# EMULSION LIQUID MEMBRANE: STABILITY AND EFFICIENCY FOR CADMIUM REMOVAL USING VEGETABLE OILS

**by**

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## LIST OF ABBREVIATIONS

| | |
|---|---|
| AAS | Atomic Absorption Spectrophotometer |
| Aliquat 336 | Trioctylmethylammonium chloride |
| BLM | Bulk liquid membrane |
| ELM | Emulsion liquid membrane |
| D2EHPA | Di-(2-ethylhexyl)phosphoric acid |
| HLB | Hydrophile-lipophile balance |
| O/W | Oil-in-water |
| ppm | Parts per million |
| SLM | Supported liquid membrane |
| TOA | Trioctylamine |
| TIOA | Tri-iso-octylamine |
| rpm | Revolution per minute |
| W/O | Water-in-oil |
| W/O/W | Water-in-oil-in-water |
| wt% | Weight percent |

# LIST OF SYMBOLS

| | | |
|---|---|---|
| $\beta$ | Emulsion breaking efficiency | % |
| $C_o$ | Initial concentration of cadmium | ppm |
| $C_t$ | Final concentration of cadmium | ppm |
| $D(t)$ | Diameter of the emulsion globule at time t | µm |
| $D(0)$ | Initial diameter of the emulsion globule | µm |
| $E$ | Removal efficiency | % |
| $\varepsilon$ | Membrane breakage | % |
| $\mu$ | Viscosity | mPa.s |
| $P_o$ | Water permeation coefficient | dimensionless |
| $R_{w/o}(0)$ | Initial W/O volume ratio | dimensionless |
| $R_{w/o}(t)$ | W/O volume ratio at time t | dimensionless |
| $S(t)$ | Change of the emulsion globule diameter | dimensionless |
| $\delta$ | Emulsion swelling | % |
| $V_b$ | Volume of separated water phase | mg/L |
| $V_e$ | Initial volume of water in the emulsion | mg/L |
| $V_s$ | Volume of the internal phase leaked | L |
| $V_i$ | Initial volume of the internal phase | L |
| $V_{Ext}$ | Initial volume of the external phase | L |

**MEMBRAN CECAIR EMULSI: KESTABILAN DAN KECEKAPAN BAGI PENYINGKIRAN KADMIUM MENGGUNAKAN MINYAK SAYURAN**

## ABSTRAK

Penggunaan Membran Cecair Emulsi (ELM) bagi pengekstrakan ion kadmium telah diuji. ELM terdiri daripada fasa dalaman dan membran yang membentuk emulsi W/O (air dalam minyak) utama yang diserak di fasa luaran. Bagi menerapkan pembangunan mampan, minyak sayuran yang merupakan pelarut mesra alam telah digunakan dalam formulasi ELM bagi menggantikan pelarut konvensional iaitu bahan kimia berasaskan petroleum. Kajian mengenai keserasian pelarut bersama pembawa (aliquat 336) dan surfaktan(Span 80). telah dijalankan untuk mengenalpasti potensinya bagi digunakan dalam formulasi ELM. Minyak jagung menunjukkan potensi yang memberangsangkan bagi digunakan sebagai pelarut untuk ELM. Fokus kajian adalah untuk menyiasat kestabilan emulsi iaitu, kepecahan membran dan pembengkakan emulsi. Kesan parameter formulasi emulsi telah dikaji untuk mengenalpasti formulasi emulsi terbaik dengan mengambil kira kestabilan emulsi dan juga kecekapannya dalam penyingkiran ion kadmium dari fasa luaran. Parameter yang terlibat ialah kepekatan pembawa dan surfaktan, masa emulsifikasi dan nisbah permulaan bagi isipadu W/O (air dalam minyak). Keputusan menunjukkan bahawa penggunaan 3 wt% Aliquat 336 dan juga Span 80, nisbah isipadu W/O pada 0.33 dan proses emulsifikasi selama 15 minit telah menghasilkan emulsi yang stabil dan penyingkiran ion kadmium yang maksimum. Formulasi yang digunakan ini telah merekodkan 0.05% kepecahan membran dan 34.10% pembengkakan emulsi. ELM yang dibangun juga telah berjaya menyingkirkan 98.20% ion kadmium dan setanding dengan ELM yang dibangunkan mengguna pelarut berasaskan petroleum.

# EMULSION LIQUID MEMBRANE: STABILITY AND EFFICIENCY FOR CADMIUM REMOVAL USING VEGETABLE OILS

## ABSTRACT

The application of Emulsion Liquid Membrane (ELM) in the extraction of cadmium ions was explored. ELM consists of internal and membrane phase that form the primary W/O (water-in-oil) emulsion which to be dispersed in the external phase. In promoting sustainable development, vegetable oil which is environmentally benign diluent was incorporated in the formulation of ELM, replacing the hazardous conventional petroleum derivatives diluent. The oil's potentialities to be used as diluent in ELM was confirmed via a compatibility study with the carrier (Aliquat 336) and surfactant (Span 80). It is learned that corn oil showed a promising potential to be employed as diluent in ELM formulation. This study focused on the investigation of emulsion stability, namely membrane breakage and emulsion swelling. The effect of emulsion formulation parameters of the vegetable oil based ELM were investigated to obtain its best formulation, by taking into consideration emulsion stability as well as its effectiveness for cadmium removal from the external phase. The parameters involved are carrier and surfactant concentration, emulsification time as well as initial W/O volume ratio. These parameters were found to affect the stability and efficiency of the ELM developed. Data obtained shows that a stable emulsion and maximum cadmium removal efficiency were achieved with the usage of 3 wt% Aliquat 336, 3 wt% Span 80, W/O volume ratio of 0.33 and 15 mins of emulsification. At this condition, 0.05 % and 34.10 % membrane breakage and emulsion swelling was recorded, respectively. The prepared ELM was found to effectively remove 98.20% cadmium ions, comparable to the ones developed using petroleum derivatives as diluent.

# CHAPTER 1

# INTRODUCTION

## 1.1 Background

Rapid industrialization which begun in 1960s has raised many critical issues regarding environmental pollution. One of them is the emission of heavy metal with a great potential to pollute the environment. In fact, Elbagermi et al. (2013) reported on the dramatic increasing trend of heavy metal emission since the onset of industrial revolution. In the year 2013 alone, Department of Environment Malaysia reported that a total of 103,994.37 metric tonnes of industrial waste containing heavy metals were generated from various industries in this country (DOE, 2014). Among the most common heavy metal found in a polluted water includes arsenic, copper, cadmium, lead, chromium, nickel, mercury and zinc (Muchie and Akpor 2010). Apart from its ability to harm the ecosystem, extensive study carried out by World Health Organization (WHO) revealed that exposure to these metals will eventually cause deleterious health effects in humans though some of them are nutritionally essential for a healthy life, but in a very small quantity (Sa'idi, 2010).

As for cadmium, it is a toxic metal occurring naturally in the environment and it is considered as a pollutant emanating primarily from industrial and agricultural sources (Salmani et al., 2013). Due to its high solubility, cadmium can be easily absorbed by living organisms and eventually enters our food chain (Barakat, 2011). Study conducted by Kadaruddin (2000) discovered that as much as 53 rivers in Malaysia were badly contaminated with cadmium from various sources, mainly manufacturing. It is reported that the wastewater coming from this source is normally acidic (Kumbasar, 2008b) with the pH range of 1.36 to 4.91 (Siyanbola et al., 2011) at concentration ranging from 0.1 to 100 ppm (Trihadiningrum et al., 2014).

Tremendous efforts have been carried out in minimizing the concentration of heavy metal in an aqueous media using various physico-chemical treatment methods (Kurniawan et al., 2006). However, Emulsion Liquid Membrane (ELM) which was invented by Li (1968) has shown a promising potential in the field of separation. In case of metal removal from aqueous media, ELM was reported to be successfully used in extracting numerous types of heavy metal from aqueous solution for instance, chromium (Kumbasar, 2008a), copper (Alaguraj et al., 2009) and cobalt (Mohamed et al., 2013). Moreover, development of several pilot plants for recovery of copper, chromium, and nickel have proved the technical feasibility of ELM process at larger scale (Mat et al., 2006). On the other hand, Othman et al. (2004) reported that ELM has been applied commercially in removing zinc from wastewater in Austria's viscous fibre industry and it recorded greater than 99.5% extraction efficiency.

ELM is a developed form of solvent extraction, with the difference that extraction and stripping process occur synchronously in the same unit (Bjorkegren and Fassihi, 2011). In principal, ELM consists of internal (W) that contains stripping agent and external feed phase (W). These two phases were separated by the immiscible organic membrane phase (O). The membrane phase consists of carrier and surfactant where they were used for in transporting the insoluble solute from the external phase and stabilization of the emulsion, respectively. These two components were dissolved in a diluent to form the membrane phase. In this multiple emulsion system, the primary W/O (water-in-oil) emulsion is normally prepared first before dispersing it in a second external aqueous phase (W) that contains the targeted solute thus, forming W/O/W (water-in-oil-in-water) emulsion system, as illustrated in Figure 1.1. (Chiha et al., 2010).

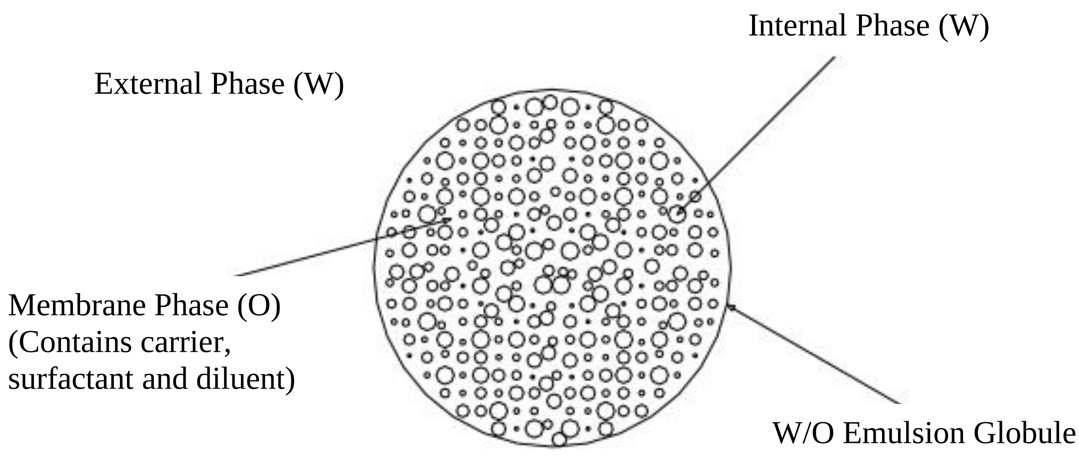


**Figure 1.1:** Illustration of emulsion globule in ELM (Kargari et al., 2006)

Comparing to the existing method for heavy metal separation, ELM was reported to be highly selective, having large interfacial area for mass transfer, high efficiency, allow reusability and able to conduct extraction and stripping process in a single unit (Miron et al., 2015). Besides being highly effective, ELM was estimated to be about 40% cheaper than the conventional extraction processes for heavy metal removal in industry (Sengupta et al., 2006). Furthermore, ELM in different formulation is extremely versatile and useful for numerous applications. This includes mineral recovery, hydrocarbon separation and a number of biochemical and biomedical applications (Alaguraj et al., 2009).

## 1.2 Problem Statement

Human exposure to cadmium either by ingestion or inhalation could cause headache, nausea, diarrhea and abdominal cramps (ATSDR, 2008) while Aziz et al. (2008) reported that several health problems such as kidney damage, renal disorder, asthma, cough, seizures and ataxia were caused by excess exposure to cadmium. On top of that, high concentration of cadmium in human body will inhibit the production of progesterone (Godt et al., 2006) and laboratory data implicate cadmium as a prostate carcinogen (Sahmoun et al., 2005). Extensive usage of cadmium in the production of nickel-cadmium batteries as well as in plating and smelting industries has further resulted in high cadmium concentration in the industrial effluent (Wittman and Hu, 2002). Existing techniques for cadmium ions removal from aqueous media are precipitation, ion exchange and adsorption (Miron et al., 2015). Unfortunately, these techniques face some inherent limitations for example low efficiency, sensitive operating condition, production of secondary sludge, high capital and operating costs as well as high cost for further disposal (Chang et al., 2011). Therefore, a study for an alternative technique in removing cadmium from aqueous phase using ELM is indeed necessary.

In complying with the principle of sustainable development, vegetable oils have been incorporated in various configurations of liquid membrane such as bulk (Manna et al., 2012) and supported (Narayanan and Palanivelu, 2008), but its application in the emulsion type is still scarce. Commonly, ELM uses petroleum derivatives such as kerosene (Basualto et al., 2006) and hexane (Chaouchi and Hamdaoui, 2015) as its diluent. These chemicals were classified as non-renewable, flammable, difficult to handle, easily volatile and hazardous to humans and aquatic life. Also, price inconsistency due to limited supply of petroleum based diluent could affect the total operational cost of ELM. Due to these constraints, the application of petroleum derivatives as diluent have therefore been called into questions and application of safer solvent is indeed crucial in ELM formulation.

Despite its beneficial characteristics for separation of solute, ELM suffers from emulsion instability. Stability of emulsion could be disrupted by membrane breakage, coalescence and emulsion swelling (Chakraborty et al., 2010). As a consequent, poor solute extraction efficiency can be expected and at certain extent, it is nullified. Djenouhat et al. (2008b) claimed that the most influencing factors in emulsion stability was found to be emulsion formulation and method of emulsion preparation. Unfortunately, the effect of these aspects on membrane membrane breakage and swelling were less reported and observed at the same time.

ELM has been applied widely for heavy metal removal from aqueous solution. For cadmium extraction, Mortaheb et al. (2009) and Kumbasar (2009) claimed that the ELM system developed by them has successfully removed more than 90% of cadmium ions from an aqueous solution. Both researchers have highlighted the importance of a thorough study on the influence of emulsion formulation towards the efficiency and stability of ELM. According to Chiha et al. (2010), carrier and surfactant concentration, emulsification time and W/O volume ratio have greatly influenced the efficiency and the stability of ELM. In fact, not much work have been done to optimize the parameters involved in ELM system by taking into consideration these two important aspects at the same time.

## 1.3 Research Objectives

The primary objective of this research is to incorporate vegetable oil as an environmentally benign diluent in ELM formulation and hence, to investigate the effect of emulsion formulation on ELM stability and efficiency. Listed below are the measureable objectives:

i. To evaluate the compatibility of vegetable oil prior to its application as diluent in ELM formulation.
ii. To investigate the occurrence of membrane breakage and emulsion swelling in ELM.
iii. To study the effect of emulsion formulation parameters in achieving minimal emulsion instability and at the same time, highest cadmium removal efficiency.

## 1.4 Research Scope

This research will be focused on the extraction of cadmium ions from an aqueous solution using ELM which will be developed using vegetable oil as diluent. The compatibility of the vegetable oil with the other membrane phase components (carrier and surfactant) will be looked at before a diluent selection is made. Also, the stoichiometry of the extraction reaction will be determined. Effect of four emulsion formulation parameters; carrier concentration, surfactant concentration, emulsification time as well as initial W/O volume ratio will be thoroughly investigated, in obtaining the best emulsion formulation hence, a stable emulsion and maximum cadmium removal efficiency could be achieved. Finally, the possibility of demulsification assisted by ultrasonication will be tested.

## 1.5 Thesis Organization

This thesis is divided into 5 chapters.

**Chapter 1:** In this chapter, a brief overview of the study will be made. Primarily, it discusses the heavy metal emission from various sources as well as the efforts carried out to curb this issue, including the application of ELM. Also, the problem statements and the objectives of this research is outlined.

**Chapter 2:** This chapter describes the literature of this research. This includes the types of liquid membranes, the transport mechanism and basic configuration of ELM. In this section, a thorough review on the stability of ELM and its application for removal of cadmium will be provided.

**Chapter 3:** The details of chemicals and methodology involved in this study will be outlined in this chapter. Besides, the analytical equipment used throughout this study will be introduced and the procedure will be clearly stated.

**Chapter 4:** This chapter presents the data obtained from the experimental work. The discussion on the diluent compatibility, ELM stability as well as extraction efficiency will be provided. Identification of the optimal condition in achieving minimal membrane instability and highest removal efficiency will be made and discussed. Finally, the possibility of demulsification process will be looked at.

**Chapter 5:** In this chapter, the conclusion of the research as well as some recommendations will be provided. The conclusion will verify whether the objectives of this study were achieved successfully or not while the recommendations is aimed for future improvement.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Liquid Membrane Configurations

Liquid membrane technology has gained increasing attention due to its huge potential in replacing conventional technique available for solute separation. Basically, there are three different configurations of liquid membrane. They are bulk, emulsion and supported which differ in the aspect of design, formulation as well as way of contact with the feed phase (Parhi, 2013). The similarities between these three configurations of liquid membrane is that they require the assistance of an extracting reagent, either stagnant or flowing between the feed and the internal phase to specifically remove the targeted solute (Kislik, 2010). In addition, liquid membrane in different configurations were found to be useful in various discipline such as engineering, biotechnology, biomedical as well as physiology where they were normally prepared to match their specific application (Araki and Tsukube, 1990). Table 2.1 summarizes the applications of these three different form of liquid membrane and their purposes.

Bulk Liquid Membrane (BLM) is the simplest form of liquid membrane. It consists of three main phases; feed (F), membrane (M) and stripping (S) phase, as shown in Figure 2.1(a). The membrane phase is responsible in solute extraction as it consists of carrier which helps to transport the solute into the stripping phase. However, its main disadvantage is it requires high amount of solvent which contributes to high operational cost. In the study by Kaur and Vohra (2009), they recovered acetic and propionic acid from a dilute solution,