

Liquid Membrane Component Selection for Succinic Acid Extraction

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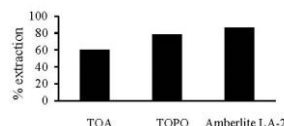
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Graphical abstract



Abstract

Succinic acid has received an upsurge interest in many industries due to its high product values and can be used in various applications. The purification cost for succinic acid from fermentation process was higher than the production cost, and the stock for succinic acid is limited. Thus, it is essential to develop an economical method to extract and purify the succinic acid. One of the promising methods is emulsion liquid membrane (ELM) process. In this study, ELM system will be developed to recover succinic acid from a simulated succinic acid fermentation broth through the selection of liquid membrane component using liquid-liquid extraction method. Several parameters such as different types of carrier, diluent, and stripping agent were investigated. The results show that the suitable carrier is Amberlite LA-2 with 87.2% of succinic acid extraction, the diluent is kerosene with 5% 1-octanol and the stripping agent is sodium hydroxide (NaOH) were selected as a main component for liquid membrane formulation.

Keywords: Liquid-liquid extraction; separation; succinic acid; fermentation; Amberlite LA-2

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1.0 INTRODUCTION

In many countries, succinic acid is receiving a great demand as alternative and renewable energy due to limitations of succinic acid reserves. Currently, lacking of crude oil supply and the cost for oil which continues increases, biological production of succinic acid from an alternative biomass has become a topic of worldwide interest. Bio-based succinic acid is a potential substitute for the current petrochemical production process which can cause harmful effect to the environment. However, compared with petrochemical-derived succinate, biological succinate production is still not economically viable because of its low product concentration in the fermentation broth and complicated product recovery. The production of succinic acid by fermentation, the separation process of succinic acid is complicated due to its by-produced acids, carbon sources, and salts.

The increasing use of biobased succinic acid as a replacement is expected to fuel market growth, as stated by the new market research report on succinic acid market. The main problems for succinic acid are the very high cost of downstream processing which accounts for 50–70% of the total production cost [1], and high production of acetic acid, which is a major by-product and a serious inhibitor during its microbial production. It is necessary to minimize the production cost of the biotechnological process in order to increase its competitiveness with the petrochemical process.

For economical separation process of succinic acid from the fermentation broth, few possible alternatives such as precipitation, electro dialysis, distillation and extraction have been reported [2]. These traditional methods are not suitable for the separation of succinic acid because it produces high amount of sludge and it requires a much more complex process for commercial use. In addition, it also requires expensive equipment and services. Reactive extraction method is also being proposed by a number of researchers [3]. Reactive extraction is a separation process between extractants and the materials extracted. Extractants such as hydrocarbon solvents, phosphorus solvents, and aliphatic amines have been used in reactive extraction method [4-5]. Kawano *et al.* [6] investigated the extraction of acetic and propionic acid using reactive extraction method. The study has found that the extractability of the secondary amine is larger than the tertiary amine. Hong and Hong [7] investigated that succinic acid can be separated using a mixture of tripropylamine with various types of diluents. From the previous study, it has been found that aliphatic amines are more effective for the separation of carboxylic acids from aqueous solution [8].

Recently, emulsion liquid membrane (ELM) process was done to extract succinic acid from aqueous solution. The study reported that the extraction rate of succinic acid is mainly depends on types of carrier used [9]. Emulsion liquid membrane also proposed by Lee and Hyun [10]. Based on the research, the degree of extraction of acetic acid reached to 99% while using trioctylamine as extractant. The extraction of acetic acid from the

mixtures of acetic-succinic acid solution was carried out by Lee and Kim [11]. A high concentration of mixtures were used in the feed phase to determine the degree of extraction for acetic acid in the emulsion liquid membrane system and high extraction of acetic acid was obtained with an appropriate emulsion liquid membrane formulation. Hence, the liquid membrane component selection was done for emulsion liquid membrane formulation by the liquid-liquid extraction process in order to get high extraction of the product.

Therefore, an objective of this research is to extract succinic acid from an aqueous mixture of succinic and acetic acid by using liquid-liquid extraction method. This is an essential part in emulsion liquid membrane formulation which is based on liquid-liquid extraction process. It consists of important components such as carrier, diluent, and stripping agent. Generally, an amine extractant must be used in the form of a solution in organic diluents due to high viscous and corrosive properties. This research will investigate the effect of different types of extractant in various diluents and stripping agent.

2.0 EXPERIMENTAL

2.1 Materials

Succinic acid (Sigma), acetic acid (Sigma), kerosene (Fluka), trioctylamine (Merck), tri-n-octylphosphine oxide (Merck), 1-octanol (Merck), 1-hexanol (Merck), sodium hydroxide (Sigma), sodium carbonate (Sigma), and amberlite LA-2 were used in this study. All the chemicals are the analytical grade reagents and used without further purification. The equipment required to measure succinic acid concentration was high performance liquid chromatography (HPLC). Amberlite LA-2, tri-n-octylphosphine oxide (TOPO), and trioctylamine (TOA) were used as extractant and dissolved in different types of diluents such as kerosene, 1-hexanol, and 1-octanol. Sodium carbonate and sodium hydroxide was used as stripping agent. The pH of an aqueous solution was measured by a pH meter (Mettler-toledo). For agitation of solutions a mechanical shaker was used (IKA-KS 130 Basic, Germany).

2.2 Liquid-Liquid Extraction of Succinic Acid

The initial concentrations of succinic acid and acetic acid were 50 g/L and 18.8 g/L, respectively. The initial acids concentration used was based on the concentration of acid in the actual fermentation broth [12]. An equal volume of aqueous solution (10 mL) and organic solutions (10 mL) were mixed together in a conical flask and shaken at 320 rpm for a period of 18 hours. The concentration of carrier, diluents and stripping were kept constant at 0.5 M. The solution was then carefully transferred into a separating funnel and let for phase separation about 15-20 minutes. Then, an aqueous solution was separated from the organic phase. The concentration of succinic acid in the aqueous phase was determined using High Performance Liquid Chromatography (HPLC). All experiments are carried out in room temperature ($\pm 27^\circ\text{C}$). The extraction (E) is defined as follows:

$$E = \frac{C_{B_0} - C_{B_{\text{raff}}}}{C_{B_0}} \quad (1)$$

Where C_{B_0} is the initial concentration of succinic acid in the aqueous phase and $C_{B_{\text{raff}}}$ is the concentration of succinic in the raffinate phase respectively.

The stripping process was carried out to identify the types of stripping agent required to strip succinic acid from succinic acid loaded organic solution. An organic phase is taken from the extraction process and mixed with stripping agent (10 mL) by using mechanical shaker at 320 rpm for 18 hours. After that, the mixture is carefully poured into separating funnel for phase separation (15-20 minutes). Then, the aqueous phase was separated from the organic phase and undergoes succinic acid analysis using High Performance Liquid Chromatography with Ultra Aqueous C18 column and UV detector at wavelength of 210 nm. In order to get the optimum conditions for succinic acid extraction, several parameters were studied. The parameters involved in this study are different types of carrier (Amberlite LA-2, trioctylamine (TOA), and tri-n-octylphosphine oxide (TOPO)), different types of diluents (kerosene, 1-hexanol, 1-octanol), and different types of stripping agent (sodium hydroxide and sodium carbonate).

3.0 RESULTS AND DISCUSSION

3.1 Selection of Carrier

The selection of carrier is one of the important factor in liquid-liquid extraction process. Figure 1 presents the percentage of succinic acid extraction using different types of carrier. It was observed that higher succinic acid extraction was obtained in amberlite LA-2 which is 86.3% of succinic acid, compared to TOA and TOPO. Amberlite LA-2 is a secondary amine while TOA is a tertiary amine. TOPO is an organophosphorus extractant. It has been widely used as extractant in the organic acid recovery and metal extraction. However, TOPO was not preferable because of its higher price compared to amine extractants. Ricker *et al.* [13] stated that the usage of TOPO in the acetic acid recovery may cause difficult recovery due to high boiling temperature. Currently, tertiary amine has been chosen in the extraction study because of its ability to react reversibly with carboxylic acid and makes the recovery of extracted acid and extractant easier [13]. Secondary amines are more favorable to extract carboxylic acid compared to tertiary amines. This is due to the extractability of the secondary amine is much higher than the tertiary amine. Since Amberlite LA-2 is a secondary amine, the base strength is lower in the molecule and makes the extractability become easier. However, Hong and Hong [13] attempted that tertiary amine provides good ability to react reversibly with carboxylic acid. On the other hand, extractability of the extractant was determined by its ability to form acid-amine complexes. Even though secondary amine can form amide formation with carboxylic acid [3], it can be solved by using active diluents, such as alcohol group. The properties for extractant not just depend on the basicity of the molecule, but also rely on the solvent used for succinic acid extraction. Therefore, Amberlite LA-2 has been chosen for this study.

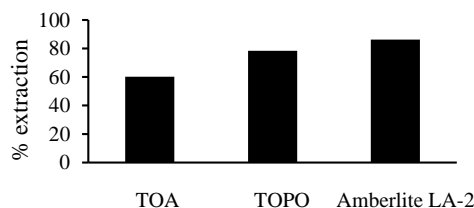


Figure 1 Effect of types of carrier used in liquid-liquid extraction. (Experiment conditions: [succinic acid]: 50 g/L, [acetic acid]: 18.8 g/L, [Carrier]: 0.5 M, mechanical shaker speed: 320 rpm, shaker time: 18 hours)

3.2 Selection of Diluents

Diluents should be chosen based on its immiscibility with the aqueous solution, volatility, viscosity, and the number of carbon in the compound. In this study, kerosene was used as a main diluent in the succinic acid extraction because of its high dielectric constant and low viscosity. Kerosene as an aliphatic diluent are preferred compared to aromatic diluent because of its low solubility in water and produce better emulsion stability in the ELM process [15]. Figure 2 shows the extraction performance of using kerosene as a diluent and the effect of adding modifier. From the result, it shows that 86.3% of succinic acid has been extracted using only kerosene as a diluent. From the observation, during the extraction process the third phase was formed. It was confirmed by Hong *et al.* [3] that the mixture of secondary amine and carboxylic acid will form third phase formation. This can be avoided by adding an active diluent such as alcohol group as a modifier. The result shows that by adding 5% 1-octanol the percentage of extraction increase to 89.5%. This indicate that the phase modifier can modify the polarity of the solvent and induce an important effect on the solute extraction and transport through the liquid membrane as stated by Cascaval *et al.*[16].

On the other hand, 1-octanol as an active diluent also provides better performance in extractability. The potential of alcohol group (1-octanol) in the extraction of succinic acid was investigated. The result shows that 1-octanol has high potential to be as assisting accelerator agent which is 89.5% of succinic acid was extracted. Succinic acid can be favorable into 1-octanol due to high solubility in the organic solvent. This proves that 1-octanol can be used as a membrane additive in the liquid membrane as it can increase the extraction rate. It has been reported that alcohol group is expected to induce an important effect on the solute extraction and transport to the liquid membrane [15]. On the other hand, Lee [9] reported that the degree of succinic acid extraction was higher by increasing the concentration of 1-octanol in the membrane phase. However the used of 1-octanol as a diluent of membrane phase is not recommended due to volatility of an alcohol group.

In the ELM process, this modifier also acts as a stabilizer in the emulsion liquid membrane system which can increase the membrane stability. Thus, kerosene in 1-octanol was chosen as diluents in the succinic acid extraction.

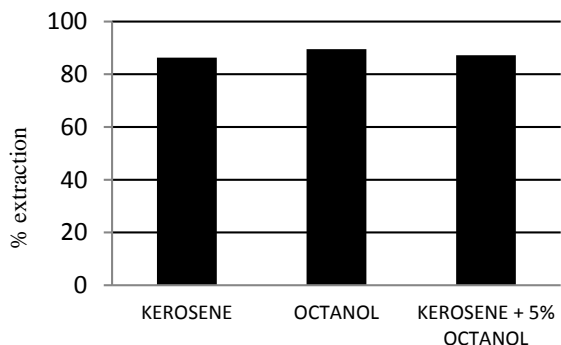


Figure 2 Effect of different diluents on the extraction of succinic acid (Experimental conditions: [Succinic acid]: 0.5 M; [Amberlite LA-2]: 0.5 M; volume of aqueous : 10 mL; volume of organic : 10 mL)

3.3 Selection of Stripping Agents

Acid loaded organic solution from liquid-liquid extraction process was then examined in stripping process using two types of stripping agents which are sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3). The results are shown in Figure 3. It indicates that NaOH perform better to strip succinic acid compared to Na_2CO_3 , which were 99.4% and 84.3% of succinic acid was recovered, respectively. Even though Na_2CO_3 shows lower percentage of succinic acid extraction, it can stabilize the emulsion in the liquid membrane system depends on its concentration. The use of sodium hydroxide as a stripping agent enabled more efficient transport of succinic acid from the succinic acid solution to the receiving phase in liquid-liquid extraction system. Sodium hydroxide is the most preferable stripping agent in order to extract succinic acid because of the larger reaction capacity of NaOH with acid keeps higher hydrogen ion gradient between the feed and the stripping phases [11]. Hence, NaOH was chosen as the best stripping agent.

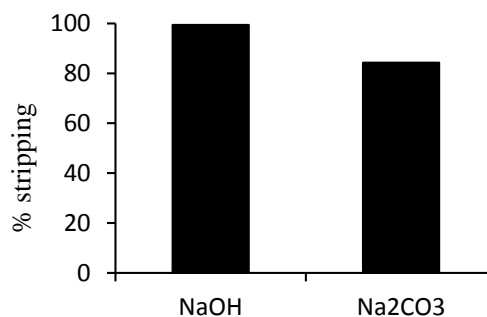


Figure 3 Effect of types of stripping agent on the percentage of succinic acid extraction using liquid liquid extraction (Experimental conditions: [Amberlite LA-2] : 0.5 M; [NaOH] : 0.5 M; [Na_2CO_3] : 0.5 M; agitation speed = 320 rpm; T = room temperature ($25 \pm 1^\circ\text{C}$)).

4.0 CONCLUSION

The selection of liquid membrane component for the extraction of succinic acid was investigated using liquid-liquid extraction method. The most suitable liquid membrane components are Amberlite LA-2 as a carrier, kerosene with 5% 1-octanol as a diluents and NaOH as a stripping agent. Using this formulation, the percentage of succinic acid extraction and stripping are 87.2% and 99.4%, respectively.

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