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Recovery of L-tryptophan from crystallization wastewater by combined membrane process

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ABSTRACT

The combined membrane process of electrodialysis (ED) and reverse osmosis (RO) was carried out to recover the L-tryptophan from its crystallization wastewater which had 0.5–1.5% residual L-tryptophan and around 15% impurity of NaCl salt. In the process of ED desalination, the operating current should be controlled below the limiting current density to avoid the polarization phenomenon. The pH of dilute solution significantly affected the recovery ratio of L-tryptophan, and the salt removal ratio varied with current density and voltage. The operating current density also had a great impact on the performance of the electrodialytic desalination process. After ED desalination, two methods including raising the temperature and adjusting the pH of the dilute solution coming from ED process were used to increase the solubility of L-tryptophan in aqueous solution during the RO concentration process. It was observed that the recovery ratio of L-tryptophan was closely correlated with not only the pH of RO feed but also the salt removal degree of ED process. After the treatment of the combined ED and RO process, 60.4% of the optimal recovery ratio of L-tryptophan was achieved, and the purity of final product of L-tryptophan reached 98%.

1. Introduction

L-Tryptophan, an essential amino acid to life, has been used widely in the production of pharmaceuticals such as infusion agents, and additives for food and animal feeds [1]. At present, it is mainly produced via three methods such as chemical synthesis method [1–5], biochemical synthesis method [6] and microbial fermentation method [7–9]. In this study, the L-tryptophan to be recovered is produced by chemical synthesis method, and is separated and purified from its reaction mixture by means of isoelectric crystallization under low temperature [5]. After separation, however, about 0.5–1.5% residual L-tryptophan still remains in the isoelectric crystallization wastewater which also contains around 15% NaCl. Nowadays, this crystallization wastewater is generally treated to recover the residual L-tryptophan by using ion-exchange or heat evaporation method [10]. But in the case of the ion-exchange, a large amount of acid and alkaline agents are consumed in order to regenerate the ion-exchange resins, which will greatly increase the operational cost of ion-exchange process. On the other hand, the wastewater produced from this process to reactivate and wash the ion-exchange resin will cause serious environmental pollution and increase the burden on subsequent wastewater treatment. For the heat evaporation, it also has some obvious disadvantages during the recovery of L-tryptophan such as high energy consumption and relative poor purity of end product due to the existence of impurity of NaCl. Thus, a more economical and environmentally friendly method is desired to recover the L-tryptophan from the crystallization wastewater.

Reverse osmosis (RO) membrane is applicable to the recovery and concentration of end materials in a solution at temperatures near room temperature without bringing about phase change. The concentration process using RO membrane which has a very important advantage of less energy consumption has been attracting much attention and finding its uses in a variety of fields [11]. The typical examples of this use are the desalination of seawater and the production of pure water. Electrodialysis is a unit operation for the separation or concentration of ions in solution based upon their selective electromigration through the semi-permeable ion-exchange membrane [12–14]. Its largest application area is in the desalination of brackish water for the production of potable water [13–15].

Nowadays, there is another promising application of both reverse osmosis and electrodialysis that is the separation and purification of amino acids from dilute aqueous solutions produced

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by fermentation, chemical synthesis or enzymatic synthesis. For example, Ogawa et al. [11] concentrated the aqueous solution of amino acids such as tyrosine, phenylalanine cystine and methionine by means of RO membrane. McGregor [16] separated the L-phenylalanine from clarified bioreactor harvest media by using RO process. In addition, Kaneko et al. [17] purified the lysine with the reverse osmosis membrane. For the electrodialysis, Shen et al. [18] used it to separate and purify the glutamine from its fermentation broth. Similarly, Zhang et al. [19] recovered the glutamic acid from its isoelectric supernatant by means of electrodialysis.

In this study, the combined process of RO and ED was proposed to recover the residual L-tryptophan from its crystallization wastewater which is produced by chemical synthesis method. It is well known that the RO process is limited by high osmotic pressure that is proportional to the concentration of solute, thus the ED process was performed to remove the salt NaCl in the L-tryptophan crystallization wastewater prior to the concentration process of RO, which not only reduced the operation pressure of the subsequent RO process to make this concentration process easier, but also removed the impurity of NaCl in the L-tryptophan crystallization wastewater to improve the purity of the final L-tryptophan product. After ED treating, the concentration process using RO membrane was carried out, and then the resulting RO concentrate was crystallized under low temperature to obtain the final L-tryptophan product. At the same time, the permeate coming from the RO process was reused to the synthesis procedure of L-tryptophan.

2. Experimental

2.1. Materials, reagents and membranes

The standard L-tryptophan (p*I*: 5.89) and the isoelectric crystallization wastewater of L-tryptophan used in the experiments were provided by Hangzhou Henrui Biological Products Co., Ltd., China, and the main characteristics of the wastewater was shown in Table 1. The ethanol, HCl and NaOH used in the experiments were all analytical grade and directly used without further purification.

The heterogeneous ion-exchange membranes used in the experiments were provided by Hangzhou Superfiltration Membrane Technology Co., Ltd., of China, and their main characteristics are listed in Table 2. The reverse osmosis element (Model: TFC®-2012-75) was purchased from Shanghai Rum-Tech CO., Ltd of China, and its characteristics are listed in Table 3.

2.2. Analytical methods

The L-tryptophan in aqueous solution was determined by high performance liquid chromatograph (HPLC) (Column: Hypersil BDS C 18 5 μm, UV 280 nm, flow phase: molar rate of methanol and water of 1:1, flow rate: 1 ml/min, LC-10AT, Shimadzu Corporation, Japan). The NaCl analysis was carried out by ion chromatograph (Column: CS12A 4 × 250 mm, eluent: 20 mM MSA, flow rate: 1 ml/min, DX120, Dionex Corporation, USA). The final product of L-tryptophan recovered was analyzed for its physical performance and chemical structure via elemental analysis, infrared spectra (IR), high performance liquid chromatograph (HPLC) and melting-point measurement.

Table 1
Characteristics of the L-tryptophan crystallization wastewater.

Parameter	Crystallization wastewater of the L-tryptophan
pH	2.42
Concentration of L-tryptophan (mg/L)	11,900
Concentration of NaCl, mol/L (ppm)	1.485 (86877.5)[a]

[a] The concentration of NaCl in L-tryptophan wastewater at isoelectric point which was adjusted by adding NaOH.

Table 2
Specifications of the electrodialytic stack used and properties of ion-exchange membrane.

Parameter	Anionic (AH)	Cationic (CH)
[a]Thickness (mm)	0.6 ± 0.05	0.6 ± 0.05
[b]Ion-exchange capacity	≥1.8 mol/kg	≥2.0 mol/kg
[a]Electric resistance (Ωcm^2)	20	15
[a]Temperature range allowance (°C)	0–40	
[a]pH range allowance	1–14	
[c]Membrane overall size (mm × mm)	400 × 200	
[c]Membrane effective size (m^2)	0.0403	
[c]Number of cell pairs	40	
[c]Overall membrane surface area (m^2)	1.612	
[c]Intermembrane channel (mm)	0.9	

[a] Data from the manufacture.
[b] Data from the literature.
[c] Experimentally measured.

2.3. Solubility testing of L-tryptophan

First, the standard L-tryptophan in excess of its normal solubility 5–10 times was stirred into the deionized water (500 ml) in order to make L-tryptophan supersaturated in water. Then, two methods such as adjusting the pH of suspension and changing the suspension temperature were used to change the solubility of L-tryptophan, and the pH of solution was adjusted by HCl or NaOH. Subsequently, the resulting suspension was filtered under vacuum to remove the excess non-dissolved solid L-tryptophan, and then the filtrate was evaporated at 80 °C in vacuo. After evaporation, the wet solid L-tryptophan was further dried for 10 h at 50 °C under vacuum. Finally, the solubility of L-tryptophan in water was calculated in terms of the practical weight of dissolved L-tryptophan.

2.4. Electrodialysis

A laboratory-scale electrodialyser (Hangzhou Superfiltration Membrane Technology Co., Ltd., China) was used to desalinate the L-tryptophan crystallization wastewater. This apparatus was equipped with two Ru/Ti electrodes and a sheet-flow stack containing 40 cation- and 40 anion-exchange membranes, separated by spacer gaskets (thickness: 0.90 mm) which ensured a flow parallel to the membranes themselves. Their main characteristics are shown in Table 2. The direct current generator could supply voltage (Φ) and current (I) in the following ranges: 0–150 V and 0–20 A. The dilute (D), concentrate (C) and electrode rinsing solutions were stocked in three PVC tanks and re-circulated through the electrodialysis stack by means of three magnetic pumps with a nominal capacity of 1.5 m^3 h^{-1} and a total discharge head of 5 m of water. The electrodialyser could be operated under a constant voltage or constant current condition, and its cell was illustrated in Fig. 1.

Before the desalination experiment, the ED stack was routinely cleaned by performing a series of cycles of 30 min each with NaCl solution (50 g/L), tap water and deionized (DI) water at room temperature. After cleaning, 5.0 L of isoelectric crystallization wastewater of L-tryptophan was added in the dilute compartment, and 10 L of tap water (conductivity: about 225 μs/cm) was added in the concentrate compartment. The electrode rinsing was carried out by using a NaCl solution (conductivity: about 1000 μs/cm) at an initial pH value of 6.5–7.0 to assure adequate electric conductivity in the electrode rinsing channels. All batch recycle runs were carried out under a constant recirculation flow rate and at temperature below 40 °C. The pH (PHS-307, Hangzhou YaMei electron instruments Co. Ltd, China) of wastewater in dilute compartment was always kept at isoelectric point (pI = 5.89 ± 0.05) which was