PALM OIL BASED EMULSION LIQUID MEMBRANE FORMULATION FOR SUCCINIC ACID EXTRACTION PERFORMANCE

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To my beloved parents, family, and friends

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ABSTRACT

Emulsion liquid membrane (ELM) process has received significant attention due to its simple operation and high selectivity to the target solute. One of the potential applications of ELM is in the separation and purification of succinic acid from fermentation process. The most important aspects for a successful ELM process are liquid membrane formulation and emulsion stability. In this study, the formulation of ELM was investigated to find a suitable carrier, diluent and stripping agent. The stability of water-in-oil (W/O) emulsion was studied by investigating the ratio of organic to internal phase, homogenizer speed, emulsifying time, and surfactant concentration. The stability of water-in-oil-in-water (W/O/W) was investigated by varying sorbitan monooleate (Span 80) and polyoxyethylenesorbitan monooleate (Tween 80) concentrations, agitation speed, and agitation time. Experiments on the effect of stripping agent concentration, treat ratio, carrier concentration, pH of external phase, modifier concentration, extraction time, and agitation speed were carried out in batch process to find the most influencing parameters for succinic acid extraction. The optimum recovery of succinic acid was studied using response surface methodology (RSM). The favourable conditions for ELM application in the succinic acid recovery was determined by varying the external feed concentration and potential of liquid membrane recycling. The results show that palm oil as a diluent, Amberlite LA2 as a carrier, and sodium carbonate (Na_2CO_3) as a stripping agent were selected in liquid membrane formulation. The most stable condition of W/O emulsion was obtained at 3:1 organic to internal phase ratio, 7000 rpm of homogenizer speed, 5 minutes of emulsification time, and 3% (w/v) of Span 80 concentration. The most stable W/O/W emulsion was obtained at 5% (w/v) Span 80, 1% (w/v) Tween 80, 300 rpm agitation speed, and 3 minutes agitation time. At the best condition of 0.01M Na_2CO_3, 1:3 treat ratio, 0.7M Amberlite LA2, 10% modifier, pH 2, and 3 minutes of extraction time, the extraction of succinic acid was up to 70%. The most significant parameters of stripping agent and carrier concentrations, and treat ratio were selected for RSM optimization study and the results show that 38.9% and 36.3% of succinic acid was recovered from aqueous solution and fermentation broth respectively. The ELM purification of succinic acid showed that at favourable condition, 84% of succinic acid was recovered with almost 100% purity and the liquid membrane is good up to the second cycle. The findings of this study show that ELM process is a promising technology to extract and recover succinic acid from bio-based production.

ABSTRAK

Proses membran cecair emulsi (ELM) telah mendapat perhatian yang sewajarnya berikutan prosesnya yang mudah dan kememilihan yang tinggi terhadap bahan larut. Salah satu potensi aplikasi ELM ialah dalam proses pemisahan dan penulenan asid suksinik daripada proses penapaian. Perkara yang paling penting bagi menjayakan proses ELM adalah rumusan membran cecair dan kestabilan emulsi. Dalam kajian ini, rumusan ELM dikaji bagi mencari agen pembawa, pelarut, dan agen pelucutan yang sesuai. Kestabilan emulsi air-dalam-minyak (W/O) telah diselidik dengan mengkaji nisbah fasa organik kepada fasa dalaman, kelajuan penghomogenan, masa pengemulsian, dan kepekatan surfaktan. Kestabilan air-dalam-minyak-dalam-air (W/O/W) telah disiasat dengan mengubah kepekatan Span 80 dan Tween 80, kelajuan pengadukan, dan masa pengadukan. Eksperimen untuk kesan kepekatan agen pelucutan, nisbah rawatan, kepekatan pembawa, pH fasa suapan, kepekatan pengubahsuai, masa pengekstrakan, dan kelajuan pengadukan telah dijalankan dalam proses berkelompok untuk mencari parameter yang paling mempengaruhi terhadap pengekstrakan asid suksinik. Perolehan optimum asid suksinik telah dikaji dengan menggunakan kaedah gerak balas permukaan (RSM). Keadaan yang sesuai bagi aplikasi ELM bagi perolehan asid suksinik telah ditentukan dengan mengubah kepekatan suapan luaran dan keupayaan kitar semula membran cecair. Keputusan menunjukkan bahawa minyak sawit sebagai bahan pencair, Amberlite LA2 sebagai pembawa, dan natrium karbonat (Na_2CO_3) sebagai agen pelucutan telah dipilih dalam rumusan membran cecair. Keadaan W/O yang paling stabil didapati pada nisbah 3:1 bagi fasa organik kepada fasa dalaman, 7000 rpm kelajuan penghomogenan, 5 minit masa pengemulsian, dan 3% (w/v) kepekatan Span 80. Emulsi W/O/W yang paling stabil telah diperoleh pada 5% Span 80, 1% (w/v) Tween 80, 300 rpm kelajuan pengadukan, dan 3 minit masa pengadukan. Pada keadaan terbaik, iaitu 0.01M Na_2CO_3, 1:3 nisbah rawatan, 0.7M Amberlite LA2, 10% kepekatan pengubahsuai, pH 2, dan 3 minit masa pengekstrakan, 70% asid suksinik telah diekstrak. Parameter yang paling mempengaruhi iaitu kepekatan agen pelucutan, pembawa, dan nisbah rawatan telah dipilih dalam kajian pengoptimuman menggunakan RSM, dan keputusan menunjukkan 38.9% dan 36.3% asid suksinik masing-masing telah diperoleh daripada larutan akueus dan air penapaian. Pada keadaan yang bersesuaian, penulenan asid suksinik menunjukkan 84% asid suksinik telah diperoleh dengan hampir 100% ketulenan dan membran cecair boleh digunakan sehingga kitaran kedua. Penemuan kajian ini menunjukkan proses ELM adalah teknologi yang berpotensi untuk mengekstrak dan memperoleh asid suksinik daripada pengeluaran berasaskan bio.

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LIST OF SYMBOLS

$[A]_f$	-	Final acid concentration in the external phase
$[A]_i$	-	Initial acid concentration in the external phase
$[A]_{int}$	-	Acid concentration in the internal phase
C_i	-	Solute concentration
D_i	-	Diffusion coefficient of solute I
J_i	-	Diffusive mass transport flux of solute I
U_T	-	Rotor speed
$V_{e,f}$	-	Volume of external phase after extraction
$V_{e,i}$	-	Volume of external phase before extraction
V_{int}	-	Volume of internal phase
X_1, X_2, X_3	-	Independent variables
d_{32}	-	Sauter mean diameter
d_i	-	Droplet diameter
k_i	-	The corresponding mass transport coefficient
$y_{i,exp}$	-	Experimental response value
$y_{i,cal}$	-	Calculated response value
$\beta_i, \beta_{ii}, \beta_{ij}$	-	Regression coefficient
D	-	Dissociation constant
M	-	Molar
pH	-	Logarithmic measure of hydrogen ion concentration
pKa	-	Acid dissociation constant at logarithmic scale
R	-	Coefficient of correlation
R^2	-	Coefficient of determination
T	-	Temperature
w/v	-	Weight per volume
x	-	Direction of diffusion

γ	-	Gamma
δ	-	Hildebrand solubility parameter
Y	-	Predicted response
n	-	Number of sample
δ	-	Thickness of the diffusional layer

LIST OF ABBREVIATIONS

AARD	-	Absolute average relative deviation
ANOVA	-	Analysis of variance
BBD	-	Box-Behnken design
BLM	-	Bulk liquid membrane
BOD	-	Biochemical oxygen damand
CAS	-	Chemical Abstracts Service
CCD	-	Central composite design
DOE	-	Department of Energy
DOE	-	Design of Experiment
ELM	-	Emulsion liquid membrane
HLB	-	Hydrophilic-lipophilic balance
HPLC	-	High performance liquid chromatography
IUPAC	-	International Union of Pure and Applied Chemistry
LLE	-	Liquid-liquid extraction
LM	-	Liquid membrane
O/W	-	Oil-in-water
OFAT	-	One-factor-at-a-time
PB	-	Placket-Burman
RSM	-	Response surface methodology
SCP	-	Single cell protein
SLM	-	Supported liquid membrane
SSF	-	Solid state fermentation
TR	-	Treat ratio
UV	-	Ultraviolet
W/O	-	Water-in-oil
W/O/W	-	Water-in-oil-in-water

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Liquid membranes (LMs) are liquids that separate two aqueous phases of the source (feed) and the receiving (product) phases and are immiscible in these phases. These separation systems are being explored widely in many fields such as organic and inorganic chemistry, wastewater treatment, chemical engineering, biomedical engineering, and biotechnology. Research and development activities within these fields involve various applications of LM technology, such as removal of organic compounds, recovery of precious metals, removal of toxic metals, gas separations, and recovery of pharmaceutical compounds and fermentation products.

Liquid membrane technology can be divided into three types which are bulk liquid membrane (BLM), emulsion liquid membrane (ELM), and supported liquid membrane (SLM). Currently, ELM is introduced as an alternative technique to the separation process. ELM process consist of four main stages which are emulsification, dispersion and extraction, settling, and demulsification. Firstly, water-in-oil (W/O) emulsion is formed by emulsifying strip solution and liquid membrane phase in the presence of surfactant. After that, the emulsion is dispersed into an external feed phase containing the solute of interest. When the extraction is complete, the emulsion phase is separated from the external phase, and demulsified to recover the membrane phase and the internal phase.

ELM fulfils the promise of providing several attractive characteristics such as relatively low energy consumption due to it is operated at ambient temperature and pressure (Othman *et al*., 2006; Chakrabarty *et al*., 2010), fast extraction and high efficiency due to large available mass transfer area (Kaminski and Kwapinski, 2000; Rajasimman and Karthic, 2010), potential for removing various toxic substances down to very low levels (Frankenfeld and Li, 1987; Skelland and Meng, 1999), high selectivity particularly with the use of carrier agents in the liquid membrane phase that react exclusively with the target solutes (Frankenfeld and Li, 1987; Bartsch and Way, 1996), and easy regeneration of the spent emulsions by a demulsification process (Li and Calo, 1992). With these advantages the ELM process becomes an alternative and a promising technology to apply in research and industry. ELM was invented by Li (1968) for hydrocarbon separations. Since then, the ELM process was widely studied for industrial separations such as in removing various types of metal ions (Zhao *et al.*, 2010; Ahmad *et al.*, 2012; Bjorkegren and Karimi, 2012; Othman *et al.*, 2016), organic compounds (Yordanov and Boyadzhiev, 2004; Mortaheb *et al.*, 2008; Ng *et al.*, 2010; Lee and Kim, 2011; Jiao *et al.*, 2013; Fang *et al.*, 2016), and inorganic compounds (Marr and Koncar, 1993; Anitha *et al.*, 2015; Zhang *et al.*, 2016).

Recent development in the ELM process of organic compound is in downstream process of bio-succinic acid separation. This is due to the increasing demand of succinic acid as a building block chemical such as poly (1,3-propylene succinate), 1,4-butanediol, n-methyl pyrrolidinone, γ-butyrolactone, and tetrahydrofuran (Ranucci *et al.*, 2000; Lee and Hyun, 2010; Lee, 2011). On the other hand, there are various types of application of succinic acid as a specialty chemical such as plant growth stimulants, food ingredients, detergents, chelators, and corrosion inhibitors (Zeikus *et al.*, 1999). Therefore, with a wide range of applications, succinic acid demand is estimated to increase considerably. The current global production of succinic acid is 30,000 to 50,000 tons annually. In addition to that, the market price of succinic acid is US$ 2,400 – 3,000 per ton (Cheng *et al*., 2012).

However, the main drawback related to ELM is the emulsion instability which is governed by emulsion breakage. Membrane breakage in ELM systems involves the rupture of the emulsion and leakage of internal phase and extracted solute to the

external phase. This causes the decrease in the volume of the stripping phase (Ho and Kamalesh, 1992). As a result, the driving force for mass transfer, which is concentration gradient is reduced and increases the external feed concentration, thereby lowering the extraction efficiency. The instability can be attributed to the emulsion formulation in terms of the choice of carrier, diluent, surfactant, stripping agent, emulsification procedure, and process condition. The carrier should be selective to the target succinic acid solute while the stripping agent and the type of surfactant must be properly chosen to minimize the co-transport of water during the extraction process.

The diluent is very important, since it is the major component of the membrane phase and is crucial for emulsion stability. Diluent should have a low solubility in water in order to create the membrane phase, it should also provide high carrier solubility, high-boiling point, non-toxic and relatively cheap (Chakraborty *et al.*, 2010; Othman *et al.*, 2011). Most studies have commonly used kerosene as an organic diluent due to its low viscosity, readily available and non-polar character. However, kerosene is not considered environmentally friendly and harmful to human. Alternatively, palm oil (cooking oil) can be chosen as a renewable organic diluent, as it is readily available and may contain natural surface-active agents, which improve the stability of an emulsion (Chow and Ho, 1996). Besides that, palm oil possesses a low melting point, low specific gravity, high flash point and non-volatile. Most importantly, palm oil has a low dielectric constant (~3) which makes them non-polar and their aliphatic property allows them to be immiscible in the external phase. In addition, palm oil was proven to work well in extraction of heavy metal, dye, acetic acid, and phenol (Narayanan and Palanivelu, 2008; Muthuraman and Teng, 2009; Badgujar and Rastogi, 2011; Bjorkegren and Karimi, 2012).

1.2 Problem Statement

The ELM process is very unique and promising in the extraction of the targeted species due to high interfacial area for mass transfer, economical, low energy

consumption, simultaneous extraction and stripping process, efficient for low solute concentration, and requirement of small quantity of solvent (Hong *et al.*, 2001; Othman *et al.*, 2005; Gupta *et al.*, 2013). Nevertheless, the various advantages of the ELM process still have been limited for industrial applications due to the emulsion globules are unstable against fluid shear.

The prepared emulsion should be sufficiently stable during the dispersion for solute extraction. Unstable emulsion resulted in emulsion breakage or swelling. Emulsion breakage cause release of the internal stripping solution and the extracted solute which reduce the extraction performance (Ho and Kamalesh, 1992; Wan and Zhang, 2002). Meanwhile, emulsion swelling resulting in destructive effect to the system because it can reduce membrane thickness, diluting the recovered solute, and decreasing the driving force for the extraction (Kulkarni *et al*., 2002; Park *et al*., 2004). On the contrary, too stable emulsion may result in difficulties during demulsification for solute recovery.

Many studies were carried out to investigate the emulsion liquid membrane stability (Gheorghe *et al*., 2008; Othman *et al*., 2009; Sulaiman *et al*., 2013; Bjorkegren and Karimi, 2015). Their study found that the primary emulsion can be stable, ranging from a few minutes to 24 days, depending on the emulsion formulation and condition of emulsification. Besides that, an appropriate condition also crucial to maintain the emulsion stability during the extraction process. Worst condition can result in 80% of emulsion breakage which is very undesirable (Othman *et al*., 2009; Hasan *et al*., 2009). Therefore, the effects of several factors on liquid membrane and emulsion stability were investigated in this study.

On the other hand, an important component of ELM, which is diluent must be properly chosen to promote an environmentally friendly process. An alternative vegetable oil diluent such as palm oil can be used to replace kerosene due to its readily available and possessing the characteristics of a good diluent. Therefore, the possibility of using palm oil as ELM component was investigated in the liquid membrane formulation for the extraction of succinic acid.

In order to obtain a stable emulsion and high performance of succinic acid extraction, the selectivity of the ELM formulation, including the carrier, stripping agent, and diluent is very important. Investigation of process parameters during the extraction also important in order to understand the process of succinic acid extraction using the ELM process. Besides that, the optimization process was carried out using response surface methodology (RSM) method to find the relation between the parameter of succinic acid recovery. In addition, for the prospects of economical process, the capability of recycling liquid membrane was also investigated.

1.3 Objectives of Study

The main focus of this study is to determine the possibility of developing the ELM purification of succinic acid using green formulation. In summary, the objectives of this study are:

i. To formulate green emulsion liquid membrane for succinic acid extraction;
ii. To study and optimize the factors affecting stability of emulsion liquid membrane;
iii. To investigate the affecting parameter of succinic acid extraction using an emulsion liquid membrane followed by recovery optimization using RSM.

1.4 Research Scopes

The aim of this study is to develop green ELM system for the extraction of succinic acid from fermentation broth. First of all, an emulsion liquid membrane was formulated to extract succinic acid. In order to formulate the ELM process, suitable components in the system are required for selectively extract succinic acid from the mixture. Therefore, the formulation was initiated by the screening of liquid membrane components, where liquid-liquid extraction (LLE) was carried out with few types of carriers (TOA, Amberlite LA-2, TDA), diluents (kerosene and palm oil) and stripping agents (NaOH, Na_2CO_3). This screening process can determine the appropriate

condition range for extraction of succinic acid from simulated solution. The composition of simulated solution is based on the actual fermentation broth.

Then, the stability of the ELM system was investigated by manipulating the organic to internal ratio (1 to 3), homogenizer speed (5000 to 12000 rpm), emulsifying time (3 to 15 minutes), and concentration of surfactant (1 to 10% w/v) during the emulsification stage. Span 80 was used as the surfactant in this study. Besides that, the stability of water-in-oil-in-water (W/O/W) was also studied by varying Span 80 concentration (1 to 7% w/v), Tween 80 concentration (0 to 4% w/v), agitation speed (200 to 500 rpm), and agitation time (1 to 7 minutes). The influence of these parameters on the emulsion droplets and globules size distribution was determined under the microscope.

Next, the application of liquid membrane for succinic acid extraction was studied. The parameters investigated were the effect of stripping agent concentration (0.005 – 0.01M), emulsion to external treat ratio (1:1 – 1:7), concentration of carrier (0.3 – 1.0M), pH of the external solution (1 – 7), modifier concentration (0 – 15%), extraction time (1 – 7 minutes), and effect of extraction speed (100 – 400 rpm). The influences of different parameters were examined using traditional one-factor-at-a-time (OFAT) approach. These parameters were investigated to determine the optimum condition of ELM process for succinic acid extraction. Meanwhile, the range of the most significant parameters was determined for the next objective.

Research on application of ELM for succinic acid covered the extraction study but very limited in product recovery aspect. Therefore, this study extend the research of ELM by considering recovery and enrichment ratio. Response surface methodology (RSM) was applied to optimize the influencing parameter on the succinic acid recovery. A set of statistical experimental design was created to optimize the process parameters including stripping agent concentration (0.005 – 0.035M), carrier concentration (0.5 – 0.9M), and treat ratio (1:1 – 1:5). A total of 15 experimental runs were required based on a three variable Box Behnken design created using Statistica 8.0 (Stat Soft). Equations of model obtained were validated through statistical tests known as the analysis of variance (ANOVA). Response surfaces were plotted to

determine individual and interactive effects of the test variables on the percentage recovery of succinic acid. The optimum condition obtained from RSM study was applied for succinic acid recovery from simulated and real broth.

In addition, to establish a favourable procedure for succinic acid recovery, the experiment was conducted to determine recovery performance and purity of simulated succinic acid from different external feed concentration (10 – 80 g/l) and real fermentation broth. On the other hand, the capability of recycling liquid membrane was carried out for the prospect of an economical process.

1.5 Significance of Study

Due to the increasing demand of succinic acid in many applications, it is essential to extract and recover succinic acid from biological production. ELM was implemented as promising alternative separation technology to the existing conventional process. It provides tremendous advantages of high transport efficiency due to the large interfacial area for mass transfer, simple operation, low energy consumption, simultaneous extraction and stripping process, efficient for low solute extraction, and low operating cost. Besides, the use of palm oil as diluent can promote a more environmental friendly process.

1.6 Research Outline

This thesis contains five chapters, which are presented in a sequential order. As an introduction, Chapter 1 presents a brief introduction of the research background, problem statement, research objectives and scopes, and significance of the study. Chapter 2 provides a review of succinic acid characteristics and applications, ELM technology, green ELM, ELM stability, ELM extraction of succinic acid, and optimization using RSM. In Chapter 3, the materials and methods including chemical

and reagents used, experimental procedure for liquid membrane component screening, emulsion liquid membrane extraction, RSM optimization, succinic acid fermentation, and analytical procedures were provided. Meanwhile, data obtained were analysed and discussed in Chapter 4. Finally, Chapter 5 suggests the conclusion and recommendation for future work.

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