Journal of Membrane Science 469 (2014) 428–435

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Recovery of fumaric acid from fermentation broth using bipolar electrodialysis

Krystyna Prochaska*, Marta J. Woźniak-Budych

Institute of Chemical Technology and Engineering, Poznan University of Technology, Pl. Skłodowskiej-Curie 2, 60-965 Poznań, Poland

ARTICLE INFO

Article history:
Received 3 February 2014
Received in revised form
1 July 2014
Accepted 3 July 2014
Available online 9 July 2014

Keywords:
Fumaric acid
Biotechnological conversion of glycerol
Bipolar electrodialysis
Ion-exchange membranes
limiting current density

ABSTRACT

Separation of fumaric acid from fermentation broth was carried out by bipolar electrodialysis using a laboratory ED set-up with an effective membrane stack area of 64 cm^2. The limiting current density was calculated on the basis of experimental current–voltage curves and optimal conditions of the process performance were proposed. Bipolar electrodialysis of post-fermentation broth from biotechnological conversion of glycerol was preceded by preliminary experiments regarding monocomponent, binary and ternary model solutions of fumaric acid. The influence of current density, pH and composition of fumaric acid model solutions on the efficiency of the process was analysed and discussed. Results of this report have proven that bipolar electrodialysis can be used as one of the purification steps towards recovery of fumaric acid from fermentation broth.

1. Introduction

Fumaric acid has been widely used in food products and beverages since 1940 [1]. Nowadays, it is used in the chemical and fodder industries [2]. It can also act as raw material for polymerisation, especially in production of unsaturated polyester, alkyd and paper resins [3]. In medicine it is used to treat psoriasis and other skin conditions. Moreover, recent studies indicate that fumaric acid can be applied as a supplement in cattle feed [4].

A number of microorganisms are able to generate fumaric acid but only a few produce it in significant quantities. Roa Angel et al [5] have shown the possibility of fumaric production by fermentation using *Rhizopus* strains. The highest productivities of fumaric acid are achieved using *Rhizopus arrhizus* (107.0 g/L) and *Rhizopus oryzae* (92.0 g/L) strains with glucose as a carbon source. The lowest productivity is obtained using Rhizopus nigricans (20.0 g/L). The same authors have observed that during fermentation the broth by-products like succinic acid, citric acid and lactic acid are also generated. Song et al [6] suggest that *Escherichia coli* strains under aerobic condition are able to produce 28.2 g/L of fumaric acid from glucose with acetic acid as a major by-product. Nakajima-Kambe et al [7] have proposed bioconversion of maleic acid to fumaric acid using *Pseudomonas alcaligenes* strain. In this report various organic acids such as malonic, itaconic, adipic and succinic one are used as carbon sources. The maximum productivity of fumaric acid was obtained after 6 hours of incubation and at elevated temperature (45 °C) using maleic acid as a major carbon source. Kordowska-Wiater et al [8] have suggested a genetic modification of two protoplasts: *Rhizopus oryzae* and *Rhizopus microsporus* to improve fumaric acid production from glycerol, when used as the only carbon source in the medium. The protoplast fusion led to a 1.5-fold increase in fumaric acid production.

During the fermentation process, some amounts of unreacted glycerol and lactic acid are determined as by-products. It should be pointed out that during each fermentation process, fumaric acid is obtained as sodium or calcium salt. Moreover, apart from fumaric salts, other components such as acetic acid, lactic acid, succinic acid or citric acid can be formed in the fermentation broth. Therefore, many additional operations are necessary to purify fumaric acid from the broth.

The traditional techniques such as extraction [9], ion-exchange [10], adsorption [11,12] and more environmentally friendly techniques like nanofiltration [13,14], dialysis [15], conventional electrodialysis [16], electro-electrodialysis and bipolar electrodialysis [17,18] can be used for organic acid separation from fermentation broth. Hong et al have reported that fermentation coupled with reactive extraction technique offers several advantages, such as a high product yield and the removal of carboxylic acid directly from the broth [19]. Siebold et al [20] selectively purified lactic acid from a ternary mixture of citric acid and acetic acid using Hostarex A337 dissolved in Cyanex 923/kerosene. Likewise, Da Silva and Miranda [21] have reported that a combination of weak base resin (Purolite, Brazil) as adsorbent and n-propanol as eluent ensured the best recovery of propionic acid from the broth. The results presented by Tongwen and Weihua [22]

* Corresponding author. Tel.: +48 61 6653601; fax: +48 61 665 3649.
E-mail address: krystyna.prochaska@put.poznan.pl (K. Prochaska).

http://dx.doi.org/10.1016/j.memsci.2014.07.008
0376-7388/

indicate that bipolar electrodialysis can be used to produce citric acid from it salts solution. Chukwu and Cheryan [23] have proposed conventional electrodialysis to separate acetic acid from unreacted glucose and other nutrients, such as calcium and magnesium salts.

In this study bipolar electrodialysis process (EDBM) was used to purify and concentrate fumaric acid from fermentation broth containing various by-products such as acetic acid, succinic acid, citric acid and mineral salts.

2. Experimental part

2.1. Materials

2.1.1. Model solutions

In these experiments monocomponent, binary and ternary model solutions containing fumaric acid in concentrations from the range 1.45–2.90 g/L, acetic acid (0.60–6.00 g/L) and 0.10 g/L of sodium chloride at pH=8 (corrected by the addition of sodium hydroxide) were analysed. Compositions of model solutions are shown in Table 1. All components of model solutions were purchased from Sigma-Aldrich.

2.1.2. Fermentation broth

Clarified post-fermentation broth from biotechnological conversion of glycerol containing fumaric acid (2.78 g/L), citric acid (0.19 g/L), cordycepic acid/mannitol (2.67 g/L), glycerol (4.2 g/L) and pH=6.4 was studied. Electrical conductivity of the broth was equal to 11.27 ± 0.01 mS/cm^2. The method of fermentation of glycerol to fumaric acid is described by Kordowska-Wiater et al [8]. The authors of this report have analysed only the major products in the broth, like organic acids (fumaric, lactic) and glycerol. However from the purification point of view, identification of other components present in the fermentation nutrient is also necessary. Thus, before electrodialysis, the composition of the fermentation broth was thoroughly examined and as a result the cordycepic acid (generally known as mannitol) was also identified. According to the authors [8], cordycepic acid was introduced to the broth as an osmotic stabiliser.

Prior to bipolar electrodialysis experiment, the fermentation broth was purified using nanofiltration technique as reported in our previous work [24].

2.2. Research equipment and methods

Three-chamber ED laboratory setup connected to a peristaltic pump (Verder), DC power supply (NDN) and multifunction metre CX-505 (Elmetron) measuring pH-value, conductivity and temperature of working solutions were used to perform bipolar electrodialysis process. Three types of membranes produced by PCCell GmbH were checked in this study: bipolar membrane PC 200bip (BM), anion-exchange membrane PC 200D (AEM) and cation-exchange membrane PC SK 250 (CEM). Their properties are listed in Table 2. The spacing between the membranes was 10 mm in thickness. The active area of membrane stack was equal to 0.0064 m^2. The cathode was made of steel 314 and the anode was made of titanium plated with iridium. In each compartment, solutions were circulated at a flow rate of 6.2 L/h.

Table 1
Composition of model solutions using in the experiments.

Model solutions	Symbol of model solutions	Concentration of components, g/L			pH
		Fumaric acid	Acetic acid	Sodium Chloride	
Monocomponent	I	1.45	–	–	8.00
	II	2.90	–	–	
Binary	III	1.45	0.60	–	
	IV	1.45	6.00	–	
	V	2.90	0.60	–	
Ternary	VI	2.90	0.60	0.10	

Table 2
Properties of the membranes used in the EDBM processes.

Membrane	AEM	CEM	BM
Symbol	PC 200D	PC SK 250	PC 200bip
Manufacturer	PCCell GmbH		
Thickness (μm)	99	164	222
T_{max} (°C)	50	–	40
pH range	0–12	1–14	0–12
Area resistance (Ω/cm^2)	2	1.5–2	1–2.5
Voltage drop (V)	–	–	1.2–2.2
Selectivity (%)	> 91	> 95	–
Efficiency (%)	–	–	> 98

The process was carried out at room temperature under constant electric field conditions ensuring current density from the range 60–120 A/m^2. During experiments, the conductivity, pH-value and temperature of working solutions were controlled. Concentration changes in concentrate and diluate compartments were measured in samples collected at regular intervals of time. All electrodialysis experiments were conducted until a constant value of conductivity was obtained. The temperature of working solutions during EDBM process changed in the range 25–26.5 °C. The voltage changes as a function of time were recorded to evaluate electrical resistance of the stack. Two types of cell configurations used in experiments are described below.

The arrangement presented in Fig. 1a consists of an anion-exchange membrane (AEM) and bipolar membrane (BM) placed between electrodes connected to DC sources. Fumaric salts solution was fed to the diluate chamber (1), while fumaric acid solution was introduced to the concentrate chamber (2), between AEM membrane and the cation side of BM membrane. In the chamber (3), between the anion side of the bipolar membrane and anode, sodium sulphate solution was added to ensure the current flow during the process. When a constant electric field was applied, fumarate anions passed through the AEM membrane to the concentrate chamber and simultaneously H^+ and OH^- ions were generated in the transition region of the BM membrane. Both, fumaric anions and hydrogen ions entered the concentrated chamber, forming fumaric acid molecules. This configuration can be used to convert organic salts into organic acids and to separate them from the other components.

The arrangement presented in Fig. 1b consists of a cation-exchange membrane (CEM) and bipolar membrane (BM). Fumaric salts solution was introduced to the concentrate chamber (2), between CEM membrane and the cation side of BM membrane. Sodium hydroxide solution was fed to the diluate chamber (1) and to ensure the current flow, sodium sulphate solution was added to the electrode chamber (3). When a constant electric field was applied, Na^+ ions passed through CEM membrane to the diluate chamber and simultaneously H^+ and OH^- ions were formed in the transition region of BM membrane. In this stack configuration, fumaric acid is generated by replacing Na^+ with H^+ ions in the compartment between the cation-exchange membrane and the cation side of the bipolar membrane. This kind of arrangement can be applied to desalinate the organic acids solutions.

2.3. Analytical methods

Concentration of fumaric acid was determined by polarography using Metrohm 797 VA Computrance. Concentrations of chloride anions were identified by Mohr method (Metrohm 702 SM Titrion).