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Alpha-ketoglutaric acid production using electrodialysis with bipolar membrane

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ABSTRACT

Environmentally friendly process of production of alpha-ketoglutaric acid (AKG) from model water solutions by bipolar membrane electrodialysis (EDBM) was carried out. Two-chamber EDBM stack with the anion exchange membrane-bipolar membrane (AM-BM) configuration was used to transport AKG ions through AM from the diluate to concentrate chamber and convert them to AKG acidic form. The influence of initial pH of diluate solution, initial concentration of AKG salts in the diluate and concentrate chambers and current efficiency was evaluated by considering such factors as voltage drop, alpha-ketoglutaric acid concentration, current efficiency and energy consumption for 1 kg of AKG production. Under optimum conditions the process EDBM allows achievement of a high concentration of AKG, high current efficiency and low energy consumption, equal to 4.83 g/L, 71.8%, 3.72 kW h/kg, respectively, while the corresponding results obtained after 180 min EDBM process without optimization were 1.6 g/L, 24% and 15.26 kW h/kg, respectively. In addition, the obtained results indicate that bipolar membrane electrodialysis may be used for the production of AKG from actual post fermentation broth in the future.

1. Introduction

Alpha-ketoglutaric acid (AKG) is a low molecular organic compound which is classified as a keto acid or oxoacid having in its structure both carboxyl groups as well as ketone groups [1]. It should be noted that keto acids having a carbonyl group in the alpha position are key intermediates in the amino acid metabolism and tricarboxylic acid (TCA) cycle [2]. In addition, a wide range of applications of this compound, e.g. in food industry, chemical industry, agriculture and especially in medicine and pharmacy (used as dietary supplement, component of infusion solutions, an agent that improves nitrogen balance in patients with burns etc.) is the reason for increasing demand for this metabolite expected in the coming years [3–5]. As well known, the majority of alpha-ketoglutaric acid is produced by chemical synthesis from diethyl succinate and diethyl oxalate [6]. However, this synthesis process is multi-step, low yielding and needs dangerous substrates such as cyanides, toluene and sodium metal, which can generate toxic waste [7,8]. Therefore, increased interest in biotechnological methods for conversion of carbon sources (glycerol, ethanol, n-paraffins) into organic compounds using microorganisms can be an alternative eco-friendly way of obtaining valuable raw materials [9]. Due to the multitude of by-products present in actual post-fermentation broth, the process of AKG production requires multiple purification steps (filtration, precipitation and acidification) [7]. Furthermore, it is important that the AKG present in actual fermentation broth occurs mainly in the form of AKG salt. Therefore, the acidification allows conversion of the salt to the acidic form. However, on the one hand, in the acidification step it is necessary to use large amounts of mineral acids (which may have a negative impact on the environment). On the other hand, this process can generate a considerable amount of wastes [10]. It appears that the use of membrane separation techniques including bipolar membrane electrodialysis (EDBM) can allow the efficient, wasteless and environmentally safe obtaining of valuable raw material [11,12]. Moreover, membrane-based processes show high potential for scaling up from laboratory to industrial level. Unfortunately, the main disadvantage of using the electrodialysis process are the operation cost (connected with high electric energy consumption) which are greater than that of the precipitation process.

Bipolar membrane (BM) consisting of cation and anion exchange layer can split water into OH^- and H^+ ions at the intermediate layer under reverse bias conditions and directly convert organic salts into organic acids [13,14]. According to literature, various organic acids and bases have been produced by EDBM. For example in 2002 Xu et al. [15] have presented the process of production of citric acid from

Abbreviations: AKG, alpha-ketoglutaric acid; EDBM, bipolar membrane electrodialysis; AM, anion exchange membrane; BM, bipolar membrane; TCA, tricarboxylic acid cycle

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sodium citrate by bipolar membrane electrodialysis. The same authors have reported that the highest citric acid concentration obtained after 200 min of EDBM process was equal to 30 g/L. In 2011 Wang et al. [12] have suggested that EDBM can be used for the production of monoprotic, diprotic and triprotic organic acids such as acetic acid, oxalic acid and citric acid, from aqueous solutions containing salts of the corresponding acids. Similarly Fu et al. [16] have used bipolar membrane electrodialysis to convert sodium succinate into succinic acid. In addition, many literature reports indicate that EDBM can be effectively used for the production of other organic acids, especially lactic acid [17], fumaric acid [18], tartaric acid [19], salicylic acid [20] and amino acids [21].

In this study bipolar membrane electrodialysis process was used to produce alpha-ketoglutaric acid from model solutions with sodium alpha-ketoglutarate and to evaluate the influence of initial pH of diluate solutions, initial concentration of AKG in the concentrate and diluate chamber and current density, on the performance of EDBM process. Moreover, the optimized bipolar membrane electrodialysis was carried out.

2. Material and methods

2.1. Materials

The study of alpha-ketoglutaric acid production from model solutions was performed with sodium alpha-ketoglutarate as a substrate. All sodium alpha-ketoglutarate solutions were prepared by adding NaOH to water solutions of alpha-ketoglutaric acid. Moreover model solutions were prepared with deionized water of conductivity not exceeding 3 μS/cm, their pH were adjusted in range 3–10 by the addition of sodium hydroxide. In addition, the conductivity of initial solutions of alpha-ketoglutaric acid is shown in Table 1. All components of model solutions were purchased from *Sigma-Aldrich*.

2.2. Bipolar membrane electrodialysis equipment and methods

In this study a two-chamber laboratory EDBM setup with a stack consisting of 1 bipolar (PC 200bip) and 1 anion-exchange (PC 200D) membrane (produced by PCCell GmbH, Germany) was used. The spacing between the membranes was 10 mm in thickness and the effective surface area of each membrane was equal to 64 cm^2. Additionally, the two-chamber laboratory EDBM setup was connected to a peristaltic pump (Verder, Poland) DC power supply (NDN) and a multifunction meter (Elmetron, Poland) measuring the pH, temperature and conductivity of working solutions. The cathode was made of steel 314 and the anode was made of titanium plated with iridium. In each compartment, solutions were circulated at the flow rate of 5.6 L/h. The process was carried out at 25 ± 2 °C and under constant current density from the range 65–125 A/m^2. During the EDBM processes, the pH-value, temperatures of diluate and concentrate solutions were controlled. In each experiment the model solution was fed to the diluate chamber while the solution of sodium alpha-ketoglutarate at the concentration from the range 0.3–5 g/L and pH of 8.5 was fed into the concentrate chamber, which allowed a decrease in the cell voltage at the beginning of the experiment. In EDBM processes the diluate and concentrate samples were collected at regular time intervals and analyzed. The voltage changes as a function of time were recorded to evaluate electrical resistance of the stack. All EDBM experiments were conducted for 180 min. Fig. 1 shows the electrodialysis membrane stack with AM-BM configuration consisting of 1 anion exchange membranes (AM) and 1 bipolar membranes (BM), which could be used to convert the sodium alpha-ketoglutarate into alpha-ketoglutaric acid. The electrolyte solution (0.3 M Na_2SO_4) was placed between the bipolar membrane and the anode. During the EDBM processes, when the constant electric field was applied, alpha-ketoglutarate ions present in diluate solution were transported across the anion exchange membranes to the concentrate chamber. At the same time, alpha-ketoglutarate salt was converted into alpha-ketoglutaric acid in the concentrate chamber with the H^+ ions produced from the water split by the bipolar membrane.

Table 1
The change in conductivity of AKG solution with different initial concentration.

Concentration, g/L	Conductivity, mS/cm
3	3.42
5	4.69
7	5.74
10	6.96

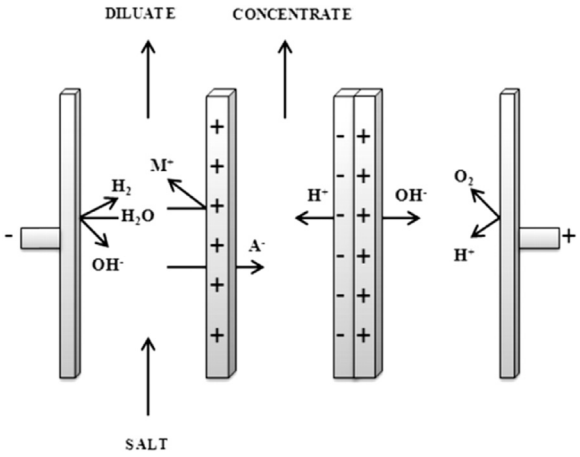

Fig. 1. Schematic of two-chamber laboratory EDBM configuration (AM-BM) (modeled after [12]).

2.3. Analytical methods

The contents of alpha-ketoglutaric acid and its salts in the starting solution and the product obtained in EDBM processes were determined using high performance liquid chromatography HP Agilent 1100 Series (Germany) equipped with an autosampler, interface (HP 35900), RI Detector (HP 1047 A), pump (HP1050), and separating column Rezex ROA-Organic Acid H+(8%), Phenomenex®. The eluent of 2.5 mM H_2SO_4 solution was constantly supplied at the rate of 0.9 ml/min. The column temperature and that at the input to the detector was 40 °C, P = 0.56 MPa. All samples were acidified to pH ≤ 2 by addition of 0.1 ml 25% H_2SO_4 to 1 ml of sample before analysis.

3. Calculations

The average value of energy consumed for 1 kg of alpha-ketoglutaric acid production was determined using the equation:

$$E = \frac{U \cdot I \cdot t}{m} \quad (1)$$

where: E – energy consumption needed to produce 1 kg of AKG, kW h/kg; U – voltage, V; I – current, A; m – mass of the final product, g; t – time, h;

The average value of the current efficiency was calculated on the basis of the following equation:

$$CE = \frac{F \cdot z \cdot V \cdot \Delta C_{dil}}{n \cdot I \cdot \Delta t} \cdot 100\% \quad (2)$$

where: CE – current efficiency, %; F – Faraday's constant (96,485), C/mol; I – current, A; z – valence of ions; V – diluate volume, L; ΔC_{dil} – change of AKG concentration in diluate chamber, mol/L; n – number of