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Membrane assisted recovery and purification of bio-based succinic acid for improved process sustainability

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ABSTRACT

Three membrane-assisted technologies – electrodialysis, nanofiltration, and Donnan dialysis – were investigated with the objective of developing a green and sustainable integrated downstream process for the recovery of biologically produced succinic acid from carob pod-based fermentation broths. For electrodialysis, heterogeneous and homogenous anion-exchange membranes (including such with monovalent-anion-permselective transport properties) were tested with synthetic model solutions in order to select the most suitable membrane. For nanofiltration, six polymeric membranes were tested to filter the obtained electrodialysis concentrates, and according to the results obtained, three of them (NF270, NF-DK and NF-DL) were selected for further experiments. The performance of these membranes was compared in a diafiltration operation mode with model carboxylates solutions and with simulated fermentation broths, all showing rejections above 90% for succinate and reaching negative rejections for acetate and formate. However, reduced fluxes and fouling were observed in the experiment with simulated fermentation broth containing a carob pod extract. Therefore this medium was treated by electrodialysis, producing a concentrate rich in ionic species, including succinate, but leaving behind the non-ionic and high-molecular mass species. This concentrate was treated by nanofiltration, thus achieving an almost complete removal of accompanying formate and acetate species. Finally, Donnan dialysis was employed to replace the metallic cations in the succinate salts in the nanofiltration retentate by H^+. The results showed approximately 76% of cations removal, which was traduced in the same percentage of obtained free succinic acid. Thus, the proposed integrated membrane-assisted process represents a promising new alternative to the existing downstream technologies for bio-based succinic acid recovery.

1. Introduction

Succinic acid (SA) has been recognized as one of the most promising chemicals that can be produced from renewable sources [1–3]. Biological production of SA involves fermentation of natural carbohydrates, and can be accomplished by different types of bacteria and yeasts, including *Anaerobiospirillum succiniciproducens* [4–6], *Actinobacillus succinogenes* [7,8], *Escherichia coli* [9] and *Saccharomyces cerevisiae* [10]. Moreover, SA can be produced from a variety of feedstocks including glycerol [6,9,11], corn stover [12], sugar cane and molasses [13], rice straw [14], and, more recently, carob pod flour [15].

Although some companies have already begun the implementation of industrial production of bio-based SA [16,17], the need of further process development and optimization remains well-known. In parallel with the efforts to optimize the production stage, a number of studies are addressing the complex problems associated with the SA downstream processing [18,19]. It has been reported that when producing organic acids by fermentation, 50–80% of the processing costs are typically attributed to the recovery and purification of the desired product [18,20,21]. The main challenges in SA recovery are its relatively low concentration in the fermentation broth, the presence of byproducts including other carboxylic acids (formate and acetate), and the requirement for pH control during fermentation, which leads to the obtainment of carboxylic acids present as salts instead of as their free forms, in the final product [22].

A common downstream process for SA recovery can be described as follows [23]: after microbial cells removal (by centrifugation and/or membrane filtration), a primary recovery step is performed, which involves evaporation for removal of water and volatile compounds, SA precipitation, liquid–liquid extraction, conventional electrodialysis or adsorption with anion-exchange

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resins, active charcoal, molecular sieves, or zeolites. The conversion of the succinate salt(s) formed into free SA, involves a dedicated step (e.g., acidification by cation-exchange resins, bipolar electrodialysis or thermal methods for salt splitting). A final SA purification requires either distillation or crystallization. However, in practice, not all steps are always necessary, often they may be combined (integrated), and their order may be changed [24].

Taking into account that membrane processes are considered as some of the most environmentally friendly methods currently available, in this work three complementary membrane-based processes, namely electodialysis (ED), nanofiltration (NF) and Donnan dialysis (DD) were investigated with the aim of recovering and purifying SA from simulated fermentation broths.

ED was first proposed for this application by Glassner and Datta, who employed conventional electrodialysis to recover, purify and concentrate sodium succinate from fermentation broth [25]. They reported a recovery of 80% of the succinate present in the broth, but also of 60% of the acetate present. Later on, Moon et al. investigated the performance of a batch ED for desalting and separation of binary and quaternary acid mixtures, while varying the composition of the initial feed and the current density [26]. Similar ED studies have been performed to recover other carboxylic acids salts [27–29].

Referring to the recovery and/or purification of carboxylic acids using NF, several studies have been reported so far. Timmer et al. tested NF membranes for dewatering a lactic acid fermentation broth [30]. Kim et al. studied NF for the removal of contaminant multivalent anions and cations from an ammonium lactate containing solution, finding that the accumulation of impurities (mainly sulfate) caused difficulties in running the process [31]. Kang and Chang employed NF to recover sodium succinate and remove by-products from a simulated fermentation broth. They registered the rejection of each salt for single, binary, ternary and quaternary organic acid salts solutions containing succinate, formate, acetate and lactate. NF of this quaternary acid salts solution in a diafiltration mode was carried out for 36 h. With time, the succinate rejection increased and the rejection of the by-products decreased as the concentration ratio of succinate to by-products increased [32]. Despite the promising results, the authors concluded that further research is needed in order to evaluate the feasibility of applying NF to fermentation broths with various compositions.

An important, and often limiting, SA purification step is the conversion of the obtained succinate salt(s) into a free SA form. Membrane-assisted processes studied to perform this conversion include bipolar electrodialysis [25] and ion substitution electrodialysis [33]. Compared to these options, Donnan dialysis appears as an interesting and possibly more feasible alternative, due to its relatively easier operation and lower energy requirements [34]. In order to transform a SA salt into its free acid form, an appropriate DD-based process should utilize a cation-exchange membrane (CEM) and an acid-containing receiver, capable of supplying the required protons across the membrane to the salt-containing feed compartment. Such a strategy has been successfully employed for recovery of alum from a water treatment plant [35] and for recovery of metal cations from lime [36], but to the best of the authors' knowledge, has not been reported so far for SA downstream.

2. Materials and methods

2.1. Materials

A model solution with the composition presented in Table 1 was employed for all experiments, unless otherwise specified. It mimics the composition of the fermentation broth reported by Carvalho et al. using a carob pod extract as substrate [15]. Succinic, acetic and formic acids were purchased from Sigma-Aldrich (minimal purities of 99.0, 99.8 and 85.0%, respectively). Inorganic salts and yeast extract were purchased from Panreac. All reagents were employed without further purification. For the experiments with simulated fermentation broth, roasted carob flour purchased from a local store was employed.

Table 1
Model solution composition.

Component	MW (g/mol)	Concentration (g/L)	Concentration (mol/L)
$NaH_2PO_4 \cdot H_2O$	137.99	8.50	0.0616
K_2HPO_4	174.18	15.50	0.0890
$NaHCO_3$	84.01	12.60	0.1500
SA	118.09	10.00	0.0847
FA	46.03	7.14	0.1551
AA	60.05	6.66	0.1109
NaOH	40.00	As needed for pH=6.8 (Aprox. 12 g/L)	Aprox. 0.3000

2.2. Electrodialysis equipment and membranes

The ED experiments were performed in an electrodialysis unit ED-Z mini (Mega, Czech Republic), which consists of a control unit (adjustable outputs of voltage from 0 to 20 V and current from 0 to 3.9 A) and 3 independent recirculation circuits, each equipped with a centrifugal pump and a liquid storage container (for diluate, concentrate and electrodes rinse solution, respectively). The unit was equipped with 2 membrane pairs consisting in three Ralex CMH cation-exchange membranes and two anion-exchange membranes (AEMs) to be tested (Neosepta AXE 01, Neosepta ACS, Ionics A103 QDP or Ralex AMH). All these AEMs are strongly basic – with quaternary ammonium fixed charged groups – with characteristics (according to the manufacturer) summarized in Table SM1 of the Supplementary material. The effective working area of each ion exchange membrane was 64 cm^2.

2.3. Electrodialysis operation

ED experiments were carried out in a batch operation mode at a temperature of about 23 °C in an air-conditioned laboratory. The diluate and concentrate containing containers were initially filled in with the model solution (Table 1) unless otherwise specified. The electrode rinse solution (Na_2SO_4, 20 g/L in distilled water), the concentrate and the diluate were re-circulated through the corresponding compartments of the ED stack at a constant flow rate (45 L/h for the electrode rinse solution and 15 L/h for the other two circuits). The experiments were run in constant current mode, with current values ranging from 0.75 to 2.0 A (corresponding to current densities from 1.2 to 3.2 mA/cm^2). During all experiments, stack voltage and current, as well as pH, conductivity and volume change were monitored for each circuit. 2.5 mL samples were taken periodically from the diluate and concentrate compartments. At the end of each run, a sample from the electrodes rinse solution was withdrawn and analyzed in order to confirm that no transport of organic acid ions has occurred to the electrode compartments. The experiments were terminated according to each experiment's objective.

2.4. Nanofiltration equipment and membranes

Dead-end NF experiments were performed at a room temperature (~23 °C) in a cylindrical stainless steel MetCell (Membrane Extraction Technology, LTD, UK), with an active membrane