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Copper Extraction Using LIX 84 as a Mobile Carrier in the Emulsion Liquid Membrane Process

Izzat Naim Shamsul Kahar[a], Ahmad Syuhaib Ali[b], Norasikin Othman[a,b*], Norul Fatiha Mohamed Noah[a,b] & Sazmin Sufi Suliman[a]

[a]Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b]Centre of Lipids Engineering and Applied Research (CLEAR), Ibnu Sina Institute for Scientific and Industrial Research (ISI-SIR), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

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ABSTRACT

Extensive research has been conducted to address the growing global demand for copper by exploring effective methods of extraction and recovery across various industries. The emulsion liquid membrane (ELM) has emerged as a viable option for efficiently extracting and recovering metals from waste solutions. Due to its advantageous features, the extraction and recovery of copper from a simulated copper solution was investigated. In the ELM, various parameters can affect the stability and efficiency of copper extraction which include agitation speed, treat ratio (TR), stripping agent, and carrier concentration. However, certain parameters such as homogenizer speed, emulsification time, surfactant concentration, extraction time, and pH of the simulated feed solution were kept constant in this study. The most favourable parameters for achieving maximum copper extraction and recovery were determined such as TR of 1:3, agitation speed (250 rpm), LIX 84 (0.2 M) in kerosene as the carrier, and H_2SO_4 (0.5 M) as the stripping agent. Using these conditions, approximately 74% of the copper was extracted while 37% was recovered with an acceptable ELM stability indicated by a 20% membrane swelling. This research demonstrates the significant potential of the ELM process for extracting copper from wastewater generated by various industries.

***Keywords*: Emulsion liquid membrane, liquid waste, metal recovery, copper, LIX 84

1.0 INTRODUCTION

The World Health Organization stated that heavy metals are hazardous in nature [1]. The most prevalent heavy metals discovered in wastewater are nickel, cadmium, chromium, arsenic, copper, lead, zinc, and others, all of which pose health and environmental problems [2]. Excessive levels of heavy metals have negative consequences and alter the physicochemical properties such as pH, chemical oxygen demand and heavy metal limits in the environment [3]. According to Mansourri and Madani [4], heavy metals over allowable limits often have deleterious impacts on humans, other organisms, and the environment because most heavy metals even at low concentrations are toxic. The discharge of agricultural, industrial, and municipal wastewaters and sewage into rivers is a significant source of heavy metals released into the aquatic environment [5]. Copper is considered a significant heavy metal in various industries such as mechanical, electrical, electronic and others [6].

* Corresponding to: Norasikin Othman (email: norasikin@cheme.utm.my)
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Moreover, copper is also recognized as a valuable metal that was used for various applications such as electrical materials, telecommunications, power generation, petroleum refining, transportation, and industrial machinery parts [7] owing to its appealing physical properties including high electrical conductivity, malleability and ductility. Therefore, copper extraction and recovery from industrial waste effluents is a promising alternative approach for reducing reliance on primary mining. In addition, it is necessary to conserve valuable raw materials and preserve the environment from heavy metal contamination.

Many commercial methods for recovering valuable metals including copper from industrial waste have been developed such as ion-exchange, solvent extraction, precipitation, electrolysis, cementation, and membrane technology [8]. Ion-exchange offers a high treatment capacity and removal efficiency [9] while solvent extraction and precipitation is a well-known established separation technology [10]. The cementation process is easy to control because pH control is not necessary and electrolysis is an effective technology for recovering valuable metals [10, 11]. However, these methods possess their own limitations which could hinder the recovery rate of copper. ELM extraction processes have certainly some appealing features, including simplicity in operation, simultaneous extraction and stripping, high efficiency, and a larger interfacial area [12–15]. ELM extraction can also be customized so that their separation behaviours could be tailored based on the specific task, particularly in liquid membrane formulation. Moreover, the technology is also appealing when dealing with very dilute solutions [14, 15]. Hence, an attempt has been made to recover and reduce copper content from wastewater using liquid membrane technology. There are several studies that have been reported for the extraction of copper from sulfate medium using ELM as shown in Table 1. However, there is a lack of research on the copper recovery or enrichment of copper in the internal phase. To the best of our knowledge, no previous research has been conducted on the extraction, recovery, and enrichment of copper in the same studies simultaneously using the ELM process as conducted in this current study.

Despite the well-known benefits of the ELM process, there are a few industrial application limitations due to ELM stability issues. This demonstrates the importance of stability for a successful ELM process. The emulsion must be stable enough to withstand leakage but not so stable that it can be easily demulsified. [24]. The use of stabilizer [25], nanoparticle [26, 27], mixed surfactant [28, 29] or variable surfactant concentration [30, 31] can improve the stability of ELM.

This research focused on the extraction and recovery of copper from simulated copper solution in a sulfate medium using the ELM process. The affecting parameter such as agitation speed, treat ratio, concentration of carrier and stripping agent on the copper extraction and recovery were investigated. Additionally, the ELM stability was studied to ensure efficient extraction and recovery of copper.

Table 1 Extraction and recovery of copper from sulfate medium

[Carrier]	Diluent	[Surfactant] (w/v)	[Stripping agent]	Performance	Reference
LIX 84 I (0.04M)	Kerosene	Span 80 (3%)	H_2SO_4 (1.5M)	E = 88% R = –	[16]
LIX 54 (0.06M)	Toluene	Span 83 (8%)	H_2SO_4 (0.1M)	E = 85% R = –	[17]
D2EHPA (0.6M)	Hexane	Span 80 (4%)	H_2SO_4 (0.15M)	E = 95% R = –	[18]
D2EHPA (0.02M)	Kerosene	Span 80 (4%)	H_2SO_4 (0.5M)	E = 95% R = –	[19]
D2EHPA (0.1M)	Sunflower oil	Span 80 (3.25%)	HCl (1.44M)	E = >94% R = –	[20]
LIX 984N-C (0.2M)	Kerosene	Span 80 (3%)	H_2SO_4 (1.5M)	E = >80% R = –	[21]
LIX 664N (1.18M)	Kerosene	Span 80 (2%)	H_2SO_4 (1.85M)	E = 97% R = –	[22]
LIX 84 (0.4M)	Kerosene	Span 80 (3%)	H_2SO_4 (1.5M)	E = >80% R = –	[23]
LIX 84 (0.20M)	Kerosene	Span 80 (3%)	H_2SO_4 (0.5M)	E = 74% R = 37%	This study

Note that "–", E and R denotes not reported extraction and recovery, respectively.

2.0 METHODS

2.1 Materials

The ELM components comprise of diluent, carrier, surfactant and stripping agent. In this experiment, kerosene (Sigma-Aldrich) was used as a diluent to dissolve 2-hydroxy-5-nonylacetophenone oxime (LIX 84, 99% purity, Cognis) (carrier), The sorbitan monooleate or Span 80 (Sigma-Aldrich) and sulphuric acid (H_2SO_4, 98% purity, Merck) were used as surfactant and stripping agent in this experiment. Copper (II) sulphate pentahydrate ($CuSO_4{\cdot}5H_2O$, ≥98% purity, Sigma-Aldrich) diluted in distilled water was used as simulated solution. The chemicals used were all analytical grade reagents that were utilized without further purification.

2.2 Preparation of External Feed Solution

The simulated copper solution was prepared by dissolving the required amount of copper (II) sulphate pentahydrate in distilled water and the solution pH was measured using a portable Smart Sensor AS218 digital pH meter with accuracy ±0.05. The desired concentration of copper (100 ppm) in the simulated solution with pH= 4.53 was used as the main sample.

2.3 Emulsion Liquid Membrane Process

In order to conduct the ELM process, an equal volume of 5 ml of organic liquid membrane solution (3% (w/v) of Span 80 and LIX 84 in kerosene) and aqueous stripping solution (H_2SO_4) with 1:1 internal to organic (I:O) ratio were emulsified constantly at 12000 rpm using a Heidolph Silent Crusher homogenizer to achieve a stable primary (W/O) emulsion for 5 minutes. As such, carrier (0.02–0.2 M) and stripping agent (0.5–1.5 M) concentrations were varied to study their effect on ELM stability and the extraction process for copper. Then, the W/O emulsion that have been prepared was dispersed into the with external feed solution for 3 minutes for the formation of double (W/O/W) emulsion as a mixture. Afterwards, the mixture was poured into a separating funnel for 30 minutes to allow for complete phase separation. The volume of emulsion (before and after) the extraction process was measured to determine the apparent breakage/swelling. Meanwhile, the aqueous phase was then analysed using Perkin Elmer flame atomic absorption spectrometry. Additionally, liquid membrane viscosity was measured using a rotary viscometer. For the demulsification process, the loaded emulsion phase was heated for 24 hours at 70°C to achieve complete phase separation [32]. Table 2 depicts the parameter ranges investigated. In this study, the experiments were carried out at room temperature (26 ± 1˚C).

Table 2 Parameters of the extraction process and stability

Parameters	Range
Agitation speed, rpm	250, 300, 350
Treat Ratio	1:3, 1:4, 1:5, 1:6
[LIX 84], M	0.02, 0.1 , 0.2
[H_2SO_4], M	0.5, 1.0, 1.5

2.4 Analytical Procedure

The extraction, recovery performance, enrichment and membrane swelling/breakage were calculated using the mass balance principle and volume of the emulsion respectively using the following equation [13, 14]:

$$\text{Extraction (\%)} = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

$$\text{Recovery (\%)} = \frac{C_{internal}}{C_i \times \left(\frac{A}{B}\right)} \times 100 \tag{2}$$

$$\text{Enrichment} = \frac{C_{internal}}{C_i} \tag{3}$$

$$\text{Swelling/Breakage (\%)} = \frac{V_f - V_i}{V_{internal}} \times 100 \tag{4}$$

In the equations, C_i represents the concentration of copper ions in the external phase before extraction, C_f represents the concentration of copper ions in the external phase after extraction, and $C_{internal}$ indicates the concentration of copper ions in the internal phase after the demulsification process. A represents the volume of the external aqueous phase (mL) and B represents the volume of the internal phase (mL). Meanwhile, V_i is the volume of external phase before extraction, and V_f is the volume of external phase after extraction while $V_{internal}$ indicates volume of the internal phase. In this study, the experiments were conducted in triplicate with standard deviation less than 5%.

3.0 RESULTS AND DISCUSSION

3.1 Effect of Agitation Speed

The effect of agitation speed on W/O/W emulsion stability is shown in Figure 1. The result shows that the emulsion swelling increases gradually from 20 to 30% when the agitation speed increases up to 350 rpm. This result is in accordance with Sulaiman *et al.* [33] who stated that the higher agitation speeds can cause rapid emulsion globule to swell and rupture tread-off due to an increase in the rate of water transport into the emulsion. As a result, more water molecules were transported from the external phase into the internal phase which is also in agreement with Kumbasar [34] and Noah *et al.* [35]. Therefore, 250 rpm was selected as the best agitation speed in this study for further experiment.

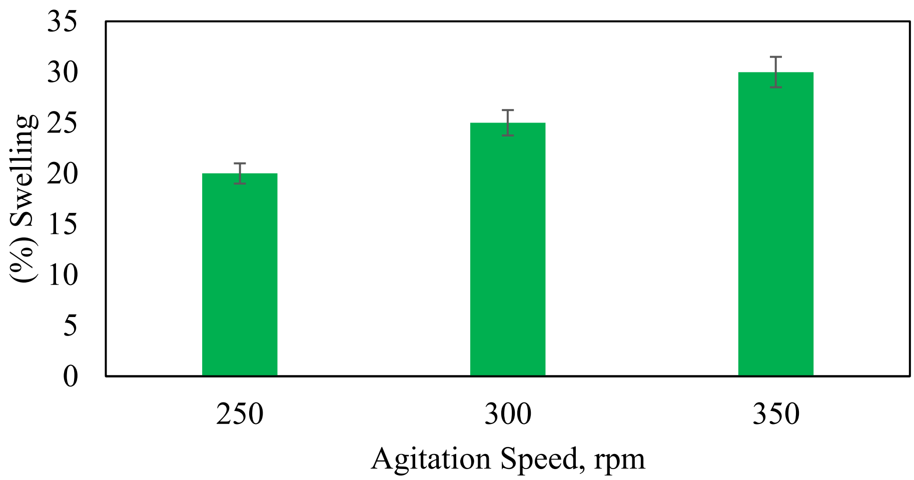

Figure 1 Effect of agitation speed on W/O/W emulsion stability in copper extraction (Experimental conditions: [LIX 84] = 0.02 M; [H_2SO_4] = 0.5 M; [Span 80] = 3% (w/v); I:O = 1:1; TR = 1:3; Emulsification time = 5 min; Homogenizer speed = 12000 rpm; Extraction time = 3 min)

3.2 Effect of Treat Ratio

It is critical to choose a suitable treat ratio (TR) because it controls the interfacial mass transfer across the ELM. Figure 2 shows the effect of the treat ratio towards W/O/W emulsion stability. The results show that increasing the TR from 1:3 to 1:4 has little effect on emulsion swelling, indicating that the ELM system has achieved effectiveness of stability. However, the emulsion swelling increases up to 30% when the TR is increased from 1:4 to 1:6 which is in accordance with results presented by Chiha *et al*. [18]. According to Datta *et al*. [36], a high TR is not preferred because it provides a larger size with a smaller contact area which is in agreement with Hasan *et al*. [37]. Furthermore, a high TR results in a larger emulsion size and may result in membrane breakage. When the TR is too high, the membrane breaks due to the difference in osmotic pressure causing the emulsion globule to rupture [30]. Thus, the TR of 1:3 is chosen as a suitable TR to be used in the next experiment.

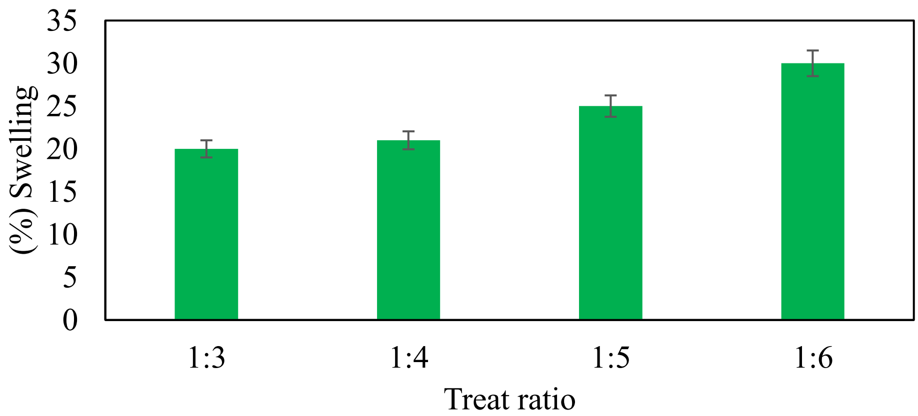

Figure 2 Effect of treat ratio on W/O/W emulsion stability in copper extraction (Experimental conditions: [LIX 84] = 0.02 M; [H_2SO_4] = 0.5 M; [Span 80] = 3% (w/v) ; I:O = 1:1; Agitation speed= 250 rpm; Emulsification time = 5 min; Homogenizer speed = 12000 rpm; Extraction time = 3 min)

3.3 Effect of Carrier Concentration

The carrier assists the extraction of solutes from an aqueous solution via a liquid membrane or into an organic phase. Furthermore, carrier concentration influences transport behaviour, extraction efficiency, membrane stability and selectivity in ELM processes [38]. In this study, the influence of LIX 84 concentration on copper extraction and emulsion stability is depicted in Figure 3. The results show that increasing the LIX 84 concentration from 0.02 to 0.2 M resulted in an increase in copper extraction from 30 to 74%. These results align with the research conducted by Hao and Ho [39], who suggest that higher carrier concentrations enhance the extraction capacity, enabling a greater partitioning of copper into the organic membrane phase. In addition, the result shows that liquid membrane viscosity increases from 55.4 to 75.1 cP with the increase of LIX 84 concentration as depicted in Figure 4. According to Kulkarni *et al.* [40], high liquid membrane viscosities improve emulsion stability by restraining water transport into the internal phase which is in accordance with Noah *et al.* [41]. As a result, the water molecule transport from the external to the internal phase will be reduced. However, 20% of emulsion swelling is observed in all studied ranges of LIX 84 concentration indicating that under this favourable condition it gives an insignificant effect on W/O/W emulsion stability. Based on the results discussed considering the extraction performance and swelling condition, 0.2 M of LIX 84 is recommended as a suitable amount of concentration for copper extraction.

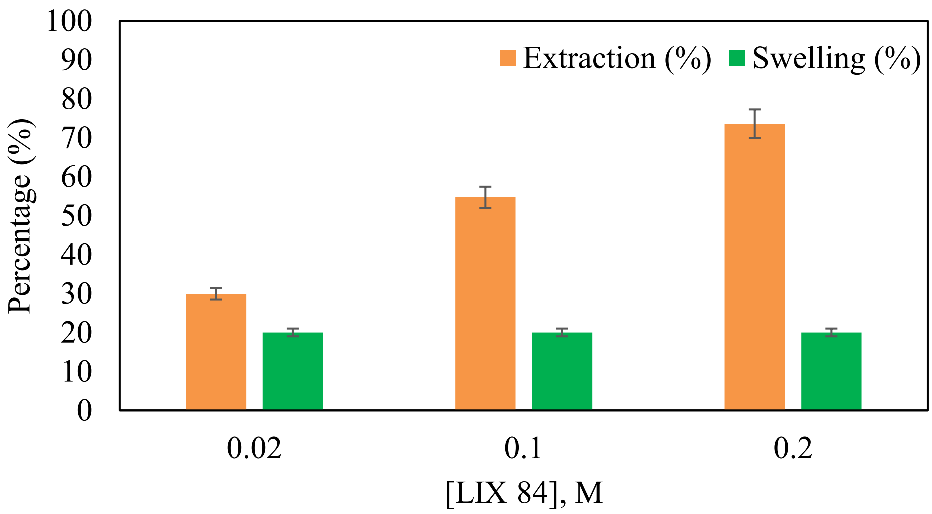

Figure 3 Copper extraction and W/O/W emulsion stability at various LIX 84 concentrations (Experimental condition: $[H_2SO_4]$ = 0.5 M; [Span 80] = 3% w/v; I:O = 1:1; TR = 1:3; Agitation speed = 250 rpm; Emulsification time = 5 min; Homogenizer speed = 12000 rpm; Extraction time = 3 min)

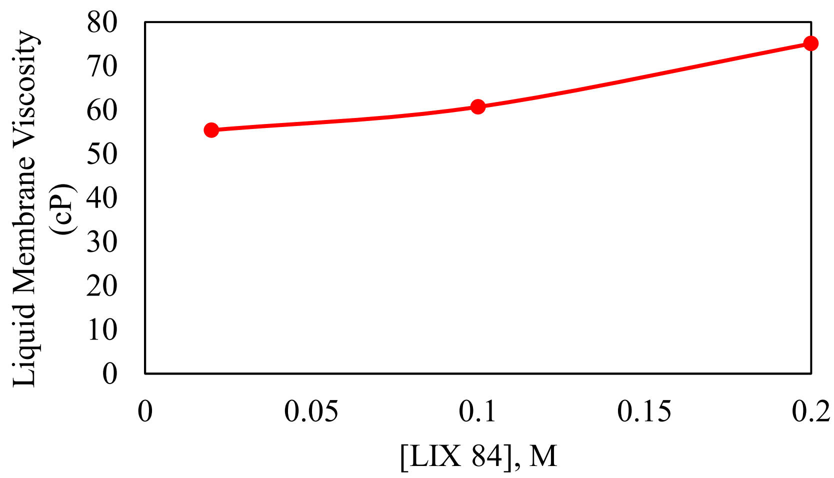

Figure 4 Effect of LIX 84 concentration on liquid membrane viscosity

3.4 Effect of Stripping Agent Concentration

The effect of H_2SO_4 concentration on the extraction, recovery, W/O/W emulsion stability and the enrichment of copper were depicted in Figure 5. The results show that the emulsion swelling observed was less than 25% but the extraction of copper decreased from 74 to 46%. After the extraction process, the loaded emulsion phase was taken to undergo a demulsification process for the recovery of copper where the recovery of copper decreased from 37 to 18% with the increase in the H_2SO_4 concentration.

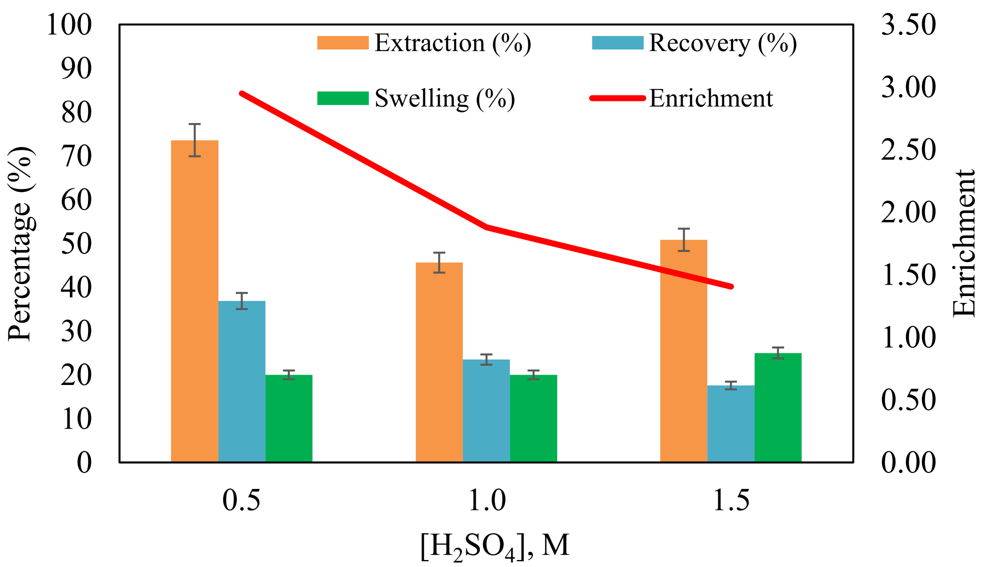

Figure 5 Copper extraction, recovery, and W/O/W emulsion stability at various H_2SO_4 concentration (Experimental condition: [LIX 84] = 0.2 M; [Span 80] = 3% w/v; I:O = 1:1; TR = 1:3; Agitation speed = 250 rpm; Emulsification time = 5 min; Homogenizer speed = 12000 rpm; Extraction time = 3 min)

In addition, the enrichment of copper was also decreased from 2.95 to 1.41 times with the increase in H_2SO_4 concentration. Goyal *et al.* [42] claimed that an increase in the internal phase concentration resulted in a higher pH difference between the external and internal phases. This, in return, increases the ionic strength difference between the two phases. As a result, water molecules were forced to move from the external to the internal phase, destabilizing the emulsion and decreasing copper extraction, recovery, and enrichment. This result is aligned with a previous study reported by Sabry *et al*. [43] in which emulsion swellings increase due to osmosis as the H_2SO_4 concentration exceeds 1.0 M, which in return, dilutes the internal phase. Furthermore, a low pH difference between the internal and external phases should be maintained to avoid swelling [44]. The best condition for stability, extraction, and recovery process of copper from simulated waste solution with a pH of 4.53 is tabulated in Table 3.

Table 3 Summary of the best condition for extraction and recovery of copper from sulfate medium

Parameters	Experimental Condition
Agitation Speed, rpm	250
Treat Ratio	1:3
[LIX 84], M	0.2
[H_2SO_4], M	0.5

4.0 CONCLUSION

The copper extraction and recovery from simulated wastewater using ELM were studied by manipulating several parameters. A high copper extraction (74%), recovery (37%) and enrichment (2.95 times) from aqueous waste solutions were achieved with 0.5 M stripping agent (H_2SO_4), 0.2 M carrier (LIX 84) and a TR of 1:3 with an agitation speed of 250 rpm. Thus, the ELM process could be beneficial to the industries for treating copper from wastewater even at very low metal concentrations. In addition, the metals can be concentrated or enriched from a very dilute stream from various industries for the purpose of recovery. In order to ensure the high recovery and stability of ELM can be enhanced, further studies are recommended.

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