW h/kg. Hence, the ED process is effective for desalination and recovery of THR. Removal of Cl^- and NH_4^+ (up to 99%) is the most effective, while Mg^{2+} (87.3%) and Fe^{x+} (72.4%) are removed in lesser amount. Membrane fouling occurs after the ED process, which enhances the membrane area resistance from 1.8–2.1 to 2.5–2.7 $\Omega \cdot cm^2$.

Keywords: l-threonine; Fermentation broth; Electrodialysis; Ion exchange membrane; Desalination

1. Introduction

Amino acids are important fermentation products that have been used in food, animal feed, pharmaceutical and cosmetic industries with annual growth rate of 5%–7% [1]. l-Threonine (THR) is one of the eight essential amino acids needed by the human body as well as one of the components of amino acid infusion, and hence, it is important in medical treatment. THR is a type of neutral amino acid and contains both $–NH_2$ and –COOH groups, showing zwitterionic characterization. THR can be normally classified into three types including acidic THR^+, basic THR^- and neutral $THR^\pm$. The different types of amino acid can be transformed through the addition of acid or alkali [2]. The fraction of each type is greatly dependent on the solution pH. The structural formula of THR with respect to pH is shown in Fig. 1. The THR has carboxyl ($pK_1 = 2.15$) and amino groups ($pK_2 = 9.12$) with the isoelectric point of 6.16. The isoelectric point of 6.16 can possess the highest concentration of non-ionic form of THR. The distribution of THR species with respect to pH is shown in Fig. 2.

Nowadays, THR is produced by protein hydrolysis and chemical synthesis but mainly by fermentation method [3,4]. The combination of biotechnology and chemical technology plays an increasingly important role to prepare and extract amino acid. The fermentation broth contains complicated components such as excessive salts and macromolecules [5], from which the amino acid is mainly extracted by the isoelectric crystallization [6]. However, the isoelectric crystallization

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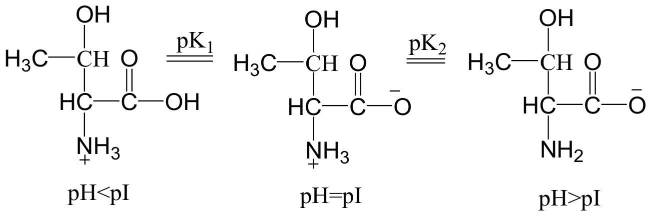


Fig. 1. Structural formula of THR with respect to pH.

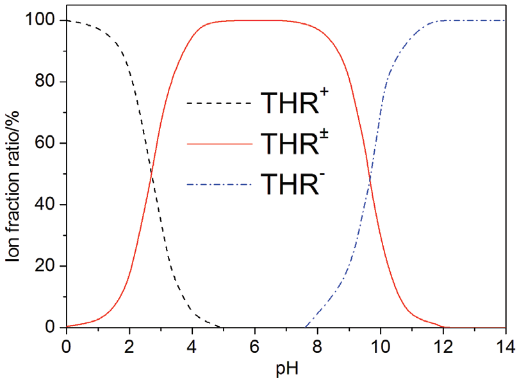


Fig. 2. Distribution of THR species with respect to pH.

has the defects such as complex steps, low yield, product of large amount of crystallization mother liquor and discharge of large sewage. At present, ion exchange is used to produce pure amino acids in the fermentation industry [7], for the amino acid can be exchanged with the ions in the resin. The exchange is based on the tiny solubility difference between amino acid and inorganic salts in mixed solvent [8]. The inorganic salts have competitive adsorption on the resin and thus can be removed. Nevertheless, the regeneration of resin consumes excessive acid and base and induces secondary pollution. Hence, a green and efficient desalination technology is necessary for the removal of inorganic salts from the THR fermentation broth.

Electrodialysis (ED) is an electrochemical separation process, with electric potential to drive ions migration through ion exchange membranes [9]. The ED has the advantages including no consumption of acid and alkali, low running costs and less chemical pollution. Hence, the ED has been widely applied in many fields such as treatment of saline water [10,11] and fermentation broth. For example, glutamine [12] and l-phenylalanine [5] were separated and purified from the simulated fermentation broth. Both experimental data and theoretical equations were applied for numerical calculation of the demineralization ratio. Lysine was produced from L-lysine·HCl using an electrodialyzer with four compartments, and a proline modeling solution is desalted in five- and six-chamber ED apparatus [13,14].

The above work, though has achieved some progress, is still insufficient due to following reasons. First, the simulation solution and fermentation broth are likely to cause membrane fouling due to their complex composition, which may influence the membrane performances. Second, desalination from THR fermentation broth is still seldom reported. Finally, most of the ED processes use commercial membranes but the membrane categories are limited, which may restrict the ED performances in some aspects.

Therefore, in this work, self-prepared membranes will be attempted to desalt the THR fermentation broth. The leakage and loss of THR need to be reduced, and the membrane fouling needs to be investigated. The operation voltages, membrane types and initial feed pH will be optimized to elevate the ED capacity and reduce the energy consumption and the loss of THR.

2. Experimental procedures

2.1. Materials

Microfiltration equipment was supplied by Hefei ChemJoy Polymer Materials Co., Ltd. Microfiltration membrane based on cellulose ester had the pore size of 0.22 μm and effective area of about 0.025 m^2, which was supplied by Haining Chloe Membrane Filtration Equipment Co., Ltd. THR fermentation broth was supplied by Shantou Jiahe Biologic Technology Co. Ltd., China. The initial broth pH and conductivity were around 3.85 and 10.15 mS/cm, respectively. The broth contained protein, sugars, inorganic salts and high concentration of THR, whose solid and ash contents [15] were 12.54 and 0.21 wt%, respectively. Other reagents such as NaCl, Na_2SO_4, NaOH, H_2SO_4 and active carbon were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd., China. Deionized water was used in experiments.

Commercial ion exchange membranes CJMA-2 and CJMC-2 were supplied by Hefei ChemJoy Polymers Co., Ltd., China, while JAM-2 and JCM-2 were purchased from Beijing Tingrun Membrane Technology Development Co., Ltd., China. The main properties of these membranes are listed in Table 1.

2.2. Preparation of CEM-412 and AM-QP-30 membranes

Anion-exchange membrane (AEM) AM-QP-30 and cation-exchange membrane (CEM) CEM-412 were prepared according to procedures modified from our previous work [16–18]. The AM-QP-30 membrane was synthesized from the sol–gel reaction of quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO), tetraethoxysilane and monophenyl triethoxysilane. The QPPO/SiO_2 solution was then mixed with polyvinyl alcohol (PVA) to obtain a casting solution. The casting solution was cast onto the PET fibers and then heated at 130°C for 8 h [16].

The CEM-412 membrane was prepared according to procedures of our previous work [18] but amplified in large-scale here. Multisilicon copolymer was prepared by copolymerization of sodium styrene sulfonate (2.67 mol) and γ-methacryloxypropyl trimethoxy silane (3.9 mol). The copolymer was concentrated through rotary evaporation, and then dropped into 65°C 10 wt% PVA solution (1.18 kg). The mixture solution was taken sol–gel reaction for 26 h to obtain a casting solution. The casting solution was cast onto PET fibers (thickness of 0.105 mm) through a casting device from Shandong Tianwei Membrane Technology Corporation of China. The obtained membrane was further heated at 130°C for 3 h. The main properties were measured and listed in Table 1.

Table 1
Main characteristics of the membranes used in ED experiments

Supplier	Membranes	Thickness, mm	Water uptake^a,%	Area resistance^b, Ω·cm^2		Transport number, %	IEC_A^c, meq/g	IEC_C^d, meq/g
				Original	After ED			
Self-prepared [16–18]	CEM-412	~0.15	40–50	~2.1	~2.5	~76	–	0.33
	AM-QP-30	~0.15	22	~1.8	~2.7	~92	0.7–1.0	
Hefei ChemJoy Polymers Materials Co. Ltd., China	CJMC-2	0.2	35	~1.1	~2.5	98	–	1.50
	CJMA-2	0.145	32	~2.5	~3.9	92	1.25	–
Beijing Tingrun Membrane Technology Development Co., Ltd., China	JCM-2	0.16–0.23	33–40	~2.3	~2.7	95–99	–	1.8–2.2
	JAM-2	0.16–0.23	24–28	~1.1	~2.8	90–95	1.8–2.0	–

[a] Water uptake was calculated as the relative weight gain on hydration per gram of the dry sample.
[b] Membrane area resistance was measured in 0.5 mol/L NaCl [19].
[c] IEC_A is the anion exchange capacity determined by titration in meq/g of Cl^- form.
[d] IEC_C is the cation exchange capacity determined by titration in meq/g of Na^+ form.

2.3. Pretreatment of the THR fermentation broth

The fermentation broth was dark yellow with presence of suspended solid particles. The broth was pretreated by microfiltration (MF) and active carbon to reduce the pollution of ED equipment and to minimize membrane fouling.

Microfiltration equipment was running under the positive pressure of 0.10 MPa [20] by using the MF membrane. The volume of filtered solution was recorded every 10 min to calculate the flux. All experiments were performed at room temperature. The filtered solution was further decolorized by the active carbon, whose dosage was about 1 wt% [21]. The solution was stirred for 20 min, and then the decolorized solution was collected for the following ED desalination.

2.4. ED apparatus

Three kinds of AEMs and CEMs were immersed in 0.5 mol/L NaCl solution for about 12 h and washed by water. Then they were used in ED experiments.

The whole separation process and membrane stack are shown in Fig. 3. The membrane stack was self-assembled including (1) a cathode and an anode composed of titanium-coated ruthenium, which were connected with an electrical source (GX1761SL5A, Hangzhou Yuhang Siling Electrical Instrument Co., Ltd.); (2) two pieces of CEM and a piece of AEM, each of which had an effective area of 20 cm^2. The CEM and the AEM were alternately assembled between the electrodes. Two neighboring membranes were separated by a Plexiglas spacer (10 mm thickness) and a silicon rubber; (3) beakers containing three solutions, which came from the diluted, concentrated and electrode chambers. The initial volume of each solution was 250 mL. The solutions were circulated by submersible pumps (AP1000, Zhongshan Zhenghua Electronics Co. Ltd., China) with flow rate of 300 mL/min. The diluted chamber was filled with the pretreated broth, the concentrated chamber was added with 0.02 mol/L NaCl, and the electrode chamber was supplied by 0.2 mol/L Na_2SO_4. The solution in each chamber was circulated for 0.5 h to eliminate visible bubbles, so that the influence of gas bubbles on the conductivity of membrane stack can be removed [16].

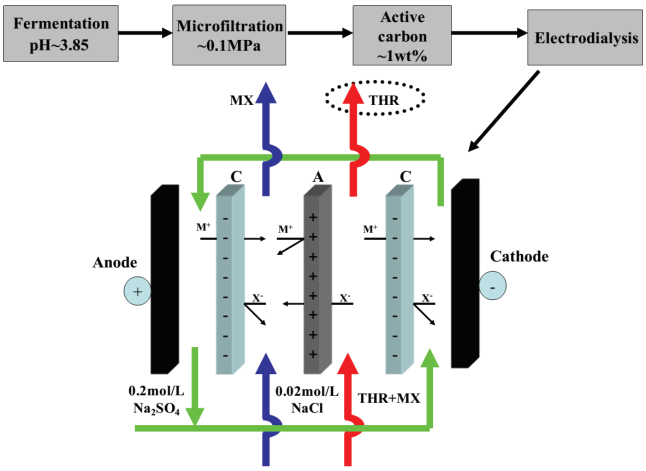


Fig. 3. ED process for removing the salts (MX) from the fermentation broth (M^+, cation; X^-, anion; A, anion-exchange membrane; C, cation-exchange membrane).

2.5. Analytical methods

The THR concentration was determined by the automatic amino acid analyzer (S-4330D, SYKAM Co., Ltd., Germany). The concentration of protein was determined using an ultraviolet spectrophotometer (UV-2450) at 260 and 280 nm. Decolorization ratio was determined by UV-2450 at 420 nm. The solution conductivity was measured by conductivity meter (LE703, METTLER TOLEDO). The pH value and temperature of diluted solution were regularly monitored by an acidity meter (LE438, METTLER TOLEDO).

The concentration of NH_4^+ was determined by ammonia gas-sensitive electrode (PNH3–1, Shanghai Ray Magnetic Instrument Co., Ltd., China). The concentration of Cl^- was determined by potentiometric titration (ZDJ-4A, Shanghai Ray Magnetic Instrument Co., Ltd., China). The concentrations of Ca, Mg, Na, Fe, P and S were determined by ICP-OES (Optima 7300DV, inductively coupled plasma emission spectrometer). Membrane surface morphology was observed with a scanning electron microscopy (SEM; Sirion 200). The membrane area resistance was measured by a device from Hefei ChemJoy Polymer Materials Co., Ltd., which was designed according to the principle previously reported [22].

2.6. Calculation

Filtration liquid flux (J, L/(h m^2)) of the MF process was calculated as Eq. (1) [23]:

$$J = \frac{Q}{A} \tag{1}$$

where Q is volume per unit time (L/h); A is effective membrane area (m^2).

Desalination ratio (D_r, %) was calculated as Eq. (2):

$$D_r = \frac{\delta_0 - \delta_t}{\delta_0} \times 100\% \tag{2}$$

where δ_0 and δ_t are the conductivities in the diluted chamber at time 0 and t, respectively.

THR recovery ratio (R, %) was determined by Eq. (3):

$$R = \frac{C_t V_t}{C_0 V_0} \times 100\% \tag{3}$$

where C_0 and C_t are the THR concentrations in the diluted chamber before and after the ED process, respectively; V_0 and V_t are the volume of diluted chamber before and after the ED process, respectively.

The water recovery rate (η, %) was calculated as Eq. (4) [11]:

$$\eta = \frac{V_t}{V_0} \times 100\% \tag{4}$$

Ion removal ratio (φ, %) was calculated as Eq. (5):

$$\varphi = 1 - \frac{c_t}{c_0} \times 100\% \tag{5}$$

where c_0 and c_t are the contents of inorganic salt (mg/L) in diluted compartment at time 0 and t (min), respectively.

Energy consumption (E, kW h/kg) of the ED process was calculated as Eq. (6) [24]:

$$E = \int_0^t \frac{UIdt}{m} \tag{6}$$

where U (V) is the voltage across ED stack; I (A) is the current applied; t is the time (h); m (kg) is the THR weight in the diluted chamber at time t.

3. Results and discussion

3.1. Pretreatment of MF and decolorization

Usually bacteria must be quickly removed in MF process to prevent the rancidity of fermentation broth, and thus positive pressure of 0.10 MPa is applied here [20]. The flux in Fig. 4 is about 62.93 L/m^2·h within 10 min, then decreases to 12.85 L/m^2·h at 30 min and gradually becomes stable.

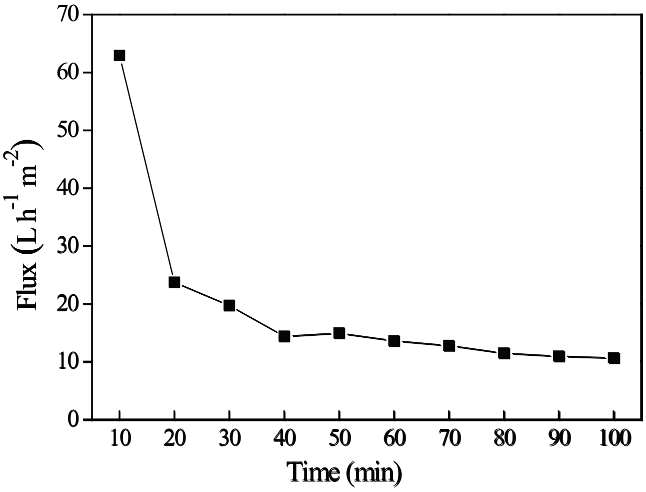


Fig. 4. Flux of microfiltration at 0.1 MPa.

The MF and active carbon decolorization can remove a part of protein and pigment, as shown in Table 2. The MF operation can remove 33.0% protein and 59.1% pigment. The combination of MF with active carbon can remove 86.8% protein and 88.6% pigment. The less residual biomass and polysaccharides in the broth may have less negative effects on subsequent ED process [25]. The concentrations of THR and Cl$^-$ ions are stable or even slightly increase, indicating the ions are all permeated after the pre-treatment. The slightly increase may be attributed the reduced volume after the pre-treatment of MF and decolorization.

Previous reports showed the effectiveness of flocculation for pre-treatment [26]. Nevertheless, as the product of THR is generally used in the food or medicine industry, no chemical reagents such as flocculants are added in our work to avoid the safety and health hazards. The method of centrifugation was also tried for pre-treating fermentation broth together with MF, ultrafiltration, etc [27]. However, the energy consumption is high and the treatment efficiency may be inadequate. For instance, small molecules such as pigment cannot be removed by centrifugation. The focus of this research is to explore the potential of membrane separation and hence, MF together with active carbon decolorization is adopted as the pretreatment for the following ED process.

3.2. Optimization of operation voltage

3.2.1. Current density and desalination ratio

The broth is first pretreated by the MF and active carbon decolorization, and then desalted by ED process until its conductivity reduces to about 0.5 mS/cm, which indicates that the desalination reaches the standard requirements [28]. Self-prepared membranes CEM-412 and AM-QP-30 are used first.

The current density increases continuously in Fig. 5(a) as the voltage increases from 10 to 50 V, for the membrane stack resistance is relatively stable at certain concentrations. The stack resistance is mainly composed of compartment resistance, membrane resistance and electrode resistance [29]. The current density rises first but then falls as the running time prolongs, which is determined by the change of the resistance in different chambers. The resistance of concentrated chamber decreases as the ions concentration increases, which reduces the whole membrane stack resistance initially. However, the resistance of diluted solution rises sharply as ions are mostly removed in later stage.

The desalination ratio in Fig. 5(b) rises rapidly at the beginning of ED process, and then becomes gradually gentle in later stage. The rapid and then gentle increase should be attributed to the variation of current density, which increases first but then falls as the time prolongs. High desalination ratio can be reached in shorter time at high voltage, for the ion transport rate increases with the voltage unless the limiting current density is reached [27]. For instance, 360 min running under 10 V has not yet reached the end of desalination, while 64 min can complete the desalination requirements under 50 V.

Fig. 5(c) shows that the pH of feed solution decreases at first and then increases under all operation voltages. The initial decrease of pH should be due to the leakage of H^+ ions through the AEM, since H^+ ions can be produced by the hydrolysis of anode compartment and transported to the recovery compartment under the electric field. During the later operation stage, the salt is exhausted in feed solution and the conductivity is reduced to a certain extent. Hence, the leaked H^+ ions migrate out of feed compartment, leading to the increase of pH.

Table 3 shows the concentrations of Cl^-, NH_4^+ and THR in the diluted chamber before and after ED process. The concentration of Cl^- or NH_4^+ is lower than 6 mg/L, indicating that they can be effectively removed after ED process. The removal ratio of Cl^- and NH_4^+ is higher than 99% under different operation voltages, which are higher than the desalination ratio (87.4%–95.8%), indicating that the Cl^- and NH_4^+ can be transported more easily through the membrane when compared with some other ions. Meanwhile, the change of THR concentrations after ED process is insignificant, indicating that the THR is less

Table 2
Effect of MF and decolorization on the composition of fermentation broth

Projects	THR, g/L	Protein retention, %	Decoloration ratio, %	Cl^-, mg/L	NH_4^+, mg/L
Untreated	132.4	–	–	569.3	440.3
MF	125.3	33.0	59.1	579.8	423.6
MF + decolorization	134.0	86.8	88.6	575.1	431.9

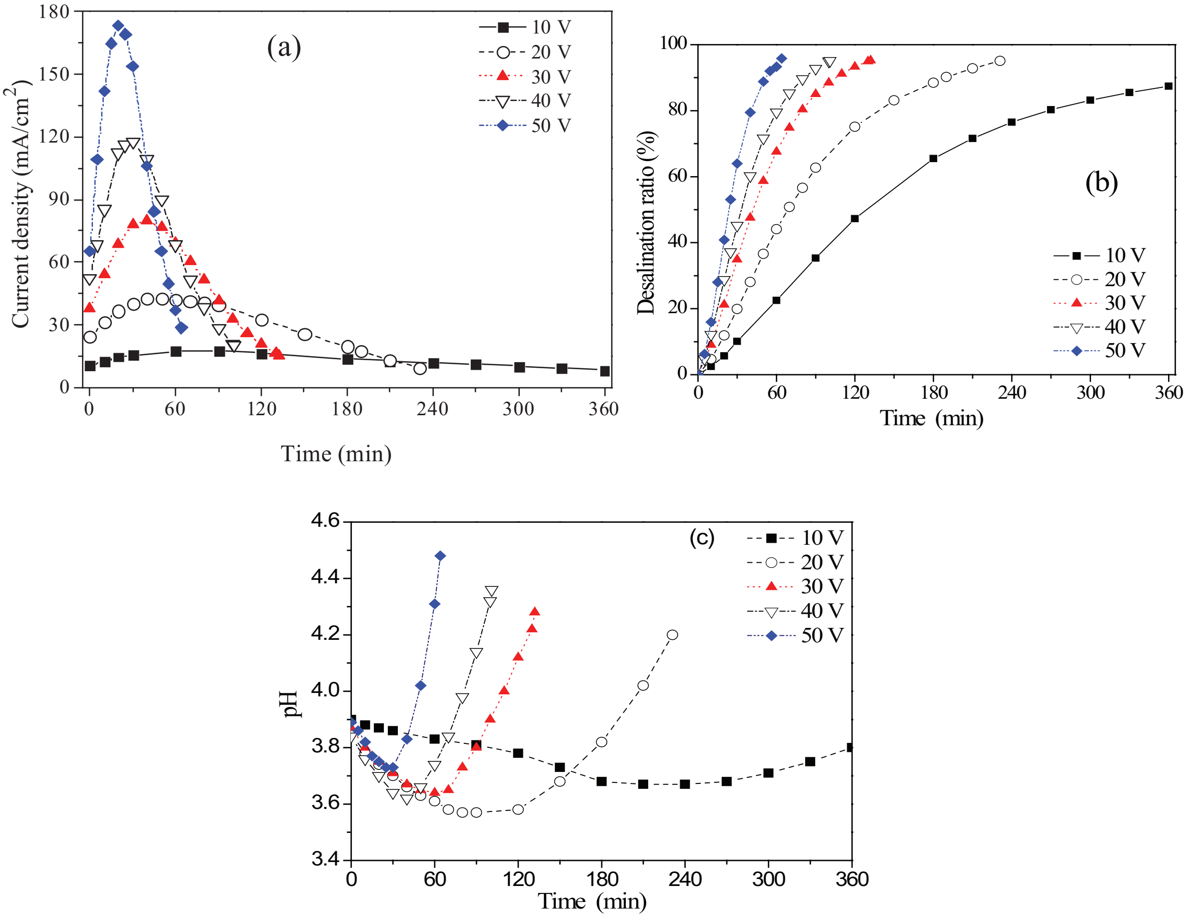


Fig. 5. (a) Current density, (b) desalination ratio and (c) pH at various operation voltages.

Table 3
Concentrations of Cl^-, NH_4^+ and THR in the diluted chamber before and after ED

Voltage, V	Cl^-, mg/L			NH_4^+, mg/L			THR, g/L	
	Before ED	After ED[a]	Removal ratio, %	Before ED	After ED	Removal ratio, %	Before ED	After ED
10	583.8	<5.0	>99	440.3	3.5	99.1	115.72	110.21
20					3.0	99.5	123.83	119.29
30					3.8	99.3	116.30	123.09
40					5.6	99.1	118.14	123.12
50					4.3	99.3	106.88	117.57

[a]The Cl^- concentration is lower than the detecting limit of potentiometric titration.

likely to be lost. The THR concentration even increases somehow after ED process under higher voltages (30–50 V), since the feed solution can be concentrated due to the more obvious water osmosis as will be discussed in the following section.

3.2.2. Energy consumptions, water recovery rate and THR recovery ratio

The ED process is accompanied with water permeation [30] and heat generation. The water recovery rate in Fig. 6 decreases with the increase of operation voltage. High voltage would accelerate the migration of hydrated ions, resulting in more obvious permeation of water through the membrane. At the same time, the enhanced temperature of diluted solution increases with the voltage after ED (Fig. 6), indicating more energy is lost due to the heat generation.

The energy consumption in Fig. 7 increases from 0.70 to 6.08 kW h/kg as the voltage increases, for more electrical energy will be consumed to generate the heat energy at higher voltage. The THR recovery ratios are higher (81.9%, 81.8%) under 10 and 30 V. The loss of some THR should be attributed to the THR transport from the diluted chamber to concentrated chamber. On one hand, THR is amphoteric and thus partially dissociated. It can be transferred from the diluted chamber to the concentrated chamber under electric field; on the other hand, THR is a weak acid, which can diffuse from the diluted chamber to the concentrated chamber under concentration gradient.

In conclusion, voltage of 30 V can obtain relatively high THR recovery ratio, rapid desalination and low energy consumption after taking into account all the factors comprehensively. Hence, 30 V is chosen as the optimal voltage for the following research.

3.3. Comparison of self-prepared and commercial membranes

Commercial membranes CJMC-2/CJMA-2 and JCM-2/JAM-2 are compared with the self-prepared membranes (CEM-412/AM-QP-30) in treating the broth, and the results are shown in Fig. 8. As aforementioned, voltage is kept constant at 30 V and ED running is ended when the conductivity of diluted chamber reduces to 0.5 mS/cm. Fig. 8(a) demonstrates that the JCM-2/JAM-2 and CJMC-2/CJMA-2 membranes need longer time to reach the end of desalination when compared with the self-prepared membranes, indicating the superiority of self-prepared membranes. Membranes CEM-412 and AM-QP-30 not only have lower thickness, but also contain ion exchange groups and –OH groups of PVA. The –OH groups are hydrophilic and thus may reduce the membrane fouling and area resistance after ED process. For example, though the self-prepared membranes have similar area resistance to the commercial membranes before ED, they have lower area resistances than the commercial membranes after ED (Table 1).

Three types of membranes show almost the same current densities in the initial 20 min, as shown in Fig. 8(b). After running 30–40 min, the peak value appears at 75.3 mA/cm² for JCM-2/JAM-2 membranes, and at 55.4 mA/cm² for CJMC-2/CJMA-2 membranes. The values are all lower than

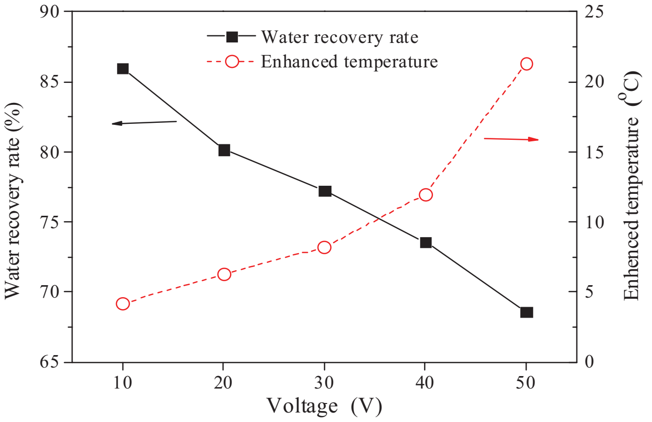


Fig. 6. Water recovery rate and enhanced temperature of the diluted solution after ED process.

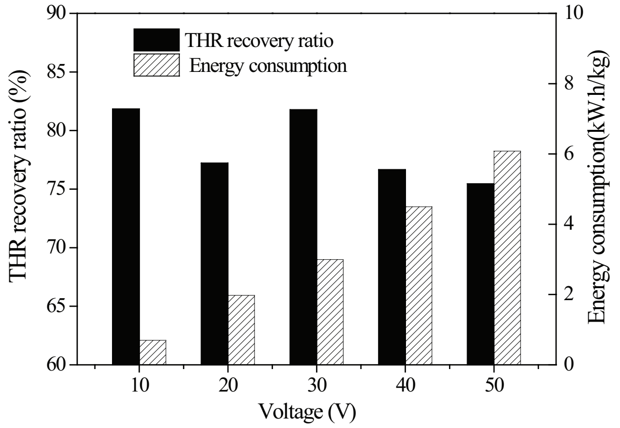


Fig. 7. THR recovery ratio and energy consumption at various operation voltages.

that of self-prepared membranes (79.6 mA/cm^2), illustrating the lower stack resistance of self-prepared membranes.

Water recovery rates of commercial membranes are in the range of 86.0%–87.6%, which are higher than that of self-prepared membranes (77.3%), as shown in Fig. 8(c). The higher water recovery rate indicates that the water osmosis is more serious for self-prepared membranes. The self-prepared membranes contain plenty of PVA-OH groups, which are hydrophilic and thus can accelerate the water migration [31]. Besides, self-prepared membranes have higher current density and heat generation at constant voltage, which may also be beneficial for the water osmosis. The higher heat generation is also shown in Fig. 8(c). The enhanced temperature of diluted solution is 8.2°C for self-prepared membranes, while 4.7°C for the commercial membranes.

Energy consumption of THR is calculated for the diluted solution, as shown in Fig. 8(d). The values of the self-prepared membranes are higher than those of the commercial membranes within 132 min. However, the time to reach the end of the desalination is much shorter, and the total process energy consumption is lower, which also illustrates their advantages in reducing energy consumption. Overall, self-prepared CEM-412/AM-QP-30 membranes are used for subsequent investigations due to the advantages of desalination ratio and energy consumption.

3.4. Influence of initial feed pH

The pH of feed solution should significantly affect the ED performances. The pH of feed solution is 3.85 initially, and then varies to 2.00, 6.16 (isoelectric point of THR) or 9.00 by adding concentrated H_2SO_4 (95%–98%) or 10 mol/L NaOH [2]. Self-prepared membranes are used at the voltage of 30 V.

The desalination ratio in Fig. 9(a) increases more slowly at pH of 2.00 or 9.00, while more quickly at initial feed pH of 6.16. The pH of 6.16 can reach the end of desalination in about 106 min. The slower desalination ratio at pH of 2.00 or 9.00 should be attributed to two reasons. The pH of 2.00 or 9.00 needs more addition of H_2SO_4 or NaOH, which enhances the ions concentration. Besides, when pH is varied from the isoelectric point, THR would exist in high concentration of ionic form such as THR$^+$ or THR$^-$, which can also migrate through the membrane and reduce the current efficiency.

The current densities are higher at pH of 2.00 and 9.00, whose peak values are close to 200 mA/cm^2, as shown in Fig. 9(b). However, the time to reach peak values is longer than that of other pH. The higher current density and longer time should be attributed to the more addition of H_2SO_4 or NaOH, which enhances the solution conductivity and thus reduces the stack resistance. However, the enhanced ions concentration prolongs the desalination time.

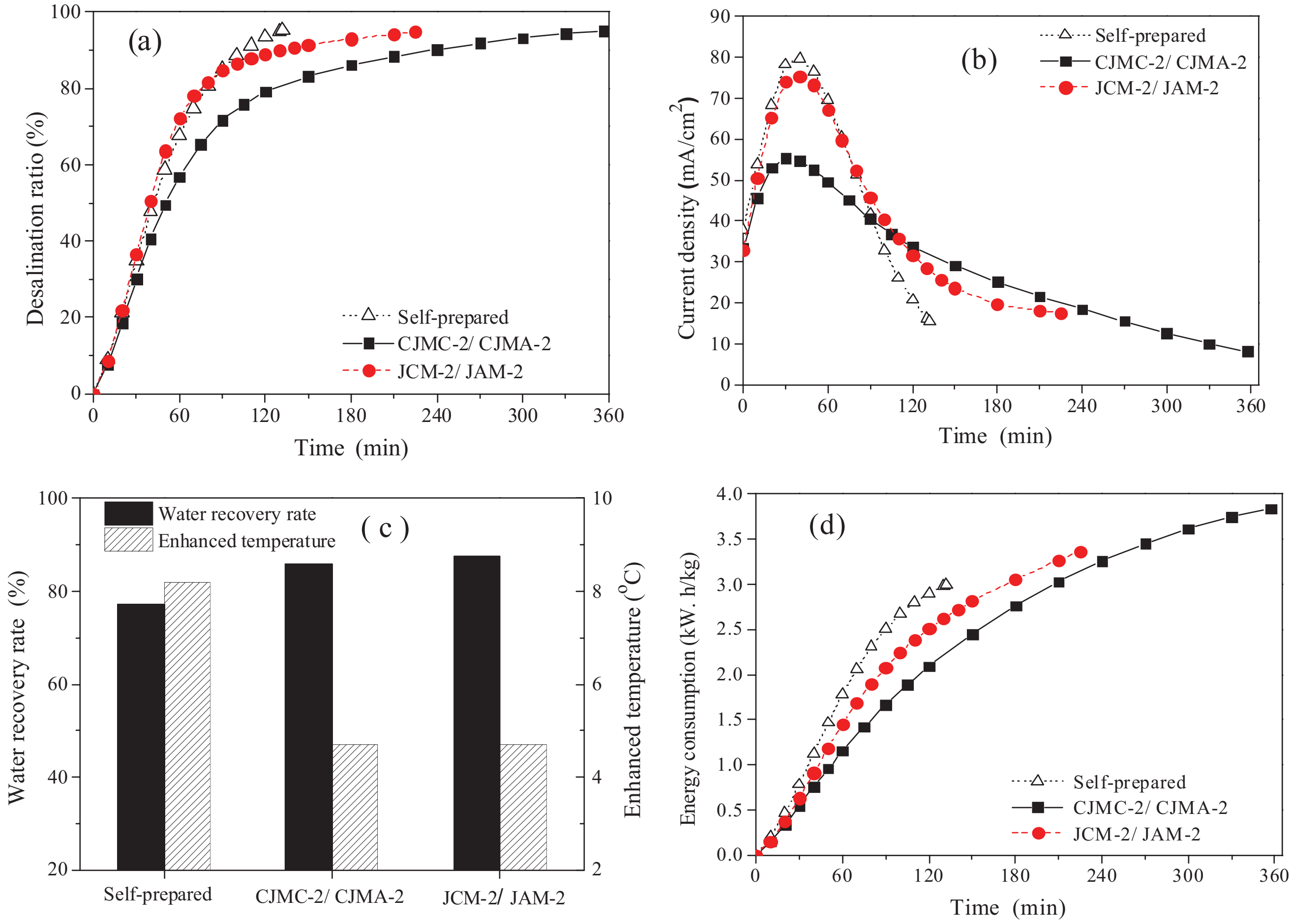


Fig. 8. Effect of membrane types on the ED performances including: (a) desalination ratio; (b) current density; (c) water recovery rate and enhanced temperature of the diluted solution; and (d) energy consumption of THR in diluted solution.

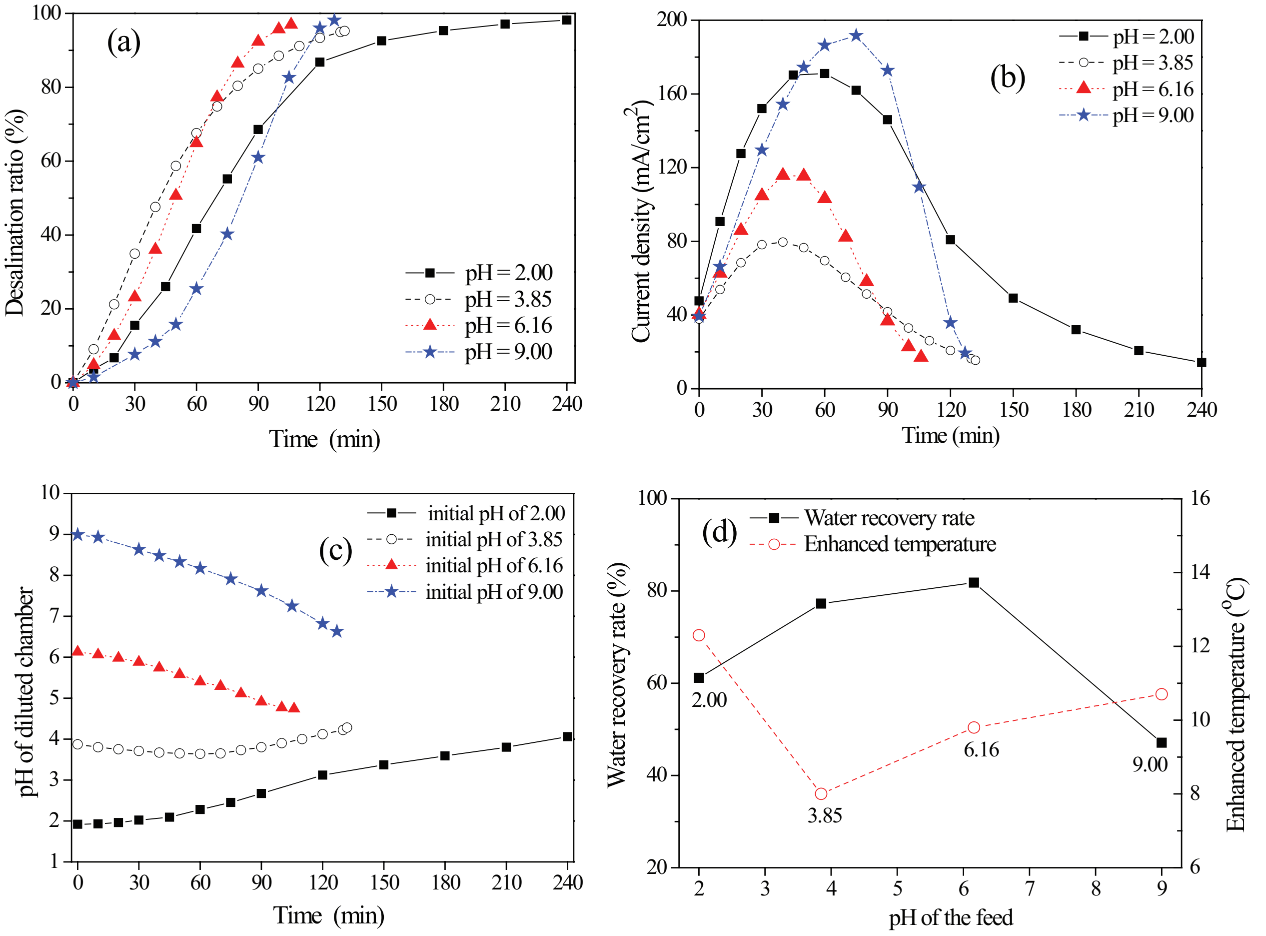


Fig. 9. Effect of initial feed pH on the ED performances including: (a) desalination ratio; (b) current density; (c) pH of diluted chamber; (d) water recovery rate and enhanced temperature.

The pH of diluted chamber increases with the time when the feed solution is acidic (initial pH of 2.00), while the pH decreases when the feed solution has initial pH of 6.16 or 9.00, as shown in Fig. 9(c). When the electric potential is applied to system, on one condition, cations (also H^+ for pH 2.00) move to cathode passing through the CEM. Thus, after a while the pH of solution increases because H^+ transport from feed (THR + MX) compartment to cathode compartment. On the other condition, anions (also OH^- for pH 9.00) pass through the AEM and thus the pH decreases. The feed solution with initial pH of 3.85 is not added with acid or alkali, but the pH of diluted chamber also increases somehow after running 60 min. It is because the salt content is low during the later stage, and H^+ transport from feed compartment to cathode compartment becomes prominent.

Water recovery rate is maximum when the initial feed pH is at isoelectric point (6.16), as shown in Fig. 9(d). Water recovery rate is reduced when initial pH is about 2.00 and 9.00. When feed pH deviates away from isoelectric point, the hydrated ions migrate more significantly, which elevate the water osmosis, current density and heat generation. The temperature of diluted solution increases more significantly (Fig. 9(d)). High temperature may affect the quality of the THR fermented broth, which is unfavorable to crystallize the broth and purify THR.

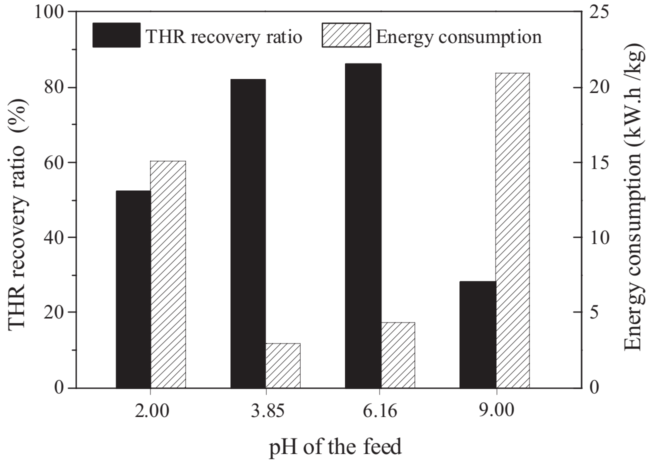


Fig. 10. Energy consumption and THR recovery ratio with respect to the initial feed pH.

Fig. 10 shows the energy consumptions and THR recovery ratios at different initial feed pH. THR recovery ratio increases first from 52.32% to 86.11%, and then decreases to 28.08% as pH increases. THR mainly exists in the form of THR^+ at pH 2.00, and is partially dissociated to the form of

THR^- at pH 9.00 (Fig. 2). When the inorganic ions migrate out of diluted chamber, the transfer of THR will increase in the form of positive or negative ions, reducing the yield of THR product. Moreover, the transport of THR would enhance the energy consumption, for more energy is consumed and more THR is lost. For example, the energy consumption at pH 2.00 and 9.00 is in the range of 15.1–21.0 kW h/kg, which is much higher than that at pH 3.85 and 6.16 (3.0–4.4 kW h/kg).

Overall, the ED performances can be controlled by the initial feed pH. The recommended pH is 6.16 (isoelectric point) in consideration of the relatively high THR recovery ratio and low energy consumption. Under the initial feed pH of 6.16, the ions concentration before and after ED is summarized in Table 4. Monovalent ions are transported preferably. The total desalination ratio is 98.19%, which contains above 99% removal of Cl^- and NH_4^+, 97.52% of Na^+, 97.44% of SO_4^{2-}, 94.42% of PO_4^{3-}, 92.10% of Ca^{2+}, 87.29% of Mg^{2+} and 72.40% of Fe^{x+}. The ions removal ratio is related to their valence state and hydrated radius. Lower valence and smaller hydrated ionic radius are favorable for fast removal [32].

3.5. Membrane fouling

Membrane fouling is a serious problem influencing the membrane performances [23] and hence is investigated by digital photos and SEM graphs. The digital photos in Fig. 11 show that membrane AM-QP-30 darkens obviously from yellow to dark grey after ED. The membrane surface might be covered with pigment and some particles. Membrane CEM-412 changes from white to pale yellow. Some pigment may be deposited on the membrane surface which is close to the cathode chamber.

Membrane AM-QP-30 and CEM-412 surface is further observed by SEM graphs before and after ED, as shown in Fig. 12. The surface is clean and plane before ED, while the surface is deposited by a considerable mass of particles. The particle sizes are in the range of 1–10 μm, which may be partly composed of the pigment remained after the pre-treatment. The fouling may affect the membrane performance [33] such as potential difference [34], inducing the enhanced membrane area resistance (Table 1). The area resistance of AM-QP-30 increases from ~1.8 to ~2.7 Ω·cm², and the value of CEM-412 increases from ~2.1 to ~2.7 (close to cathode chamber) or ~2.2 Ω·cm² (close to anode chamber). However, the enhanced area resistance of self-prepared membranes is less significant than those of commercial membranes (Table 1), which may be attributed to the hydrophilic PVA-OH groups within self-prepared membranes.

Membrane fouling is one of the main concerns of ED process, especially for complicated solution such as the fermentation broth. However, our research indicates that the hydrophilic PVA–OH groups may reduce the membrane fouling. Besides, the ED process is more convenient and environmental friendly than the traditional methods of isoelectric crystallization and ion exchange, which consume other chemicals and produce secondary pollution [6,7]. Hence, the ED process has high potential for desalination of fermentation broth.

4. Conclusions

L-Threonine (THR) fermentation broth contains macromolecules and excessive salts, which are first pre-treated by MF and active carbon. The pre-treatment can remove 86.8% protein and decolorize 88.6% pigment, while retain nearly

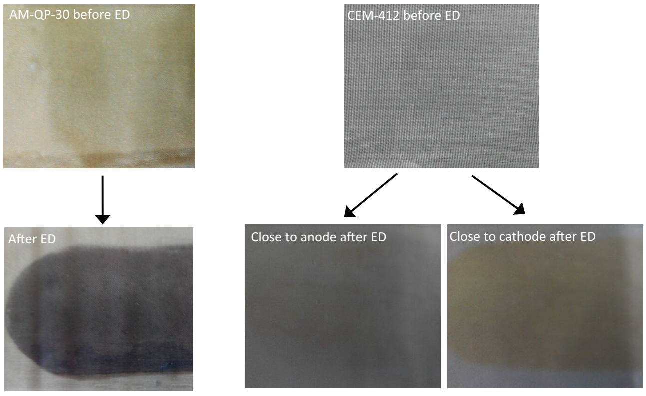
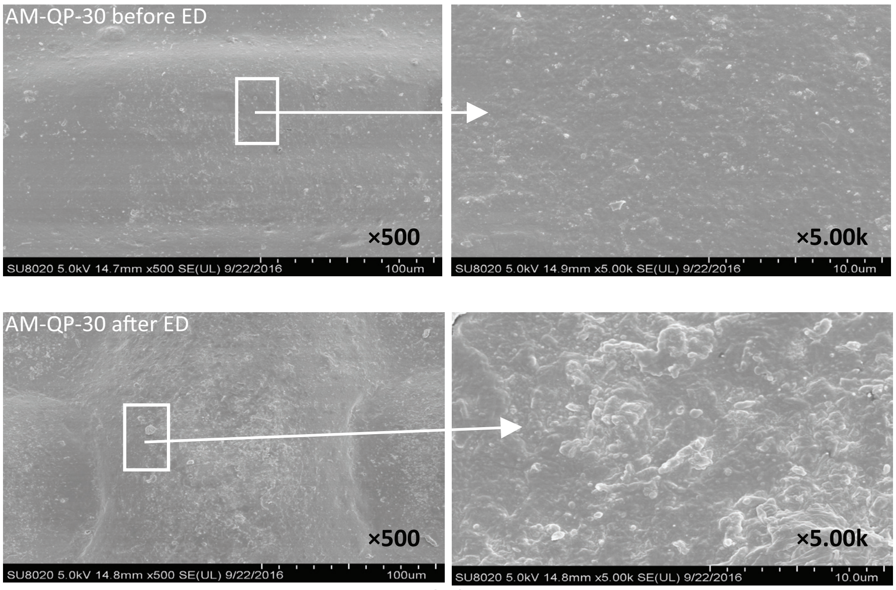


Fig. 11. Digital photos of self-prepared membranes AM-QP-30 and CEM-412 before and after ED (30 V with the initial feed pH of 6.16).

Table 4
Concentrations of inorganic ions before and after ED running, which uses self-prepared membranes under 30 V with the initial feed pH of 6.16

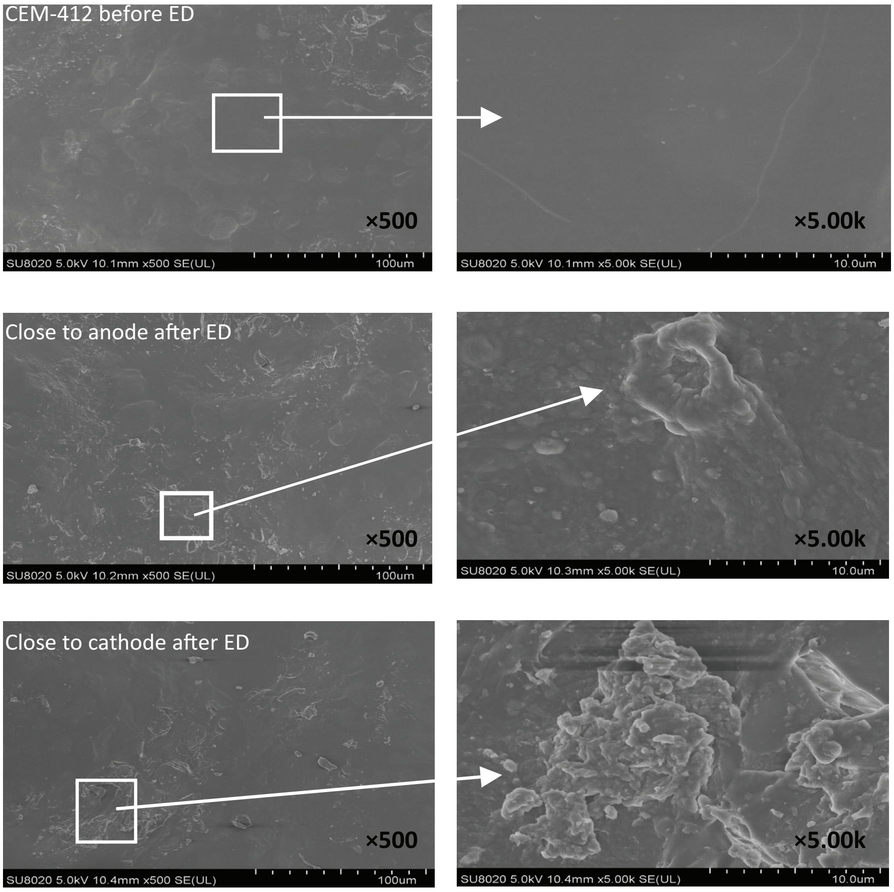
Species[a]	Before ED, mg/L		After ED, mg/L		Ion removal ratio, %
	Diluted chamber (feed)	Concentrated chamber	Diluted chamber	Concentrated chamber	
Na^+	1,500	487.8	37.2	5,340	97.52
Cl^-	750	630.2	<5	1,496	>99
SO_4^{2-}	1,661	–	42.6	1,276	97.43
Ca^{2+}	66.7	–	5.3	134	92.05
Mg^{2+}	44.2	–	5.6	117	87.33
Fe^{x+}	13.2	–	3.6	40	72.73
PO_4^{3-}	134.5	–	7.5	256	94.42
NH_4^+	342.5	–	2.7	299.7	99.21

[a] Species concentration measured by ICP-OES should be the total concentration of one element, but here only ion form is represented. The exact form of "Fe" cannot be confirmed and thus "Fe^{x+}" is used.



(a)

(a) SEM graphs ofmembrane AM-QP-30



(b)

(b) SEM graphs ofmembrane CEM-412

Fig. 12. Membrane SEM graphs with the magnification of 500 (left) and 5,000 (right) before and after ED (30 V with the initial feed pH of 6.16).

all the THR and inorganic salts such as NH_4^+ and Cl^-. The pretreated broth is then desalinated by a lab scale ED stack, whose performances are adjusted by the operation voltage, membrane category and initial feed pH.

Higher voltage can increase the desalination ratio, but decrease the water recovery rate and increase the energy consumption. Self-prepared CEM-412 and AM-QP-30 membranes can achieve higher desalination efficiency, and lower total process energy consumption than commercial membranes. When the initial feed pH is adjusted as 6.16 (isoelectric point of THR), the end of desalination can be reached in the shortest time (106 min). The desalination ratio is 96.94% with the THR recovery ratio of 86.11%. The energy consumption is 4.36 kW h/kg. Membrane fouling occurs after the ED process, which elevates the membrane area resistance. Further improvement may be investigated through the increase of repeat unit number, and decrease of membrane fouling and THR leakage.

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Symbols

THR – L-Threonine
ED – Electrodialysis
PVA – Polyvinyl alcohol
AEM – Anion-exchange membrane
CEM – Cation-exchange membrane
QPPO – Quaternized poly(2,6-dimethyl-1,4-phenylene oxide)
IEC_C – Cation exchange capacity
IEC_A – Anion exchange capacity
SEM – Scanning electron microscope
MF – Microfiltration
J – Filtration liquid flux of microfiltration during pre-treatment
D_r – Desalination ratio of all the ions in the THR fermentation broth
φ – Ion removal ratio for one type of ion
R – THR recovery ratio in the diluted chamber
η – Water recovery rate in the diluted chamber
E – Energy consumption of THR in the diluted chamber

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