EVALUATION OF EMULSION LIQUID MEMBRANE ON PHARMACEUTICAL WASTE FROM AQUACULTURE WASTEWATER

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by

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LIST OF SYMBOLS

A	Number of PLS or PCA components in the model
a	Number of the PLS or PCA component
b	PLS regression coefficient
b	Number of blocks (b=1,2,3.....,K)
C	Coarse APM block
$\boldsymbol{C}_p$	Pooled covariance matrix for the two classes

LIST OF ABBREVIATIONS

BLM	Bulk Liquid Membrane
ELM	Emulsion Liquid Membrane
HCL	Hydrochloric Acid
HLB	Hidrophile-lipophile Balance
NaOH	Sodium Hydroxide
NH_3	Ammonia
rpm	Radian per Minute
SLM	Supported Liquid Membrane
Span 80	Sorbitan Monooleate
TOA	Trioctylamine
UV-vis	Ultra Violet Visible

ABSTRAK

Teknologi membran cecair mengalami peningkatan yang ketara dalam kedua-dua penyelidikan dan aplikasi sebagai kaedah pemisahan industri pada masa ini. Membran cecair dapat digunakan untuk mengasingkan zat terlarut tertentu dari campuran dan bahkan mengeluarkan zat terlarut terhadap kecerunan kepekatannya. Terdapat tiga fasa cecair dalam sistem membran cecair: fasa umpan, fasa organik membran cecair, dan fasa penerimaan. Membran cecair yang disokong atau membran cecair emulsi (tidak disokong) boleh dibuat. Membran cecair emulsi adalah membran cecair yang menyebarkan fasa membran emulsi ke fasa umpan yang akan dirawat. Kaedah ini disiasat sebagai proses alternatif untuk pemulihan ibuprofen dari sisa farmasi. Formulasi ELM dikaji untuk mencari komponen yang paling sesuai. Selain itu, beberapa parameter yang mempengaruhi prestasi ELM juga sedang dikaji. Parameter yang terlibat adalah kelajuan pengadukan, masa pengemulsi, kepekatan agen pelucutan, nisbah dalaman ke membran, dan peratusan berat surfaktan dan pembawa. Berdasarkan hasilnya, komponen yang paling sesuai untuk ELM adalah minyak tanah sebagai pengencer, trioctylamine sebagai pembawa, dan amonia sebagai agen pelucutan. Juga didapati bahawa, keadaan optimum untuk kajian membran cecair emulsi ini diperoleh pada kelajuan pengadukan 300 rpm, masa pengemulsian 15 minit, nisbah 1: 3 dalaman untuk membran, kepekatan pelucutan 0.1 M, dan 6 wt% dan 2wt% untuk peratusan berat pembawa dan surfaktan masing-masing yang menghasilkan kecekapan 84%. masa pengemulsi, kepekatan agen pelucutan, nisbah dalaman ke membran, dan peratusan berat surfaktan dan pembawa. Berdasarkan hasilnya, komponen yang paling sesuai untuk ELM adalah minyak tanah sebagai pengencer, trioctylamine sebagai pembawa, dan amonia sebagai agen pelucutan. Juga didapati bahawa, keadaan optimum untuk kajian membran cecair emulsi ini diperoleh pada kelajuan pengadukan 300 rpm, masa pengemulsian 15 minit, nisbah 1: 3 dalaman untuk membran, kepekatan pelucutan 0.1 M, dan 6 wt% dan 2wt% untuk peratusan berat pembawa dan surfaktan masing-

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EVALUATION OF EMULSION LIQUID MEMBRANE ON PHARMACEUTICAL WASTE FROM AQUACULTURE WASTEWATER.

ABSTRACT

Liquid membrane technology is undergoing a significant increase in both research and application as an industrial separation method at the moment. A liquid membrane can be used to isolate a specific solute from a mixture and even extract a solute against its concentration gradient. There are three liquid phases in a liquid membrane system: feed phase, liquid membrane organic phase, and receiving phase. Either a supported liquid membrane or an emulsion (unsupported) liquid membrane can be made. Emulsion liquid membranes are liquid membranes that disseminate the emulsion's membrane phase into the feed phase to be treated. This method was investigated as an alternative process for the recovery of ibuprofen from pharmaceutical waste. The formulations of ELM were studied in order to find the most suitable component. Besides that, some parameter affecting the performance of ELM was also being studied. The parameter involved are agitation speed, emulsifying time, concentration of stripping agent, internal to membrane ratio, and the weight percentage of surfactant and carrier. Based on the result, the most suitable component for ELM was found to be kerosene as diluent, trioctylamine as carrier, and ammonia as stripping agent. It is also being found that, the optimal condition for this emulsion liquid membrane study was obtained at 300 rpm of agitation speed, 15 minutes of emulsification time, a ratio of 1:3 internal to membrane, 0.1 M concentration of stripping agent, and 6 wt% and 2wt% for the weight percentage of carrier and surfactant respectively which yield 84% of efficiency.

CHAPTER 1

INTRODUCTION

Chapter 1 introduces an overview of this research including the significance of emulsion liquid membrane (ELM) for extraction of ibuprofen from aquaculture wastewater. In general, this chapter summarizes the research background of pharmaceutical waste from aquaculture wastewater and emulsion liquid membrane technology for extraction of ibuprofen, the problem statement and also the objectives of this final year project.

1.1 Background

Aquaculture industry has become one of the most important industry, providing supplies such as food, income, nutrition and livelihood for the people in the entire world. The increasing demand for these sources has directly contribute on the rapid growing of this industry every year. Although this trend is beneficial for the economic development, it is somehow cause several adverse impacts towards the environment because of the waste generation. One of the example of waste generated by the industry is pharmaceutical waste. Based on J.Liu and Y.Cui research (J.Liu & Y.Cui, 1997), almost 500 type of pharmaceutical were used for prevention and treating purpose on approximate 170 type of aquaculture diseases. Therefore, it was reported that approximately more than 30 mg/L of pharmaceutical waste were generated and discharged every day (Fawell J. & Ong C.N., 2012).

Ibuprofen, one of the pharmaceutical used in aquaculture industry is the third most popular, highly prescribed and most saleable over the counter medicine in the world (Marchlewicz et al.,2015). In Southeast Asian countries, this compound has been highly and commonly detected on water surface. The concentration of Ibuprofen alongside other pharmaceutical waste detected in several Southeast Asian countries was shown in Table 1.1.

Table 1.1 Pharmaceutical waste detected in several Southeast Asian countries (Nor Haslina Hashim et al.,2016)

Country	Location	Compound	Conc. (ng/L)
Taiwan	Taiwanese River	Ketoprofen	110–620
		Ibuprofen	<12–30
		Diclofenac	24–62
Vietnam	Hanoi	Ketoprofen	<40–330
		Ibuprofen	100–1100
		Diclofenac	<140–310
		Naproxen	80–380
Singapore	Marina Bay	Naproxen	>12-24
		Ketoprofen	>3-23
		Diclofenac	>4-26
		Ibuprofen	>37-60
	Rochor Canal	Naproxen	20
		Ketoprofen	25
		Diclofenac	Below Detection
		Ibuprofen	139
Malaysia	Langat and Muar Rivers	Caffeine	138–760
		Diclofenac	Non Detect–54

People start to concern about the emerging of Ibuprofen waste towards the environment since it is an environmental risky substance (Bouissou-Schurtz et al., 2014). Its toxicity can affect other living organisms. For example, Flippin et al. (2007) has study the effect of Ibuprofen on a fish which resulting in reduced spawning while increasing the number of egg simultaneously. In other research, Ibuprofen was observed to cause membrane damage in digestive gland and increase the lipid eroxidation level in mussels of Mytilus galloprovincialis (Gonzales-Rey and Bebianno, 2012).

In order to overcome this issue, there are many wastewater treatment technologies that have been introduced to remove or extract the pharmaceutical waste from aquaculture wastewater. One of the most promising technology is emulsion liquid membrane (ELM), a process involving a selective liquid membrane phase in which simultaneous extraction or stripping occurs. This technology has been used widely in various potential area such as wastewater treatment, pharmaceutical (Araki et al, 1990), pulp and paper (Ooi et al, 2015), textile industries, electroplating, mining, semiconductor, dairy, food and beverage processing, biotechnology industries, tanning and leather industries. Compared to other conventional technique, ELM has a simpler operation, low energy consumption and also can achieves higher efficiency. The main function of EML are for recovery and removal of hydrocarbons and metal ions from wastewater (Li & N.N., 1998).

Emulsion liquid membrane is also known as double emulsion system. This system consists of two immiscible phase emulsion which will be dispersed in the third phase called as external phase. The liquid membrane phase refers to the phase in between the encapsulated phase in the emulsion and the external phase. Usually the encapsulated phase and the external phase are miscible. However, with the membrane phase, they are not miscible (Chakraborty et al., 2003). The solute extraction between the two miscible phase is achieved by mass transfer through the membrane phase.

In general, an emulsion liquid membrane process will have four main steps (Norasikin Othman et al, 2014). The first step is emulsification. In this step, preparation of emulsion is done by emulsifying both internal and membrane phase. The second step is dispersion and extraction. By using the prepared emulsion in previous step, it will be dispersed into external feed phase. The external feed phase contain solute that will be extracted. Next step, emulsion and feed solution will be separated by settling process. After that, membrane phase will be recovered in the last step which known as demulsification process.

1.2 Problem Statement

In order to reduce the amount of pharmaceutical waste in aquaculture wastewater which been discharged to environment especially water body, an effective wastewater treatment technology is required. Most of the conventional technique with the use of permeable and semipermeable membranes such as microfilters, ultrafilters, osmosis, reverse osmosis and dialysis has problems like high capital costs, low mass transfer rate, low selectivity, and large equipment size. Emulsion liquid membrane is proposed for this project due to its simpler operation, low energy consumption, large interfacial area and high efficiency as compared to other techniques. ELM technique will be used in this project for extraction of Ibuprofen, one of the common content in pharmaceutical waste from aquaculture wastewater. Since the major drawback of this technology is related to its stability, the stability of ELM will be test by observing its emulsion breakage time and droplet size distribution. Its optimum operating condition will be determined as well by varying the process parameters. The data for each parameter will then be compared to determine the suitable and optimum value to obtain the most stable EML for ibuprofen extraction.

1.3 Objectives

I. To formulate emulsion liquid membrane for ibuprofen extraction.

II. To investigate the affecting parameters of ibuprofen extraction through emulsion liquid membrane

III. To evaluate the effectiveness of emulsion liquid membrane formulation on ibuprofen extraction.

CHAPTER 2

LITERATURE REVIEW

Chapter 2 presents the previous researches and discoveries available from credible scientific records and references which are related to this final year project topic. This chapter covers the overview of liquid membrane, types of liquid membrane, transport mechanism, formulation of emulsion, parameter in emulsion liquid membrane and the demulsification process.

2.1 Liquid Membrane

Liquid membrane (LM) processes refer to the process that involve a selective liquid membrane phase (P.K.Parhi, 2013). In this process, the extraction process and stripping process will occur simultaneously. Basically, the separation of molecule is achieved by the mean of permeation and transfer process where the solute permeate via the liquid phase and transferred from feed phase to the receiving phase. Noble RD et al (Noble RD et al, 1987) had studied the general characteristic of liquid membrane process. They stated that liquid membrane process is a rate of process in which the separation does not occurs when the equilibrium between phase achieved but it is due to chemical potential gradient. In addition, the LM process can be defined based on its mechanism, not fabrication's materials.

The LM process can be classified into three different types based on its module design configurations (V. Kislik,2009). There are bulk liquid membrane (BLM), immobilized or supported liquid membrane (SLM or ILM), and emulsion liquid membrane (ELM).

2.1.1 Bulk Liquid Membrane

The bulk liquid membrane (BLM) is one of the most basic liquid membranes, with higher membrane stability but lower solute fluxes. In bulk liquid membrane (BLM), two main components which are a bulk aqueous feed and receiving phases will be separated by a bulk organic, water-immiscible liquid phase. Both feed and reception phases may be separated from the liquid membrane in two ways, with or without the existence of microporous supports (layered BLM). However, Bartsch RA et.al (Bartsch RA et.al,1996), in their study suggested that only layered BLM has a potential for a practical application. This explain why most of the reviewers for liquid membrane subject only considering layered BLM for their study. An illustration of BLM process is shown in Figure 2-1 below.

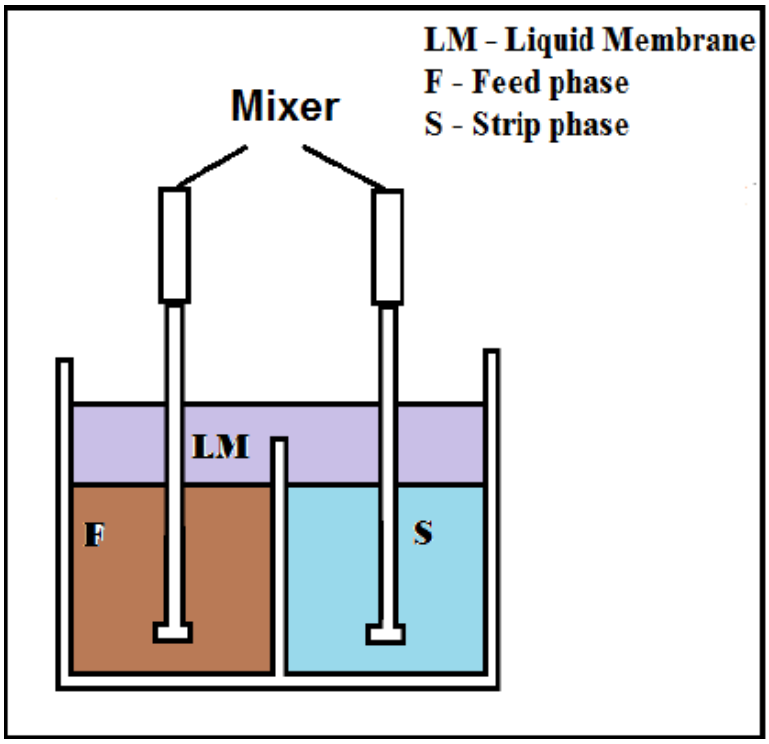


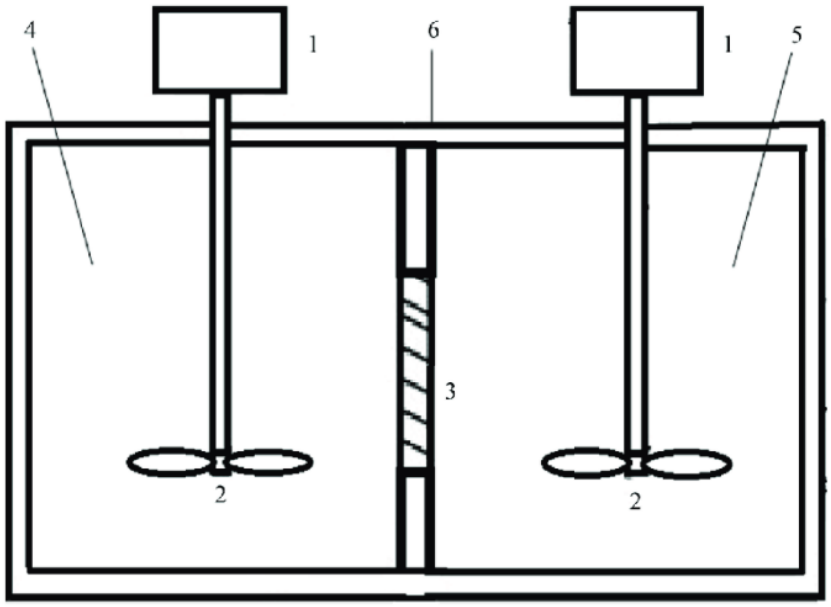
Figure 2-1 Schematic diagram for BLM (Mohammed, Ahmed & Hussein, Maad, 2018).

The common encountered problem in LM technology is the stability of membrane itself. But, based on Siu Hua Chang (Chang, Siu,2015), unlike other liquid membrane technologies, BLM does not appear to have a problem with membrane stability as long as the source, membrane, and receiving phases are all agitated properly. The reason is due to the bulky-membrane structure in BLM that help to eliminates the likelihood of membrane rupture or quick carrier exhaustion, resulting in high membrane stability. Furthermore, as compared to other types of liquid membranes, BLM has the benefit of being simple and inexpensive to be produced (S.H. Chang et al.,2011).

2.1.2 Supported Liquid Membrane

One of the main component in liquid membrane is the thin layer of organic phase. Together with a dissolved reagent, this thin layer usually exists between two different compositions of aqueous phases. Immobilization of the thin layer could turn it into a suitable inert microporous support. As the name implies, it will act as a structural support as it interposed in between two different aqueous solutions (B. Swain et.al,2004, D.N. Mondal et.al,2011).

Supported liquid membranes can be divided into two categories based on their size, shape, surface area, and applications: flat sheet supported liquid membrane (FSSLM) and hollow fibre supported liquid membrane (HFSLM). The simplest form of liquid membrane is the flat sheet supported liquid membrane, which uses a microporous solid support for the liquid membrane. The schematic diagram for flat sheet supported liquid membrane can be seen in Figure 2-2 below.



Flat-sheet supported liquid membrane (FSSLM) system used in the current study. 1: Motors, 2: agitators, 3: flat-sheet membrane chamber, 4: feed phase, 5: strip phase, 6: Plexiglass body.

Figure 2-2 Schematic diagram of FSSLM (Kamran Haghighi et.al, 2019)

From the figure, the extractant-impregnated solid support is clamped between two half cells using gaskets, generating two compartments (for feed and strip solution) which are stirred by mechanical stirred.

For hollow fiber supported liquid membrane (HFSLM), a hollow fibre module is used to extract metal ions. Based on the study conducted by A. Gabelmana and S. T. Hwang (A. Gabelmana & S. T. Hwang,1999), the module's exterior cell is made of a single nonporous substance that prevents the solution inside from being moved. Many thin threads are neatly packed in orderly rows inside the shell as shown in Figure 2-3.

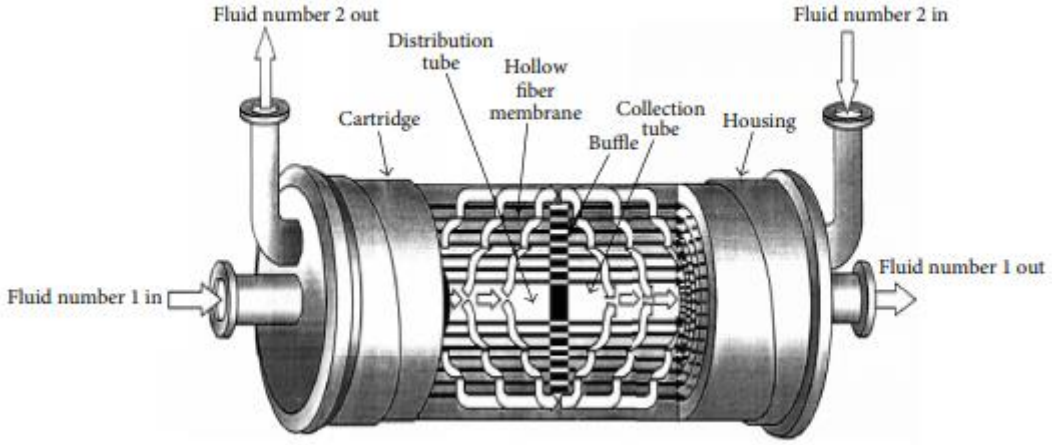


Figure 2-3 Diagram of HFSLM (A. Gabelmana & S. T. Hwang,1999)

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Flat sheet SLM is useful for research, but the surface area to volume ratio is too low for industrial applications. Spiral-wound and hollow-fiber SLMs have much higher surface areas of the LM modules (103 and 104 m2/m3, respectively). The main problem of SLM technology is the stability: the chemical stability of the carrier, the mechanical stability of porous support, etc. In term of research purpose, flat sheet SLM seems very useful due to its simplicity beside the fact that it is not applicable for industry application because of very low surface area to volume ratio.

2.1.3 Emulsion Liquid Membrane

Also known as a double emulsion process, ELM was first invented in 1968 by Li.N.N (Li, 1998) for hydrocarbon separation process. The ELM consists of three major phase which are membrane, internal and external phase. Furthermore, it has been identified that this ELM process is made up of four main components basically are carrier, diluent, stripping agent and surfactant. Figure 2.4 below illustrated the steps involved in ELM process.

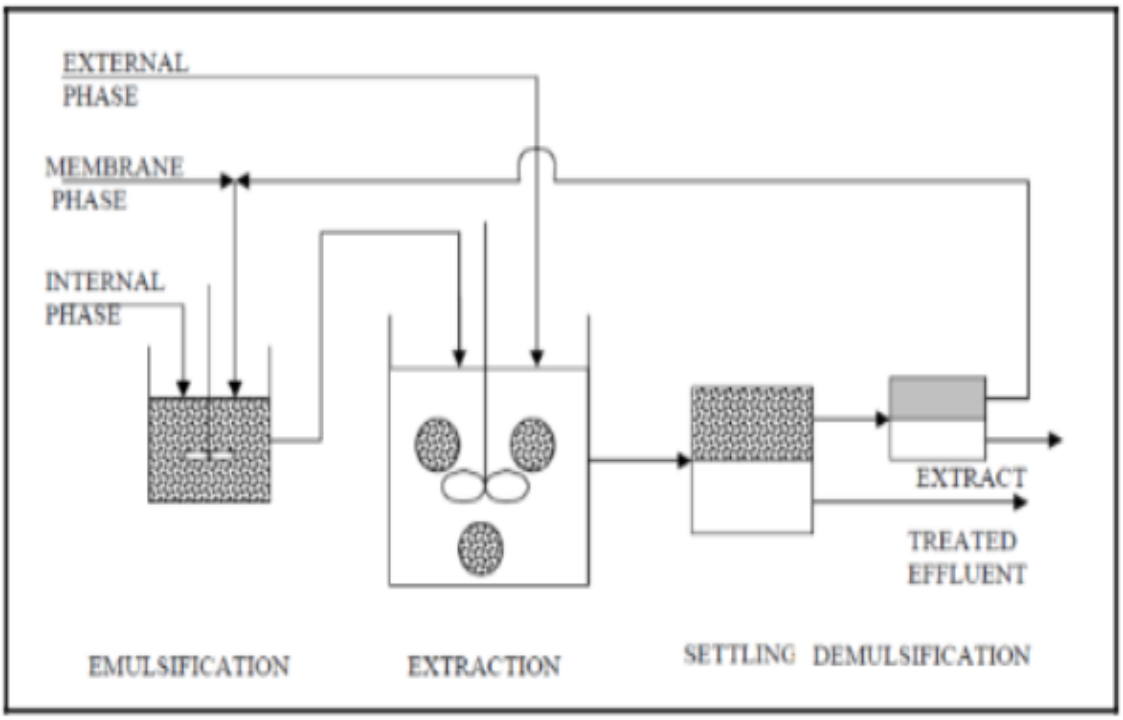

Figure 2-4 Emulsion liquid membrane process (F.Wang et al, 2001)

Based on Figure 2.4, the internal and membrane phase will first be emulsified before been dispersed into external feed phase. The feed phase contains the solute to be extracted. Next, the solution of emulsion and feed solution will be separated in settling step before entering demulsification step where the membrane phase will be recover back to be reused in emulsification step.

The system of EML has two different types. It can be either water-oil-water emulsion or oil-water-oil emulsion. For water-oil-water type, the emulsion will be dispersed in external aqueous phase while for oil-water-oil, it will be dispersed in external organic phase. Between both type, the most commonly used is water-oil-water emulsion. The preparation step of water-oil-water emulsion is shown in Figure 2-5 below.

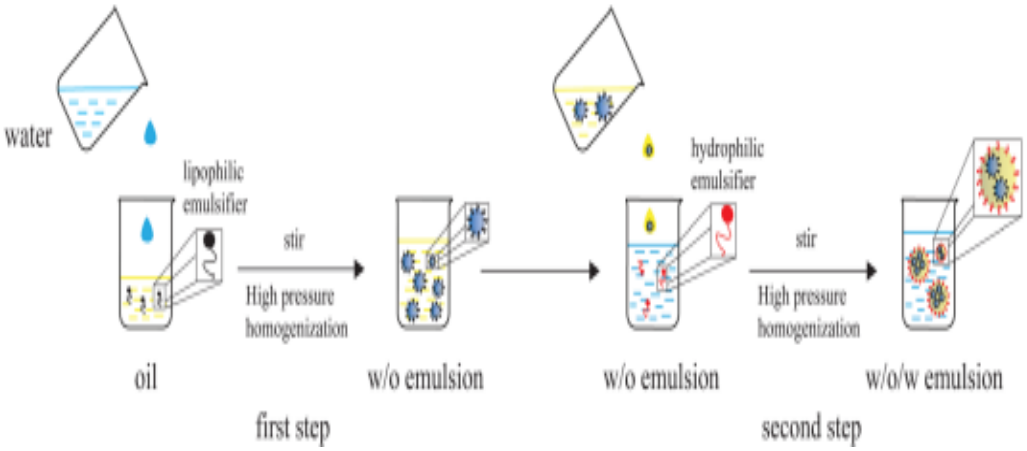

Figure 2-5 Preparation of water-oil-water emulsion (Jun Wang et al, 2017)

Bartsch RA et al, (Bartsch RA et al, 1996) had pointed several benefits of using ELM in their study. That's include the possibility of high fluxes, a very selective separation process, and less amount of carrier required due to small inventory in the membrane. Other than that, compared to other conventional process, ELM possessed some advantage such as simple operation but high extraction efficiency, high interfacial area for better mass transfer rate, simultaneous extraction and stripping process, and relatively low cost and energy requirement. (S. Chaouchi et al, 2015).

2.2 Transport Mechanism

Solute diffusion through the membrane is the main rate-determining stage in solute permeation through a liquid membrane. However, the introduction of additives, specialised carriers, chemical reagents, external electric or photoelectric impulses can improve the separation. Among various types of separation mechanism, they are all usually classified into two main types, simple and facilitated.

2.2.1 Simple Transport

In simple transport mechanism, any immiscible liquid can serve as a membrane between two liquid or gas phases containing a solute at varying concentrations, because the liquid surfactant membrane is a thin film of liquid (oil or aqueous) consisting of surfactants and their solvents between a feed and a receiving phase (J.D Way et.al,1982). The solute is mainly soluble in LM, and because of that, it is able to passes through by simple transport. When concentration equilibrium is reached, permeation stops. The solute does not react chemically with LM and is meant to be in the same form in all three phases (feed, LM, and receiving). This form of permeation has little technical significance and is solely useful for emulsion stability research. Figure 2-6 below shows the mechanism of simple transport.

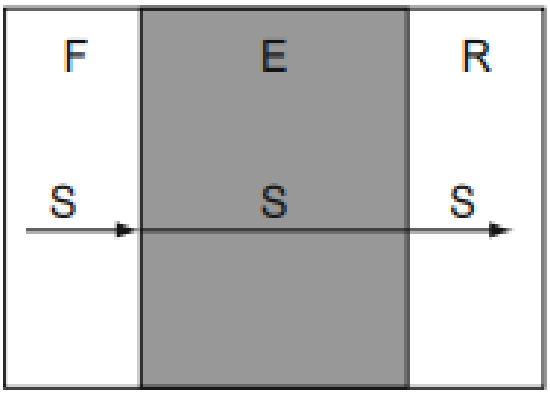

Figure 2-6 Mechanism of simple transport

2.2.2 Facilitated Transport

One of the most important applications of supramolecular chemistry is carrier-assisted transport (facilitated transport) via liquid membranes. Partitioning, complexation, and diffusion

can all be used to characterize the transport. The mechanism of facilitated transport is shown in Figure 2-7 below.

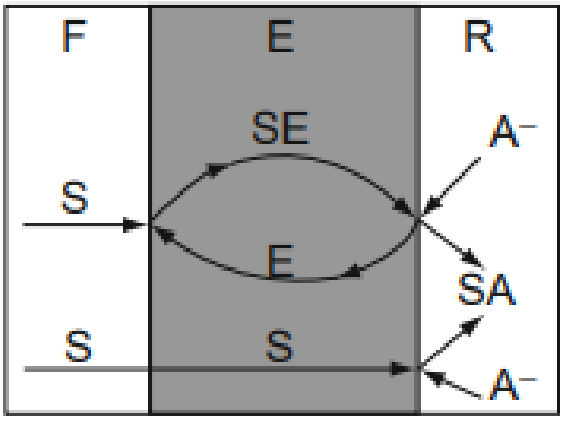

Figure 2-7 Mechanism for facilitated transport

By optimizing the flux through the membrane phase and the capacity for diffusing species in the receiving phase, the effectiveness of separation across a liquid membrane is improved in this type of transport. In order to achieve this improvement, two mechanisms have been introduced.

For the first mechanism, the mass transfer rate through the membrane phase is boosted by including a stripping agent in the internal phase that interacts with the solute and produces a membrane insoluble product (C.J. Lee & C.C. Chan,1990). The second mechanism, in the membrane phase, a reactive component or carrier is introduced to convey diffusing species across the membrane to the internal phase, thereby facilitating their transfer via the membrane.

2.3 Formulation of Emulsion

The formulation of the liquid membrane process, which includes the selection of the carrier, strip agent, surfactant, and diluents, is critical. The success of the procedure is frequently determined by the components used and their composition.

2.3.1 Carrier

Based on IUPAC (IUPAC,1993), carrier or also known as an extractant, is a reagent that forms a complex or other adducts in the solvent with the substance that partitions over the extraction system's phase boundary. There are three types of carriers namely extractant involving compound formation, ion association and solvation.

Utilization of carrier in liquid membrane offers some benefits and advantages. Larger fluxes than in polymer membranes are feasible by combining the advantages of high diffusion coefficients in liquids with the carrier's additional carrying capacity. Other than that, it is possible to utilise an expensive extractant. Because of the limited solvent inventory associated with the membrane and the carrier's nonvolatile nature, only minimal amounts of carrier are used. Next, coupled transport allows one to pump ions against their concentration gradient. Thus, the ions can be concentrated. Lastly, the carrier's selective character allows for significantly better separations than would be possible based purely on relative solubility and diffusion. Table 2-1 below shows the list of extractant used in ELM process.

Table 2-1 Extractant used in ELM process (N.Othman et.al,2003)

Type of extractant	Metal ions	Feed solution	Surfactant	Stripping solution	Diluent
Group1					
Cyanex 272	Cu	$CuSO_4$	ECA5025 DNP-8	6N H_2SO_4	Tetradecane
LIX 63/LIX 64N		Cu salt	Span 80	HCl	Kerosene
LIX 860		$CuSO_4$	ECA 5025 DNP-8	0.25-2.5M H_2SO_4	Kerosene
Acorga P17/Acorga P50		Cu salt	Span 80	H_2SO_4	Tetradecane
KELEX 100/SME 529					
Cyanex 272	Ni	$NiNO_3$	ECA5025 DNP-8	6N H_2SO_4	Tetradecane
D2EHPA		$NiCl_2$		HNO_3	Kerosene
PC-88A		$NiSO_4$	Span 80	dil H_2SO_4	*n*-Heptane

Group 2					
Adogen 364	Cd	Pure Cd	Span 80	NaOH	Dimethyl benzene
Primene JMT	Ag	Ag salt	Not mentioned	H_2SO_4	Tetradecane
Aliquat 336	Mo	Na-Mo salt	Monesan	NaOH	Kerosene, heptane
Aliquat 336	Cr	Cr(IV)	Span 80	NaOH	Kerosene
Group 3					
Calix[4]arene					
Carboxyl/*p*-tert-octylcalix[*n*]arene (1,4,6)	Rare earth	Lanthanide chloride	$2C_{18}\Delta^9GE$	H_2SO_4	Toluene
Cyanex 272/DEHPA	Zn	$ZnSO_4$	ECA5025 DNP-8	6N H_2SO_4	Tetradecane
D2EHPA		$ZnCl_2$	Span 80	HNO_3	Kerosene
DEHMTPA		$ZnSO_4$	ECA5025 Span 80	Thiourea	*n*-Dodecane
D2EHPA	Ag	$AgNO_3$	Span 80	HNO_3	Toluene
D2EHPA	Pb	$Pb(NO_3)_2$	ECA5025	HCl	Toluene
PC-88A	Co	$CoSO_4$	PX 100	H_2SO_4	Paraffin oil
MSP-8	Pd	Simulated Waste	ECA4360 Span 80	H_2SO_4	*n*-Heptane
TOA	Hg	$HgCl_2$	Span 80	NaOH	Toluene

2.3.2 Stripping Agent

A stripping agent is a chemical specie that is added to the liquid membrane's product phase to react with the target specie or the complex target specie carrier at the membrane/product interface, resulting in a membrane insoluble product or simply releasing the target specie in the product phase. Depending on the solute to be extracted, an acid or base can be utilised as an internal phase or as a stripping phase in the ELM process. The rate of solute extraction increases as the amount of internal reagent in the emulsion increases.

2.3.3 Surfactant

Surfactant is a combination of the words "surface acting agent". Surfactants are amphipathic organic molecules, which means they include both hydrophobic and hydrophilic groups (their "tails" and "heads"). The surfactant's amphipathic structure causes not only surfactant concentration at the surface and a reduction in the solvent's surface tension, but also molecule orientation at the surface, with the hydrophilic group in the aqueous phase and the hydrophobic group oriented away from it, as shown in Figure 2-8.

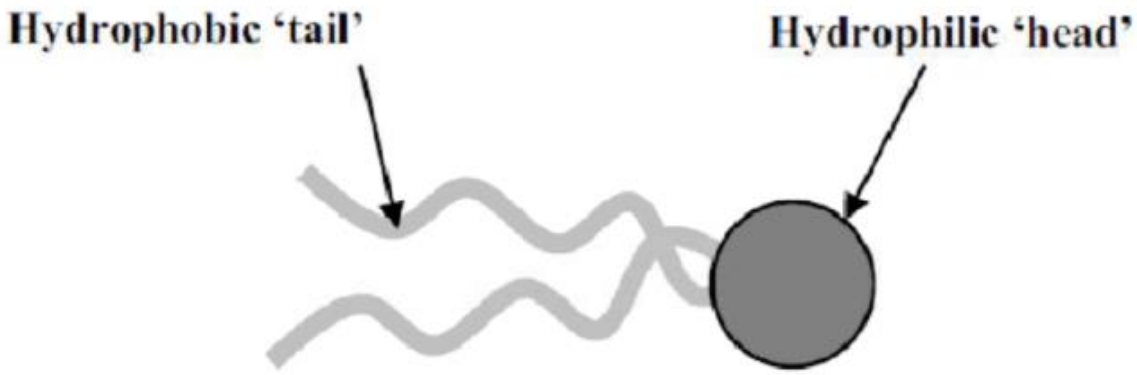

Figure 2-8 Structure of surfactant (Akil Ahmad et.al,2014)

Cationic groups (organic amines, especially those with three hydrocarbon chains connected to the nitrogen atom), anionic groups (fatty acids or sulphates with hydrocarbon chains), and nonionic groups are all examples of hydrophilic groups. Meanwhile, lipophilic groups might be long, straight, or branched chain hydrocarbons, cyclic hydrocarbons, aromatic hydrocarbons, or a mixture of these (Lin,2001).

The balance between the hydrophilic and lipophilic portions of surfactants' molecules is broadly used to classify them. In an arbitrary range of 1-40, the hydrophilic-lipophilic balance (HLB) number shows the polarity of the molecules, with the most often used emulsifiers having a value between 1 and 20. In the range of 1-10, HLB is soluble in oil rather than water. Those with an HLB of 10-20 are more water soluble than oil. The HLB number of a mixture made up of x percent HLB A surfactants and y percent HLB B surfactants is calculated using the formula below.

$$\mathrm{HLB}\,(A+B) = (Ax + By)\,/\,(x+y) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2\text{-}1)$$

2.3.4 Diluent

When choosing the right diluents, several factors must be taken into account. Specific gravity, viscosity, flash point, and polar nature are examples of these qualities. N-hexane, kerosene, cyclohexane, benzene, toluene, carbon tetrachloride, and chloroform are the most often used diluents. In comparison to aromatic diluents, aliphatic diluents are often chosen. Table 2-2 below shows the physical properties of various diluent.

Table 2-2 Physical properties of various diluent
(Sekine and Hesegawa, 1977, Rydberg et al., 1992).

Diluents	Chemical formula	Molecular weight (gmol)	Density (g/mL)	Viscosity (cP)	Dielectric constant
n-hexane	C_6H_{14}	86.17	0.65937	0.23	1.88
Kerosene	-	-	0.80	0.02	2.0 – 2.2
Cyclohexane	C_6H_{12}	84.16	0.77855	0.98	2.02
Benzene	C_6H_6	78.11	0.87903	0.65	2.28
Toluene	C_7H_8	92.13	0.86694	0.59	2.24
Carbon tetrachloride	CCl_4	153.82	0.965	0.97	2.24
Chloroform	$CHCl_3$	119.38	1.563	0.57	4.81

Aromatic products have greater specific gravities than aliphatic products, which can interfere with dispersion and coalescence in a solvent containing them. When the solvent is heavily loaded with metals, the difference in specific gravity between the loaded solvent and the aqueous phase can be insignificant, making separation difficult. Ritcey and Ashbrook (Ritcey and Ashbrook, 1984) stated that, as the concentration of extractant rises, the density of the solvent rises as well, making the density of the diluent an issue to consider.

Metal loading, on the other hand, has an impact on the solvent's viscosity. With increasing metal loading, the viscosity rises. To reduce viscosity effects and enhance the pace of phase separation, it is important to run the solvent extraction system at a higher temperature. The solubility in aqueous solution and the flash point are essential factors to consider when determining the applicability of diluents. Because it flashes easily at low temperatures, the diluent with a very low flash point poses an environmental concern. As a result, it's best to utilize diluents with a significantly greater flash point.

The polarity of the diluents is the most essential element. The extraction of metals decreases as the polarity of the diluent increases. Metal ions can have a decreased extraction coefficient when the diluent interacts with the extractant. As a result, diluents with a lower dielectric constant were recommended for maximum extraction.

2.4 Parameter in emulsion liquid membrane (ELM)

Stability of liquid membrane is the main concern for the ELM technique. ELM is very dependent on the process parameters. The suitable value for each parameter need to be determined to prevent the breakage of emulsion. The parameters involved in ELM are hydrophilic-lipophilic value, concentration of mixed surfactant, homogenizer speed, emulsification time and organic-to-internal ratio.

Hydrophilic-lipophilic balance value often been used as evaluation of ELM stability and portioning features (E.Magnusson et al, 2016). Basically, more than one surfactant can be used in emulsion to create an interaction among themselves (D.J. McClements et al., 2018). This interaction will change the characteristic of surfactant, stability and the functionality of the emulsion simultaneously. According to V.B. Fainerman et al. (V.B. Fainerman et al., 2016), they suggest that the electrostatic repulsion strength could be increase by combining two surfactants (Span 80 and Tween 80). A strong electrostatic repulsion will stabilize the droplets against aggregation.

While the combination of surfactants may enhance the emulsion stability, its concentration somehow has a similar effect on stability. There is high possibility for the rupture of membrane occur at low concentrations of blended surfactants. A thinner membrane and larger droplet size that formed at low concentration leads to weaker coalescence resistance

between emulsion droplets (Z.Y.Ooi et al, 2016). As the concentration increased, droplet size will be reduced together with the surface tension. As the results, enhancement of adsorption layer strength occur, producing more stable emulsion droplets.

Homogenizer is used to generates intense disruptive forces which will affect the emulsion stability. The disruptive force generated will be depends on the homogenizer speed (Hakansson et al., 2013). Oil and water phase will automatically break into small droplets due to low disruptive force produced from low energy (low homogenizer speed). The activity of stirred to dissipate oil droplets will be inhibited resulting to a larger emulsion droplet.

Emulsification time is very crucial in determining the stability of liquid membrane. If the time provided for emulsification process is insufficient, the interfacial activity of the surfactants for adsorption at water-oil interphase might be hindered. When this happen, the configuration of surfactant molecule become unorganized in the interfacial area. Unorganized surfactants cannot provide a strong and rigid membrane layer. Otherwise, it will provide high interfacial tension. This will cause the membrane rupture to occur easily due to droplets coalescence and large droplets.

In order to achieve a stable water-oil emulsion, the organic-to-internal ratio must exceed 1:1 (Luo et al., 2014). At equal ratio, a thinner membrane layer will be produced. This thin layer is weak against droplet coalescence. Yildirim et al. (Yildirim et al., 2017) in their study suggest that a greater breakage percentage of membrane will occur at high internal phase volume. As the result, instead of water oil will be dispersed, instigating the hydrophilic part of the emulsion to dissolve in the internal phase easily.

2.5 Demulsification

One of the most important procedures in the application of emulsion liquid membranes is demulsification. Demulsification is primarily used in the oil industry to remove water and salts from crude oil, as well as in waste treatment operations to recover the membrane phase, which includes organic solvent, surfactant, extractant, and valuable solute ions. Centrifugation, thermal breaking, and the electrostatic technique are the example of typically used method in demulsification.

By comparing those method, thermal breaking and centrifugation hardly become the first choice for demulsification due to their drawbacks. Thermal breaking requires a lot of energy to breakdown emulsion droplets, and it cannot be used on all emulsions because some components are thermally unstable. Centrifugation necessitates a lot of mechanical effort and a lot of money. Conventional breaking procedures are unable to separate systems with very tiny droplets and little density difference between the dispersed and continuous phases (Strathman, 2001).

Electrical emulsion breaking in other hand, works at room temperature, has no moving parts, requires little energy, and allows the separation of microscopic droplets from the continuous phase (Luo et.al.,2001). In fact, one of the most effective and simple demulsification procedures is the electrostatic approach in a high voltage field. Electrostatic forces induce dispersed water droplets to consolidate and develop into larger drops, which then fall easily due to gravity or electric forces. This explained why electrostatic demulsification technique is favorable and has been used widely especially in wastewater treatment (G.Lu et al.,1997).

CHAPTER 3

METHODOLOGY

Chapter 3 disclose the overall experimental aspects of the final year project including the overall research flow diagram along with the emulsion liquid membrane (ELM).

3.1 Research Flow

In general, this final year project focused on the evaluation of emulsion liquid membrane on pharmaceutical waste from aquaculture wastewater. The overall activity of the research is shown in Figure 3.1 below.

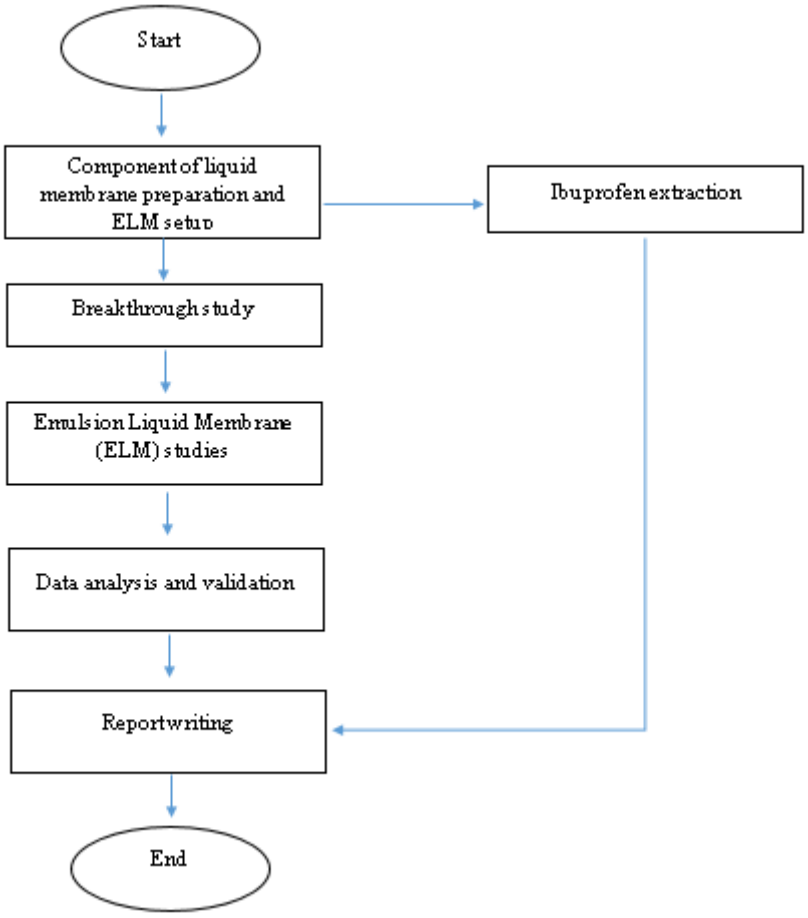

Figure 3.1 Flow diagram of research project on evaluation of ELM

3.2 Liquid Membrane Component Selection

Carrier, stripping agent, diluents, and surfactant are the four main components of liquid membranes. Each component was chosen from the literature to screen out possible components in the emulsion liquid membrane technique for extracting ibuprofen.

3.3 Emulsion Liquid Membrane Preparation

The membrane phase was prepared by dissolving adequate amounts (2,4,6,8 wt%) of surfactant and carrier in diluent. This was done to ensure the homogeneity of the solution. Next, the membrane phase solution was mixed under magnetic stirrer at 350 rpm for 5 minutes. After that, internal phase (0.1, 0.15, 0.2 M) will be added to the organic membrane phase. Then, ultrasonic probe was inserted into the mixture. The probe tip was symmetrically placed at the aqueous-organic interface and ultrasonic irradiation started. Emulsification was carried out based on parameters.

3.4 Extraction Process

3.4.1 Preparation of Ibuprofen Solution

Ibuprofen solution was prepared by dissolving 10 ppm of ibuprofen in deionized water. Next step, hydrochloric acid was added to adjust the pH of solution.

3.4.2 Ibuprofen Extraction