



Influence of different resins on the amino acid recovery by resin-filling electrodialysis



Fangfang Yuan^{a,b}, Qian Wang^a, Pengbo Yang^a, Yuan Tian^a, Wei Cong^{a,*}

^a National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China

^b University of Chinese Academy of Sciences, Beijing 100049, PR China

ARTICLE INFO

Article history:

Received 9 July 2015

Received in revised form 22 August 2015

Accepted 24 August 2015

Available online 25 August 2015

Keywords:

Resin-filling electrodialysis

Lysine

Glutamate

Water dissociation

ABSTRACT

Compared to the concentration and separation of inorganic salts, recovery of amino acids by electrodialysis (ED) is normally more difficult due to their weak dissociation ability, relatively complex structure and zwitterionic properties. In this work, three kinds of resins, inert resin, 001 × 4 resin (strongly acidic) and 201 × 4 resin (strongly basic), were added in the diluted compartments of membrane stack to facilitate the transport of amino acids. The effect of the property and quantity of resin-filling on the ED behavior of glutamate (acidic) and lysine (basic) was investigated respectively. It was found that the promotion effect of different resins on the transport of amino acids was in this order: 201 × 4 > 001 × 4 ≥ inert resin. For inert resin, when the percentage of resin filling in the compartments reached 25% or 50%, the improvement in transport of amino acids was most significant. This was attributed to the influence of resins on the hydraulic conditions in the diluted compartments. As for 201 × 4 and 001 × 4 ion exchange resins, the higher quantity of resin-filling produced more obvious positive effect on the migration of amino acids as compared to inert resin, which was caused by the superior conductive and catalytic ability of the functional groups.

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1. Introduction

Amino acids are widely used in food and agricultural industries as nutritional supplements and chelating agents respectively, and they are also important ingredients in the production of drugs, biodegradable plastics, and chiral catalysts. Nowadays, most amino acids can be produced by fermentation at industrial scale, while the separation of amino acids from the fermentation broth is still challenging. The traditional down-stream separation and purification process [1] is quite complicated, normally consisting in several steps like filtration, acidification, neutralization, crystallization, evaporation, ion exchange, etc. This process has some inherent disadvantages, such as relatively low recovery, high labor intensity and enormous chemical consumption [1,2].

Electrodialysis (ED), with alternating cation-exchange and anion-exchange membranes in a direct current field, is considered as a promising technology for the separation and purification of amino acids [3,4]. Compared with the traditional separation methods for fermentation products, ED has attracted more and more attention in recent years, especially for biorefinery applications [5,6] concerning its advantages in energy and environment issues. It is well known that ED can be successfully applied for the recovery of inorganic ions [7,8]. However, the recovery of organic ions by ED is more difficult because the migration of organic ions across ion exchange membranes in the ED process is unsatisfactory due to their weak dissociation ability and complex chemical structure [3,6,9,10]. Moreover, the charge pattern of amino acids (as zwitterionic molecules) is greatly influenced by the pH value [6], making the migration of amino acids more complicated.

Inspired by electro-deionization technology, ion exchange resins were added into the compartments of electrodialyzer during the recovery of organic ions like tartaric acid [2,11] and citric acid [12] by ED. It was proved that introducing resins into ED process indeed improved the process performance. Nevertheless, to the best of our knowledge, there has been few reports yet regarding the resin-filling ED process for the recovery of amino acids, and the optimization of such integrated process is still required.

In this work, three kinds of resins, named inert (without functional group), 001 × 4 (strongly acidic ion exchange resin) and 201 × 4 (strongly basic ion exchange resin) respectively, were introduced into the diluted compartments of membrane stack used for amino acids separation and extraction. The effect of resin property and quantity filling in the compartments on the migration of glutamate (Glu, acidic amino acid) and lysine (Lys, basic amino acids) in ED process was investigated and the potential mechanisms behind various phenomena were discussed. The outcome of this work not only offers a simple strategy to improve amino

* Corresponding author.

E-mail address: weicon@ipe.ac.cn (W. Cong).

acids recovery from fermentation broth by ED, but also serves as valuable guide for process design in industrial production.

2. Experimental

2.1. Chemicals and resins

Glutamate, lysine hydrochloride, sodium sulfate, hydrochloric acid and ammonium hydroxide were of analytical grade and used without further purification. 001 × 4 (strongly acidic resin), 201 × 4 (strongly basic resin), and D301R (weakly basic resin) resins were purchased from Tianjin Nankai Hecheng Science & Technology Co., Ltd. The inert resin without functional group was supplied by Jiangsu Suqing Water Treatment Engineering Group. The main characteristics of the resins are listed in Table 1 (TEC: the total exchange capacity.).

2.2. Stack operation with resins

Electrodialyzer supplied by Sanyuan Bada Co. (Beijing, China) was used in this study. Fig. 1 shows the schematic diagram of membrane stack with alternating cation-exchange membranes (Xiangfeng Co. Ltd.; Shanghai, China) and anion-exchange membranes (Guangya Co. Ltd.; Hebei, China). Moreover, two pieces of bipolar membranes (Guangya Co. Ltd.; Hebei, China) were placed on both sides of the membrane stack, which effectively prevented ions from transferring between the electrode compartments and the adjacent compartments [13]. The H^+ and OH^- ions generated by the bipolar membranes in compartments 1 and 5 can be neutralized by each other in the reservoir tank, so it will have little effect on the pH change of the concentrate. The ED stack consists of diluted, concentrated and electrode compartments. The effective area of each membrane was 50 cm^2 , and the width of the diluted and concentrated compartments were 4 mm and 1.2 mm, respectively. Thus the volume of each diluted compartment was 20 mL ($50\text{ cm}^2 \times 0.4\text{ cm}$), and the diluted compartments were filled with resins. In order to investigate the influence of the quantity of resins on the ED process, the volume of resins filling in each compartment was 0, 5, 10 or 20 mL, namely 0%, 25%, 50% or 100% of the volume of the diluted compartment. It is worth mentioning that the ionic types of resins were adjusted suitably by immersing the resins into the same electrolyte solutions as in the diluted compartments.

The ED process was carried out in batch using a constant voltage of 20 V generated by an ac–dc rectifier (HB17300SL; Hossoni electric Co. Ltd.; Zhejiang, China). Solutions were pumped into the compartments continuously from reservoir tanks using peristaltic pumps (HIGHFLO-8007, Kflow; Taiwan, China). The flow rate of each stream was 3.7 cm/s. The solution temperature was maintained at 30 °C by a water bath (DC-1015; Ningbo Haishu Safe Co. Ltd.; Zhejiang, China).

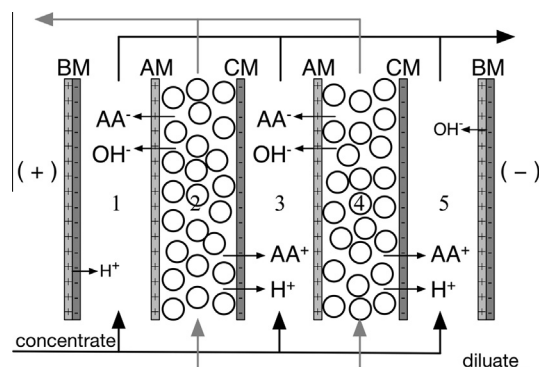


Fig. 1. Principle of resin-filling electrodialysis stack for the recovery of amino acid (AM, anion-exchange membrane; CM, cation-exchange membrane; BM, bipolar membrane).

The ED process involved three independent streams: electrode stream, feed stream and concentrated stream. The electrode stream was 0.2 mol/L Na_2SO_4 . In the Glu recovery process, the feed stream circulating in diluted compartments was 0.25 mol/L or 0.5 mol/L Glu- NH_3 (500 mL). To increase initial conductivity, 0.1 mol/L $NH_3 \cdot H_2O$ (300 mL) was circulated in the concentrated compartments as initial stream. For the Lys recovery process, the initial feed and concentrated streams were 0.25 mol/L or 0.5 mol/L Lys-HCl (500 mL) and 0.1 mol/L $NH_3 \cdot H_2O$ (300 mL), respectively. The concentration of amino acids was determined by a biosensor (Model SBA 40C, China) every 15 or 20 min. Volume variation for each solution was determined by monitoring the scale on the reservoir tank.

2.3. FT-IR measurement

Using the transmission technique FT-IR spectrums were obtained for the virgin strongly basic 201 × 4 resin and that used in ED operation. The samples were dried for 4 h under vacuum at 50 °C. FT-IR spectra were taken at 0.48 cm^{-1} resolution in the range $4000\text{--}400\text{ cm}^{-1}$ by an infrared spectrometer (Thermo Fisher Nicolet iS5).

2.4. Calculation

Generally, average current efficiency, energy consumption and transfer rate of amino acid [13] were used to evaluate the performance of ED process, which were calculated as follows.

The average current efficiency η (%) was calculated according to:

$$\eta = \frac{zF(C_0V_0 - C_tV_t)}{MN \int_0^t Idt} \times 100\% \quad (1)$$

Table 1
Main characteristics of the resins.

Resin type	Matrix structure functionality	TEC, mmol/g (Dry) mmol/g (Wet)	Moisture content, %	Density (wet), g/mL true wet density apparent wet density	Particle diameter, mm ≥ 95%
Inert	Styrene-DVB /	/	50–60	1.04–1.31 0.60–0.74	0.3–1.25
001 × 4	Styrene-DVB –SO ₃ [−]	≥ 4.5 ≥ 1.3	55–65	1.20–1.24 0.74–0.84	0.3–1.25
201 × 4	Styrene-DVB –N ⁺ (CH ₃) ₃	≥ 3.8 ≥ 1.1	50–60	1.04–1.08 0.60–0.70	0.3–1.25
D301R	Styrene-DVB –N(CH ₃) ₂	≥ 4.8 ≥ 1.4	50–65	1.03–1.07 0.61–0.71	0.3–1.25

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