Formulation of liquid membrane phase for the extraction of levulinic acid using supported liquid membrane

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ABSTRACT: Supported liquid membrane (SLM) is a simple and low-cost technique that promises a highly selective separation and recovery of organic acids from biomass products. In the present work, the liquid membrane was formulated using different types of diluents: 2-ethyl-1-hexanol, 1-octanol, kerosene, and different carriers: trioctylamine (TOA), tridodecylamine (TDA), a mixture of 50% TOA and 50% TDA, Aliquat 336 and tri-n-octyl phosphine oxide for levulinic acid (LA) extraction. The highest LA extraction from 10 g/L LA aqueous solution was 86% using a liquid membrane formulated from 0.3 M of TOA in 2-ethyl-1-hexanol. Discovering liquid membrane formulation in SLM is vital for achieving high extraction of LA.

Keywords: *Biomass; Supported liquid membrane; Levulinic acid; tri-n-octylamine.*

1. INTRODUCTION

At present, LA produced from biomass fermentation has gained significant attention due to concerns over fossil fuel depletion, increasing oil prices, and environmental issues. However, the main challenge in this biological process is the downstream recovery of LA. SLM is getting more attention for selective separation of the biomass product in the biorefinery industry [1]. The thin microfiltration membrane support pores are incubated with the liquid membrane phase in the SLM system. The liquid membrane phase is made of carrier and diluent.

The type of carrier, diluent, and carrier concentration are essential factors in the liquid membrane formulation. In the present work, different carriers were dissolved in different diluents to determine the best carrier-diluent combination for LA extraction.

2. MATERIALS AND METHODS

2.1. Preparation of membrane support

According to our previous publication, the membrane support was fabricated using the vapor-induced phase separation technique [2]. Dope solution was made from 15 wt% PES, 42.5% PEG 200 and 42.5% DMaC. 0.1% graphene was added to the dope solution relative to the total PES content in the polymer solution.

2.2. Supported liquid membrane system

The membrane support (11 cm × 5 cm) was incubated for 24 hours in different types of liquid membrane formulation, as shown in Table 1. In another experiment set, the TOA carrier concentration varied at 0.3 M, 0.4 M, 0.5 M, and 0.6 M in 2-ethyl-1-hexanol. The setup for the SLM system was similar to that by Harruddin et al. [2]. 10 g/L LA feed solution and 0.5 M NaOH stripping solution were circulated counter-currently at 50 ml/min in the SLM system for 8 hours.

2.3. Calculation of the extraction yield

The concentration of the final LA after the SLM process was assayed using Synergy Hydro C18 HPLC column (Phenomenex, 250 mm × 4.6 mm, 4 µm particle size) at 221 nm UV detection. The LA extraction yield was calculated using Equation (1)

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

where, $[LA]_{fi}$ and $[LA]_{fo}$ are LA's initial and final concentrations in the feed phase, respectively.

3. RESULTS AND DISCUSSION

3.1. LA extraction yield

The extraction yield of LA using different organic liquid formulations is presented in Table 1. The highest and lowest LA extractions were shown by 0.5 M TOA in 2-ethyl-1-hexanol (74%) and a mixture of 50% TOA and 50% TDA in kerosene (5%), respectively. Active diluents (2-ethyl-1-hexanol and 1-octanol) showed higher LA extraction in most carriers than an inactive diluent (kerosene), except for the TOPO carrier. The polar properties of the active diluent and its specific functional groups provide an excellent solvating medium for the solute complex [3].

2-ethyl-1-hexanol showed better LA extraction compared to 1-octanol for most of the carriers tested except for Aliquat 336. 2-ethyl-1-hexanol and 1-octanol have the same molecular formula but different molecular structures. 2-ethyl-1-hexanol has a branched (CH_3) structure compared with the straight-chain structure of 1-octanol. Therefore, 2-ethyl-1-hexanol has a lower boiling point and lower viscosity than 1-octanol. Hence, the viscosity of the final organic liquid phase is low. Thus, the diffusivity of the solute complex within the liquid membrane is enhanced and improved the overall transport of the carrier-solute complex in the SLM system. Nevertheless, 1-octanol is a suitable diluent for Aliquat 336 carrier, which gives 67% LA extraction compared to other diluents.

Kerosene has the lowest viscosity among the diluents tested for LA extraction in this study. Theoretically, low viscosity diluent will improve the transport mechanism in the SLM system and increase the extraction yield [4]. However, there was less efficient LA extraction than the 2-ethyl-1-hexanol and 1-octanol in most of the carriers tested. This is because the kerosene is an inactive diluent with low solvating power, resulting in low acid distribution and diminishing the extraction efficiency. Based on the above result, the TOA carrier dissolved in 2-Ethyl-1-hexanol diluent showed the best performance and was chosen for further experiments.

Table 1 Extraction yield of LA from aqueous solution using different types of carriers and diluents

Carrier	Diluent		
	2-Ethyl-1-hexanol*	**1-Octanol**	**Kerosene**
0.5 M TOA	74 %	59 %	8 %
0.5 M TDA	47 %	39%	7 %
0.5 M (50% TOA:50%	67 %	50 %	5 %
0.5 M Aliquat 336	62 %	67 %	49 %
0.5 M TOPO	22%	9 %	36 %

* The result is extracted from our previous study [5]

3.2 Effect of TOA carrier concentration

The extraction yields of LA using different concentrations of TOA in 2-ethyl-1-hexanol are represented in Figure 1. Based on the results, it was found that 0.3 M of TOA is the best concentration for LA extraction in SLM, with an extraction yield of 86%. The LA extraction decreased with increasing TOA concentration. The extraction of LA after 8 hours using TOA concentrations of 0.4 M, 0.5 M, and 0.6 M were 80%, 74%, and 62%, respectively. Increasing the concentration of TOA in diluent will increase the viscosity of the liquid membrane phase. Thus, diffusion coefficients are reduced, thus affecting the extraction efficiency. Furthermore, at high carrier concentration, the formation of acid-amine complexes is increased; this can slow down their movement through the SLM system [6]. Loss of carrier is also a possible occurrence at high carrier concentration due to reduction of the carrier interfacial within the SLM phase [6].

4. CONCLUSION

The carrier and diluent type had a significant influence on the LA extraction using the SLM system. The best diluent for TOA and TDA carriers was the 2-ethyl-1-hexanol. The best diluent for Aliquat 336 and TOPO was 1-octanol and kerosene, respectively. The highest LA extraction achieved was 86% using 0.3 M TOA with 2-ethyl-1-hexanol.

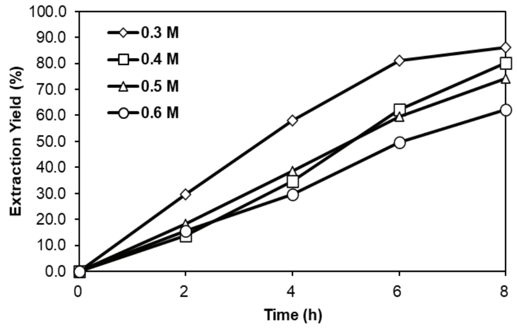

Figure 1 Extraction yield of LA from aqueous solution using different TOA concentrations in 2-Ethyl-1-hexanol

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