



Recovering L-malic acid from a beverage industry waste water: Experimental study of the conversion stage using bipolar membrane electro dialysis

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ABSTRACT

Recovery of L-malic acid from a by-product of alcoholic fermentation process containing mainly sugars, alcohols, minerals, malate and other organic salts was investigated in order to ensure a cost-effective valorisation. Environmental-friendly process could consist in a two-stage electro dialysis process associating concentration electro dialysis (CED) and bipolar membrane electro dialysis (BMED). The feasibility of the CED stage has been assessed in a previous study [1]. BMED with two-compartment cell (BP/C) was investigated on a model potassium malate solution over the range 0.4–1.2 equiv. L⁻¹ giving current efficiency, L-malic acid recovery and specific energy consumption of 87–97%, 93–97% and 1.15–1.27 kWh kg⁻¹ L-malic acid, respectively. These performances were confirmed by runs on real concentrate obtained from the previous CED stage. However, specific energy consumption was significantly increased (50%) by the presence of anionic impurities, stressing the importance of a very efficient preliminary purification step. At last, the two-stage electro dialysis process allowed malate purity to be raised from 9% in the initial effluent to more than 70%.

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1. Introduction

Waste water from food processing often contains valuable molecules whose extraction may lower their polluting load and compensate at least partly for their discarding cost. The object of this study is a dark brown liquid with an intense apple flavour arising from a fermentation process involved in the elaboration of alcoholic beverages. Among the four most abundant compounds (Table 1), L-malate appears as the most promising one [1]. Indeed, a growing interest is observed for organic acids due to the wide spectrum of their applications and the possibility of producing them through fermentation. Regarding L-malic acid, most of its current applications are in food and pharmaceutical industries [1]: its sensorial and technological properties make it the second most used acidulant in the food sector, just after citric acid; it is used as pH corrective and anti-oxidant in nutritive solutions and contributes to the formulation of medicines. At last, due to its strong reactivity (moderate MW = 134 g mol⁻¹ and two acidic groups: pK₁ = 3.4, pK₂ = 5.11), it is regarded as a potentially interesting cross-linker for the production of bio-based polymers.

Organic acids are generally obtained as dilute salts in solutions containing impurities such as proteins, enzymes, sugars, and inorganic salts. Purification and concentration can be achieved through electro dialysis without any of the environmental drawbacks associated with conventional technologies [2]. The interest of a two-stage electro dialysis process is now well-assessed [3]: a first concentration electro dialysis step (CED) alternating homopolar anion- and cation-exchange membranes to concentrate and purify organic salts and a subsequent electro dialysis step with bipolar membrane (BMED) to achieve acid conversion by water splitting: indeed, BMED should be fed with a concentrated solution in order to achieve high current density and minimise the surface area of the costly bipolar membrane; the feed should also contain no more than a few ppm of divalent cations to avoid hydroxide precipitation [4,5]. Most of the studies recently published focus on lactic acid which is currently dominating the market [6–9] but this two-stage process proves also beneficial for citric, tartaric, gluconic, itaconic and propionic acids [2]. However, no examples of application to malic acid could be found.

Regarding BMED, a three-compartment cell is recommended for obtaining pure acid and base from the salts of strong acids [4]. When processing weak acids, high electrical resistance of the acid compartment, diffusion of the non-dissociated acid, high resistance of the anion-exchange membrane to the transfer of organic anions and low mobilities of organic anions (these two last problems being as more accurate as the MW is large (>200 g mol⁻¹) and the valence is high [10]) may lead to high energy consumption and poor current

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Table 1
Composition of the wastewater under study.

| | | | | | | | | |
|----------------------------------|------------|--------|-------------------------------|-------------------------------|-------|------------------------------------|-------------------------------------|-------|
| Alcohols (g L ⁻¹) | Ethanol | 131.00 | Minerals (g L ⁻¹) | SO ₄ ²⁻ | 1.50 | Organic acids (g L ⁻¹) | Malate | 24.40 |
| | Glycerol | 43.25 | | PO ₄ ³⁻ | 1.10 | | Lactate | 1.20 |
| | Sorbitol | 31.45 | | Cl ⁻ | 0.14 | | Acetate | 1.10 |
| Polyphenols (g L ⁻¹) | | 1.70 | | K ⁺ | 14.80 | | Citrate | 0.65 |
| Sugars (g L ⁻¹) | Saccharose | 7.23 | | Na ⁺ | 0.45 | | pH | 5.8 |
| | Glucose | 2.35 | | Ca ²⁺ | 0.38 | | Conductivity (mS cm ⁻¹) | 16.6 |
| | Fructose | 4.03 | | Mg ²⁺ | 0.37 | | Malate purity ^a (%) | 9 |

^a Mass ratio between malate ion and all species analysed.

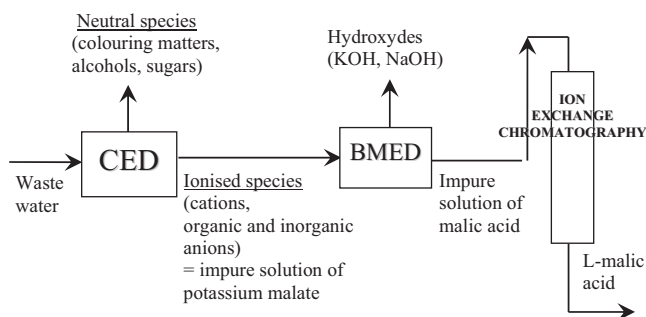


Fig. 1. Global process scheme.

efficiency. A two-compartment cell associating bipolar with cation-exchange membranes (BP/C) is therefore preferred [4,11,12]. High conversion level (>95%) may be reached depending on applications. Ion-exchange chromatography generally ensures final purification.

The feasibility of the first step (CED) for the extraction of malate from the current wastewater was assessed in a previous study [1]. The non-ionised impurities (sugars, alcohols and colouring matter, mainly) were retained better than 96% in the diluate. More than 84% malate could be recovered with current efficiency better than 90%. Monoselective cation-exchange membrane (Neosepta CMX-S) proved very efficient in removing divalent cations from the purified stream. The best transfer flux (316 g malate h⁻¹ m⁻²) was observed for Neosepta (CMX-Sb/AXE 01) arrangement. Concentration through a series of ten consecutive batches allowed a malate concentration of 130 g L⁻¹ to be reached, complying with criteria for a subsequent BMED stage [5].

The objective of the present work was to assess the feasibility of BMED as the second stage of the process (Fig. 1). Acid recovery, cation transfer rate, current efficiency and energy consumption were investigated on a BP/C configuration, in relation with initial concentrations in the acid and base compartments.

2. Materials and methods

2.1. Electrodialysis pilot

A two-compartment electro dialyzer TS-2-10 from EURODIA (Rungis, France) was used. Its electric supply allowed the pilot to be operated in a bipolar mode. It may contain up to ten cell pairs, each one with a 0.02 m² effective membrane area. Cationic and bipolar membranes were arranged alternately so that the repeating unit (cell) contains two compartments. Diluate or "acid" compartment received the effluent. Concentrate or "base" compartment was fed by a KOH solution. A NaOH solution at 1.5 mol L⁻¹ (conductivity about 20 mS cm⁻¹) was circulated through the electrode compartments. Temperature was regulated at 25 °C tanks to a plate heat-exchanger interposed on the electrolyte circuit and fed from a water bath. The experiments were run in a batch recycle mode: malate (Mal) and KOH solutions were pumped from their respective tanks and circulated through the acid and the base compartments respectively and then recycled. The initial volumes of solutions

in the two tanks were 2 L. Circulation flow rates were 300 L h⁻¹ for both acid and base compartments and 400 L h⁻¹ for the electrolyte. Experiments were stopped when the conductivity in the acid compartment decreased below 3 mS cm⁻¹. During all trials, pH and conductivity were monitored in each circuit, as well as current intensity and total tension. After each run, the volumes in the two compartments were measured.

2.2. Ion-exchange membranes

NEOSEPTA membranes (Tokuyama Soda, Japan) were purchased from Eurodia (Rungis, France). CMB is a cation-exchange membrane recommended for use in bipolar arrangements and concentrated basic solutions; however, concentration in the base compartment should not exceed 2 N, according to the suppliers' specifications. Bipolar membrane was BP1E. The stack was used with seven cells (total effective area 0.14 m²).

2.3. Experimental procedures and operating conditions

As a limited volume of concentrated malate solution was available from the preliminary CED stage, a first series of experiments was run with pure K₂Mal solutions (model solutions). Referring to Pourcelly [4], a minimal initial feed conductivity of 20 mS cm⁻¹ is required, corresponding to K₂Mal concentrations of approximately 0.12 mol L⁻¹ at 25 °C. Higher concentrations are generally implemented for reducing the membrane area and consequently both investment and operating costs: Bailly [5] recommends a minimal feed concentration in organic salt of 1 equiv. L⁻¹ corresponding here to 0.5 mol L⁻¹ (67 g L⁻¹) malate. Consequently, K₂Mal model solutions were prepared from pure DL-malic acid and KOH so as get solutions with conductivities and malate concentrations ranging from 27 to 65 mS cm⁻¹ and 0.2 to 0.6 mol L⁻¹ (0.4–1.2 equiv. L⁻¹), respectively; pH was consistent with the pH of the real solution (5.8).

The second series with the real solution should confirm the results obtained. In this second series, no intermediate rinsing was done in order to investigate possible occurrence of fouling.

KOH concentration in the base compartment must be high enough to ensure sufficient conductivity at the beginning of the operation. However, considering the chemical resistance of the membranes, it must not exceed 2 N (corresponding approximately to 112 g L⁻¹ or 388 mS cm⁻¹) at the end of the operation. A too high concentration may also slow down the transfer of potassium from the acid towards the base compartment. In specific cases, the choice of the concentration also takes into account the final destination of the base solution: for example, when the acid is produced by fermentation, base is recycled for pH control of the biological reactor and high concentration may be needed. This is however not the case here. Two concentrations were used: 0.04 and 0.09 mol L⁻¹, corresponding to conductivities from 9 to 25 mS cm⁻¹.

The tension drop per elementary cell should be maintained in the range of 1.5–3 V for 100 mA cm⁻² current density [4]. Taking account of the tension drop at the electrodes (approximately 6 V), overall tension should not exceed 25 V in the seven-cell

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