Conversion of dipotassium malate to malic acid by electromembrane processes

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Abstract

Conversion of dipotassium malate to malic acid was carried out through conventional electrodialysis and through electrolysis in combination with cation-exchange membranes. For the first method, hydrochloric acid was added to dipotassium malate, and the potassium chloride that formed was removed by electrodialysis. For the second method, H+ generated at the anode during electrolysis of water migrated through cation-exchange membranes and converted dipotassium malate to malic acid.

Keywords: Electromembrane process; Malic acid

1. Introduction

L-malic acid can be produced from fumaric acid by enzymatic conversion. The salt of L-fumaric acid is converted to the salt of L-malic acid by addition of a water molecule to the double bond. The reaction takes place at neutral pH. The product of this reaction is a solution containing 0.8 M dipotassium malate and 0.2 M dipotassium fumarate (80% conversion). When the mixture is acidified, most of the fumaric acid is precipitated, as its solubility is only 0.04 M at 18°C.

We used two electromembrane processes to transform dipotassium malate to malic acid.

1.1. Conventional electrodialysis

By adding HCl to a mixture of dipotassium malate and dipotassium fumarate, L-malic acid, fumaric acid and potassium chloride are obtained (Fig. 1). About 80% of the fumaric acid precipitates out of solution. The pH must be below 1.5 to ensure complete transformation of dipotassium malate to malic acid. KCl can be removed completely by electrodialysis, because it completely dissociates to ions. The weak malic acid and the

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slightly dissociated fumaric acid remain in the mother solution.

1.2. Combination of electrolysis and cation-exchange membranes

The H\(^+\) that was generated at the anode during decomposition of water was used to replace K\(^+\) ions (Fig. 2). Since L-malic and fumaric acids have a low dissociation constant, most of the cations that arrived at the cathode through the cation-exchange membrane were K\(^+\), and the electrical efficiency was high.

For this configuration, we used a unit with only three compartments, compared to the four compartments used for the same purpose by Belafi-Bako et al. [1].

For industrial purposes, bipolar electrodes may be used (Fig. 2).

During the operation, potassium fumarate converted to fumaric acid and precipitated out of solution, so a 10-micron filter was required to prevent precipitation onto the membrane.

Recovery of citric and lactic acid from fermentation processes by electrodialysis with bipolar membranes is given in [3] and [4], respectively.

2. Experimental

2.1. Conventional electrodialysis

The experiments were carried out with a laboratory electrodialysis unit consisting of eight Teflon\textsuperscript{TM} cells: two electrode cells (thickness — 40 mm), three brine cells (thickness — 10 mm) and three diluate cells (thickness — 10 mm), (Fig. 1). The surface area of each cell was 12 cm\(^2\).

A peristaltic pump was used to circulate the brine and the diluate solutions, at a linear velocity of 2 cm/s. The cells were separated by Tokuyama-AM-3 anion-exchange membranes and Asahi-CMT cation-exchange membranes (Fig. 1). The mixture of about 0.8 M dipotassium malate and about 0.2 M dipotassium fumarate was obtained from Amgal Co. (Israel). Concentrations of malic acid and fumaric acid were determined by HPLC.
2.2. Combination of electrolysis and cation-exchange membranes

The experiments were carried out with a laboratory unit and a bench-scale unit (Fig. 2). The laboratory unit consisted of six Teflon cells (thickness — 10 mm: two anode cells, two cathode cells and two malic acid cells. The surface area of each cell was 12 cm². Three electrodes were used. Two were titanium sheets, plated on one side with a 2-microns thick layer of platinum. One of these served as the anode, the other served as the bipolar electrode. The third electrode was a stainless steel sheet, which served as the cathode. Between the anode and cathode many units with bipolar electrodes may be introduced.

An Asahi-CMT cation-exchange membrane was used to separate the cells. A peristaltic pump was used to circulate the solutions at a linear velocity of 2 cm/s.

The bench-scale unit experiments were carried out with Teflon cells 0.8 mm thick, having a total surface area of 120 cm² (Fig. 3). Both experiments required a filter on the acid line to remove the fumaric acid that had precipitated out of solution during acidification.

3. Results and discussion

3.1. Conventional electrodialysis

In these experiments, a concentrated solution of HCl (32%) was introduced into a mixture of dipotassium malate (0.78 M) and dipotassium fumarate (0.2 M) until the Cl⁻ concentration reached 2.3 M, resulting in a mixture of malic acid, fumaric acid potassium malate and HCl (Fig. 1). The portion of the fumaric acid that had precipitated was removed through filtration. Of the remaining mixture, 0.2 L was introduced into the laboratory
Electrodialysis unit. Removal of 97% of the KCl and HCl from the solution required 10 h of operation at a current density of 50 mA/cm² (Fig. 4). Because the concentration of electrolytes is very high, a higher current density can be used, but it will increase the voltage drop and the energy requirement.

The loss of malic acid during this operation was 31.5% and that of fumaric acid was 55%. The high loss of weak carboxylic acid was due to the relatively low pK of malic acid and fumaric acid: 3.4 and 3.0, respectively. In previous research, when sodium chloride (4 M) was removed from cacodylic acid, which has a pK of 6.1, only a 5% loss of acid was reported [2]. Loss of the weak acid was due to the high concentration of malate and fumarate ions present in the solution, which migrated — together with chloride ions — through the anion-exchange membrane.

The average electrical efficiency in this experiment was 65%, due to the high concentration of electrolytes.

3.2. Electrolysis combined with cation-exchange membranes

H⁺ ions generated at the anode during electrolysis of water were used to replace the potassium ions in our mixture (Fig. 2). The H⁺ ions reacted immediately with the malate and fumarate ions present in the solution to produce the corresponding weak acid. The K⁺ ions that migrated to the cathode created potassium hydroxide (about 0.5 M), which can be recycled. Only small amounts of malate and fumarate anions migrate through the cation-exchange membrane to the anode.

By increasing the current density to 150 mA/cm², the time required for 97% replacement of K⁺ with H⁺ was significantly reduced (Fig. 5), without diminishing the electrical efficiency. A higher current density can be used, but it must be followed by higher linear velocity to prevent temperature increase in the cells.

During the operation, the pH decreased from 6.8 to about 1.5, and the K⁺ concentration decreased...
Fig. 4. Decrease of chlorides, malic acid and fumaric acid concentration vs. time during electrodialysis at current density of 50 mA/cm².

Fig. 5. Conversion of dipotassium malate and dipotassium fumarate (150 ml, 1.0 M) to corresponding acids at different current densities in laboratory unit.
from 1.9 M to about 0.025 M (Fig. 6). By using Amberlite® 120 cation-exchange resin (Rohm and Haas), it was possible to further decrease the K⁺ concentration in solution to less than 0.0025 M. The voltage drop between the cathode and the anode in the bench-scale unit was relatively high because it was necessary to decompose the water and overcome the overpotential near the electrodes. As the current density increased, the voltage also increased rapidly up to 10 mA/cm², followed by a relatively low rate from 20–150 mA/cm² (Fig. 7).

Advantages of such an operation over conventional electrodialysis:

- Loss of malic acid decreased from 31.5% with electrodialysis to 6.7%
- Current efficiency improved from 65% to 80%
- High current density (up to 200 mA/cm²) may be used, thus reducing membrane and electrode surface areas
- Addition of HCl not needed; KOH can be recycled

Disadvantages:

- Voltage drop per unit at 50 mA/cm² was higher (about 4.0 V) than with conventional electrodialysis (about 0.8 V). This large difference is due to the fact that in conventional electrodialysis, up to several hundred of cell-pairs are introduced between the two electrodes, while in electrolysis with cation-exchange membranes, every unit has an anode and a cathode.
- Large surface areas of expensive electrodes needed.

Due to the high voltage drop between electrodes, the energy requirement per ton of malic acid was high (3266 kWh, average of 5 cycles). The current density was 70 mA/cm² and the voltage drop between electrodes was 4.6V. The high cost of the energy required for combining electrolysis with membranes is offset by not needing to add acid, which conventional electrodialysis requires.

Fig. 6. Changes in potassium concentration and pH vs. time during conversion of potassium malate to malic acid by electrolysis combined with membrane process in a bench scale unit. Current density was 70 mA/cm².
4. Conclusions

Conversion of dipotassium malate to malic acid by a process involving addition of HCl to the mixture and removal of KCl by conventional electrodialysis is not efficient because of the high loss (31.5%) of malic acid due to the relatively low pK value (3.4) for this weak acid.

Conversion of dipotassium malate to malic acid by a process of electrolysis combined with cation-exchange membranes is more efficient, as losses of malic acid during the process are relatively low (6.7%) and the need to add acid to the process is eliminated. On the other hand, the energy requirement is high — about 3300 kWh per ton of malic acid.

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References