



Experimental results and optimization via the design of experiment (DOE) of the copper ion recovery from aqueous solutions using emulsion liquid membrane (ELM) method

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ABSTRACT

Copper ion recovery from aqueous solutions is of particular importance due to the need for an environment free of industrial pollution. The emulsion liquid membrane (ELM) has a high potential to recover and remove metal ions. In this research, first, using a liquid–liquid extraction method, the parameters affecting the extraction of copper ion were investigated. Then, by identifying the influential parameters on the test process, using the ELM method, the parameters affecting the copper ion separation were examined using a bi-functional polyethylene glycol carrier. In addition, the design of the experiment with Design Expert 10 software was used to investigate and compare with laboratory results. For this purpose, the central composite design method was used to study the factors affecting the copper ion separation. In conclusion, by optimizing the operational conditions, about 99% extraction efficiency for copper ion was achieved.

Keywords: Emulsion liquid membrane (ELM); Liquid–liquid extraction; Design of experiment (DOE); Central composite design (CCD); Copper ion recovery

1. Introduction

Currently, having a pollution-free environment is a major concern of researchers in the field of biotechnology. Researchers have attempted to develop methods to prevent further damage to the environment by implementing ways to mitigate pollution. Industrial wastewater containing heavy metals is one of the most important pollutants that cause significant damage to our environment [1].

Copper is one of the widely used metals in heavy industries, which can be found in the untreated wastewater streams. Since copper does not decompose in the biological systems and environment, it accumulates in soil and

water and harms the ecosystem. Therefore, there are strict environmental regulations to strip industrial wastewater from the copper before releasing them to the environment. Considering the importance of this element in various industries, studying the extraction of this metal from aqueous solutions to prevent the environmental problems caused by effluents is necessary [2].

So far, various methods such as chemical deposition, ion exchange, coagulation and flocculation, electrochemical purification, adsorption, solvent extraction (SE) and membrane technology have been utilized for the removal of heavy metals [3]. Among the mentioned methods, membrane

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processes have become of particular importance in the separation field [4].

Emulsion liquid membrane (ELM) as one of the membrane processes has important advantages such as high mass transfer rates and stability (caused surface-active reagents such as surfactants). Norman Li introduced ELM for the separation of hydrocarbons, for the first time in 1962. Since then, there have been many published research on the separation of heavy metals from aqueous solutions using ELM [5].

Any ELM is often produced by vigorous agitation of two immiscible fluids forming an emulsion (e.g. water in oil, W/O) followed by gentle dispersion into the third phase (to form W/O/W emulsion). It should be noted that the membrane phase consists of the oil phase (including a surfactant and a carrier) which separates its internal contents (water and stripper reagent), from the external phase, (water and heavy metals). During synthesis, surfactants and additives are added to the mixture to prevent emulsion break and increase the membrane stability before and during the extraction process. The extraction process is relatively quick and takes about a few minutes to complete. Then, the W/O/W emulsion is processed in the phase settling step to separate most of the stripped phase (wastewater) from the bottom of the container. Then the W/O/W globules on the surface of the liquid are sent to the de-emulsification unit, and phases are separated. Finally, the oil phase is recycled [6]. Fig. 1 shows an overview of the synthesis process of ELM.

So far, much research has been done to separate copper ions from aqueous solutions using ELM. Martin and Davies [7] investigated the feasibility of using emulsion membranes

for copper ion separation and investigated factors affecting mass transfer such as the membrane composition, pH of aqueous phases, types of acid and stirring rate. Kondo et al. [8] separated copper ion by ELM using hydrochloric acid in the internal phase and benzoyl acetone (as the copper chelating agent) in the organic phase. Lorbach and Marr [9] compared the copper separation efficiency via ELM using stearic acid and LIX 64N carriers. They concluded that the emulsion formed by LIX 64N was more stable.

ELM has been utilized for extraction and purifications on many materials from aqueous solutions such as heavy metals [10–12], drugs [13,14] and organic toxins such as phenol [15].

There are some data on the magnitude of influence of parameters such as initial copper concentration, pH, carrier concentration, emulsifier concentration, membrane viscosity and composition of the receptor phase (internal phase). However, it is challenging to conduct an explicit evaluation of parameters influencing the separation efficiency. Therefore, utilizing bi-functional emulsifiers that act both as carrier and emulsifier is desirable and promotes the simplicity of the system. Kakoi et al. [16] showed that the use of bi-functional emulsifiers at low concentrations, aside from improving the stability of the emulsion, it also enhances the extraction rate. For example, two types of C18/C18Δ9 QA and 2C18Δ9 QA bi-functional emulsifiers have been shown to be much more effective in emulsion stability than conventional Span 80 and PX100 commercial emulsifiers [17]. Polyethylene glycol (PEG) is a strong candidate as a bi-functional emulsifier due to its low cost and availability. However, the main problem with PEG is its solubility in the oil phase solvent (diluent). Therefore, high-density solvents such as dichloroethane or chloroform should be present in the oil phase to

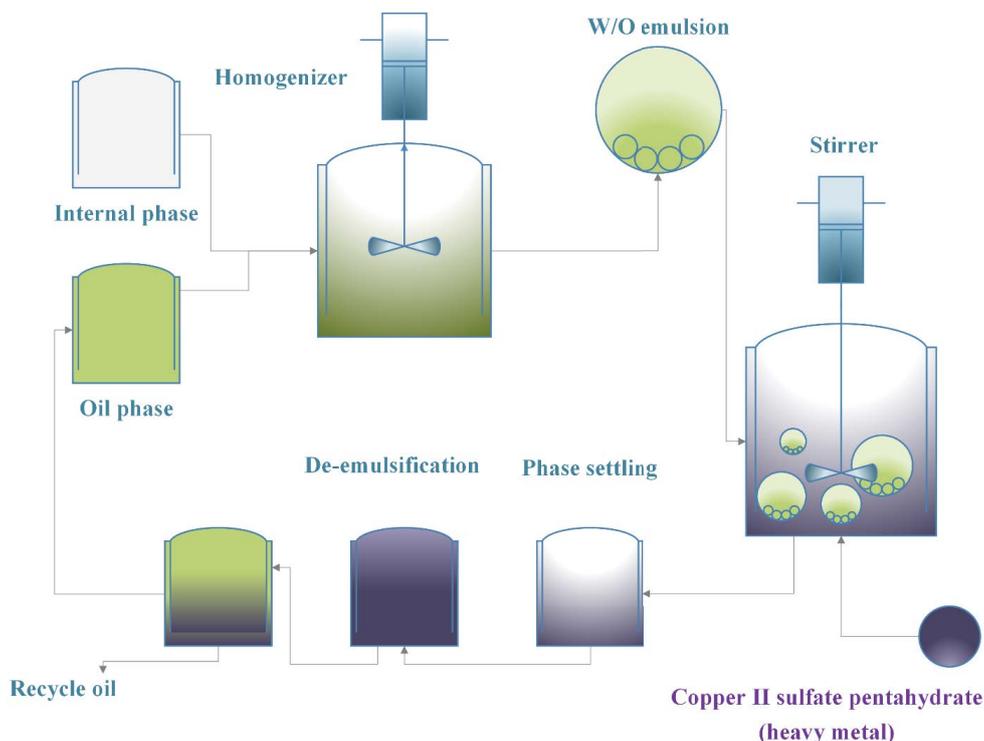


Fig. 1. Schematic of the emulsion liquid membrane process.

enhance PEG solubility [18]. In general, the type, molecular structure and mass of the bi-functional carriers have a great impact on the extraction and selectivity process. However, unfortunately, there has been limited work on such carriers.

Altogether, the response surface methodology (RSM) is used to investigate the levels of influencing factors. RSM combines both statistical and mathematical approaches, which are useful for the development, improvement and optimization of products and processes. There are several ways to design experiments in RSM, such as central composite design (CCD) and Box–Behnken design (BBD). CCD is the most commonly used RSM that considers 5 levels of each factor's surface and is a highly rotational method [19].

In the past, most research has been done on ELM using one factor at the time method (OFAT), but currently, due to the effectiveness of the design of experiment methods (DOE), researchers have considered these methods for designing experiments. For example, Asadian and Ahmadi [10] investigated the extraction of gallium from chloride solutions by ELM using an optimized BBD method. In another study, Rosly et al. [15] investigated the effect and optimized the phenol removal parameters using ELM via experimental design methods. In a comprehensive study by Benderrag et al. [12], the extraction of Cd(II) ions by ELM using Triton X-100 as a degradable surfactant was investigated using CCD.

To the best of our knowledge, no research has yet been done on the ELM separation of copper ions using PEG carrier by implementing the DOE. For this purpose, in this research, the extraction of copper metal ions from aqueous solutions method using PEG with potassium thiocyanate (KSCN) and ammonium thiocyanate (NH_4SCN) ligands under different operating conditions is studied for both via the conventional SE and ELM methods. Besides, to compare the results of OFAT and DOE methods in copper recovery experiments using ELM, Design Expert 10 software was used, and an empirical equation was reported. Then the achieved empirical equation via CCD to attain maximum recovery of copper ion.

2. Materials and methods

2.1. Reagents

Copper(II) sulfate pentahydrate (Merck, Germany) with a molecular weight of 249.68 was used in all experiments to prepare the feed solution as the external phase. Sodium hydroxide (NaOH) solution (Merck, Germany) was used as the internal phase. Bi-functional PEG (Sigma-Aldrich, molecular weight (MW) ~20,000, USA) was used as the carrier. Tween® 20 (Germany) (polysorbate, Merck, Germany) was used as the surfactant. 1,2-dichloroethane (Merck, Germany) was used as the organic phase, KSCN and NH_4SCN and KSCN (Merck, Germany) were used as ligand forming agents. Sulfuric acid (Merck, Germany) was used to adjust the pH. Deionized water was also used in all solutions.

2.2. Apparatuses

The pH meter (3505-meter, Jenway, USA) was used to measure the pH of aqueous solutions. HIELSCHER UIP1000hd laboratory (Germany) ultrasound homogenizer

with variable power was used to make emulsions. In all experiments, a SHIN SAENG model SDS-41D (Korea) laboratory mixer was used to stir the solutions. Perkin-Elmer's AA300 atomic absorption device was used to determine the concentration of copper ions in the feed samples. Fourier-transform infrared (FTIR) spectroscopy (Bruker Tensor 27, USA) was used to identify the bonds and chemical structure of the samples. The samples were placed in a spectrophotometer, and the spectra of each sample were obtained at wavelengths of 200 to 4,000 cm^{-1} . The KOKASAN H-11n (Japan) centrifuge was used to precisely separate the emulsion and the organic phase from the external phase. For weighing materials in all experiments, RADWAG Model AS220/C digital scale with 0.001 g accuracy was used. In all experiments, a 500 mL glass container was used as the extraction medium. Stainless steel with four flat diagonal blades and a 4° angle was used to stir the solutions while extracting. Fig. 2 shows an overview of the experimental set up used in this study. Samples were taken at certain time intervals from the aqueous phase in the SE and ELM experiments using disposable syringes (~10 cc). To perform the phase mixing in the experiments, and to maintain isothermal conditions, a shaking water bath (Model SWBR27, Shel Lab Co.) was used.

2.3. Preparation of solutions

2.3.1. External phase (feed solution) and membrane phase

A solution of copper(II) sulfate pentahydrate (100 ppm) was used as the external phase (feed phase). Sulfuric acid (1 M) and sodium hydroxide (1 M) solutions were used to adjust the pH of the feed phase. Either KSCN or NH_4SCN as the ligand-forming agent was added to the feed phase.

1,2-dichloroethane was used as the solvent; PEG was used as the carrier and the emulsifier in the membrane phase. Moreover, Tween® 20 (Germany) emulsifiers and sodium hydroxide stripping agents were also added to ELM.

2.3.2. Emulsion liquid membrane

The organic solution was made by mixing 1,2-dichloroethane and PEG at 150 rpm for 3 min. Then the internal aqueous phase containing the sodium hydroxide (stripping agent) was gradually added to the stirring solution at 600 rpm for 3 min. The mixture was then subjected to ultrasound at 75 W for 10 min to provide W/O emulsion. All the above steps were performed at the controlled temperature. The emulsions containing two emulsifiers were prepared by the addition of Tween® 20 hydrophilic emulsifiers to the W/O emulsion and stirred for 3 min. Finally, the W/O emulsion was slowly added to the stirring feed solution to form ELM.

2.4. Extraction experiment

2.4.1. SE experiments

The experiments were performed by mixing 15 mL of the external (feed) phase and 15 mL of the organic phase with the shaker. Samples were taken with 10 mL disposable syringes and centrifuged to separate the organic and aqueous phase. Finally, the atomic adsorption

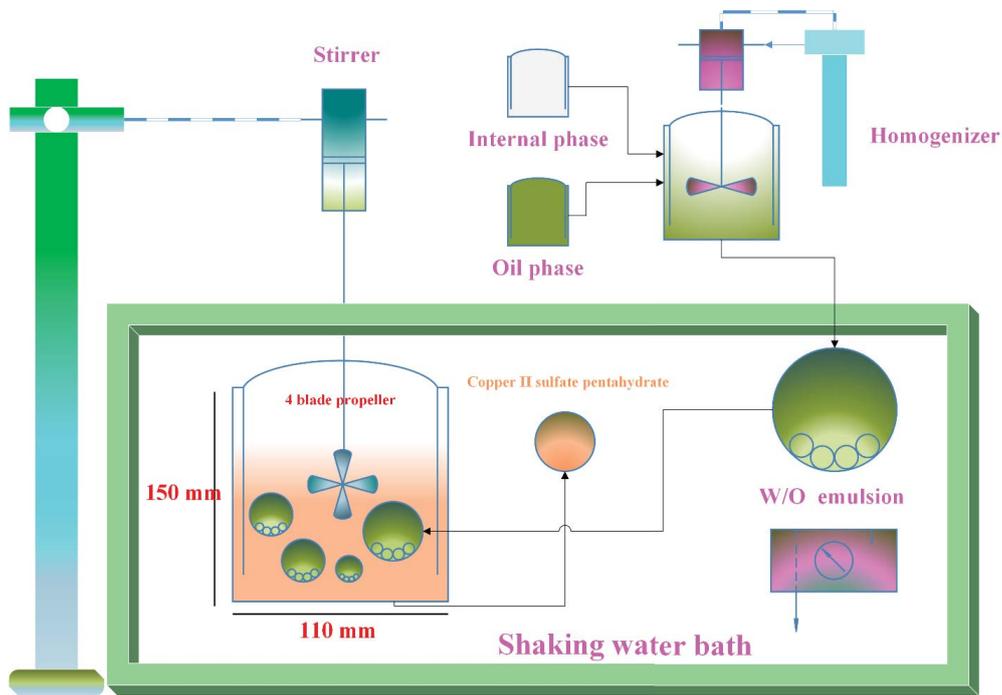


Fig. 2. Schematic representation of the experimental setup.

spectrophotometer was used to measure the amount of copper ion extraction. The experiments were conducted at a controlled temperature (30°C) [20].

2.4.2. ELM experiments

Initially, the external phase (feed) was prepared by diluting a concentrated copper sulfate solution with deionized water (~100 mL), and its pH was adjusted. Then the W/O emulsion phase is added to the stirring external phase to form ELM. If the emulsion phase composition was not suitable or the stirring conditions were not selected correctly, the emulsion swoll and formed a continuous phase, and the extraction halted. The location of the stirrer was important to uniformly disperse the ELM while avoiding its breakage and its accumulation on the surface of the feed solution. The samples taken at specific times, after separating their emulsion layer was analyzed using atomic adsorption spectrophotometer [21].

2.4.3. Analytical procedure and calculation

Atomic adsorption spectrophotometer was used to determine the concentration of different metals in solutions [21,22]. Atomic absorption apparatus was calibrated by standard solutions of 5, 10 and 15 ppm. All samples were diluted 10 times before being measured by the device. The percentage of extraction ($E\%$) was calculated from the following relation [21]:

$$E\% = \left[\frac{C_0 - C_t}{C_0} \right] \times 100 \quad (1)$$

where C_0 is the initial concentration of metal ions in the external solution and C_t is the concentration of metal ions in the treated solution after time interval t .

The influential factors and their considered values (level) for the SE and liquid membrane extraction experiments are reported in Tables 1 and 2, respectively.

3. Result and discussion

3.1. Separation of copper ions with the SE method

3.1.1. Effect of carrier concentration

In the SE process, PEG molecules accumulated on the interface of the organic and aqueous phases. Then PEG transported the captured copper molecules in the feed side by reacting with them and forming a complex to the organic phase [23].

The type and molecular mass of bi-functional carriers have a great impact on the extraction and selectivity process. So far, limited work has been done on such carriers [24]. Bi-functional agents act in a unique way; their hydrophilic head reacts with metallic ions. They also manipulate the hydrophilicity of the metal complexes and promote the complex hydrophilicity [24]. In acidic solution, copper ions reacted with thiocyanate ligands (SCN) and formed $\text{Cu}(\text{SCN})_4^{2-}$. The resultant then complexed with PEG [25].



In order to investigate the effect of carrier concentration, different PEG solutions with concentrations ranging from 0 to 1.2 mm in the organic phase were synthesized. The solutions contained either KSCN or NH_4SCN ligands

Table 1
Levels and values of factors considered in emulsion liquid membrane (ELM) tests

Sample	Symbol	High (-1)	High (+1)
Feed phase pH	A	2	6
H ₂ SO ₄ concentration, mol/L	B	0.1	2
Surfactant concentration, wt. %	C	1	6
Carrier concentration, wt. %	D	0.1	0.5
Feed phase/emulsion volume ratio	G	1	10
Feed phase concentration, ppm	H	100	500
W/O/W emulsion stirring time, min	J	1	20
W/O/W emulsion stirring speed, rpm	K	250	650

Table 2
Levels and values of factors considered in solvent extraction (SE) tests

Sample	Symbol	High (-1)	High (+1)
Feed phase pH	A	1	6
Surfactant concentration, wt. %	B	0	4.5
Mixing time, min	C	0	50
Carrier concentration, wt. %	D	0	1.2
Ligand concentration (M), mol	F	0.1	0.4
Type of ligand (M), mol	J	0	0.6

separately. As shown in Fig. 3a, where the carrier concentration is zero, for both ligands used, the extraction rate is negligible (~1%–4%). With an increase in the PEG concentration up to 0.2 mm, the extraction rate increases ~80% for the KSCN and ~60% for NH₄SCN ligands. As the concentration of the carrier increases, the number of molecules capable of extracting the desired ions increase and thus, the percentage of extraction is elevated. Therefore, it is evident that the concentration of PEG is directly related to the extraction efficiency.

3.1.2. Effect of ligand concentration

One important parameter in the process of extraction of metal ions by organic solvents is the number of ligands that surround the metal ions. This number determines the number of carrier molecules that are bonded to the metal ions and expresses the stoichiometry of the system [26]. Fig. 3b demonstrates the effect of ligand concentration on copper extraction. Experimental results were obtained by selecting three levels of 0.1, 0.2 and 0.4 M for NH₄SCN ligand at different pH and after 15 min of extraction process at 25°C. According to the results, an increase in the amount of ligand increased extraction efficiency. In fact, at low ligand concentrations, a small number of copper cations were complexed, and most of them remained as free cations in the aqueous phase. These free cations remained in the aqueous phase and were less likely to enter the PEG containing organic phase [2]. As the concentration of the ligand increased, due to the equilibrium reaction of the complex formation, most of the free hydrophilic copper cations in the aqueous solution were converted to Cu(SCN)₄²⁻ complexes, with less hydrophilic properties. The resulting complexes were more

inclined towards the organic phase. As a result, the rate of copper extraction increases as the concentration of ligand increases from the feed phase to the organic phase.

As demonstrated in Fig. 3b, as the concentration of the ligands increases from 0.1 to 0.2 M, there is a 20%–40% increase in the extraction rate at different pHs. In addition, with an increase in the concentration of the ligands from 0.2 to 0.4 M, the extraction rate increased by ~30%–40% at different pH. Fig. 3b, at concentrations above 0.4 M the process of copper complex formation is almost complete; the increase in ligand concentration does not have much effect on the rate of complex formation. Therefore, the extraction rate does not very much. Nevertheless increasing the ligands concentrations past 0.4 M, due to promoting the steric hindrance did not improve copper capture.

3.1.3. Effect of ligand type

The effect of ligand type (KSCN and NH₄SCN) on the extraction of copper ions by SE process, at different concentrations of PEG at pH = 2 and aqueous to organic phase ratio 1:1 at 25°C is shown in Fig. 3c. It can be seen from Fig. 3c, both ligands were capable of achieving a high percentage of separation. However, in experiments where the SCN⁻¹ ions were sourced from KSCN, the extraction rate was always between 5% and 22% higher than when the SCN⁻¹ ions were obtained from NH₄SCN. This difference could be related to a higher dissociation constant of KSCN [27,28].

3.1.4. Effect of stirring time

Since extraction is a dynamic process, the final extracted percentage depends on the stirring time. If a system is at

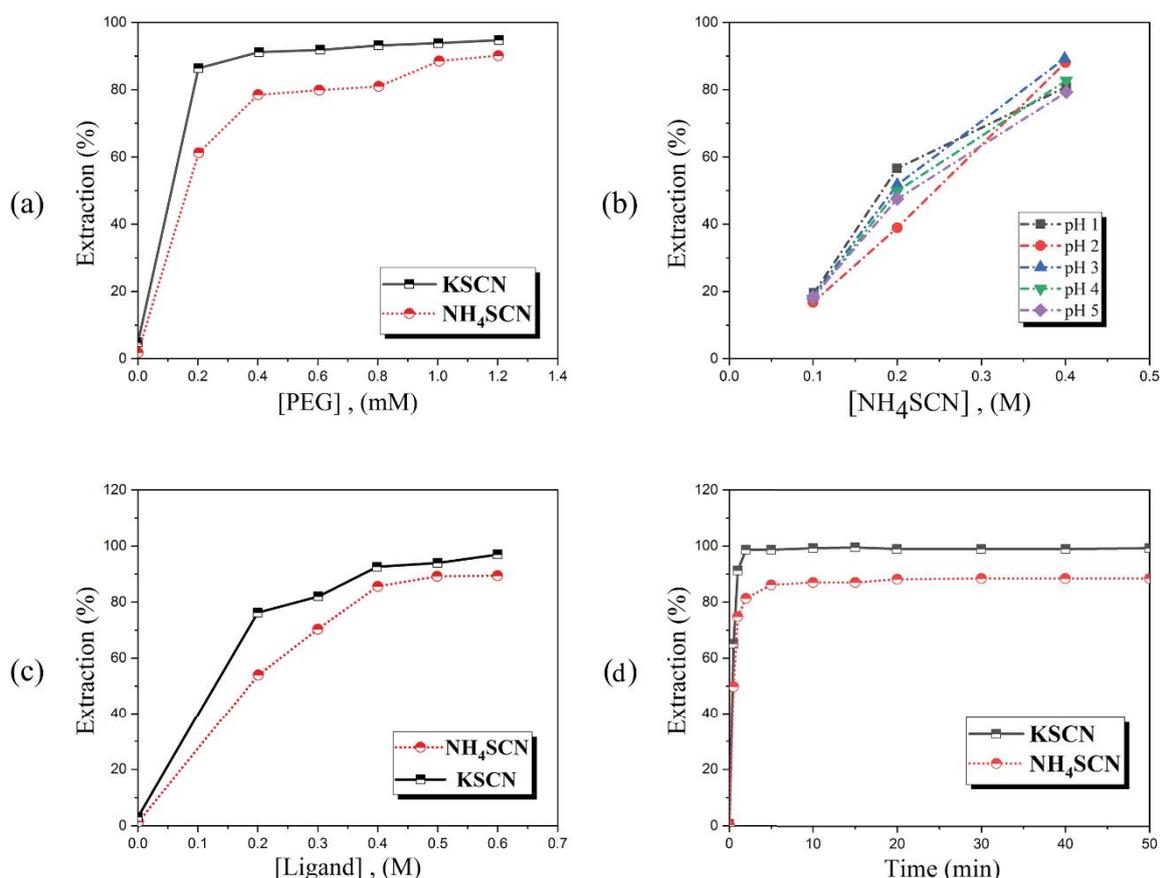


Fig. 3. Effect of (a) changes in PEG concentration (pH = 2; [KSCN] = [NH₄SCN] = 0.4 M; 1:1 A:O v/v; time: 15 min), (b) ligand concentration (initial Cu 100 ppm; [PEG] = 0.4 mM; 1:1 A:O v/v; time: 15 min), (c) type of ligands (initial Cu 100 ppm; [PEG] = 0.4 mM; pH: 2; 1:1 A:O v/v; time: 15 min), and (d) mixing time on extraction rate by SE process (initial Cu 100 ppm; [KSCN] = [NH₄SCN] = 0.4 M; [PEG] = 0.4 mM; pH: 2; 1:1 A:O v/v).

its equilibrium, there would not be any changes in the extraction value vs. stirring time, and the extracted value is the maximum attainable separation. However, if the stirring time is less than the equilibrium time, maximum copper extraction will not be carried out by the organic phase [29]. Fig. 3d demonstrates the effect of stirring time on copper extraction using KSCN and NH₄SCN ligands. In addition, the extraction percentage in the aqueous medium is approximately constant after about 5 min. Hence, it can be concluded that the copper extraction kinetics are relatively quick, and the system gets to the equilibrium after 5 min.

3.1.5. Effect of feed phase pH

The extraction of copper from aqueous solutions containing NH₄SCN ligands (0.4 M) in the pH range of 1–6 and after 15 min of experiments is shown in Fig. 4a. As shown in Fig. 4a, the highest extraction rate was obtained at pH 2. The extraction rate decreased with an increase in pH from 2 to 5, possibly due to a decrease in the complex formation rate.

Nevertheless, at acidic pH (~1) the extraction rate decreased again. This drop was attributed to the protonation of the thiocyanate ion in highly acidic environments. In other words, H⁺ competed with Cu⁺ for association with

thiocyanate ions. Hence, the copper-thiocyanate complex formation decreased, and the copper extraction rate was lowered [25]. At pH above 2, some of the copper cations precipitated as hydroxide and did not participate in complex formation. Therefore, the equilibrium extraction concentration decreased [30].

The effect of pH on the copper extraction percentage at different concentrations of NH₄SCN ligands is presented in Table 3. The concentrations varied from 0.1 to 0.4 M, while pH ranged from 1 to 5. All samples were taken after 15 min of stirring time. In general, according to Table 3, the maximum percentage of copper extraction at any ligand concentration was always obtained in aqueous solutions with pH = 2. Therefore, the optimum pH for copper extraction from the feed was found to be ~2.

3.1.6. Effect of emulsifier concentration

The effect of emulsifier (surfactant) concentration (0%–4.5% vol.) in the organic phase on the extraction rate is shown in Fig. 4b. Emulsifier reduces the interfacial tension between the contact surfaces of the phases, and facilitates mass transfer [31]. Tween® 20 emulsifiers have been used for this work. The results showed that surfactants

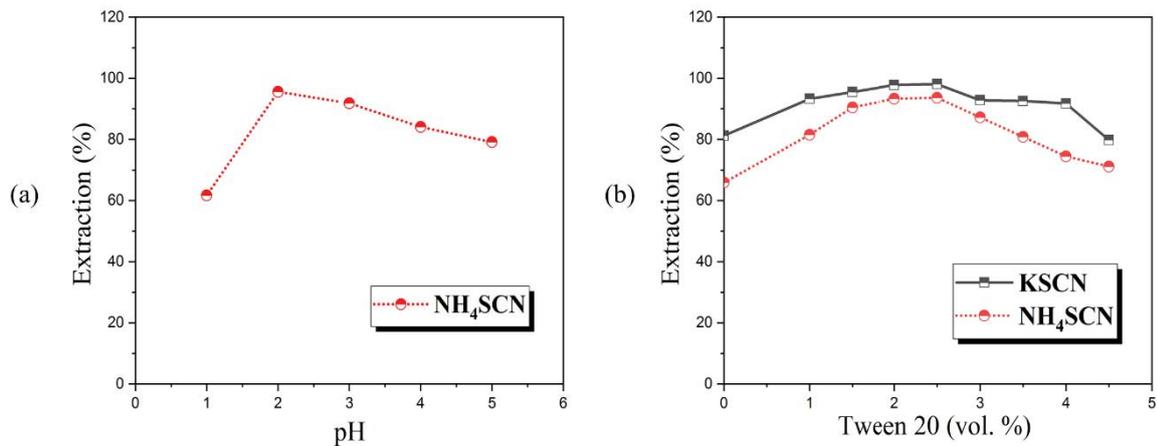


Fig. 4. Effect of (a) pH changes (initial Cu 100 ppm; [PEG] = 0.4 mM; [NH₄SCN] = 0.4 M; 1:1 A:O v/v; time: 15 min) and (b) emulsifier concentration (initial Cu 100 ppm; [PEG] = 0.4 mM; pH = 2; [KSCN] = [NH₄SCN] = 0.4 M; 1:1 A:O v/v; time: 15 min) on extraction rate in SE process.

Table 3

Investigation of the pH effect on the copper extraction (100 ppm initial) for different NH₄SCN ligands concentration (~0.1 to 0.4 M)

pH	Ligand concentration (M), %		
	0.1	0.2	0.4
1	19.02	48.80	61.44
2	18.50	50.10	95.30
3	19.00	51.80	91.60
4	16.50	38.97	84.50
5	19.70	39.14	79.80

with concentrations up to 2.5 vol.% in the organic phase increased the extraction rate by 16% and 27%, using NH₄SCN and KSCN, respectively. However, increasing the surfactant concentration beyond 2.5% resulted in the formation of a layer between two phases, thereby reduced the extraction rate [5,17].

3.2. Separation of copper ions with ELMs

3.2.1. Mechanism of the copper ions separation

3.2.1.1. Facilitated mass transport by carrier agent

The facilitated mechanism was used to investigate the mass transfer mechanism of metal ions separation using ELM. The facilitated mechanism is composed of the following steps:

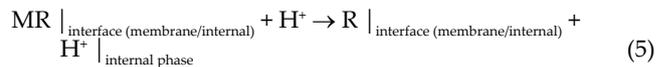
- Mass transfer in the formed film extended from the bulk of the external phase to the interface of the external phase and membrane phase (organic phase);
- Mass transfer at the interface of the external phase and the membrane phase where the reaction of metal ions (Mⁿ⁺) with the carrier (HR) occurs;



- Mass transfer of the formed complex (MR) through the membrane phase, from the interface with the external phase to the interface with the internal phase;



- Mass transfer of ion metal-carrier (MR) at the interface between the membrane phase and the internal phase and reaction with protons in the internal phase. In this step, metal ions are transferred from the membrane phase to the internal phase;

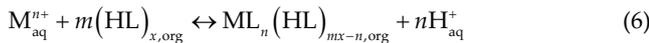


- Mass transfer of metal ions from the internal interface of the membrane to the bulk of the internal phase (aqueous phase);
- Carrier diffuses in the opposite direction of metal complexes within the membrane from the external membrane interface to the internal membrane interface;

It should be noted that the mass transfer of metal ions occurred when the pH in the internal phase was lower than the external phase. It is assumed that the protons concentration difference between the two aqueous phases (i.e., internal and external phases) played an important role in the required driving force is the separation of the metal ions and the diffusion of carrier molecules in the opposite direction compared to metal ions.

3.2.1.2. Extraction by cation exchange (acidic carrier)

Organic molecules that contain exchangeable protons are called acidic carriers (cation exchangers). In a cation exchange extraction system, the extraction of a cation is accompanied by the substitution of extraction molecules equivalent to the electric charge of that cation. For the extraction of Mⁿ⁺ metal ion by acidic extractor (HL) the reaction equation can be written as Eq. (6):



In Eq. (6) (M_{aq}^{n+}) is the concentration of metal ions in the feed, (HL_{org}) is the amount of carrier used, $\text{ML}_{n,\text{org}}$ is the ion metal-carrier complex, ($n\text{H}_{\text{aq}}^{+}$) is the proton released during metal complex formation, and m is the number of molecules of carriers engaged in the reaction (coordination number). In this equation $n = 2$ is the oxidation rate of the metal.

The extraction reaction for Cu^{2+} can be written as:



From Eq. (7), the equilibrium constant (K_{ex}) may be expressed as:

$$K_{\text{ex}} = \frac{[\text{CuL}_2(\text{PEG})_{(mx-2)}]_{\text{org}} \times [\text{H}^{+}]_{\text{aq}}^2}{[\text{Cu}^{2+}]_{\text{aq}} \times [(\text{PEG})_x]_{\text{org}}^m} \quad (8)$$

Eq. (7) can be also written as:

$$\log \left[\frac{[\text{CuL}_2(\text{PEG})_{(mx-2)}]_{\text{org}}}{[\text{Cu}^{2+}]_{\text{aq}}} \right] = \log K_{\text{ex}} + m \log [(\text{PEG})_x]_{\text{org}} - 2 \log [\text{H}^{+}]_{\text{aq}} \quad (9)$$

The distribution coefficient (D) can be expressed as a function of metallic species concentration ratio in organic and aqueous phases at equilibrium condition as:

$$D = \left[\frac{[\text{CuL}_2(\text{PEG})_{(mx-2)}]_{\text{org}}}{[\text{Cu}^{2+}]_{\text{aq}}} \right] \quad (10)$$

By substituting the distribution coefficient in Eq. (9), Eq. (11) is obtained:

$$\log D = \log K_{\text{ex}} + m \log [(\text{PEG})_x]_{\text{org}} + 2\text{pH} \quad (11)$$

By plotting $\log D$ vs. $\log[\text{PEG}]$, in constant pH, a line with a slope equal to the number of acidic ligands in the extraction complex is obtained. Therefore, according to Fig. 5, the number of carrier molecules (HL) associated with each extracted copper complex can be estimated to be ~ 2 ($R^2 = 0.99$) which is in accordance with the coefficients reported in Eq. (7) ($\text{CuL}_2(\text{PEG})_{mx-2}$).

3.2.1.3. Mechanism of copper ion separation

In this study, a carrier-facilitated mechanism was used to investigate the extraction mechanism of copper ions from aqueous solutions using the ELM technique. Fig. 6 shows a schematic of copper ion transport via the carrier-facilitated mechanism. In this mechanism, the permeate (metal

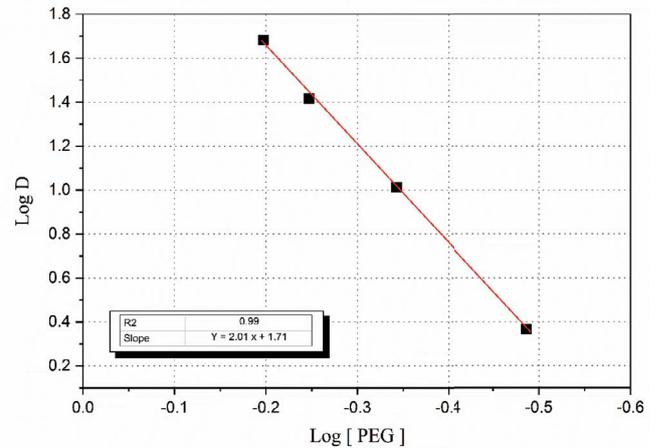


Fig. 5. Plot of $\log D$ vs. $\log[\text{PEG}]$ (pH = 2; A:O = 1:1 v/v).

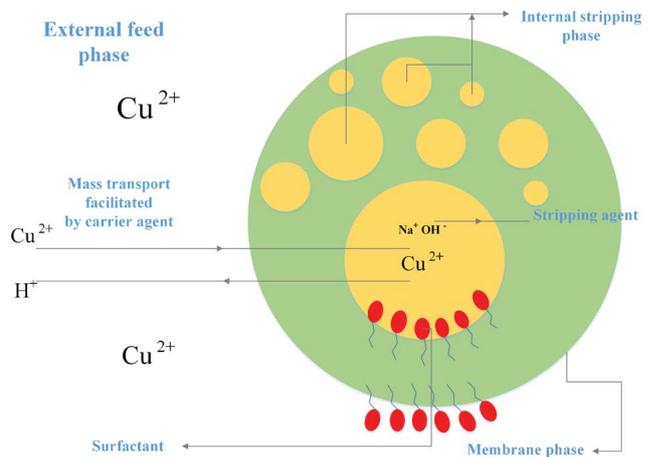


Fig. 6. Schematic representation of Cu recovery mechanism by ELM process.

ion) passes through the membrane phase with the aid of a carrier (complexing or extracting material) [32]. The carrier component improves the penetration of the desired component, while the chemical reactions take place at both external and internal interfaces of the aqueous phase membranes. As shown in Fig. 6, the soluble carrier agent in the membrane phase initially reacts with copper ions at the external phase interface, with the feed phase in the form of a copper-carrier complex. Then, the copper-carrier complex penetrates the membrane phase. The formed complex then diffuses through the membrane until it reaches to internal the interface of the membrane phase and internal phase where the ion exchange reaction occurs at low pH. Finally, the copper-carrier complex releases the extracted copper ions and takes up protons in return. The process continues until the system reaches the equilibrium [33–35]. This phenomenon can be represented by FTIR analysis. Fig. 7 shows the FTIR analysis of PEG before and after copper ions extraction. As shown in Fig. 7, the peak of the O–H groups (3440 cm^{-1}) decreased after extraction, which indicated the chemical exchange of hydrogens by copper cations. The results also showed that some of

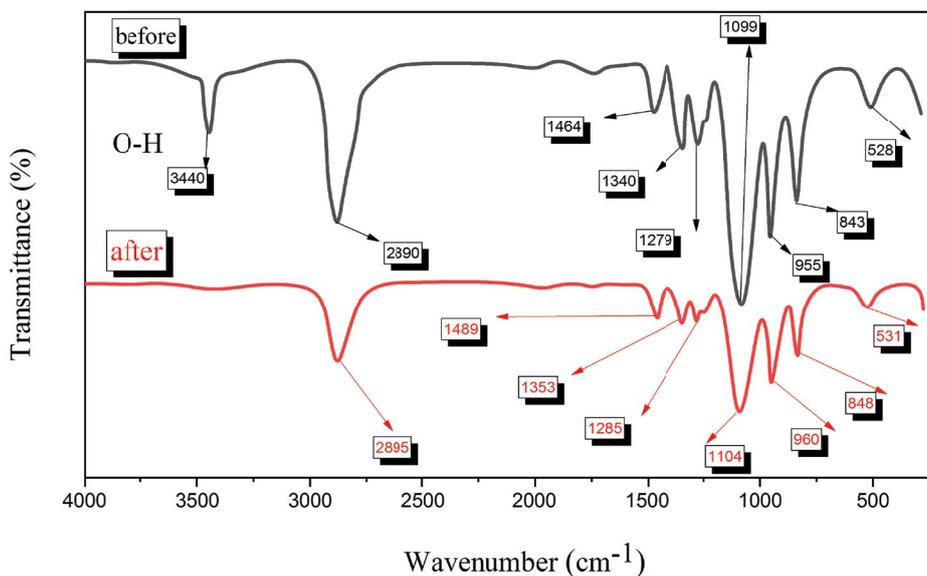


Fig. 7. FTIR spectra of polyethylene glycol (PEG) before and after Cu separation.

the copper ions covalently bonded with carbon atoms in the organic phase to form (C–Cu–C) group [36].

3.2.2. Effect of feed phase concentration

The results of liquid–liquid extraction experiments showed that copper ions concentration ranging from 25 to 150 ppm was suitable for ELM experiments. As shown in Fig. 8a, the Cu concentration in the feed phase with an initial concentration of 25 ppm reached zero after 2 min indicating a complete extraction. The extraction time for copper initial concentration of 50, 100 and 150 ppm was 5, 15 and 20 min, respectively. In experiments with an initial copper concentration of 150 ppm, even after 20 min, the copper concentration was near 20 ppm, indicating that more time was needed to further extraction. The results showed that the time required for extraction increases with increasing concentration in the external phase [37].

3.2.3. Effect of carrier concentration

The extraction rate is a function of both the metal–extraction complex formation ability and the carrier concentration in the organic phase [21]. It is stated that a low carrier concentration results in a low extraction rate due to the small number of formed complexes [5]. In addition, at low PEG concentrations, the emulsifier adsorption rate at the oil–water interface and its mass transfer through the membrane decrease. As illustrated in Fig. 8b, at a concentration of 0.1 mM, the extraction was slow, and after 15 min, the concentration of copper in the external phase reached only to about 27 ppm. The extraction time required to get to 27 ppm was reduced to 0.5 min after the concentration of PEG was increased to 0.2 mM. Therefore, by increasing the concentration of PEG, to 0.4 mM after 10 min, extraction efficiency was above 96%. It can be stated that as the concentration of PEG increases, the number of complexes and

consequently, the rate of extraction increased [38]. Although in general, this trend held, a further increase in PEG concentration to 0.5 mM demonstrated an adverse impact on the separation process (copper ion concentration ~38 ppm after 5 min). Therefore it can be concluded that there was an optimum carrier for maximum copper extraction beyond which a further increase in the carrier concentration, decreased the separation efficiency due to increase the membrane phase viscosity (lower diffusion) and decreased its stability [39,40].

The optimum PEG concentration in the membrane phase was 0.4 mM increasing the amount of PEG increased the viscosity and decreased the extraction rate.

3.2.4. Effect of internal phase concentration

The effect of internal phase stripping concentration on the copper ions extraction in the feed phase at different times is plotted in Fig. 8c. It is evident from Fig. 8c that as the internal phase concentration increased from 0.1 to 0.3 M, the concentration of copper ions in the feed phase decreased. Also, an increase in the concentration of sodium hydroxide in the internal phase led to an increase in the ability to strip the copper–PEG complex arriving at the internal interface of the membrane and decreased the surface polarization, thereby increasing the extractive drive force [41]. In the experiment using 0.1 M concentration in the internal phase, the concentration of the feed phase reached 16 ppm after 15 min. In addition, by increasing the concentration from 0.1 to 0.2 and 0.3, the concentration of copper ions reached 7 and 1.5 ppm after 15 min, respectively.

Notwithstanding, increasing the concentration of the stripping agent in the internal phase to values greater than 0.3 M, made the membrane more unstable, broke the globules, and mix the internal phase with the external phase, thereby stopping the extraction. One can notice in Fig. 8c that when a concentration of NaOH equal to 0.4 M was used, the concentration of copper ions dropped to 12 ppm after 5 min.

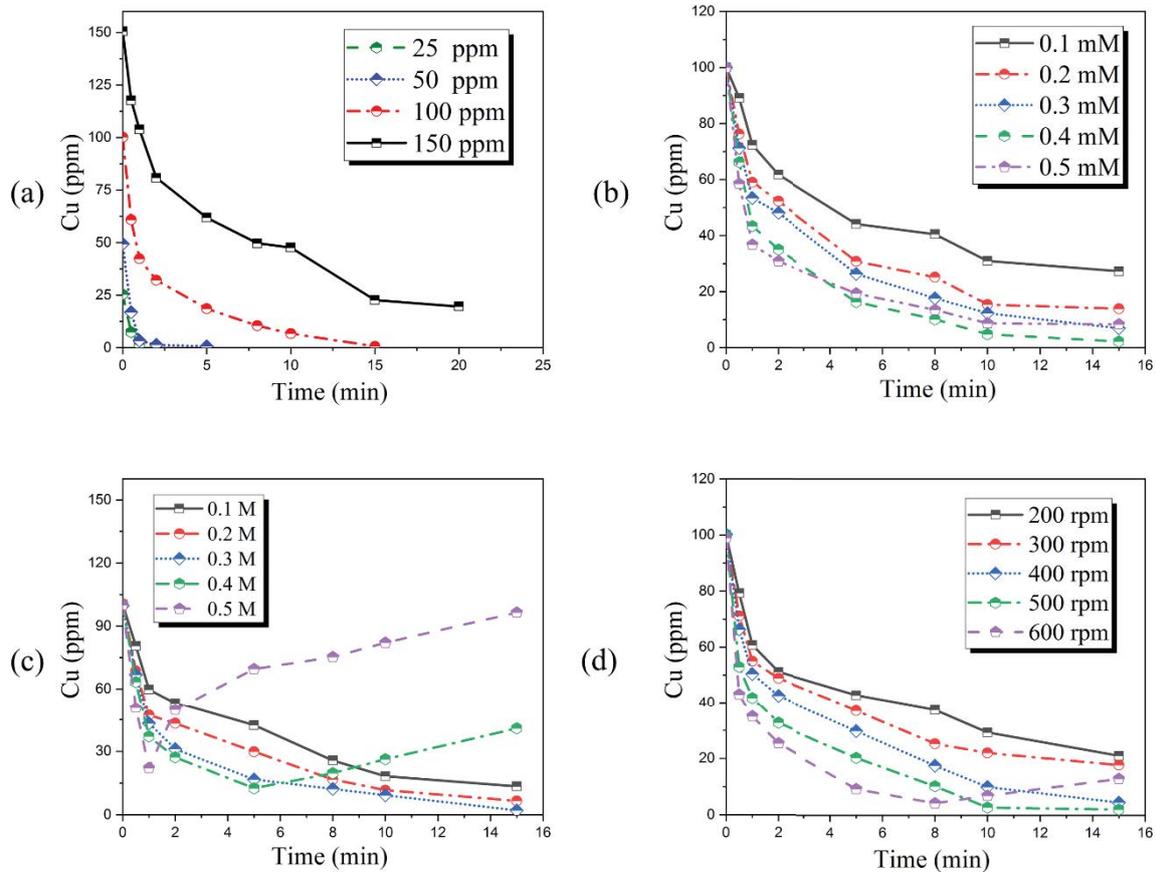


Fig. 8. Effect of (a) feed phase concentration ([internal phase (NaOH)] = 0.3; pH feed phase = 2; [PEG] = 0.4 mM; [KSCN] = 0.4 mM; stirring rate 500 rpm), (b) carrier concentration ([internal phase (NaOH)] = 0.3; pH feed phase = 2; Cu concentration in feed phase = 100 ppm; [KSCN] = 0.4 mM; stirring rate 500 rpm), (c) internal phase concentration ([PEG] = 0.4 mM; pH feed phase = 2; Cu concentration in feed phase = 100 ppm; [KSCN] = 0.4 mM; stirring rate 500 rpm) and (d) W/O/W emulsion stirring rate on extraction rate using ELM process ([internal phase (NaOH)] = 0.3 [PEG] = 0.4 mM; pH feed phase = 2; Cu concentration in feed phase = 100 ppm; [KSCN] = 0.4 mM).

However, after 5 min, the copper ion concentration in the feed phase increased over time, indicating, globules breakage and mixing of aqueous phases. Therefore, the stability of the globules decreased with an increase in the internal phase concentration. The globule's destabilization increased further (breakage time ~1 min) with further NaOH concentration increase (0.5 M).

3.2.5. Effect of W/O/W emulsion stirring rate

One of the important factors on the membrane stability and the extraction efficiency via ELM is the mixing rate of the external phase which directly affects the mass transfer of the dissolved component in the solution [31]. Fig. 8d represents the copper ion concentration vs. time at different stirring rates. As shown in Fig. 8d, as the stirring rate, increased from 200 to 500 rpm the concentration of copper in the external phase decreased from 29 to 10 ppm after 10 min. In addition, with a further increase in the stirring rate to 500 rpm copper concentration near zero. It can be stated that an increase in the stirring rate increased the shear force applied to the emulsion globules and decreases the size of the globules. It should be noted that in ELM, the overall

mass transfer is a function of available external surface of globules and membrane thickness. Therefore, downsizing the globules via stirring leads to an increase in the total surface area of the globules and the rate of diffusion within them (due to the reduction in the membrane thickness). The combination of the mentioned parameters leads to an improvement in mass transfer [42]. Nevertheless, by further increasing the stirring rate to 600 rpm, due to the excessive shear stress destroyed the globules. Therefore, there is a limit beyond which the stirring rate causes the emulsion breakdown by excessive thinning the membrane thickness to the extent that globules burst due to uncontrolled osmotic swelling [43].

3.2.6. Effect of feed phase/emulsion volume ratio

During the extraction, the volume of the phases may change due to the phase transfer components from one phase to another or due to the slight dissolution of one phase to another [43]. Fig. 9a shows a diagram of changes in copper ion concentration overtime at different feed phase/emulsion volume ratio. The results are illustrated in Fig. 9a. In general, with an increase in the emulsion to feed phase

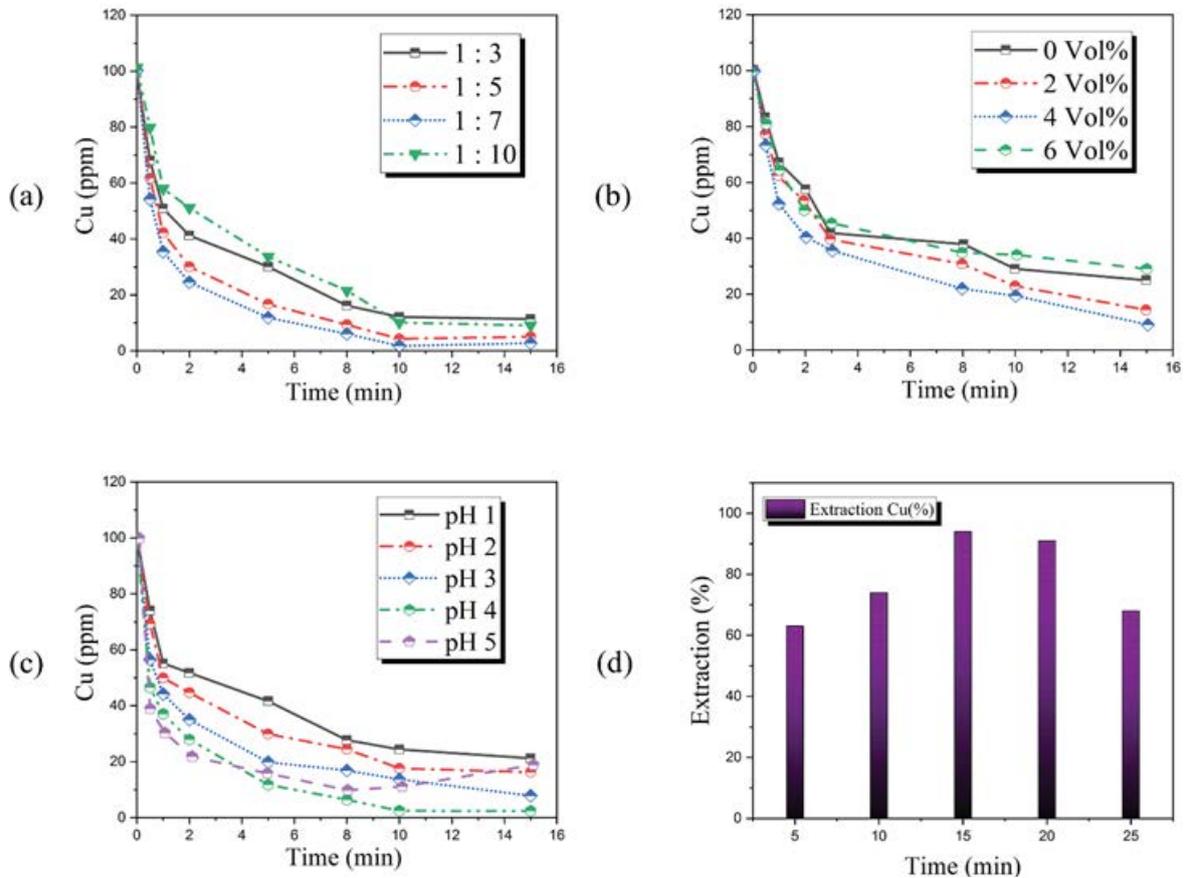


Fig. 9. Effect of (a) feed phase/emulsion volume ratio ([internal phase (NaOH)] = 0.3 [PEG] = 0.4 mM; pH feed phase = 4; Cu concentration in feed phase = 100 ppm; [KSCN] = 0.4 mM; Tween 20:4 vol.%), (b) Tween 20 emulsifier concentration ([internal phase (NaOH)] = 0.3 [PEG] = 0.4 mM; pH feed phase = 4; Cu concentration in feed phase = 100 ppm; [KSCN] = 0.4 mM; feed phase/emulsion volume ratio 1:7), (c) feed phase pH ([internal phase (NaOH)] = 0.3 [PEG] = 0.4 mM; Tween 20:4 vol.%; Cu concentration in feed phase = 100 ppm; [KSCN] = 0.4 mM; feed phase/emulsion volume ratio 1:7) and (d) W/O/W emulsion stirring time on extraction rate using ELM process ([internal phase (NaOH)] = 0.3 [PEG] = 0.4 mM; Tween 20:4 vol.%; Cu concentration in feed phase = 100 ppm; [KSCN] = 0.4 mM; feed phase/emulsion volume ratio 1:7; pH feed phase = 4).

ratio, the extraction rate increased. Therefore, by decreasing the emulsion to external aqueous phase ratio from 10:1 to 5:1, after 15 min, the concentration of copper in the external aqueous phase (feed) reached to ~1.5 ppm. This is due to the increased membrane capacity for extraction and stripping, which is due to an increase in the number of created globules and increased mass transfer rate. On the other hand, with a further reduction of the phase volume ratio to 3:1, the extraction rate, after 15 min, was ~12 ppm. This was because increasing the emulsion content in the feed prevented the globules formation and therefore reduced the mass transfer rate and extraction rate.

3.2.7. Effect of Tween® 20 emulsifier concentration

In this work, PEG was used as both an emulsifier and a carrier. Moreover, studies showed that emulsion blends could lead to higher extraction efficiencies in ELM [44]. Therefore, to investigate this effect, the Tween emulsifier was added to the oil phase. Fig. 9b demonstrates the copper concentration in the feed phase vs. time for 2% (v/v) and 4% (v/v) Tween emulsifier concentrations. The results in Fig. 9b shows

that the copper concentration for 2% (v/v) and 4% (v/v) Tween emulsifier concentrations, after 15 min, decreased from 25 to 14 and 9 ppm, respectively. Moreover, by increasing the Tween 20 hydrophilic emulsifier concentration to 4% by volume, the diameters of droplets decreased, resulting in a faster mass transfer rate. Nevertheless, by increasing the emulsifier concentration to 6% by volume, the increase in the viscosity of the organic phase had an adverse effect on the emulsion formation and extraction process [45].

3.2.8. Effect of feed phase pH

Experiments in liquid–liquid extraction by copper ion extraction show that the pH value of the external phase had a significant effect on the amount of extracted copper ion. [46]. A pH range between 1 and 5 was adapted from liquid–liquid extraction and was used in ELM tests. The results in Fig. 9c show that extracted copper increased with an increase in pH from 1 to 4, indicating the effect of cation exchange on the extraction. On the contrary, increasing from 4 to 5 not only did not improve the extraction efficiency but due to an increase in globule's instabilities and breakage,

the separation efficiency dropped over time. As a result, the internal phase seeps out and the metal ion concentration in the feed phase increases. Due to the instability of the emulsion cells at higher pH and the possibility of the formation of metal hydroxides in the external phase, pH above 5 was not investigated in this study. Finally, pH = 4 was used as the optimum pH.

3.2.9. Effect of W/O/W emulsion stirring time

Fig. 9d shows a diagram of copper ion concentration variation vs. time at different W/O/W emulsion stirring time. The results showed that the emulsion break increased with an increase in the stirring time. It seems that high stirring time increased the rate of water transfer into the internal phase on the globules and swoll them. Therefore, there should be an optimal stirring time to maximize extraction rate while keeping the emulsion stability. Kankekar et al. [47] reported 8 min for the optimum stirring time. Studies on uranium and gold extraction showed that the optimum time was 5 and 20 min, respectively Kulkarni et al. [48] Kargari et al. [49].

It should be noted, that due to a higher mass transfer rate at the early stages of experiments, most of the copper ions were extracted within the first half of the stirring time (Fig. 9d). Moreover, as the stirring time continued, the globule swelling and breakage increased, leading to an increase in the copper concentration. According to Fig. 9d, the maximum beneficial extraction time was obtained to be between $t = 15\text{--}20$ min.

3.3. Optimization using DOE

There are several methods used in RSM for the DOE, one of which is the CCD method [50]. In the CCD method, the total number of experiments is N .

$$N = 2K + 2^K + n_0 \tag{12}$$

where K is the number of independent variables, n_0 is the number of repetitions of the experiments in the central points. The model used in RSM is generally a quadratic relation. The RSM method defines a model for each dependent variable expressing the main factors on each variable. The quadratic relation (Eq. (13)) describes the behavior of the system [51].

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j + \varepsilon \tag{13}$$

where Y is the predicted response, β_0 is a constant, β_i is the linear coefficient, β_{ii} is the squared coefficient, β_{ij} represents the binary interaction and ε is the system error value. Eq. (13) is solved using software Design Expert 10 to estimate the response of the independent variables. The significance of each sentence in the regression equation is examined, and the significance of the model is determined by analysis of variance (ANOVA) for each response [52].

Table 4 shows the factors that are expected to influence the test process with their high and low levels. Five important factors were identified, which included carrier concentration, feed phase pH, feed phase/emulsion volume ratio, W/O/W emulsion stirring rate and time. Copper removal percentage was selected as the response. For optimization, we used 5 factors affecting the system and using CCD type 1/2 and double replication for greater accuracy. Thus, 64 experiments were carried out for copper ion extraction experiments, 52 of which were for non-central points and 12 for central points. The design matrix with the percentage of copper removal in each test is given in Table 5. The normal plot, residual plot, predict vs. actual, Box-Cox, leverage and Cook's distance were used to assess adequacy. Moreover, the ANOVA table was used to evaluate model accuracy.

3.4. Investigated adequacy and accuracy of the selected model

3.4.1. Adequacy of the selected model

The results are shown in Figs. 10a–f report the adequacy of the selected factors by CCD model using Design Expert 10. Figs. 10a and b show the normality of the data and the absence of deviations from the model. Variances constant is another way to demonstrate the adequacy of the model using the residual graph. According to the residual data in Fig. 10c, the variance will remain the same when a specific trend is not followed [53]. Fig. 10d shows the Box-Cox diagram for checking the data normality. According to the results shown in the Box-Cox diagram, there is no need to transform for normalizing the data [54]. The other two diagrams to check for data normality are the Leverage and Cook's distance diagrams are shown in Figs. 10e and f. These two diagrams vary between 0 and 1 and represent the risk of overfitting in the model [55]. By looking at these two graphs, we find that outliers that overfitting risks do not exist in the optimization.

3.4.2. Accuracy of the selected model

ANOVA is used to check the accuracy of the model [56]. The results of the ANOVA model are shown in Table 6.

Table 4
Levels of factors in the central composite design (CCD)

Factors	Symbol	−α	−1	0	+1	+α
Feed phase/emulsion volume ratio	X_1	1	3	5	7	9
Carrier concentration, wt.%	X_2	0.05	0.2	0.35	0.5	0.65
Feed phase pH	X_3	1	2	3	4	5
W/O/W emulsion stirring time, min	X_4	5	10	15	20	25
W/O/W emulsion stirring rate, rpm	X_5	200	300	400	500	600

Table 5
Central composite design (CCD) extraction of copper ion

Run	X_1 : feed/emulsion ratio	X_2 : carrier concentration	X_3 : feed phase pH	X_4 : stirring time	X_5 : stirring speed	Removal Cu%
1	9	0.35	3	15	400	63.21
2	5	0.35	3	25	400	88.12
3	3	0.5	2	10	300	76.9
4	5	0.35	5	15	400	89.06
5	3	0.5	2	20	500	97.95
6	5	0.65	3	15	400	95.12
7	3	0.5	4	10	500	98.8
8	1	0.35	3	15	400	74.84
9	7	0.2	2	10	300	43.6
10	7	0.2	2	20	500	80.12
11	3	0.5	4	10	500	98.09
12	7	0.5	4	20	500	95.34
13	1	0.35	3	15	400	81.54
14	5	0.35	3	5	400	78.12
15	3	0.2	4	20	500	86.8
16	7	0.5	2	20	300	60.12
17	5	0.35	1	15	400	74.1
18	9	0.35	3	15	400	61.67
19	3	0.2	4	20	500	94.12
20	5	0.35	3	15	400	75.9
21	7	0.5	2	20	300	62.91
22	7	0.5	2	10	500	97.01
23	5	0.35	3	15	400	88.12
24	7	0.2	2	10	300	48.7
25	5	0.35	3	15	400	83.12
26	5	0.35	3	15	400	86.09
27	5	0.35	3	15	600	85.29
28	7	0.2	2	20	500	76.34
29	5	0.35	3	15	400	86.9
30	7	0.2	4	10	500	76.6
31	7	0.2	4	20	300	68.1
32	3	0.5	2	20	500	91.89
33	5	0.35	3	15	400	93.2
34	5	0.05	3	15	400	68.12
35	3	0.5	2	10	300	78.9
36	3	0.2	4	10	300	64.34
37	5	0.35	3	15	400	89.36
38	7	0.5	4	10	300	70.71
39	5	0.05	3	15	400	63.9
40	3	0.2	2	20	300	38.09
41	5	0.35	3	5	400	78.12
42	3	0.2	2	10	500	87.56
43	7	0.5	4	20	500	98.12
44	7	0.2	4	10	500	81.7
45	5	0.35	3	15	400	90.18
46	5	0.35	3	25	400	87.45
47	3	0.2	4	10	300	50.08

(Continued)

Table 5 Continued

Run	X_1 : feed/emulsion ratio	X_2 : carrier concentration	X_3 : feed phase pH	X_4 : stirring time	X_5 : stirring speed	Removal Cu%
48	5	0.35	3	15	400	91.23
49	5	0.35	3	15	400	82.8
50	3	0.5	4	20	300	98.03
51	3	0.2	2	10	500	79.43
52	5	0.35	3	15	200	43.6
53	7	0.5	2	10	500	90.78
54	3	0.5	4	20	300	95.34
55	5	0.35	3	15	600	89.12
56	5	0.65	3	15	400	99.6
57	7	0.5	4	10	300	72.13
58	7	0.2	4	20	300	66.8
59	5	0.35	3	15	400	80.2
60	5	0.35	1	15	400	78.34
61	5	0.35	3	15	200	35.46
62	5	0.35	3	15	400	76.9
63	5	0.35	5	15	400	89.38
64	3	0.2	2	20	300	37.23

As can be seen in Table 6, the p -value is significant, and the lack of fit is non-significant, stating the accuracy of the chosen model [57]. Due to a great advantage of Design expert 10 software, the selected models can be improved by the elimination of non-significant terms. Table 7 shows the results of the modified ANOVA. It can be seen that the F -value has increased significantly, demonstrating the improvement of the quality of the selected mode (mean = 78.29, standard deviation = 4.28). All other statistical information regarding the accuracy of the model is reported at the bottom of Table 7. By using the values reported in Table 7, a quadratic linear regression equation can be written as follows:

$$\begin{aligned} \text{Removal Cu} = & 34.35 - 3.07 \times X_1 + 8.93 \times X_2 + 4.57 \times X_3 + \\ & 1.47 \times X_4 + 12.28 \times X_5 - 2.91 \times X_1 X_2 - 2.90 \times \\ & X_2 X_3 + 4.64 \times X_3 X_4 - 3.46 \times X_3 X_5 - 3.17 \times \\ & X_1^2 - 4.90 \times X_5^2 \end{aligned} \quad (14)$$

3.5. Investigation the relationship of response with relevant variables

3.5.1. Surface plot graphs

Figs. 11a–d shows the surface plot diagram of the factors influencing the optimization process. Fig. 11a represents the investigating two factors X_1 and X_2 (feed phase/emulsion volume ratio, and the carrier concentration, respectively) vs. the response (copper removal %) while X_3 , X_4 and X_5 (feed phase pH, stirring time and stirring rate, respectively) were kept constant at their central points. Therefore, if factor X_1 (feed phase/emulsion volume ratio) is at a low level of 3–5 and carrier concentration factor (X_2) at its high level of 0.3–0.5, the highest response (copper removal %) would be copper ion recovery which confirms the results reported

in section 3.2.6 [58]. Fig. 11b shows the results of carrier concentration (X_2) and W/O/W emulsion stirring rate (X_5) factors vs. copper removal %, while X_1 , X_3 and X_4 are at their central points. According to the results shown in Fig. 11b, for X_2 between 0.3–0.5 wt.% and X_5 is between 350–450, the highest rate of copper ion separation can be achieved. As mentioned before, the extraction rate has a direct relationship with the formation of the metal-carrier complex and the carrier concentration in the organic phase. Nevertheless, it was mentioned that the carrier concentration could have an adverse effect on copper separation at sufficiently high concentrations (section 3.2.3) [22]. Fig. 11c shows the feed phase pH (X_3) and W/O/W emulsion stirring time (X_4) factors vs. copper recovery, while X_1 , X_2 and X_5 are kept constant. It is evident from Fig. 11c that for X_3 in the middle range ~3–4.5 wt.% and X_4 in the range of ~10–20, the highest rate of copper ion separation is achieved. The effect of pH and W/O/W emulsion stirring time are explained in sections 3.2.8 and 3.2.9, respectively [12]. In Fig. 11d the effect of feed phase pH (X_3) and W/O/W emulsion stirring rate (X_5) vs. Cu removal while X_1 , X_2 and X_4 are constant is reported. It can be stated that for X_3 in the range of ~3–4.5 wt.% and X_5 in the range of 4–4.50 wt.%, the highest copper separation can be achieved.

3.6. Optimization

Based on the results in sections 3.4–5, the optimum points for maximum extraction are presented in Fig. 12. As shown in Fig. 12, if feed phase/emulsion volume ratio (X_1), the carrier concentration (X_2), the feed phase pH (X_3), W/O/W emulsion stirring time (X_4) and the W/O/W emulsion stirring rate (X_5) were ~3.6, ~0.5, ~4, ~13 and 465, respectively, the highest extraction rate (more than 99%) would be achieved. To verify the optimization results, we performed an experiment with the optimal conditions suggested by

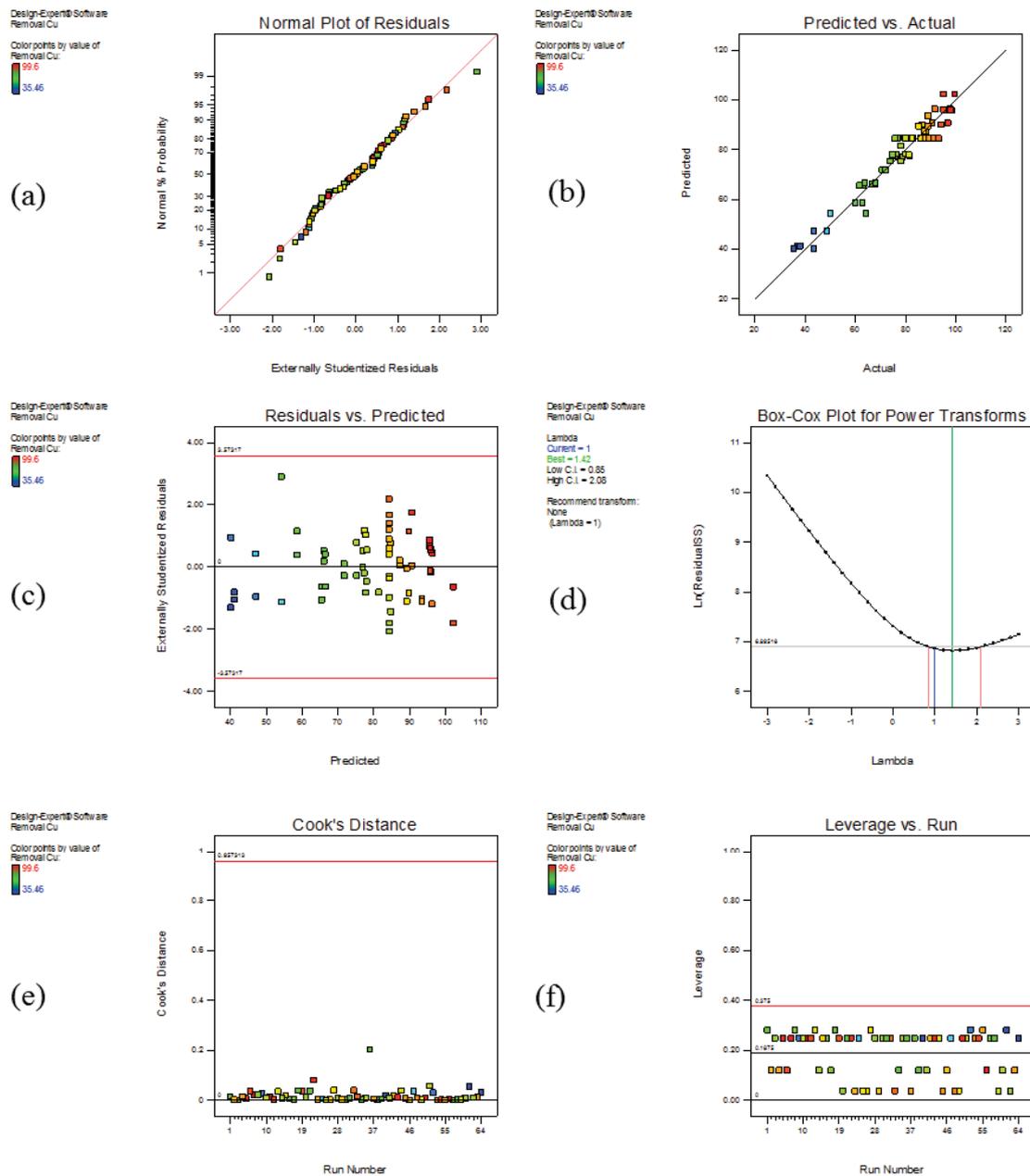


Fig. 10. Diagrams of (a) normal plot, (b) predict vs. actual, (c) residual plot, (d) Box-Cox charts, (e) Cook's distance chart and (f) leverage chart for model adequacy in CCD method.

the software in the laboratory to separate the copper ions with the ELM technique. Based on the results, we were able to separate 98% of copper ions.

4. Conclusions

The SE process was investigated to recover copper ions, and the effect of various factors such as the concentration of carrier, ligand agent type, the ligand concentration, pH and stirring time was investigated. In addition to the above factors, the effect of using an emulsifier on the SE process was investigated. The following conclusions were obtained from the studies on these factors:

- PEG and thiocyanate ligand were suitable carriers for copper extraction.
- Extraction rate was directly proportional to the ligand concentration.
- Adding a small amount of emulsifier increased the extraction process efficiency significantly.
- KSCN ligand was more effective than NH_4SCN in copper ion extraction.
- Although the stirring time to reach equilibrium condition for copper extraction depended on experimental conditions such as pH and ligand concentration, the equilibrium condition was reached after ~5 min.

Table 6
Analysis of variance in CCD design for copper removal

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value	
Model	16,234.71	20	811.74	39.71	<0.0001	Significant
X_1 – feed/emulsion	453.07	1	453.07	22.16	<0.0001	
X_2 – carrier concentration	3,830.79	1	3,830.79	187.38	<0.0001	
X_3 – feed phase pH	1,004.40	1	1,004.40	49.13	<0.0001	
X_4 – stirring time	103.93	1	103.93	5.08	0.0293	
X_5 – stirring speed	7,236.60	1	7,236.60	353.97	<0.0001	
X_1X_2	270.80	1	270.80	13.25	0.0007	
X_1X_3	24.03	1	24.03	1.18	0.2843	
X_1X_4	14.14	1	14.14	0.69	0.4102	
X_1X_5	1.62	1	1.62	0.079	0.7794	
X_2X_3	23.41	1	23.41	1.15	0.2906	
X_2X_4	0.020	1	0.020	9.540E-004	0.9755	
X_2X_5	269.06	1	269.06	13.16	0.0008	
X_3X_4	688.48	1	688.48	33.68	<0.0001	
X_3X_5	382.19	1	382.19	18.69	<0.0001	
X_4X_5	3.48	1	3.48	0.17	0.6820	
X_1^2	602.09	1	602.09	29.45	<0.0001	
X_2^2	7.65	1	7.65	0.37	0.5440	
X_3^2	0.61	1	0.61	0.030	0.8632	
X_4^2	0.11	1	0.11	5.607E-003	0.9407	
X_5^2	1,431.94	1	1,431.94	70.04	<0.0001	
Residual	879.09	43	20.44			
Lack of fit	193.57	6	32.26	1.74	0.1387	Not significant
Pure error	685.51	37	18.53			
Corr. total	17,113.80	63				

Table 7
Analysis of variance optimized in CCD design for copper removal

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value	
Model	16,160.05	11	1,469.10	80.10	<0.0001	Significant
X_1 – feed/emulsion	453.07	1	453.07	24.70	<0.0001	
X_2 – carrier concentration	3,830.79	1	3,830.79	208.86	<0.0001	
X_3 – feed phase pH	1,004.40	1	1,004.40	54.76	<0.0001	
X_4 – stirring time	103.93	1	103.93	5.67	0.0210	
X_5 – stirring speed	7,236.60	1	7,236.60	394.55	<0.0001	
X_1X_2	270.80	1	270.80	14.76	0.0003	
X_2X_5	269.06	1	269.06	14.67	0.0003	
X_3X_4	688.48	1	688.48	37.54	<0.0001	
X_3X_5	382.19	1	382.19	20.84	<0.0001	
X_1^2	599.24	1	599.24	32.67	<0.0001	
X_5^2	1,436.65	1	1,436.65	78.33	<0.0001	
Residual	953.75	52	18.34			
Lack of fit	268.24	15	17.88	0.97	0.5077	Not significant
Pure error	685.51	37	18.53			
Corr. total	17,113.80	63				

Std. Dev. = 4.28; Mean = 78.29; C.V.% = 5.47; Press = 1,387.11; R-squared = 0.9443; Adj. R-squared = 0.9325; Pred. R-squared = 0.9189; Adeq. Precision = 33.455.

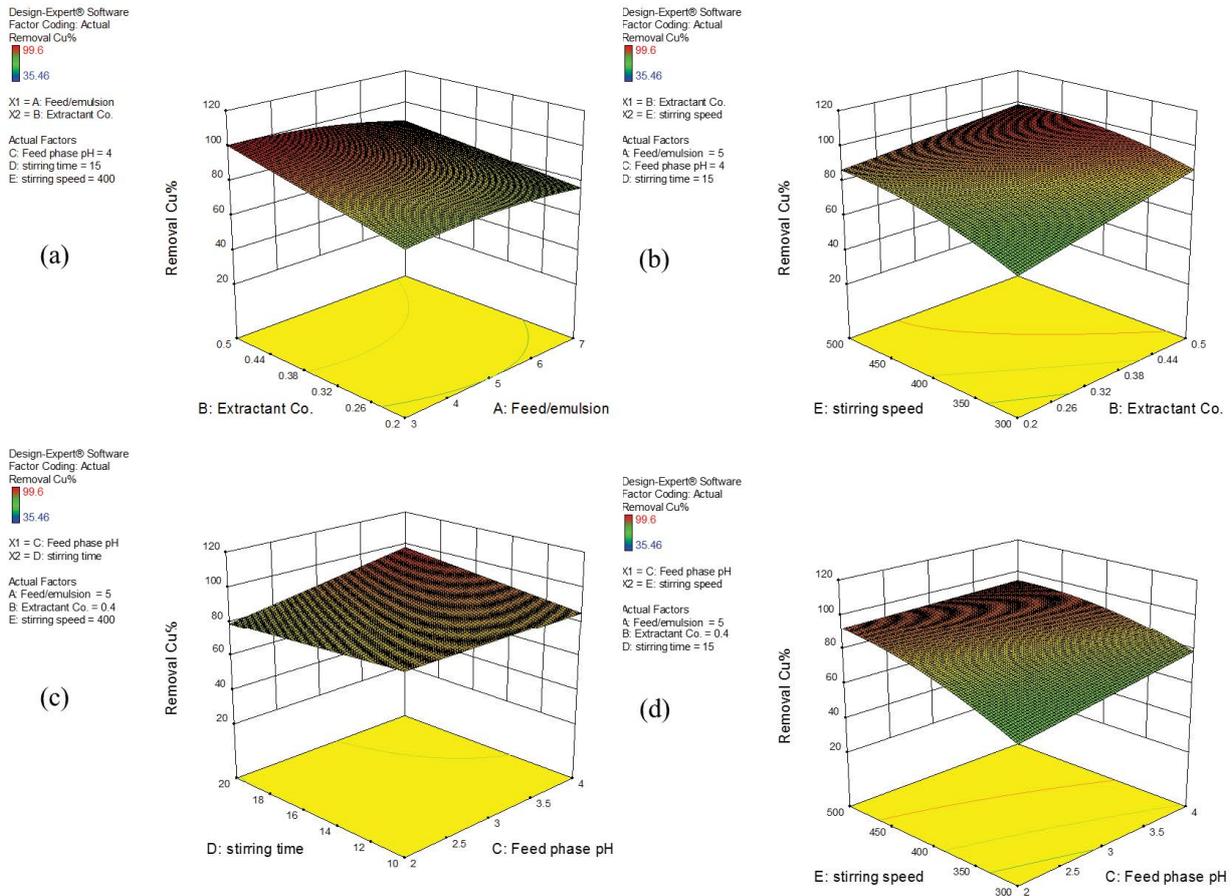


Fig. 10. Fig. 11. Plot of the response surface (a) feed phase/emulsion volume ratio (X_1) and the carrier concentration (X_2), (b) carrier concentration (X_2) and W/O/W emulsion stirring rate (X_5), (c) feed phase pH (X_3) and W/O/W emulsion stirring time (X_4) and (d) feed phase pH (X_3) and W/O/W emulsion stirring speed (X_5) with response rate.

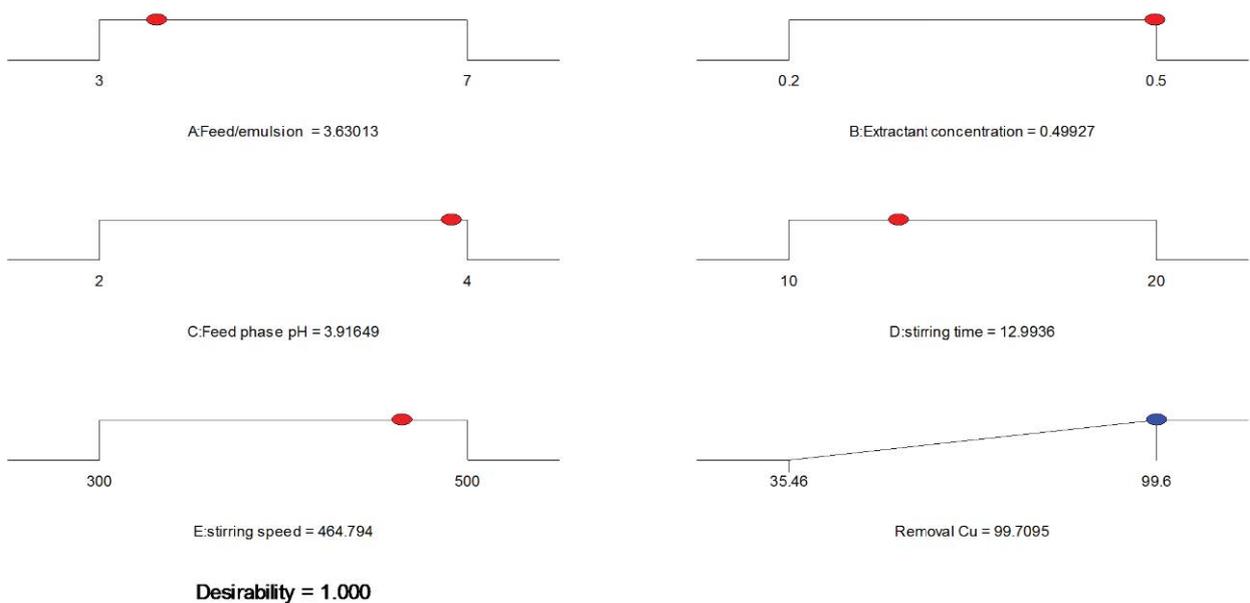


Fig. 12. Optimum conditions to get the most response (highest Cu recovery).

- Investigation of feed pH variations and its effect on the copper ion extraction process show that the optimum extraction percentage is obtained at pH 2.

According to the results in ELM, an increase in the internal phase concentration, carrier concentration, emulsion to external phase ratio and stirring rate had a direct impact on the extracted copper ion concentration. On the contrary, an increase in the external phase concentration lowered the amount of extracted copper. The following statements are concluded in the extraction of copper ion using ELM.

- Increase in the stirring rate increased the extraction rate up to 180 rpm. A further increase in stirring rate beyond 180 rpm, increased emulsion failure and decreased extraction rate.
- Increase in the concentration of sodium hydroxide in the internal phase, initially, increased the extraction process driving force. However, increasing the internal phase concentration to more than 0.3 M resulted in osmotic swelling of membranes and early emulsion failure.
- Optimum concentration for PEG in the membrane phase was 0.35 mM. Increasing the concentration of PEG, reduced the extraction rate.
- By increasing the copper concentration in the external phase, the equilibrium time for the copper extraction process was increased.
- An increase in the emulsion volume ratio in the external phase sped up the copper ion extraction process.
- Experimental results showed that the concurrent use of Tween 20 and PEG increased the extraction of copper ions.

In this study, DOE with Design Expert 10 software was used to investigate the factors affecting copper ion separation. The results showed that the maximum extraction (~100%) would achieve if: the feed phase/emulsion volume ratio = 3.6, carrier concentration = 0.5, feed phase pH = 4, W/O/W emulsion stirring time = 13 min and W/O/W emulsion stirring rate = 465 rpm. Experiments verified the conditions suggested by the software, and the results showed that 98% of copper ions were extracted.

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