Desalination and Water Treatment
www.deswater.com

25 (2011) 291–296
January

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doi: 10.5004/dwt.2011.1999

Production of L-lysine from L-lysine monohydrochloride by electrodialysis

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Received 11 May 2010; Accepted in revised form 14 June 2010

ABSTRACT

Production of L-lysine from L-lysine monohydrochloride was carried out by electrodialysis, using four-compartment electrodialysis apparatus with two cation-exchange membranes and one anion-exchange membrane. The process feasibility was tested with an effective membrane area of 25 cm^2. Effects of L-Lys·HCl concentration, the molar ratio of L-Lys·HCl and NaOH, and the operation voltage were compared and discussed in terms of ionic transport. The Cl$^-$ removal ratio, the current density, the current efficiency, and the energy consumption were presented and the optimum experimental parameters were determined. It was suggested that optimum operating conditions were as follows: the initial concentration of L-Lys·HCl is 0.3 mol L^{-1}, the molar ratio of L-Lys·HCl and NaOH 3:5 and the constant voltage 30 V.

Keywords: Electrodialysis; L-lysine; L-lysine monohydrochloride; Production

1. Introduction

L-lysine (L-Lys) is an essential amino acid generally considered as a fundamental substance of human body, which is very important in regulating metabolic balance and promoting the body's absorption of cereal protein [1]. It has been widely used in pharmaceuticals, food, and feed industry. Commercial L-Lys is usually produced as L-lysine monohydrochloride (L-Lys·HCl), since L-Lys is difficult to preserve and easy to absorb moisture as a natural protein. However, L-Lys·HCl is not commonly suitable for eating directly, and Cl$^-$ needs to be removed in order to gain the L-Lys of high medical and edible value [2].

The production methods of L-Lys include hydrolysis, synthesis and fermentation. Among them fermentation is the most primary route [3]. After fermentation, L-Lys is usually recovered from broth by ion-exchange process. Although high recovery for L-Lys is achieved, large amount of acid and base are consumed in order to regenerate ion-exchange resins, which increase overall operational cost. In addition, wastewater from the process of reactivating and washing the ion-exchange resins also causes serious environmental pollution.

Electrodialysis is an electro-membrane process in which ions are transported through ion-exchange membranes from one solution to another under the drive of an electric field force between two electrodes [4]. The main advantages of this method are higher recovery ratio, lower energy consumption and less pollution. Until now, many literature papers have been devoted to the production or separation of amino acids by electrodialysis, such as L-tryptophan [5], glutamic acid [6], tyrosine [7], and phenylalanine [8]. Aghajanyan et al. [9] reported the separation of L-proline with a five and six-chamber electrodialysis apparatus. Kinetic curves of proline's migration through ion-exchange membrane were inves-

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tigated, and the optimal current density was found with a desalting degree of about 94.6%. Grib et al. [10] presented the recovery of phenylalanine from an industrial waste stream by electrodialysis. The process were successful in removing 98% of salts (e.g., Na_2SO_4 and $(NH_4)_2SO_4$), with an average current efficiency of 98%, and the loss of phenylalanine did not exceed 5%. In addition, separation of L-Lys, methionine, and glutamic acid by electrodialysis [11] was also studied. It was showed that L-Lys streams through cation-exchange membrane and glutamic acid through anion-exchange membrane reached a maximum at a neutral range of pH. With an increase in current density, the stream of L-Lys and glutamic acid through membranes also increased. Obviously, electrodialysis has been successful used in the production or recovery of several amino acids, however, few literature papers have reported the production of L-Lys from L-Lys·HCl.

In this paper, the production of L-Lys from L-Lys·HCl using an electrodialyzer with four compartments is investigated. Effects of several parameters including L-Lys·HCl concentration, the molar ratio of L-Lys·HCl and NaOH, and the operation voltage are presented. The optimum experimental parameters of the whole operation system, such as the removal ratio of Cl^-, the current efficiency, and the energy consumption are also studied.

2. Experimental

2.1. Material

The heterogeneous ion-exchange membranes were purchased from Zhejiang Qianqiu Environmental Water Treatment Co., Ltd. (China), and their main characteristics are listed in Table 1.

L-lysine monohydrochloride, sodium hydroxide and sodium sulphate were commercially obtained and used without further purification. Deionized water was used throughthly.

2.2. Methods

First, L-Lys·HCl and NaOH with different concentrations were mixed and reacted for some time. The reaction equation can be written as Eq. (1):

$$\text{L-Lys}\cdot\text{HCl+NaOH} \rightarrow \text{L-Lys+NaCl+H}_2\text{O} \qquad (1)$$

Table 1
Main characteristic of the ion-exchange membranes

Membrane	Cation-exchange membrane	Anion-exchange membrane
Water content, %	40–55	30–45
Exchange capacity, mol kg^{-1}	≥2.0	≥1.8
Area resistance, Ω·cm^2	12	13
Thickness, mm	0.42	0.42
Transport number, %	90	92

Then the reacted solution was desalinated and NaCl was removed by electrodialysis. As shown in Fig. 1, the laboratory-scale electrodialyzer consisted of one anode, one cathode, one piece of anion-exchange membrane, as well as two pieces of cation-exchange membranes inserted between them with the inter-membrane distance of 8 mm. There were four compartments from left to right: anode compartment (compartment 1) containing 0.5 mol L^{-1} of Na_2SO_4 solution, concentrating compartment (compartment 2) containing 0.2 mol L^{-1} $NaNO_3$ solution, desalting compartment (compartment 3) composed of the reacted mixture of L-Lys·HCl and NaOH solution, and cathode compartment (compartment 4) composed of 0.5 mol L^{-1} Na_2SO_4 solution. Each compartment with the volume of 25 mL was connected to a separate external 500 mL beaker, allowing for continuous recirculation by four submerged pumps (AT-301, ATMAN) with the flow rate of 15 L h^{-1}. The size of ion-exchange membrane was 7 cm×7 cm with an effective area of 25 cm^2. The voltage during operation was controlled by a DC power (DF1731SLL3A, Zhongce Electronics Co., Ltd., China).

After electrodialysis, most of Cl^- and Na^+ ions from compartment 3 transferred across the ion-exchange membranes and concentrated in compartment 2 and compartment 4, respectively, under the drive of the electric field force. The pH of the solution in compartment 3 was controlled to be of the isoelectric point (9.74) of L-Lys, so that its loss across the ion-exchange membrane reached a minimum level.

During the electrodialysis, such parameters as current density, pH of each compartment, and removal ratio of Cl^- were recorded and calculated as below once in a while. All measurements were carried out for three times at constant temperature (20 ± 0.5°C), and their mean value was taken as the final result. The estimated error is about ±5%.

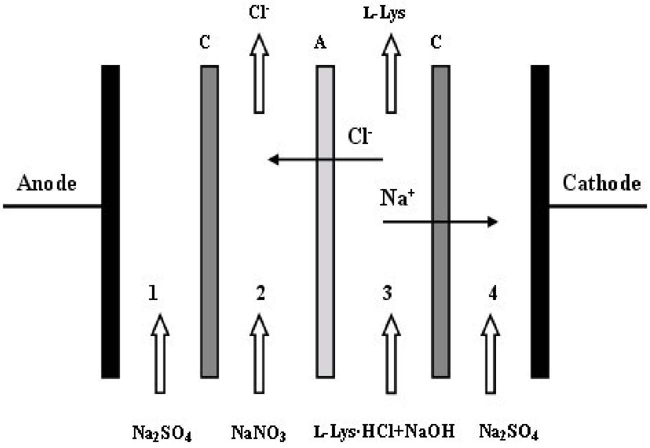

Fig. 1. Schematic of the electrodialyzer for L-Lys production.

2.3. Calculation

The operation process performance of electrodialysis was expressed by removal ratio of Cl^-, energy consumption, and current efficiency.

Since most Cl^- ions transferred across the anion-exchange membrane and concentrated in compartment 2, no Cl_2 was measured in compartment 1. Thus the removal ratio of Cl^- can be calculated as R_m in Eq. (2):

$$R_m = \frac{n(t)}{n_S(0)} \times 100\% \tag{2}$$

where $n(t)$ is the mole amount of Cl^- in compartment 2 (mol); $n_s(0)$ the mole amount of initial L-Lys·HCl (mol) in compartment 3.

Energy consumption (kW h kg^{-1}), EC is defined as Eq. (3):

$$\mathrm{EC} = \frac{\int_0^t IUdt}{m} \tag{3}$$

where m is the mass of Cl^- removed (kg); I the current (A); t the time (h); U the voltage (V).

Current efficiency (%), CE is defined as Eq. (4):

$$\mathrm{CE} = \frac{zF\Delta n}{\int_0^t Idt} \times 100\% \tag{4}$$

where Δn is the mole amount of Cl^- removed (mol); z the ionic valency; F the Faraday constant (96,500 C mol^{-1}).

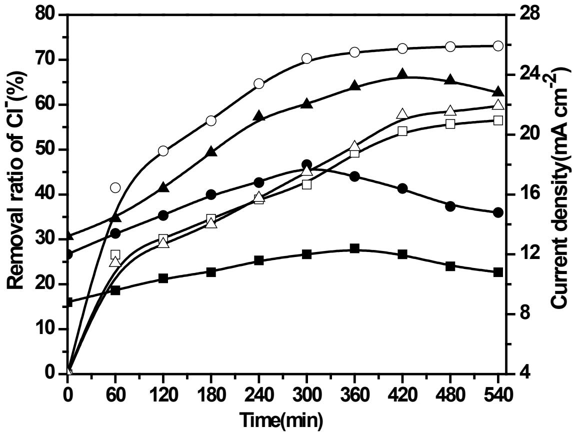

Fig. 2. Variation of current density and removal ratio of Cl^- with time at different molar ratios of L-Lys·HCl and NaOH (Current density: ■ 1:5; ● 3:5; ▲5:5; Removal ratio of Cl^-: □ 1:5; ○ 3:5; △ 5:5).

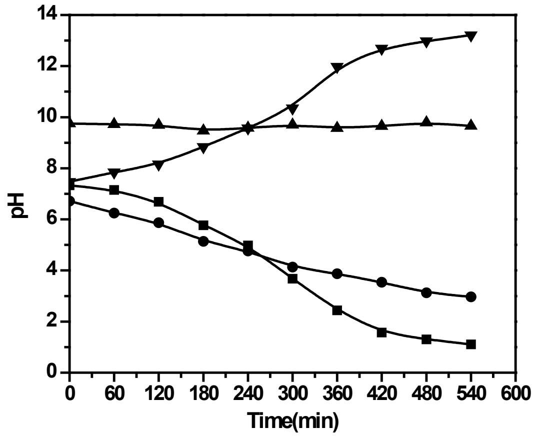

Fig. 3. Variations of solution pH with time (■: compartment 1; ●: compartment 2; ▲: compartment 3; ▼: compartment 4).

3. Results and discussion

3.1. Effect of feed liquid

3.1.1. Effect of molar ratio of L-Lys·HCl and NaOH

The voltage was kept constant in 30 V, and the pH of the solution in compartment 3 was controlled to be 9.74. The concentration of NaOH was fixed to as 0.5 mol L^{-1}, and the molar ratio of L-Lys·HCl and NaOH were changed to be 1:5, 3:5 and 5:5. During the electrodialysis, both the current density and removal ratio of Cl^- were recorded, and their variations with electrodialysis time are shown in Fig. 2. pH of the solution in each compartment as a function of electrodialysis time is shown in Fig. 3, the current efficiency and energy consumption are shown in Fig. 4.

In Fig. 2, both current density and removal ratio of Cl^- increase with the increase of time at the beginning of electrodialysis. However, the current density reaches its maximum value and decreases with time, and Cl^- removal ratio almost keeps constant, after it reaches a higher value. It should be noted that the molar ratio of L-Lys·HCl and NaOH were 3:5, namely, NaOH is excessive from the point of stoichiometric view according to Eq. (1). When the electrodialysis starts, both Cl^- and excessive OH^- in compartment 3 were transferred to compartment 2 across the anion-exchange membrane, while Na^+ transferred to compartment 4 across the cation-exchange membrane under the drive of electric field force. As a result, the decrease of the electric resistance in compartment 2 and 4 causes the increase of current density and Cl^- removal ratio. With such a transport process going on, more and more Cl^- and Na^+ transferred out from compartment 3, which results in the increase of the electric resistance in compartment 3 [12], and thus the sharp decrease in the overall current density. In fact, such an experimental trend can be observed during the whole procedure of electrodialysis, which is in accordance with the results investigated by Kumar [13]. On the other hand, with the same electrodialysis time, the current density increases with the rising of molar ratio of L-Lys·HCl and NaOH. The explanation to such an experimental trend can be rendered below: As mentioned above, the concentration

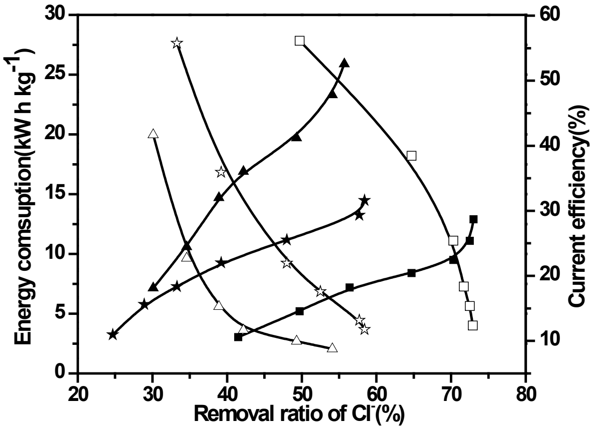

Fig. 4. Variation of energy consumption and current efficiency with removal ratio of Cl^- at different molar ratios of L-Lys·HCl and NaOH (Energy consumption: ▲ 1:5; ■ 3:5; ★ 5:5; Current efficiency: △ 1:5; □ 3:5; ☆ 5:5).

of NaOH here was fixed to as 0.5 mol L^{-1}, and the molar ratio of L-Lys·HCl and NaOH were altered through changing the amount of L-Lys·HCl. The higher molar ratio means the larger amount of L-Lys·HCl. Although the pH was controlled to be of the isoelectric point of L-Lys·HCl, there are still a little amount of cation (L-Lys^+) and anion (L-Lys^-) dissociated. The more amount of L-Lys·HCl, the more the dissociated ions are. Consequently, increase of the ion amount raises the current density undoubtedly.

It also can be seen from Fig. 2 that final Cl^- removal ratio at the molar ratios of L-Lys·HCl and NaOH 1:5, 3:5 and 5:5 are 56.5%, 73.1% and 59.7%, respectively. The removal ratio first increases and then decreases with the molar ratio, and when the molar ratio is 3:5, the Cl^- removal ratio achieves the maximum. As a matter of fact, the ionic transport in such an electrodialysis system is a little complicated. Taking compartment 3 into consideration, the main ionic transports are as the following: substantial Cl^- and excessive OH^- (except molar ratio 5:5) together with slight L-Lys^- transfer across anion-exchange membrane, and abundant Na^+ and little L-Lys^+ across the cation-exchange membrane. Since the concentration of NaOH is fixed at 0.5 mol L^{-1}, the increase of the molar ratio means the raising of the concentration of L-Lys·HCl, which lead to the rising removal ratio of Cl^- from the point of chemical reaction equilibrium. Moreover, because of smaller volume and larger mobility, OH^- is much easier to transfer to compartment 2 than Cl^-. The more the excessive OH^- (the less the molar ratio), the more limited the transport of Cl^- is, and thus the lower removal ratio of Cl^- is. However, when the molar ratio increases to be higher than 3:5 (i.e., 5:5), the Cl^- removal ratio also decreases. That means the molar ratio increases too much is disadvantageous to the production of L-Lys.

In addition, pH of the solution in each compartment except compartment 3 also changes with the electrodialysis time as shown in Fig. 3, when applied voltage was 30 V, initial molar ratio of L-Lys·HCl and NaOH 3:5, and initial L-Lys·HCl concentration 0.3 mol L^{-1}, respectively. When the electrodialysis process begins, the electrode reaction occurs as below:

Anode reaction:

$$2OH^- - 2e \rightarrow H_2O + \frac{1}{2}O_2 \uparrow \qquad (5)$$

Cathode reaction:

$$2H^+ + 2e \rightarrow H_2 \uparrow \qquad (6)$$

Initially, anolyte in compartment 1 offers nearly pH 7.3 because Na_2SO_4 solution is neutral, and afterwards it decreases to some extent due to formation of H^+ by water splitting. Likely, pH of catholyte in compartment 4 is initially close to7.4, which is increased substantially due to the consumption of H^+ according to Eq. (6). The pH of compartment 3 was kept to be close to 9.74 as mentioned in section 2.2, while the pH of compartment 2 decreases with time on account of immigration of H^+ from compartment 1. As a matter of fact, similar relationship between pH of each compartment and electrodialysis time can be observed during all of our experiments, and explanations are also analogous.

As shown in Fig. 4, for including, the energy consumption increases with Cl^- removal ratio for different molar ratios (e.g., 1:5, 3:5, and 5:5). As illustrated above, current density decreases when the electrodialysis is progressing, causing the increase of the electric resistance contributed to the energy consumption. In order to remove the same ratio of Cl^-, the energy consumption decreases with the increase of molar ratio below 3:5. When the molar ratio is lower than 3:5, i.e., 1:5, the concentrations of L-Lys·HCl and NaOH are 0.1 and 0.5 mol L^{-1}, respectively. Obviously, low overall ionic concentration results in high electric resistance, which is the main reason for high energy consumption. However, when the molar ratio is higher than 3:5 (i.e., 5:5), the energy consumption also increases. From Fig. 2 it can be found that the electrodialysis time needed to reach an equal removal ration of Cl^- for the molar ratio of 5:5 is much longer than that for 3:5. The longer the electrodialysis time, the higher the energy consumption is.

In addition, the current efficiency can also be influenced by the molar ratios of L-Lys·HCl and NaOH. The current efficiency decreases with the increase of time, which conforms to the typical trends reported by Xu [14]. In addition, the current efficiency is 30.0%, when the molar ratio of L-Lys·HCl and NaOH is 3:5 in Fig. 4. While the ratio is less or larger than 3:5 (e.g., 1:5 or 5:5), the current efficiency also decreases to some extent.

Therefore, among different molar ratios of 1:5, 3:5 and 5:5, taking the Cl^- removal ratio and energy consumption together with current efficiency into comprehensive consideration, it can be concluded from Figs. 2–4 that the optimum molar ratio is 3:5. At such a molar ratio, the ultimate Cl^- removal ratio can achieve 73.1%, with the energy consumption of 12.9 kW h kg^{-1} and current efficiency of 30.0%, respectively.

3.1.2. Effect of initial L-Lys·HCl concentration

In this part, the effect of initial L-Lys·HCl concentration was investigated with a molar ratio of L-Lys·HCl and NaOH of 3:5, the voltage of 30 V, and the pH value of solution of 9.74. Various electrodialysis experiments were carried out at the L-Lys·HCl concentrations of 0.15 mol L^{-1}, 0.3 mol L^{-1} and 0.6 mol L^{-1}. Obtained removal ratio of Cl^-, current density, energy consumption and current efficiency are shown in Figs. 5 and 6.

The order of the removal ratio with various initial L-Lys·HCl concentrations is: 0.3 mol L^{-1} > 0.15 mol L^{-1} > 0.6 mol L^{-1}, the current density order is: 0.6 mol L^{-1} > 0.3 mol L^{-1} > 0.15 mol L^{-1} with similar electrodialysis time. The energy consumption is: 0.15 mol L^{-1} > 0.6 mol L^{-1} > 0.3 mol L^{-1} and the current efficiency 0.3 mol L^{-1} > 0.15 mol L^{-1} > 0.6 mol L^{-1} at the close Cl^- removal ratio. Since the molar ratio of L-Lys·HCl and NaOH is kept constant, the decrease of the initial concentration of L-Lys·HCl (0.15 mol L^{-1}) means less amount of OH^- in compartment 3, which increases the electrical resistance of the whole electrodialysis system and thus results in an lower current density. Therefore, the removal ratio of Cl^- and current efficiency decrease; however, the energy consumption increases contrarily. When the concentration is higher than 0.3 mol L^{-1} (i.e., 0.6 mol L^{-1}), the Cl^- removal ratio decreases instead, and thus the energy consumption increases and current efficiency decreases, respectively. Above experimental facts indicate that increase or decrease of the concentration too much (i.e., 0.15 mol L^{-1} or 0.6 mol L^{-1}) is both disadvantageous to the production of L-Lys.

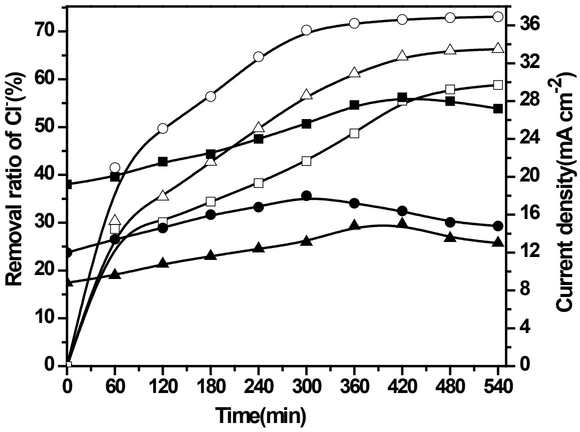

Fig. 5. Variation of current density and removal ratio of Cl^- with time at different initial concentrations of L-Lys·HCl (Current density: ▲ 0.15 mol/L; ● 0.3 mol/L; ■ 0.6 mol/L; Removal ratio of Cl^-: △ 0.15 mol/L; ○ 0.3 mol/L; □ 0.6 mol/L).

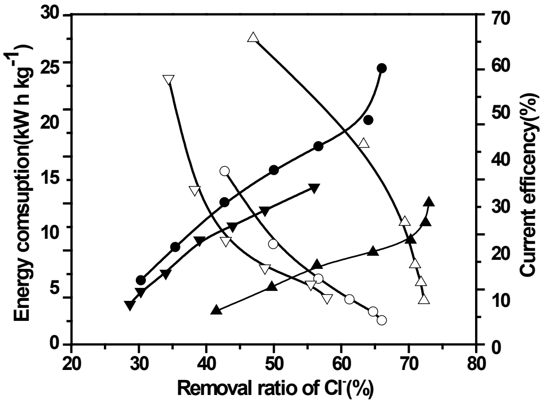

Fig. 6. Variation of energy consumption and current efficiency with removal ratio of Cl^- at different initial concentrations of L-Lys·HCl (Energy consumption: ● 0.15 mol/L; ▲ 0.3 mol/L; ▼ 0.6 mol/L; Current efficiency: ○ 0.15 mol/L; △ 0.3 mol/L; ▽ 0.6 mol/L).

3.2. Effect of voltage

In order to study the effect of operation voltage, several experiments were carried out at various voltages of 20, 30 and 50 V, respectively. The initial concentration of L-Lys·HCl was 0.3 mol L^{-1} and NaOH was 0.5 mol L^{-1}, and the operation was carried out at pH of 9.74. Removal ratio of Cl^- as a function of time at different voltages is shown in Fig. 7, and the comparisons of operation process performance parameters are also listed in Table 2.

In Fig. 7 and Table 2, the process of electrodialysis can be strongly affected by operation voltage. Higher voltage always results in larger removal ratio of Cl^-. After 9 h of electrodialysis, the Cl^- removal ratio reaches 61.4% and 73.1%, respectively, when voltage is varied from 20 to 30 V. However, there are no obvious difference in removal ratio at 30 V and 50 V. Though the higher voltage (i.e., 50 V) can improve the Cl^- removal ratio compared with that at 30 V, it makes against the current efficiency and energy consumption as shown in Table 2. When Cl^- transfer is kept constant, polarization may occur at high operation voltage resulting in the competitive transfer of hydroxyl ion with Cl^-, which inevitably decreases the current efficiency and increases the energy consumption. Moreover, heat emitting transformed from part of electric energy maybe occurs, which is also another loss to the energy consumption and current efficiency [15]. Therefore, though less time that is taken to reach the maximum removal ratio of Cl^- with the increase of operation voltage, the energy consumption increases and current efficiency

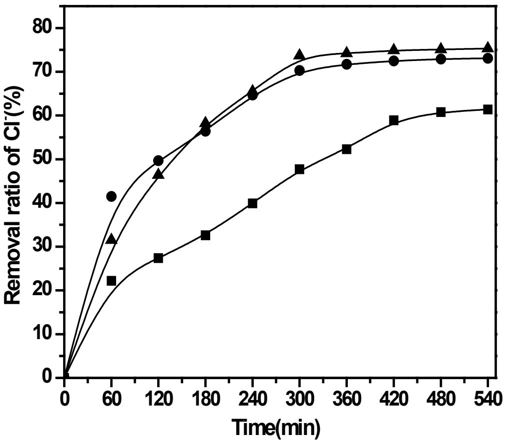

Fig. 7. Variation of removal ratio of Cl^- with time at different voltages (■ 20 V; ● 30 V; ▲ 50 V).

Table 2
Comparison of operation process performance parameters at different voltages

Voltage (V)	Removal ratio of Cl^- (%)	Energy consumption (kW h kg^{-1})	Current efficiency (%)
20	61.4	9.1	44.6
30	73.1	12.9	30.0
50	74.9	23.7	28.8

decreases conversely. Therefore, considering removal ratio of Cl^- to be the most important process performance parameter, and then the energy consumption and current efficiency, it is not difficult to determine the optimal operation voltage as 30 V.

4. Conclusions

A four-compartment electrodialysis process was proved to be successful in production of L-Lys from L-Lys·HCl. Effects of such parameters, such as the molar ratio of L-Lys·HCl and NaOH, initial L-Lys·HCl concentration, and the operation voltage on operation process performance were studied. The obtained optimum values at pH 9.74 of above parameters were 3:5, 0.3 mol L^{-1}, and 30 V, respectively. Moreover, the corresponding removal ratio of Cl^- is the highest as 73.1%, the energy consumption is the lowest as 12.9 kW h kg^{-1}, and the current efficiency is 30.0 %. Future work will be focused on improving the removal ratio of Cl^- and current efficiency.

Acknowledgements

Financial supports from Doctoral Research Foundation of Southwest University of Science and Technology (No. 06zx7119) and Opening Foundation of Key Laboratory of Solid Waste Treatment and Resource Recycle (Southwest University of Science and Technology) (No.09zxgk03) are greatly appreciated. The authors also wish to thank Dr. C.H. Huang and Q.H. Li from University of Science and Technology of China for their kind help in the experimental aspects.

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