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Malic acid production using a biological electrodialysis with bipolar membrane

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ABSTRACT

Malic acid is a valuable organic acid and important acidulant in food and pharmaceutical industries and can be produced using electrodialysis with bipolar membrane (EDBM). The aim of this study was to investigate the possibility of malic acid production using a system integrating EDBM and biochemical process, i.e., the microbial electrodialysis and chemical-production cell (MEDCC). With an applied voltage of 1.0 V, the MEDCC successfully conversed 0.3 M malate into 0.23 M malic acid, which was about four times as that produced in the EDBM (0.06 M). The maximum current density in the MEDCC was five times higher than that in the EDBM (10 vs. 1.9 A/m^2). The specific electric consumption for the malic acid production in the MEDCC was 0.34 kWh/kg, which was only 10–30% of that in the reported EDBMs. In the MEDCC, the energy from the anode biodegradation provided about 50% of the total energy demand (0.68 kWh/kg) during the malic acid production. Our results show that the MEDCC should be a promising method for organic acid production with advantages of lower electrical consumption and diverse substrates utilized by exoelectrogens.

1. Introduction

Electrodialysis with bipolar membranes (EDBM) has been proposed recently as an economical and environment-friendly method to produce, separate, and converse chemicals in the industrial field [1]. In the EDBM, a bipolar membrane (BPM), which consists of a cation-selective layer and an anion-selective layer, is used to separate the system into functional chambers. With the capability of BPM to dissociate water into H^+ and OH^-, the EDBM can directly convert organic salts into organic acids without wastewater production. With a suitable applied voltage (e.g., 0.9–1.1 V), the water dissociation rate in the BPM can be 50 million times faster than that in aqueous solutions [2]. Coupling with conventional electrodialysis, the EDBM can convert salts into corresponding acids and bases [3,4]. The process does not consume any additional acid, which is with the risk of wastewater discharge, and requires much less energy than an electrolytical production process. Organic acid production using the EDBM should be highly valuable because organic acids are widely used in industries, such as for buffer solutions, rust removal, nutrients, and preserves [4]. Several organic acids have been produced in the EDBM, including acetate acid, propionic acid, citrate acid, and gluconic acid [5–8].

However, several factors have limited the development of EDBM in practice, such as high costs of BPM, high energy consumption, and high maintenance costs. To dissociate water and transfer ions during the operation, a direct electrical field with high current density must be applied on the EDBM continuously [4]. Lameloise and Lewandowski [9] reported that production of one kilogram malic acid from 0.19–0.55 mol/L potassium malate using EDBM with an effective membrane area of 0.02 m^2 consumed 1.15–1.27 kWh with current density of 50 mA/cm^2. Alvarez et al. [3] showed that in an EDBM with three compartments, 15–20 kWh of electricity with current density of 750 A/m^2 was required to produce one kilogram of salicylic acid. High electricity requirement in the EDBM results in high costs for maintenance and total process. The energy consumption can take up to 20% of the total costs during the gluconic acid production using the EDBM [10]. Therefore, it is necessary to develop strategies to reduce the energy requirement in the EDBM.

To treat groundwater with nitrate, Wisniewski et al. [11] combined electrodialysis with a membrane bioreactor. Nevertheless, the two components were actually independent. An integration of electrodialysis with biochemical process should combine the biological reaction with ion separation, thus results in a synergic effect of optimized utilization of materials and energy.

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In this study, a new device integrated the EDBM and exoelectrogens, called the microbial electrodialysis and chemical production cell (MEDCC) [12], was applied for organic acid production. In the MEDCC, electricity from substrate biodegradation by exoelectrogens (i.e., bioenergy) is utilized, which greatly reduces applied energy requirement of the system. In addition, the applied voltage can accelerate the electron transfer process between exoelectrogens and the anode electrode. Therefore, it is hypothesized that the MEDCC should have a synergic effect of optimized utilization of energy. As a typical organic acid and one of important acidulants in food and pharmaceutical industries [9,13], L-malic acid was investigated in this study. The objective of this research was to examine the feasibility of L-malic acid production and energy consumption using the MEDCC. Acid recovery, current efficiency, and energy consumption were measured in the MEDCC and results were compared with those in the EDBM.

2. Materials and methods

2.1. MEDCC setup

The MEDCC reactor was described by Chen et al. [12] and its schematic structure is shown in Fig. 1. The reactor was made of plexiglass, which was drilled with a hole in a diameter of 3 cm. Effective volumes of the anode chamber, the acid-production chamber, the desalination chamber, and the cathode chamber were 30, 10, 10, and 30 mL, respectively. A piece of BPM (Fumasep-FBM, FuMA-Tech GmbH, Germany) with the same size of the hole cross section area was installed between the anode and acid-production chambers. Similarly, a piece of cation exchange membrane (CEM) (Ultrex CMI-7000, Membranes International, USA) was installed between the acid-production and desalination chambers, and a piece of anion exchange membrane (AEM) (Ultrex AMI-7001, Membranes International, USA) between the desalination and cathode chambers. The graphite brush anode and the cathode were the same as described by Chen et al. [12]. As the control, an EDBM reactor was constructed with the same structure of MEDCC but without microbes in the anode chamber.

The MEDCC for malic acid production was started from a matured MEDCC with desalinating NaCl solution. Initially, 0.04 M L-malic acid solution and 0.017 M NaCl were applied in the acid-production and cathode chambers, respectively. The anodic solution contained (in 1 L deionized water): 1 g CH_3COONa, 4.0896 g Na_2HPO_4, 2.544 g NaH_2PO_4, 0.31 g NH_4Cl, 0.13 g KCl, 12.5 mL trace metal solution, 12.5 mL vitamin solution, and the initial pH of the solution was adjusted to 7.0. Different L-sodium malate solutions (Na_2Mal) (0.2, 0.3, 0.4, 0.5, and 0.6 M) were tested in the desalination chamber. Four fixed voltages (0.4, 0.6, 0.8, and 1.0 V) were applied to the MEDCC circuit using a power supply (Itech, IT6700, China). An external resistance (10 Ω) was connected between the negative lead of the power supply and the cathode, and the positive lead of the power supply was connected to the anode. The solutions in all chambers were refreshed when the current was lower than 1.5 mA. As a control experiment to examine the effect of microbes, the EDBM was operated with the same conditions as the MEDCC. The experiments for each treatment were carried out at 30 ± 1 °C in duplicate and at least for three cycles of stable voltage outputs in the cells. Differences between values of the treatments were considered to be statistically significant at $p < 0.05$.

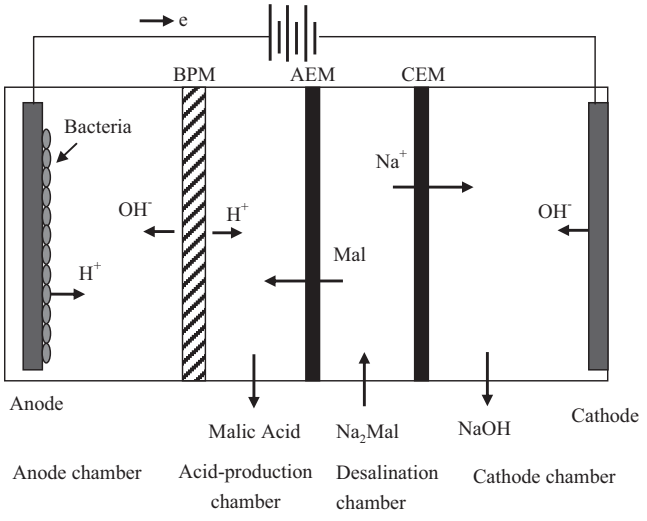

Fig. 1. Schematic structure of MEDCC for malic acid production.

2.2. Analyses and calculations

Concentrations of L-malate were determined using high performance liquid chromatography (1100 LC, Agilent Instruments, Inc., USA) with a C8 column (150 mm × 4.6 mm Column). The mobile phase was 0.5 M H_2SO_4 solution and the detected wavelength was 210 nm. The flow rate was controlled at 0.6 mL/min at 35 °C. The chemical oxygen demand (COD) in the anode chamber was measured using a dichromate standard method [14]. Solution conductivities and pH values were measured using a conductivity meter (Mettler Toledo, FE30K, Swiss) and a pH meter (Mettler Toledo, FE 20, Swiss), respectively.

Voltages cross the external resistance were recorded using a data acquisition system (model 2700, Keithley Instruments, Inc.). The voltage and external resistance were used to calculate the current. The current density (A/m^2) was estimated with the current normalized by the projected area of cathode electrode. The current efficiency (η) was determined as follows [9]:

$$\eta = 100\% \frac{F(C-C_0)V}{\int_0^T Idt} \quad (1)$$

where F is the Faraday constant (96,500 C equivalents^{-1}), C_0 and C are the initial and final concentrations of malic acid in the acid-production chamber (M), respectively, V is the volume of the acid-production chamber (L), I the current in the circuit (A), and T the operation time (s).

The total energy consumption in the MEDCC included the electricity input from the power supplier and the energy from acetate utilization by exoelectrogens in the anode chamber [9]. Thus the total specific energy consumption (i.e., the energy consumption for the production of 1 kg L-malic acid, kWh/kg) was calculated by

$$E = E_E + E_S \quad (2)$$

where E_E and E_S are the specific energy consumption from the electricity and from the substrate removal (kWh/kg), respectively, and calculated by

$$E_E = \frac{\int_0^T UIdt}{3600(C-C_0)MV} \quad (3)$$

$$E_S = \frac{n_S \Delta H_S}{3600(C-C_0)MV} \quad (4)$$

where M is the malic acid molar weight (134 g/mol), U the applied voltage (V), n_s the number of moles of substrate consumed during a batch cycle based on COD removal in the anode chamber (a conversion factor of 0.78 g COD/g sodium acetate is used), and ΔH_s (870.28 kJ/mol) is the combustion heat of the substrate [15].