Journal of Membrane Science 482 (2015) 76–82

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Bipolar membrane electrodialysis in aqua–ethanol medium: Production of salicylic acid

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ARTICLE INFO

Article history:
Received 25 October 2014
Received in revised form
13 January 2015
Accepted 14 February 2015
Available online 2 March 2015

Keywords:
Bipolar membrane
Electrodialysis
Aqua–ethanol medium
Salicylic acid

ABSTRACT

To overcome the low solubility of salicylic acid (SAH) in the production process by bipolar membrane electrodialysis (BMED), the water–ethanol mixture as solution medium was introduced in the BMED technique. The results indicated that the highest acid concentration was obtained when ethanol content was 50 v/v%, and the current efficiency reached 98.2%. Moreover, the BMED stack of BP–C (BP, bipolar membrane; C, cation exchange membrane) configuration was proved as most cost-effective configuration, and using this configuration the highest current efficiency could reach 99.6% and the lowest energy consumption was 2.1 kW h kg^{-1}.

1. Introduction

Salicylic acid (SAH) as an important chemical raw material has been used as an intermediate product to synthesize drugs (such as aspirin) and cosmetics (used for the treatment of seborrheic dermatitis) [1]. Currently, the production of salicylic acid is based on the Kolbe–Schmitt reaction by the following reaction [2] (Fig. 1). Firstly, sodium phenolate is synthesized by the reaction between phenol and NaOH. Secondly, the intermediate is transformed into sodium salicylate (SANa) through carboxylation reaction under conditions of high pressure, high temperature and CO_2 atmosphere. Thirdly, the salicylic acid is obtained by acidification using enormous amount of H_2SO_4. However, this process will not only consume considerable H_2SO_4 and generate numerous waste solutions of Na_2SO_4 with a concentration higher than 0.1 w/w% [3], but also cause a waste of acid and the secondary salt pollution.

As an environment friendly and technical advanced process, bipolar membrane electrodialysis (BMED) has been used as an alternative for the production of salicylic acid [4]. A key part of the BMED is a bipolar membrane, which is manufactured by the composition of a cation-exchange layer, water splitting layer and an anion-exchange layer. Under interaction of the gradient of potential difference and water splitting layer catalysis, water was dissociated into H^+ and OH^- which moved into corresponding compartment and formed acid/base, respectively. In this case, BMED is a good choice in order to get an environment friendly method. Furthermore, BMED also has the advantage of technical advancements and economical competence [5,6]. Because of these remarkable advantages, it has attracted more and more attention from all over the world, and also, it has found many applications in chemical synthesis, food processing, and environmental protection [7–10], especially in cleaner production of organic acids [11].

However, some acids like long-chain organic acids are hardly or not soluble in water and thus limit the conversion of organic acid salts into organic acids by BMED. There are few reports on the production of aromatic acids by BMED. As reported by Alvarez [4], in order to increase the solubility of the salicylic acid, experiments were performed at 40 °C. However, at this temperature, the solubility can only increase to 3.7 g L^{-1}, and higher temperatures will shorten membrane life. In order to overcome this shortcoming, Kameche [12] proposed the electro-membrane processes in ethanol–water mixtures for the conversion of linear organic acid salts ($C_nH_{2n+1}COONa$, with $n=2$–7) into their corresponding acids. Luo [13] developed two-phase electro-electrodialysis (TPEED) for recovering and concentrating citric acid. Later then, our group produced sebacic acid using TPBMED [14]. However, the organic acids produced in ethanol–water mixtures reported above are aliphatic acids. To solve this problem, in this work a mixture of water and ethanol can be used as the media for BMED for increasing salicylic acid solubility. Furthermore, this work could also provide the feasibility of BMED processes in aqua–ethanol medium for the conversion of aromatic acid salts into their corresponding aromatic acids.

Therefore, the aim of this work is to investigate an alternative process for the production of salicylic acid using BMED in water–ethanol medium, which produces the salicylic acid at room

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http://dx.doi.org/10.1016/j.memsci.2015.02.030
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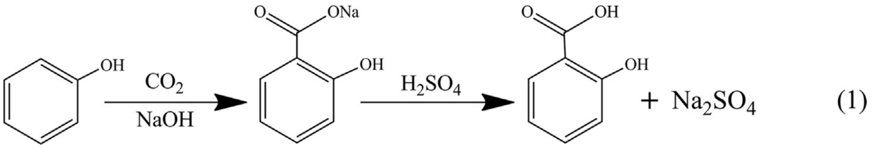

Fig. 1. Production of salicylic acid by the Kolbe–Schmitt reaction.

Table 1
Properties of the membranes applied to the BMED stacks[a].

Membrane	Thickness (μm)	IEC (meq g^{-1})	Area resistance ($\Omega\ cm^2$)	Voltage drop (V)	Current efficiency (%)
Neosepta AMX	120–180	1.4–1.7	2.0–3.5		
Neosepta CMX	220–260	1.5–1.8	2.0–3.5		
Neosepta BP-1	200–350	–	–	1.2–2.2	> 98%

[a] The data are collected from the product brochure provided by the company.

temperature and avoids the waste solution of sodium sulfate. To evaluate the influence of ethanol content, current density, sodium salicylate concentration, and stack configurations on the performance of BMED process, a series of experiments were conducted as follows.

2. Experimental

2.1. Materials

Membranes used in the experiments are Neosepta AMX (anion-exchange membrane, Tokuyama Co., Japan), Neosepta CMX (cation-exchange membrane,Tokuyama Co., Japan), and Neosepta BP-1 (bipolar membrane, Tokuyama Co., Japan). Their properties are listed in Table 1. All the chemicals used were analytical grade and used as received. Distilled water was used throughout.

2.2. Setup

This lab-scale experimental set-up comprised of (1) a cathode and an anode, which was made of titanium coated with ruthenium; (2) alternatively arranged anion-exchange membranes (A), cation-exchange membranes (C) and bipolar membranes (BP). The effective area of each membrane was 7.07 cm^2. These membranes were arranged between anode and cathode. Two electrodes were connected with a direct current power supply (TN-XXZ02, Yangzhou Shuanghong Electronics Co., Ltd.). As shown in Fig. 2, four configurations (BP–A, BP–C, BP–A–C and BP–A–A) were considered for construction of a laboratory-scale BMED stack. Taking the BP–A–C configuration as an example, there were four independent solutions circulating through correponding compartment named anode, acid, feed and cathode that layed between cathode and anode, which were separated by a bipolar membrane, an anion-exchange membrane and a cation-exchange membrane. Two neighboring membranes were separated by two silicon rubber (total thickness of 1 mm). Every compartment was connected to a 0.25 L beaker, allowing for the circulation of external solutions by peristaltic pumps (BT-100S, Baoding Lead Fluid Technology Co., Ltd. with the speed of 11 L h^{-1}). Before applying current, the solution of each compartment was circulated for half an hour, and all the visible gas bubbles were eliminated.

In the stack of BP–C configuration (Fig. 2b), sodium salicylate (SANa) and salicylic acid (SAH) exist in one compartment, and thus, a mixture of ethanol and water was chosen as the solvent. However, in other stacks (BP–A, BP–A–A, BP–A–C) (Fig. 2a, c, d), SANa and SAH are in different compartments, so SANa and SAH are, respectively, dissolved in water and a mixture of ethanol and water. In additon, $LiNO_3$, due to its high solubility in ethanol–water mixtures,was added as an electrolyte to reduce the electrical resistance of the mixture and decrease stack voltage. Na_2SO_4 was added as a supporting electrolyte and electrode rinse solution. If not specifically mentioned, all the experiments for parameters optimization were conducted using BP–C (1-unit) configuration.

2.3. Determination of acid concentration

Changes in salicylic acid concentration were determined by acid–basic titration with a calibrated NaOH solution using phenolphthalein as an indicator.

The concentration of salicylic acid, C_{SAH}, was calculated as

$$C_{SAH} = \frac{C_{OH} V_{OH}}{V_{SAH}} \tag{1}$$

where C_{OH} (mol L^{-1}) is the concentration of the calibrated NaOH solution, V_{SAH} (L) is the volume of the acid cycle, and V_{OH} (L) is the volume of NaOH used for titration.

2.4. Calculation of current efficiency and energy consumption

The current efficiency η was calculated as follows:

$$\eta = \frac{(C_t - C_0)VF}{It} \times 100\% \tag{2}$$

where C_t and C_0 (mol L^{-1}) are the concentrations of salicylic acid at time t and 0, respectively; V (L) is the volume of the acid cycle ($V \le 0.25$ L); F is the Faraday constant (96,485 C mol^{-1}); and I (A) is the current applied.

The energy consumption (kW h kg^{-1}) was calculated as follows:

$$E = \int_0^t \frac{UIdt}{C_t VM} \tag{3}$$

where E (kW h kg^{-1}) is the energy consumption; U (V) is the voltage drop across BMED stack; I (A) is the current applied; C_t (mol L^{-1}) is the concentration of SAH at time t; V (L) is the volume of the acid cycle ($V \le 0.25$ L); and M is the molar mass of SAH (138.12 g mol^{-1}).

3. Results and discussion

3.1. Effect of ethanol content on the production of salicylic acid

Fig. 3 shows the effect of ethanol content on the production of salicylic acid using BP–C configuration. Fig. 3a shows the effect of ethanol content on the concentration of salicylic acid under the current density of 14 mA cm^{-2}. Obviously, the concentration of salicylic acid increases with the elapse of operating time, and there is no significant difference when the ethanol content is in the range of 40–80 v/v% in the ethanol–water mixture. When the ethanol content increases from 40 v/v% to 50 v/v%, the acid concentration has a slight increase. On one hand, the solubility of salicylic acid increases by the addition of ethanol; on the other