Study on stripping phase conditions on the levulinic acid extraction using supported liquid membrane

V. Rajendaren[1], S. M. Saufi[1,*], M. A. K. Zahari[1], A. W. Mohammad[2]

[1]Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Pahang Darul Makmur, Malaysia
*Email: smsaufi@ump.edu.my
Phone: +6095492823; Fax: +6095492889
[2]Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor Darul Ehsan, Malaysia

ABSTRACT

Levulinic acid (LA) is one of the top-twelve platform chemicals that can be produced from the biomass resources. LA production from the biomass is an environment friendly and sustainable compare to the petroleum based process. However, the separation and recovery of the LA from the biomass products is the main challenging process for reducing the overall LA production cost. Supported liquid membrane (SLM) is the most effective technique to extract and recover the desired product from the biomass products in a single step. Hence, it had a potential to be used for LA extraction. The study of the operation parameters in SLM system is very important to improve the yield of extraction and recovery of the product. In this study, different types of stripping agents such as sodium hydroxide (NaOH), sodium carbonate, hydrochloric acid, trimethylamine, and water were tested in the SLM system to extract levulinic acid (LA). By using 0.3 M trioctylamine in 2-ethyl-1-hexanol as liquid membrane phase, it was found that NaOH was the best stripping agent to extract LA. The concentration of the NaOH stripping agent was varied from 0.25 M to 1 M. The best stripping agent concentration was 0.5 M, which gave an LA extraction of 86% from a 10 g/L LA aqueous solution. The flow rate of the feed and stripping phase was investigated from 25 mL/min to 125 mL/min. SLM operated at 75 L/min was found to be adequate in reducing the boundary layer thickness at both sides of the SLM phases without any leakage of the liquid membrane and breakage of the matrix support. At the best stripping condition, 89% of the LA was extracted using 0.5 M NaOH that operated at flow rate of 75 mL/min.

Keywords: Supported liquid membrane; liquid extraction; stripping phase; levulinic acid.

INTRODUCTION

Levulinic acid (LA) is listed as one of the twelve top value added chemicals derived from biomass from over 300 biomass products [1]. The separation or recovery of organic acids like LA from other biomass byproducts is the most challenging and costly part in biorefinery [2–6]. Recently, supported liquid membrane (SLM) has gained significant attention in

downstream process due to its high degree of selectivity and capacity during separating or recovering the desired component from the mixture [7–9]. Moreover, optimization study on the operation parameters of the SLM system can further improve the efficiency of the process.

Stripping is an important parameter in the SLM system. During this step, the extracted component via carrier in the organic liquid membrane phase will be released to the stripping phase by the stripping agent. The carrier is regenerated and restarts the extraction cycle [8,9]. This process occurs simultaneously in the SLM and prevents the accumulation of extracted components in the liquid membrane phase, hence, improving the permeation and flux [10]. The stripping agents for back extraction should have a high degree of stripping and not affect the extraction efficiency of the carrier after stripping [11]. The concentration of the stripping agents is also an important parameter that should be considered in the SLM operation. If the concentration is too high, it has a high possibility for the stripping agent to move into the feed phase through the membrane's pores [12].

An aqueous solution of an electrolyte such as acid and base is a type of stripping agent that is commonly used for the recovery of organic acids in the SLM. Sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) and volatile ammonia (NH_3) are examples of base stripping agents that can strip the acid and form sodium salt or ammonium salt at the stripping phase [7,11–13]. Furthermore, trimethylamine (TMA) is a water-soluble and volatile base used in the stripping phase for extracting the acid without the formation of a salt byproduct [14–16]. However, TMA is a toxic material that can affect the bioactivity of the enzyme [17]. Back extraction using acid such as hydrochloric acid (HCl) can also be used to produce undissociated acid, but later, it would have to undergo the distillation process to regenerate the HCl.

It was reported that the succinic acid extraction yield had increased when the striping agent concentration increased from 0.01 M to 0.5 M due to the delayed accumulation of acid complex in the membrane layer and 0.5 M of Na_2CO_3 was recorded as the best stripping agent concentration for the process [18]. The results also indicated that Na_2CO_3 was performed better and resulted high succinic acid extraction yield compared to NaOH [18,19]. However, some studies reported that NaOH performs better than Na_2CO_3 because of its larger reaction capacity with acid, which keeps higher hydrogen ion gradient between the feed and the stripping phases [20]. NaOH also showed a better recovery of lactic acid than HCl [11]. Keshav and Wasewar [15] has tested various concentrations of NaOH (0.02–1.0 M) and TMA (0.05–0.31 M) as the stripping phase for the recovery of propionic acid from loaded organic phase. Based on the results, 100% of acid in the organic phase was extracted when the molar ratio of NaOH or TMA is slightly higher than the molar ratio of the acid in the organic phase.

Apart from that, the flow rate of the feed and strip phases are important operation parameters in the SLM system [21]. The stirring or pumping of the flow streams affects the existing pressures in the organic LM phase. Normally, the flow rate for both feed and stripping sides are set at the same value. Using different values can cause different pressures existing in the LM, thus, leading to the leakage of LM from the matrix support [22]. The effect of different flow rates as 1.35, 2.07 and 2.79 L/h at both feed and stripping streams in the SLM for glucose extraction were investigated by [23]. Based on the study, increasing the flow rate of both streams and reducing the boundary layer thickness between the phases and membrane lead to a high degree of glucose extraction and recovery. Harruddin et al. (2017)

[24] studied the effect of different feed flow rates and it was found that 75 mL/min is the optimum flow rate for the acetic acid removal by their SLM system.

Hence, a study on the best operating condition of the SLM process is important to enhance the LA extraction. In the current study, a custom-made hybrid graphene-polyethersulfone membrane was fabricated and used as the membrane support in the SLM system. The effect of stripping operation parameters such as types of stripping agents and concentrations, and SLM flowrates were investigated.

METHODS AND MATERIALS

Materials

Polyethersulfone (Radel® A, Solvay, USA) was used as the base polymer for membrane fabrication. Dimethylacetamide (DMac) and polyethylene glycol (PEG 200) were purchased from Sigma Aldrich and used as a solvent and an additive, respectively. Distilled water was used as a coagulation medium. The graphene nanopowder was used as an inorganic compound, in which it was supplied by Low Dimensional Materials Research Centre, University of Malaya, Malaysia. For organic LM phase preparation, trioctylamine (TOA) was supplied by Sigma Aldrich and used as carriers, whereas the 2-ethyl-1-hexanol from Merck was used as diluents. NaOH (Merck), Na_2CO_3 (Merck), HCl (Fisher Scientific), TMA (Nacalai Tesque), and deionized water (H_2O) were used as stripping agents. The LA was bought from Sigma Aldrich and used as the feed.

Membrane Fabrication

Vapor inducing phase separation (VIPS) technique was used to fabricate a microporous PES/graphene mixed matrix membrane. The casting solution was prepared from 15 wt % PES, 42.5 wt % polyethyleneglycol (PEG 200) and 42.5 wt % dimethylacetamide (DMac). The graphene nanopowder with an amount of 0.1 wt % relative to the total amount of PES in the casting solution was added to increase the hydrophobicity of the membrane support. The graphene nanopowder was premixed with DMac solvent (50% based on the total wt % of DMac solution) and ultrasonic for a day. Later, the 42.5 wt % of PEG 200, 15 wt % of PES and the balanced wt % of the DMac were added together with the premixed solution and continuously stirred for up to two days at room temperature until a homogeneous dope solution was formed. The prepared solution was degassed at room temperature for a day. The polymer solution was casted onto a glass plate at a thickness of 400 μm by using a semi-automatic casting machine. The cast film was immediately exposed to 86–89% of humidified environment for 30 seconds. Later, it was immersed into a water coagulation bath at 40 for 30 minutes. Then, the solidified film was immersed into another new water coagulation bath at room temperature for a day and was dried at room temperature for two days. The prepared membrane support was cut into 11 cm × 5 cm size [25].

Field Emission Scanning Electron Microscope

The membrane was fractured via freeze fracture technique by using liquid nitrogen. The membrane was then coated with platinum and its morphology was observed using Field Emission Scanning Electron Microscopy (FESEM) model JEOL JSM-5410LV, Japan.

SLM System
A LM was prepared from 0.3 M TOA and 2-ethyl-1-hexanol. The membrane support was immersed into the LM for a day and the excess LM on the surface of SLM was removed using filter paper. The SLM was fixed into the cell membrane, as shown in Figure 1. 10 g/L LA solution was used in the feed phase. The effect of 0.5 M of each stripping agent (NaOH, Na_2CO_3, HCl, TMA, and H_2O) at the stripping phase on the LA extraction yield was evaluated. The concentration of the best stripping agent that ranged from 0.25 M, 0.5 M, 0.75 M, and 1 M was also evaluated. Two-channel peristaltic pump was used to pump the solutions into the membrane cell in counter-current flow, as shown in Figure 1. The effect of flow rate of the feed and stripping phases that ranged from 25 mL/min, 50 mL/min, 75 mL/min, 100 mL/min, and 125 mL/min on the extraction yield of LA was investigated. The samples were taken from the feed phase every two hours for the period of eight hours [25].

LA Extraction Percentage
The samples were analyzed by using the Synergy Hydro C18 high performance liquid chromatography (HPLC) column (Phenomenex, 250 mm × 4.6 mm, 4 µm particle size) that is connected to the Agilent HPLC 1200 system. The 0.02 M potassium dihydrogen phosphate was adjusted to a pH value of 2.9 and used as a mobile phase. The LA was detected through an ultraviolet (UV) detector at 221 nm wavelength. The column was operated for 22 minutes at 30℃ with a flow rate of 8 mL/min. Equation (1) was used to calculate the percentage of LA extraction during the SLM process [25].

$$\text{Extraction (\%)} = \frac{[LA]_{fi} - [LA]_{fo}}{[LA]_{fi}} \times 100\% \tag{1}$$

where, $[LA]_{fi}$ is the initial concentration of LA in the feed phase, and $[LA]_{fo}$ is the final concentration of LA in the feed phase.
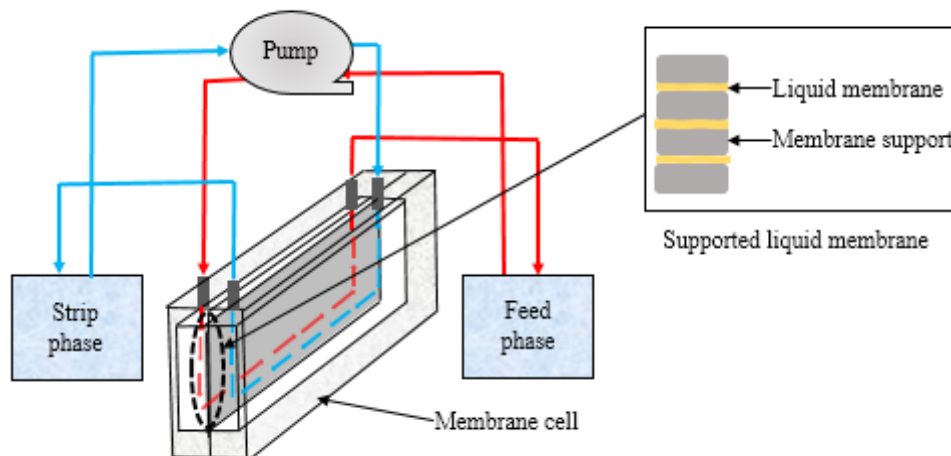

Figure 1. SLM system

RESULTS AND DISCUSSION

Membrane Morphology

The cross sectional structure of the hybrid PES/graphene membrane support was showed in Figure 2. It shows a long cylindrical microvoid structure that connected from the top to the bottom surface of the membrane. This same type of the membrane was successfully used for extraction of acetic acid using SLM process previously [9].
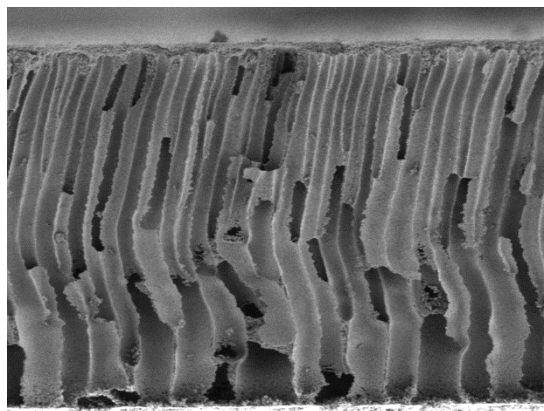

Figure 2. Cross section of PES/graphene hybrid membrane.

Effect of Types of Stripping Agents

In the SLM system, the pH difference between the feed and stripping phases plays a vital role in LA extraction [18]. Therefore, two types of alkaline striping phase were tested, which were NaOH and Na_2CO_3. The extraction yield of LA using various types of stripping agents at 0.5 M concentration was showed in Figure 3. The extraction yield of LA stripped using NaOH is higher, with 86% compared to Na_2CO_3, of only 59%. The initial pH values of aqueous Na_2CO_3 and NaOH were recorded as 9.83 and 13.54, respectively. Hence, NaOH is a strong base and it dissociates completely in water to form one mole of Na^+ and OH^-. Meanwhile, Na_2CO_3 is a weak base that dissociates in water to form two moles of Na^+ and one mole of CO_3^{2-}. The total molar concentration of sodium ions (Na^+) in Na_2CO_3 and NaOH are 1 mol/L and 0.5 mol/L, respectively. It has been stated that the stripping phase with higher concentration of sodium ion can extract more acid [18,19]. However, the OH^- group possesses high base strength than the CO_3^{2-} does. Therefore, the NaOH easily undergoes base ionization in water and efficiently reacts and extracts the acid from the loaded carrier compared to the Na_2CO_3.

The LA extraction yield for acid-based stripping solution of HCl showed the least, with only 14%. The HCl and LA are classified as acid and both can be extracted by TOA. However, the HCl is a strong acid and a good proton donor, which easily dissociates into a proton, H^+ and effectively reacts with the lone pair in amine (TOA) compared to the LA. Moreover, it has been stated that HCl can easily displace the organic acid from the loaded carrier [11,26,27]. In this case, the HCl at the stripping phase was extracted via the carrier and the HCl had also displaced the LA from the loaded carrier in the LM. Therefore, HCl resulted in the least LA extraction yield. Hence, HCl is not recommended for acid-back extraction in this SLM system.
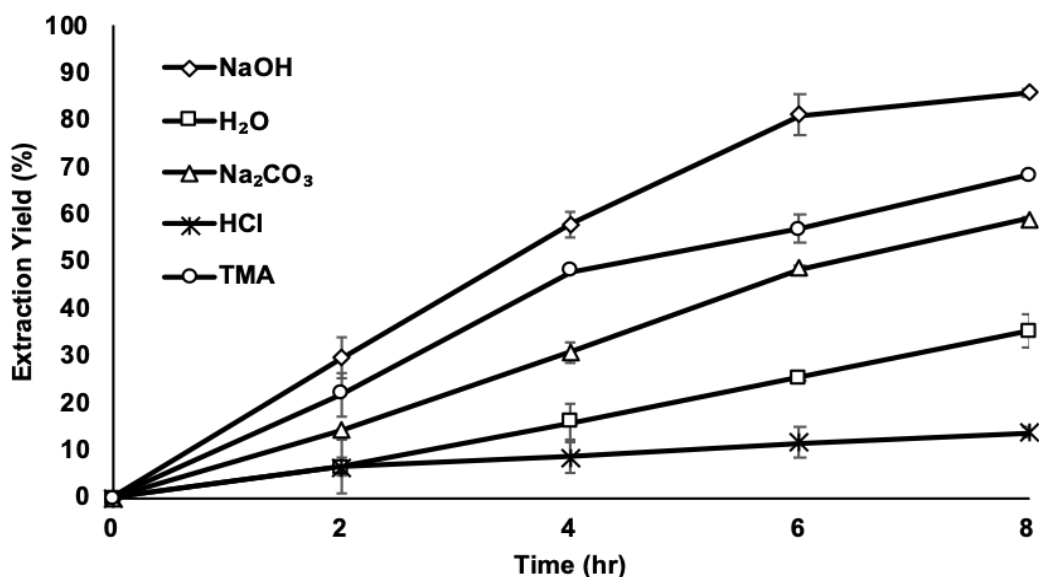
Figure 3. Extraction yield of LA using 0.5 M of various types of stripping agents.
(Experimental condition: feed phase - 10 g/L LA; LM phase - 0.3 M TOA in 2-ethyl-1-
hexanol; flow rate - 50 mL/min)

In eight hours, 35% of LA was extracted using the H_2O stripping phase. Water is a neutral compound with pH 7, resulting in a low pH difference between the feed and stripping phases compared to other striping agents. The extraction yield using H_2O is low compared to the NaOH, Na_2CO_3 and TMA, which possessed high pH values of 13.54, 9.83 and 11.50, respectively. Theoretically, high pH difference between the feed and stripping phases provide a better stripping efficiency [11].

Stripping using TMA showed an LA extraction yield of 68%. TMA can dissolve in water and has a high capability of re-extracting the organic acid from the loaded carrier [11]. Hence, it is suitable to be used as a stripping agent at the stripping phase of SLM. By using TMA as the stripping phase, the formation of salt byproduct can be prevented [28]. Furthermore, it is a high volatile base that can be easily separated from the extracted LA by distillation process at low temperature [11]. However, the extraction yield using TMA is still low compared to the NaOH stripping agent. Therefore, NaOH was selected for further study to investigate the effect of the stripping agent concentration on the LA extraction yield.

Effect of Stripping Agent Concentration
Based on Figure 4, the LA extraction was increased when the NaOH concentrations were increased from 0.25 M to 0. 5 M. Further increment on the NaOH concentration to 0.75 M and 1 M had reduced the LA extraction yield. 0.5 M of NaOH was recorded as the best concentration for stripping with the extraction yield of 86%. 0.25 M of NaOH resulted in the very least extraction yield of 75% because it only possessed a small amount of Na^+ to extract the acid. It consisted of more H_2O molecules, which acts as a barrier for the Na^+ to interact

with the acid-amine complex in the LM. The increase in NaOH concentration can cause an increase in the space availability for Na^+ at the stripping phase. Therefore, it rapidly interacted with the acid-amine complex and easily extracted the LA. This prevented the accumulation of acid complex in the LM, thus improving the efficiency of stripping. However, further increase in the NaOH concentrations to 0.75 M and 1 M had decreased the extraction yield to 79% and 77%, respectively. This is because a further increase in the stripping concentration had caused an increase in the viscosity of the NaOH solution. According to the Poiseuille's Law, the flow rate is inversely proportional to the viscosity of a solution. Hence, the additional NaOH had increased the viscosity and reduced the flow rate at the stripping phase. The low flow rate level is insufficient to prevent and reduce the boundary layer formation on the surface of SLM at the stripping phase, as shown in Figure 5.
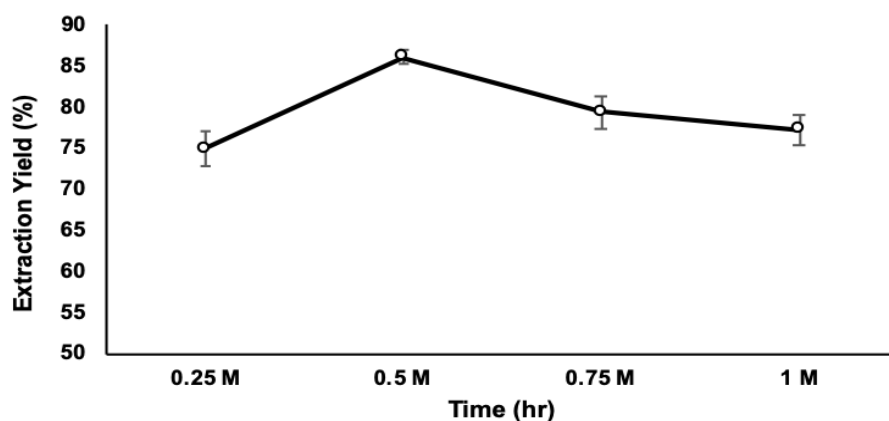

Figure 4. Extraction yield of LA using different concentrations of NaOH stripping agents. (Experimental condition: feed phase - 10 g/L LA; LM phase - 0.3 M TOA in 2-ethyl-1-hexanol; flow rate - 50 mL/min)
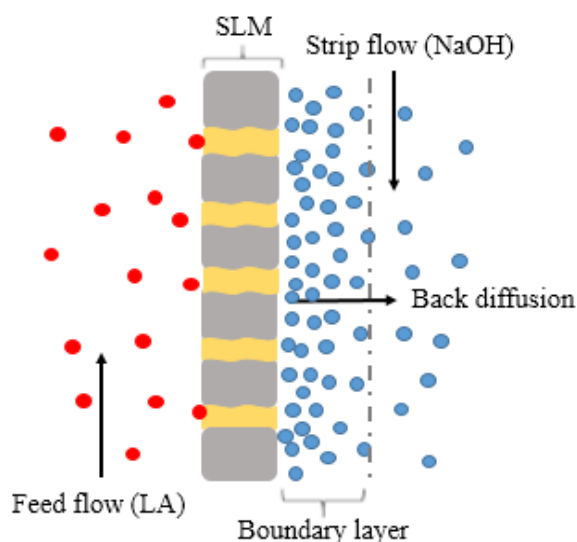

Figure 5. Formation of boundary layer on the surface of membrane support in SLM process

Thicker boundary layer can increase the osmotic pressure close to the membrane surface, in which it can diffuse the Na^+ back from the membrane support to the bulk solution. Thus, it will reduce the LA extraction yield. Furthermore, the pressure that exists at the stripping phase increases when high concentration of stripping agent was used. This will induce an imbalance pressure between the feed and stripping phases, causing the leakage of LM from the membrane support [22]. Hence, 0.5 M of NaOH was chosen as the best stripping agent concentration for LA extraction in this study.

Effect of SLM Flow Rate
In this study, the flow rates of the feed and stripping phases were kept at the same value to avoid the leakage of LM from the membrane support and breakage of the membrane support. Different flow rates at the feed and stripping phase can lead to different pressures existing in the SLM [22]. The effect of the SLM flow rate from 25 mL/min to 125 mL/min on the LA extraction yield is showed in Figure 6. The LA extraction yield increased, as the flow rate increased from 25 mL/min to 75 mL/min, reaching a maximum extraction at 75 mL/min and then decreased as the flow rate increased from 75 mL/min to 125 mL/min. The lowest LA extraction yield (74%) was obtained at 25 mL/min because it was insufficient to reduce the boundary layer formation near the membrane surface in both the feed and stripping phases. 75 mL/min is the best flow rate that resulted in the highest extraction yield of 89%. It had successfully reduced the boundary thickness at both sides of the SLM without any leakage of the LM and breakage of the matrix support. Further increase in flow rate to 100 mL/min and 125 mL/min did not improve the extraction efficiency, but had reduced the LA extraction yield to 82% and 79%, respectively. This is because too high flow rate can cause high pressure in the SLM due to the formation of turbulence flow at both the feed and stripping phases. This phenomenon can cause high possibility for LM leakage and matrix support breakage [22].
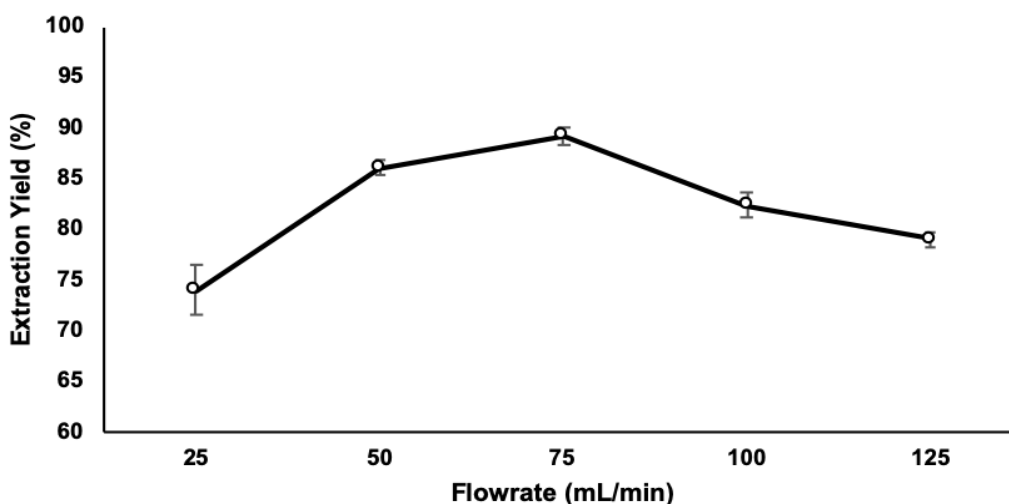

Figure 6. Extraction yield of LA after eight hour using different SLM flow rate. (Experimental condition: feed phase - 10 g/L LA; LM phase - 0.3 M TOA in 2-ethyl-1-hexanol; stripping phase - 0.5 M NaOH)

Table 1 showed the LA extraction yield using various methods. The lowest LA extraction yield obtained from this study is 13.8% when HCl was used as the stripping agent. Thereafter, NaOH was selected as the best stripping agent. By adjusting the stripping operation parameters, the LA extraction yield increased to the highest value of 89%. This value is higher than the conventional liquid-liquid extraction process that using methyl-iso-butyl ketone (MIBK) [29] and dichloromethane [30] extractant. Although, the extraction yield using SLM process is lower compare to the reactive liquid extraction process [30], SLM process had advantage in term of single operation step compare to reactive liquid extraction method. Another variation of liquid membrane, which is bulk liquid membrane (BLM) showed higher LA extraction yield than the SLM process using in this study [31]. However, BLM requires a large amount of organic liquid membrane compared to SLM and will increase the overall separation cost [32]. Thus, SLM is a more preferable technique than BLM.

Table 1 Different types of extraction methods for LA separation

Methods	Description	Yield (%)	Reference
Supported Liquid Membrane (SLM)	Extraction of LA from 10 g/L LA aqueous solution using 0.3 M TOA and 2-ethyl-1-hexanol liquid membrane incubated in hybrid PES/graphene membrane support.	89	This study
Physical Extraction	Extraction of LA from 0.1099 mol·kg^{-1} LA using Methyl-iso-butyl ketone (MIBK)	41.07	[29]
	Extraction of LA from 0.5 kmol. m^{-3} of LA solution using dichloromethane	37.8	[30]
Reactive extraction	Extraction of LA from 0.2795 mol·kg^{-1} LA using mixture of Aliquat 336 and dichloromethane	67.55	[29]
	Extraction of LA from 0.5 kmol. m^{-3} of LA solution using mixture of TOA in dichloromethane	98.7	[30]
Bulk Liquid Membrane (BLM)	Extraction of LA from 6.015 %w/w of LA solution using mixture of tributyl phosphate in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	98.63	[31]

CONCLUSIONS

In this study, the operation parameters in the SLM such as the types and concentrations of stripping agents and SLM flow rate were tested. These parameters have a great impact on the extraction efficiency of LA. The best stripping solution is NaOH solution at 0.5 M operated using flow rate of 75 mL/min. The system was able to extracted 89% of LA from 10 g/L aqueous LA feed solution using 0.3 M TOA in 2-ethyl-1-hexanol as the organic liquid membrane phase. In conclusion, SLM is a simple low cost process which able to promote highly selective separation with a small amount of organic liquid membrane. However, loss of liquid membrane and short life time of membrane support are the main problems in SLM that required further improvement. In order to enhance the extraction yield of the LA, optimization of the membrane support can be considered in the future studies. Less attention has been given on the development of the best membrane support in SLM process in the past studies due to the use of commercial membrane support.

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