이온교환막을 이용한 청정 유기산 생산 기술

최재환, 김양훈*, 문승현*
공주대학교 화학공학과
광주과학기술원 환경공학과*

Cleaner Technologies for Recovery of Organic Acids using Ion-Exchange Membranes

Jae-Hwan Choi, Yang-Hoon Kim*, and Seung-Hyeon Moon*
Department of Chemical Engineering, Kongju National University,
182, Shinkwan-dong, Kongju, Chungnam, 314-701, Korea
Department of Environmental Science and Engineering,
Kwangju Institute of Science and Technology
1 Oryong-dong, Buk-gu, Gwangju, 500-712, Korea*

1. Introduction

The conventional fermentation process producing calcium lactate salt precipitate that must be reacidified by a strong acid, yields calcium salt as by-product. It causes severe drawbacks such as high chemical cost and waste generation. A number of processes for lactic acid recovery from fermentation broth without precipitation have been studied including solvent extraction, adsorption, direct distillation, and electrodialysis [1]. Ion exchange is by far the most frequently employed process in recovery of ionized forms of bioproducts facing severe environmental problems in wastewater treatment.

The use of ion-exchange membranes, however, can virtually eliminate the salt waste generated from the regeneration step of the ion-exchange process. Electrodialysis (ED) is an ion-exchange membrane process that uses an electrical potential as a driving force. Applications of ED can be found in the environmental and biotechnological industries as well as in the production of table salt [2]. In this regard, ED process becomes one of the most important membrane processes for environmentally clean technology and is considered to be more effective than other separation methods.

2. Cell configurations for recovery of organic acids

2.1 Conventional electrodialysis

It is the most widely used cell configuration of ED processes in a commercial scale. An ED cell arrangement consists of anion- and cation-exchange membranes in an alternating pattern between an anode and cathode. If an electrical current is applied between the electrodes the diluate stream is to be desalted and simultaneously the concentrate stream is to be concentrated as a result of salt transfer across the ion-exchange membrane.

2.2 Ion substitution

These configurations allow a feed stream to be modified in its ionic composition. The solution to be modified flows between the same type membranes (e.g. two cation or two anion membranes), then permeable ions will leave the solution in one direction through a membrane while equivalent ions of the same charge will enter the solution through the other side of the compartment from a make-up solution flowing in the adjacent compartment of the latter membrane.

2.3 Double decomposition

It is a cell configuration of an ED process where two streams exchange their counterions like chemical reaction called metathesis. Stream 1 and stream 2 contain M^+X^- and L^+Y^- salt, respectively. M^+ and X^- in each stream move countercurrently through cation, anion membrane and also L^+ and Y^- in other stream transfer through cation, anion membrane. M^+ joins Y^- and L^+ joins X^- in the stream 3 and 4, producing M^+Y^- and L^+X^- salts.

2.4 Three compartment water-splitting electrodialysis (WSED)

The potential of ED processes has been greatly extended by the invention of bipolar membrane, consisting of an anion and a cation selective layer joined together. The bipolar membranes split water into hydrogen ions and hydroxyl ions [3]. The bipolar membrane process is a unique electrodialysis operation, which can be used to generate equimolar quantities of acid and base from their corresponding salts. In the WSED configuration, H^+ and OH^- generated from a bipolar membrane join Cl^- in the acid compartment and Na^+ in the base compartment, respectively, for electroneutrality, resulting in producing hydrochloric acid and sodium hydroxide from sodium chloride salt. Figure 1 shows the schematic diagram of the configuration consists of a bipolar membrane operated in conjunction with cation and anion membranes.

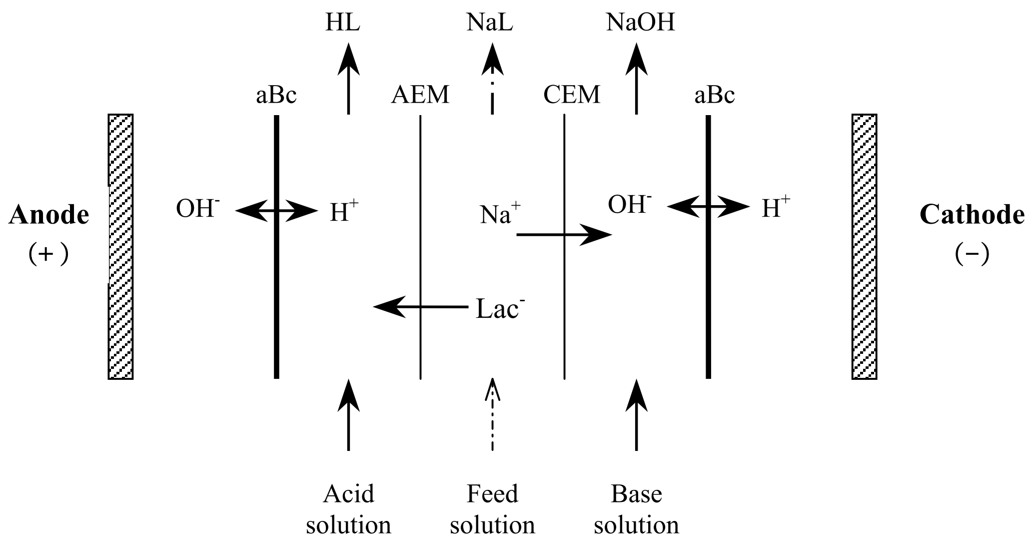

Fig. 1 Principle of three-compartment water-splitting electrodialysis. AEM: anion-exchange membrane, aBc: bipolar membrane, CEM: cation exchange membrane.

2.5 Two compartment WSED

This configuration consists of a bipolar membrane operated in conjunction with a cation or an anion membrane. It is suitable for converting salts of weak acids (e.g. Na salts of organic acids) or salts of weak bases (e.g. NH_4NO_3) into a mixed acid/salt stream and a relatively pure base or acid stream. It is particularly advantageous when the salt stream is a concentrated solution (1-5N) because of the competing transport of ions of the same charge.

3. Recovery of lactic acid using ion-exchange membrane process

The development of ED processes for the recovery of lactic acid is illustrated in Fig. 2. In the figure, the route (a) represents the two-stage ED where desalting ED is performed as the first step of the two-stage ED process to recover and partially purify lactic acid. The second step, WSED, which consisted of a series of bipolar membrane and cation-exchange membrane (two compartment WSED), is employed for acidification of sodium lactate. Prior to operating the WSED, the hardness materials, such as calcium and magnesium ions, should be removed by an ion-exchange column to prevent membrane fouling due to hydroxide precipitates of hardness compounds. In order to simplify the process, Lee studied a hybrid using nanofiltration and WSED where nanofiltration replaced desalting

ED and ion-exchange of the two-stage process (the route (b) in Fig. 2). The system, however, has a low lactic acid recovery and a significant flux decline in nanofiltration and consequently, frequent cleaning cycles were required during the operation [4]. Another simplified ED process for lactic acid recovery is the one-stage ED (the route (c) in Fig. 2). Free lactic acid could be recovered from fermentation broth directly without pretreatment, such as desalting ED or ion-exchange for removal of hardness metals and foulants.

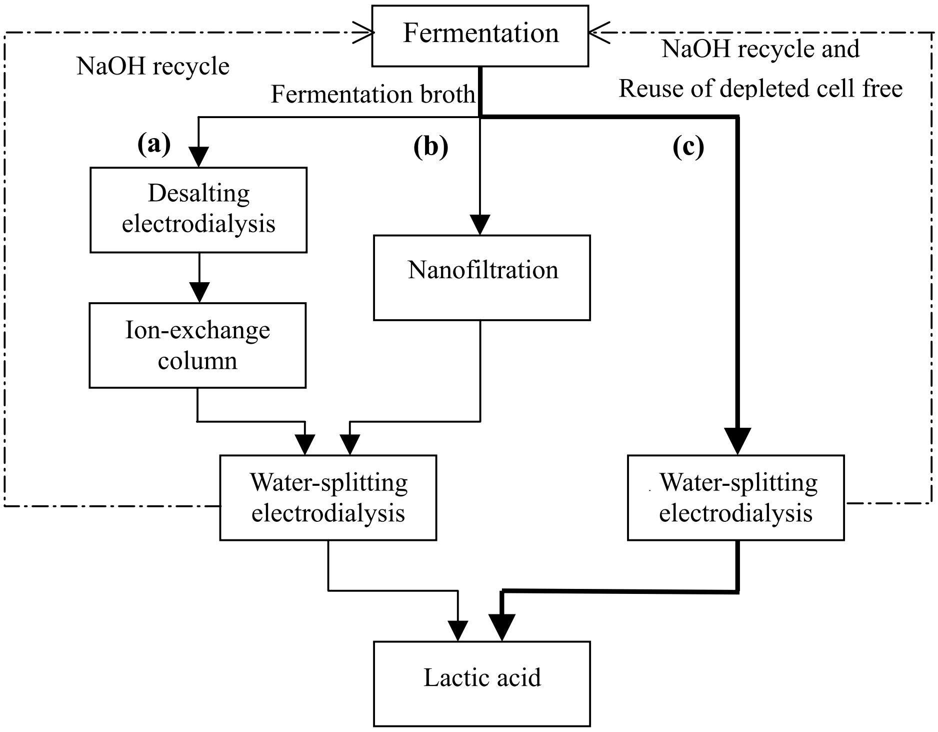

Fig. 2. Process flow sheet diagram of the integrated processes for lactic acid recovery. (a) Two-stage electrodialysis, (b) Hybrid of nanofiltration and water-splitting electrodialysis, (c) One-stage electrodialysis.

The one-stage ED process using three-compartment WSED (Fig. 1) has been examined by laboratory experiments to determine their economic feasibility for application in the lactic acid recovery process. The experiments were carried out with synthetic solutions and fermentation broth. Experimental results are summarized in Table 1. The stack for the first experiment was equipped with AM-1 and CM-1 membranes, the current being supplied initially at 12 A. The feed solution was a synthetic solution containing lactate 80.8 g/L and initially, the acid compartment was filled with 0.1 % lactic acid. The results show a high lactic acid recovery (98.2 %) with a current efficiency of about 80 % being achieved. The energy consumption for the recovery of 1 kg of lactic acid was about 1.35 kWh. When fermentation broth was used as the feed solution, the initial current of the experiments was fixed at 8 A to prevent possible rupture of the membrane from a high initial voltage drop, which was caused by organic or inorganic compounds in the fermentation broth. In spite of impurities in the fermentation broth, the recovery of lactic acid and the current efficiency was 96.4 % and 80.4 %, respectively.
For minimizing the acidification of the fermentation broth and blocking the transport of divalent ions, the experiments were performed using ACM and CMS membranes instead of AM-1 and CM-1

membranes. The removal rate of hardness metals shows significant improvement by using the CMS membrane as shown in Table 1. Thus, the CMS membrane was expected to be more effective in removing hardness metals than other cation-exchange membranes. However, energy consumption for the cell configuration of ACM/CMS (3.8 kWh/kg) was 3.2 times higher than that of AM-1/CM-1.

Table 1. Summary of three-compartment water-splitting electrodialysis operation

Membranes	Initial feed concentration (Lactate g/L)	Operating current (A)	Lactic acid recovery (%)	Current efficiency (%)	Energy consumption (kWh/kg)
BP-1 AM-1 CM-1	80.8 (synthetic soln.)	12	98.2	79.9	1.4
BP-1 AM-1 CM-1	63.2 (fermentation)	8	96.4	80.4	1.2
BP-1 ACM CMS	58.4 (fermentation)	8	97.8	77.3	3.8

4. Conclusion

Electrodialysis is an attractive process in the point of fast treatment, effective separation of ionic materials, concentration of product, and no by-product generation. This process can make lactic acid recovery simpler and can reduce wastes generation. Even though deployment of the ion-exchange membrane process is an early stage in Korea, recent development in bipolar membrane, high conductivity and fouling resistant membranes, and hybrid membrane systems, may extend the application of electrodialysis to recovery of many organic acids, amino acids, peptides as well as non-ionized or large molecule bioproducts such as carbohydrates and proteins.

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