SAKARYA UNIVERSITY
JOURNAL OF SCIENCE
e-ISSN: 2147-835X
http://www.saujs.sakarya.edu.tr
Received
08-02-2018
Accepted
23-04-2018
Doi
10.16984/saufenbilder.392118

Extraction of propionic acid by emulsion liquid membrane using trioctylamine in toluene

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Abstract

The extraction of carboxylic acids by emulsion liquid membranes has also attracted attention in biotechnology, due to the high selectivity for the desired product, high separation rate and lower costly. The emulsion type liquid membrane system consists of three phases (water/organic/water) in which the organic phase acts as a membrane between the aqueous internal phase and the aqueous external phase. The main parameters such as surfactant concentration, mixing speed, feed phase pH, carrier concentration, and feed phase concentration were investigated. In the optimum conditions, extraction efficiency was obtained 71% in 10 minutes using trioctylamine (5% w/w) as a carrier, Span 80 (4% w/w) as a surfactant, toluene (91% w/w) as a diluent, sodium carbonate (10% w/w) as a stripping solution, mixing speed 300 rpm and feed phase pH 2,5.

Keywords: propionic acid, trioctylamine, emulsion liquid membrane

1. INTRODUCTION

Most of the carboxylic acids that are being used in food and pharmaceutical industry are produced by fermentation with the improvement of the biotechnology. Separation of carboxylic acids from fermentation broth, reaction mixtures and waste solutions has gained importance recently. Despite being produced by fermentation, recovery of biomass product is not practical due to the impairing the biomasses and high cost recovery expenses.

Carboxylic acids in existing processes are removing the microorganisms from the fermentation foam and then precipitation of insoluble calcium salts. As this recycle technique is a complicated process, liquid-liquid extraction and liquid-membrane techniques are suggested as an alternative to traditional precipitation process. But liquid-liquid extraction has many disadvantages due to the toxicity of the solvents and study with bacteria. This problem can be solved by using ultrafiltration [1,2], reverse osmosis [3,4], nano-filtration [5], membrane electro dialysis [6], emulsion liquid membrane [7,8], supported liquid membrane [9,10] as systems [11-14].

Emulsion Liquid Membrane (ELM) is a proper technique for the recovery of fermentation products. ELM is more efficient technique then liquid-liquid extraction, using solvent and solution with less values are its superiority. Extraction and stripping occur together on the large surfaces of liquid membranes prepared with the minimum amount of carrier in the ELM systems. Separation process of carboxylic acids with liquid membranes has attracted attention in biotechnology as it has provided high selectivity, separation speed and energy efficiency for the desired product. There are studies in which extraction of propionic acid

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was conducted by using reactive and liquid-liquid extraction systems [15-22].

Propionic acid that is produced by fermentation method, is a valuable chemical for agricultural applications and is being used protective compound in food and pharmaceutical industry.

ELM system consists of three phases; water/organic/water (W/O/W) that organic phase is moved as a membrane between internal aqueous phase and external aqueous phase. In this study, extraction of propionic acid was provided in aqueous solution.

2. EXPERIMENTAL

2.1. Materials

Propionic acid (Merck), surfactant Span 80 (Fluka), tertiary amine: trioctylamine (Merck), toluene and sodium carbonate (Sigma-Aldrich) were used in this study.

2.2. Preparation of membrane

(W/O) type emulsion was prepared mixing with surfactant Span 80 (sorbitan monooleate), carrier Alamine 300 (trioctylamine) and diluent (toluene) and stripping solution (Na_2CO_3) at 2000 rpm. (W/O/W) type emulsions were formed by adding mixture to feed solution. The mixing process was stopped at different periods and samples were taken from the aqueous phase. The acid concentration was measured by High Performance Liquid Chromatography (HPLC, Shimadzu LC-20AD and Hypersil C18 ODS Column).

The effects of surfactant concentration, mixing speed, carrier concentration, pH and concentration of feed solution parameters were investigated in this study. Two phases were occurred; feed phase and membrane phase at the end of the experiment. Emulsion was broken into its constituent using a high-voltage splitter with niobium electrodes.

3. RESULTS AND DISCUSSION

3.1. Effect of surfactant concentration

The surfactant was being used in order to increase the emulsion stability and decrease the surface tension in ELM processes. Span 80 (sorbitan monooleate) has been widely used in various industrial applications. Surfactant concentration added to the membrane phase was changed between (3-5%). As it can be seen in Figure 1, surfactant addition has increased emulsion stability and extraction rate. Too little surfactant renders the membrane weak. 50% extraction efficiency was occurred in 10 minutes with 4% (w/w) concentration. The extraction efficiency was shown equation 1.

$$\eta = 1 - \frac{c}{c_o} \tag{1}$$

c : Actual concentration, c_o: Initial concentration

Excess of surfactant increases the interface resistance and membrane viscosity and decreases the extraction.

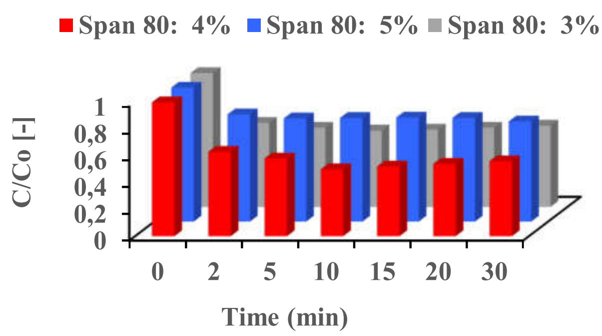

Figure 1. Effect of the surfactant concentration on the extraction rate (Diluent: Toluene, extractant: trioctylamine (5% w/w), feed phase concentration: propionic acid (10% w/v), feed phase pH: 2,5, stripping phase: Na_2CO_3 (10% w/v), mixing speed: 300 rpm)

3.2. Effect of mixing speed

Mixing speed is one of the parameters that affect the mass transfer rate in ELM processes. It affects the emulsion stability and diameter of emulsion drops. Mixing speed was changed 250, 300 and 500 rpm.

Increase on the mixing speed causes obtaining smaller emulsion drops and faster mass transfer speed. However unlimited increase causes a break of emulsion and decreases on the extraction that is effective parameter for propionic acid transport. The best appropriate mixing speed was found as 300 rpm.

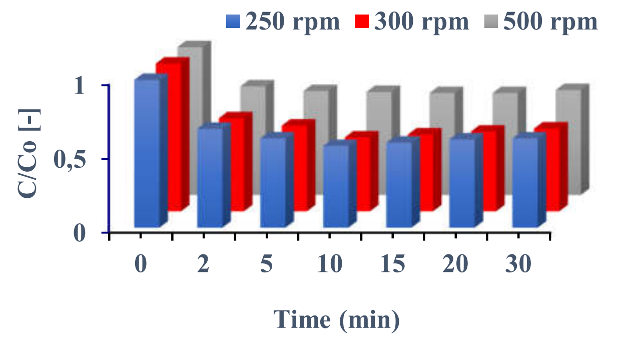

Figure 2. Effect of the mixing speed on the extration rate (Diluent: Toluene, surfactant: Span 80 (4% w/w), extractant: trioctylamine (5% w/w), feed phase concentration: propionic acid (10% w/v), feed phase pH: 2,5, stripping phase: Na_2CO_3 (%10 w/v))

3.3. Effect of feed solution pH

pH value of feed solution has an important role in ELM processes. Initial pH of the feed solution was differentiated between 1 and 4 in order to search the effect of pH on propionic acid extraction.

In order to change pH, HCI and NaOH were added to feed phase. The extraction rate decreased in Figure 3, when the HCI was added to feed phase. The competitive of HCl against the propionic acid has decreased the extraction of propionic acid. The best extraction efficiency was occurred in 10 minutes with pH: 2.5.

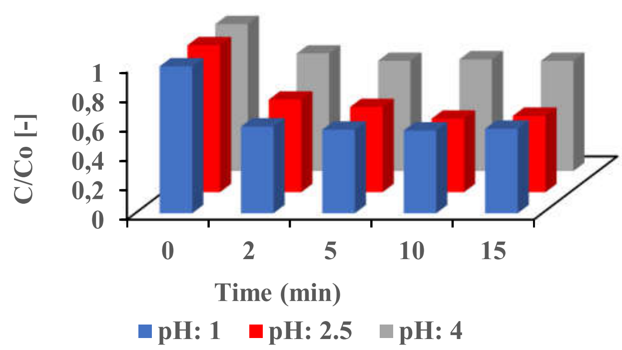

Figure 3. Effect of the feed solution pH on the extraction rate (Diluent: Toluene, surfactant: Span 80 (4% w/w), extractant: trioctylamine (5% w/w), feed phase concentration: propionic acid (10% w/v), stripping phase: Na_2CO_3 (10% w/v), mixing speed: 300 rpm)

3.4. Effect of extractant concentration

Tertiary amine (Alamine 300) that is used as carrier reacts with carboxylic acids. Extracted acid and extractant are possible easily recycled. This characteristic is being used in liquid membrane processes. Extracting ability of the extractants is identified by the formation of acid-amine complexes.

Characteristics of carriers are connected with the used solution as well as the basic characteristics of the molecule. During the solvent selection, immiscibility, volatility, viscosity and carbon number in the compound features with liquid solution are considered. Because of high dielectric constant and low viscosity, toluene was selected as solvent in propionic acid extraction in this study.

As it can be seen in the Figure 4, extraction of propionic acid has increased with the increase of the concentration of carrier agent.

Increase of carrier concentration more than (5% w/w) was caused defection on stability of emulsion. Extraction efficiency was decreased.

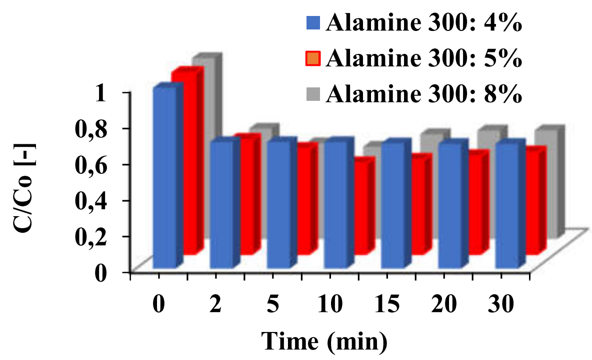

Figure 4. Effect of the extractant concentration on the extraction rate (Diluent: Toluene, surfactant: Span 80 (4% w/w), feed phase concentration: propionic acid (10% w/v), feed phase pH: 2,5, stripping phase: Na_2CO_3 (10% w/v), mixing speed: 300 rpm)

3.5. Effect of initial feed concentration

The different concentration of propionic acid in feed solutions was measured in the optimum conditions. Extraction has decreased with the increase of initial feed concentration, as it can be seen in the Figure 5.

The membrane was filled up with propionic acid complex and as there was no sufficient Na_2CO_3 in stripping agent, extraction was decreased. As the initial feed concentration was 10% (w/v), 50% acid was extracted. When the concentration was decreased to 1% (w/v), extraction efficiency was increased to 71% in 10 minutes.

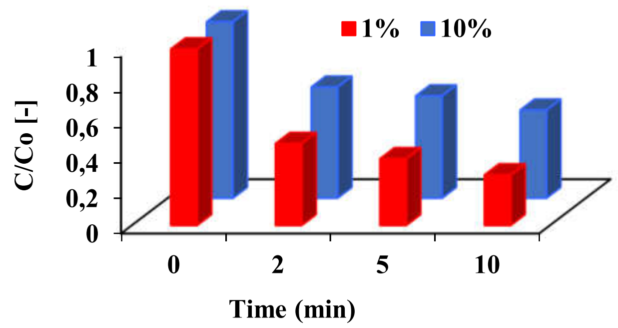

Figure 5. Effect of the feed solution concentration on the extration rate (Optimum conditions: Diluent: Toluene (91% w/w), surfactant: Span 80 (4% w/w), extractant: trioctylamine (5% w/w), stripping phase: Na_2CO_3 (10% w/v), mixing speed: 300 rpm, feed phase pH: 2,5)

3.6. Transport mechanism of propionic acid

Alamine 300 contains R_3 basic nitrogen atom. It reacts with organic and inorganic acids in order to form amine based salt. Produced amine salts can create ion change reactions with other anions easily. Reaction with secondary and tertiary amines, ionized propionic acids have performed between the interfaces of aqueous and membrane phases.

The study in which sodium carbonate was used as stripping agent can be explained with the mechanisms below:

Formation of amine salt between interfaces of feed and membrane phases (2). Transfer of amine salt following stripping in interface of a membrane and internal phases (3). Deterioration of amine carbonate in the sub surfaces of membrane feed phases to carbon dioxide and transfer for the formation of amine (4).

$$R_3N_{org} + C_2H_5COOH_{aq} \rightarrow R_3NH^+C_3H_5O_2^-{}_{org} \quad (2)$$

$$2R_3NHC_3H_5O_{2_{org}} + Na_2CO_{3_{aq}} \rightarrow 2C_3H_5O_2Na_{aq} + \\ + (R_3NH)_2CO_{3_{org}} \quad (3)$$

$$(R_3NH)_2CO_{3_{org}} \rightarrow 2R_3N_{org} + CO_{2_{aq}} + H_2O_{aq} \quad (4)$$

4. CONCLUSIONS

In the extraction created with the mixture of a membrane and prepared by using carrier Alamine 300 in Toluene with the emulsion type liquid membrane process, 71% propionic acid extraction was occurred just in 10 minutes. The optimum conditions obtained from the experiments: surfactant Span 80 (4% w/w), extractant Alamine 300 (5% w/w), diluent toluene (91% w/w), stripping phase Na_2CO_3 (10% w/w), mixing speed 300 rpm, feed phase pH 2,5.

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