
Simultaneous Removal and Recovery of Heavy Metal By Emulsion Liquid Membrane: Kinetic Study

Nur Ilyani Najmi Binti Zainuddin^a, Meor Muhammad Hafiz Bin Shah Buddin^a

^aFaculty of Chemical Engineering, Universiti Teknologi MARA, Selangor, Malaysia

Abstract

The presence of heavy metal in industrial effluents has become one of the major factors leading to environmental pollution and human health deficiencies. Owing to this issue, the emulsion liquid membrane (ELM) has been discovered as an advanced and effective technique for heavy metal removal from aqueous solution. This study is aimed to conduct component selection and kinetic study for ELM in favour of Cd(II) and Cu(II) ions removal from synthetic wastewater. On top of that, the selectivity of extraction process in ELM system was identified. Two different types of facilitated carrier; di-(2-ethylhexyl) phosphoric acid (D2EHPA) and trioctylamine (TOA) were studied and compared. Membrane phase was incorporated of 0.05 wt% of carrier and 0.95 wt% of kerosene. HCl and NaOH are as the stripping agent accompanied by the carrier were kept constant at 1M concentration while the feed phase was maintained at pH 4. The results revealed that D2EHPA is more preferred as carrier compared to TOA due to higher extraction efficiency (>98%) achieved. Furthermore, it was analysed that both carriers are being more selective toward Cu(II) removal. The system's ability to remove Cu(II) ions from the feed phase was identified through the use of dimensional reduced concentration, R_f . It was identified that the reaction rate constants for extraction and stripping on Cd(II) removal were found to be 7.66 h⁻¹ and 22.95 h⁻¹ for D2EHPA system and 0.11 h⁻¹ and 2.49 h⁻¹ for TOA system. Meanwhile, as for Cu(II) extraction, reaction rate constants for extraction and stripping obtained for D2EHPA system were 3.66 h⁻¹ and 2.87 h⁻¹, whereas 0.17 h⁻¹ and 3.20 h⁻¹ for TOA system.

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1.0 Introduction

Rapid progress of the industry nowadays has greatly affected the environment and human beings. Heavy metals are known to be a threat to the environment and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons (Jaishankar, Mathew, et al., 2014). Heavy metals are non-biodegradable and toxic or poisonous even at low concentration where they represent dangerous threats to society as well as to the flora and fauna. They can be accumulated in human body causing serious illness such as kidney failure, cancer, nervous system damage or even fatalities (Al-Saydeh et al., 2017). For instance, cadmium is a highly toxic nonessential heavy metal that is well recognized for its adverse influence on the enzymatic systems of cells, oxidative stress and for inducing nutritional deficiency in plants. Humans may get exposed to this metal primarily by inhalation and ingestion and can suffer

from acute and chronic intoxications (Jaishankar, Tseten, et al., 2014). Removal of heavy metals from wastewater has recently become main considerable interest subjected to legislation and regulation due to highly toxic element. Various techniques have been developed to remove metal ions from industrial effluents and wastewaters. They are precipitation, solvent extraction, chemical and electrochemical, ultrafiltration, reverse osmosis, flotation and coagulation (Gunatilake, 2015; Peters & Shem, 1993). However, owing to the disposal of sludge, their high cost, low efficiency and inapplicability to a wide range of pollutants, most of these processes are unacceptable in the way to overcome the barrier towards a sustainable future with favorable environment (Samiey et al., 2014).

Liquid membrane technology was invented by Li in 1968 (Norman, 1968). Since then, liquid membrane technology has been known as auspicious technique in

order to overcome these drawbacks that has potential to substitute existing separation and purification technologies. Liquid membrane is an homogeneous, non-porous and insoluble liquid, usually an organic solvent which is selective for a solute, separating two other liquid phases. To date liquid membrane may be classified into three types (Figure 1) which are bulk liquid membrane (BLM), supported liquid membrane (SLM) and emulsion liquid membrane (ELM).

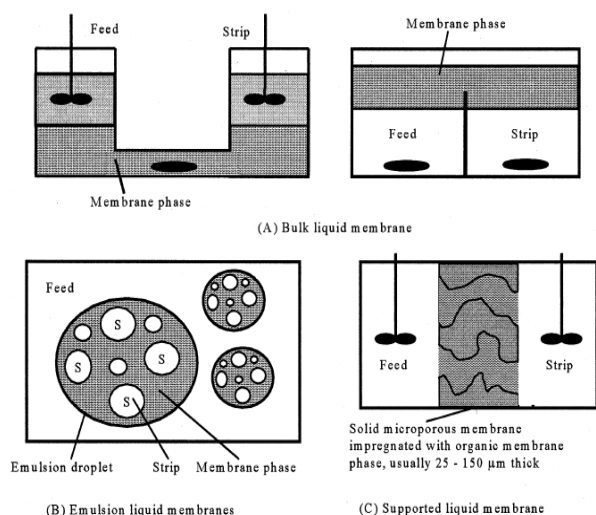


Figure 1: Schematics of (A) a BLM, (B) an ELM, (C) a SLM (Yang et al., 2003)

Generally, ELM processes are a three phase dispersion system, where primary emulsion consist of organic and stripping phase is dispersed in the feed or effluent phase, which is the phase to be treated. ELM operates in such a way that the primary water-in-oil (W/O) emulsion is prepared first prior to its dispersion in a aqueous solution. At the inner interface, the complex decomposes by the reversal of the equilibrium reaction and the metal ion is delivered into the internal phase and the regenerated carrier goes back into the membrane phase. This configuration allows the formation of water-in-oil-in-water (W/O/W) emulsion. The advantages of this process are extraction and stripping occurred simultaneously in one single step operation and equilibrium limitation can be removed. Furthermore, using ELM to recover the heavy metal can overcome high mass transfer area at low cost compared to other liquid membranes.

Emulsion liquid membrane (ELM) offers myriad benefits such as significant high driving force and selectivity advantages which enhancing separation performance due to single step of extraction and stripping processes (Kumar et al., 2019). This study will utilize ELM technique to minimize the concentration of heavy metals from an aqueous

solution. Though ELM offers many attractive advantages, but its formulation is an important aspect to look at due to ELM method still have to deal its major drawback which always correlate with instability of emulsion where this can be referred to the emulsion formulation in terms of the selection of carrier, stripping agent, diluent, surfactant and emulsion procedure. The carrier should be selective or high tendency in forming complex to the target metal ions that need to be recovered while the stripping agent and diluent must be properly chosen as it have significant effect on emulsion stability and to minimize the water transport through the membrane during the extraction process. A thorough study on the component selection must be conducted to ensure its effectiveness. In fact, kinetics of the extraction and stripping process is the main interest of many researchers (León et al., 2016; Religa et al., 2009) Determination of liquid membrane components, especially of carrier and stripping agent must be taken into account. The process of component selection is highly likely able to reduce the issue of emulsion instability (Chakraborty et al., 2010) and eventually, maximum heavy metal removal is achieved.

This study will utilize the emulsion liquid membrane (ELM) technique for binary heavy metal (Cu(II) and Cd(II)) removal from aqueous solution. Specifically, the study will conduct a component selection process and its effectiveness on extraction and stripping of solute will be looked at. Experiments will be carried out by using different types of carrier (di-(2-ethylhexyl) phosphoric acid and trioctylamine) and stripping agent (hydrochloric acid and sodium hydroxide). This screening process will able to determine the most suitable carrier for copper and cadmium metal extraction. Simultaneously, the kinetics of the extraction and stripping process by using varying components will be looked at. In the end, the study will reveal the best carrier and stripping agent by taking into consideration of its efficiency as well as kinetics.

1.1 Theory

In principal, ELM consists of internal (W) and external (W) phase and they were separated by the immiscible organic membrane phase (O) thus, forming W/O/W (water-in-oil-in-water) emulsion system. In this multiple emulsion system, the primary W/O emulsion is prepared first before dispersing it in a

second aqueous external phase (W) (A. Ahmad et al., 2015).

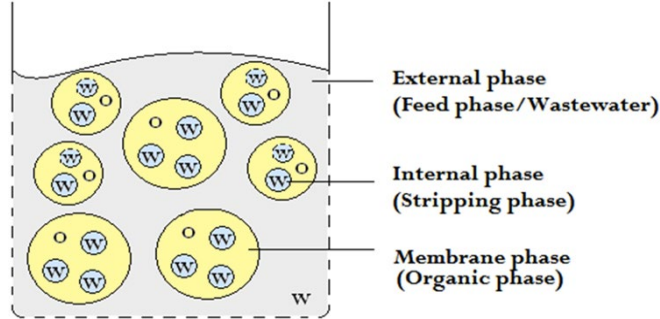


Figure 2: The phases in a water-in-oil-in-water emulsion (w/o/w). O = Oil (Yellow) and W = Water (Gray for external phase and blue for internal phase) (Pirmoradi & Ashrafizadeh, 2017).

The most important emulsion class is the double emulsions which is known as complex liquid dispersion system. Water-in-oil-in-water emulsions (W/O/W) are the common double emulsions that have been applied due to their ability to entrap water-soluble material (Pirmoradi & Ashrafizadeh, 2017). Above shown in Figure 2 is the schematic representation of a W/O/W emulsion.

The general extraction reaction of a metal ion (Mn^{+}) with extractant (HR) was explained by:

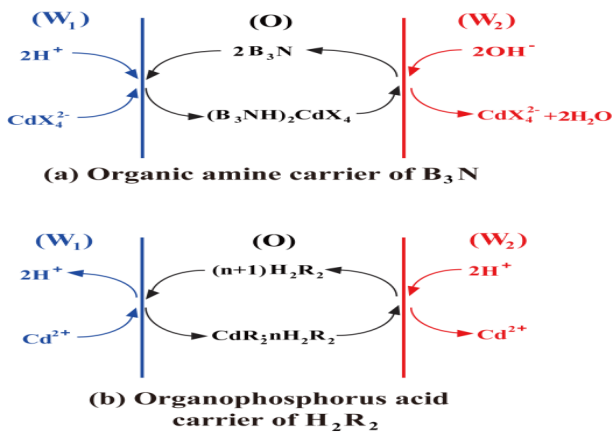
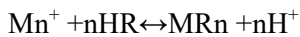


Figure 3: Schematic diagrams of selective separation of Cd(II) using liquid membrane with organic amine carrier (a), and organophosphorus acid carrier (b) (Zeng et al., 2018).

The kinetic data determines the constant reaction rate of k (h^{-1}) values. The variation rate of the metal

reduced concentration in each phase can be described by the following equations (León et al., 2016)

$$\frac{dR_f}{dt} = -k_1 R_f \quad (1)$$

$$\frac{dR_m}{dt} = k_1 R_f - k_2 R_m \quad (2)$$

$$\frac{dR_p}{dt} = k_2 R_m \quad (3)$$

Integration of these differential equations, leads to expressions of variation of R_f , R_m , and R_p with time:

$$R_f = \exp(-k_1 t) \quad (4)$$

$$R_m = \frac{k_1}{k - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \quad (5)$$

$$R_s = 1 - \frac{1}{k - k_1} [k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \quad (6)$$

2.0 Methodology

2.1 Material

Chemicals used in this experiment are di-(2-ethylhexyl) phosphoric acid (D2EHPA), trioctylamine (TOA), Kerosene, Copper (II) Sulphate, Cadmium (II) Nitrate, Hydrochloric acid (HCl), Sodium Hydroxide (NaOH), Acetic acid, and Sodium acetate. Deionized water is used for all solution preparation.

2.2 Liquid Membrane Component Selection

The current study focuses on the selection of carrier and stripping agent of the ELM system for Cd(II) and Cu(II) ions removal from wastewater. Carrier concentration was kept constant at 0.5 wt%, dissolved in kerosene. Comparison study was conducted to select best carrier between D2EHPA and TOA. The stripping agent accompanied the carrier mentioned are HCl and NaOH where the concentration was kept constant at 1M.

2.3.1 Batch Extraction Process

Experiments are constructed to predetermine or choose the appropriate type of carrier to recover copper and cadmium metal. As the amount of cadmium and copper extracted is the main parameter of interest, the most suitable carrier must have high tendency forming complexes with metal ion and also easy to strip out using appropriate stripping agent.

The batch extraction process was performed by contacting an equal volume (30ml) of aqueous feed phase (copper and cadmium solution) and membrane phase using a magnetic stirrer starting at 1 hour to 6 hours at one hour interval. Both solutions were mixed at 400 rpm for each run. Once the process ended, the content of the beaker was allowed to settle and separate by gravity. Feed phase was sampled using syringe to measure its content of heavy metal. The concentration of copper and cadmium in the sample were analyzed using atomic absorption spectrophotometer (AAS) at wavelength of 324.8 nm for Cu(II) and 228.85 nm for Cd(II) to evaluate extraction efficiency. The carrier screening procedures were repeated for other type of carrier, TOA. Extraction efficiency, EE (%) as given by the following equation:

$$EE(\%) = \frac{C_{f0} - C_{ft}}{C_{f0}} \times 100 \quad (7)$$

where C_{f0} is the initial concentration of Cu(II) in the feed phase, and C_{ft} , C_{mt} , and C_{pt} are the concentrations of Cu(II) in the feed, membrane, and product phase, respectively, at time t .

2.3.2 Batch Stripping Process

Batch stripping agent screening experiment was carried out to identify the best stripping agent to strip copper and cadmium metal from solute loaded organic solution. The loaded organic phase was taken from extraction process from Section 2.3.1 as stripping process is the reverse extraction step. An equal volume of stripping agent at specified concentration 1M and metal loaded organic solution were mixed at 1 hour to 6 hours with one hour time interval hours at stirring speed of 400 rpm. Then, the stripping process sample were allowed to settle and separate. Once phase separation is completed, sampling was made to measure the concentration of heavy metal in the stripping phase. Then, the concentration of copper and cadmium ions were measured using AAS. The stripping procedures were repeated for other stripping agent.

2.3 Kinetic study

Kinetics of extraction and stripping process were looked at. The aim of this section is to compare the kinetics of the extraction and stripping process for different carrier and stripping agent.

Using experimental data obtained, R_f , R_m and R_s will be calculated. R_f , R_m and R_s are dimensionally reduced concentrations of Cd(II) and Cu(II) ions in the feed, membrane and stripping phases, respectively.

Dimensionless reduced concentration of metal ions in the feed phase:

$$R_f = \frac{C_{ft}}{C_{f0}} \quad (8)$$

Dimensionless reduced concentration of metal ions in the membrane phase:

$$R_m = \frac{C_{mt}}{C_{f0}} \quad (9)$$

Dimensionless reduced concentration of metal ions in the product phase:

$$R_p = \frac{C_{pt}}{C_{f0}} \quad (10)$$

where C_{f0} is the initial concentration of Cu(II) in the feed phase, and C_{ft} , C_{mt} , and C_{pt} are the concentrations of Cu(II) in the feed, membrane, and product phase, respectively, at time t .

Data of Cu(II) and Cd(II) ions in external phase as well as stripping phase was also used to evaluate the kinetics of the process. Equations (1) to (6) are useful in predicting the kinetics of the extraction and stripping process.

3.0 Results and discussion

3.1 Kinetic Study on Cd(II) Extraction

Extraction of Cd(II) ions were studied using two different types of facilitated carrier; D2EHPA and TOA. In this experiment, both concentration of carriers were fixed at 0.05 wt%. The data of R_f , R_m and R_s are illustrated through Figure 4 for D2EHPA system while Figure 5 displays data obtained for TOA system. Both figures showed model curves of dimensionless reduced concentration of Cd(II) in the feed (R_f), membrane (R_m) and stripping (R_s) phase using different carrier and stripping agent. The total of R_f , R_m and R_s is equals to unity.

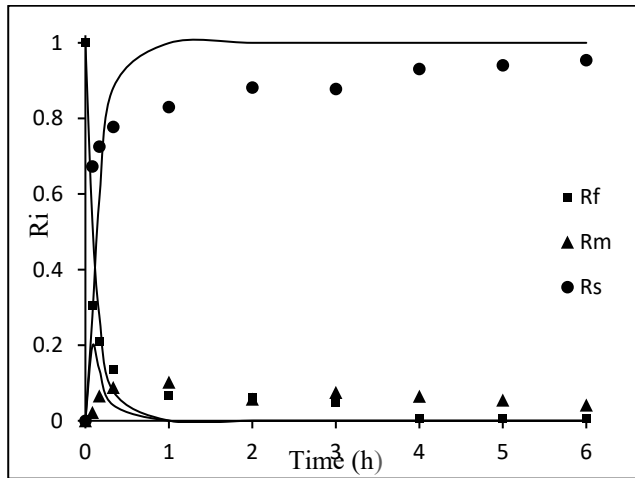


Figure 4: Effect of time on Cd(II) ions removal by using D2EHPA as extractant and HCl as stripping agent on R_f in feed phase, R_m in membrane phase, and R_s in stripping phase. (Points, experimental values; lines, model values)

Based on the data available in Figure 4, it can be inferred that extraction of Cd(II) ions by using D2EHPA as carrier in the liquid membrane is possible. As the extraction time prolongs, R_f decreases. The trend reflects that the concentration of the ions in the feed phase is decreasing. Longer contact time between the phases played an important role as the system is progressing towards its equilibrium. Trend reported in the figure is in line with the one reported by Basualto et al. (2006) where the authors reported on the success of Cd(II) ions extraction using D2EHPA at 0.1 mol/L of concentration. The author recorded higher efficiency due to higher concentration of carrier used. Meanwhile, the same trend applies when TOA was used as the carrier, as shown in Figure 5. However, the system recorded much less R_f compared to D2EHPA. This is because of the characteristics of the carrier itself. D2EHPA is classified as acidic carrier while TOA is a basic type (Kusumastuti et al., 2018). Characteristics of carrier dictates the pH of the wastewater to be treated.

Based on Figures 4, the trend of R_m is sigmoidal while R_s is decreasing monoexponentially. Shah Buddin et al. (2019) reported similar trend. The significance of increasing R_s is that the stripping of the Cd(II) ions from the membrane phase is successful and the solute now is concentrated in the internal phase. As for TOA system, no such trend can be concluded. It is highly possible due to insufficient time for the system achieve equilibrium, or at least, it is moving towards equilibrium. Or else, low concentration of carrier could cause the recorded data (A. L. Ahmad et al., 2011). However, the kinetic rate constant value will be predicted based on the available data, as discussed

later.

By applying Equation (4), (5) and (6), the model was plotted and it can be interpreted that R_f decreases monoexponentially over time, R_s increases as sigmoid form curve, and R_m time dependence present increase then decreasing at ascending rates.

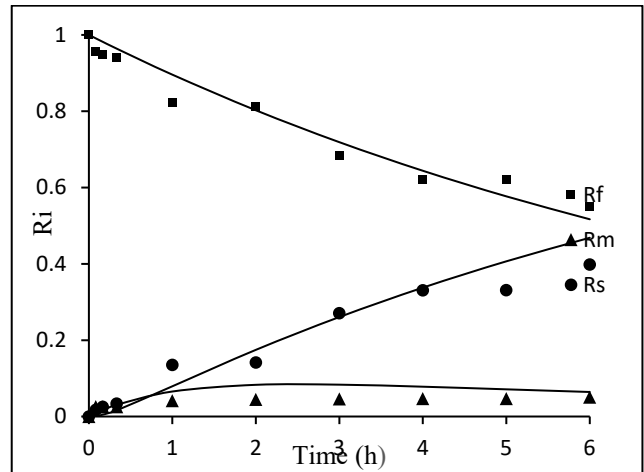
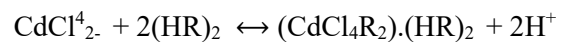


Figure 5: Effect of time on Cd(II) ions removal by using TOA as extractant and NaOH as stripping agent on R_f in feed phase, R_m in membrane phase, and R_s in stripping phase. (Points, experimental values; lines, model values)

The reaction equation of Cd(II) on the feed phase and stripping phase of the liquid membrane interface can be described as follows :

For (Carrier; D2EHPA, Stripping Agent; HCl) (Basualto et al., 2006)

Feed phase:

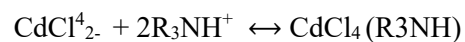


Stripping phase:



For (Carrier; TOA, Stripping Agent; NaOH) (Shah Buddin et al., 2019)

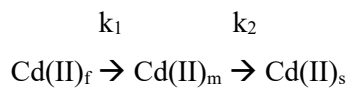
Feed phase:



Stripping phase:



The results in Figure 4 and Figure 5 proposed that Cd(II) transport meets the kinetic laws of two consecutive first-order irreversible reactions, extraction (rate constant, k_1) and stripping (rate constant, k_2) reactions:



The irreversibility must be assumed because R_f and R_m tend to be zero, while R_s tends to be one, hence the transport of Cd(II) from the feed phase to the stripping phase appears to be practically complete (León et al., 2016).

Table 1: Reaction rate constants for extraction (k_1) and stripping (k_2) process of Cd(II) ions through ELM

Carrier	D2EHPA	TOA
Extraction reaction rate constant, k_1 (h^{-1})	7.66	0.11
Stripping reaction rate constant, k_{2s} (h^{-1})	20.99	3.98
Membrane reaction rate constant, k_{2m} (h^{-1})	22.90	0.99
Average value of k_2 (h^{-1})	22.95	2.49
R^2 for k_1	0.936	0.970
R^2 for k_{2s}	0.803	0.970
R^2 for k_{2m}	0.536	0.816

The value of k_1 and k_2 as tabulated in Table 1 were used to plot the predicted model line as seen in both Figure 4 and 5. Experimental data available was compared with the model. As a result, kinetics data of the system can be determined. The value of k_1 was derived directly from the Equation (4) by iteration until a constant value was determined. Meanwhile, the initial value of k_2 was identified by using the other two equations. As can be seen from the plotted graph, the experimental results for both different type of carriers was found to be well matched with the models shown in Equations (4), (5) and (6), where the R^2 values for R_f , R_m and R_s data were found to be 0.936, 0.536 and 0.807 for D2EHPA carrier while 0.970, 0.816 and 0.970 for TOA carrier.

3.2 Kinetic Study on Cu(II) Extraction

In this study, two different types of carrier including D2EHPA and TOA were examined on the extraction of Cu(II) ions. Experiments were carried out to extract Cd(II) and Cu(II) ions simultaneously. Figure 6 displays the result value of R_f , R_m , and R_s on Cu(II) ions extraction for D2EHPA system while Figure 7 showed the data for TOA system. Both figures indicate results of dimensionless reduced concentration of Cu(II) ions in the feed phase, membrane phase and

stripping phase over the time using extractants. Note that the sum of R_f , R_m , and R_s are all equal to one.

According the data shown in Figure 6, it can be implied that the removal of Cu(II) ions is achievable due to present of D2EHPA as carrier in the liquid membrane. As the extraction time increases, R_f value seems to decrease reaching zero and thus this trends reflects a decline in ion concentration in the feed phase. Longer contact time played a major role as the system progresses toward its equilibrium. The pattern shown in the figure is consistent with report by Son-Ki et al. (1988) where it was revealed that during the initial stage, the copper extraction speed decreases by approximately 15 to 20 minutes then it becomes almost constant as time prolongs. This can be attributed to an increase in the mass transfer rate due to interfacial turbulence where it also means that resistances to mass transfer are important in the current process. Whereas, when TOA was used as the carrier, the same pattern occurs as shown in Figure 6. However, compared to D2EHPA, the system registered much less R_f . This is due to the carrier's own characteristics which applied as basic extractant. The trend in the figure is the same as reported by (León et al., 2016) where the author found low removal of Cu(II) ions by TOA may result from variations in the diffusion coefficient of the different Cu(II)-carrier complexes in the membrane phase. Also, the phenomenon was observed due to the differences in the formation of complexes which affects the co-transport mechanism of the system.

Based on Figure 6, R_f was found to decrease, reaching zero value as the time increased due to extraction of Cu(II) ions from the feed phase. Meanwhile, R_s value increased approaching one as this proved Cu(II) ions were stripped in the stripping phase. The solid line represented the model curve where it was found to be fitted with the experimental data and achieved highest R^2 . The value of R^2 were found to be 0.944, 0.881, and 0.944 for data of R_f , R_m , and R_s , respectively.

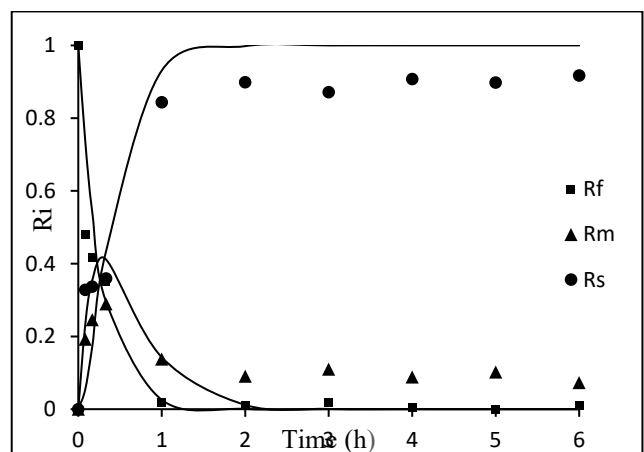


Figure 6: Effect of time on Cu(II) ions removal by using D2EHPA as extractant and HCl as stripping agent on R_f in

feed phase, R_m in membrane phase, and R_s in stripping phase. (Points, experimental values; lines, model values)

Referring to Figure 7 where TOA was used, it can be seen that R_f values is decreasing with time while R_m values has the opposite trend. Theoretically, the Cu(II) ions were extracted from the feed phase and were stripped from stripping phase. However, the value of R_f and R_m did not achieve nearly to one or zero, as compared to D2EHPA as carrier. Thus, this showed that the extraction efficiency of Cu(II) ions by using TOA is not as high as D2EHPA used as carrier which will be further discussed at Section 3.3. As can be seen from the graph, the experimental data is said to be fitted with the models shown in Equation (4), (5), and (6), following the highest R^2 values calculated which were 0.958, 0.774, and 0.973 for data of R_f , R_m , and R_s .

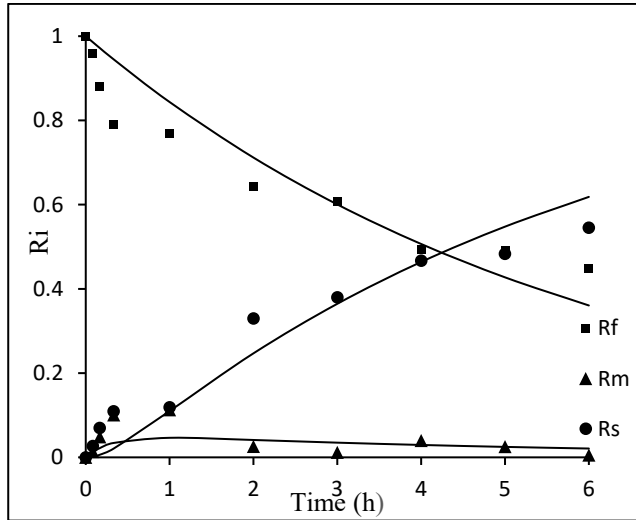
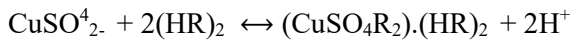


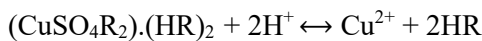
Figure 7: Effect of time on Cu(II) ions removal by using TOA as extractant and NaOH as stripping agent on R_f in feed phase, R_m in membrane phase, and R_s in stripping phase. (Points, experimental values; lines, model values)

For (Carrier; D2EHPA, Stripping Agent; HCl) (Kamaruddin et al., 2019)

Feed phase:

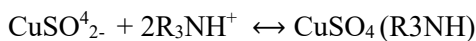


Stripping phase:



For (Carrier; TOA, Stripping Agent; NaOH) (Alaguraj et al., 2009)

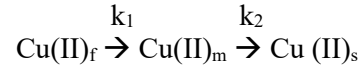
Feed phase:



Stripping phase:



The results in Figure 6 and Figure 7 proposed that Cd(II) transport meets the kinetic laws of two consecutive first-order irreversible reactions, extraction (rate constant, k_1) and stripping (rate constant, k_2) reactions:



The irreversibility must be assumed because R_f and R_m tend to be zero, while R_s tends to be one, hence the transport of Cu(II) from the feed phase to the stripping phase appears to be practically complete.

Table 2: Reaction rate constants for extraction (k_1) and stripping (k_2) process of Cu(II) ions through ELM.

Carrier	D2EHPA	TOA
Extraction reaction rate constant, k_1 (h^{-1})	3.66	0.17
Stripping reaction rate constant, k_{2s} (h^{-1})	5.48	2.99
Membrane reaction rate constant, k_{2m} (h^{-1})	2.87	3.20
Average value of k_2 (h^{-1})	4.18	3.10
R^2 for k_1	0.944	0.937
R^2 for k_{2s}	0.944	0.966
R^2 for k_{2m}	0.881	0.405

The reaction rate constants tabulated in Table 2 were used to plot the model line fitted in Figure 6 and Figure 7. Experimental data obtained was compared with those models. As a result, kinetic data of the system can be determined. The value of k_1 was derived by iteration from the equation (4) until a constant value had been added and k_2 was then identified with the other two equations. As can be seen, Cu(II) ion extraction or stripping process is greater using D2EHPA as carrier due to the higher values of both the extraction and the stripping rate constants. The lower values of these rate constants in the carrier lead to much lower maximum fluxes and extraction and stripping efficiencies (León et al., 2016). This results also

indicated that the use of D2EHPA as extractant and HCl as stripping agent with 1M of concentration is much preferable rather than using TOA extractant. A similar kinetic study has been conducted previously on metal ions removal and the results achieved lower value of R_f and higher value R_s which indicating better extraction and stripping efficiency (Shah Buddin et al., 2019). However, different type stripping agent was used in the respective study and this could be one of the factors that contributed to low efficiency reported in this current study.

3.3 Selectivity of Carrier

Simultaneous extraction of Cd(II) and Cu(II) ions from synthetic wastewater was tested. Performance of two different types of carrier; D2EHPA and TOA were examined to check their selectivity in removing Cd(II) and Cu(II) metal ions. The concentration of carrier in kerosene was fixed at 0.05wt%. Figure 8 and Figure 9 illustrated the extraction efficiencies (EE%) of both metals by respective carrier along the extraction time.

Referring to Figure 8, it showed the metal extraction efficiency, EE(%) data for Cu(II) reached approximately 98% at one hour extraction time by 0.05wt% of D2EHPA while about only 85% of Cd(II) is extracted using the same type and concentration of carrier. The Cd(II) ions started to be 99% extracted at four hours of extraction time. Figure 8 showed the same trend of result which can be supported through optimization study conducted by Kamaruddin et al. (2019) which the author also found extraction efficiency of Cu(II) achieved higher than Cd(II) using D2EHPA as carrier. The author also concluded that aqueous pH, and interaction effects of contact time and concentration of D2EHPA played an important role in achieving the best percent extraction efficiency. This results suggest D2EHPA has higher selectivity on Cu(II) ions compared to Cd(II).

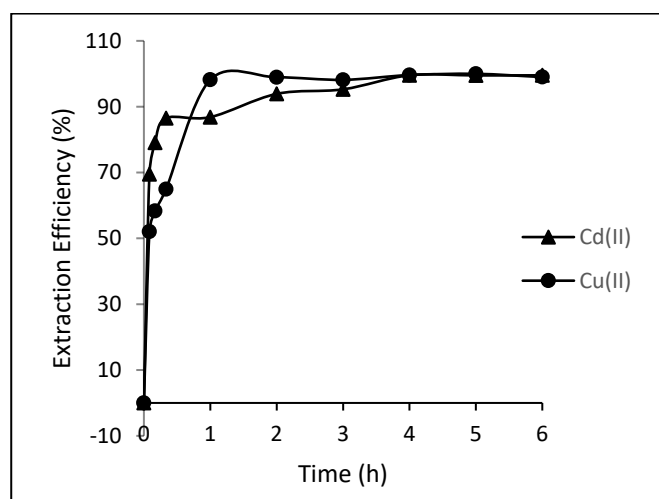


Figure 8: Extraction efficiency on Cd(II) and Cu(II) removal using D2EHPA as carrier.

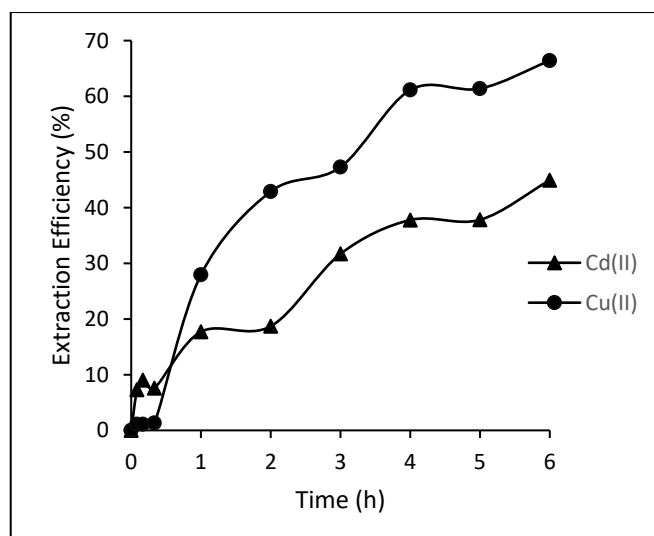


Figure 9: Extraction efficiency on Cd(II) and Cu(II) removal using TOA as carrier.

On the other hand, for TOA as carrier used in this experiment, Figure 9 clearly displayed that higher extraction efficiency (42%) of Cu(II) ions at two hours extraction time as compared Cd(II) ions which only achieve 18% extraction efficiency. Comparing the results at 6 hours extraction time, Cu(II) ions could remove as much as 66% while only 44% of Cd(II) ions could be removed using same type and concentration of carrier, 0.05 wt% of TOA. Contradict results were reported by A. Ahmad et al. (2015) where the author achieved higher Cd(II) removal efficiencies (>95%) even though there was slightly decreasing of efficiency after 15 minutes extraction time. This highly likely due to the chemistry of amine metal extraction. The influence of the diluents used, the aqueous media and ionic compound types, as well as the amine structure itself as TOA contributed to the observation made in the current study (Othman, 2006). It is suggested from Figure 9 that TOA has higher selectivity towards Cu(II) than Cd(II) ions.

4.0 Conclusions

Concurrent removal of Cd(II) and Cu(II) ions from wastewater through ELM system using two different carrier; D2EHPA and TOA has been studied. The results of extraction efficiency, EE% of using D2EHPA carrier was found to achieve up to 98% at 4 hour extraction time for both Cd(II) and Cu(II) ions. Meanwhile, at the same extraction time mentioned, using TOA as carrier could only obtained extraction efficiency approximately 61% for Cu(II) and 38% for Cd(II). This results prove that in comparison of both extractant, D2EHPA is highly preferable rather than TOA. On top of that, it was also found that D2EHPA and TOA are being more selective towards Cu(II) ions compared to Cd(II) which attained lower extraction

efficiency. A kinetic study of Cd(II) and Cu(II) transportation via ELM was also performed using a kinetic model. The rate constants of the reactions for Cd(II) was calculated by numerical analysis of experimental results with a k_1 value and average k_2 value of 7.66 h^{-1} and 22.95 h^{-1} for D2EHPA system, whereas for TOA system calculated k_1 value and average k_2 value were 0.11 h^{-1} and 2.49 h^{-1} . As for Cu(II) extraction, calculated k_1 value and average k_2 value for D2EHPA system were 3.66 h^{-1} and 2.87 h^{-1} , meanwhile 0.17 h^{-1} and 3.20 h^{-1} for TOA extractant. Model were found to be fitted with experimental data thus showing that both extractants are capable of removing Cd(II) and Cu(II) ions in an aqueous solution. As to conclude, D2EHPA is selected as the best ELM component referring to this study operation condition; 0.05wt% extractant, 0.95wt% kerosene as diluent, 1M of HCl as stripping agent, and feed phase condition at acidity pH 4.

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References

- Ahmad, A., Buddin, S., & Ooi, B., Extraction of Cd (II) ions by emulsion liquid membrane (ELM) using aliquat336 as carrier. *Am. J. Chem.*, 2015. 5: p. 1-6.
- Ahmad, A. L., Kusumastuti, A., Derek, C. J. C., & Ooi, B. S., Emulsion liquid membrane for heavy metal removal: An overview on emulsion stabilization and destabilization. *Chemical Engineering Journal*, 2011. 171(3): p. 870-882.
- Al-Saydeh, S. A., El-Naas, M. H., & Zaidi, S. J., Copper removal from industrial wastewater: A comprehensive review. *Journal of industrial and engineering chemistry*, 2017. 56: p. 35-44.
- Alaguraj, M., Palanivelu, K., & Velan, M., Removal of Cu (II) using emulsion liquid membrane. *International Journal of ChemTech Research*, 2009. 1(3): p. 722-726.
- Basualto, C., Poblete, M., Marchese, J., Ochoa, A., Acosta, A., Sapag, J., & Valenzuela, F., Extraction of cadmium from aqueous solutions by emulsion liquid membranes using a stirred transfer cell contactor. *Journal of the Brazilian Chemical Society*, 2006. 17: p. 1347-1354.
- Chakraborty, M., Bhattacharya, C., & Datta, S. (2010). Emulsion liquid membranes: Definitions and classification, theories, module design, applications, new directions and perspectives. In *Liquid membranes* (pp. 141-199): Elsevier.
- Gunatilake, S., Methods of removing heavy metals from industrial wastewater. *Methods*, 2015. 1(1): p. 14.
- Jaishankar, M., Mathew, B. B., Shah, M. S., & Gowda, K., Biosorption of few heavy metal ions using agricultural wastes. *Journal of Environment Pollution and Human Health*, 2014. 2(1): p. 1-6.
- Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., & Beeregowda, K. N., Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary toxicology*, 2014. 7(2): p. 60-72.
- Kamaruddin, M. A., Ismail, N., Osman, U. N., & Alrozi, R., Sustainable separation of Cu (II) and Cd (II) from aqueous solution by using solvent extraction technique with di-2-ethylhexylphosphoric acid (D2EHPA) as carrier: optimization study. *Applied Water Science*, 2019. 9(6): p. 141.
- Kumar, A., Thakur, A., & Panesar, P. S., A review on emulsion liquid membrane (ELM) for the treatment of various industrial effluent streams. *Reviews in Environmental Science and Bio/Technology*, 2019. 18(1): p. 153-182.
- Kusumastuti, A., Qudus, N., Anis, S., & Ahmad, A. L., Emulsion Liquid Membrane For Cadmium Removal: Determination of Liquid Membrane Components. *Journal of Physical Science*, 2018. 29: p. 227-242.
- León, L., León, G., Senent, J., & Guzmán, M., Kinetic study of copper (II) simultaneous extraction/stripping from aqueous solutions by bulk liquid membranes using coupled transport mechanisms. *Metals*, 2016. 6(9): p. 212.
- Norman, N. L., Separating Hydrocarbons With Liquid Membranes. United States Patent Office, 1968. 3: p. 410-794.
- Othman, N. (2006). *Selective Emulsion Liquid Membrane Extraction of Silver from Liquid Photographic Wastes*. Universiti Teknologi Malaysia,
- Peters, R. W., & Shem, L. (1993). *Separation of heavy metals: removal from industrial wastewaters and contaminated soil*. Retrieved from
- Pirmoradi, M., & Ashrafizadeh, S. N., Removal of nitrate from water by bulk liquid membrane. *Desalination and Water Treatment*, 2017. 58: p. 228-238.

- Religa, P., Gawroński, R., & Gierycz, P., Kinetics of chromium (III) transport through a liquid membrane containing DNNSA as a carrier. *International journal of molecular sciences*, 2009. *10*(3): p. 964-975.
- Samiey, B., Cheng, C.-H., & Wu, J., Organic-inorganic hybrid polymers as adsorbents for removal of heavy metal ions from solutions: a review. *Materials*, 2014. *7*(2): p. 673-726.
- Shah Buddin, M. M. H., Azrai, N. A., Roseli, E. A. R., Wahet, F., & Ahmad, A. L., Kinetic Study of Cd(II) Ions Extraction Using Trioctylamine as Carrier in Bulk Liquid Membrane (BLM). *Journal of Physical Science*, 2019. *30*(2): p. 157-168.
- Son-Ki, I., Hwa-Young, L., & Dong-Hui, L., Kinetic study of the extraction of copper(ii) by di(2-ethylhexyl)phosphoric acid in a Lewis-type cell. *Journal of Membrane Science*, 1988. *37*(2): p. 181-191.
- Yang, X., Fane, A., & Soldenhoff, K., Comparison of liquid membrane processes for metal separations: permeability, stability, and selectivity. *Industrial & engineering chemistry research*, 2003. *42*(2): p. 392-403.
- Zeng, L., Liu, Y., Yang, T., Yang, Y., & Tang, K., Simultaneously enhanced ELM selectivity and stability by difunctional additives for batch and continuous separation of Cd (II)/Cu (II). *Chemical Engineering Research and Design*, 2018. *140*: p. 261-272.