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Downstream Processing of Lactic Acid by Membrane-Based Solvent Extraction*

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ABSTRACT

Lactic acid has extensive use in the food and chemical industry. About half the lactic acid used in the world is produced by fermentation of carbohydrates using lactic acid bacteria. The recovery of lactic acid from the fermentation broth is more difficult than the fermentation itself. In the present work a study of membrane-based solvent extraction as a separation unit for the continuous downstream processing of lactic acid from fermentation broth was carried out. The experiments were performed using simulated fermentation broths made of lactic acid in acetate buffer or distilled water as the feed solution. The effects of membrane material, organic carrier, and pH of the feed solution on membrane extraction efficiency were investigated. A separation degree of 35% was obtained by using a polyetheretherketone (PEEK-WC 14%) membrane with 5% trioctylamine as the organic carrier in *n*-heptane. The experimental results obtained with the simulated system encourage the use of membrane-based solvent extraction with a real fermentation broth.

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INTRODUCTION

Aliphatic hydroxy acids containing one or more carboxyl groups are an important group of additives which have extensive uses in the food and chemical industry. Lactic acid is primarily used as an acidulant and as a preservative. Lactate polymers can be used as environmentally benign packaging materials, thanks to their strength, biodegradability, and availability from renewable resources. These applications have great potential for expanding the market of carboxylic acids, provided more economical and efficient downstream separation processes can be developed.

In the last twenty years, liquid membranes have been proposed as a new extraction technique, either in the form of double emulsions or in the form of a liquid held in the pores of a porous solid support. However, both types of liquid membranes proved to be unstable and were found to cause substantial losses of extractant (1, 2). An indirect contact method has been proposed to overcome the instability problem, but the flux across such membrane is often unsatisfactory.

The general objectives of this work are to study and optimize a membrane-based solvent extraction process (MBSX) for the separation of lactic acid from fermentation broths.

Membrane-based solvent extraction is a sequential two-step extraction process, used to selectively separate or to concentrate a solute from an aqueous phase to another via an organic enrichment step. In this system, contact between feed, organic solution, and stripping is established by the porous membranes which are preferentially wetted by one of the phases. A controlled pressure drop is then necessary to stabilize the separated-multiphase system (3).

The main advantages of membrane-based solvent exatraction, compared with traditional solvent extraction, are the high surface contact area per unit volume between the aqueous and organic phases without phase mixing, and the fact that relatively large equipment is not needed. The extractant and the feed can be brought into contact at high speed, even if their densities are identical, and there are no problems with ''flooding'' or ''loading'' (4).

The advantages promised by a hollow fiber membrane may be compromised in the following ways:

Fiber walls may offer major resistance, retarding the extraction

Choosing the membrane has an important effect on process performance (chemical resistance to organic solvents, porosity, pore diameter, wall thickness, Δp_{cr}, etc.)

Production of an emulsion squanders one main advantage; the emulsion can be avoided by a static pressure difference

Membrane-based solvent extraction with different kinds of membranes has been used for the separation of organic acids (5–7), proteins (8, 9), and metals (10).

In the present work membrane-based solvent extraction was investigated for continuous downstream separation of fermentation broths. The effects of membrane material, organic carrier, and feed solution pH on the separation efficiency of lactic acid were studied. After optimization, the membrane process was integrated into a previously studied continuous fermentation (11).

THEORY

The membrane extraction process described here employs an organic carrier which picks up the anions of lactic acid from the feed solution to an extraction module and releases them during contact with the stripping solution in a reextraction module. Figure 1 shows the mechanism of separation of a carboxylic acid by MBSX using a tertiary amine as carrier. At the interface between the feed and the extractant solution (Phase I and Phase II, respectively), the first step is activation of the carrier (12, 13):

$$R_3N + H^+ \leftrightarrow R_3NH^+ \tag{1}$$

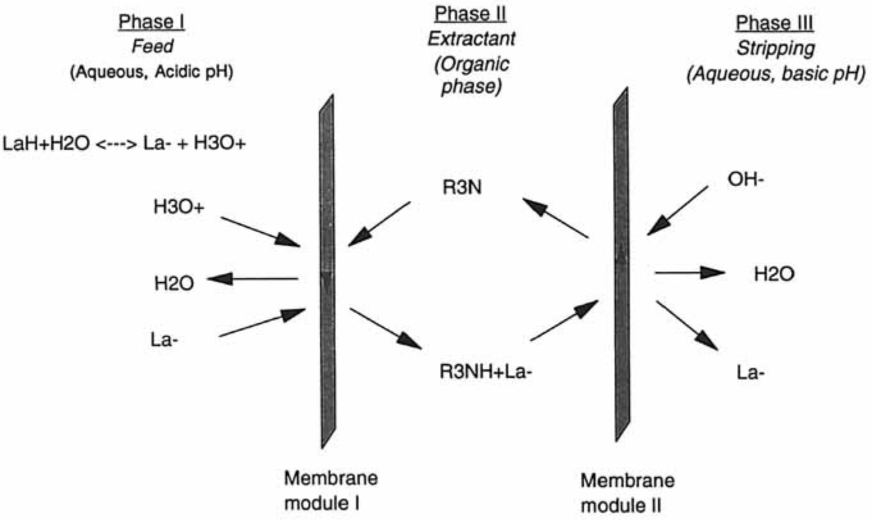

FIG. 1 Mechanism of separation of lactic acid by membrane-based solvent extraction.

where the equilibrium is described by

$$K_{\mathrm{Eq}} = \frac{[\mathrm{R_3NH^+}]}{[\mathrm{R_3N}][\mathrm{H^+}]} \tag{2}$$

The second step is the reaction between the activated carrier and the lactic acid anion:

$$\mathrm{R_3NH^+ + La^- \leftrightarrow R_3NH^+La^-} \tag{3}$$

where the equilibrium is described by

$$K_{\mathrm{Eq}} = \frac{[\mathrm{R_3NH^+La^-}]}{[\mathrm{R_3NH^+}][\mathrm{La^-}]} \tag{4}$$

At the interface between the extractant and the stripping solution (Phase II and Phase III, respectively), the release of lactic acid anions and the regeneration of carrier occur:

$$\mathrm{R_3NH^+La^- + OH^- \leftrightarrow R_3N + La^- + H_2O^-} \tag{5}$$

This equilibrium is described by

$$K_{\mathrm{Eq}} = \frac{[\mathrm{R_3N}][\mathrm{La^-}]}{[\mathrm{R_3NH^+La^-}][\mathrm{OH^-}]} \tag{6}$$

Using a pH gradient concentration between the feed and the stripping solution, lactic acid can be separated with cotransport of H^+ ions.

Most experiments have been carried out using a microporous hydrophobic membrane. The organic phase wets the membrane and its transport to the other side of the membrane is prevented by maintaining the pressure of the aqueous phase equal to or higher than that of the organic phase (14). The aqueous–organic interface is thus immobilized at each pore mouth on the aqueous side of the membrane.

The transport of the solute from the aqueous feed to the organic extractant is governed by the solute partition into the organic solvent, by the reaction between solute and carrier, and by the transport rate across the organic phase.

MATERIALS AND METHODS

The membrane extraction system (Fig. 2) consists of two hollow fiber modules. In the first module (Module I), the extraction of lactic acid from the feed solution (at acidic pH) into the organic phase (extractant) is carried out. In the second one (Module II), the lactic acid is reextracted from the organic phase into a stripping solution (at basic pH). Table 1 lists the different membranes used.

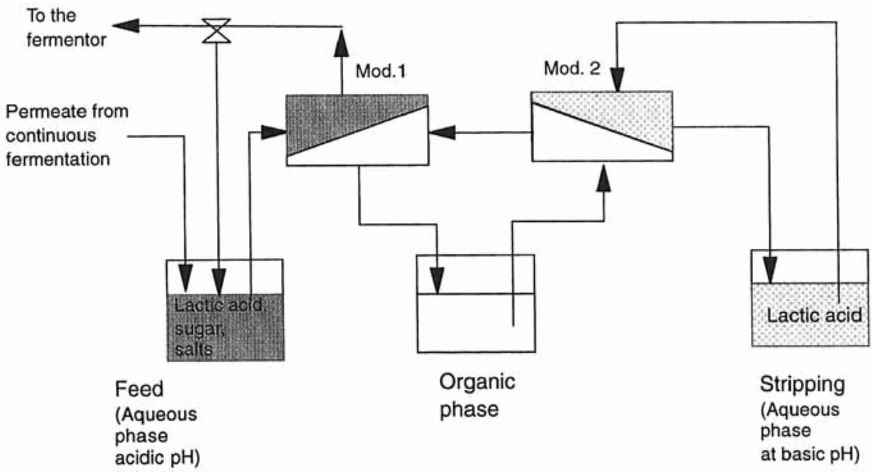

FIG. 2 Membrane-based solvent extraction system.

The feed solution consisted of 13.53 g/L L(+)-lactic hemizinc salt [equal to the concentration of 10 g/L L(+)-lactic acid] or 10 or 20 g/L D,L-lactic acid (from Sigma) in pure water or in a 0.1 M acetate buffer solution in the pH range between 2 and 5.5.

The extractant phase consisted of one of the following organic carriers:

Secondary amine Amberlite LA-2 (Sigma)
Trioctylamine (TOA) (Sigma)
Quaternary ammonium salt Aliquat 336 (Aldrich)

TABLE 1
Type of Capillary Membranes Tested for Extraction of Lactic Acid

Membrane[a]	Source	NMWCO (kDa)	Inner diameter (mm)	Outer diameter (mm)
PEEK-WC (14%)	Own production		1	1.5
PEEK-WC (18%)	Own production		1	1.9
Polyamide	Berghof	50	1.1	2.2
Polysulfone	Berghof	30		
Polypropylene	Accurel pp.		1.8	2.7

[a] The PEEK-WC membranes were made in our laboratory by phase inversion using 14 or 18% PEEK-WC polymer in dimethylacetamide (DMA).

TABLE 2
Operational Conditions under Which the Experiments Were Carried Out

	Axial flow rate (mL/s)	Temperature (°C)	pH	Initial volume (mL)
Feed	5	22	2–5.5	250
Extractant	8	22	—	250
Strip	12	22	11.4	125

Because of their high viscosity and cost, the carriers were diluted in such organic solvents as *n*-heptane (Carlo Erba), dodecane (Sigma), and oleyl alcohol (Fluka). The concentrations of organic carriers were 5 and 10% (w/w).

The stripping solution was made of 1 M sodium carbonate solution, set at pH 11.4 with sodium hydroxide.

Table 2 lists the operational conditions in which the experiments were carried out.

The lactic acid concentration in both aqueous phases was determined by the enzymatic test of Boehringer and by HPLC. A SumiChiral OA 5000 column from Chromopack was used for liquid chromatography. The mobile phase was 2×10^{-3} M $CuSO_4$ in 95/5 water/isopropanol at a flow rate of 1 mL/min and a wavelength of 254 nm.

RESULTS AND DISCUSSION

The hollow-fiber-in-tube modules (Fig. 2) consisted of 4 or 6 fibers glued by an epoxy resin (from Chimica Standard, Catania). The feed solution was recirculated through the lumen side of Module 1. The extractant solution was recirculated through the shell side of Module 1 and the lumen side of Module 2. The stripping solution was recirculated through the shell side of Module 2. In all experiments the solutions were recirculated in a countercurrent flow configuration.

Effect of Membrane Material

Five types of membrane materials and three types of organic solvents were examined for the separation of lactic acid. The first experiments were carried out to optimize the extraction process from the feed to the organic phase. For this reason the stripping circuit was not used initially.

Figure 3 describes the time course of lactic acid (LaH) for the different kinds of membranes used. In these experiments the feed solution was 13.5

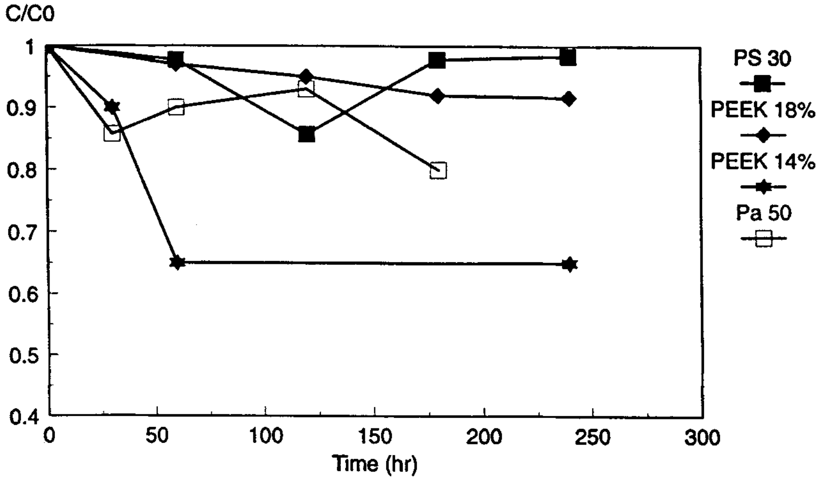

FIG. 3 Concentration profile of lactic acid in the feed as a function of different kinds of membranes.

g/L L-LaH hemizinc salt in 0.1 M buffer at pH 4.5–5 with 5% TOA in *n*-heptane or dodecane. The use of the different organic solvents did not show a significant influence on the separation process. The results showed that the PEEK-WC 14% membrane gives a separation of about 35% against the 10–15% of the other membranes. The lower performance of PEEK-WC 18% compared to PEEK-WC 14% could be due to its lower porosity and greater wall thickness.

In order to avoid leakage between the organic and the aqueous phase, it was necessary to wash the membrane with EtOH and then dry it with a vacuum pump before each experiment. In this way, membranes which show a certain degree of swelling when in contact with the organic phase can be completely regenerated to the original shape.

Another important way to keep the two phases separated is to use cocurrent flow at the beginning of the experiments to stabilize the system and then to swich to countercurrent flow using a transmembrane pressure of about 0.2 bar from the organic to the aqueous phase.

Effect of Carrier

The effect of carrier on the separation efficiency is described in Fig. 4. Experiments have been carried out using a PEEK-WC 14% membrane, a feed solution of 13.5 g/L L-LaH hemizinc salt in 0.1 M buffer at pH 4,

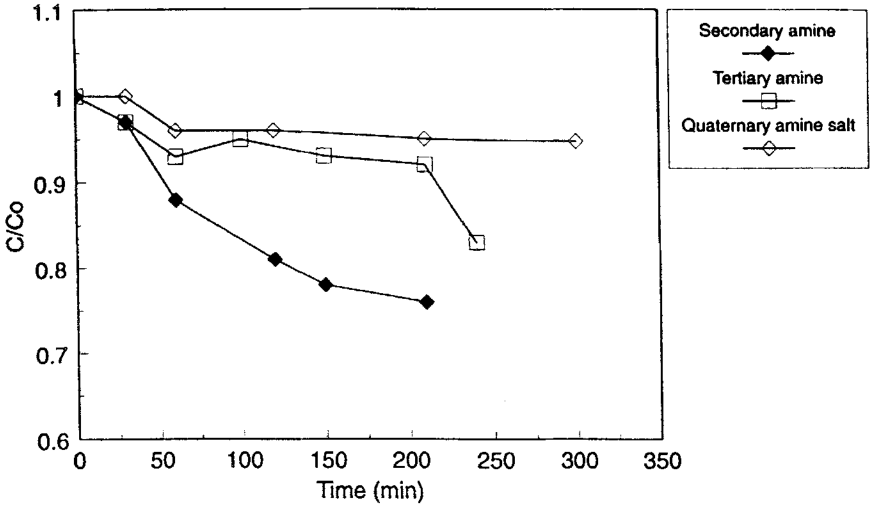

FIG. 4 Time course of lactic acid as a function of different carriers.

and 5% of carrier in *n*-heptane. As indicated in the figure, the quaternary ammonium salt separated about 8% of LaH, tertiary amine separated about 15%, and secondary amine separated about 25%, so that the best performance is obtained with secondary amine, as already described in the literature (15).

Experiments have also been carried out using a carrier concentration of 10% and an initial D,L-LaH concentration of 20 g/L in water with an initial pH of about 2.

LaH in pure water was taken as the feed solution in order to avoid competitive reaction with the buffer anions. In these experiments the stripping circuit was also connected to the system to speed up the whole process. The profile illustrated in Fig. 5 shows that higher separation was reached with the secondary amine.

Effect of pH

The investigated membrane-based solvent extraction process will be integrated with continuous fermentation for the downstream separation of lactic acid. The fermentation medium in which lactic acid is produced has to have pH values between 5 and 6. For this reason, the extraction efficiency has also been investigated as a function of pH. Figure 6 describes the average results of three different series of experiments carried

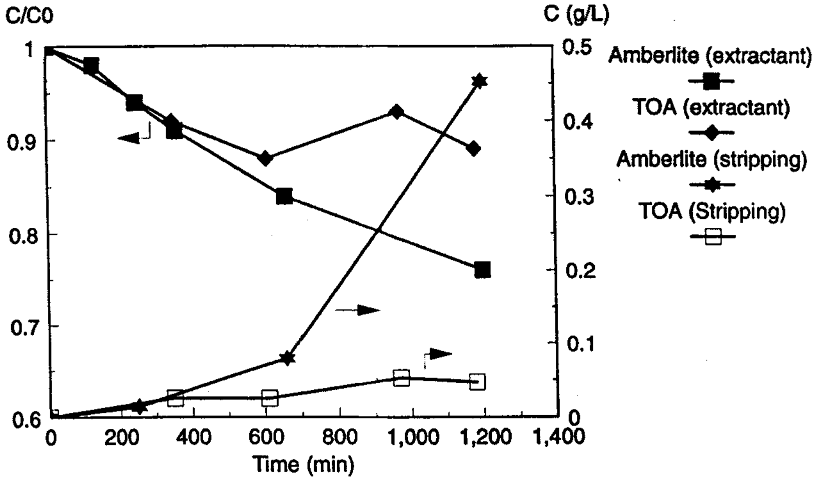

FIG. 5 Concentration profile of lactic acid in the feed and in the stripping solution.

out with PEEK-WC 16 and 18%, 20 g/L D,L-LaH in water, and 10% TOA in *n*-heptane. These results refer to the degree of separation calculated after 250 minutes of extraction of lactic acid. The pH did not seem to influence the separation process prior to this time. Further studies on the observed behavior are in progress.

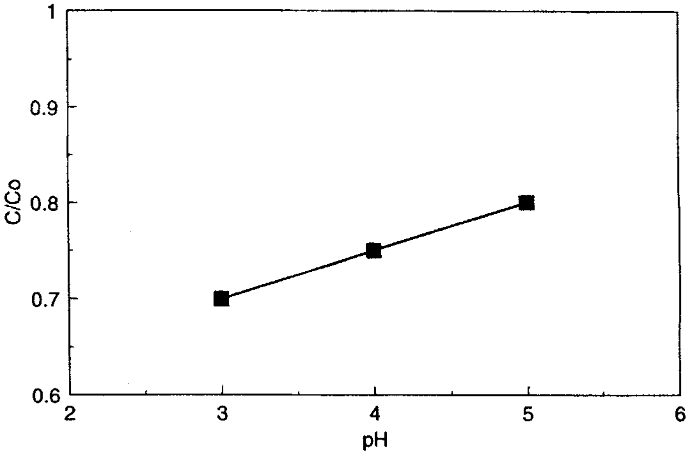

FIG. 6 Effect of pH on lactic acid extraction.

CONCLUSIONS

A membrane-based solvent extraction process for the separation of lactic acid using simulated fermentation broths made of lactic acid in acetate buffer solution or in pure water was studied.

Five different membranes were tested, and the highest performance was shown by the PEEK-WC 14% membrane using a capillary membrane module with an internal/external surface area of about 22.5×10^{-4} m^2/34×10^{-4} m^2, respectively. A degree of separation of 35% in about 1 hour (for the extraction of lactic acid from the aqueous feed into the organic phase) was obtained.

The morphology of the membrane has a strong effect on the separation process. The PEEK-WC 18% membrane, which has a pure water permeate flux about 25% less than PEEK-WC 14%, also showed a lower performance.

The effect of organic carriers was investigated. In agreement with the literature, the secondary amine promoted the highest separation process.

In general, the results show that membrane-based solvent extraction can be competitive with liquid membrane extraction (16) but is less efficient than a liquid emulsion membrane (17).

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