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Fumaric acid separation from fermentation broth using nanofiltration (NF) and bipolar electrodialysis (EDBM)

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ABSTRACT

The suitability of two techniques: nanofiltration (NF) with ceramic membrane and bipolar electrodialysis (EDBM), in separation and concentration of fumaric acid from fermentation broth obtained during biotechnological conversion of glycerol, was investigated. The influence of composition, concentration and pH of fumaric acid model solutions on the efficiency of nanofiltration process was studied. It was found that the retention of fumaric salts increased strongly with increasing pH of the initial solution, while the retention of glycerol was lower than 6%, irrespective of pH. In the second step, the influence of electrodialysis stack configuration, current density, pH and concentration of fumaric acid in model solutions on the efficiency of bipolar electrodialysis was analysed. Then, after NF pretreatment, EDBM process of simulated solutions as well as fermentation broth was performed. The current density equal to 50 A/m^2 was found sufficient to achieve a 53% desalination of fumaric acid from fermentation broth. Moreover, the results obtained showed that bipolar electrodialysis stack, consisting of anion-exchange and bipolar membranes, allowed selective separation of fumaric acid from the broth.

The results suggest that NF with ceramic membrane as well as EDBM can be effectively applied as a removal step of fumaric acid from fermentation broth.

1. Introduction

Fumaric acid (IUPAC) is widely used in industry, for example as flavour additive, food ingredient in food industry, intermediate in pharmaceutical industry and as a precursor of many important organic chemicals such as aspartic acid, maleic acid or succinic acid [1].

Nowadays, fumaric acid is mostly produced by microbial fermentation process. Many different microorganisms such as *Rhizopus nigricans, Rhizopus arrhizus, Rhizpous formosa, Pseudomonas alcaligenes* are used for bioconversion of various carbon sources, including glycerol crude fraction for fumaric acid production [2,3]. On the basis of literature data, *R. oryzae* is able to produce large amounts of fumaric acid as a major product. As reported by Xu et al. [4] *R. oryzae* strain generates more than 27 g/L of fumaric acid as a salt with the productivity of 0.33 g/L/h during bioconversion of mixture of glucose and xylose as a carbon source.

The success of fermentation process is also strongly dependent on purification and separation steps, because large amounts of by-products, like organic acids (lactic acid, succinic acid, acetic acid, citric acid) or/and mineral salts, proteins and sugars are often formed [5,6]. In fact, many techniques are necessary to separate and concentrate organic acid from fermentation broth. The literature data indicates that traditional techniques based on precipitation [7], crystallization [8], reactive extraction [1] or adsorption [9] can be replaced by membrane techniques, such as nanofiltration [10], ultrafiltration [11], dialysis [12], conventional electrodialysis or/and bipolar electrodialysis [13–15], which can be more expensive, however – what is of crucial meaning – they are more environmentally friendly.

All these methods can be applied to isolate low molecular-weight organic acid from fermentation broth in one major operation unit. However, these techniques can be coupled in a hybrid system, i.e. consisting of nanofiltration with conventional electrodialysis [16], as well as electro-electrodialysis with back extraction [17] or complex extraction with reverse osmosis [18] etc.

The study was undertaken to check the possibility of using the processes of nanofiltration and bipolar electrodialysis in a hybrid system proposed for recovery of fumaric acid from fermentation broth. Taking into account the results obtained in our lab previously, it can be assumed that the proposed hybrid system NF + EDBM will exhibit high transport efficiency of fumaric acid, and also owing to the proposed configuration of the stack of bipolar electrodialysis, it is expected to ensure selective separation of organic acids.

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2. Experimental section

2.1. Materials

Several model solutions were prepared, containing fumaric acid in concentrations from the range 1.4–5.8 g/L and pH > 11 adjusted by the addition of sodium hydroxide, mixture of fumaric acid (1.4–5.8 g/L) with glycerol (2.5 g/L) and post-fermentation broth (solution 7) from biotechnological conversion of glycerol. All components of model solutions were purchased from Sigma–Aldrich.

The fermentation broth (solution 7) applied in our investigation was delivered by one of the collaborators in the frames of the project: "Biotechnological conversion of glycerol to polyols and dicarboxylic acids." The method of fermentation of glycerol is protected under the copyright of Kordowska-Wiater et al. [3]. Compositions of model solutions and fermentation broth applied in this investigation are listed in Table 1.

2.2. Nanofiltration experiment

The applied nanofiltration pilot scale module (Intermasz) was equipped with tubular ceramic monochannel membrane (Inopor) with cut-off 450 Da and the effective surface area equal to 0.0125 m^2. All of the experiments were carried out at temperature equal to 25 ± 2 °C and at transmembrane pressure (TMP) from the range 0.4–1.4 MPa. Model solutions containing fumaric acid and a mixture of fumaric acid with glycerol were separated using a pilot scale NF system with recycling of the ratentate to the feed vessel at the cross-flow rate of 3.5 m/s. After each experiment, the ceramic membrane in the module was cleaned to recover its initial permeability according to the following procedure: (i) washing with ultrapure water (10 min at 30 °C), (ii) alkaline bath – 1% of sodium hydroxide (45 min at 70 °C), (iii) washing with ultrapure water (10 min at 50 °C), (iv) washing with ultrapure water (10 min at 40 °C) until the pH neutralization, (v) acid bath – 0.5% nitric acid (10 min at 50 °C), (vi) washing with ultrapure water (10 min at 40 °C), (vii) washing with ultrapure water (10 min at 30 °C) until the pH neutralization. Moreover, before each nanofiltration experiment, the permeate flux of water was checked and compared with the initial one.

2.3. Bipolar electrodialysis experiment

Bipolar electrodialysis experiments were performed using a three-chamber laboratory set-up connected to a peristaltic pump (Verder), DC power supply (NDN) and multifunction meter (Elmetron) measuring pH-value, conductivity and temperature of working solutions. Fig. 1 shows the configuration of the electrodialysis stack consisting of commercial membranes of two types, produced by PCCell company: the bipolar membrane PC 200bip (BM) and the anion-exchange membrane PC 200D (AM), separated by polycarbonate spacer of 10 mm in thickness. The active area of membrane stack was equal to 0.0064 m^2. The anode was made of titanium plated with iridium and the cathode was made of steel 314.

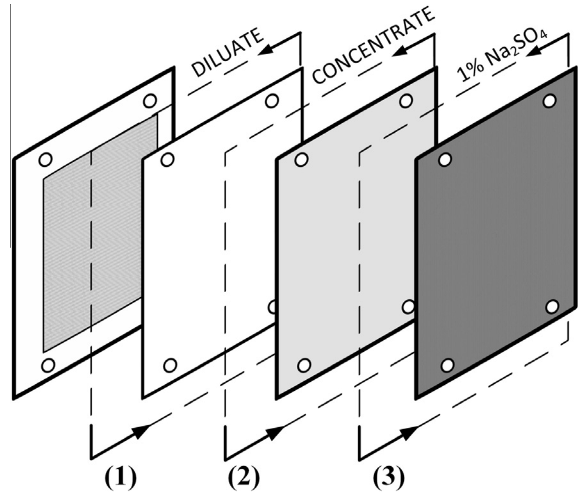

Fig. 1. Bipolar electrodialysis stack configurations.

Fumaric salt solution and fumaric acid solution were introduced to chambers (1) and (2), respectively. To ensure the current flow, sodium sulphate solution (10 g/L) was added to the electrode chamber (3). When a constant electric field was applied, fumaric anions passed through the AM to the concentrate chamber (2), and simultaneously hydrogen ions were generated by the BM. Both fumaric anions and hydrogen ions entered the concentrate chamber (2) and molecules of fumaric acid were formed. The other ingredients of model solutions which were not able to pass through the AM remained in diluate chamber (1). Moreover in the electrode chambers (1), the following reactions took place at the anode and cathode.

$$H_2O - 2\bar{e} = \frac{1}{2}O_2 \uparrow + 2H^+ (\text{Anode compartment}) \quad (1)$$

$$2H_2O + 2\bar{e} = H_2 \uparrow + 2OH^- (\text{Cathode compartment}) \quad (2)$$

Bipolar electrodialysis process (EDBM) was carried out at temperature equal to 25 ± 1 °C under a constant electric field ensuring current density from the range 50–80 A/m^2. The fluxes of working solutions were equal to 6.2 L/h. Each experiment continued until the conductivity of the working solutions (in concentrate and diluate chamber) remained unchanged. During the EDBM process, the concentrations of the components, conductivity, pH-value and temperature of the concentrate and diluate solutions were controlled.

Table 1
Composition of model solutions and post-fermentation broth.

	Concentration (g/L)									
	Solution 1, NF	Solution 2, NF	Solution 3, NF	Solution 4, EDBM		Solution 5, EDBM		Solution 6, EDBM		Solution 7 (the broth) NF-EDBM
Fumaric acid	2.90	2.90	2.90	D[a] 2.90	K[a] 1.40	D 2.90	K 2.90	D 5.80	K 2.90	2.00
Glycerol	–	–	2.50	–		–		–		–
Succinic acid	–	–	–	–		–		–		0.05
Citric acid	–	–	–	–		–		–		0.20
Cl^-	–	–	–	–		–		–		0.32
pH	3	11	11	11		11		11		6

[a] D, K – diluate and concentrate chambers, respectively.