Al-Kimia, 12-1-2024, 49-63
Available online at: http://journal.uin-alauddin.ac.id/index.php/al-kimia

Utilization of Green Diluent on the Removal for Heavy Metal Contaminants Using Emulsion Liquid Membrane

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Received: March, 22, 2024/Accepted: June, 30, 2024
doi: 10.24252/al-kimiav12i1.46283

Abstract: *Growing industries and human activities have increased the amount of waste containing heavy metals, potentially toxic to human health and the environment. Conventional methods for handling heavy metal wastes have limitations, so the current emerging technique is emulsion liquid membrane (ELM), which is easy and inexpensive and leads to green chemistry. The composition of ELMs generally consists of surfactant, extractant, stripping agent, and diluent. In this article, the focus is on the use of environmentally sustainable diluents derived from vegetable oils. The diluent acts as a solvent for the extractant, helping form a stable emulsion and lowering the emulsion breakage percentage. This article aims to evaluate the potential use of vegetable oils as diluents in the Emulsion Liquid Membrane (ELM) process to improve emulsion stability and heavy metal extraction efficiency.*

Keywords*: diluent, emulsion liquid membrane, heavy metals, vegetable oil*

INTRODUCTION

As industries and human activities advance, such as mining, electroplating, metallurgy, chemical production, and agriculture, waste generation has also escalated (Yang et al., 2019). These wastes typically contain significant concentrations of heavy metals. Unlike organic contaminants, heavy metals are non-biodegradable, more likely to bioaccumulate in organisms, and many of their ions are toxic or carcinogenic. Heavy metals such as arsenic (As), lead (Pb), chromium (Cr), cadmium (Cd), zinc (Zn), cobalt (Co), nickel (Ni), silver (Ag), and uranium (U) pose severe threats to both human health and the environment (Imdad & Dohare, 2022).

Several conventional techniques have been employed for treating heavy metal contamination, including chemical precipitation, ion exchange, adsorption, electrodialysis, and coagulation/flocculation (Shrestha et al., 2021). However, these methods have certain limitations, such as incomplete removal of heavy metals, environmental unsustainability, secondary sludge production, and high operational costs (Chang et al., 2011; Manzak & Tutkun, 2011; Shrestha et al., 2021).

An emerging separation method, the emulsion liquid membrane (ELM), has shown promise in addressing these challenges. ELMs have been used to separate contaminants such as metals, weak acids/bases, inorganic compounds, and hydrocarbons due to their broad interfacial area, which enables high mass transfer and selective removal capabilities (Ahmad et al., 2011a). This technique offers considerable potential owing to its advantages, including the use of environmentally friendly chemicals, simplicity, cost-effectiveness, low energy consumption, and the efficiency of combining extraction and stripping phases in a single step (Dâas & Hamdaoui, 2010; Kumar et al., 2018).

The ELM process involves a separation system in which internal and external phases are separated by a thin layer of homogeneous, non-porous organic solution, typically in a W/O/W configuration (Daraei et al., 2019). The composition of the ELM generally includes a surfactant, extractant, stripping solution, and diluent (Ahmad et al., 2011b). The diluent plays a critical role in the process, acting as the primary component of the membrane phase, enhancing emulsion stability and reducing emulsion breakage (Björkegren et al., 2015; Zereshki et al., 2018). Commonly used diluents, such as kerosene, n-heptane, toluene, and dodecane, are petroleum-based (Othman et al., 2016). These diluents are preferred due to their low viscosity, availability, and non-polarity (Ahmad et al., 2016). However, they are also associated with high costs, flammability, volatility, and environmental hazards due to their toxicity (Daraei et al., 2019; Rosly et al., 2020).

As an alternative, green solvents, such as vegetable oils—palm oil, sunflower oil, cooking oil, corn oil, and rice bran oil—can be used as diluents in the ELM process. These oils are environmentally compatible, cost-effective, renewable, have low dielectric constants and melting points, and possess surface-active properties that improve emulsion stability (Kazemi et al., 2014; Zereshki et al., 2018). Therefore, this review focuses on using eco-friendly diluents in the ELM technique for heavy metal separation, promoting environmental sustainability.

RESULTS AND DISCUSSION

Role of Diluents in Emulsion Liquid Membrane

Each diluent utilized in the ELM process serves a crucial role as it constitutes the primary component of the membrane phase. The diluent is an organic phase that functions as a solvent for the extractant and assists in formulating a stable emulsion (Admawi & Mohammed, 2023a). There are several requirements in the selection of diluents, which are poor solubility in internal and external water phases, compatibility with extractants and surfactants, ability to create new phases, intermediate viscosity, sufficient density different from the water phase, low toxicity, and high flash point (Ahmad et al., 2011a)

During the ELM process, complexes will form at the outer membrane interface and diffuse into the internal membrane interphase. Correctly choosing the oil phase ensures membrane stability and efficient metal transport (Ahmad et al., 2019). Elevated diluent viscosity typically enhances emulsion stability but may concurrently impede mass transport due to increased diffusion resistance (Shere & Cheung, 1988). A significant density difference between the external and oil phases will facilitate post-extraction separation (Anarakdim et al., 2020a). The diluent should have limited solubility in water to prevent interaction with the aqueous phase and potential breakage of the emulsion (Othman, 2006).

The efficiency of extracting a diluent is closely tied to its polarity or dielectric constant, with a lower dielectric constant enhancing extraction capability. A high distribution coefficient indicates that the substance exhibits lower solubility in water but more excellent solubility in organic solvents. An increased distribution coefficient correlates with excellent membrane permeability to the substance (Ahmad et al., 2019).

Furthermore, diluent-carrier interaction may decrease removal efficiency. Hence, utilizing a diluent with a lower dielectric constant is more effective for maximizing metal removal.

Green Diluent (Vegetable Oil)

As per the World Health Organization guidelines, the acceptable level of hydrocarbons in water should not exceed 0.05 mg/L. However, diluents derived from petroleum dissolve in water within the range of 10 mg/L, posing environmental risks if discharged into natural ecosystems (Raval et al., 2022; Zereshki et al., 2021). Petroleum hydrocarbons can enter the environment through leaching and seepage during extraction, storage, and refining operations. Oil spills cause oxidative stress in soil by filling air-containing pore spaces with hydrocarbons, leading to significant metabolic changes in plants and high levels of cell-damaging reactive oxygen species (ROS). Additionally, their hydrophobic nature disrupts water distribution in the soil, causing uneven water distribution and potential water shortages (Alkio et al., 2005; Kuppusamy et al., 2019). Thus, it is necessary to change petroleum-based organic solvents with more environmentally friendly diluents, such as vegetable oils.

Vegetable oils are lipid materials obtained from various fruits and seeds of plants, such as soybeans, palm fruits, sunflower seeds, cotton seeds, coconuts, corn, peanuts, rice grains, and so on. As a biological substance, vegetable oil is non-hazardous, biodegradable, and sustainable (Admawi & Mohammed, 2023a). Vegetable oils consist of nonpolar lipids (<92%), polar lipids (<4%), free fatty acids (<2%), and unsaponifiable materials (phytosterols, tocopherols, and hydrocarbons) (<2%) (Othman et al., 2019). Vegetable oils have a high triglyceride content, i.e., more than 90% by weight (Orsavova et al., 2015). Triglycerides, formed from glycerol and three fatty acids, are esters. They represent nonpolar lipid substances, which exhibit poor solubility in polar solvents like water, thereby favoring the dissolution of nonpolar solutes through the principle of "like dissolves like" (Bettelheim et al., 2010). This characteristic renders oils rich in triglycerides efficient in extracting nonpolar compounds from aqueous solutions so they can be used to treat organic waste from various industries.

Vegetable oils can be extracted as soluble at low concentrations, often with carrier molecules or extractants. Solute ions or molecules found in low concentrations tend to be polar, whereas vegetable oils are nonpolar. Consequently, these solutes exhibit limited solubility in nonpolar diluents like vegetable oils. The dielectric constant of a solvent provides an approximate indication of its polarity. Solvents with a dielectric constant of more than 15 are polar, and less than 15 are nonpolar (Marcus, 2004). Vegetable oil has a much lower dielectric constant (<5), making it a highly nonpolar solvent (Chang, 2014).

Vegetable oils have a higher viscosity than petroleum oils due to the intermolecular attraction between the long-chain fatty acids contained in them, which increases the resistance to mass transfer (Mei et al., 2020; Othman et al., 2019). In addition, environmentally friendly diluents have shallow vapor pressure and high flash points. The vegetable oil's low vapor pressure suggests minimal volatility, whereas its high flash point signifies reduced flammability (Chang, 2020).

Palm Oil

Crude palm oil consists mainly of triglycerides. The triglyceride chain fatty acids in palm oil vary in carbon number and structure, determining the chemical and physical properties. The fatty acid chains vary from 12 to 20 long carbons, with an equal distribution between saturated and unsaturated forms (Björkegren & Karimi, 2011). Palm oil possesses phospholipids as natural surfactants, which increase the emulsifier content overall (Ahmad et al., 1996).

The performance of palm oil as a diluent in ELM was observed by Björkegren et al. (2015) with a membrane phase formulation including tri-n-octylmethylammonium chloride (TOMAC) as carrier, hydrophilic surfactants Tween 80 and Span 80, and butanol as co-surfactant. Cr (VI) extraction with palm oil-based ELMs resulted in a removal efficiency of 97% - 99% after less than 10 minutes. In addition, chromium ion separation was also carried out by Noah et al. (2018) using various types of diluents such as palm oil, corn oil, and kerosene. Figure 1 illustrates how the type of diluent impacts chromium extraction efficiency. The findings showed that palm oil, corn oil, and kerosene worked well, where almost 100% of chromium was successfully extracted. These suggest applying palm and corn oil as eco-friendly alternatives for separating metal ions in ELM.

Palm and corn oils exhibit high viscosities of 83.2 and 55.3 cP, respectively, in contrast to kerosene, which has a viscosity of 2.2 cP. The drawback of this heightened viscosity is its tendency to elevate resistance to mass transport within the membrane phase, making the extraction rate less efficient. Therefore, the minimal concentration of chromium ions allows ample time to overcome the reduced extraction efficiency resulting from viscosity effects, ensuring the efficient extraction of all chromium ions. The study results showed that most chromium extraction occurred rapidly, implying that mass transport resistance might not be the primary factor limiting the rate of oil (Björkegren et al., 2015; Noah et al., 2018).

Noah et al. (2018) reported that high-viscosity palm oil produces higher mass transfer resistance emulsion. Research conducted by (Othman et al., 2016) has combined palm oil with kerosene to decrease diluent viscosity. This study chose TOMAC as the carrier in the organic phase consisting of 30% by volume kerosene and 70% palm oil. The kerosene and palm oil mixture resulted in an increased mass transfer rate and high chromium (VI) extraction efficiency. The study also showed that by using the correct ratio of kerosene and palm oil and the optimal agitation speed, chromium extraction efficiency could be increased to close to 100%. Adding kerosene to palm oil reduces the viscosity of the organic membrane phase. This is due to the higher hydrophobicity of kerosene compared to palm oil and its lower solubility in water (Rosly et al., 2019).

Sunflower oil

Sunflower oil, derived from sunflower seeds (*Helianthus annuus*), is a non-volatile oil predominantly composed of linoleic acid triglycerides (Keshav et al., 2009). Sunflower oil has a low dielectric constant (about three) and a very high flash point (121°C), so it can be used as a diluent (Admawi & Mohammed, 2023b).

Raji et al. (2020) have investigated the stability and mass transfer of ELMs and compared the efficiency of sunflower oil with other organic diluents. Figure 2 shows sunflower oil as a diluent in ELM, yielding almost perfect extraction results under optimal conditions in less than 20 minutes.

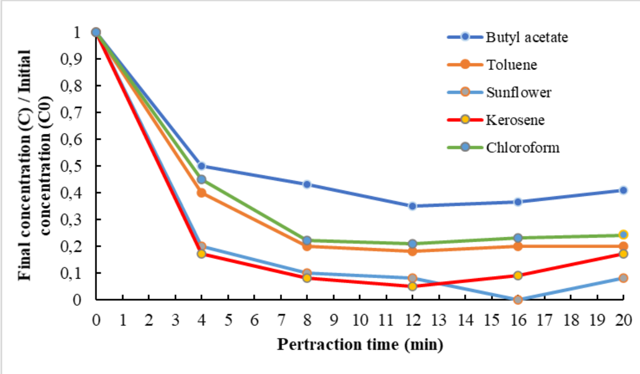


Figure 1. Effect of diluent type (Raji et al., 2020).

Employing sunflower oil in the ELM led to a lower overall mass transfer coefficient than kerosene. The increased viscosity of sunflower oil contributed to forming a more stable liquid membrane, resulting in better extraction than kerosene and other diluents (Raji et al., 2020).

Table 1. Viscosity value of diluent (Raji et al., 2020).

Diluent	Viscosity (cP)
Sunflower oil	39.1
Kerosene	1.64
Toluene	0.55
Chloroform	0.53
Butyl acetate	0.685

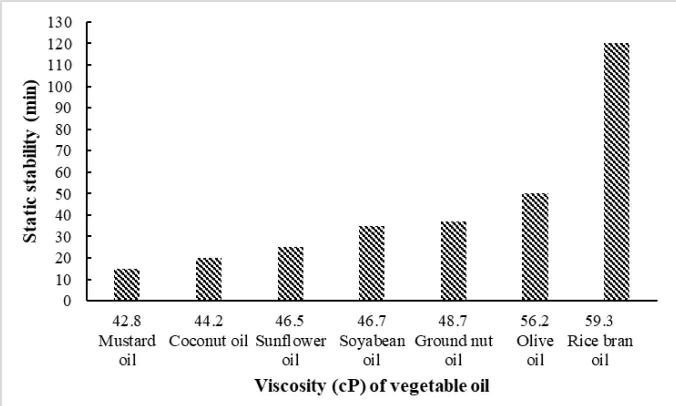
The use of sunflower oil as a diluent has been done by Zereshki et al. (2021) to separate Cu (II) ions from water-based solutions. The study showed sunflower oil-based ELM extraction improved emulsion stability for up to 132 min and efficiently extracted over 94% of copper ions under optimal conditions.

Another study related to the use of sunflower oil for chromium separation by ELM was conducted by Anarakdim et al. (2020b), who used a combination of two hydrophilic emulsifiers, two lipophilic emulsifiers, and tri-n-octylphosphine oxide as a carrier. The result obtained a removal efficiency of Cr (VI) ions up to 96%. Chromium ion separation was also conducted by Davoodi-Nasab et al. (2017), and the results stated that 99% of Cr (VI) ions could be extracted within 10 minutes at optimal conditions.

Rice Bran Oil

Rice bran oil makes a stable ELM because it has a balanced ratio of fatty acids, namely saturated fatty acids (such as palmitic (16: 0)- 24%), monounsaturated fatty acids (such as oleic acid (18:2)- 42%, insoluble in water), and polyunsaturated (such as linoleic acid (18:1)-34%, soluble in water), which is close to the WHO recommendation of 1:1. 5:1 (saturated: monounsaturated: polyunsaturated) (Dhamodaran et al., 2017; Narayanan & Palanivelu, 2008; Shi et al., 2016). In addition, rice bran oil is the second most viscous vegetable oil (59.3 cP), which directly helps to improve ELM stability (Dhamodaran et al., 2017; Ng et al., 2010). This oil also has several properties, such as a density of 910 g/L, non-toxic, economical, and inert diluent (Friedman, 2013; Pal & Keshav, 2016).

Purtika et al. (2022) have researched the effect of green diluents (vegetable oils) on the stability of emulsion liquid membranes. It was found that vegetable oils such as rice bran oil, sunflower oil, peanut oil, soybean oil, olive oil, coconut oil, and mustard oil have different effects on the stability of ELM, with the highest statistics obtained being the use of rice bran oil which can be shown in Figure 3.



. **Figure 2**. Effect viscosity of various vegetable oils as green diluent on static stability (min) ELM (Purtika et al., 2022).

The statistical stability of ELM resulting from using rice bran oil was 120 ± 2 min, which is sufficient time for extraction. Rice bran oil achieved the most excellent stability due to its highest absolute viscosity of 59.3 cP among various vegetable oils, which is advantageous for emulsion stability since viscosity plays a crucial role. Additionally, this oil possesses a well-balanced fatty acid composition falling within the optimal range for stable emulsions. It contains surface-active agents such as oryzanol, polycosanol, and ferulic acid, which reduce the interfacial tension between water-oil phases and prevent internal phase droplet aggregation. Therefore, the oxidative properties of rice bran oil increase and contribute to emulsion stability (Purtika et al., 2022).

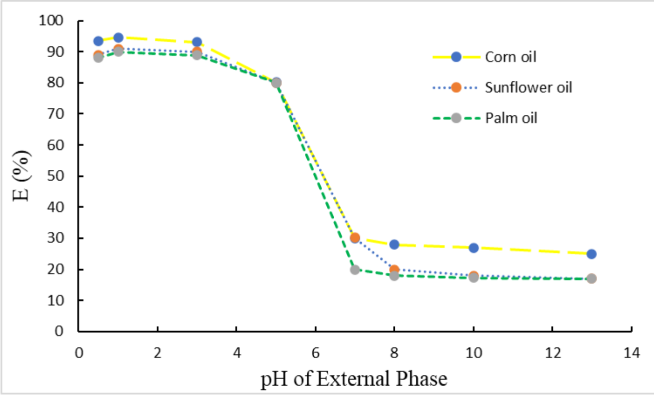
In a study by Kumar et al. (2019), Cr (VI) separation using green ELM with tridodecylamine as an extractant was carried out. The study explored using rice bran oil as a green solvent and optimized the process parameters for efficient extraction. The use of rice bran oil has shown stable emulsion results. Rice bran oil could solubilize the surfactant (span 80) and extractant (TDDA) agents, facilitating stable ELM formation. The findings indicated that the ELM based on rice bran oil successfully achieved Cr (VI) extraction efficiency up to 97 ± 2% and dynamic stability up to 150 ± 2 min below optimum conditions.

Corn Oil

Corn oil consists of aliphatic polyunsaturated fatty acids, with linoleic and oleic acids being the main components (Kedari et al., 2010). Corn oil has a viscosity of 55.3 cP, low dielectric constant (~3), low specific gravity (0.919), and high flash point (Chang, 2014). These properties allow corn oil to dissolve carriers and surfactants to form stable emulsions effectively.

Sunflower, corn, and palm oil were studied to ascertain the suitability of Aliquat 336 as a carrier and span 80 as surfactants dissolved in oil for use in Emulsion Liquid Membrane

(ELM) formulations. It was found that corn oil showed the best performance in removing Cd (II) ions, i.e., 98.6% of cadmium ions were effectively eliminated from the external aqueous phase. The use of Span 80 was studied to see the stability of the emulsion in corn oil, and it was found that the emulsion formulation produced a stable emulsion, showing no significant phase separation for at least 1 hour (Ahmad et al., 2015).



. **Figure 3**. Cadmium removal efficiency using Aliquat 336 dissolved in various vegetable oils (Ahmad et al., 2015).

Waste Cooking Oil

Waste cooking oil is obtained from various vegetable oils left over from the frying of food that has been used up. Waste cooking oil produces substances during the frying process, such as polar components (monoglycerides, diglycerides, phospholipids), oxidized fatty acids, impurities, and food debris (Dewa et al., 2021). Waste cooking oil cannot threaten food safety and costs less than fresh, unused vegetable oil while exhibiting non-toxic, non-flammable, non-volatile, and biodegradable green solvents (Chang, 2014). Waste cooking oil will be equivalent to fresh, unused oil carrying pollutants through liquid membranes because of its similar fatty acid composition and average molecular weight (Banerjee & Chakraborty, 2009).

Sujatha and Rajasimman (2021) have conducted arsenic extraction from wastewater solution with ELM, which consists of waste cooking oil as a diluent. The results showed that ELM using waste cooking oil has successfully extracted arsenic from wastewater solution with maximum extraction efficiency reaching 99.0%. In addition, waste cooking oil as a diluent showed good stability for six use cycles. However, after the sixth cycle, there was a decrease in emulsion stability and arsenic extraction.

Another study related to ELM waste cooking oil was carried out by Sujatha et al. (2021a) to separate nickel from an aqueous solution. This study found that ELM can selectively transfer nickel into the internal phase to achieve a maximum extraction efficiency of 98.7% and has the potential to be used repeatedly for up to 7 cycles.

Sujatha et al. (2021b;2022) also extracted Pb and Cd using an emulsion liquid membrane of waste cooking oil, a non-toxic solvent as a diluent. The viscosity and density of waste cooking oil were measured, resulting in 32 cSt and 877 kg/m3 at room temperature, respectively. The results showed that using waste cooking oil as a diluent in ELM gave positive results in extracting cadmium and lead. The waste cooking oil-based ELM used showed a maximum lead extraction efficiency of 97.39% and cadmium extraction efficiency of up to 97.40% at optimum conditions.

Another study by Khalil et al. (2022) observed that 95.17% of Zn ions were extracted at optimum conditions. The density and viscosity of waste cooking oil were 798 kg/m3 and 64.4 cP at room temperature, respectively. In contrast to the characteristics of previously reported cooking oil by Sujatha et al. (2022), the oil utilized in this study exhibits a lower density and increased viscosity. In general, the elevated viscosity of vegetable oils stems from the intermolecular attraction among the long fatty acids. (Chang 2014).

The higher content of free fatty acids, glycerol, and water in waste vegetable oil due to oxidation, hydrolytic, and cracking reactions that occur during frying is feared to affect its efficiency in extracting substances (Khalil et al., 2022; Yaakob et al., 2013). However, the results of the studies that have been conducted prove that frying oil has no impact on extraction efficiency and results in high extraction efficiency.

Table 2. Study on the composition of emulsion liquid membrane for heavy metal contaminant removal.

Targeted solute	Surfactant	Extractant	Diluent	Internal phase reagent	Extraction efficiency (%)	Reference
Cr (VI)	Tween 80 + Span 80	TOMAC	Palm oil	NaOH	99%	(Björkegren et al., 2015)
Cr (VI)	Span 80	TOMAC	Palm oil	NaOH	97%	(Noah et al., 2018)
Cr (II)	Span 80	D_2EHPA	Sunflower oil	HCl	94%	(Zereshki et al., 2021)
Cr (VI)	Tween 20 + Tween 80 and PGPR + Span 80	TOPO	Sunflower oil	Na_2CO_3	96%	(Anarakdim et al., 2020b)
Cr (VI)	Span 80	Aliquat 336	Sunflower oil	NaOH	99%	(Davoodi-Nasab et al., 2017)
Cr (VI)	Span 80	TTDA	Rice bran oil	NaOH	97%	(Kumar et al., 2019)
Cd (II)	Span 80	Aliquat 336	Corn oil	NaOH	98.6%	(Ahmad et al., 2015)
As (III)	Span 80	Aliquat 336	Waste cooking oil	NaOH	99%	(Sujatha & Rajasimman, 2021)
Ni (II)	Span 80	Cyanex 301	Waste cooking oil	H_2SO_4	98,70%	(Sujatha et al., 2021a)
Pb (II)	Span 80	D_2EHPA	Waste cooking oil	H_2SO_4	97.39%	(Sujatha et al., 2021b)
Cd (II)	Span 80	D_2EHPA	Waste cooking oil	HCl	97,40%	(Sujatha et al., 2022)
Zn (II)	Span 80	D_2EHPA	Waste cooking oil	H_2SO_4	95,17%	(Khalil et al., 2022)
Cr (VI)	Span 80	TOMAC	Palm oil + kerosene (7:3)	NaOH	100%	(Othman et al., 2016)

CONCLUSIONS

An emulsion liquid membrane is a promising technique to remove heavy metal contaminants from industrial and household effluents. The selection of membrane phase constituents, such as diluents, will affect the stability of the emulsion. The use of vegetable oil-based diluents in the ELM process is environmentally friendly, low-cost, and renewable compared to petroleum-based diluents. The higher viscosity of vegetable oils will aid in forming more stable emulsions but may limit mass transportation. However, the studies observed did not show inefficient extraction results. Results showed that most heavy metals were successfully extracted within a few minutes. Research shows that palm, sunflower, rice bran, corn, and waste cooking oil can be used as diluents in ELM to improve the extraction efficiency of heavy metals such as chromium, arsenic, nickel, lead, and cadmium. Based on the percent extraction efficiency results, palm oil with a combination of surfactants Tween 80, Span 80, and TOMAC carrier is shown to be most effective as a diluent because its high viscosity improves emulsion stability and extraction efficiency. Thus, this study showed the potential of using vegetable oils as diluents in heavy metal extraction processes, which can be a more environmentally friendly alternative.

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