COPPER AND NICKEL EXTRACTION USING EMULSION LIQUID MEMBRANES

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To my beloved parents and brothers

ABSTRACT

Emulsion liquid membrane (ELM) technique is a modified technique that combines the traditional solvent extraction and stripping in a single unit operation. The characteristics of ELM include the large interfacial area and high selectivity when treating heavy metal ions. Through the study of applying ELM technique in extracting and stripping some heavy metal ions such as copper and nickel from single cation bearing solutions, this thesis targets at the extraction and separation of different metal ions including copper, nickel and calcium from a synthetic wastewater stream by using the minimum reagent and energy consumption. A two-stage mixer-settler was eventually built-up and implemented to test the extraction and separation efficiency of ELM.

It was noticeable that ELM technique can remove more than 99% of copper and nickel ions from its single cation bearing solutions under the optimum operating conditions. As in both copper and nickel extraction tests, the ELM formed is water-in-oil-in-water emulsion, where the internal water phase is sulfuric acid, with the oil phase being kerosene containing metal extractant & surfactant and the external water phase being cation bearing solution. The surfactant used is oil-soluble SPAN 80 (Sorbitan monooleate) for all tests.

As for copper extraction, the extractant used was LIX 984N, four factors were screened out as important ones that could significantly affect the copper extraction efficiency: extractant concentration; W/O/W emulsion stirring time; W/O/W emulsion stirring speed; and $CuSO_4$ solution/emulsion volume ratio. The other factors were not important thus they were fixed at constant value: surfactant concentration of 2.0 wt %; Cu^{2+} concentration of 500 ppm; ultrasonic time for primary emulsion of 1 minute, oil/H_2SO_4 volume ratio of 5 and $CuSO_4$ solution pH of 3.5. The optimum operating condition of copper extraction is determined to be: $CuSO_4$ solution/primary emulsion volume ratio of 3.2; extractant concentration of 6.7 wt %; H_2SO_4 concentration of 4.6 mol/L; W/O/W emulsion stirring time of 24 minutes; and W/O/W emulsion stirring speed of 415 rpm (1 rpm = $\frac{1}{60}$ Hz $= \frac{\pi}{30}$ rad/s).

As for nickel extraction, the extractant used was Cyanex 301, the optimum laboratory conditions were: extractant concentration of 7.2 wt %; stripping solution (H_2SO_4) concentration of 0.5 mol/L; $NiSO_4$ solution pH of 4.5; and $NiSO_4$ solution/emulsion volume ratio of 3.5. A series of comparison tests between ELM technique and traditional solvent extraction technique were performed and the following results were found: The loading capacity tests showed that emulsion phase had a higher nickel extraction capacity (8.128 g Ni (II)/100 g Cyanex 301) than the organic phase (5.240 g Ni (II)/100 g Cyanex 301). The kinetics tests showed that nickel ion concentration in the aqueous feed phase decreased by first order kinetics for both the emulsion phase and the organic phase, where they had a mass transfer coefficient of 2.823×10^{-7} (m/s) and 3.192×10^{-7} (m/s) respectively.

After the process optimization and chemical characteristics have been explored for ELM treating copper and nickel ions separately, the selective extraction and separation of copper and nickel from calcium ion in a synthetic wastewater solution mimicking the nickel mine tailings from Sudbury, Ontario was investigated. The solution had a copper concentration of 10 ppm, nickel concentration of 20 ppm; an averaged calcium concentration of 250 ppm and its pH was 4.0. Two stages were implemented. It was found that in the first stage, LIX 984N was used as copper extractant and copper ion was effectively separated from nickel and calcium ions, the optimum operating conditions were: extractant concentration of 0.97 wt %, H_2SO_4 concentration of 0.5 mol/L, W/O/W emulsion stirring time of 22.5 minutes and synthetic solution/emulsion volume ratio of 4.0. The copper removal rate was 96.7% while nickel and calcium removal rate was only 0.9 % and 1.3%; In the second stage, a mixture of LIX 984N and Cyanex 301 at a volume ratio of 1 to 1 was used as extractant, and the optimum operating conditions were: extractant concentration of 6.7 wt %, H_2SO_4 concentration of 5.7 mol/L, W/O/W emulsion stirring time of 25 minutes and synthetic solution/emulsion volume ratio of 3.5. The nickel removal rate was 99.0% while the calcium removal rate was 0.55%. A two-stage bench-scale mixer-settler proved the process of using ELM to extract and separate these metal ions was successful under these optimum conditions obtained.

RÉSUMÉ

La technique de la membrane liquide émulsion (MLE) est une technique modifiée qui combine l'extraction traditionnelle au solvant et le stripage dans une seule opération unitaire. Les caractéristiques de la MLE comprennent la grande surface interfaciale et une grande sélectivité lors du traitement des ions de métaux lourds. Par à l'étude de l'application de la technique MLE pour extraire et déshabille des ions métalliques lourds tels que le cuivre et le nickel à partir de solutions simples de cations, cette thèse vise l'extraction et la séparation de différents métaux tels que le cuivre, le nickel et le calcium, en utilisant le réactif et la consommation d'énergie minimum. Un mélangeur-décanteur à deux étages a finalement été construit et mis en œuvre pour tester l'efficacité d'extraction et de séparation de la MLE.

Il est apparu que la technique MLE peut éliminer plus de 99% des ions cuivre et nickel de ses solutions de palier cationiques uniques dans les conditions de fonctionnement optimales. Comme dans les tests d'extraction de cuivre et de nickel, la MLE formé est une émulsion eau-dans-huile-dans-eau (E/H/E), dans laquelle la phase aqueuse est de l'acide sulfurique, la phase huileuse étant un agent d'extraction et un tensioactif contenant du kérosène. Le surfactant utilisé est SPAN 80 qui est soluble dans l'huile pour tous les tests.

Pour l'extraction du cuivre, l'agent d'extraction utilisé était le LIX 984N, quatre facteurs ont été éliminés comme étant importants, ce qui pourrait avoir une incidence importante sur l'efficacité de l'extraction du cuivre: concentration de l'agent d'extraction; temps d'agitation de la MLE; Vitesse d'agitation de la MLE; et le rapport solution $CuSO_4$/volume d'émulsion. Les autres facteurs n'étant pas importants, ils ont été fixés à une valeur constante: concentration en tensioactif de 2.0% en poids; Concentration en solution de $CuSO_4$ de 500 ppm; temps ultrasonore pour l'émulsion primaire de 1 minute, le rapport de volumique huile/H_2SO_4 de 5 et solution de $CuSO_4$ pH de 3.5. La condition de fonctionnement optimale de l'extraction du cuivre est déterminée comme étant: rapport $CuSO_4$/volume d'émulsion primaire de 3.2; concentration d'agent d'extraction de 6.7% en poids; concentration en H_2SO_4 de 4.6 mol/L; émulsion temps d'agitation de la MLE 24 minutes;

et vitesse d'agitation de la MLE de 415 tours/min.

Pour l'extraction du nickel, l'agent d'extraction utilisé était le Cyanex 301, les conditions de laboratoire optimales étaient: une concentration d'agent d'extraction de 7.2% en poids; concentration de solution (H_2SO_4) de 0.5 mol/L; solution de $NiSO_4$ pH 4.5; et le rapport solution de $NiSO_4$/volume d'émulsion de 3.5. Une série de tests de comparaison entre la technique MLE et la technique traditionnelle d'extraction par solvant ont été réalisées et les résultats suivants ont été trouvés: Les tests de capacité de charge montrent une capacité d'extraction du nickel supérieure (8.128 g Ni (II)/100 g Cyanex 301) pour la phase emulsion et (5.40 g de Ni (II)/100 g de Cyanex 301) pour la phase organique. Les essais de cinétique ont montré que la concentration en ions nickel dans la phase d'alimentation aqueuse diminuait par la cinétique du premier ordre tant pour la phase émulsion que pour la phase organique, avec un coefficient de transfert de masse de 3.192×10^{-7} (m/s) et 2.823×10^{-7} (m/s) respectivement.

L'extraction sélective et la séparation du cuivre et du nickel de l'ion calcium dans une solution synthétique d'eaux usées imitant les résidus miniers de nickel de Sudbury, en Ontario, ont été étudiées. La solution avait une concentration de cuivre de 10 ppm, une concentration de nickel de 20 ppm; une concentration moyenne de calcium de 250 ppm et son pH était de 4.0. Deux étapes ont été mises en œuvre. Dans la première étape, LIX 984N était utilisé comme extractant du cuivre et que l'ion cuivre était efficacement séparé des ions nickel et calcium, les conditions opératoires optimales étaient: concentration d'agent d'extraction de 0.97% en poids, concentration en H_2SO_4 de 0.5 mol/L, Temps d'agitation de la MLE de 22,5 minutes et rapport de la solution synthétique / volume de l'émulsion de 4.0. Le taux d'élimination du cuivre était de 96.7% alors que le taux d'élimination du nickel et du calcium était de seulement 0.9% et 1.3%; Dans la seconde étape, un mélange de LIX 984N et Cyanex 301 dans un rapport volumique de 1 à 1 a été utilisé comme extractant, et les conditions opératoires optimales étaient: concentration en extractant de 6.7% en poids, concentration en H_2SO_4 de 5.7 mol/L, Temps d'agitation de la MLE de 25 minutes et rapport volume de solution synthétique/volume d'émulsion de 3.5. Le taux d'élimination du nickel était de 99.0% tandis que l'élimination du calcium était de 0.55%. Un mélangeur-décanteur en deux étapes

à l'échelle du laboratoire a prouvé que le procédé consistant à utiliser la MLE pour extraire et séparer ces ions métalliques était un succès dans les conditions optimales obtenues.

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CONTRIBUTION OF AUTHORS

The thesis is presented as a “manuscript-based thesis” consisting of Chapter 2 of literature reviews and Chapters 3, 4 and 5 that are based on three manuscripts, where 2 manuscripts were published and one was under review. All the manuscripts are co-authored by Professor Kristian E. Waters as research supervisor and Dr. Ozan Kökkılıç as a research associate for help with design of experiment. Chapter 4 is also co-authored by Christopher M. Marion, Ravinder S. Multani for their work on zeta-potential analysis and article review. Chapter 5 is also co-authored by Raymond Langlois, Xuejuan Song, Yong Qin for their work on mixer-settler set-up and running. The information of manuscripts for Chapters 3, 4 and 5 is as follows:

1. Ma, H., Kökkılıç, O., & Waters, K. E. (2017). "The use of the emulsion liquid membrane technique to remove copper ions from aqueous systems using statistical experimental design." Minerals Engineering 107(Supplement C): 88-99.
2. Ma, H., Kökkılıç, O., Marion, C. M., Multani, R. S., & Waters, K. E. (2018). "The extraction of nickel by emulsion liquid membranes using Cyanex 301 as extractant." The Canadian Journal of Chemical Engineering 96:1585–1596.
3. Ma, H., Kökkılıç, O., Langlois, R., Song X. J., Qin, Y., & Waters K. E. (2018). " Selective separation of copper and nickel ions from aqueous solutions containing calcium by emulsion liquid membranes using central composite design." The Canadian Journal of Chemical Engineering, minor revision.

All the experiments and chemical & statistical analysis were performed by the candidate, beyond the noted contributions of the co-authors the whole work presented in this dissertation was performed and written by the candidate.

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NOMENCLATURE AND ABBREVIATIONS

A/O	Acid to organic phase ratio
AMD	Acid mine drainage
ANOVA	Analysis of variance
$CaSO_4 \cdot 2H_2O$	Calcium sulfate dihydrate
CCD	Central composite design
Coef	Regression coefficient
$CuSO_4$	Anhydrous cupric sulfate
Cyanex 272	Bis(2,4,4-trimethylpentyl) phosphinic acid
Cyanex 301	Bis(2,4,4-trimethylpentyl)dithiophosphinic acid
D2EHPA	Di-(2-ethylhexyl) phosphoric acid
DF	Degree of freedom
DOE	Design of experiment
ELM	Emulsion liquid membrane
Eq. pH	Equilibrium pH
ext	External
FFD	Fractional factorial design
FTIR	Fourier transform infrared spectroscopy
HLB	Hydrophilic-lipophilic balance
H_2SO_4	Sulfuric acid
ICP-OES	Inductively coupled plasma optical emission spectroscopy
iep	Isoelectric point
int	Internal
IX	Ion-exchange
LIX 84N-I	2-hydroxy-5-nonylacetophenone oxime
LIX 860N-I	5-nonylsalicylaldoxime

$NiSO_4 \cdot 6H_2O$	Nickel sulfate hexahydrate
NSERC	Natural sciences and engineering research council
OFAT	One factor at a time
O/W	Oil in water
O/W/O	Oil in water in oil
PC-88A	2-ethyl hexyl phosphonic acid and mono 2-ethyl hexyl ester
ppm	Parts per million = mg/L^{-1}
PVR	Phase volume ratio = V_{org} / V_{aq}
RO	Reverse osmosis
RPM	Revolutions per minute
RSM	Response surface methodology
SD	Standard deviation
Span-80	Sorbitan monooleate
SX	Solvent extraction
Tween 60	Polyethylene glycol sorbitan monostearate
V_{aq}	Volume of aqueous phase
Versatic 10	Neodecanoic acid
V_{org}	Volume of organic phase
W/O	Water in oil
W/O/W	Water in oil in water
wt %	Weight percentage
ζ-potential	Zeta potential

CHAPTER 1. INTRODUCTION

1.1 INTRODUCTION

According to the survey released by Statistics Canada in 2014 [1.1], the manufacturing industries discharged 3,226.8 million cubic meters of water; of this, 34.0% was not treated prior to release. Regarding the mining industry, a total of 587.9 million cubic meters were discharged where 43.8% was not treated before discharge, and 47.6% only underwent primary or mechanical treatment [1.1]. Generally, the waste water released by the mining industry contains heavy metal ions (Cr, Pb, Zn, Cu, Ni, Cd, Co, etc.) [1.2-1.6], which are usually toxic, meaning that they not only damage local fauna and flora, but also a threat to humans due to the accumulation of toxic metals in the food chain [1.7-1.8]. One example of where heavy metal ions are commonly found is acid mine drainage (AMD), where a high concentration of these ions in the water are caused by the oxidation of the sulphide minerals in the presence of water [1.9-1.11]. In the meantime, authorized limits of heavy metal ions are generally required to be low. Thus, in order to reduce the metal contents to a legal limit, a certain cost will be accrued. Statistics Canada shows that the water cost associated with effluent treatment of the manufacturing industries and the mining industries in 2011 were $393.8 million and $87.7 million dollars, respectively [1.1]. These numbers mean that wastewater treatment continues to increase since daily manufacturing and mining activities are still growing.

Many different techniques have been utilized to remove these heavy metal ions, and potentially produce a revenue stream from the wastewater. These methods include, but are not limited to: chemical precipitation, ion-exchange, adsorption, flotation, flocculation, coagulation, reverse osmosis, evaporation, electrochemical treatment, and solvent extraction [1.12-1.15]. Depending on different requirements, these techniques are generally effective in removing heavy metal ions. However, the selection of one over another method in a real situation may differ, and the choice depends on the composition of wastewater, the energy & materials costs, the location & space requirements, etc. Out of these methods, solvent extraction (SX) is an effective hydrometallurgical technique in removing these metal ions from concentrated solutions (where the concentration of metal ion is usually higher than 0.5g/L) [1.16-1.22]. However, when facing a wastewater stream with much lower concentrations of heavy metal ions, SX is not always a good choice due to the high solvent consumption, solvent loss and phase separation difficulties during the operation process [1.23]. One solution to this problem is to increase the contacting surface area between organic solvent and the wastewater solution. Based on this idea, different techniques have been proposed including liquid membranes, colloidal gas aphrons and air-assisted solvent extraction [1.24].

As one of the very promising techniques, liquid membranes have attracted researchers for the past two decades [1.25]. Membrane system usually has an immiscible or semipermeable liquid barrier between the feed and receiving phases, it possesses two characteristics which distinguish itself from conventional solvent extraction. The first property is the large surface area as a result of its micrometer size droplets. This does not only improve mass transfer (extraction) rate when compared to conventional SX, it also helps treat the dilute solutions with a low organic/aqueous ratio and energy & materials saving can be achieved. The second property is the stripping process which can regenerate the extractant. This significantly increases the loading capacity of metal extraction [1.26]. Generally liquid membranes can be divided into three major groups: bulk, supported and emulsion liquid membrane (ELM) [1.25, 1.27]. ELMs usually achieve the highest mass transfer area among these three types of membranes thus it is preferred in many applications [1.25].

Emulsion liquid membranes, also termed a “double emulsion”, was first used by Li to separate hydrocarbons from wastewater in 1968 [1.28-1.29]. Two types of emulsion liquid membranes can be usually observed: water-in-oil-in-water (W/O/W) emulsion and oil-in-water-in-oil (O/W/O) emulsion, where the immiscible membrane phase separating the external and internal phase is oil and water [1.27, 1.30-1.35]. For metal ion removal from a wastewater stream, a W/O/W type emulsion is commonly used. The external water phase is wastewater solution and the internal water phase is a strong acid liquor, while the middle oil phase will be organic diluent containing oil soluble metal extractant and surfactant. The metal cation from the external solution will firstly diffuse to the interface between the feed and the emulsion membrane phase, where it will rapidly complex with an extractant molecule. This metal-extractant complex formed will move freely inside the oil phase until it reaches the internal stripping liquor; a higher concentration of H^+ in the stripping liquor will always dissociate the metal cation from its complex prior to moving into the stripping liquor [1.36]. This carrier-facilitated coupled transport relies heavily on the chemical potential gradient of H^+ between the feed and the stripping phase. The attractive features of ELM include: the emulsions have very large surface area to volume ratio with rapid separation; it combines extraction and stripping in one single stage; the operation is simpler with higher efficiency and lower investment & materials cost; it could selectively extract one metal from others; it also has lower solubility of organic substances in the water; the process is generally environmental friendly; and it has the potential of continuous operation [1.25, 1.33].

In the past few decades, there are many examples of the ELM technique being used to remove or recover metal ions such as copper, nickel, zinc, cobalt, chromium, uranium, cadmium, mercury, rare earth metal ions, to name but a few [1.37-1.51]. The separation of different metal ions, such as cobalt and nickel, zinc and copper, lead and cadmium can also be achieved by ELM [1.42-1.44, 1.51-1.55]. Because of the advantages associated with ELM technique, lab-scale mixer-settlers [1.34, 1.42-1.44] or even pilot-scale plants have been built, these include the three pilot-scale plants for zinc removal from wastewater located in Glanzstoff, AG, Austria (700 m^3/h capacity), CFK Schwarza, Germany (200 m^3/h capacity) and AKZO Iede, the Netherlands (200 m^3/h capacity) [1.30]. However, no commercial large-scale plant currently exists, partially due to the stability issue associated with emulsions, where membrane leakage, coalescence, and emulsion swelling can often be observed during operation [1.25, 1.33, 1.56]. In addition to the chemical characteristics and properties of ELM, the effects of parameters during the process, process optimization, and technical comparisons between ELM and traditional SX are not fully understood and are somewhat under-reported. These questions or problems should be solved.

1.2 THESIS OBJECTIVE

The objective of this thesis is to apply the ELM technique to treat a synthetic wastewater solution containing heavy metal ions such as copper and nickel. Based on the information obtained, it also aims at obtaining a detailed description of process parameters when using a lab-scale two-stage mixer-settler to separate heavy metal ions, thus providing insight into possible scale-up and continuous process development. Specific objectives are as follows:

(i) ELMs generation and characterization.

(ii) While applying ELM technique treating copper / nickel ion solution, investigating the influences of operating parameters; interactions of these parameters; process optimization and the chemical principles & properties behind.

(iii) Comparing the ELMs with SX on different physical & chemical properties.

(iv) Examining the feasibility in removing and separating copper and nickel ions in the presence of calcium ions using ELMs.

(v) Examining the breakage and recyclability of ELMs

1.3 THESIS STRUCTURE

This thesis is a manuscript-based thesis, consisting of 6 chapters, Chapters 3, 4, 5 being either published or submitted for peer-review. The outline of each chapter is as follows:

Chapter 1:

This chapter discusses the introduction, thesis objective and structure.

Chapter 2:

In this chapter, a detailed literature review of heavy metal ions pollution and corresponding removing techniques; principles of emulsion & liquid membrane; ELM theories and models, the current & recent research of heavy metal ions including copper, nickel extraction by ELM is given.

Chapter 3:

This chapter details copper ion extraction using the ELM technique in order to explore the important operating parameters and obtain the optimal parameters under different conditions. In addition, the complex formation between the copper cations and bidentate ligands are detailed by means of FTIR. This chapter was presented at the conference "Sustainable Minerals '16" (Falmouth, UK) and subsequently published in Minerals Engineering as:

Ma, H., Kökkılıç, O., & Waters, K. E. (2017). "The use of the emulsion liquid membrane technique to remove copper ions from aqueous systems using statistical experimental design." Minerals Engineering 107(Supplement C): 88-99.

Chapter 4:

Based on the previous information obtained in Chapter 3, this chapter shows that the process of nickel ions extraction using ELM technique have also been optimized. The emulsion was also successfully recycled. In addition, the chemical characteristics of ELM and comparison between ELM and traditional solvent extraction was made. This chapter was published in the Canadian Journal of Chemical Engineering as:

Ma, H., Kökkılıç, O., Marion, C. M., Multani, R. S., & Waters, K. E. (2018). "The extraction of nickel by emulsion liquid membranes using Cyanex 301 as extractant." The Canadian Journal of Chemical Engineering 96:1585–1596.

Chapter 5:

This chapter details the use of the ELM technique to selectively recover copper and nickel from calcium in a synthetic process water designed to mimic a tailings pond from Vale's operations in Sudbury (Ontario, Canada). This chapter is currently under review in the journal “The Canadian Journal of Chemical Engineering” as:

Ma, H., Kökkılıç, O., Langlois, R., Song X. J., Qin, Y., & Waters K. E. (2018)." Selective separation of copper and nickel ions from aqueous solutions containing calcium by emulsion liquid membranes using central composite design." The Canadian Journal of Chemical Engineering, minor revision.

Chapter 6:

This chapter discusses the major conclusions of this project, the contributions to the original knowledge as well as suggestions for future work.

Appendix A:

The optical microscopy images of organic and ELM phase droplets under different conditions.

Appendix B:

Derivation procedures of the diffusion transport model.

Appendix C:

A detailed comparison between ELM and SX technique.

Appendix D:

The reaction mechanisms between LIX 984N & Cyanex 301 and copper & nickel ions.

Appendix E:

The effect of multiple ionic species in solution.

Appendix F:

The implementation of ELM technology in a metallurgical operation.

Appendix G:

The proposed continuous process flowsheet for pilot-scale plant treating wastewater stream using ELMs.

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CHAPTER 2. A REVIEW OF THE EXTRACTION OF HEAVY METAL IONS FROM WASTEWATER BY EMULSION LIQUID MEMBRANES

2.1 ABSTRACT

This chapter provides a comprehensive review of the generation, characterization, physical & chemical properties and applications of emulsion liquid membranes (ELM) from more than 200 published papers & books so far. It will firstly give a brief discussion about wastewater heavy metal ions and the current methods of treatments, then it will discuss the formation of emulsion liquid membranes as well as the transport mechanisms and corresponding models for ELM; it will then discuss the stability of ELM as well as emulsion splitting methods; these are then followed by the most important part of this chapter – the latest research and findings of the extraction of heavy metals such as copper and nickel using ELMs technique during the past few decades.

2.2 HEAVY METAL IONS FROM WASTEWATER AND METHODS OF TREATMENTS

As defined, heavy metal ions usually refer to elements having atomic weights between 63.5 and 200.6 and a specific gravity greater than 5.0 [2.1-2.2]. They exist in all forms of waste effluents including mining tailings, manufacturing discharges, smelting and metal plating processes [2.3]. They are usually not considered to be biodegradable. Many heavy metal ions are toxic, or the accumulation of heavy metals ions can be harmful to living organisms [2.4-2.6]. For example, in excess amounts, copper can cause many problems to human beings such as vomiting, convulsions and cramps [2.6]; nickel is a human carcinogen and it may cause serious lung and kidney problems such as pulmonary fibrosis and gastrointestinal distress [2.4]; mercury may cause nausea, nephrotic syndrome and neurotic disorder to human beings [2.7]; lead, one of the most common heavy metal in wastewater, may cause brain dysfunction and severe kidney disease [2.8]; cadmium as well as chromium may cause lung problems such as lung inflammation, scarring or even cancer

[2.5, 2.9]. In order to minimize the negative effects brought by these heavy metal ions to the environment, governments around the world have set strict regulations regarding the heavy metal ion concentrations allowed in wastewater discharges; the authorized heavy metal ion concentration in mining effluent set by the Canadian government is given in Table 2.1:

Table 2.1 The maximum authorized heavy metal ion concentration in mining effluent set by the Canadian government [2.10]

Item	**Metal**	**Maximum authorized monthly mean concentration**	**Maximum authorized concentration in a grab sample**
1	Copper	0.30 mg/L	0.60 mg/L
2	Lead	0.20 mg/L	0.40 mg/L
3	Nickel	0.50 mg/L	1.00 mg/L
4	Zinc	0.50 mg/L	1.00 mg/L

One main source of wastewater containing heavy metal ions is acid mine drainage (AMD). Although the formation of AMD is a complicated process with a combination of chemical and microbiological process, it generally includes the oxidation of pyrite and pyrrhotite [2.11-2.14], as such it often contains iron as well as many different heavy metal ions. These heavy metal ions concentration may vary and were sometimes distributed unevenly among the tailings, causing difficulty in treatment. An example of AMD from Montalbion silver mine, northern Queensland (Australia) is given in Table 2.2.

Table 2.2 Heavy metal ion concentration from a representative acid mine drainage sample obtained from Montalbion mine, Australia [2.15]

Element	Concentration (mg/L)
Al	27.7
Ba	0.081
Cd	0.561
Co	0.273
Cu	12.9
Fe	12.1
Mn	18.5
Ni	0.172
Pb	0.052
Zn	60.7

As concluded by Fu & Wang (2011) [2.5] as well as other researchers, various methods have been implemented towards removing heavy metals ions from wastewater, these methods include solvent extraction [2.16-2.21]; chemical precipitation [2.22-2.24], ion exchange [2.25-2.26], adsorption [2.27], solid membrane filtration [2.28-2.29], liquid membrane technique [2.30-2.33], coagulation and flocculation [2.34-2.35], floatation [2.36] as well as electrochemical treatment [2.37-2.39]. Their advantages & disadvantages are listed in Table 2.3a and Table 2.3b.

Table 2.3a The advantages and disadvantages of various methods treating heavy metal ions from wastewater (adapted from Fu & Wang (2011)) [2.5]

Techniques		**Advantages**	**Disadvantages**	**Ref.**
Chemical precipitation	Hydroxide precipitation	Simple, low cost and ease of pH control	Large volumes of low-density sludge, some metal hydroxides are amphoteric causing problem for others, metal precipitation may be inhibited	[2.40-2.42]
	Sulfide precipitation	High degree of metal removal over a broad pH range, better thickening and dewatering characteristics	Possible production of toxic H_2S fumes, colloidal precipitates may cause some separation problems	[2.22, 2.43]
	Chemical precipitation combined with other methods	Higher metal removal, the possibility of materials recycling	Cases are individual, not many supporting references exist	[2.44-2.46]
	Heavy metal chelating precipitation	Better meet the increasingly stringent environmental regulations, more effective and simplified process	Chelating compounds can block the hydroxide precipitation reaction	[2.47-2.49]
Ion exchange		High treatment capacity, high removal efficiency and fast kinetics,	Difficulty in treating concentrated metal solution, not very selective, highly sensitive to pH	[2.50-2.53]
Adsorption	Activated carbon adsorbents	Large micropore and mesopore resulting high surface area	Commercial coal-based activated carbon is depleting	[2.54-2.56]
	Carbon nanotubes adsorbents	Superior adsorption capability	Its discharge into water may pose a risk to humans	[2.57-2.61]
	Low-cost adsorbents	Generally cheaper and easily available, using waste as absorbent	Efficiency may be low	[2.62-2.67]
	Bioadsorbents	High effectiveness, the use of inexpensive biosorbents, ideal for dilute heavy metal wastewater	Difficulty in separation of biosorbents afterwards	[2.68-2.70]
Solid membrane filtration	Ultrafiltration	High removal efficiency, binding selectivity and metal concentrates for reuse,	Not widely spread in use, operational cost is high	[2.71-2.72]
	Reverse osmosis	Able to remove a wide range of dissolved species	High power consumption	[2.73-2.74]
	Nanofiltration	Ease of operation, reliability; comparatively low energy consumption, high efficiency of pollutant removal	High operation cost and may soften water	[2.75-2.78]
	Electrodialysis	High separation selectivity	High operation cost and energy consumption	[2.79-2.80]

Table 2.3b The advantages and disadvantages of various methods treating heavy metal ions from wastewater (continued from previous table)

Techniques		Advantages	Disadvantages	Ref.
Solvent extraction		Selective, metal solution can be concentrated, process recyclability	High capital cost & solvent consumption, limited to high metal concentrations (>500 mg/L)	[2.16-2.21]
Liquid membrane technique	Emulsion liquid membrane	Large contacting surface area, higher efficiency, relatively lower cost, extraction & stripping in the same process	Unstable and breakage of emulsion droplets may occur	[2.31-2.33]
	Bulk liquid membrane	Simplicity in operation, simultaneous separation and preconcentration	Relatively low interfacial area to volume ratio	[2.81-2.82]
	Supported liquid membrane	High interfacial area, low solvent loss, no loading and flooding limitations	Issues with chemical stability of the carrier and the mechanical stability of porous support	[2.83-2.87]
Coagulation and flocculation		Function efficiently over wide pH ranges and water temperatures as well as lower dosages	Limitation in treatment, needs to be followed by other techniques	[2.88-2.91]
Flotation		Extensive usage, be selective	Limited pH, extra chemicals may be needed	[2.92-2.94]
Electrochemical treatment		Able to meet the stringent environmental regulations	Relatively large capital investment and the expensive electricity supply	[2.95-2.97]

Although the techniques listed above can be used to treat industrial effluents containing a high level of metal ions, when facing the wastewater that contains a much lower metal ion concentration (less than 500 mg/L), most techniques would incur a lower removal or separation efficiency as well as high operating cost. The emulsion liquid membrane technique can be used to solve these problems, it has a high removal efficiency and very large contacting surface area. Thus, this thesis will focus on the emulsion liquid membrane technique and the details of which will be described in the following sections.

2.3 Emulsion Liquid Membrane Generation

An emulsion refers to the dispersion of one liquid phase (dispersed phase) in another immiscible phase (continuous phase) [2.98]. They are usually in the form of water in oil (W/O) or oil in water (O/W). Emulsion liquid membrane (ELM) is often referred to an emulsion in emulsion, or double emulsion; usually two forms of ELM exist including water-in-oil-in-water (W/O/W) or oil-in-water-in-oil (O/W/O), where the middle immiscible phase behaves as the liquid membrane separating the internal and external phases [2.99-2.104]. Two steps are usually involved in the formation of ELM, which are the formation of primary emulsion and the formation of emulsion liquid membrane. In order to prepare the primary emulsion, water or oil droplets need to be broken up into many smaller ones to suspend in the surrounding liquid. The deformation of a droplet is opposed by Laplace pressure-a pressure difference between the convex and concave side of a curved interface [2.105].

$$\Delta P = P_{inside} - P_{outside} = \gamma\ (1/R_1 + 1/R_2) \qquad \text{Equation 2.1}$$

where γ represents the surface tension and R_1 and R_2 represent the principal radii of curvature. Generally, a larger external stress needs to be applied to the mother droplet, which means that a very large pressure gradient occurs in order to deform the droplets. Although this could be done by high stresses in laminar flow, in most cases, when droplets are suspended in water or other low-viscosity liquid, droplet break up occurs in the turbulent flow, where inertial effects (liquid chaotic motion such as pressure fluctuations or cavitation) play the main role, although high shear stresses are sometimes required [2.106-2.107]. The following devices are generally used for emulsification: mechanical stirrers, high-pressure homogenizers (such as ultrasonicator) and rotor–stator systems (such as colloidal mills); the comparisons of these devices are made in Table 2.4:

Table 2.4 The comparisons of emulsification devices (adapted from Ahmad *et al.* (2011)) [2.108]

Devices	Emulsification through	Advantages	Disadvantages	Ref.
Mechanical stirrers	Shear stresses	High availability and process controllable	High energy consumption	[2.109]
High-pressure homogenizers	Turbulence and cavitation effects	High pressure may lead to very fine droplets, droplets are usually homogenized	Excessive temperature increase, high energy dissipation & difficulty in controlling droplets size	[2.110-2.111]
Rotor–stator systems	Mechanical and hydraulic shear causing turbulence	High efficiency, short processing time and very high shear condition	Not designed for multi-sample, high-throughput application	[2.112-2.115]

The addition of an emulsifier (surfactant) is necessary in order to form a stable emulsion. The emulsifier usually has a polar head (hydrophilic) and a non-polar tail (lipophilic), and the non-polar tail will go into oil phase while the polar head will remain in the water phase [2.105]. Figure 2.1 shows a typical structure of an emulsifier molecule in O/W emulsion.

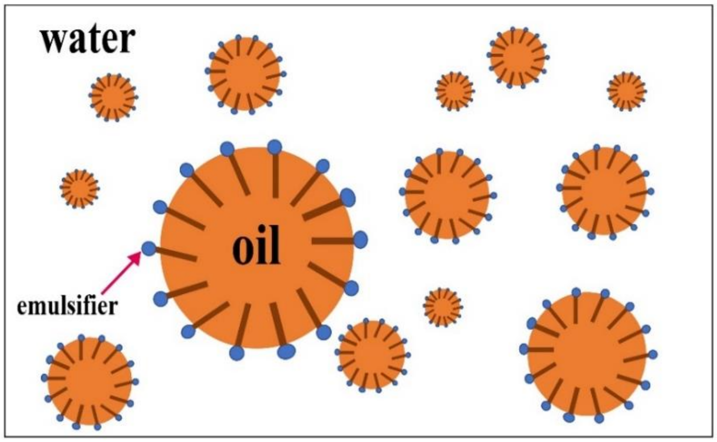


Figure 2.1 A typical structure of emulsifier molecule in O/W emulsion

The types & effects of emulsifiers have been discussed by many other researchers and are thus only briefly mentioned here. The emulsifier does not only lower the surface tension (γ) in order to facilitate the break-up of emulsion droplets, but also prevent the formed emulsion droplets from recoalescence [2.98-2.99].

After the primary emulsion is formed (it could be W/O or O/W emulsion), an emulsion liquid membrane will be generated by stirring the primary emulsion in water or oil depending on the matrix, the stirring usually conducted using a mechanical stirrer with the speed low enough that the formed internal droplets are not disrupted. During this process, an additional surfactant may be required depending on the system. Even when it is needed, the concentration will generally be low [2.116]. A typical structure of ELM droplet can be seen in Figure 2.2.

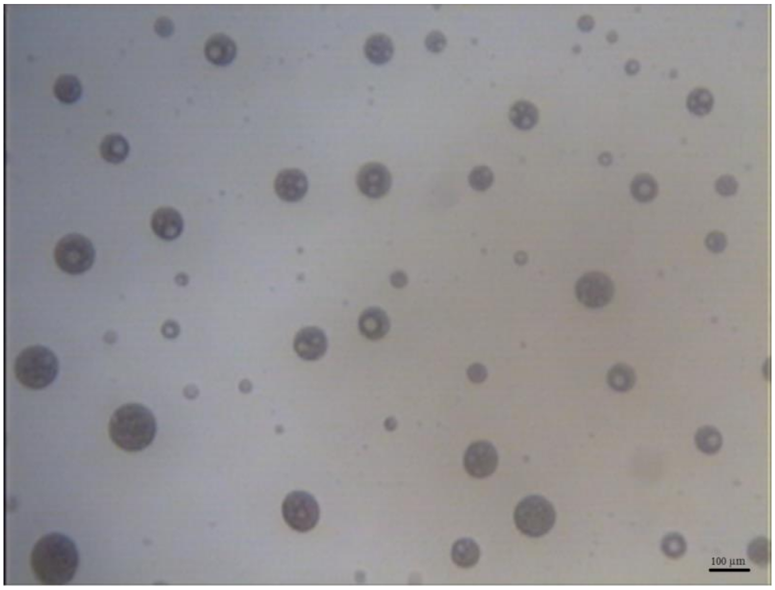


Figure 2.2 A typical structure of ELM droplet

2.4 ELM MECHANISM AND MODELS

For the extraction of heavy metal ions using emulsion liquid membrane, solution-diffusion model is the most widely accepted mechanism [2.33, 2.98]. It can be divided into two types including simple permeation mechanism and facilitated transport mechanism. They are discussed in the following subsections separately.

2.4.1 Simple permeation mechanism

Here the solute in the external liquid phase is dissolved into the liquid membrane, the dissolved solute has a certain diffusivity that can be transported into the internal receiving phase. This mechanism was driven by the concentration difference of the solute between the inside and outside of the liquid membrane (from high concentration to low concentration) [2.117]. However, this is rare and in in most cases the second mechanism applies.

2.4.2 Facilitated transport mechanism

In order for the maximum amount of solute to diffuse into the membrane phase and transport these solute into receiving phase, two mechanisms may be utilized:

- The first one is passive transport mechanism, which is done through the incorporation of a stripping liquor inside the receiving phase. Once the solute moving in the membrane phase reacts with the stripping agent, a membrane insoluble product is produced [2.118-2.121]. The examples include phenol removal when NaOH is used as the receiving stripping liquor and nickel oxalate particles precipitate when using oxalic acid solutions as the stripping liquor [2.122-2.123].
- The second one is more widely used, where a carrier (or extractant) exists in the membrane phase, thus, the solute diffusion and chemical reactions occur in both the membrane phase and internal receiving phase [2.124-2.127]. Depending on the system requirement, the carrier can be acid, basic or chelating. Especially for metal ion transport, the carriers are usually acid such as -COOH or chelating products such as commercially available LIX products [2.30-2.32]. The whole process is as followed: Firstly, when a solute enters into the interface between the membrane and the external phase, it will usually form a solute-carrier complex that is soluble in the membrane phase - this reaction is reversible [2.32]. This complex can diffuse freely inside the membrane phase, and once it reaches the interface between the membrane and internal phase it will dissociate and the solute will dissolute back into the internal phase [2.128-2.129]. It can be seen that this process combines both solvent extraction and stripping in the same step [2.32, 2.130]. Through this way, the carrier molecule can be regenerated and reused many times, meaning that a lower amount of carrier is required when using ELM than conventional solvent extraction. The percentage metal removal can be calculated by comparing the difference of metal concentration in aqueous phase before and after extraction process. Figure 2.3 shows a typical process for metal ion extraction by ELM using $NiSO_4$ solution as an example. In this example, HR represent a nickel extractant (such as Cyanex 301) and NiR_2 represents the nickel-extractant complex.

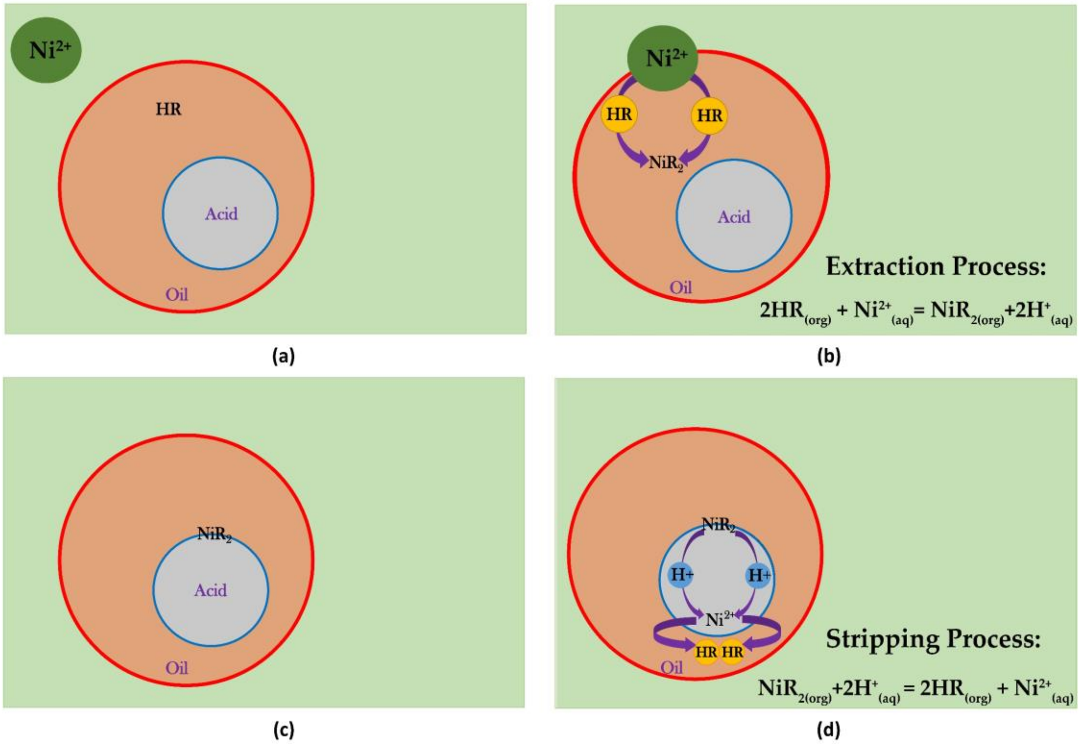


Figure 2.3 The extraction of nickel ions by ELM technique: (a) The formation of ELM globules in $NiSO_4$ solution; (b) The formation of nickel-extractant complex by solvent extraction; (c) The nickel-extractant complex moves freely inside the ELM globule; (d) The regeneration of nickel ions inside the internal liquor by stripping.

2.4.3 ELM models

Fick's first law is usually used to describe the mass transport of solute into the membrane (permeation) phase, this is driven by the potential gradient of the solute through the external phase and the membrane phase [2.33]. The equation is as follows:

$$J = -D\frac{dC}{dx} \qquad \text{Equation 2.2}$$

J is the solute diffusion flux; D represents the solute diffusion coefficient; C is the solute concentration while x is the membrane thickness. If it is steady-state diffusion, a linear concentration gradient exists, thus the equation can be written as follows:

$$J = -\frac{D}{x}\Delta C = k\Delta C \qquad \text{Equation 2.3}$$

Here k is the mass transport coefficient of the solute across the membrane. However, if there is a large chemical potential existing over a thin membrane, the equation should be expressed by Fick's second law [2.98]:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad \text{Equation 2.4}$$

Many different models have been proposed ever since Li used ELM to separate hydrocarbons. Depending on where mass transfer is concentrated (membrane film or throughout the emulsion droplet), these models include but are not limited to: spherical shell model [2.118]; membrane film model [2.131]; advancing front model [2.132]; reversible reaction model [2.120] and advancing stripping model [2.133]. They are only briefly mentioned here and a comparison of the models in its simplest form of every type is made in Table 2.5.

Table 2.5 A comparison of current proposed ELM models (adapted from Chakraborty *et al.* (2011)) [2.134]

Terms	Models	Conditions	Ref.
Spherical shell model	$\ln\frac{C_{ini}}{C_{fin}} = D'(\frac{V_E}{V_W})t$	C_{ini} and C_{fin}: The initial and final concentration of metal ions; D': The diffusion rate constant; V_E/V_W: The volume ratio of emulsion phase and aqueous phase; t: The contacting time.	[2.118, 2.135-2.137]
Unsteady-state membrane film model	$\frac{\partial C_m}{\partial t} = D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_m}{\partial r}\right)$ $C_m = 0$ at $t = 0$ ($r < R_o$); $C_m = \alpha C_c$ at $r = R_o$ ($t > 0$); $C_m = 0$ at $r = R_i$ ($t > 0$).	C_m and C_c is the concentration of the solute in the membrane phase and external phase; D is the solute diffusivity through the membrane phase; R_o and R_i represent the radius of the ELM droplet and the internal droplet, respectively.	[2.131]
Advancing front model	$\frac{\partial C_m}{\partial t} = D_{eff}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_m}{\partial r}\right) - \frac{\partial C_d}{\partial t}$ $\frac{\partial C_i}{\partial t} = K_f C_m - K_b C_d$	C_m and C_d are the solute concentrations in the membrane phase and internal phase; C_i is the internal reagent concentration; D_{eff} is an effective molecular diffusivity; and K_f and K_b are the rate constants of the forward and backward reactions, respectively.	[2.138-2.140]
Reversible reaction model	$\frac{\partial C_{Am}}{\partial t} = \frac{D_{eff}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{Am}}{\partial r}\right)$ $-\left(\frac{1-f_m}{f_m}\right)\left(\frac{\partial C_{Ai}}{\partial t} + \frac{\partial C_{Pi}}{\partial t}\right)$ $t = 0$, $C_{Am} = 0$ ($R > r \geq 0$); $r = R$, $C_{Am} = k_{bm} C_{Ab}$ ($t \geq 0$); $r = 0$, $\frac{\partial C_{Am}}{\partial r} = 0$ (for all t); $\frac{\partial C_{Ab}}{\partial t} = -\frac{3D_{eff}}{Rf_b}(1-f_b)f_m\frac{\partial C_{Am}}{\partial r}\|_{r=R}$	Where C_{Am} and C_{Ab} is the solute concentration in the membrane phase and external phase; C_{Ai} and C_{Pi} are the unreacted solute and product concentration; R is the mean globule radius in the internal phase; k_{bm} is the solute partition coefficient between bulk and membrane phases; f_m and f_b are the volume fractions of membrane and bulk phases; and D_{eff} is the mean effective diffusivity.	[2.120, 2.122, 2.141-2.150]
Advanced stripping model	$J = \left[\frac{1}{K} + (\frac{1}{\alpha D_m})(\frac{R}{R_f})(R - R_f) + \frac{1}{\alpha\varphi k_1}\right]^{-1}$ $C_{e,t} = 0$, $R_f = R$, $C_e = C_{e,0}$.	Where J is the solute flux; C_e is the metal ion concentration; R is the emulsion globule radius; R_f is the radius of unreacted core in emulsion; $1/D_m$ represents the membrane phase diffusion resistance within emulsion globule; $1/k_1$ is the interfacial reaction; 1/K is the combined overall resistance; φ is the volume fraction of internal aqueous phase to the emulsion.	[2.151]

2.5 EMULSION STABILITY & SPLITTING TECHNIQUE

2.5.1 Emulsion stability

Emulsion stability is a perennial issue, with formed emulsion being generally thermodynamically unstable [2.98]. Take water in oil (W/O) emulsion for example, during the emulsification process, large water globules will be breaking down into many smaller droplets and these droplets are uniformly dispersed in the oil matrix. This not only significantly increases the total surface area of water droplets, but also increases the total configurational entropy [2.105]. This phenomenon can be shown in second law of thermodynamics:

$$\Delta G = \Delta A\gamma - T\Delta S \qquad \text{Equation 2.5}$$

Here ΔG is the change in Gibbs energy during emulsion formation process; ΔA is the change of total surface area of droplets; γ is the surface tension between the mother droplet and the surrounding immiscible phase; TΔS is equal to the entropy of dispersions during emulsification. Usually ΔAγ is much higher than TΔS, this means that the Gibbs energy formed can not be compensated by the entropy dispersion in the droplets [2.105]. Thus, this formation is thermodynamically unstable.

Emulsion stability is usually a relative term, the stability measurement of emulsion droplets can be very complicated and sometimes it is difficult to perform a quantitative measurement. As such, various methods have been proposed including: droplet counting and size distribution analysis using optical microscope or dynamic light scattering; zeta-potential measurements to predict the electrostatic repulsion force between droplets; other stability tests such as shaking, thermal cycling and freeze-thaw, etc. [2.108].

Before the emulsion droplets are deformed, they are balanced by interaction forces including the Van der Waals attraction, electrostatic repulsion from the double layers of colloidal dispersions or steric repulsion depending on the type of surfactant that is used [2.107]. Once the balance force can no longer support the emulsion droplets, the following emulsion breakdown process may occur: flocculation, sedimentation, creaming, Ostwald ripening (disproportionation), phase inversion and coalescence [2.105], the schematic representation of each term is shown in Figure 2.4.

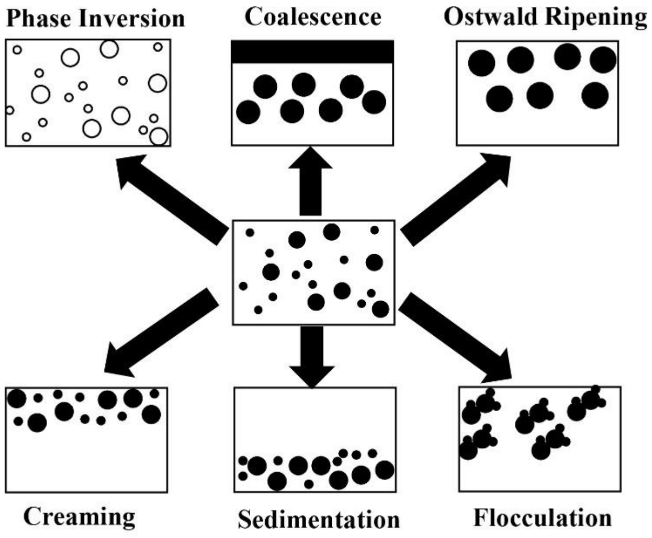


Figure 2.4 Various emulsion breakdown processes (adapted from Tadros (2009)) [2.105]

In most circumstances, for example, a water in oil (W/O) emulsion, the break-down of emulsion can be broken down into four steps. The first step is that some large groups are formed due to the flocculation of many small dispersed internal droplets, it should be noted that the droplets still exist without coalescence; the second step is that these small droplets coalescence into large drops and the numbers of emulsion droplets are thus decreased; the third step involves with the sinkage of formed large droplets into the water & oil interface by gravity, then the last step is that these drops coagulate, meaning the emulsion droplets are broken [2.116].

2.5.2 Emulsion splitting technique

Although emulsion droplets will deform inherently, some emulsion droplets are relatively stable and can last for several weeks or months. After using ELM to extract heavy metal ions, the emulsion has to be broken. ELM splitting can be complicated, depending on the characteristics and properties of the emulsion as well as the system requirement. Various methods have been proposed, including heating, such as conventional and microwave demulsification [2.152]; mechanical methods such as gravity separation and centrifugal force [2.153]; chemical methods such as the addition of a chemical de-emulsifier [2.154]; electrical methods such as high-voltage electrostatic splitter [2.155]. The comparison of the advantages and disadvantages of these techniques can be found in Table 2.6

Table 2.6 The advantages & disadvantages of different emulsion splitting techniques

Methods		Advantages	Disadvantages	Ref.
Heating	Conventional	Simple	High cost caused by high energy consumption	[2.156]
	Microwave	Very effective, very short time needed, environmental friendly	Radiation may harm the extractant efficiency, no commercialization yet	[2.152, 2.157]
Mechanical	Gravity settler	Simple and least expensive	Sedimentation speed may be slow	[2.153]
	Centrifugal separators	Reliable, fast	High operating cost	[2.158]
Electric field	Electrostatic splitter	Very effective and harmless	High voltage is always required causing safety concern	[2.159]
Chemical	De-emulsifier	Easy integration into equipment already existed, small capital cost	Emulsifier may be difficult to remove afterwards.	[2.160-2.161]
	pH adjustment	Demulsification usually takes place very rapidly	Further treatment such as neuralization may be needed	[2.158]

These methods maybe used solely or combined. An example of process plant schematic of breaking emulsion using high-voltage electric field is shown in Figure 2.5.

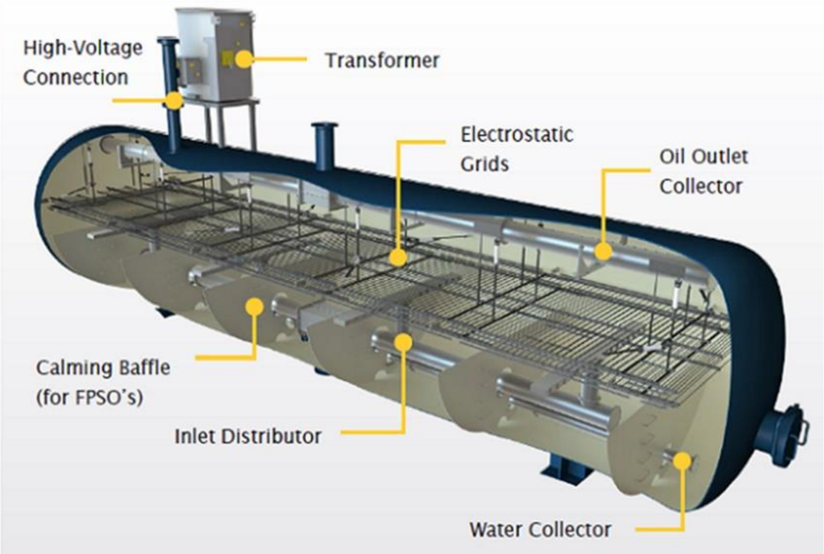


Figure 2.5 A plant process schematic of breaking emulsion using high-voltage electric field [2.162]

2.6 EXTRACTION OF HEAVY METAL IONS USING ELM

The extraction of heavy metal ions from waste stream using ELM has been a popular topic ever since ELM was invented in 1968. Studies generally focus on the extraction efficiency, process kinetics, process optimization, separation mechanism, mass transfer modeling in the extraction of metals such as copper, nickel, zinc, cadmium, cobalt, mercury and chromium. The ELM formed is always a water-in-oil-in-water (W/O/W) emulsion, where the internal water phase is usually very strong acid (such as H_2SO_4) or basic (such as NaOH); the external phase is the waste water stream and the oil phase being a commonly seen diluent (such as kerosene) containing oil-soluble metal extractant (such as LIX 64N) and hydrophobic surfactant (such as SPAN 80) to stabilize the primary water in oil emulsion [2.30]. A process schematic of utilizing ELM to extract heavy metal ions is shown in Figure 2.6.

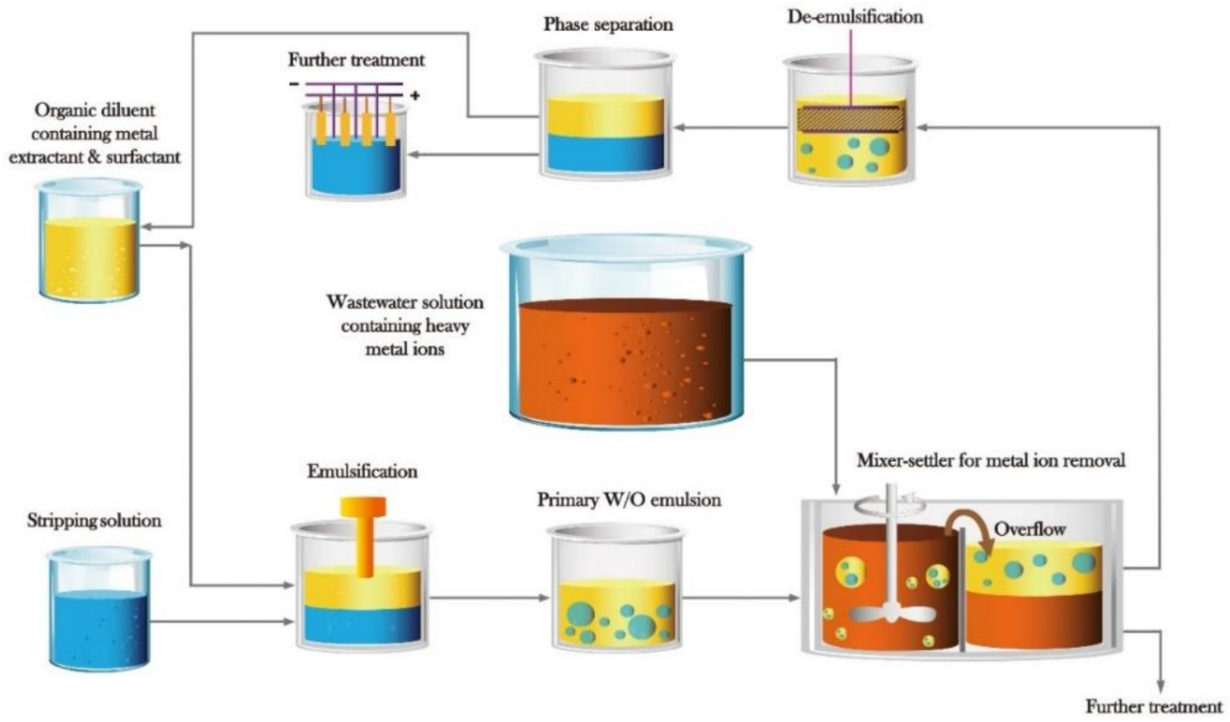


Figure 2.6 Process schematic showing ELM removing heavy metal ions process

A summary of the compositions of ELM for some commonly seen heavy metal ions (Cu, Ni, Zn, Co, Cr, Cd) removal is listed in Table 2.7.

Table 2.7 A summary of the compositions of ELM for some heavy metal ions removal

Solute	Internal liquor	Diluent	Surfactant	Extractant	Ref.
Copper	H_2SO_4	Hexane/Heptane/Dodecane	SPAN80	D2EHPA	[2.163]
	H_2SO_4	Kerosene	SPAN80	LIX-860 N-IC	[2.32]
	H_2SO_4	Kerosene	SPAN80	LIX 984N-C	[2.164]
	H_2SO_4	Kerosene	SPAN80	LIX 84	[2.165]
	H_2SO_4	Kerosene	SPAN80	LIX 7950	[2.166]
	H_2SO_4	Kerosene	SPAN80	LIX 64N	[2.137]
	H_2SO_4	Shellsol T	ECA 4360J	LIX 54	[2.167]
	H_2SO_4	Isopar M	Paranox 100	Acorga M5640	[2.168]
	HNO_3	Kerosene	SPAN80	D2EHPA	[2.169]
	NaOH	Isopar M	Paranox 100	LIX 64N	[2.170]
Nickel	HCl	Kerosene	SPAN80	D2EHPA	[2.171]
	EDTA	Kerosene	SPAN80	DBHQ	[2.101]
	HCl	Kerosene	SPAN80	LIX 63&2BDA	[2.172]
	HNO_3	Toluene/Heptane/Xylene/Dodecane	SPAN80	D2EHPA	[2.173]
	H_2SO_4	n-Heptane	SPAN80	D2EHPA	[2.174]
	Methane sulfonic acid	Mixture of xylene, heptane, toluene, dodecane	SPAN80	D2EHPA	[2.175]
Zinc	H_2SO_4	Shellsol T	ECA 4360	D2EHPA	[2.176]
	H_2SO_4	Kerosene	SPAN80	D2EHPA	[2.31]
	H_2SO_4	n-Heptane	SPAN80	PC-88A	[2.177]
	H_2SO_4	Shellsol T	ECA4360J	DTPA	[2.178]
	H_2SO_4, LiCl	Shellsol T	ECA4360J	DEHTPA	[2.113]
	H_2SO_4	Isododecane	SPAN80	D2EHPA	[2.179]
Cobalt	H_2SO_4	Kerosene	ECA 4360J	TOA	[2.102]
	HCl	Kerosene	SPAN80	CYANEX 301	[2.125]
	H_2SO_4	Cyclohexane	SPAN80	CYANEX 923	[2.180]
	HNO_3	Cyclohexane.	SPAN80	D2EHPA	[2.181]
Chromium	NaOH	Kerosene	SPAN80	Aliquat 336	[2.182]
	NaOH	Kerosene	SPAN80	TOMAC	[2.183]
	NaOH	Kerosene	SPAN80	Cyanex 923	[2.184]
	NaOH	Kerosene	Paranox 106	Aliquat 336	[2.185]
	NaOH	Cyclohexane	SPAN80	TOPO	[2.186]
	NaOH	Hexane, Heptane, Dodecane	SPAN80	TBP	[2.187]
	KOH	Kerosene	SPAN80	Aliquat 336	[2.188]
	KOH	Kerosene	SPAN80	TOA	[2.189]
	$(NH_4)_2CO_3$	Kerosene	SPAN80	TBP	[2.190]
	$(NH_4)_2CO_3$	Kerosene	ECA 4360J	TOA	[2.191]
	$(NH_4)_2CO_3$	Kerosene	ECA 4360J	Amberlite LA-2	[2.192]
	$(NH_4)_2CO_3$	Kerosene	ECA 4360J	TOPO	[2.193]
	LiOH	Kerosene	SPAN80	TOA	[2.194]
	$(NH_4)_2S_2O_8$	Kerosene	SPAN80	PC-88A	[2.195]
Cadmium	NH_4OH	Kerosene	SPAN80	Aliquat 336	[2.100]
	NH_4OH	Kerosene	SPAN80	TOA	[2.196]
	NH_4OH	Kerosene	SPAN80	Amberlite LA-2	[2.197]
	NaOH	Oxylene	SPAN80	TOA	[2.198]
	NaOH	Dimethylbenzene	SPAN80	TIOA	[2.199]
	HCl	Kerosene	Arlacel C	Cyanex 302	[2.200]
	HCl	Kerosene	SPAN80	D2EHPA	[2.201]
	HNO_3	Paraffin oil	SPAN80	D2EHPA	[2.202]
	H_2SO_4	Kerosene	SPAN80	D2EHPA	[2.104]

It should be noted that ELM not only can be used to remove metal ions from single cation bearing solutions, it is also efficient in separating some metal ions from others that co-exist in solution. This can be attributed to the difference in metal selectivity of the extractant in the membrane phase or the stripping liquor in the internal phase. Examples include, but are not limited to, the separation of: cobalt and nickel; zinc and copper; and chromium and nickel.

Many reports have been focused on the metal ions removal from single cation solutions using ELM, these metals include copper, nickel, cobalt, zinc, chromium, cadmium, mercury, lead, silver, gallium, molybdenum, uranium, ruthenium, platinum and palladium. Each metal has different physical and chemical properties during this process and needs to be discussed separately. Since the scope of this thesis is to remove and separate copper, nickel from calcium ions, only copper and nickel are discussed here:

2.6.1 Copper

As one of the most common metals in the world, copper has been extensively utilized in recorded history. The removal of copper from wastewater has also been an area of research interest. In the past few decades, much research has been reported on the copper removal by ELM. These can be generally classified into three sections, which are: process operating parameters [2.30, 2.32, 2.163-2.165, 2.169, 2.203-2.212]; kinetic studies during copper permeation process [2.32, 2.112, 2.137, 2.167, 2.171, 2.204, 2.211-2.220] and industrial applications [2.153, 2.159, 2.168, 2.170, 2.221]. They are discussed further in the following sections:

2.6.1.1 Copper process operating parameters

Many different operating parameters are associated with the ELM extraction process, including the ones during the formation of primary emulsion: extractant concentration, surfactant concentration, the internal phase concentration, the volume ratio of internal phase/organic phase, the primary emulsion formation speed, the primary emulsion formation time; and those parameters associated with the formation of double emulsion and copper extraction including: the volume ratio of primary emulsion/external phase, the pH of the external phase, the copper concentration of the feed phase, the double emulsion stirring time and double emulsion stirring speed [2.163-2.164, 2.169, 2.203, 2.209-2.210, 2.212]. These parameters have been investigated by many researchers. It should be noted that each work was performed under different conditions, thus the conclusions usually differ. However, many common characteristics have been found and are as follows:

Extractant concentration: according to Sengupta *et al.*, extractant concentration is vital since copper loading in the membrane phase usually governs the rate of extraction [2.164, 2.203]. Most work used oxime as the copper extractant due to the fact that oxime carrier contained some p-nonylphenol that could prevent crud formation and allows clear phase separation. Zheng *et al.* points out that a higher extractant concentration is preferred during the process since it will favor complex formation at the membrane-feed stream interface, thus the copper ions transfer flux will be increased [2.208]. However, as stated by Valenzuela *et al.* and Sengupta *et al.*, an excessive increase in extractant concentration will make the oxime aggregate, increasing the viscosity of the membrane as well as impeding the diffusion of copper into the ELMs [2.30, 2.165]. In addition, the interface tension between the membrane and the feed phase will increase, resulting in an increase in emulsion droplet size as well as a decrease in contacting surface area, meaning the extraction rate will thus be lowered. Emulsion breakdown may also occur.

Surfactant concentration: the surfactant has a significant influence on membrane stability, although it was reported by Mikucki & Osseo-Asare that with an increase in surfactant concentration, the amount of copper extracted initially increased [2.206-2.207], this increase was attributed to the increased stability of the emulsion globules and the kinetics of metal extraction. However, once the surfactant concentration increases beyond a certain point, although the emulsion droplets were more stable, Mikucki & Osseo-Asare found that both the interfacial viscosity and the chances of association of hydrophobic tails of the surfactant with the internal droplets were increased, the membrane thickening also brought an increased diffusion distance for metal ions [2.206]. All these factors generated higher interfacial resistances and resulted in a rate decrease in interfacial chemical reactions, and thus impeded the copper extraction.

Internal phase concentration: Zheng *et al.* pointed out that although mass transfer of the stripping phase was not the rate controlling step in the extraction process, a higher concentration of H^+ in the internal phase would lead to a very large concentration gradient across the membrane, this could increase the speed of copper complex dissociation, favoring the copper transport across the membrane [2.208]. However, a much higher concentration of H^+ will degrade the extractant as well as lower its acid-activity coefficient.

<u>The volume ratio of internal phase/organic phase</u>: Sengupta *et al.* stated in their research papers that an increase of the volume ratio of internal phase/organic phase did not only increase the overall extracting capacity of the ELMs, but also brought a faster extraction rate [2.164, 2.203]. The reason raised from the denser packing of stripping droplets and this helped form a thinner membrane thus the diffusion path length for the copper complex within the emulsion globule was shortened.

<u>The primary emulsion formation speed & time</u>: although these influence the composition and droplets size of the internal droplet of the W/O emulsion, they have not been reported to have significant impact on copper extraction process.

<u>The volume ratio of primary emulsion/external phase</u>: normally it is known that an increase in this value can improve overall extraction capacity was well as copper extraction rate [2.204].

<u>The pH of the external phase</u>: it is found by Valenzuela *et al.* and Sengupta *et al.* that the copper was very strongly extracted starting from pH of 2.0 [2.32, 2.165]. At pH 1, Sengupta *et al.* reported a case of more than 80% recovery of copper using LIX 984N [2.165]. Mohamed & Ibrahim stated that the copper permeation percent increased once pH increased [2.205]. Kondo *et al.* reported in his research that in the low pH range, the initial extraction rate varied inversely as the 0.5 power of hydrogen-ion concentration, but in the high pH range it became independent of pH [2.212]. Also, rupture of emulsion globules may also occur by changing the pH of the feed phase.

<u>The copper concentration</u>: It was found by Matsumiya *et al.* that copper extraction efficiency was 88–91% for 0.05–0.5 mg of copper and 80–82% for 1.0 mg of copper [2.209]. The increase in copper concentration will help a faster saturation of copper in internal droplets.

<u>Double emulsion stirring speed & time</u>: a higher stirring speed will lead the formation of smaller globules, resulting in an increased interfacial area, the copper extraction rate is thus increased. A longer stirring time also gives sufficient time for copper to be extracted and diffuse through the

membrane. However, they also bring a negative effect to membrane stability, as stated by Frankenfeld *et al.*, Valenzuela *et al.* and Sengupta *et al.*, the emulsion globules were more likely to be ruptured and swelling occurred under very high stirring speed & time since there existed very intense drop-drop interactions [2.30, 2.165, 2.204].

To summarize, it was found that the copper extraction reaction occurs in a short time, in this process, in order to keep a higher copper extraction rate, an adequate membrane viscosity and higher interfacial area between the membrane phase and continuous phase should be maintained while keeping emulsion stability in a reasonable range. These can be achieved by adjusting the process operating parameters. Some results have been reported regarding process optimization - according to Chiha *et al.*, a D2EHPA concentration of 20% (w/w), a H_2SO_4 concentration of 0.3 mol/L and a double emulsion stirring speed of 200 rpm are required for high copper removal [2.163]. However, all these experiments were performed using the one factor at a time (OFAT) method, which means that all other factors were fixed while an optimization value was achieved for one factor by changing its values at different levels. This method may not be accurate and it does not guarantee the conditions obtained are indeed optimal. In addition, many interactions between factors exist including different chemical and physical interactions are not discussed. This problem needs to be solved.

2.6.1.2 Kinetics during copper permeation process

Although the models that predict the copper permeation behavior have already been proposed in Section 2.4.3, much research has also focused on the kinetics & mass transfer rate of the copper permeation process. As reported by Raghuraman *et al.*, Teramoto *et al.*, Valenzuela *et al.* and others, a typical copper complexion with LIX extractant (RH) can be described as [2.32, 2.122, 2.213, 2.220]:

$$Cu^{2+} + 2RH \leftrightarrow CuR_2 + 2H^+ \qquad \text{Equation 2.6}$$

The thermodynamic equilibrium constant K can be defined as:

$$K= \frac{\{CuR_2\}\{H^+\}^2}{\{Cu^{2+}\}\{RH\}^2} \qquad \text{Equation 2.7}$$

It is reported by Raghuraman *et al.* that the K value is 328.0 and 75.48 when using tetradecane as the organic solvent and LIX 860 and LIX 984 as the copper extractant, separately [2.213]. They also noted that this K value could be used over a large range of pH and ionic strength. Frankenfeld *et al.* reported in their research that K was not only a function of the specific liquid ion exchange agent, but was also affected by the organic solvent properties [2.204]. A spherical shell model was utilized, and it was found that the copper permeation rate was lower when having a more viscous liquid membrane. This rate also increased with an increase in external phase/emulsion phase ratio; this enhancement was possible with the use of oil-soluble complexing agents. One interesting work involved with the comparison of facilitated transportation and simple diffusion under similar membrane viscosity, they mentioned that the rate of the facilitated transport of copper was 3 to 7 times faster than the simple diffusion of ammonia through membranes with comparable viscosity [2.204].

Nakashio & Kondo noted that copper extraction rate was more affected by the H^+ concentration in the low pH range, and that copper extraction rate varied inversely as the 0.5 power of H^+ concentration. The rate was also proportional to the extractant concentration (benzoylacetone) as well as the square root of copper concentration of the feed phase [2.215].

Physical mass transfer parameters for copper within the membrane were investigated by Völkel *et al.*, and they found that the copper mass transfer was affected by many factors such as the membrane viscosity, extractant concentration, copper concertation as well as stripping solution concentration and its dropsize distribution [2.137]. The mass transfer value ranged from 0.1×10^{-3} to 1.18×10^{-3} cm/s, where it increased with higher stirring speed since it caused an increased degree of dispersion [2.137].

Hu and Wiencek conducted a comparison of copper extraction using conventional solvent extraction and emulsion liquid membranes, they found that the cooper reaction permeation rate was 9.28×10^{-6} and 2.23×10^{-6} cm/s for solvent extraction and ELM respectively [2.214]. However, despite the relatively slow kinetics, ELM showed exceptional extraction capacity when the extraction approached or exceeded equilibrium. In addition, they showed that ELM can extract copper even from a very low feed concentration [2.214].

It was known that average copper fluxes must be equal to the mass transfer rates of copper and extractant species. Based on the research from Kondo *et al.* while using unsteady-state membrane film model [2.211-2.212], Valenzuela *et al.* calculated the mass transfer coefficients of copper and LIX 860 in the membrane are 3.56×10^{-3} and 1.1×10^{-4} cm/s, separately [2.32]. In another paper that they published [2.219], they calculated the diffusion coefficient of extractant and the forward reaction constant to form copper-LIX 860 complex was 1.23×10^{-5} cm^2/s and 5.2×10^{11} $cm^3/mol\cdot s$, a model was thus proposed [2.219]:

$$1\text{-}\left(\frac{[Cu]}{[Cu_0]}\right)^{1/2} = Q\frac{[HX_0]t}{2[H^+]^{1/2}[Cu_0]^{1/2}} \qquad \text{Equation 2.8}$$

Where Cu_0 and HX_0 represents initial copper and extractant concentration, while Q is a constant.

Based on a reversible reaction model, Teramoto *et al.* found that the copper permeation rate was negatively affected by the feed solution flow rate while it was positively affected by the copper concentration using SME529 as copper extractant [2.220]. In subsequent research which investigated the influence of other process parameters, they found that higher H^+ concentration in feed phase brought down the mass transfer rate, while stripping liquor concentration, stirring speed brought positive effect. However, the extractant concentration did not show significant effects during this process. In the meantime, the addition of small amount of anionic surfactant such as sodium dodecyl sulfate to the feed phase was found to increase the mass transfer rate significantly [2.220]. Those findings were supported by work from other researchers, such as Lazarova and Boyadzhiev. They calculated the copper diffusion coefficient between the organic and aqueous phase to be approximately 76.5 [2.216]. The major conclusion of the work was that copper transfer from the feed solution to the membrane phase was controlled by copper diffusion, while inside the membrane was controlled by the chemical reaction of copper-LIX complex stripping [2.216].

In another case based on the reversible reaction model, Gameiro *et al.* reported the effects of various parameters on copper permeation rate under an assumption of a copper-LIX 54 effective diffusivity of 2.53×10^{-10} cm^2/s and a stripping rate constant of 1.2×10^{-7} m/s. They found that an increase in stripping liquor concentration, extractant concentration and stirring speed coupled with a decrease in copper concentration and the volume ratio of external phase to internal phase would enhance the extraction rate [2.112]. In further research, they reported that the extraction mechanism was significantly affected by the LIX 54 concentration, such that at a value of 0.2 kmol/m^3, the process was controlled by diffusion in the aqueous boundary layer while in the range of 0.015–0.10 kmolm^{-3}, it was controlled by chemical reaction and diffusion in the aqueous boundary layer [2.167].

Chakraborty *et al.* reported the work of extracting copper using D2EHPA as the extractant, the chemical reaction was different than using LIX [2.171]:

$$Cu^{2+} + 2(RH)_2 \leftrightarrow CuR_2(RH)_2 + 2H^+ \qquad \text{Equation 2.9}$$

They used an unsteady membrane film model and the diffusivity of copper-D2EHPA complex inside the membrane was calculated to be 3.29×10^{-10} cm^2/s. They also reported that the permeation rate of copper was affected by pH that it was very high under higher pH (>3.5) while it was extremely low under low pH (<1).

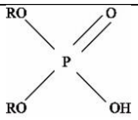
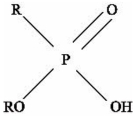
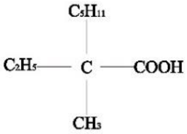
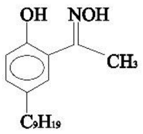
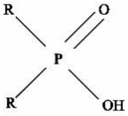
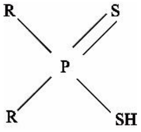
2.6.1.3 Industrial applications

Although much research has been performed on copper removal in research labs, very few reports have focused on the industrial application of this technique. In general, the pilot-scale plant contained emulsion-membrane generation circuit, extractant tanks, settlers, electrical coalescer as well as electronwinning (EW) cell. The process is usually counter-current with copper solution and emulsion flowing in opposite direction. Wright *et al.* reported their results processing 5600 gallons of copper solution at a copper mine in Arizona utilizing ELMs, with normal plant pregnant leach liquor (PLS) containing 1.43 g/L Cu; PLS diluted with mine water to 0.5 g/L Cu; and PLS diluted with mine water to 0.32 g/L Cu were treated, and copper extractions averaged 98.0%, 95.7% and 91.6% for these three solutions, separately [2.168]. 165 g/L H_2SO_4 was used as the stripping liquor while the membrane swelling and leakage were promising, averaged less than 8% and 0. 1%, separately. Draxler *et al.* showed that by using a counter-current extraction column, two copper solutions were reduced from an initial concentration of 8 g/L, 0.8 g/L to a final concentration of 0.027 g/L and 0.003 g/L, separately, while the throughput was 20 L/h and 40 L/h [2.159]. In other work it was found that 30 g/L copper can be obtained in the receiving phase using 250 g/L H_2SO_4 while the initial copper concentration has been reduced from 8 g/L to 0.04 g/L at a throughout of 200 L/h [2.153]. Li and Cahn utilized a continuously feed 4-stage cascade mixer treating aqueous flow that had a copper concentration of 2.5 g/L and a throughput of 17.4 L/h, they found that over 95% copper recovery in four mixers in cascade to give a total residence time of 12.5 min while the copper concentration in the internal phase reached 30 g/L while using 150 g/L H_2SO_4 as stripping liquor [2.170]. Their economic assessment showed that the liquid membrane process had a significant lower operating cost than solvent extraction and a considerably reduced capital cost (35%-40%).

2.6.2 Nickel

Nickel is usually found to co-exist with cobalt ions in wastewater stream, with these two metals having similar chemical properties due to their adjacent position in the periodic table. Thus, a lot of work has been focused on the removal and separation of nickel from cobalt using ELM technique. The membrane or the stripping liquid is used as a tool to selectively extract or strip one metal. Various kinds of extractants have been used for this process, whereas for copper extraction, LIX products dominate. Table 2.8 details a number of nickel extractants and their physical properties [2.222-2.238].

Table 2.8 Some common extractants and their properties for nickel extraction

Extractants	**Description**	**Chemical Formula**	**Density ($kg \cdot m^{-3}$)**	**Viscosity ($mPa \cdot s$)**	**Molar Mass ($g \cdot mol^{-1}$)**	**Aqueous Solubility ($mg \cdot L^{-1}$)**	**Ref.**
D2EHPA	Di-(2-ethylhexyl) phosphoric acid	 Where $R=C_8H_{17}$	970	40	322	182	[2.223-2.225, 2.230, 2.232]
PC-88A	2-ethyl hexyl phosphonic acid and mono 2-ethyl hexyl ester	 Where $R=C_8H_{17}$	953	36±3	306	-	[2.224, 2.233, 2.235]
Versatic 10	Neodecanoic acid		910	28.3	172	61.8	[2.229, 2.233, 2.236]
LIX 84-I	2-hydroxy-5-nonylacetophenone oxime		910	2.44	277	-	[2.234-2.235, 2.237]
Cyanex 272	bis(2,4,4-trimethylpentyl) phosphinic acid	 Where $R=C_8H_{17}$	910	142	290	38	[2.224, 2.226, 2.230, 2.238]
Cyanex 301	bis(2,4,4-trimethylpentyl) dithiophosphinic acid	 Where $R=C_8H_{17}$	950	78	322	7	[2.226-2.229, 2.231]

A number of research publications focused on the discussion of operating process parameters [2.140, 2.171-2.173, 2.175, 2.239-2.243] and process kinetics [2.140, 2.171, 2.173, 2.174-2.175, 2.213, 2.244-2.248]. They are discussed in more detail below:

2.6.2.1 Nickel process operating parameters

Since the removal of ELMs technique for all metal ions follow the same process, the operating parameters for nickel removal are the same as those for copper removal. Many findings of the parameters for nickel removal are similar to those discussed in section 2.6.1.1. Kumbasar *et al.*

performed many different tests to extract nickel or separate nickel from cobalt in acid leach solutions, ammoniacal solutions or electroplating bath solutions, respectively [2.172, 2.240, 2.242-2.243]. They found that the extractant concentration was the most important parameter during the process, and that a synergistic extractant can significantly improve the extraction efficiency, such as a mixture of LIX 63 and 2BDA or LIX 63 and D2EHPA [2.172, 2.240]. Unlike in copper extraction, the feed solution pH is a key parameter to selectively extract the targeted nickel, and high nickel removal only occurred within a narrow pH range (such as 4.0-5.75) [2.172]. They also performed process optimization using the OFAT method, when they found that in one case that more than 40% increase in nickel extraction could be achieved when operating parameters were optimized [2.172]. Table 2.9 lists the optimum parameters when extracting nickel from simulated spent Cr/Ni electroplating bath solutions:

Table 2.9 The optimum parameters for nickel removal from simulated spent Cr/Ni electroplating bath solutions [2.172]

Operating Parameter	**Optimum Value**
Extractant concentration	5.0% (v/v) LIX 63
	5.0% (v/v) PC88A
Surfactant concentration	4.0% (v/v) SPAN 80
Stripping liquor concentration	6.0 mol/L HCl
Feed solution pH	5.75
Double emulsion mixing speed	300 rpm
Emulsion/feed solution volume ratio	5/4

Under these optimum conditions, a nickel removal efficiency of more than 99% could be achieved. Although a high HCl concentration is needed to strip nickel from the complex, it should also be noted that when extracting nickel from ammoniacal solutions, a low concentration of EDTA acid (0.025 mol/L) was sufficient [2.242].

Li *et al.* also used ELM to separate nickel from cobalt while using EDTA as a stripping reagent since Ni-EDTA complex is more stable than Co-EDTA complex [2.248]. They found that an addition of NaAc-HAc buffer solution could increase the solution ionic strength thus make the metal separation easier. In Eyupoglu and Kumbasar's work [2.240-2.241], the separation factor of nickel and cobalt was calculated using Equation 2.10:

$$\beta_{Ni/Co}=\frac{(C_{Ni}/C_{Co})_{strip}}{(C_{Ni}/C_{Co})_{feed,0}} \qquad \text{Equation 2.10}$$

Where C_{Ni} and C_{Co} are the concentrations of Ni and Co in the stripping and initial feed solutions. They found that a value of 580 was achieved under optimum conditions. Kulkarni *et al.* reported that the maximum nickel extraction could be achieved with emulsion/feed solution volume ratio fixed at 1:3 while having a HNO_3 concentrtaion of 1.0 mol/L as the internal stripping liquor [2.173]. This value was low when compared with Kumbasar *et al.* [2.243], the reason being the increased swelling behavior of internal droplets with a drastic increase of HNO_3 concentration, where the mass transfer area was reduced and thus the nickel extraction was impacted [2.173]. This finding was confirmed by Hachemaoui *et al.*, where they used 0.5 mol/L HCl as the internal stripping liquor under the optimum condition, 8 % D2EHPA was used while the SPAN 80 concentration was determined to be 2 % [2.239]. The nickel and cobalt extraction efficiency can be up to 97.2 % and 98.2 % when the treatment ratio of emulsion to feed phase and the phase ratio of internal stripping phase and oil phase was 0.2 and 0.5, respectively [2.239]. However, due to the low concentration of HCl, there was not a good separation between nickel and cobalt (separation factor around 1.0). Chakraborty *et al.* studied the emulsion stability during this process, which is another perspective examining the emulsion properties [2.140, 2.171, 2.217]. They investigated the impact of these parameters including the pH of feed solution, stirring speed, surfactant concentration, internal aqueous phase concentration. They found that the emulsion was less stable at pH 1.5 than 3.5 since the rate of SPAN 80 hydrolysis was much faster at pH 1.5 [2.171]. In the meantime, with an increase of stirring speed from 400 rpm to 750 rpm, the emulsion breakage also increased from around 10% to more than 40%, such a high rupture of emulsion needed to be avoided [2.171]. Chakraborty *et al.* also noted that an intermediate value (4 wt%) of SPAN 80 was needed in order to stabilize the emulsion for solving the hydrolysis problem; while NaOH should not be used as the internal stripping phase for nickel extraction since over 40% emulsion breakage would occur. Also, it was pointed out that H_2SO_4 was better than HCl with a lower emulsion breakage. All these suggested that the emulsion stability was affected not only by the hydrogen ion concentration but also the associated anions [2.171].

Kulkarni *et al.* also worked on determining the effect of the kinds of stripping liquor on membrane stability, and they obtained a different result [2.175], where sulfuric acid yielded the maximum membrane swelling due to its highest affinity towards water, with the increase of acid concentration, the difference of osmotic pressure between the internal and external phase also increased, resulting a linearly increased emulsion swelling rate. Also for nickel extraction, they found maximum extraction occurred when methane sulfonic acid was used as an internal stripping phase. They also found that the 12 carbon atoms dodecane had higher extraction and lower swelling rate than toluene, xylene, and heptane [2.175]. The difference came from its high viscosity as well as hydrophobicity, which could maintain the membrane stability by lowering water transport into membrane. Although it was found that a higher emulsion/feed phase volume ratio would increase the degree of extraction, a trade-off was needed in order to maximize the enrichment ratio of nickel in the internal stripping phase, where they found a value between 1:5 to 1:7 was ideal [2.175].

Although all the work above shows similar characteristics of operating parameters for nickel removal while compared with those for copper removal, sometimes the contrary result can be found, for example, Chakraborty *et al.* reported that a lower nickel concentration would bring a higher extraction efficiency during their work on mass transfer analysis of nickel extraction using ELMs [2.140, 2.217]. They also reported that a variation in stripping liquor concentration did not affect nickel removal until the end of the process [2.140].

2.6.2.2 Kinetics during nickel permeation process

In the work of Chakraborty *et al.*, a mass transfer analysis of nickel extraction by ELM technique using D2EHPA as nickel extractant and HCl as stripping agent was performed [2.140]. They used the advancing front model (Section 2.4.3) based on the following assumptions: the emulsion droplets size distribution was uniform; no emulsion breakage, swelling, coalescence or internal circulation occurred during the process; the reaction between nickel ions and D2EHPA was irreversible and instantaneous at the reaction front while it shrunk toward the globule core as the reaction proceeded. They calculated the effective diffusivity of Ni-D2EHPA complex in the emulsion to be 0.7832×10^{-10} m^2/s and they obtained the following equation [2.140, 2.171]:

$$C_D = 56.23\ C_S^{-1.11} \qquad \text{Equation 2.11}$$

Where C_D represented the distribution coefficient of nickel between membrane and external phase while C_S is the equilibrium solute concentration in the aqueous phase. Based on these findings, in their later work, they found that injection method of emulsion, stirring speed, oil phase viscosity, composition of inner water phase and solute permeation rate all affected the emulsion droplet size. Raghuraman *et al.* also performed research into equilibrium constant during nickel extraction by D2EHPA, the reaction between Ni^{2+} and D2EHPA is as follows [2.213]:

$$Ni^{2+} + 2(RH)_2 \leftrightarrow NiR_2(RH)_2 + 2H^+ \qquad \text{Equation 2.12}$$

Where RH represents D2EHPA. They found that if the percentage of D2EHPA consumed during the reaction was less than 10 %, a constant equilibrium constant K of 6.95×10^{-5} was obtained. with an increase in the percentage D2EHPA reacted, K value increased [2.213]. This was attributed to the polymerization of Ni-D2EHPA complex in the membrane phase.

Juang and Jiang reported in their work that the K value was 1.40×10^{-4} while using n-heptane as the organic solvent, 6.4% (v/v) D2EHPA as the nickel extractant removing nickel from its dilute Watts rinse solution. They found that the volume ratio of emulsion phase over external phase ϕ_1 and the volume ratio of internal stripping phase and oil phase ϕ_2 were the most important factors when coming to the nickel recovery rate [2.174]. This conclusion was contrary to others', where extractant concentration and pH are always considered to be vital [2.140, 2.171].

Kulkarni and his co-workers performed a series of tests in order to obtain the distribution ratio of nickel of the membrane phase over the aqueous phase (K_D) [2.173]. Those tests were performed under different pH since the extraction of nickel is pH dependent. Table 2.10 shows their experimental results.

Table 2.10 Distribution ratio of nickel as a function of pH by using 5% D2EPHA (v/v) in xylene and dodecane [2.173]

pH	K_D for xylene	K_D for dodecane
3	0.086	0.108
4	0.101	0.143
5	0.228	0.368
6	0.432	0.692
7	1.150	2.030

It can be seen that the K_D increased with pH while the value for dodecane was always higher than xylene under the same pH. This could be understood through the fact that the acidity difference between the internal phase and external phase affected the nickel permeation rate.

In the work of liquid membrane permeation of nickel with 4-acyl-5-pyrazolones and β-diketones, Mickler *et al.* found that a higher nickel diffusion rate was obtained using 4-acyl-5-pyrazolones than β-diketones. This could be due to the lower acidity of β-diketones [2.245]. They also found that the permeation of nickel was hindered by the increased ammonia concentration of the ammoniacal solutions.

Yamashita *et al.* reported that the nickel permeation rate in ELMs were found to be depended on the hydrogen activity in the external phase, the first order of extractant concentration (LIX 63 or DOLPA) and the second order of surfactant concentration. The overall rate constant k was calculated to be 8.3×10^{10} (m^3/mol·s) [2.247].

Kakoi *et al.* measured the equilibrium constant of nickel extraction under three different extractants, LIX 860 was found to have the highest equilibrium constant (9.0×10^{-6}), while this was followed by LIX 84 (1.2×10^{-6}) and LIX 65N (8.1×10^{-7}) [2.246]. This was probably due to that the reaction rate of LIX 860 was higher than the other two extractant. They also found that the nickel extraction rate improved significantly by using an amphoteric surfactant rather than a nonionic surfactant [2.246].

Serga *et al.* investigated the influence of direct current on the extraction of nickel cations from acidic solutions, they added 5–20 vol% of tributyl phosphate (TBP) or 1–2 vol% n-trioctylamine (Oct_3N) to 20 vol% D2EHPA in order to significantly improve the electrical conductivity of the ELMs [2.244]. When current density was operated at ≤ 2.1 mA/cm^2 and ≥ 4.9 mA/cm^2 for the mixture of D2EHPA with TBP and Oct_3N, respectively, they found nickel removal was higher than 99% for both cases. Also, they can achieve a complete extraction of nickel from more acid solution with direct current applied. The flux of nickel cations increased with an increase in current density, nickel concentration and surfactant concentration [2.244]. The flux of nickel into the membrane phase and internal phase were calculated and listed in Table 2.11.

Table 2.11 Dependence of the nickel cations flow under different conditions [2.244]

Membrane composition	**Vol%**	**i (mA/cm^2)**	**Membrane phase $j_1 \times 10^{10}$ (mol/m^2·s)**	**Internal phase $j_2 \times 10^{10}$ (mol/m^2·s)**
D2EHPA	20	0.7	0.5	0.3
D2EHPA	20	2.1	2.5	0.9
TBP	20			
D2EHPA	20	4.9	3.7	1.5
Oct_3N	1.5			

2.6.2.3 Industrial applications

Not many reports have been focused on the industrial application of removing nickel using ELMs. Draxler and his co-workers reported the separation of metals including zinc, copper, nickel, cadmium, lead and chromium in a pilot plant [2.153, 2.159, 2.221]; in their trial run, they found that nickel concentration was reduced from 2200 mg/L to 360 mg/L at a throughput of 20 L/h [2.159]. This low extraction efficiency was due to the short residence time. They performed another test under the same conditions to extract nickel in a two-stage counter-current mixer-settler [2.153], they found that the nickel concentration was reduced to about 200 mg/L in the first stage and to 3 mg/L in the second stage.

2.7 CONCLUSIONS

This chapter gives a detailed background discussion of emulsion liquid membranes, the theories and principles. A literature review of the extraction of copper and nickel by ELMs are also given. It can be seen that the investigations of characteristics and properties of ELMs are still ongoing since those are not fully understood yet. The industrial applications of ELMs are limited; and process optimization was performed using the one factor at a time method; people also neglected the interactions of operating parameters during the process. The current situation needs to be improved. This thesis will continue with investigations into the application of ELM to heavy metal ions extraction from aqueous systems commonly found as effluents in the mining industry. In addition, the operating parameter optimization will be performed using a statistical design of experiment, where the effect of each parameter and the interactions between them will be explored. The focus of this thesis is using ELMs treat a copper-nickel system mimicking an acid mine drainage content that is common to Canadian operations.

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CHAPTER 3. THE USE OF THE EMULSION LIQUID MEMBRANE TECHNIQUE TO REMOVE COPPER IONS FROM AQUEOUS STSTEMS USING STATISTICAL EXPERIMENTAL DESIGN

3.1 ABSTRACT

Process water from mineral processing plants may contain a significant amount of dissolved metal ions, which may be recycled as process water, or discharged into the environment as effluent. If they are discharged into the environment they may cause significant problems for the local flora and fauna. One method of removing metal ions from aqueous systems, which has generated considerable interest over recent years, is the emulsion liquid membrane (ELM) technique, which incorporates solvent extraction and stripping. This work details the use of design of experiments applied to an ELM process for removing copper ions from a dilute aqueous solution. Initially, a fractional factorial design was used to screen out the most important factors; this was followed by a central composite design to obtain optimal operating conditions. The extraction percentage of copper was obtained as more than 99% under these conditions.

3.2 INTRODUCTION

Every year a huge volume of waste water is discharged by the mining, metallurgy and smelting industries; these waste streams may contain significant amounts of heavy metal ions [3.1-3.2]. These metals ions should be recovered for both environmental and economic considerations. Thus, the removal of heavy metal ions from waste water has been an important topic for the past several decades. For waste streams released by the mining industry, acid mine drainage (AMD) is considered to be the biggest problem [3.3-3.4].

There have been various ways for recovering heavy metal ions, the most commonly used methods being ion-exchange (IX) [3.5-3.6], adsorption [3.7-3.9], solvent extraction and chemical precipitation [3.10-3.12]. However, when facing AMD, these methods have some disadvantages. The concentration of heavy metal ions found in the drainage is usually less than 500ppm [3.13], and a significant amount of reagents are usually required for treating such large scale waterbodies. Thus, an effective way for extracting low concentration of heavy metal ions and requiring fairly lower cost must be developed.

One potentially effective method of recovering these heavy metal ions is the emulsion liquid membrane (ELM) technique [3.14-3.16]. This technique was introduced by Li in 1968 and has been researched ever since [3.17-3.24]. It works by forming a primary water in oil (W/O) emulsion as the first step in which the internal phase contains the stripping acid, and the oil phase contains the surfactant and metal extractant. The primary W/O emulsion is then sent for treatment with a solution containing heavy metal ions, and emulsion liquid membrane globules are formed during this process. In this project, the ELM globules are water (H_2SO_4 liquor) in an oil phase (copper extractant & surfactant in kerosene) in water ($CuSO_4$ solution) emulsions. The copper ions are extracted by the copper extractant in the oil phase and further stripped into the internal H_2SO_4 droplets. A schematic representation of extraction of copper ions using ELM technique is shown in Figure 3.1.

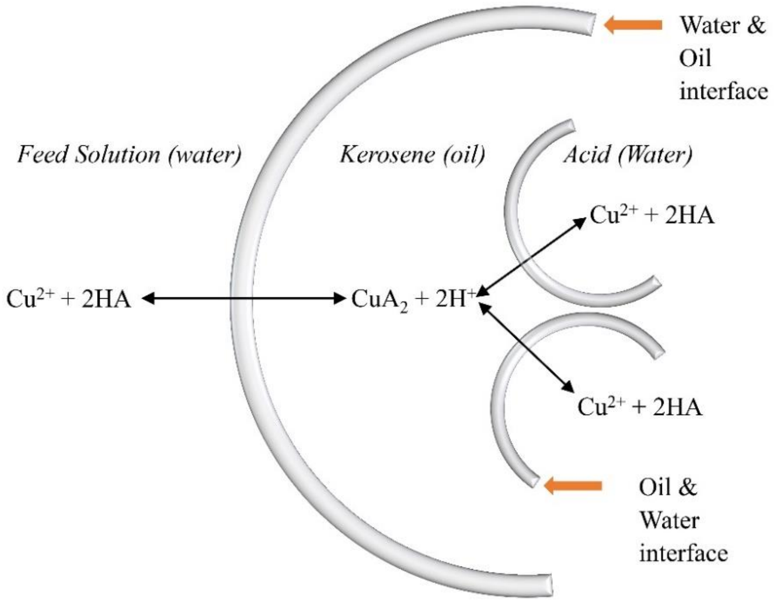


Figure 3.1 A schematic representation of extraction of copper ions using ELM technique

The copper extractant is represented by HA, and CuA_2 represents the copper-extractant complex [3.19-3.20]. Copper ions will be extracted, stripped and concentrated at the same time [3.20-3.22]. After extraction, the water phase (effluent) will be sent for further treatment such as acid neutralization prior being discharged into environment; the emulsion phase will be sent for de-emulsification such as electrostatic coalescence [3.25]. The de-emulsification process will separate the oil phase from the stripping liquor phase. The stripping liquor which is loaded with copper ions will be sent for metal deposition such as electro-winning, and the oil phase will be recycled. Figure 3.2 shows a schematic of the ELM process.

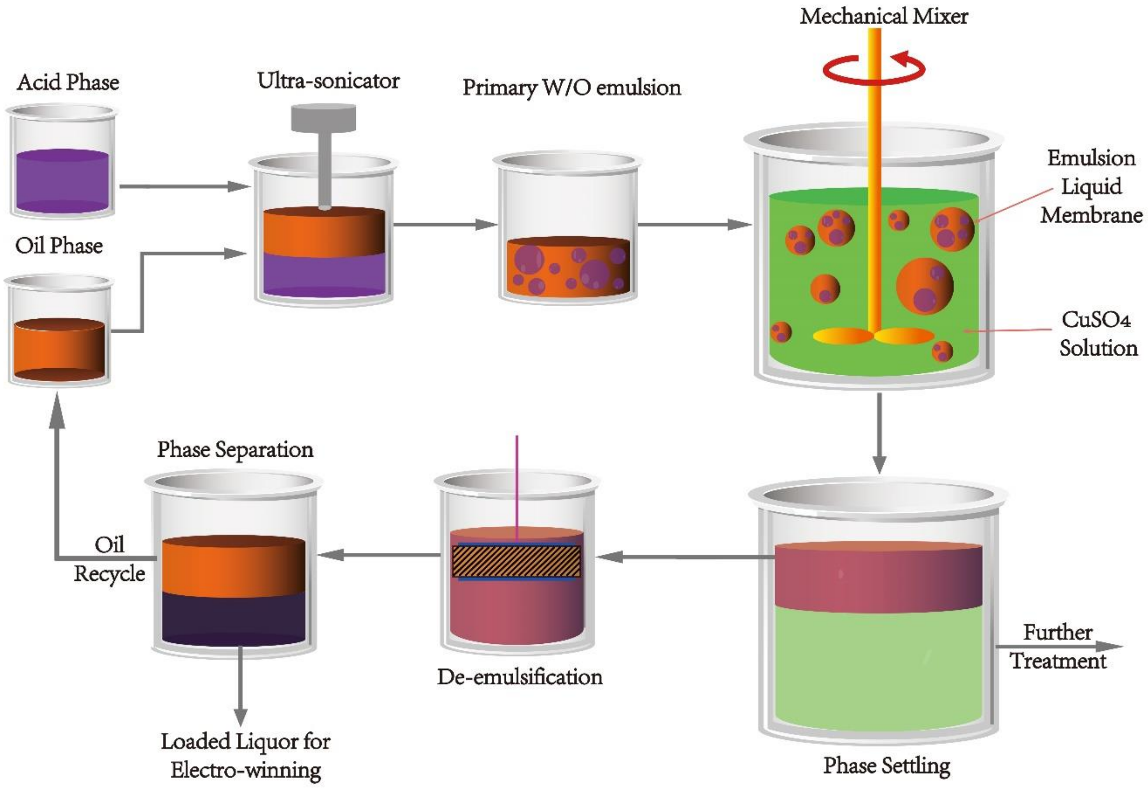


Figure 3.2 A schematic of the ELM process

Economic evaluation has indicated that ELM extraction of copper using LIX 64N could be 40% cheaper than traditional solvent extraction [3.26], and many researchers have studied the practical operation of ELM technique recovering heavy metal ions for the past few decades [3.27-3.35]. In this work, an investigation of the effects of operating parameters on copper extraction by ELM has been performed. Initially, a fractional factorial design was used to screen out the most important factors and the interactions between these factors were investigated. Then, a central composite design was used to obtain optimal lab operating conditions. Validation tests were performed to confirm the optimal operating conditions. Based on these results, the principles and theories behind this process were discussed.

3.3 EXPERIMENTS

3.3.1 Materials

For the primary water in oil emulsion, kerosene (reagent grade, Sigma-Aldrich (USA)) was selected as the organic solvent. LIX 984N (BASF) was selected as the copper extractant, which was a 1:1 volume blend of LIX 860N-I (5-nonylsalicylaldoxime) and LIX 84N-I (2-hydroxy-5-nonylacetophenone oxime) in a high flash point hydrocarbon diluent. Sulfuric acid (98%, H_2SO_4) was purchased from Fisher Scientific (USA). Sorbitan monooleate (Span-80) was purchased from Sigma-Aldrich (USA) and used as the surfactant stabilizing the primary water in oil emulsion. It is a yellow viscous liquid with a hydrophilic/lipophilic balance of 4.3. Anhydrous cupric sulfate ($CuSO_4$) was purchased from Fisher Scientific (USA) to prepare $CuSO_4$ solution. All the aqueous phases were prepared using reverse osmosis (RO) purified water (pH of 5.8 at 25°C). The pH of the $CuSO_4$ solution was adjusted using 1M sulfuric acid and 1M sodium hydroxide accordingly.

3.3.2 Experimental Protocols

3.3.2.1 Primary W/O Emulsion

In order to prepare the primary water in oil emulsion, H_2SO_4 solution was slowly added into kerosene during the process of ultra-sonication. The ultra-sonication was performed using a 24-kHz processor (Hielscher, Germany, UP400S). The ultrasonic horn tip was immersed in the oil layer before the sonication was turned on at the lowest power level (80 watts). Cold water was pumped through a water jacket to prevent heat accumulation. An emulsion with a milky appearance was formed after ultra-sonication. The primary W/O emulsion droplets ranged from 9μm to 108μm in diameter with an average value of 33 μm.

3.3.2.2 Formation and Characterization of ELM Globules

The primary water in oil emulsion was then added to a predetermined volume of $CuSO_4$ solution; small globules of the ELM droplets were produced through mechanical mixing of the primary emulsion in the $CuSO_4$ solution. The globules of ELM droplets ranged from 17 μm to 267 μm with an average value of 95 μm. An environmental scanning electron microscope (FEI Quanta 450) was used to examine the emulsion liquid membrane globules, it utilized a high vacuuming pressure thus the water phase ($CuSO_4$ solution) was quickly evaporated. The sulfuric acid droplet was surrounded by an oil droplet and isolated from the external aqueous phase, as can be seen in Figure 3.3.

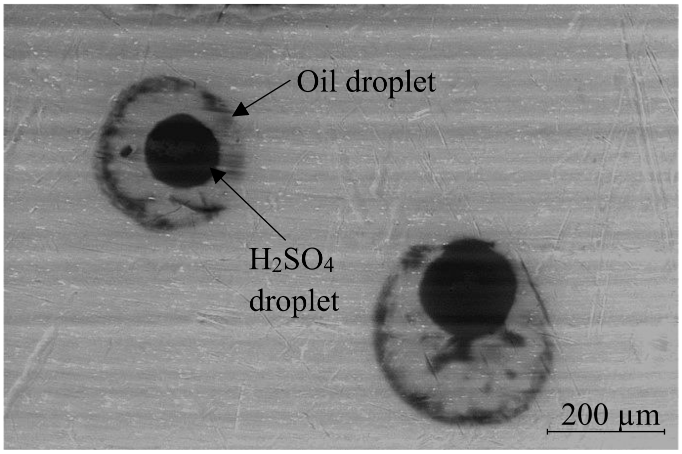


Figure 3.3 The structure of emulsion liquid membrane globules

3.3.2.3 Analysis of Percentage Copper Removal

Once the extraction process was complete, the remaining aqueous phase (effluent) was filtered (Filter Paper No. P8, Fisher Scientific, Canada) and acid digested prior being tested for copper content using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Thermo Scientific 6000 series). The percentage copper removal (y) was calculated using Equation 3.1:

$$y = \frac{C_0 - C}{C_0} \times 100\ \% \qquad \text{Equation 3.1}$$

Here C_0 is the initial concentration of copper (ppm) calculated with regard to the dilution factor and C is the final concentration of copper (ppm) measured by ICP-OES. The ICP-OES tests used a minimum of 3 measurements for each sample to reduce any associated errors.

3.3.2.4 Fourier Transform Infrared Spectroscopy (FTIR)

A Spectrum 400 spectrometer (Perkin-Elmer, USA) was employed to identify the complex formation between the copper cations and bidentate ligands in the extractant composition. Infrared spectrums of LIX 984N before and after copper extraction were recorded in the range of 4000-650 cm^{-1} with 32 scans, using a resolution of 2 cm^{-1}.

3.4 RESULTS AND DISCUSSION

3.4.1 Chemical Reactions and Theories

In the extraction of copper ions from aqueous solutions using the ELM technique, the reaction between chelating extractant and copper ions can be treated as an extractant-mediated transport process. This means that the coupled counter-transport of protons through the membrane provides the energy for uphill transport of copper ions, since the separation and concentration of copper-extractant complex into the stripping liquor is an entropy decreasing process [3.14]. The extractant can chemically react with the solute, thus the involved chemical changes are very drastic. In general, the changes can be described as subsequent partitioning, complexation and diffusion of copper ions from bulk phase to the reaction interface and then to the oil phase [3.14]. For the first two processes, the copper ions are moving towards the oil membrane from the feed solution. An interface between feed solution and oil phase is formed. The copper ions and the copper extractant will firstly go into this interface. One extractant molecule will react with one copper electron with the breaking of O-H covalent bond and the formation of Cu-O bond, since there is a place for another electron from copper ions to further reduce the energy, another extractant molecule takes the copper electron and an O-Cu-O bond forms [3.36]. This phenomena can be revealed through the comparison between infrared spectrums of LIX984N before and after copper extraction (Figure 3.4). The decrease of the band at 3381.46 cm^{-1} (hydroxy group) suggests the chemical substitution of hydrogen by a copper cation. It should be noted that the nitrogen atoms from these two extractant molecules form an N-Cu-N coordinate covalent bond with copper cations since they share electron pairs [3.36]. It should be noted that in the FTIR spectra, the bending and stretching of O-H, N-H, C-H and C=N bonds are of our concerns. Based on its structure, LIX 984N has a carbon-nitrogen bond in the oxime –C=NOH group. During the chelation process, nitrogen atom is involved in co-ordination with copper thus a decrease in the C=N stretching frequency should appear and be observed at 1690–1650 cm^{-1} of FTIR spectra. However, they are not clearly manifested since they coincide with the absorption bands associated with vibrations of the aromatic ring.

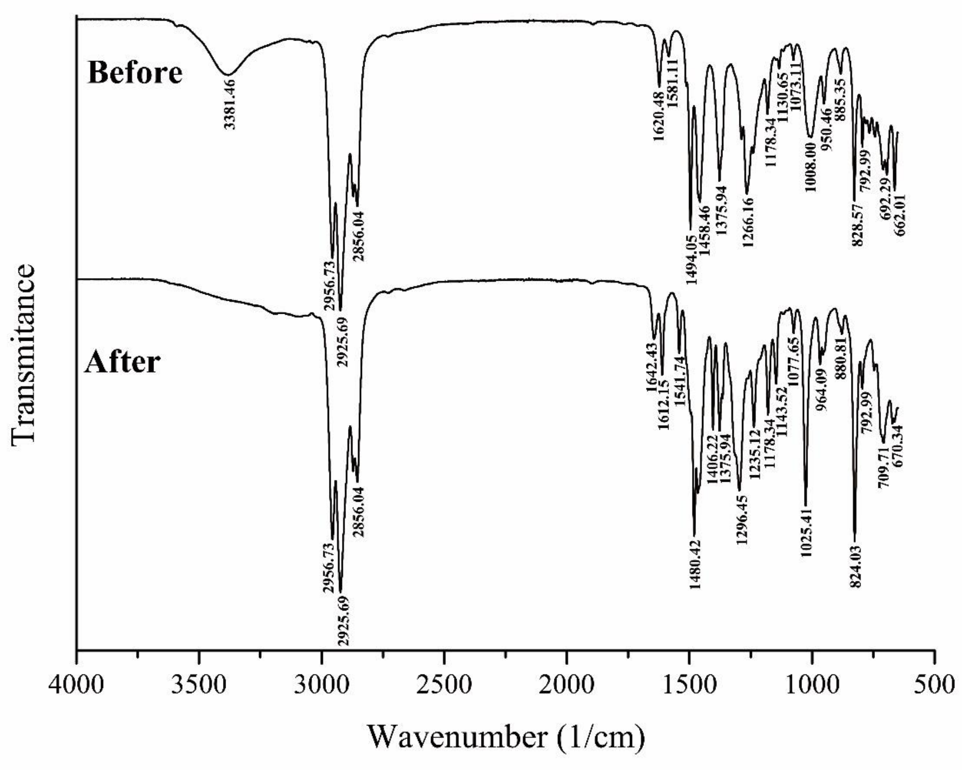


Figure 3.4 IR spectrum of LIX 984 before and after copper extraction

The copper-extractant complex is soluble in the oil phase, as such it will move freely in the membrane until it reaches interface between the stripping liquor and the oil phase. At this interface, H$^+$ will replace the copper ions so that they become free ions into the acid phase. The extractant is regenerated in the interface between the stripping liquor and the oil phase, and it will move freely into the oil phase until it reaches the interface between the feed solution and the oil phase before the copper extraction process starts again.

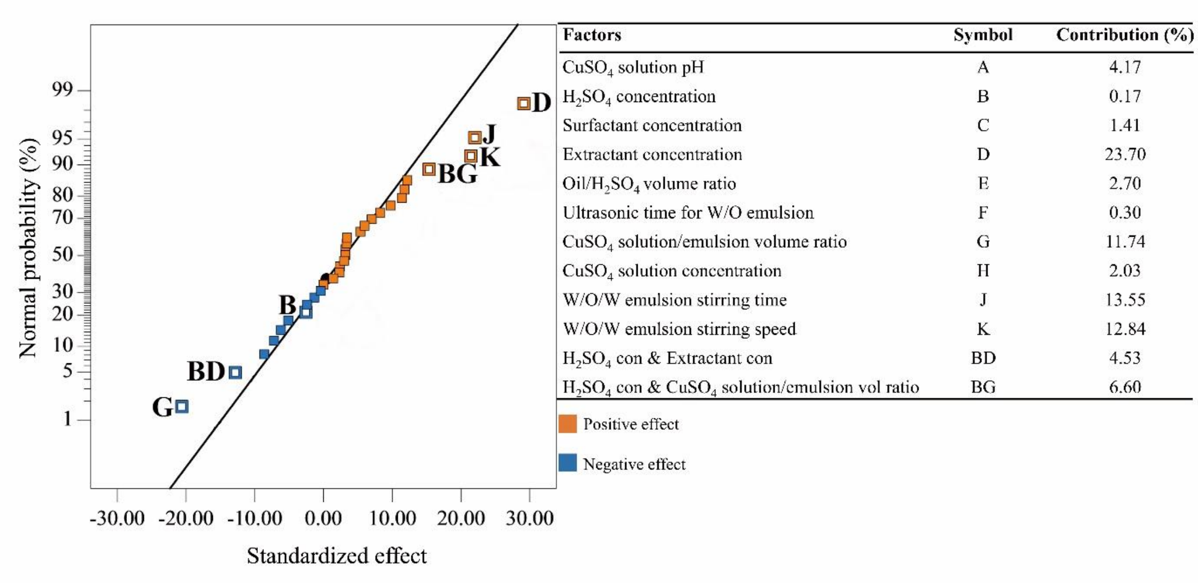
3.4.2 Selection of Important Factors

There are ten factors considered in this research. Fractional factorial design (FFD) was chosen as a method to screen out factors that were statistically important. FFD is a design that usually consists an adequately chosen fraction of a full factorial design [3.37-3.39]. Table 3.1 shows the levels and the values of these ten factors for fractional factorial design.

Table 3.1 Levels and values of factors

Factors	**Symbol**	**Unit**	**Levels**	
			Low (-1)	**High (+1)**
$CuSO_4$ solution pH	A		2	5
H_2SO_4 concentration	B	mol/L	0.1	2
Surfactant concentration	C	wt %	0.5	5
Extractant concentration	D	wt %	0.5	5
Oil/H_2SO_4 volume ratio	E		1	5
Ultrasonic time for W/O emulsion	F	min	1	5
$CuSO_4$ solution/emulsion volume ratio	G		1	10
$CuSO_4$ solution concentration	H	ppm	100	500
W/O/W emulsion stirring time	J	min	1	20
W/O/W emulsion stirring speed	K	rpm	240	600

“Minitab® Statistical Software 17” was used to develop the fractional factorial design. Percentage copper removal was chosen to be the response. The design matrix, along with the % copper removal in each test, were given in Table 3.2. The normal probability effect plot was used to evaluate the significance of factors (Figure 3.5).



Factors	Symbol	Contribution (%)
$CuSO_4$ solution pH	A	4.17
H_2SO_4 concentration	B	0.17
Surfactant concentration	C	1.41
Extractant concentration	D	23.70
Oil/H_2SO_4 volume ratio	E	2.70
Ultrasonic time for W/O emulsion	F	0.30
$CuSO_4$ solution/emulsion volume ratio	G	11.74
$CuSO_4$ solution concentration	H	2.03
W/O/W emulsion stirring time	J	13.55
W/O/W emulsion stirring speed	K	12.84
H_2SO_4 con & Extractant con	BD	4.53
H_2SO_4 con & $CuSO_4$ solution/emulsion vol ratio	BG	6.60

Figure 3.5 Normal probability plot of standardized effects for copper removal

Table 3.2 Fractional factorial design and the copper removal

RunOrder	Variables										Copper removal
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**J**	**K**	
1	5	2	0.5	5	1	1	10	100	20	600	72.28
2	5	2	5	5	5	5	10	500	20	600	96.89
3	2	2	0.5	5	5	5	10	100	20	240	18.73
4	5	2	5	0.5	5	1	10	100	1	240	23.88
5	5	0.1	0.5	5	1	5	1	500	20	240	78.68
6	5	0.1	5	5	5	1	1	100	20	240	97.16
7	5	0.1	5	0.5	1	5	10	100	20	240	13.86
8	2	0.1	5	5	5	5	10	500	1	240	12.33
9	5	2	5	0.5	1	1	1	500	20	600	17.58
10	2	0.1	0.5	0.5	1	5	10	500	20	600	17.01
11	2	0.1	5	0.5	5	1	10	100	20	600	13.79
12	2	2	5	0.5	1	5	10	100	1	600	14.09
13	2	0.1	0.5	5	5	1	1	500	20	600	98.07
14	2	2	5	5	5	1	1	100	1	600	54.73
15	5	0.1	0.5	5	5	5	10	100	1	600	66.48
16	2	2	0.5	0.5	1	1	1	100	20	240	44.21
17	2	2	0.5	0.5	5	1	10	500	1	600	24.21
18	5	2	5	5	1	5	1	100	1	240	23.23
19	5	0.1	0.5	0.5	5	1	10	500	20	240	14.83
20	5	2	0.5	0.5	1	5	10	500	1	240	11.72
21	5	2	0.5	0.5	5	5	1	100	20	600	82.34
22	2	0.1	5	5	1	5	1	100	20	600	97.34
23	2	0.1	0.5	5	1	1	10	100	1	240	15.10
24	5	2	0.5	5	5	1	1	500	1	240	32.05
25	5	0.1	0.5	0.5	1	1	1	100	1	600	32.14
26	5	0.1	5	5	1	1	10	500	1	600	20.73
27	2	2	5	0.5	5	5	1	500	20	240	14.20
28	2	2	5	5	1	1	10	500	20	240	15.61
29	2	2	0.5	5	1	5	1	500	1	600	50.15
30	5	0.1	5	0.5	5	5	1	500	1	600	30.09
31	2	0.1	5	0.5	1	1	1	500	1	240	13.43
32	2	0.1	0.5	0.5	5	5	1	100	1	240	14.95

Based on the normal probability plot (Figure 3.5) and their contributions to the response, four main important factors were selected: extractant concentration; W/O/W emulsion stirring time; W/O/W emulsion stirring speed; and $CuSO_4$ solution/emulsion volume ratio. The sequence of significance is: extractant concentration > W/O/W emulsion stirring time > W/O/W emulsion stirring speed > $CuSO_4$ solution/emulsion volume ratio. It should be noted that even though H_2SO_4 concentration does not appear to be a statistically important factor, it shows very strong interactions with $CuSO_4$ solution/emulsion volume ratio and extractant concentration as can be seen in the interaction plot (Figure 3.6).

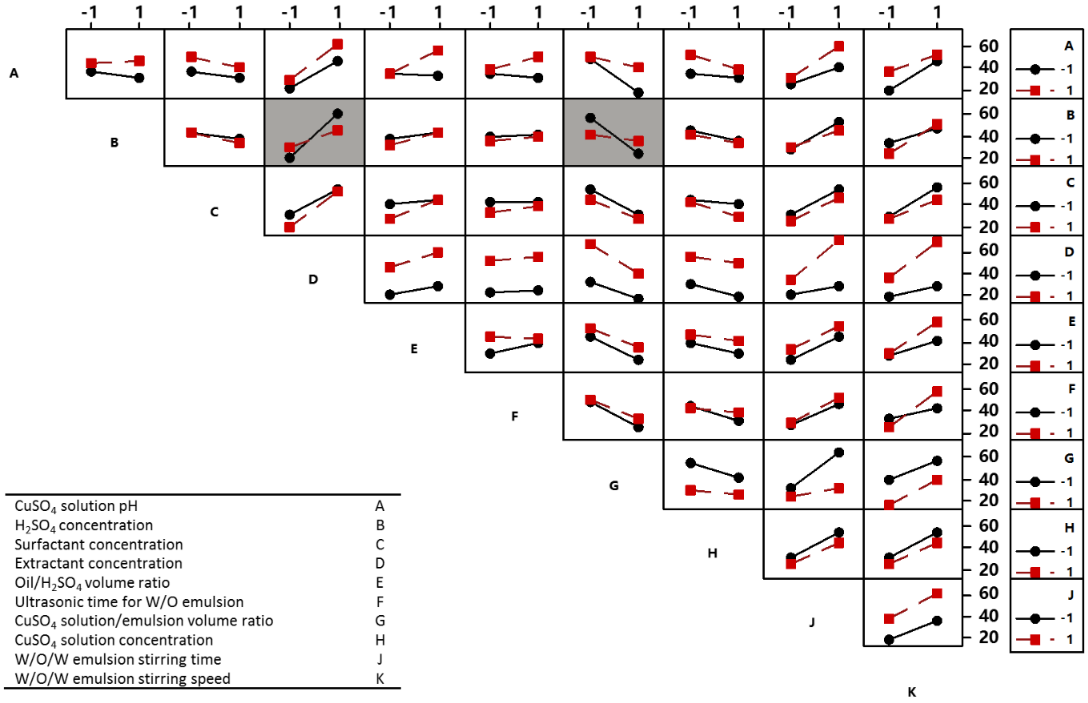


Figure 3.6 Interaction plot

These interactions also bring significant contributions (11.13%) to the response, thus H_2SO_4 concentration was considered to be an important factor for central composite design. These main effects and interactions between factors can be understood through the following discussion:

Extractant concentration has a positive effect on the reaction rate for copper extraction. It plays a vital role in this process since the extraction efficiency should be proportional to the extractant concentration. However, due to the fact that extractant molecules need to move freely inside the oil phase, the extractant concentration should not be very high due to viscosity effects. The interaction between H_2SO_4 concentration and extractant concentration can be understood through an increase in H_2SO_4 concentration promoting the copper-extractant complex stripping process thus it will regenerate more extractant.

The volume ratio of $CuSO_4$ solution/emulsion is also an important parameter for the extraction process. Since an emulsion droplet has a comparably larger surface area, it can theoretically extract copper ions from a much higher solution volume than its own volume. However, it is not ideal to set the volume ratio too high, because the copper extractant will reach its extraction capacity before all the copper ions have the chance to collide with extractant molecules. It should be noted that an increase of $CuSO_4$ solution/emulsion volume ratio means that there will be more water molecules in the system thus the leakage of H_2SO_4 from the stripping liquor will have less effect on lowering the pH of $CuSO_4$ solution.

The W/O/W emulsion speed and time refers to the total energy input to the process. The stirring speed directly affects the rate of the copper ions moving from the aqueous phase into the membrane phase. Agitation helps form emulsion liquid membrane globules. Here the stirring speed should be fast enough to enable all the extractant molecules to remove the copper ions from the aqueous phase, but not so fast as to break the liquid membrane globules; thus, a mild agitation is required during this process. The W/O/W emulsion liquid membrane globules will easily coalesce without the stabilization of oil in water surfactant. So, when the agitation stops, all the emulsion liquid membrane globules will gradually coalesce and become water in oil emulsion after all the copper ions have been extracted and stripped into the stripping liquor.

For the H_2SO_4 concentration, it was visually observed that under the same operating condition, different H_2SO_4 concentrations will lead to difference in the color of final product. Generally, at a lower value of H_2SO_4 concentration (less than 2 mol/L) the emulsion liquid membrane layers appear dark green, and the increase in H_2SO_4 concentration changes this to yellow-green and finally white. This can be explained that copper extraction and stripping occurs at the same time inside the membrane phase, since the copper-extractant complex has a dark color, if a large amount of the complex is existing in the oil phase without being stripped, the color of the emulsion phase will appear dark green, however, a higher H_2SO_4 concentration promotes the stripping rate inside the internal droplets thus less copper-extractant complex will stay in the oil phase, they are stripped into the internal droplets and concentrated as Cu^{2+} in the internal droplets, thus, the appearance of the emulsion layer will change to lighter green and will eventually change to white with the increase of H_2SO_4 concentration. It should be noted that H_2SO_4 concentration should not be very high since it may be harmful to the stability of the membrane by increasing the water permeability in the membrane; in addition, the high osmotic pressure gradient between the internal and external phases will lead to obvious swelling to the internal phase. Thus, the chances of breakage and dilution of loaded internal droplets will increase.

It should be noted that in the fractional factorial design, the $CuSO_4$ solution pH range was chosen from 2-5 because in this pH range, copper ions can be stable in the form of Cu^{2+}. Cu^{+} will only appear when the pH is greater than 5. Theoretically, the $CuSO_4$ solution pH should play an important role in the copper extraction process, this can be explained that the lower the feed solution pH, the slower the extraction rate will be since a higher amount of H^{+} in the $CuSO_4$ solution can help promote the back-extraction process (Figure 3.1), thus impeding the extraction process. In addition, since the driving force for stripping is the pH difference between the sulfuric acid and feed solution, it is easier to treat $CuSO_4$ solutions of a higher pH. However, the leakage from H_2SO_4 droplets in the liquid membrane can significantly change the feed solution pH during the reaction, and lower the $CuSO_4$ solution pH. It was found that the $CuSO_4$ solution pH changed from 2-5 (initial state) to 1.5-2.7 (final state). This pH change actually comes from two parts: one is from the leakage of H_2SO_4 droplets into $CuSO_4$ solution; the other comes from the release of H^{+} during the copper extraction process.

3.4.3 Optimization of Selected Factors

In order to optimize the selected factors, response surface method (RSM) with central composite design (CCD) was used. CCD can be used to build a second order model with minimum experiments to obtain maximum information [3.37-3.42]. Five experimental parameters including extractant concentration, $CuSO_4$ solution/emulsion volume ratio, W/O/W emulsion stirring time, W/O/W emulsion stirring speed and H_2SO_4 concentration were selected from the FFD design. Table 3.3 shows the levels of factors used in this central composite design.

Table 3.3 Levels of factors in the central composite design

Factors	**Symbol**	**Units**	**-β**	**-1**	**0**	**1**	**β**
$CuSO_4$ solution/emulsion volume ratio	X_1		2	3.5	5	6.5	8
Extractant concentration	X_2	wt %	2	3.5	5	6.5	8
H_2SO_4 concentration	X_3	mol/L	1	2	3	4	5
W/O/W emulsion stirring time	X_4	min	10	15	20	25	30
W/O/W emulsion stirring speed	X_5	rpm	200	300	400	500	600

The design matrix used in central composite design, along with the % copper removal in each test is given in Table 3.4a and Table 3.4b.

Table 3.4a Central composite design and the copper removal

RunOrder	**X_1**	**X_2**	**X_3**	**X_4**	**X_5**	**Copper removal**
1	6.5	6.5	4	25	500	98.99
2	5	5	3	20	200	39.99
3	3.5	3.5	2	25	300	31.65
4	5	5	3	20	400	76.67
5	5	5	1	20	400	73.85
6	5	5	5	20	400	82.16
7	8	5	3	20	400	62.43
8	5	5	3	20	400	90.35
9	3.5	6.5	2	15	300	76.91
10	5	5	3	20	400	88.02
11	6.5	6.5	2	15	500	92.48
12	3.5	6.5	2	25	500	99.03
13	5	5	3	20	400	83.37
14	3.5	6.5	4	25	300	96.57
15	5	5	3	20	600	86.18
16	5	2	3	20	400	45.23
17	5	5	3	20	400	73.83
18	5	5	3	20	400	83.26
19	3.5	6.5	4	25	300	96.30
20	6.5	3.5	2	25	500	76.39
21	6.5	6.5	2	25	300	62.05
22	3.5	3.5	4	15	300	52.85
23	3.5	3.5	4	25	500	85.29
24	2	5	3	20	400	76.85
25	5	5	3	30	400	83.41
26	3.5	3.5	2	15	500	83.39
27	6.5	3.5	2	15	300	52.15

Table 3.4b Central composite design and the copper removal (continued from previous table)

RunOrder	X_1	X_2	X_3	X_4	X_5	Copper removal
28	6.5	6.5	4	15	300	69.08
29	5	5	5	20	400	90.02
30	5	8	3	20	400	96.15
31	6.5	3.5	4	25	300	65.37
32	8	5	3	20	400	51.41
33	3.5	6.5	2	25	500	92.78
34	3.5	3.5	2	25	300	31.71
35	5	5	3	20	600	82.61
36	6.5	6.5	4	15	300	69.21
37	5	5	3	30	400	86.13
38	6.5	6.5	4	25	500	98.20
39	5	5	3	20	400	82.89
40	5	5	3	20	400	87.21
41	3.5	6.5	4	15	500	99.41
42	2	5	3	20	400	81.45
43	3.5	3.5	2	15	500	81.35
44	6.5	6.5	2	25	300	61.43
45	5	5	3	20	400	87.85
46	5	5	1	20	400	73.24
47	6.5	3.5	4	25	300	62.41
48	5	2	3	20	400	41.31
49	5	5	3	10	400	70.67
50	5	5	3	20	200	38.23
51	5	5	3	10	400	75.77
52	5	5	3	20	400	95.05
53	3.5	6.5	4	15	500	98.95
54	5	5	3	20	400	85.62
55	6.5	3.5	4	15	500	79.15
56	6.5	3.5	4	15	500	73.31
57	6.5	3.5	2	25	500	72.97
58	6.5	6.5	2	15	500	94.79
59	6.5	3.5	2	15	300	44.53
60	5	8	3	20	400	99.62
61	5	5	3	20	400	93.02
62	3.5	3.5	4	15	300	61.75
63	3.5	3.5	4	25	500	93.84
64	3.5	6.5	2	15	300	74.95

The values of non-significant factors were determined to be as follows:

Table 3.5 Values for non-significant factors

Factors	**Hold Value**
Surfactant concentration (wt %)	2
$CuSO_4$ solution concentration (ppm)	500
Ultrasonic time for primary emulsion (min)	1
Oil/H_2SO_4 volume ratio	5
$CuSO_4$ solution pH	3.5

The values were chosen with the following considerations:

- For surfactant concentration, a lower value could drive down the cost. However, in order to maintain the stability of primary water in oil emulsion, it was not ideal to set the surfactant concentration lower than 2%.
- For $CuSO_4$ concentration, mine tailings that have a copper concentration higher than 500 ppm can be treated using traditional solvent extraction method, so 500 ppm was a good limit for this ELM investigation.
- For ultra-sonication time, an ultrasonic time of one minute could lower the cost while maintaining the energy required for emulsification.
- For oil/H_2SO_4 volume ratio, visual observation showed that any value lower than 5 may impede the holding capacity of H_2SO_4 in the oil phase.
- For $CuSO_4$ pH, it was chosen to be 3.5 since it was close to the pH of many acid mine drainage sites.

The regression analysis was expressed as a second-order polynomial to estimate the response function (Equation 3.2) [3.37]:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j \qquad \text{Equation 3.2}$$

Y is the predicted response (% copper removal); X_i and X_j are variables; β_0 is a constant coefficient; β_i, β_{ii} and β_{ij} are coefficients that represent the linear, quadratic and cross-products of X_1, X_2, X_3, X_4 and X_5 on response; k is the number of factors. Table 3.6 shows the parameters using least squares method for the regression model. These parameters include: regression coefficient (Coef), t-value (t) and p-value (p) [3.37-3.39, 3.42].

Table 3.6 Regression model for copper removal

Term	Coef	t	p
Constant	84.230	49.810	0.000
X_1	-3.607	-4.170	0.000
X_2	11.489	13.280	0.000
X_3	4.632	5.350	0.000
X_4	1.394	1.610	0.115
X_5	12.345	14.260	0.000
X_1^2	-3.024	-3.860	0.000
X_2^2	-2.388	-3.050	0.004
X_3^2	-0.078	-0.100	0.921
X_4^2	-0.283	-0.360	0.719
X_5^2	-4.593	-5.870	0.000
$X_1 \times X_2$	-2.910	-2.750	0.009
$X_1 \times X_3$	-1.700	-1.600	0.117
$X_1 \times X_4$	0.800	0.750	0.456
$X_1 \times X_5$	-0.350	-0.330	0.740
$X_2 \times X_3$	-0.860	-0.810	0.422
$X_2 \times X_4$	1.200	1.130	0.264
$X_2 \times X_5$	-2.350	-2.220	0.032
$X_3 \times X_4$	5.180	4.890	0.000
$X_3 \times X_5$	-3.260	-3.070	0.004
$X_4 \times X_5$	0.270	0.250	0.801

A second-order polynomial model is given in Equation 3.3 (in coded units).

$$Y_1 = 84.23 - 3.607 \times X_1 + 11.489 \times X_2 + 4.632 \times X_3 + 1.394 \times X_4 + 12.345 \times X_5 - 3.024 \times X_1^2 - 2.388 \times X_2^2 - 0.078 \times X_3^2 - 0.283 \times X_4^2 - 4.593 \times X_5^2 - 2.91 \times X_1 \times X_2 - 1.7 \times X_1 \times X_3 + 0.8 \times X_1 \times X_4 - 0.35 \times X_1 \times X_5 - 0.86 \times X_2 \times X_3 + 1.2 \times X_2 \times X_4 - 2.35 \times X_2 \times X_5 + 5.18 \times X_3 \times X_4 - 3.26 \times X_3 \times X_5 + 0.27 \times X_4 \times X_5 \quad \text{Equation 3.3}$$

Where Y_1 is the percentage copper removal, X_1, X_2, X_3, X_4 and X_5 represent $CuSO_4$ solution/emulsion volume ratio, extractant concentration, H_2SO_4 concentration, W/O/W emulsion stirring time and W/O/W emulsion stirring speed accordingly.

The adequacy of the regression model for copper removal was confirmed by an analysis of variance (ANOVA) table, with the data detailed in Table 3.7.

Table 3.7 ANOVA table for copper removal

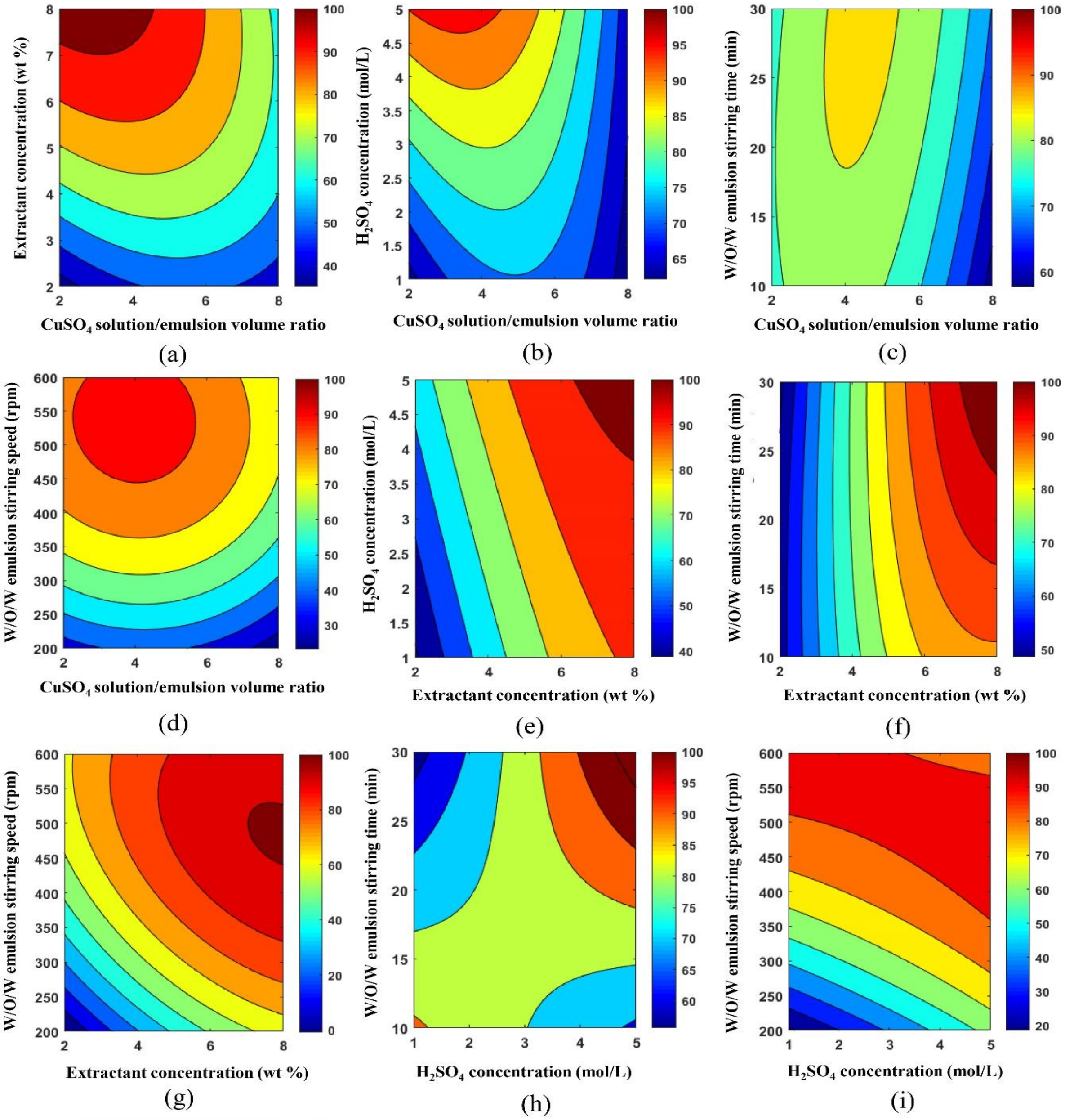
Source	**DF**	**f-value**	**p-value**	**R^2**	**SD**
Model	20	26.58	0.000	0.925	5.996

DF: degree of freedom SD: standard deviation

Considering R^2 and SD, it can be noted that this is an acceptable model from an engineering perspective.

3.4.3.1 Contour Plots

Contour plots were used to display the relationship between variables and response and in each contour plot there are two variables and other three factors held at constant values (center level); therefore, a total number of ten response surface contour plots were produced, as shown in Figure 3.7(a-j).



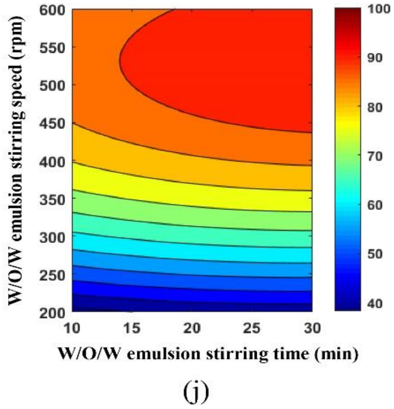


Figure 3.7 Surface contour plots showing the effects of variables on copper removal: (a) $CuSO_4$ solution/emulsion volume ratio and extractant concentration; (b) $CuSO_4$ solution/emulsion volume ratio and H_2SO_4 concentration; (c) $CuSO_4$ solution/emulsion volume ratio and W/O/W emulsion stirring time; (d) $CuSO_4$ solution/emulsion volume ratio and W/O/W emulsion stirring speed; (e) Extractant concentration and H_2SO_4 concentration; (f) Extractant concentration and W/O/W emulsion stirring time; (g) Extractant concentration and W/O/W emulsion stirring speed; (h) H_2SO_4 concentration and W/O/W emulsion stirring time; (i) H_2SO_4 concentration and W/O/W emulsion stirring speed; (j) W/O/W emulsion stirring time and W/O/W emulsion stirring speed.

Conclusions regarding the suitable ranges of variables for high copper removal were made through the observations of Figure 3.7(a-j) and listed in Table 3.8.

Table 3.8 Suitable ranges of variables for the response

Variables	**Units**	**Variables ranges for high copper removal**	**Supporting graphs**
$CuSO_4$ solution/emulsion volume ratio		3.5-4.5	Figure 3.7 (a, b, c, d)
Extractant concentration	wt %	7-8	Figure 3.7 (a, e, f, g)
H_2SO_4 concentration	mol/L	4.5-5	Figure 3.7 (b, e, h)
W/O/W emulsion stirring time	min	25-30	Figure 3.7 (c, f, h, j)
W/O/W emulsion stirring speed	rpm	450-550	Figure 3.7 (d, g, i, j)

It should be noted that for H_2SO_4 concentration, Figure 3.7 (i) shows that under all concentrations (1-5 mol/L), an optimum value of copper removal can be obtained by controlling the W/O/W emulsion stirring speed at around 510-570 rpm. This means that under this condition, the W/O/W emulsion stirring speed is a key parameter affecting the copper removal rather than H_2SO_4 concentration.

3.4.3.2 Overlaid Contour Plots

Overlaid contour plots can be used to optimize all responses simultaneously by emphasizing the overlaid region of the contour plots [3.37-3.39]. Figure 3.8 (a-j) show the overlaid contour plots. The darker areas of the overlaid contours indicate the optimum operating conditions to obtain a high copper removal (>99%).

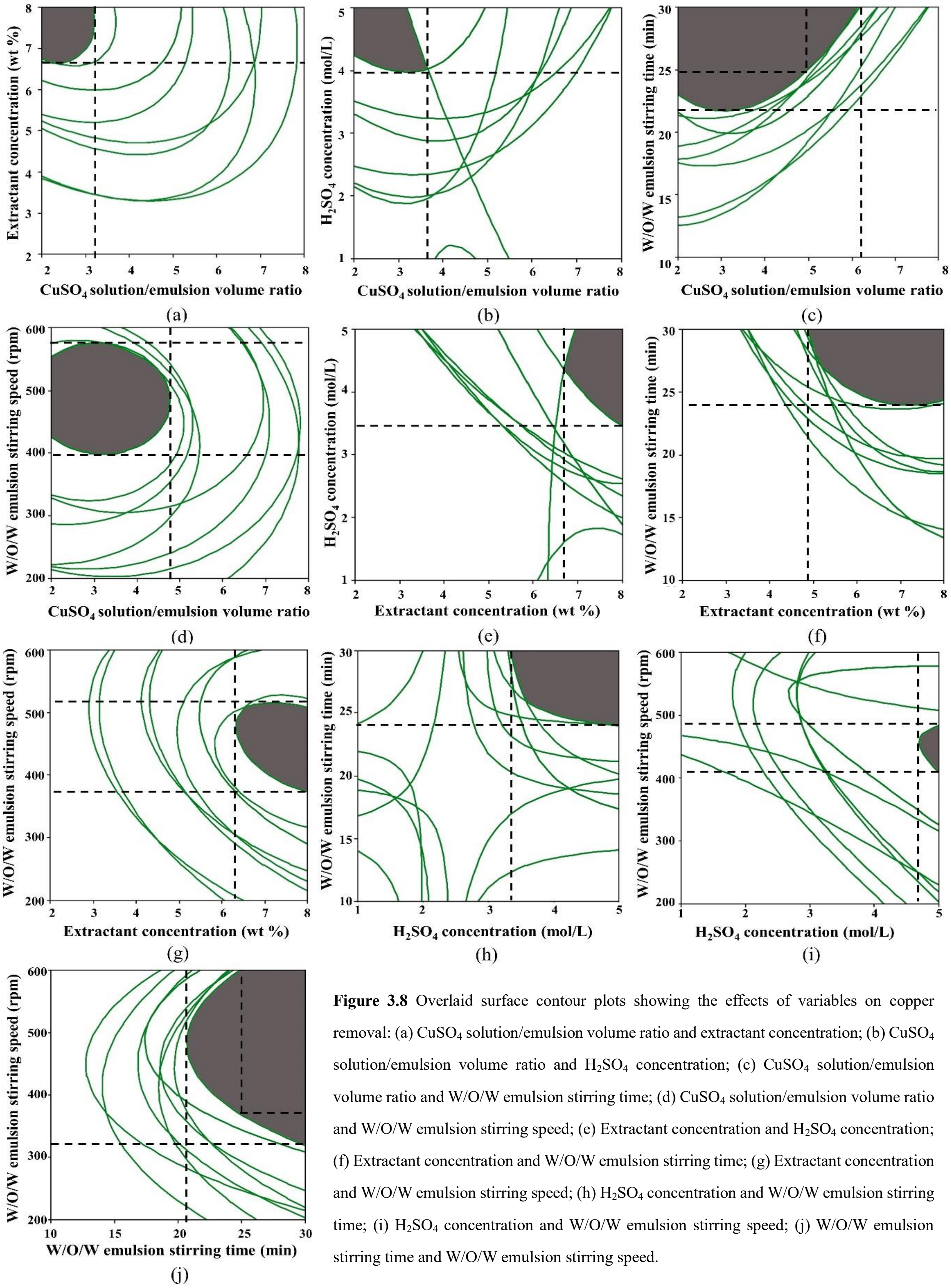


Figure 3.8 Overlaid surface contour plots showing the effects of variables on copper removal: (a) CuSO$_4$ solution/emulsion volume ratio and extractant concentration; (b) CuSO$_4$ solution/emulsion volume ratio and H$_2$SO$_4$ concentration; (c) CuSO$_4$ solution/emulsion volume ratio and W/O/W emulsion stirring time; (d) CuSO$_4$ solution/emulsion volume ratio and W/O/W emulsion stirring speed; (e) Extractant concentration and H$_2$SO$_4$ concentration; (f) Extractant concentration and W/O/W emulsion stirring time; (g) Extractant concentration and W/O/W emulsion stirring speed; (h) H$_2$SO$_4$ concentration and W/O/W emulsion stirring time; (i) H$_2$SO$_4$ concentration and W/O/W emulsion stirring speed; (j) W/O/W emulsion stirring time and W/O/W emulsion stirring speed.

It can be observed from Figure 3.8 (a) that a high extractant concentration of 6.6-8.0 wt % and a low $CuSO_4$ solution/emulsion volume ratio of 2-3.2 will lead to a high % copper removal (over 99%); Figure 3.8 (b) shows that a high H_2SO_4 concentration of 4-5 mol/L and a low $CuSO_4$ solution/emulsion volume ratio of 2-3.7 is desired. Figure 3.8 (c) shows that a wider range of $CuSO_4$ solution/emulsion volume ratio of 2-6.2 can also bring optimum copper removal if W/O/W emulsion stirring time is kept at the range 22-30 min, and a suitable optimum rectangle zone is: W/O/W emulsion stirring time of 25-30 min; and $CuSO_4$ solution/emulsion volume ratio of 2-4.9. Figure 3.8 (d) has a shape close to a local-maxima overlaid contour plot, high copper removal appears under the combination of low-middle value of $CuSO_4$ solution/emulsion volume ratio (2-4.8) and high value of W/O/W emulsion stirring speed (400-575 rpm), an even higher value of W/O/W emulsion stirring speed will not secure the response at the optimum condition; Figure 3.8 (e) indicates that suitable ranges for the variables are an extractant concentration of 6.7-8 wt % and H_2SO_4 concentration of 3.5-5 mol/L; Figure 3.8 (f) enlarges the range of extractant concentration to 4.8-8 wt % while controlling W/O/W emulsion stirring time at 24-30 min; the observation of Figure 3.8 (g) shows that the optimum range for extractant concentration is 6.3-8 wt % and W/O/W emulsion stirring speed is 380-510 rpm. Any value higher than 510 rpm for W/O/W emulsion stirring speed may negatively affect the response; Figure 3.8 (h) shows that a high H_2SO_4 concentration of 3.3-5 mol/L and a longer W/O/W emulsion stirring time of 24-30 rpm is preferred; Figure 3.8 (i) shows a much narrower range exists for H_2SO_4 concentration (4.6-5 mol/L) and W/O/W emulsion stirring speed (415-480 rpm) while Figure 3.8 (j) gives a much wider selection for W/O/W emulsion stirring time (21-30 min) and W/O/W emulsion stirring speed (320-600 rpm), there is also a larger suitable area for W/O/W emulsion stirring time (25-30 min) and W/O/W emulsion stirring speed (370-600 rpm). It should be noted that in Figure 3.8 (i), a very narrow range of H_2SO_4 concentration was selected for obtaining optimum copper removal. However, if a lower bound value of 98% is selected rather than 99%, a much wider range will appear for the range of H_2SO_4 concentration (3-5 mol/L). As such, a compromise may be made between H_2SO_4 concentration and copper removal.

From the contour plot result above, it can be seen that the $CuSO_4$ solution/emulsion volume ratio negatively affects the copper removal, such that a lower value is desired in this project. In contrast, a higher value of extractant concentration is desired and the same trend applies to the H_2SO_4 concentration. With the increase of W/O/W emulsion stirring speed, the emulsion globules will be split into smaller sizes thus the total surface area is increased. The Nernst film at the membrane interfaces will also be thinner so it positively improves the copper ions diffusion and reaction efficiency [3.14]. However, a value greater than 550 rpm in this system will make the emulsion liquid membranes globules unstable, increasing the possibility of leakages of internal droplets into $CuSO_4$ solution so that it will negatively affect the extraction rate. This can be observed in Figure 3.8 (d, g, i) where a suitable zone only appears in a certain range of W/O/W emulsion stirring speed. Also, a higher W/O/W emulsion stirring time (over 22 minutes) is desired for obtaining a high copper removal. This phenomena can be seen in Figure 3.8 (f, h, j). It should be noticed that any value lower than 21 minutes will bring added uncertainty to the response. This may be because a lower value will impede the contact time of emulsion liquid membranes with copper ions.

Based on these results, the optimum ranges for these variables can be listed: $CuSO_4$ solution/emulsion volume ratio: 2-3.2; extractant concentration: 6.7-8.0 wt%; H_2SO_4 concentration: 4.6-5.0 mol/L; W/O/W emulsion stirring time: 22-30 mins; W/O/W emulsion stirring speed: 415-480 rpm. The optimum condition was selected in order to minimize the energy and materials input and maximum output. The calculation of stationary points using the desirability function was performed to confirm the result and random points were selected as well. Validation tests were performed in order to check the adequacy of the model, shown in Table 3.9:

Table 3.9 Validation tests results

Terms		**Optimum Condition**	**Random Condition 1**	**Random Condition 2**	**Random Condition 3**
Factors	$CuSO_4$ solution/emulsion volume ratio	3.2	4.5	4.5	3
	Extractant concentration (wt %)	6.7	5.5	6	4
	H_2SO_4 concentration (mol/L)	4.6	4	3.5	5
	W/O/W emulsion stirring time (min)	24	24	24	18
	W/O/W emulsion stirring speed (rpm)	415	425	425	450
Results	Fitted result (% copper removal)	100*	100.0*	100.0*	85.7
	Avg. test result (% copper removal)	99.8	99.1	96.9	78.4
	% Error	0.20	0.90	3.10	8.52

*Any value higher than 100% is considered to be 100%

It can be seen from Table 3.9 that validation tests showed a good confirmation of the optimum condition, and random condition 1 and 2 also bring optimized results, these results are illustrated in Figure 3.9:

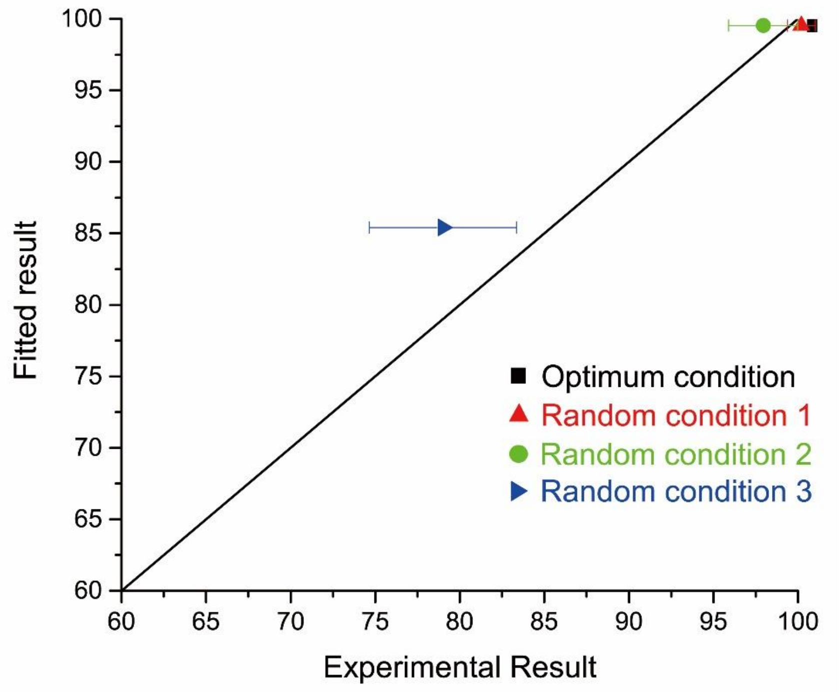


Figure 3.9 Model validation graph of experimental result and fitted result

A suggestion can be made that this process can be operated at random condition 1 in order to minimize the energy & materials input and maximize output.

3.5 CONCLUSIONS

Fractional factorial design was used to screen out five important factors: extractant concentration; W/O/W emulsion stirring time; W/O/W emulsion stirring speed; $CuSO_4$ solution/emulsion volume ratio; and H_2SO_4 concentration. Response surface methodology was then used to obtain optimal operation conditions. The optimum conditions are as follows: $CuSO_4$ solution/emulsion volume ratio = 3.2; Extractant concentration = 6.7 wt %; H_2SO_4 concentration = 4.6 mol/L; W/O/W emulsion stirring time = 24 minutes; and W/O/W emulsion stirring speed = 415 rpm. The percentage cooper removal was found to be greater than 99% under these conditions.

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LINKING PARAGRAPH BETWEEN CHAPTER 3 AND CHAPTER 4

Since the target of this thesis is to effectively extract and separate copper and nickel ions from calcium ion using ELM technique, it is necessary to know the extraction behavior of copper and nickel from its single cation bearing solution. The extraction of copper ion from $CuSO_4$ solution using ELM have been discussed in Chapter 3, it is found that out of ten operating parameters, five have been identified to be statistically insignificant using fractional factorial design, the optimization of the other five important parameters have been obtained by central composite deign, meaning that the process optimization of the extraction of copper using ELM by design of experiment method is applicable and successful. Based on the findings from Chapter 3, Chapter 4 explores nickel extraction from $NiSO_4$ solution by ELM technique, it firstly fixes the five unimportant operating parameters at their constant values as was done in Chapter 3, and an optimization of the remaining important factors have also been performed using central composite design. In the meantime, Chapter 4 explores some physical & chemical properties of ELM in order to further understand the characteristics of ELM.

CHAPTER 4. THE EXTRACTION OF NICKEL BY EMULSION LIQUID MEMBRANES USING CYANEX 301 AS EXTRACTANT

4.1 ABSTRACT

The removal of nickel ions from waste streams discharged from mining and metal plating industries has become a popular research topic over the past few decades. In this work, the emulsion liquid membrane (ELM) technique was used to remove nickel ions from synthetic aqueous solutions using bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) as the extractant. Sulfuric acid was selected as the internal stripping agent. Central composite design methodology was used to obtain the optimum conditions, with the factors selected in the design being extractant concentration, stripping agent concentration, $NiSO_4$ solution pH and $NiSO_4$ solution/emulsion volume ratio. It was found that extractant concentration, stripping agent concentration and $NiSO_4$ solution/emulsion volume ratio had a significant effect on nickel removal. Optimum operating conditions achieved a maximum nickel removal of more than 99%. Validation tests confirmed the good agreement between predicted and experimental data. The emulsion was successfully broken afterwards and the oil phase was re-tested. The effect of kinetics, loading capacity and pH variation tests between the emulsion phase and organic phase were conducted using $NiSO_4$ solution. Zeta potential measurements suggest a final pH of around 2.0 is desirable for post-reaction treatment of the emulsion droplets.

4.2 INTRODUCTION

Nickel is a silvery-white metal that is very important in modern industries, for example, nickel and its alloys are used to produce coins, batteries and stainless-steel due to its high corrosion resistance properties [4.1-4.6]. Despite its extensive usage, nickel can be toxic and hazardous [4.7-4.14]; excessive exposure to nickel may cause nausea, skin allergies and lung fibrosis in humans [4.11, 4.14-4.15]; the wastewater containing nickel ions discharged from the mining and metal plating industries may also pollute waterbodies and soil, thus damaging the local flora and fauna [4.11, 4.15].

Oxidation of mine tailings and backfill (sulfide minerals including pyrite, pyrrhotite) generates acid and mobilizes heavy metal ions such as Ni^{2+}, Cu^{2+}, Fe^{2+}/Fe^{3+}, etc. [4.15]. The emulsion liquid membrane (ELM) technique is a very promising method for removing these metal ions from acid mine drainage (AMD) [4.16-4.28]. Invented by Li in 1968, ELM has a number of attractive features when compared to conventional solvent extraction: the operation is generally simple and it combines both extraction and stripping in one stage [4.18, 4.26]; ELM also typically requires a lower volume of chemicals than solvent extraction. An economic evaluation by Frankenfeld *et al.* indicated that ELM extraction of copper using LIX 64N could be 40% cheaper than traditional solvent extraction [4.29]. However, challenging technical difficulties that limit the industrial applications of ELM include the inherent thermodynamic instability of emulsion; the water entrainment or shrinkage of double emulsion in the presence of water migration during operation and the uncontrolled release of the addenda during storage and operation [4.16, 4.19, 4.26, 4.30]. Currently there are no commercial industrial plants implementing ELM technique in the market. Thus, for the past few decades the researchers have been working closely on the study of chemical and physical properties of ELM, these include the stability of emulsion; the removal of organic waste; the extraction behavior on heavy metals such as copper, zinc, nickel, cobalt, etc. as well as the kinetics study [4.17-4.18, 4.20-4.25, 4.27-4.31]. Much progress has been made since then and various researchers have reported the implementation of ELM technique in lab-scale or even pilot-scale plant [4.22-4.24]. For example, in 1986, a two-stage mixer-settler was built in Graz, Austria to treat nickel ions from synthetic solution using ELM, where the nickel concentration was reduced from an initial concentration of 2.2 g/L to about 200 mg/L in the first stage and to 3 mg/L in the second stage [4.19]; Valenzuela *et al.* built up a batch stirred tank using ELM technique removing copper content from an actual acidic mine drainage (Cu(II) 350 mg/L, Zn(II) 250 mg/L, Fe 280 mg/L) in 2009 [4.24]; another successful application is zinc removal from wastewater (Zn(II) concentration ranging from 0.3 to 200 mg/L) at the pilot plant located in Lenzing, AG, Austria

[4.29], the plant can treat up to 75 m^3•h^{-1} of zinc bearing wastewater with zinc removal efficiency up to 99.5% [4.29]. We have previously studied the optimization of extracting copper ions from synthetic $CuSO_4$ solution using ELM technique and this work will be a continuous work focusing on the optimization of lab-scale nickel ion extracting process.

Based on the traditional solvent extraction technique, the ELM process is usually a coupled counter transport process which transfers metal ions from a feed solution to the organic phase by solvent extraction, then to the internal phase by stripping [4.30]. This transport is controlled by non-equilibrium mass transfer kinetics, thus the extractant and its concentration usually plays a vital role on the metal extraction [4.30-4.32]. Therefore, a suitable selection of extractant is vital. Currently there are many commercialized extractants for nickel extraction on the market, these nickel extractants include: D2EHPA (Di-(2-ethylhexyl) phosphoric acid); PC-88A (2-ethyl hexyl phosphonic acid and mono 2-ethyl hexyl ester); Versatic 10 (Neodecanoic acid); LIX 84-I (2-hydroxy-5-nonylacetophenone oxime); Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid) and Cyanex 301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid) [4.33-4.49].

These extractants generally have a low solubility in water, which makes them suitable for generating ELM. However, since the reaction is a process with counter-current transport of hydrogen and nickel ions, the decrease in feed solution pH is inevitable. Thus, when treating nickel ions from AMD, the requirement of good extraction performance in acid environment for extractants makes bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) an ideal choice in this work. As can be seen from its chemical nomenclature, Cyanex 301 is the dithio-substituted analog of Cyanex 272, where sulfur is acting as a proton acceptor and tends to form more stable complex with divalent 3d transition metal ions such as nickel and cobalt [4.37-4.38]. These characteristics allow Cyanex 301 to perform well when treating AMD at pH values lower than 2 [4.37, 4.50]. It should be noted here that Cyanex 301 was not stable and may be decomposed into Cyanex 272 and elemental sulphur thus it should be kept away from air oxidation during storage and transportation.

In this work, Cyanex 301 (extractant) and SPAN 80 (emulsion stabilizer) were initially dissolved into kerosene; the oil mixture was then used to form a primary emulsion with sulfuric acid by emulsification. The emulsion was a dispersion of sulfuric acid liquor droplets in the oil phase through ultra-sonication, the interfaces between water (W) and oil (O) phases were stabilized by SPAN 80 to prevent the re-coalescence of the formed H_2SO_4 droplets. This primary W/O emulsion was then sent to treat $NiSO_4$ solution, a mechanical mixer was employed during this process, W/O/W emulsion droplets were created and nickel ions extraction started. The nickel was extracted into the oil phase and further stripped in the internal water phase; Cyanex 301 was then regenerated. The process reaction is shown in Equation 4.1:

$$Ni^{2+}{}_{(aq)} + 2HR_{(org)} \leftrightarrow NiR_{2\,(org)} + 2H^{+}{}_{(aq)} \qquad \text{Equation 4.1}$$

Where HR stands for Cyanex 301, NiR_2 represents the Ni-Cyanex 301 complex, aq and org represent aqueous and organic separately.

4.3 EXPERIMENTS AND METHODS

4.3.1 Materials

Kerosene (reagent grade) purchased from Sigma-Aldrich was selected to be the organic solvent. The Cyanex 301 sample was provided by Cytec Canada, and used as the nickel extractant without further purification. Sorbitan monooleate (Span-80, Sigma-Aldrich) was used as the surfactant. Nickel (II) sulfate hexahydrate ($NiSO_4{\cdot}6H_2O$) purchased from Anachemia Canada was used to prepare synthetic $NiSO_4$ solution with nickel ions concentration of 300 ppm (5.11×10^{-3} mol/L). Instead of nitric acid (HNO_3) or hydrogen chloride (HCl), Sulfuric acid (H_2SO_4, Fisher Scientific) was selected to be the internal stripping liquor to avoid introducing new ions to the system. All the aqueous phases were prepared or diluted using reverse osmosis water (pH of 5.8 at 25°C). $NiSO_4$ solution pH was adjusted by 1 mol/L H_2SO_4 and 1 mol/L NaOH accordingly. All experiments were carried out at room temperature (~25 °C).

4.3.2 ELM Preparation and Nickel Extraction

Surfactant (SPAN 80) and metal extractant (Cyanex 301) was pre-dispersed in the kerosene, then the oil phase and the water phase (H_2SO_4 solution) were mixed up at a volume ratio of 5:1 in a beaker. The primary W/O emulsion was formed using a 24 kHz ultra-sonication processor (Hielscher, Germany, UP400S) at its lowest level (80 W), the sonication time was 1 minute. Once the ultrasonic processor was turned on, the high intensity sonic waves produced by the ultrasonic probe will propagate into the oil phase and create small voids and bubbles, the small water droplets are going into the voids to reduce surface tension thus this creates the primary water in oil emulsion, the surfactant helped stabilize these emulsion droplets during the process. The formed primary emulsion was then injected into a beaker of $NiSO_4$ solution, stirred with a Caframo Ultra Speed BDC 6015 stirrer, which was equipped with a three-blade impeller running at a rotational speed of 425 rpm. Each test duration was 15 minutes. During the mechanical stirring process, a water in oil in water emulsion (emulsion liquid membrane) formed and metal ions were extracted and stripped. Once the mixer was stopped, samples were taken from the aqueous phase using a 10-ml syringe (around 3 cm below the surface). The nickel concentration was measured using atomic absorption spectroscopy (AAS) (Perkin Elmer Atomic Absorption Spectrometer 311). The nickel removal efficiency (R %) was calculated using Equation 4.2:

$$R\ \% = ([Ni^{2+}]_{ini} - [Ni^{2+}]_{fin}) / [Ni^{2+}]_{ini} \times 100\ \% \qquad \text{Equation 4.2}$$

Where $[Ni^{2+}]$ represents the nickel ion concentration and the subscripts “ini” and “fin” stand for the initial and final nickel concentration in the aqueous solution, respectively.

4.3.3 Design of Experiments

In this process, factors that affect the extraction are: extractant concentration, surfactant concentration, $NiSO_4$ solution pH, H_2SO_4 concentration, Oil/H_2SO_4 volume ratio, sonication time for W/O emulsion, $NiSO_4$ solution/emulsion volume ratio, W/O/W emulsion stirring time and W/O/W emulsion stirring speed. However, based on previous studies [4.18, 4.51-4.55], only the extractant concentration, H_2SO_4 concentration, $NiSO_4$ solution pH and $NiSO_4$ solution/emulsion volume ratio were considered as being potential important factors and optimization tests were performed using central composite design based on these factors. Other factors were kept constant and are listed in Table 4.1.

Table 4.1 Values for non-significant factors

Factors	**Value**
Surfactant concentration (wt %)	2
Sonication time for primary emulsion (min)	1
Oil/H_2SO_4 volume ratio	5
W/O/W emulsion stirring time (min)	15
W/O/W emulsion stirring speed (rpm)	425

A central composite design (CCD) was used to obtain the optimum operating condition. CCD is a form of response surface methodology that predicts the response by a second-order equation (Equation 4.3) [4.55-4.65].

$$R = \alpha_0 + \sum_{i=1}^{k} \alpha_i X_i + \sum_{i=1}^{k} \alpha_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \alpha_{ij} X_i X_j \qquad \text{Equation 4.3}$$

R is the response (% nickel removal); X_i and X_j are variables; α_0 is a constant coefficient; α_i, α_{ii} and α_{ij} are linear, quadratic and interactive coefficients of X_1, X_2, X_3 and X_4 on response R; k is the number of variables. Since there are four variables, a total of 31 experimental runs are required [4.56-4.58]. Each experimental run has a replicate in order to test the consistency of experimental data. All the values were averaged for statistical analysis. Table 4.2 gives the levels and values of factors in CCD. "Minitab® Statistical Software 17" was used to develop the central composite design.

Table 4.2 Levels and values of factors in CCD

Factors	**Symbol**	**Units**	**-β***	**-1**	**0**	**1**	**β***
Extractant concentration	X_1	wt %	2	3.5	5	6.5	8
H_2SO_4 concentration	X_2	mol/L	0.1	0.6	1.1	1.6	2.1
$NiSO_4$ solution pH	X_3		2	3	4	5	6
$NiSO_4$ solution/emulsion volume ratio	X_4		2	3.5	5	6.5	8

*β=2

Figure 4.1 shows the nickel speciation in an aqueous solution as a function of pH, The $NiSO_4$ solution pH range was set to 2-6 because of the mainly acidic environment of mine drainage, plus the fact that pH higher than 6.5 results in nickel hydrolysis and formation of $Ni(OH)_2$. As can be seen from Figure 4.1, while pH range was between 2.5 to 6, nickel exists in two forms, one is Ni^{2+} (ionic form and accounts for 60% of total nickel), the other one is liquid $NiSO_4$ (liquid form and accounts for 40% of total nickel). When the pH is going down, more $NiSO_4$ will be transformed into Ni^{2+} form.

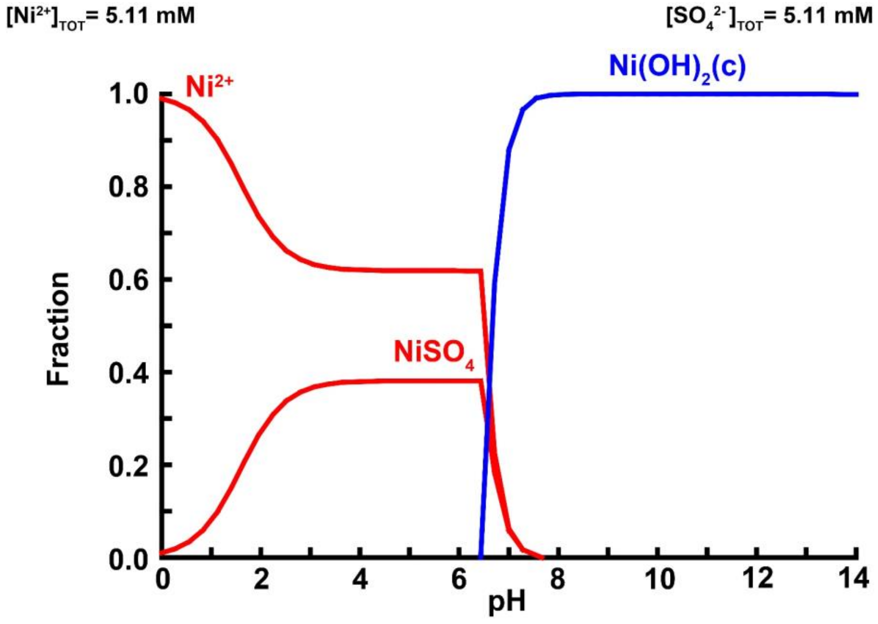


Figure 4.1 Nickel speciation as a function of pH, calculated at 25 °C using HYDRA and MEDUSA [4.66-4.67].

It should be noted that H_2SO_4 concentration was investigated in the range of 0.1 mol/L to 2.1 mol/L since preliminary tests showed that a H_2SO_4 concentration greater than 3 mol/L will significantly reduce the extraction efficiency. This can be explained through the leakage of H_2SO_4 droplets into the $NiSO_4$ solution lowering the solution pH, bringing a lower H^+ difference between the internal and external phase. Since this difference is a driving force for Ni^{2+} going towards the internal phase, the Ni^{2+} moving speed will thus be lowered. Also, the nickel extraction process is highly pH dependent, a higher acidity in the external phase will drive back the extraction equilibrium and slow down the nickel extraction speed thus impeding the extraction efficiency of Cyanex 301 (Figure 4.1). However, a higher H_2SO_4 concentration will speed up the stripping process since the difference between the feed and the internal phase acidity plays an important role in the nickel ion permeation process. Thus, a compromise must be made when determining the optimum concentration of H_2SO_4. Considering the nickel extraction process is an acid generating step, leakage of the internal droplets into $NiSO_4$ solution will further decrease the pH. It is a very difficult and an uneconomical task to maintain the $NiSO_4$ solution pH during the test. Thus, in this work $NiSO_4$ solution pH refers to the initial pH rather than the equilibrium pH, which is different from many other researchers' work [4.68-4.73].

4.3.4 Emulsion Zeta Potential Measurement

Zeta potential (ζ) is usually used to measure the electric potential of the double layers of colloidal dispersions. Since emulsion droplets are usually charged, surrounding by a cloud of ions, the voltage difference between droplet surface and the liquid beyond the charge cloud can be obtained through the zeta potential measurement. Generally, the magnitude of zeta potential indicates different levels of electrostatic repulsion between dispersed colloidal droplets [4.74]. The electrostatic repulsion force is important in keeping colloidal droplets from coalescing and aggregating. Thus, zeta potential measurements can be used as a tool to predict the stability of the colloidal system. The two most common methods for measuring zeta potential are electroacoustic and electrophoretic techniques, which use sound and light respectively. Since the electrophoretic method only works well for very diluted oil in water emulsions [4.75-4.81], for this investigation the electroacoustic technique was chosen. The measurements were carried out using a FieldESA (ParticleAnalytik, Germany) with an automatic titration unit. KCl solution (10^{-3} mol/L) was selected as the background electrolyte, 10 wt % emulsion phase (b) (Table 4.3) was added and suspended in the KCl solution by use of a mechanical stirrer. The initial pH of the mixture was always acidic (approximately 1.8) and the pH titration of the emulsion dispersion was up to 8.0 with an increase of 0.2 pH units, with a delay of 300s being set between each measurement to allow the suspension to reach equilibrium. The size of the emulsion liquid membrane droplets was measured using an optical microscope (Appendix A) and analyzed using the software "ImageJ", a median size of 19.8 μm was obtained.

4.3.5 Comparison Tests Between Organic Phase and Emulsion Phase

In order to compare the differences in chemical properties during the extraction process between traditional solvent extraction and ELM technique, a series of comparison tests were performed between the kerosene based organic phase (a) and emulsion phase (b) including: kinetics; loading capacity; and pH variation tests. The constituents of (a) and (b) are listed in Table 4.3.

Table 4.3 The constitutions of organic phase (a) and emulsion phase (b)

Terms	Constituents	Properties
(a)	Oil matrix	Kerosene
	Extractant	Cyanex 301 (7.2 wt %)
(b)	Oil matrix	Kerosene
	Extractant	Cyanex 301 (7.2 wt %)
	Surfactant	Span-80 (2.0 wt %)
	Internal stripping liquid	H_2SO_4 solution (0.5 mol/L)
	Oil/H_2SO_4 volume ratio	5
	Sonication time	1 min

It should be noticed that all the comparison tests were performed with single nickel ions using synthetic $NiSO_4$ solution, although there maybe competing ions (such as Cu, Fe, Ca, etc.) existing in real wastewater, generally they follow the Irving-William series during extraction process: Mn<Fe<Ca<Co<Ni<Cu. The details of how these competing ions perform during extraction process will be further explored and discussed in future projects.

The kinetics tests were performed by contacting (a) and (b) with $NiSO_4$ solution (initial nickel ion concentration: 300 ppm; $NiSO_4$ solution pH: 4.5; aqueous/organic volume ratio: 3.5) for 12 minutes. The Cyanex 301 loading capacity test was performed by contacting (a) and (b) with an equal volume of fresh aqueous $NiSO_4$ solution for 30 minutes (initial nickel ion concentration of 300 ppm and $NiSO_4$ solution pH of 4.5), with the test repeated until no more nickel could be extracted. A comparison of the pH variation curves was made between (a) and (b) after contacting with $NiSO_4$ solution at different initial pH (initial nickel ion concentration: 300 ppm; aqueous/organic volume ratio: 3.5), the mixture was stirred for 20 minutes and the aqueous pH was measured every minute. It should be noted that all the tests performed represent the comparison between traditional solvent extraction lab method and the ELM method.

Generally, as can be seen from the information above, the contribution of this work can be concluded into two aspects: (a) the statistical analysis of experimental results including process optimization, the discussion of main effects and interactive effects of process parameters can used as indications in practical applications; (b) the chemical property of emulsion liquid membrane was further explored and comparisons between these two techniques (ELM and conventional solvent extraction) were made quantitatively which expanded the current database and could be used as instructions allowing more comprehensive views of process selection and optimization for nickel extraction.

4.4 RESULTS AND DISCUSSIONS

4.4.1 Emulsion Zeta Potential

The zeta potential measurements were used to monitor and control emulsion stability. Figure 4.2 shows the zeta potential curve as a function of pH, where the solution was ELM droplets in KCl electrolyte during mechanical stirring. The lower and upper solid lines represent 99% confidence interval. The methods for construction of confidence and prediction intervals of zeta potential curves can be found in Marion *et al.* [4.80]. It can be seen that the ζ potential curve shows an isoelectric point (pH_{iep}) of approximately 2.1, where the pH_{iep} represents the point that ELM droplets have the lowest repulsion force between each other in the matrix. Any pH value higher than 2.1 gives a negative ζ potential value while any pH lower than 2.1 results in a positive value. As can be seen from Figure 4.2, from pH 2.1 to 8.0, the ζ potential value is decreasing and this reveals that the repulsive force between ELM droplets is increasing, thus enhances the ELM droplets stability, which means that it would require more energy input during the de-emulsification stage. Thus, the pH_{iep} is preferred in this study.

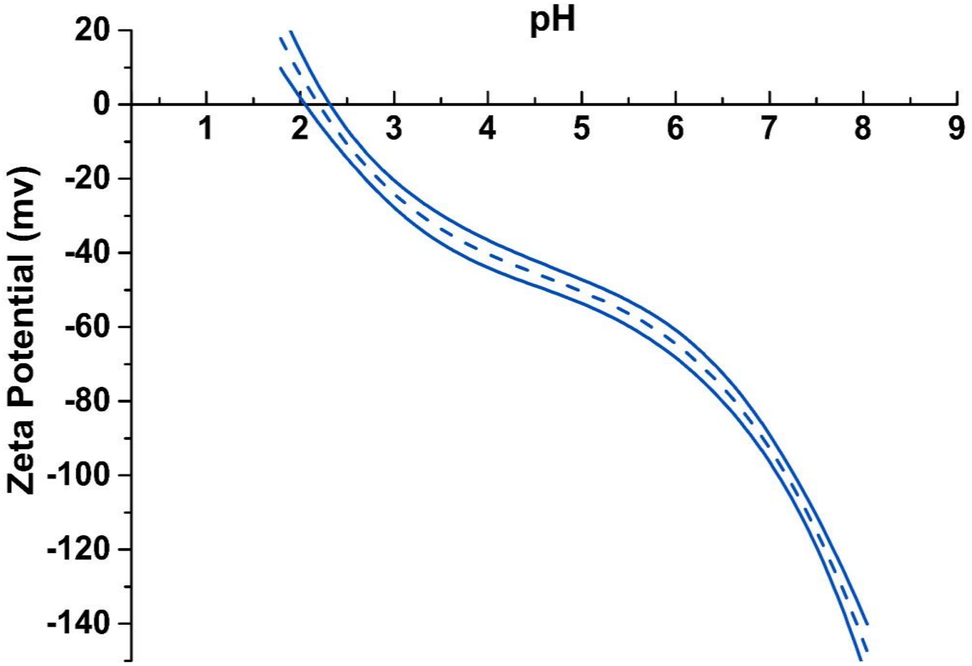


Figure 4.2 Zeta potential curve as a function of ELM pH (Error intervals shown are 99% confidence intervals)

4.4.2 Central Composite Design

The design matrix used in central composite design, along with the % nickel removal in each test is given in Table 4.4.

Table 4.4 Central composite design and the nickel removal

	Variables				**Ni removal**	**Ni removal**	
Run order	**X_1**	**X_2**	**X_3**	**X_4**	**test set 1**	**test set 2**	**Average**
1	3.5	1.6	5	3.5	54.93	54.90	54.91
2	6.5	0.6	3	3.5	98.16	99.29	98.73
3	6.5	1.6	5	6.5	74.86	72.88	73.87
4	5	1.1	4	5	71.53	78.43	74.98
5	5	1.1	4	8	52.82	47.03	49.92
6	3.5	0.6	3	6.5	54.50	45.24	49.87
7	3.5	0.6	5	6.5	54.06	54.09	54.08
8	3.5	0.6	3	3.5	92.03	94.36	93.20
9	3.5	1.6	3	6.5	56.65	44.95	50.80
10	5	1.1	4	5	82.01	82.53	82.27
11	5	0.1	4	5	98.53	94.73	96.63
12	3.5	1.6	3	3.5	60.41	61.97	61.19
13	5	1.1	4	5	70.71	73.60	72.15
14	6.5	1.6	5	3.5	73.22	74.41	73.82
15	5	1.1	4	2	95.67	95.76	95.71
16	5	1.1	4	5	77.93	75.02	76.47
17	5	1.1	4	5	68.49	79.40	73.94
18	5	1.1	4	5	72.09	74.99	73.54
19	6.5	0.6	5	3.5	99.03	99.61	99.32
20	6.5	1.6	3	3.5	75.50	70.36	72.93
21	5	1.1	4	5	72.57	59.32	65.95
22	6.5	1.6	3	6.5	74.23	70.62	72.42
23	5	1.1	6	5	55.15	60.33	57.74
24	6.5	0.6	3	6.5	65.42	64.71	65.07
25	3.5	0.6	5	3.5	73.30	71.85	72.57
26	3.5	1.6	5	6.5	46.07	50.00	48.04
27	2	1.1	4	5	60.07	51.85	55.96
28	5	2.1	4	5	41.83	46.56	44.20
29	5	1.1	2	5	44.35	36.90	40.63
30	6.5	0.6	5	6.5	82.51	82.23	82.37
31	8	1.1	4	5	87.64	90.73	89.19

The regression model including regression coefficient (Coef), t-value (t) and p-value (p) are listed in Table 4.5.

Table 4.5 Regression model for nickel removal

Term	Coef	T	p
Constant	74.19	28.5	0.000
X_1	9.18	6.53	0.000
X_2	-8.84	-6.29	0.000
X_3	1.21	0.86	0.403
X_4	-9.24	-6.57	0.000
X_1^2	0.26	0.2	0.845
X_2^2	-0.28	-0.22	0.828
X_3^2	-5.59	-4.34	0.001
X_4^2	0.32	0.25	0.809
X_1X_2	0.15	0.08	0.933
X_1X_3	2.85	1.66	0.117
X_1X_4	1.75	1.02	0.324
X_2X_3	-0.51	-0.3	0.770
X_2X_4	5.92	3.44	0.003
X_3X_4	2.85	1.66	0.117

It can be seen from Table 4.5 that out of the four main factors, extractant concentration, H_2SO_4 concentration and $NiSO_4$ solution/emulsion volume ratio are considered statistically important ($p<0.05$), while the $NiSO_4$ solution pH does not contribute a significant effect to the response. In addition, the sign of the t-values (Table 4.5) reveal that H_2SO_4 concentration and $NiSO_4$ solution/emulsion volume ratio play negative roles, while the extractant concentration plays positive roles in the response; $NiSO_4$ solution pH plays a slightly positive role in the response. This is in agreement with other work [4.4, 4.18, 4.21]. The reasons are as followed:

- For $NiSO_4$ solution pH, the change in the value was not extremely important to the system since a drastic pH decrease can be seen during the first several minutes of the extraction process; generally, it changes from an initial pH of 2-6 to an equilibrium pH of 1.7-2.0, and Cyanex 301 is a good extractant in this pH range. Although it has been previously noted that the extraction process may be pH sensitive [4.68-4.69], other work has shown that as long as the level of extractant is higher than a certain value, nickel removal will be independent of pH [4.51].

- For extractant concentration, in the extraction process a higher extractant concentration will increase the reaction rate, and improve the transportation rate of nickel-extractant complex into the membrane. However, a much higher concentration will impede the movement of the complex due to the increase in viscosity.
- For H_2SO_4 concentration, an increase will be detrimental to the extraction rate since the leakage of more acidic H_2SO_4 droplets into the $NiSO_4$ solution will significantly change the $NiSO_4$ solution pH, thus decreasing the difference in acidity between the inside and outside of the membrane, which will cause a reduction in driving force. In addition, despite its nature, Cyanex 301 will not perform well under an extremely acidic environment (when $NiSO_4$ solution pH <1.0) [4.37-4.38].
- For $NiSO_4$ solution/emulsion volume ratio, it can be noted that an increase in this ratio will be equivalent to a decrease in the relative extractant concentration, thus it will have a negative impact on the system. It can also be seen that there is a strong interaction between H_2SO_4 concentration and $NiSO_4$ solution/emulsion volume ratio, this can be explained that the higher the ratio is, the less influence it will have on the change of acidity that is due to the leakage of H_2SO_4 droplets into the $NiSO_4$ solution.

A second-order polynomial model is given in Equation 4.4 (in coded units).

$$R = 74.19 + 9.18X_1 - 8.84X_2 + 1.21X_3 - 9.24X_4 + 0.26X_1^2 - 0.28X_2^2 - 5.59X_3^2 + 0.32X_4^2 + 0.15X_1X_2 + 2.85X_1X_3 + 1.75X_1X_4 - 0.51X_2X_3 + 5.92X_2X_4 + 2.85X_3X_4 \qquad \text{Equation 4.4}$$

Where R is the percentage nickel removal, X_1, X_2, X_3 and X_4 represent extractant concentration, H_2SO_4 concentration, $NiSO_4$ solution pH and $NiSO_4$ solution/emulsion volume ratio accordingly. An analysis of variance (ANOVA) table was used to check the adequacy of the regression model, with details given in Table 4.6.

Table 4.6 ANOVA table

Source	**DF**	**f-value**	**p-value**	**R^2**	**SD**
Model	14	11.74	0.000	0.911	6.886
Lack of Fit	10	2.57	0.130		

DF: degree of freedom SD: standard deviation

It can be seen that this model has a high R^2 value (>0.90) and a low p-value (<0.05), the lack of fit has a p-value higher than 0.05, which means that it is an acceptable model from engineering point of view [4.58].

4.4.3 Model Optimization

Two-dimensional response surface plots were used to represent the empirical functional relationship between the response and factors, with the x and y axes represent two variables while keeping other factors constant at their center value (level 0 in Table 4.2). Since $NiSO_4$ solution pH is not an important factor in this process, only contour plots composing important factors (extractant concentration, H_2SO_4 concentration and $NiSO_4$ solution/emulsion volume ratio) are shown in Figure 4.3, where the color bars represent the % nickel removal.

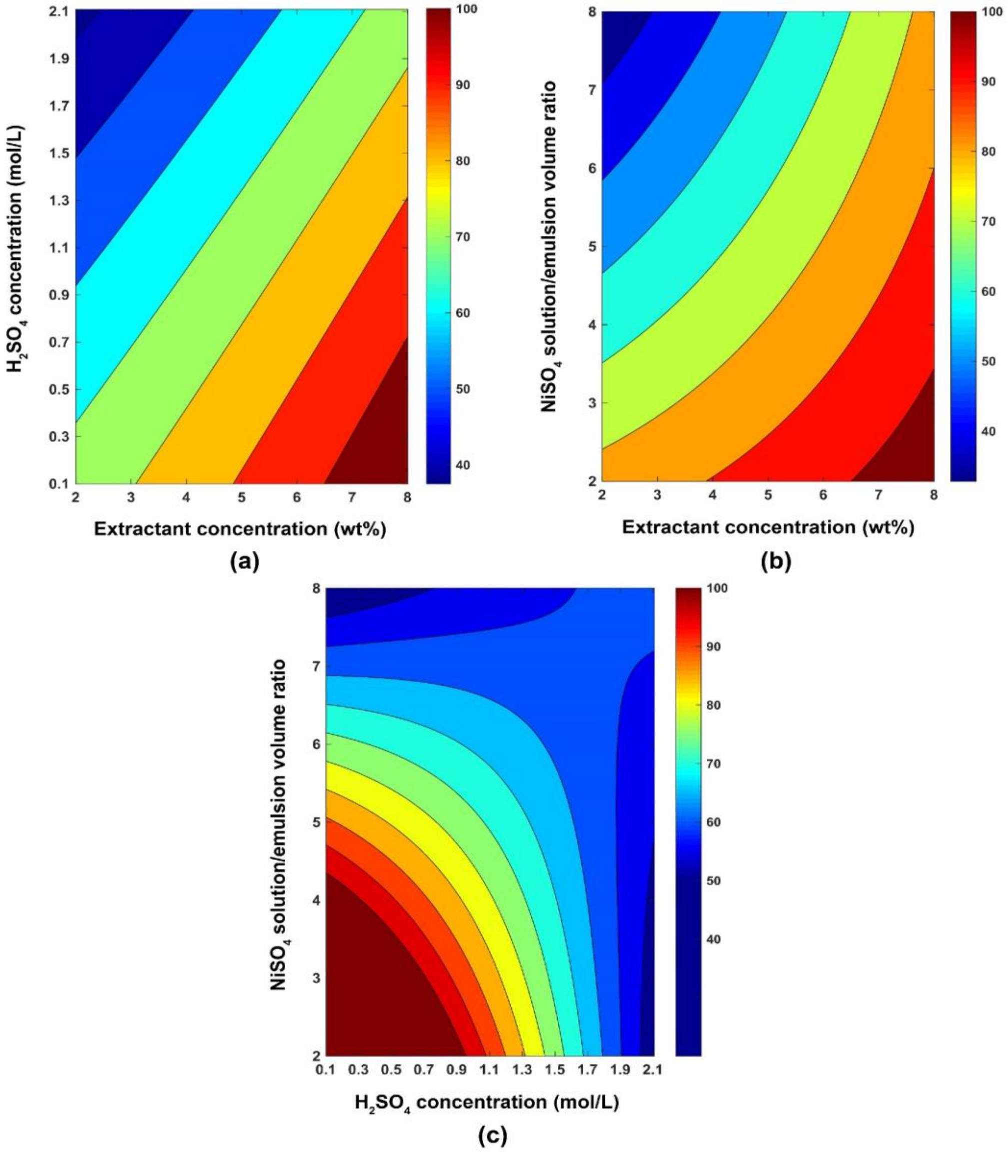


Figure 4.3 Surface contour plots showing the relationship between nickel removal and (a) Extractant concentration and H_2SO_4 concentration; (b) Extractant concentration and $NiSO_4$ solution/emulsion volume ratio; (c) H_2SO_4 concentration and $NiSO_4$ solution/emulsion volume ratio.

It can be seen that in order to achieve a high nickel removal, it is desirable to keep the extractant concentration at a higher level (6.5 -8 wt% (Figure 4.3 (a) and (b))); H_2SO_4 concentration at a lower level (0.1-0.7 mol/L (Figure 4.3 (a) and (c))) and $NiSO_4$ solution/emulsion volume ratio at a lower level (2-3.3 (Figure 4.3 (b) and (c))). Thus, an increase of H_2SO_4 concentration; $NiSO_4$ solution/emulsion volume ratio, and/or a decrease of extractant concentration may impede the nickel removal efficiency. These results confirmed the findings obtained from Table 4.5.

Overlaid surface plots (shown in Figure 4.4) were used to determine the optimum operating conditions [4.58]; these overlaid regions represent the overlaps of the operating conditions for high nickel removal (>99%).

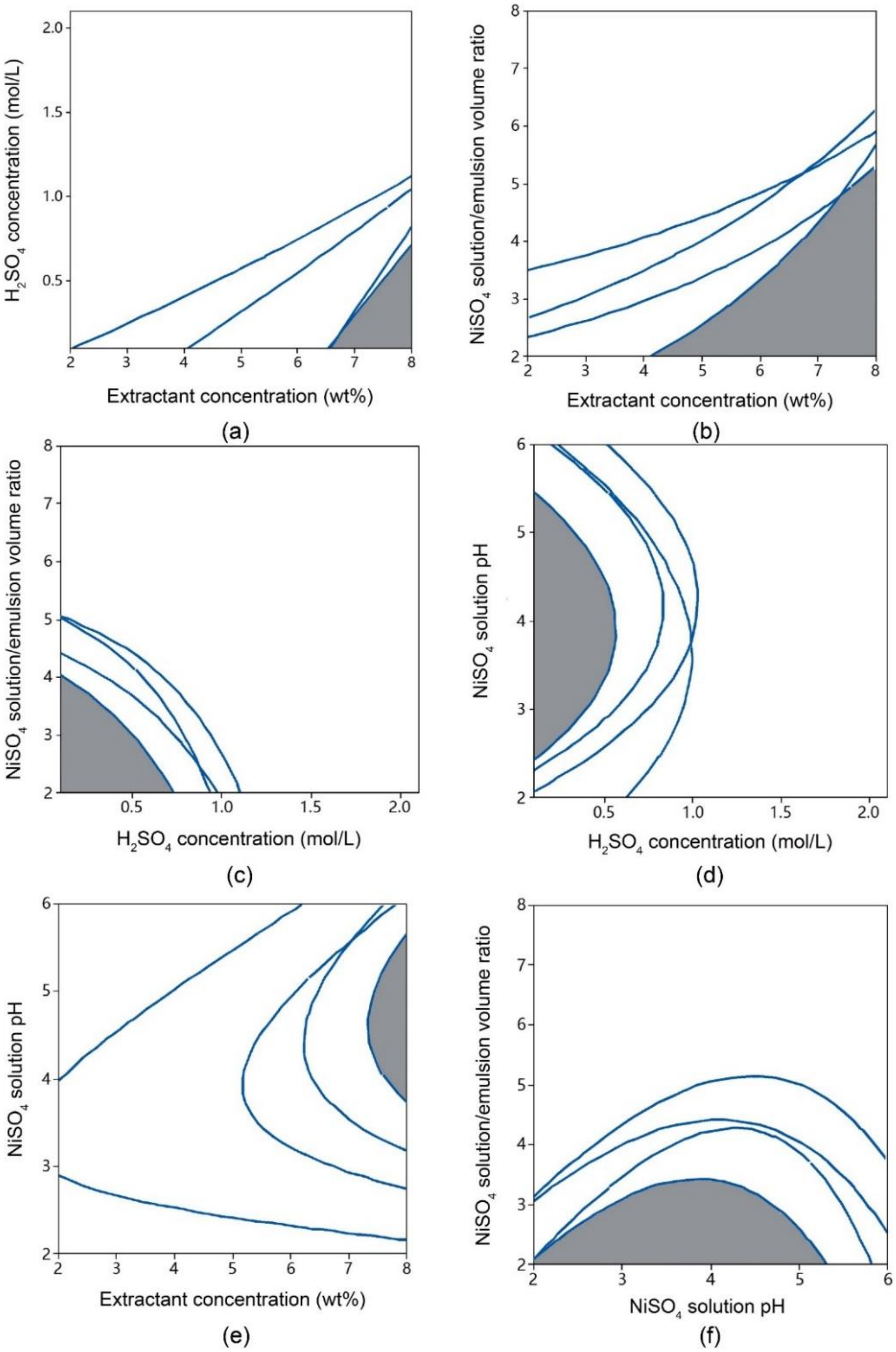


Figure 4.4 Overlaid contour plots showing the relationship between nickel removal and (a) Extractant concentration and H_2SO_4 concentration; (b) Extractant concentration and $NiSO_4$ solution/emulsion volume ratio; (c) H_2SO_4 concentration and $NiSO_4$ solution/emulsion volume ratio; (d) H_2SO_4 concentration and $NiSO_4$ solution pH; (e) Extractant concentration and $NiSO_4$ solution pH; (f) $NiSO_4$ solution pH and $NiSO_4$ solution/emulsion volume ratio.

From these plots, the optimum operating conditions have been determined to be: extractant concentration of 7.2 wt %; stripping solution concentration of 0.5 mol/L; $NiSO_4$ solution pH of 4.5; and $NiSO_4$ solution/emulsion volume ratio of 3.5.

Validation tests were performed to check the adequacy of the model by confirming the nickel extraction at optimum and random conditions, selected based on the calculations of stationary points using the desirability function. Each test was repeated three times, and the average values for nickel extraction are shown in Table 4.7 and Figure 4.5.

Table 4.7 Validation test results

Factors / Tests	Extractant concentration (wt %)	H_2SO_4 concentration (mol/L)	$NiSO_4$ solution pH	$NiSO_4$ solution/emulsion volume ratio	Result (% Nickel removal)
1	7.2	0.5	4.5	3.5	Fitted: 100* Avg. result:99.0 %Error:1.0
2	7.0	0.8	4.5	4.0	Fitted: 99.4 Avg. result:96.0 %Error:3.4
3	6.5	0.8	4.5	4.5	Fitted: 92.8 Avg. result:85.7 %Error:7.7
4	6.0	1.0	4.5	5.0	Fitted: 82.4 Avg. result:72.1 %Error:12.5

*Any value higher than 100% is considered to be 100%

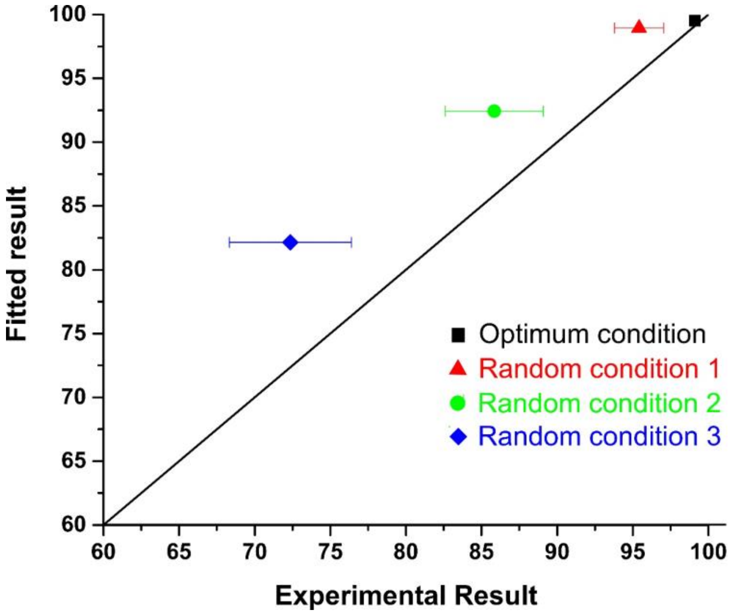


Figure 4.5 Validation graph comparing fitted (modeled) with experimental results, where the axes represent % nickel removal

It can be seen from Figure 4.5 that the experimental values fitted well with the calculated values at or near optimum conditions. It should be noted that since the model was targeting at obtaining an optimum condition, bias may appear when data points were away from optimum condition.

4.4.4 Comparison Tests Between Organic phase and Emulsion phase

4.4.4.1 Kinetics Tests

Nickel transport kinetics was studied for the first 12 minutes of the nickel extraction operation for both organic phase (a) and emulsion phase (b). In Figure 4.6, $[Ni^{2+}]_t$ represents the nickel concentration over time while $[Ni^{2+}]_{ini}$ represents the initial nickel concentration. Here, diffusion transport was considered to be the rate-controlling step in the overall transport [4.24, 4.30, 4.31, 4.51, 4.81]. The detailed model and calculations are given in Appendix B. Initially a linear regression model (Figure 4.6) based on Equation B.8 in Appendix B supported the assumption of diffusion-controlled mass transfer model. It showed that an linear relationship exists between the natural logarithm of nickel concentration and time, which means the reaction proceeds at a rate that depends linearly on time. Thus, it is a first-order kinetics reaction.

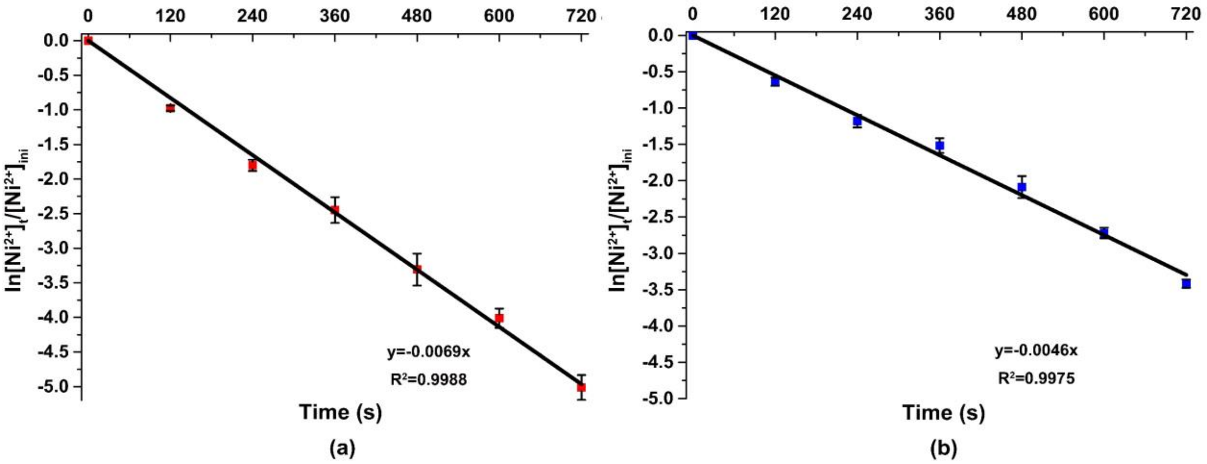


Figure 4.6 Kinetics plot for nickel ion transport: Linear regression model for the organic phase (a) and the emulsion phase (b).

Based on these results, in order to obtain least square error minimization and more accuracy in parameters estimation, an integrated form of non-linear regression model (Figure 4.7) was employed based on Equation B.9 in Appendix B [4.82-4.84]. The mass transfer coefficients for the organic phase and the emulsion phase was calculated to be 3.192 × 10^{-7} ($m \cdot s^{-1}$) and 2.823 × 10^{-7} ($m \cdot s^{-1}$). The difference in mass transfer coefficients between the organic phase and the emulsion phase can be explained that the internal sulfuric acid contained in the emulsion phase was leaked into $NiSO_4$ solution during stirring. This will increase the H^+ concentration in the feed solution, which will push the pH dependent extraction equilibrium into the reverse direction and the nickel extraction rate will be slowing down, resulting a lower mass transfer coefficient.

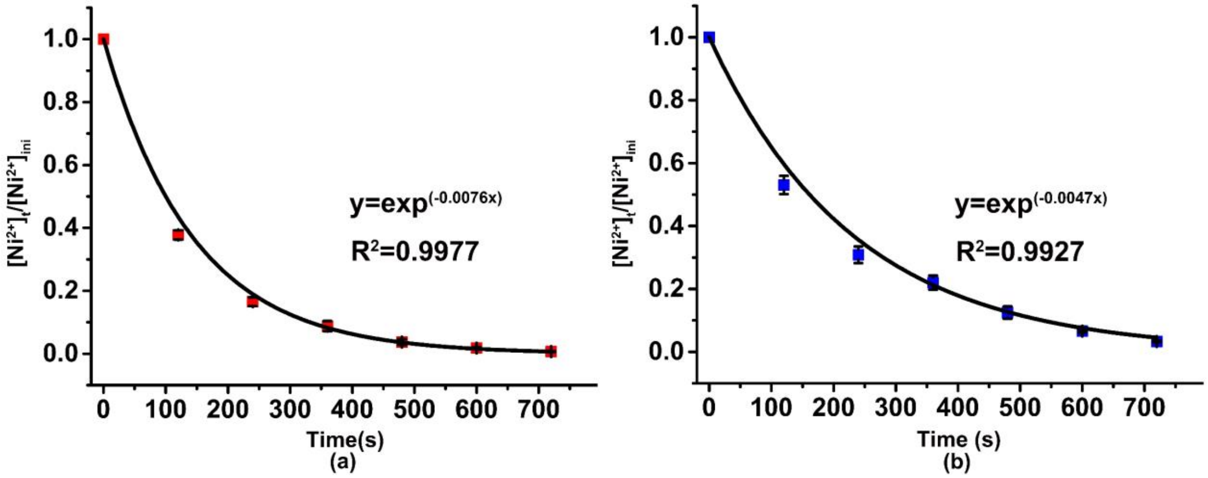
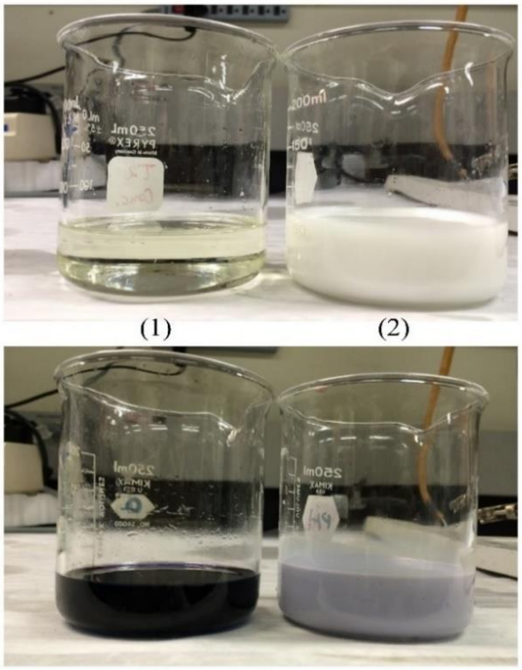


Figure 4.7 Kinetics plot for nickel ion transport: Non-linear regression model for the organic phase (a) and the emulsion phase (b) for better mass transfer coefficient estimation.

4.4.4.2 Loading Capacity Tests

Loading capacity tests of the organic (a) and the emulsion (b) phases were performed in order to compare the efficiency of Cyanex 301 in traditional solvent extraction method with the current ELM method, visually displayed in Figure 4.8 (It can be seen that for the organic phase, its color turns to purple-black while for the emulsion phase, its color turns to light purple; the difference attributed to the opaque ELM droplets).



(1) (2)

(3) (4)

Figure 4.8 The organic phase and emulsion phase before (1, 2) and after (3, 4) the nickel loading capacity test.

Figure 4.9 shows the result of loading capacity tests for the two different phases.

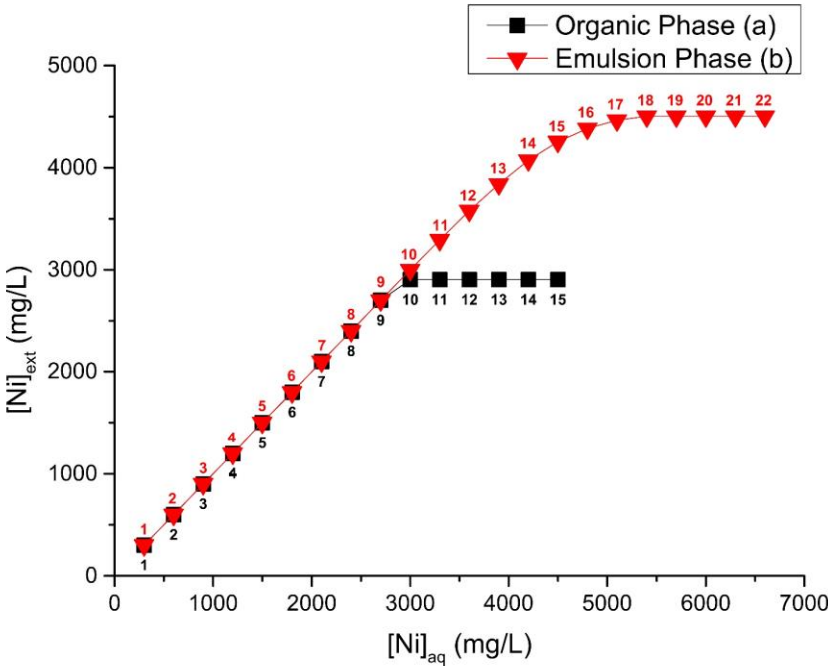


Figure 4.9 Loading capacity of the organic phase (a) and the emulsion phase (b).

In Figure 4.9, $[Ni]_{ext}$ represents the nickel concentration extracted by the organic phase or the emulsion phase and $[Ni]_{aq}$ represents the nickel concentration in aqueous phase. It can be seen that the emulsion phase has a higher loading capacity than the organic phase for the same volume of Cyanex 301. The loading capacity for organic phase was found to be 5.240 g Ni (II)/100g Cyanex 301, whereas for emulsion phase was 8.128 g Ni (II)/100 g Cyanex 301. The difference was attributed to the stripping process occurring inside the ELM droplets, in which Cyanex 301 could be regenerated and reused for nickel extraction.

4.4.4.3 pH Variation Tests

Three tests for both organic and emulsion phase were performed and an average value was used to plot the pH variation curves. Figure 4.10 shows that the $NiSO_4$ solution pH decreased after mixing with the organic phase (a) and the emulsion phase (b) until it reached equilibrium. Most of the decrease occurred within the first few minutes for both (a) and (b), which also meant that this is a fairly fast chemical reaction with the majority of the reactions occurring within the first few minutes. It is also noticeable that (b) always resulted in a lower pH than (a), this may be possibly explained by the following two reasons: firstly, the ELM method produces more acid than solvent extraction after it regenerates Cyanex 301; secondly, the internal H_2SO_4 droplets from the ELMs are leaked into the feed phase during stirring. It can be seen that for $NiSO_4$ solution with an initial pH of 4.0 and 6.0, the final pH will be approximately 2.0 after it was treated by the emulsion phase. This value is very close to the pH_{iep} obtained from zeta potential measurement (Figure 4.2). As pH_{iep} is the pH at which the emulsion droplet carries no net electric charge. Since the emulsion was reported to have an isoelectric point of about 2.1, at pH around 2.1, the emulsion droplet has the lowest net electrical charge and the droplets between each other will be more likely to have rapid coagulation or flocculation, which means the emulsion droplets have the lowest stability. This support that the selection of optimum pH being 4.5 (in the range of 4.0-6.0) will probably minimize the energy associated with emulsion breaking process afterwards.

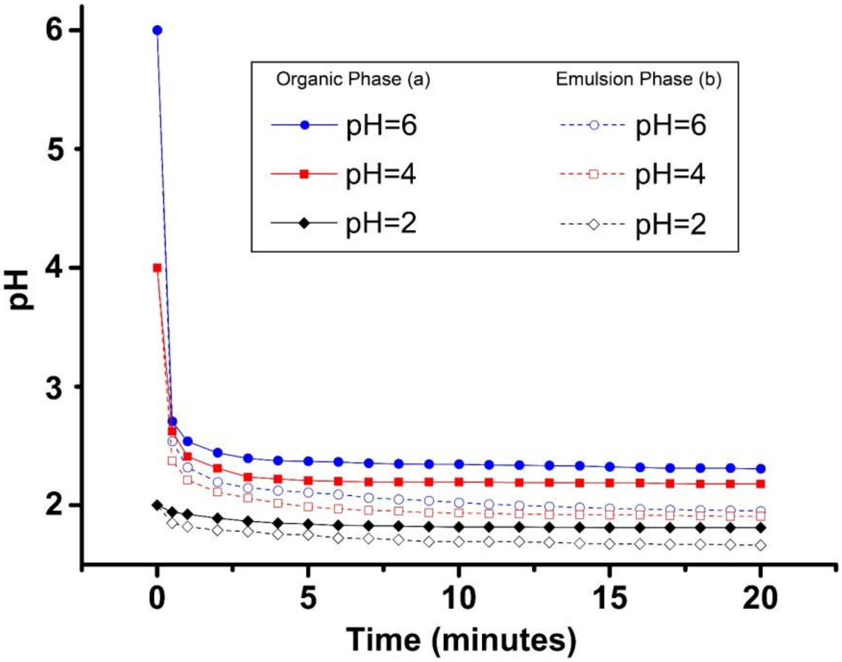


Figure 4.10 pH variation curve after mixing $NiSO_4$ solution at different initial pH of 2, 4 and 6 with the organic phase (a) and the emulsion phase (b); initial nickel ion concentration of 300 ppm.

4.4.5 Emulsion Breakage and Re-use/Regeneration

Emulsion breakage is a complex problem in many processes, with there being a number of techniques available, including: physical (thermal or centrifuge force), chemical (de-emulsifiers) and electrostatic (high-voltage splitter) methods [4.18, 4.21, 4.25, 4.26, 4.29, 4.30]. All these techniques have disadvantages, for example, the heat brought by the thermal treatment may harm the surfactant or extractant activity; the addition of extra chemicals as de-emulsifier may change the characteristics of the system; an excessive energy and a very high voltage supply was always demanded by electrostatic fields [4.11, 4.16, 4.19, 4.25, 4.29]. Thus, careful consideration should be taken prior to using one or a combination of these techniques, depending on the requirement of the process. In the case of extracting metal ions from aqueous systems using emulsion liquid membranes generated with Cyanex 301 as the extractant, Hachemaoui and Belhamel recently published work on the simultaneous extraction of nickel and cobalt [4.73]. However, the regeneration of the ELMs was not investigated.

In this work, the loaded emulsion was broken into oil phase and stripping liquor phase using a laboratory centrifuge (Model: CENTRAL CL2, Thermo) operating at 4000 rpm for 10 minutes. Iso-propanol (1 ml) was added to the system to act as a de-emulsifier. After centrifuging, the extraction experiments were performed under the optimum operating conditions (extractant concentration of 7.2 wt %; stripping solution concentration of 0.5 mol/L; $NiSO_4$ solution pH of 4.5; and $NiSO_4$ solution/emulsion volume ratio of 3.5). This process was repeated twice, i.e. three extraction experiments with one using virgin ELMs and two with regenerated ELMs.

The results of the regeneration extraction tests are shown in Table 4.8, where it can be observed that there is a decrease in nickel extraction with each regeneration stage (99.0 %; 97.2 %; 89.1 %).

Table 4.8 Nickel extraction with ELM regeneration

Extraction run	Nickel extraction [%]	SD
Virgin ELMs	99.0	0.058
Regeneration 1	97.2	1.069
Regeneration 2	89.1	3.620

The decrease in nickel removal from 99.0 % to 97.2 % (first regeneration) most likely arises from two aspects: one is the loss of extractant in the $NiSO_4$ solution during the extraction process; the other one is the adverse effect that may degrade the extractant brought by the addition of de-emulsifier. A comparison test was performed under optimum conditions with 1 ml iso-propanol added before the emulsification process and an average nickel removal of 97.2 % was obtained. This difference was confirmed to be significant by conducting Student's t-test, which supports the hypothesis that the introduction of this chemical de-emulsifier to the system had a slightly negative effect on the nickel extraction. The results proved that the emulsion could be effectively broken and a relatively high nickel removal could be maintained during the re-use of the oil phase. A schematic flow chart of this process is shown in Figure 4.11.

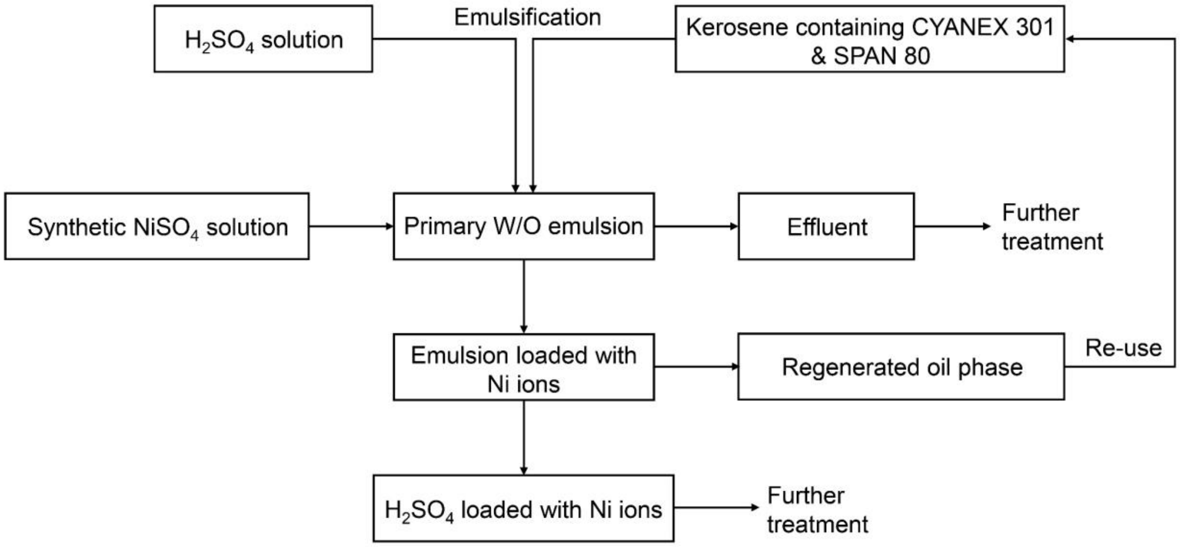


Figure 4.11 Schematic process flow chart of nickel removal by the ELM technique

4.6 CONCLUSIONS

The results indicated that nickel removal was influenced by three factors: extractant concentration; stripping agent concentration; and $NiSO_4$ solution/emulsion volume ratio. The $NiSO_4$ solution pH was not statistically significant in this study, however, analysis of the pH variation and zeta potential tests revealed that in order to reduce the energy associated with breaking the emulsion droplets, a feed phase pH between 4 and 6 was preferable. Thus, the optimum laboratory conditions were: extractant concentration of 7.2 wt %; stripping solution (H_2SO_4) concentration of 0.5 mol/L; $NiSO_4$ solution pH of 4.5; and $NiSO_4$ solution/emulsion volume ratio of 3.5. Under these conditions, nickel ion extraction greater than 99% could be achieved. Emulsion was successfully broken afterwards and the oil phase could be recycled for further usage. Nickel loading capacity tests showed that the emulsion phase has a higher nickel extraction capacity (8.128 g Ni (II)/100 g Cyanex 301) than the organic phase itself (5.240 g Ni (II)/100 g Cyanex 301). The kinetics tests showed that nickel ion concentration in the aqueous feed phase decreased by first order kinetics and a mass transfer coefficient of 3.192×10^{-7} (m/s) and 2.823×10^{-7} (m/s) was obtained for the organic phase and the emulsion phase, respectively. All the results indicate that ELM can be more efficient when compared with conventional solvent extraction method.

It was also shown that the ELMs could be regenerated, with a slight decrease in extraction efficiency. The method of ELM destabilisation and regeneration must be investigated further to ensure that this is a sustainable process.

Further investigations into scale-up and developing a continuous process should be undertaken to make an accurate comparison with traditional solvent extraction. It should also be noticed that the effects of competing ions from real mining tailing water during extraction process should be explored in future projects.

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LINKING PARAGRAPH BETWEEN CHAPTER 4 AND CHAPTER 5

Chapter 4 explores the nickel extraction from $NiSO_4$ solution using ELM technique. Based on the finding from Chapter 3, five factors have been considered as statistically unimportant and are kept at constant values, and the other four factors have been optimized using central composite design. The physical & chemical properties have also been explored by various tests. A comparison between ELM and traditional solvent extraction (SX) have been made. All these results and findings help us understand the extraction behavior of nickel and the characteristics of ELM. Chapter 3 as well as Chapter 4 build the basis for Chapter 5, which is our target of the thesis: to effectively extract and separate copper, nickel from calcium ions using ELM.

CHAPTER 5. SELECTIVE SEPARATION OF COPPER AND NICKEL IONS FROM AQUEOUS SOLUTIONS CONTAINING CALCIUM BY EMULSION LIQUID MEMBRANES USING CENTRAL COMPOSITE DESIGN

5.1 ABSTRACT

The emulsion liquid membranes technique was utilized to selectively extract copper and nickel from a synthetic aqueous solution containing calcium, which was used to mimic a tailing stream found in the Sudbury region of Canada. The results showed copper and nickel ions were successively extracted from the synthetic solution. Two central composite design and analysis of experiments were used to optimize the process and determine the main effects and interactions of experimental factors. In the first stage, copper was extracted with minimum removal of nickel and calcium. It was found that under optimum conditions, 98% of the copper was extracted, with only 0.9% nickel and 1.3% of the calcium being extracted. The subsequent copper stripping efficiency was 95.7%. In the second stage, the remaining aqueous solution was treated to remove nickel with a minimum calcium removal. During this stage, the corresponding nickel and calcium removal percentages were 99.0% and 0.55%, respectively, with nickel stripping efficiency of 84.1%. Laboratory bench-scale tests using a two-stage mixer-settler showed a good correlation with these results when moving to a semi-continuous process, which extracted 99.7% of the copper and 98.2% of the nickel, with only 2.2% calcium extraction.

5.2 INTRODUCTION

Mining waste stream can have the dual challenge of being acidic (due to oxidation of sulphide minerals) [5.1-5.3] and containing metal ions such as copper, nickel, iron, lead, zinc, cadmium, mercury, chromium and many others [5.4-5.7]. One example of mining tailing wastewater from the Sudbury region of Ontario (Canada) contains 10 ppm copper, 20 ppm nickel and an average calcium concentration of 250 ppm at a pH of approximately 4.0 [5.8]. Unlike organic waste, these metal ions are never biodegradable and they will not easily precipitate into a carbonate form due to the acidic matrix [5.9-5.12]. The accumulation of copper and nickel ions in the food chain may cause damage to the central nervous system of animals such as humans. Thus, the removal or the minimization of these metal ions is critical [5.13-5.16]. The emission standard in Ontario, Canada in 2017 regarding the discharge limit of copper, nickel and calcium ion concentration in mining tailings is listed in Table 5.1.

Table 5.1 Monthly average concentration limit for Cu, Ni and Ca in process effluent for all existing and new plants set by the Ontario government [5.17]

Element	**Concentration (mg/L)**
Copper	0.3
Nickel	0.5
Calcium	No limit

Various techniques to remove these metal ions have been investigated or implemented [5.18-5.22]. Currently, the primary method of removing heavy metals ions from mining effluents is by liming of the effluent and hydroxide precipitation through the addition of lime and an appropriate hydroxide, respectively. Although this method has advantages of low cost and ease of pH control, there are also limitations such as handling problems as well as large volumes of low-density sludge. Solvent extraction, one of the most widely used techniques in removing heavy metal ions from mining waste water, has advantages such as high efficiency and ease of operation when treating wastewater containing high metal concentrations (>500 mg/L) [5.23-5.27]. However, in this particular case, the low concentration of copper and nickel in the samples makes solvent extraction uneconomical and inefficient since it requires a long extraction time and a high solvent/aqueous ratio [5.27]. Thus, a method with higher efficiency and lower cost must be utilized.

One potential method of solving this problem is to use the emulsion liquid membranes (ELM) technique, proposed by Li *et al.* (1967) [5.28]. ELM in this work refers to a water-in-oil-in-water emulsion, and the term membrane refers to the bulk oil phase which separates the external and internal water phases [5.28-5.32]. ELM can combine solvent extraction and stripping in one step.

The transfer of metal ion from aqueous phase to organic phase is driven by the difference in chemical potential, under most circumstances, after the liquid-liquid extraction ends, the overall system is in a more stable configuration with a lower free energy [5.26]. Advantages of ELM include that the highly dispersed emulsion droplets containing metal extractant not only increase the overall contacting surface area with metal ions, but also provide a higher extracting capacity. The increased capacity occurs because the stripping process inside the droplets is able to regenerate the metal extractant [5.32-5.35]. Liquid membranes offer an inner interfacial area of approximately l0^6 m^2/m^3, therefore the kinetics of the stripping reaction are faster than in conventional solvent extraction [5.29]. A detailed comparison between ELM and traditional solvent extraction (SX) can be referred to Appendix C.

The ELM technique may also be used to selectively separate heavy metal ions, according to previous research [5.36-5.39]. For example, researchers have worked on the extraction and separation of nickel, copper and other metals from ammonium carbonate/ammonium sulfate solutions using ELM [5.40-5.42]. Calcium, nickel and copper belong to the first transition series, which means that they follow the Irving-William rule, such is that the relative stability of complexes formed by these transitions metals will be Ca<Ni<Cu [5.43-5.44]. Thus, in order to achieve the lowest Gibbs energy in the system, copper can be firstly extracted from the trinary system, and can be extracted at lower pH than the other two [5.45]. However, literature showed that these metal ions may be co-extracted or partially co-extracted by organic extractant at the same time, bringing difficulties for metal separation in the next stage. Thus, it is critical to design a process that can selectively extract copper, nickel from calcium ion [5.46-5.51]. Thus, in this paper, a two-stage operation was employed in order to selectively remove and separate copper and nickel ions from calcium ions. The first stage was designed to remove copper ions and the second stage to remove nickel ions. In both stages, a requirement of minimum extraction rate of calcium ions was set to avoid the possible precipitation of gypsum during the later stripping process.

5.3 MATERIALS AND METHODS

5.3.1 REAGENTS

Kerosene (reagent grade) purchased from Sigma-Aldrich (USA) was used as the organic solvent. The LIX 984N and Cyanex 301 samples were provided by BASF (Canada) and Cytec (Canada), respectively, and were used as the metal extractants without any further purification. LIX 984N is a 1:1 volume blend of 5-nonylsalicylaldoxime (LIX 860N) and 2-hydroxy-5-nonylacetophenone oxime (LIX84) in a high flash point hydrocarbon diluent, and Cyanex 301 is bis(2,4,4-trimethylpentyl) dithiophosphinic acid. The reaction mechanisms between these extractants and copper & nickel ions can be referred to Appendix D. Sorbitan monooleate (Span-80, Sigma-Aldrich, USA) with a hydrophilic-lipophilic balance (HLB) value of 4.3 was used as the lipophilic non-ionic surfactant for both stages since it can stabilize water in oil emulsion. Sulfuric acid (H_2SO_4, Fisher Scientific, USA) was selected to be the internal stripping liquor for both stages, diluted from an initial concentration of 18.0 mol/L. Anhydrous cupric sulfate ($CuSO_4$, Fisher Scientific, USA), nickel (II) sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$, Anachemia, Canada) and calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$, Sigma-Aldrich, USA) were used to prepare synthetic solutions containing copper, nickel and calcium ions at concentrations of 10 ppm (1.57×10^{-4} mol/L), 20 ppm (3.41×10^{-4} mol/L) and 250 ppm (6.24×10^{-3} mol/L) respectively. Isopropanol (Sigma-Aldrich, USA) was used as the chemical de-emulsifier in the emulsion break up process. All the aqueous phases were prepared or diluted using reverse osmosis water (pH of 5.8 at 25°C, conductivity of 10.5 μS/cm). The solution pH was adjusted to 4.0 using 0.1 mol/L H_2SO_4.

5.3.2 Emulsion Preparation and Metal Extraction

The surfactant (SPAN 80) and metal extractant was pre-dispersed in kerosene, and then the oil phase (10 ml) and the water phase (2 ml of H_2SO_4 solution) were mixed at a volume ratio of 5:1 in a beaker. A 24 kHz ultra-sonication processor (Hielscher, Germany, UP400S) was used at its lowest level (80 W) to form the water in oil emulsion. Depending on the sonication frequency and time (energy input), the sizes of W/O emulsion droplets varied from 1 μm to 200 μm can be observed under optical microscope with a spherical shape. The formed primary water-in-oil emulsion was then injected into the metal ion solution, and stirred using a Caframo Ultra Speed BDC 6015 stirrer. During this process, water-in-oil-in-water emulsion (emulsion liquid membranes) formed and could be seen under optical microscope by coloring the oil phase or by environmental scanning electron microscope [5.32], and the metal ions were extracted in the membrane phase and further stripped in the internal acid droplets phase. Once complete, samples were taken from the feed aqueous phase using a 10ml syringe (approximately 3 cm below the surface). The metal ion concentration was measured using atomic absorption spectroscopy (AAS) (Perkin Elmer Atomic Absorption Spectrometer 311). The metal extraction efficiency (E %) was calculated using Equation 5.1:

$$E\ \% = ([M^{2+}]_{ini} - [M^{2+}]_{fin}) / [M^{2+}]_{ini} \times 100\ \% \qquad \text{Equation 5.1}$$

Where $[M^{2+}]$ represents the metal (Ni/Cu/Ca) ion concentration and the subscripts “ini” and “fin” stand for the initial and final metal ion concentration in the aqueous solution, respectively.

5.3.3 Emulsion Breaking, Stripping Efficiency and Separation Factor

The metal extraction and stripping occurs at the same time inside the ELM droplets; therefore, the emulsion needs to be subsequently broken to release the loaded stripping liquor for further treatment. In this work, the loaded emulsion was broken into the oil phase and stripping liquor phase using a centrifuge (Model: CENTRAL CL2, Thermo), operated at 4000 rpm for 20 minutes, with the addition of 1 ml of iso-propanol as de-emulsifier. Iso-propanol (IPA) has a structure with an isopropyl group linked to a hydroxyl group, it is miscible in both water and oil since it has a polar part and a nonpolar part with no charge. When isopropanol is added, it will act by total or partial displacement of the indigenous stabilizing interfacial film agents back into the bulk oil phase. This displacement also brings a decrease in interfacial viscosity or elasticity of the protecting film, thus enhancing emulsion destabilization [5.52-5.53]. The emulsion was separated into two layers with the bottom one being H_2SO_4 solution and the top one being the organic phase. The metal ion concentration in loaded H_2SO_4 solution was then measured by AAS, and the stripping efficiency (S %) was calculated using Equation 5.2:

$$S\ \% = ([M^{2+}]_{int} * V_{int}) / ([M^{2+}]_{ini} * V_{ini} * E\ \%) \times 100\ \% \qquad \text{Equation 5.2}$$

where M^{2+} represents the metal (Ni/Cu/Ca) ion concentration while the subscripts "int", "ini" and E stand for the internal stripping liquid solution, initial aqueous solution and extraction efficiency respectively. The average copper, nickel and calcium concentration in the loaded stripping liquor will be measured, and the separation factor of β_{Cu}/β_{Ni} and β_{Cu}/β_{Ca} can be calculated using Equation 5.3:

$$\beta_{Cu/M} = \frac{(C_{Cu}/C_M)_{strip}}{(C_{Cu}/C_M)_{feed,0}} \qquad \text{Equation 5.3}$$

Where M can be Ni or Ca.

5.3.4 Central Composite Design (CCD)

For both two stages, the operating parameters (factors) involved in the process are: extractant concentration, surfactant concentration, H_2SO_4 concentration, Oil/H_2SO_4 volume ratio, sonication time for W/O emulsion, synthetic solution/emulsion volume ratio, W/O/W emulsion stirring time and W/O/W emulsion stirring speed. Based on previous research, only four parameters were considered to be important and the others were considered to be non-significant and were kept constant during the test for both stages [5.32, 5.54]. Table 5.2 list the values of the constant variables.

Table 5.2 Values for non-significant factors

Factors	Value
Surfactant concentration (wt %)	2
Sonication time for primary emulsion (min)	1
Oil/H_2SO_4 volume ratio	5
W/O/W emulsion stirring speed (rpm)	425

The values of the non-significant parameters were chosen based on the following considerations: based on our previous research [5.32], it was not ideal to set the surfactant concentration lower than 2% in order to maintain the stability of primary water in oil emulsion; an ultrasonic time of one minute could maintain the minimum energy required for emulsification while lowering the total energy cost; For oil/H_2SO_4 volume ratio, visual observation showed that any value lower than 5 may impede the holding capacity of H_2SO_4 in the oil phase. It should be noted that although W/O/W emulsion stirring speed and W/O/W emulsion stirring time together represents the total energy input to the extraction process, based on our previous research [5.32], a W/O/W emulsion stirring speed of 425 rpm is considered to be ideal, where it is fast enough to enable all the extractant molecules remove the copper/nickel ions from the aqueous phase, but not so fast as to break the liquid membranes globules.

Thus, the remaining four parameters including extractant concentration, H_2SO_4 concentration, W/O/W emulsion stirring time and synthetic solution/emulsion volume ratio were selected as being important parameters. It should be noticed that for H_2SO_4 concentration, although it was not reported by many researchers to have any significant impact on the extraction efficiency [5.52]; However, in our previous research work [5.32], it was found to chemically interfere or interact with other factors such as extraction concentration and $CuSO_4$ solution/emulsion volume ratio, these chemical interactions could bring significant affects to the response [5.32]. Thus, in this paper, H_2SO_4 concentration is considered as an important parameter.

For both the first and second stage, a response surface method (RSM) with central composite design (CCD) on these four significant factors was used to optimize the process. A second order equation model was used to predict the response of the central composite design for both stages (Equation 5.4) [5.55-5.59]:

$$E = \alpha_0 + \sum_{i=1}^{k} \alpha_i X_i + \sum_{i=1}^{k} \alpha_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \alpha_{ij} X_i X_j \qquad \text{Equation 5.4}$$

E is the response (% metal extraction); X_i and X_j are experiment variables (factors); α_0 is a constant coefficient; α_i, α_{ii} and α_{ij} represent linear, quadratic and interactive coefficients of the variables X_i and X_j on response E; k is the number of variables (k=4 for both the first and second stage). The experimental design as well as all statistical analysis was performed using "Minitab® Statistical Software 17" while surface contour plots were drawn using "MATLAB R2015b academic use".

To make a conclusion of the contribution of this work to the original knowledge, it does not only solve the problem of adequately extract and separate copper, nickel from calcium ions using ELM technique, but also provides sufficient support for the process to go towards into plant scale-up and a continuous process development through the investigations of successful operation of semi-batch bench-scale mixer-settler.

5.3.5 Semi-batch Process

To investigate the potential for using this technique as a continuous process, a two-stage small-scale mixer-settler was developed and built out of poly (methyl methacrylate) glass. The schematic view for two-stage mix-settler treating solution is shown in Figure 5.1.

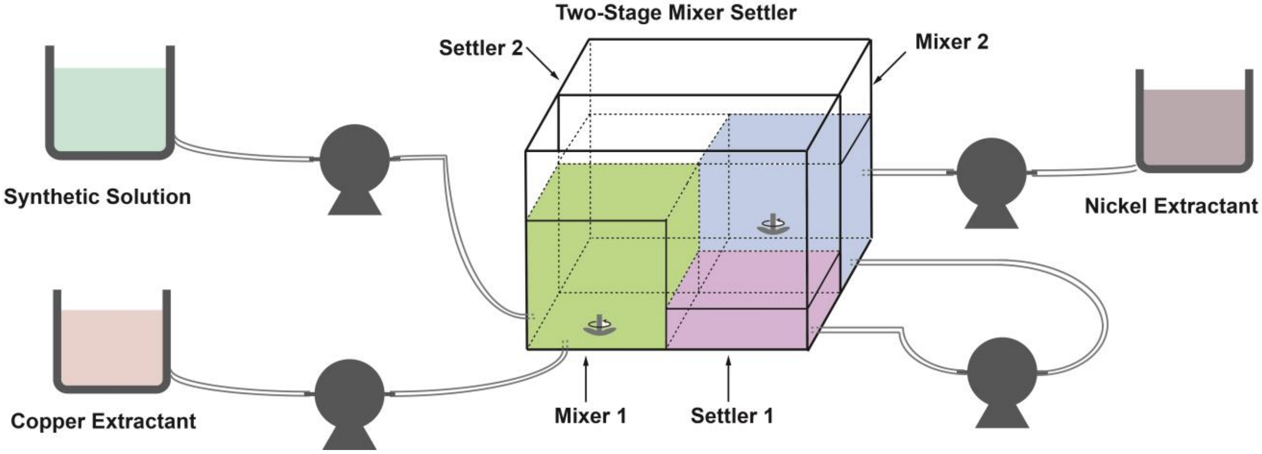

Figure 5.1 A schematic view for two-stage mix-settler treating solution containing copper, nickel and calcium

This allowed the initial extraction of copper to take place, with the aqueous stream containing the nickel to proceed to the next stage and finally a tailings stream with minimum copper and nickel to be removed. The optimum processing conditions as determined for the two extraction processes were used as a basis for this stage.

5.4 RESULTS AND DISCUSSION

5.4.1 Stage A

In this stage, the target was a high copper removal (>95%) with minimal nickel and calcium removal in order to selectively extract copper from the synthetic solution. Every copper ion is extracted by two LIX 984N molecules through a chelation reaction: $Cu^{2+} + 2HX \leftrightarrow CuX_2 + 2H^+$ [5.30]. Where HX represents LIX 984N. It can be seen the release of H^+ during the reaction will inevitably lower the solution pH. The levels and values of these four important parameters during the process are listed in Table 5.3.

Table 5.3 Levels and values of factors in stage A

Factors	**Short**	**Symbol**	**Units**	**-β***	**-1**	**0**	**1**	**β***
Extractant concentration	EC	X_1	wt %	0.4	0.6	0.8	1.0	1.2
H_2SO_4 concentration	AC	X_2	mol/L	0.2	0.4	0.6	0.8	1.0
W/O/W emulsion stirring time	ST	X_3	minute	10	15	20	25	30
Synthetic solution/emulsion volume ratio	VR	X_4		2	3	4	5	6

*β=2

5.4.1.1 Central Composited Design—Copper removal

Based on Table 5.3, after the experiments were performed in pre-determined random order, each test was replicated, the results were averaged and detailed in Table 5.4:

Table 5.4 Central composite design for stage A

Run	**Actual level of factors**				**Response (Average Extraction, %)**		
	X_1	X_2	X_3	X_4	Cu	Ni	Ca
1	1	0.8	25	5	90.6%	3.1%	5.4%
2	0.8	0.6	10	4	91.0%	1.0%	3.5%
3	0.8	0.2	20	4	99.6%	5.5%	3.7%
4	0.8	0.6	20	4	90.6%	2.0%	5.2%
5	0.8	0.6	20	4	92.0%	2.6%	5.2%
6	0.8	0.6	30	4	89.0%	3.1%	6.3%
7	0.8	0.6	20	2	89.9%	1.5%	4.3%
8	1	0.4	15	5	92.3%	2.3%	2.2%
9	1	0.8	25	3	90.1%	1.9%	6.0%
10	0.6	0.8	25	5	74.8%	3.3%	5.7%
11	0.8	1	20	4	76.6%	3.9%	6.8%
12	0.6	0.8	15	5	80.4%	4.0%	5.7%
13	0.8	0.6	20	4	93.5%	2.4%	4.7%
14	0.8	0.6	20	4	92.7%	4.8%	4.5%
15	0.6	0.4	25	5	93.2%	4.9%	2.5%
16	0.6	0.4	15	3	95.7%	5.4%	3.8%
17	0.8	0.6	20	4	91.7%	5.8%	4.1%
18	0.8	0.6	20	6	85.9%	7.0%	2.8%
19	0.6	0.4	25	3	94.3%	5.9%	4.1%
20	1	0.4	15	3	95.5%	5.1%	2.9%
21	1	0.8	15	3	92.3%	4.1%	4.5%
22	1	0.8	15	5	82.6%	4.8%	4.3%
23	0.6	0.8	15	3	87.4%	5.7%	3.7%
24	0.8	0.6	20	4	94.4%	2.4%	2.8%
25	0.6	0.4	15	5	94.3%	4.2%	1.2%
26	1	0.4	25	3	97.6%	2.7%	1.5%
27	1.2	0.6	20	4	96.0%	1.8%	1.7%
28	0.8	0.6	20	4	93.4%	4.4%	2.4%
29	0.4	0.6	20	4	84.9%	3.3%	2.8%
30	1	0.4	25	5	95.4%	3.2%	0.6%
31	0.6	0.8	25	3	85.5%	3.5%	6.0%

From Table 5.4, it can be seen that the copper removal ranged from 74.9% to 99.6% while the percent removal of other metal ions remained fairly low with an average value of 3.7% and 3.9% for nickel and calcium respectively. One of the possible reasons why copper was preferred in stage

A arises from the planar donor sets of LIX 984N that provide cavities for copper ions to form a pseudo-macrocyclic complex. Also, it should be noted that although nickel has a higher crystal field stabilization energy than copper, octahedral Cu(II) complexes are more stable than Ni(II) complexes, it could be explained that there are two possible ways of filling electrons in the e_g orbitals of Cu(II), resulting in a degeneracy energy state causing a geometrical distortion that lowers down the total energy of Cu(II) complexes [5.60-5.61]. The second order response model for Cu removal (E_{Cu}) was represented as a function of extractant concentration (X_1), H_2SO_4 concentration (X_2), W/O/W emulsion stirring time (X_3) and synthetic solution/emulsion volume ratio (X_4) in coded unit was given in Equation 5.5:

$$E_{Cu} = 92.63 + 4.43X_1 - 10.03X_2 - 0.25X_3 - 3.56X_4 - 1.52X_1^2 - 3.84X_2^2 - 1.95X_3^2 - 4.05X_4^2 + 6.04X_1X_2 + 5.27X_1X_3 + 1.36X_1X_4 - 1.13X_2X_3 - 4.76X_2X_4 + 1.97X_3X_4 \qquad \text{Equation 5.5}$$

A summarized analysis of variance table is given in Table 5.5 in order to show the adequacy of the model:

Table 5.5 Summarized ANOVA table for copper removal

Source	**DF**	**f-value**	**p-value**	**R^2**	**R^2(adj)**	**SD**
Model	14	15.24	0.000	0.930	0.869	2.105

DF: degree of freedom SD: standard deviation adj: adjusted

It can be seen from Table 5.5 that the model has a p-value less than 0.05, confirming the significance of the model. The f-value is greater than the f critical value at 5% significance level ($f_{0.05\,(14,16)} = 2.44$). Based on this information and the high R^2 and R^2(adj) value, it is shown that this model is a good fit and can be accepted from engineering point of view [5.56-5.58]. Table 5.6 shows the regression model for copper removal in order to determine the effect of each factor and the interactions between these factors, where Coef represents regression coefficient and t, p represent t-value and p-value accordingly.

Table 5.6 Regression model for copper removal

Term	Coef	T	P
Constant	92.63	116.44	0.000
X_1	4.43	5.15	0.000
X_2	-10.03	-11.67	0.000
X_3	-0.25	-0.29	0.775
X_4	-3.56	-4.14	0.001
X_1^2	-1.52	-0.97	0.348
X_2^2	-3.84	-2.44	0.027
X_3^2	-1.95	-1.24	0.233
X_4^2	-4.05	-2.57	0.021
X_1X_2	6.04	2.87	0.011
X_1X_3	5.27	2.50	0.024
X_1X_4	1.36	0.64	0.529
X_2X_3	-1.13	-0.53	0.600
X_2X_4	-4.76	-2.26	0.038
X_3X_4	1.97	0.94	0.363

As can be seen from Table 5.6, the discussion regarding the important factors that have a significant effect to the response can be divided into the following three sections:

1. Main effects: Out of the four main factors, extractant concentration, H_2SO_4 concentration and synthetic solution/emulsion volume ratio are statistically significant whereas the W/O/W emulsion stirring time is non-significant based on the p-values. Based on the signs of the regression coefficient and T value, it can be seen extractant concentration has a positive effect while H_2SO_4 concentration and synthetic solution/emulsion volume ratio have negative effects on the response. This could be explained through higher extractant concentration lead to an increased concentration of extractant molecules, bringing a higher area available to contact the metal ions during the extraction process, thus enhancing the extraction kinetics and extraction capacity; for H_2SO_4 concentration, a higher concentration will decrease the synthetic solution pH due to the unavoidable leakage of H_2SO_4, thus decreasing the extractant efficiency; for the solution/emulsion volume ratio, a high value will dilute the extractant concentration, thus leading to a negative effect to the response.

2. Quadratic effects: the quadratic effect of statistically important terms including H_2SO_4 concentration and synthetic solution/emulsion volume ratio are both negative. Statistically

speaking, negative quadratic effect means that up to a certain point, an increase of the factor will bring positive effect to the response. However, after passing that point, the increase of the factor begins to bring negative effect to the response.

3. Interactive effects: Three interactive effects are statistically important and they are: the interactive effect between extractant concentration and H_2SO_4 concentration; extractant concentration and W/O/W emulsion stirring time; H_2SO_4 concentration and synthetic solution/emulsion volume ratio. For the interactive effect between extractant concentration and H_2SO_4 concentration, it can be understood that a higher H_2SO_4 concentration will enhance the speed of extractant regeneration. The interactive effect between extractant concentration and W/O/W emulsion stirring time means that a longer W/O/W emulsion stirring time brings more time for metal-extractant complex stripping, so extractant concentration will eventually reach an equilibrium inside the emulsion. The interactive effect brought by H_2SO_4 concentration and synthetic solution/emulsion volume ratio can be explained that a higher value of synthetic solution/emulsion volume ratio means there is higher chance that swelling is happening inside the H_2SO_4 droplets. Here the swelling is driven by the difference in osmotic pressure between the internal and external phases, whereas water is transported from the external phase to the internal phase since the latter one has a higher ionic strength. This dilutes the internal H_2SO_4 concentration and thus may slow down the stripping process and thus lower down the extraction kinetics. Although W/O/W emulsion stirring time itself is not a statistical important factor, based on the interactive effects, it will still be treated as an important factor for model optimizations consideration, including surface contour plot and overlaid contour plots.

5.4.1.2 Model Optimization

Figure 5.2 shows the surface contour plots of the effects of different variables on copper removal. In each contour plot, two factors were selected as variables while the other two factors were kept constant at their central level.

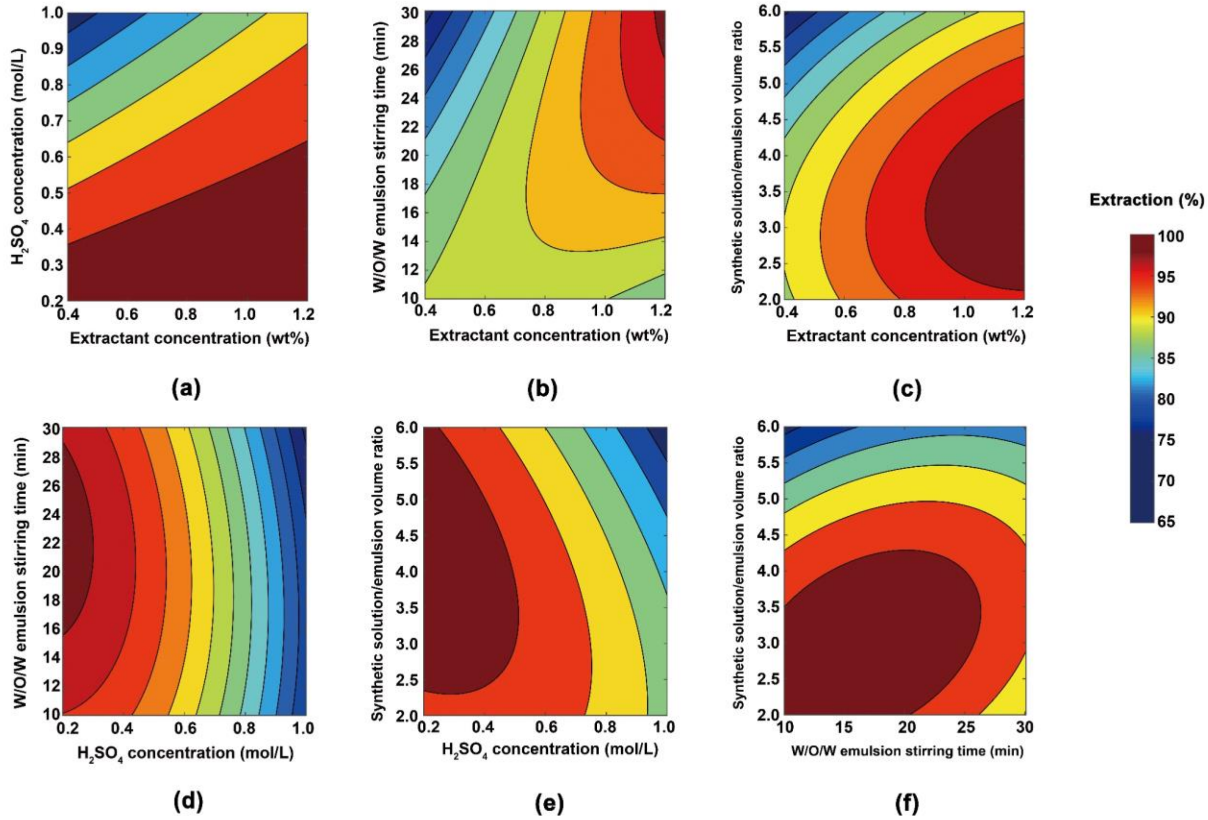

Figure 5.2 Surface contour plots showing the effects of variables on copper removal in stage A: (a) extractant concentration and H_2SO_4 concentration; (b) extractant concentration and W/O/W emulsion stirring time; (c) extractant concentration and synthetic solution/emulsion volume ratio; (d) H_2SO_4 concentration and W/O/W emulsion stirring time; (e) H_2SO_4 concentration and synthetic solution/emulsion volume ratio; (f) W/O/W emulsion stirring time and synthetic solution/emulsion volume ratio.

As can be seen from Figure 5.2, in order to achieve a high copper removal (>95%), it is recommended to have: higher extractant concentration (1.0 wt%-1.2 wt%); lower H_2SO_4 concentration (0.2 mol/L-0.4 mol/L); intermediate W/O/W emulsion stirring time (18-25 min); and an intermediate synthetic solution/emulsion volume ratio (2.5-4.0). In order to obtain an accurate optimum operating condition, overlaid contour plots were generated and shown in Figure 5.3. The shaded area represents the intersection of all contour plots where a minimum copper removal of 95% is achieved.

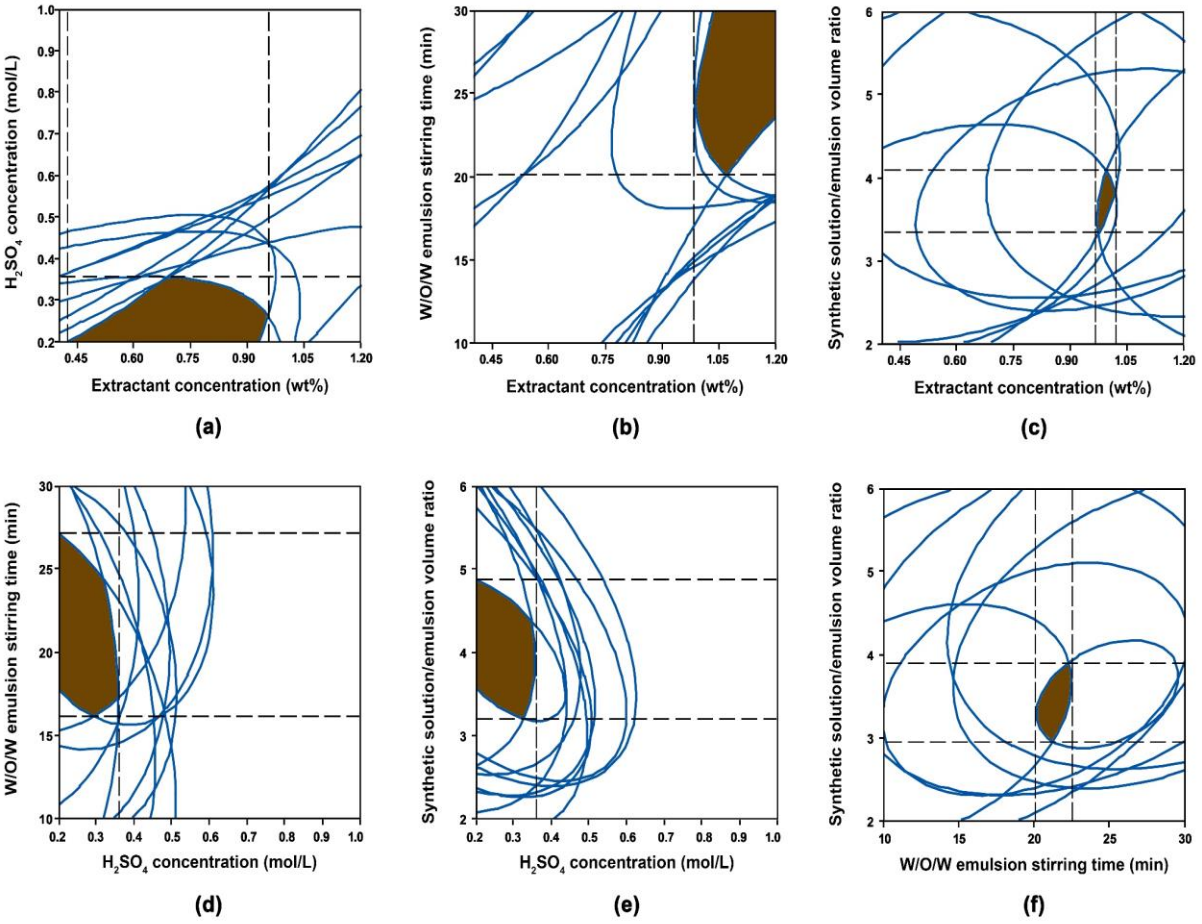

Figure 5.3 Overlaid contour plots showing the effects of variables on copper removal: (a) extractant concentration and H_2SO_4 concentration; (b) extractant concentration and W/O/W emulsion stirring time; (c) extractant concentration and synthetic solution/emulsion volume ratio; (d) H_2SO_4 concentration and W/O/W emulsion stirring time; (e) H_2SO_4 concentration and synthetic solution/emulsion volume ratio; (f) W/O/W emulsion stirring time and synthetic solution/emulsion volume ratio.

Based on Figure 5.3, in order to achieve a high copper removal (>95%), the range of the variables can be obtained and are detailed in Table 5.7.

Table 5.7 Optimum ranges of variables for copper removal over 95%

Figure	Variables			
	EC (wt %)	**AC (mol/L)**	**ST (min)**	**VR**
5.2(a)	0.45-0.96	0.20-0.36	/	/
5.2(b)	0.97-1.20	/	20-30	/
5.2(c)	0.96-1.03	/	/	3.3-4.1
5.2(d)	/	0.20-0.36	16-27	/
5.2(e)	/	0.20-0.36	/	3.2-4.8
5.2(f)	/	/	20-22.5	2.9-3.9

Based on this information, it can be seen that for extractant concentration, there is a very limited range, and the ideal value was determined to be 0.97 wt%. The optimum range of H_2SO_4 concentration was 0.2-0.36 mol/L as indicated in Table 5.7. An initial value of 0.4 mol/L was chosen, giving a copper extraction efficiency of 98.2%, this satisfied our optimization target (>95%) based on the design. Since the process involves both copper extraction and stripping process, the copper stripping efficiency must also be considered. Thus, after the loaded emulsion was collected and broken into two phases, the stripping efficiency was determined to be 90.3%, which meant that the remaining 9.7 % copper in the organic phase could not be stripped by a H_2SO_4 solution of 0.4 mol/L. It was found that higher H_2SO_4 concentrations will not only provide more chemical driving force for metal ion extraction into ELMs, but also enhance the stripping efficiency of metal ion within ELMs. For the reasons above, a compromise was made between high efficiency and lower materials cost and the value of 0.50 mol/L was chosen (Table 5.8). The W/O/W emulsion stirring time was determined to be 22.5 minutes in order to provide sufficient time for copper extraction and stripping. The synthetic solution/emulsion volume ratio was set at a maximum value of 4.0 in order to increase the treating ratio of ELM on synthetic mixed solution. The predicted copper removal rate was 96.7% using the response optimizer function in Minitab® Statistical Software 17 (Equation 5.4). The validity of the optimum point was also confirmed by 5 validation tests to ensure reproducibility. Table 5.8 shows the optimum point and response (experimental and predicted by model).

Table 5.8 Optimum point for copper removal in stage A

Test Condition				**Response (Extraction, %)**			**Stripping**
EC (wt%)	**AC (mol/L)**	**ST (min)**	**VR**	**Predicted**	**Experimental mean**	**Error (%)**	**Efficiency (%)**
0.97	0.40	22.5	4.0	97.6	98.2	0.6	90.3
0.97	0.50	22.5	4.0	96.7	98.0	1.3	95.7

After the test finished, the emulsion was broken up and an average copper stripping efficiency of 95.7% was obtained. This means that a H_2SO_4 concentration of 0.50 mol/L provides sufficient acidity to strip the majority of copper ions from the copper-LIX complex. It should be noted that an analysis showed that the nickel and calcium removal rate was only 0.9 % and 1.3%, respectively. These low values mean that there is good selectivity for copper over nickel and calcium. The average copper, nickel and calcium concentration in the loaded stripping liquor was 187.6 ppm, 8.0 ppm and 9.4 ppm respectively. The separation factor of β_{Cu}/β_{Ni} and β_{Cu}/β_{Ca} was calculated to be 46.9 and 498.9, respectively. The composition of the effluent before and after the first stage is listed in Table 5.9

Table 5.9 The effluent before and after the first stage

Term	**Initial condition**	**After stage A**
pH	4.0	2.5
Cu (ppm)	10.0	0.2
Ni (ppm)	20.0	19.8
Ca (ppm)	250.0	246.8

5.4.2 Stage B

It can be seen that after the first stage of copper extraction, the feed solution pH decreases significantly from 4.0 to 2.5. This decrease in pH is due to two reasons, namely the release of hydrogen proton during the reaction, and the leakage of internal liquor H_2SO_4 into the mixed solution. It should be noted that the surface charge of emulsion droplets usually behaves in a way that from the very acidic condition, the surface was positively charged, with an increase in pH, it would reach its isoelectric point before it turned to be negatively charged. The increase in pH above isoelectric point will bring a more stable emulsion and a higher driving force for metal ions to be extracted by the membrane phase [5.62]. This acidic pH not only makes it more difficult to extract nickel by ELM, since most extractant starts to extract nickel from a feed solution pH higher than 4.5; it also requires a higher concentration of internal stripping liquor in order to shift the pH dependent extraction equilibrium in the reverse direction (stripping). Many researchers add NaOH or lime to increase the feed pH in order to solve this problem [5.36, 5.39, 5.41]; however, this increases operation costs and might also create difficulties in subsequent nickel and calcium separation. Currently for nickel extraction, no single extractant can achieve very high extraction efficiency at lower pH with a faster kinetics, good membrane stability and stripping rate. Fouad *et al.* reported that an enhancement of extraction and stripping efficiency of copper ions at very low pH can be achieved by the synergistic effect brought by a mixture of Cyanex 301 and LIX 984N, where significant synergistic enhancement could be obtained at a volume ratio of Cyanex 301 to LIX 984N of 1 to 1 [5.30]. A synergistic effect means that a mixture of two extractants has a cooperative effect that the distribution ratio for the mixture is greater than the largest individual distribution ratio, this can significantly increase the extraction efficiency. The synergistic effect comes from the neutralization of metal ion charges by the chelating extractant and the replacement of residual water from the inner coordination sphere by the other extractant, this could render the complex formed more hydrophobic. Thus, a mixture of Cyanex 301 and LIX 984N at a volume ratio of 1 to 1 was used as the nickel extractant for stage B in our project. The reaction of nickel and the binary mixture of monomeric Cyanex 301 (HR) and LIX 984N (HX) can be expressed through Equation 5.6:

$$Ni^{2+} + HR + HX \leftrightarrow NiRX + 2H^{+} \qquad \text{Equation 5.6}$$

It should be noted that factors in stage A (extractant concentration, H_2SO_4 concentration, W/O/W emulsion stirring time and synthetic solution/emulsion volume ratio) were also considered to be important in stage B [5.62]. However, the range changed based on the characteristics of experiments and were shown in Table 5.10:

Table 5.10 Levels and values of factors in stage B

Factors	**Short**	**Symbol**	**Units**	**-β***	**-1**	**0**	**1**	**β***
Extractant concentration	EC	X_1	wt %	4	5	6	7	8
H_2SO_4 concentration	AC	X_2	mol/L	4	5	6	7	8
W/O/W emulsion stirring time	ST	X_3	minute	10	15	20	25	30
Synthetic solution/emulsion volume ratio	VR	X_4		2	2.5	3	3.5	4

*β=2

When compared with stage A, it can be seen that significant changes are made to the ranges of two factors: extractant concentration and H_2SO_4 concentration. They both required a much higher value than in stage A. The reasons for these increases are as followed:

For extractant concentration, a more acidic environment leads to a higher concentration of H^+, thus pushing the pH dependent extraction equilibrium into the reverse direction (Equation 5.6). A much higher concentration of extractant is required to prevent the extraction equilibrium moving in that direction.

For H_2SO_4 concentration, the range was set from 4.0 to 8.0 mol/L in order to maintain a relatively high nickel stripping efficiency inside the ELM droplets. This also provides a higher chemical driving force for nickel extraction such that the difference in acidity between the feed solution and the internal stripping liquor actually acts as a chemical pump during the process. It was also reported by Fouad *et al.* that the complex formed by solvent mixture of Cyanex 301–LIX 984N and copper is quite stable so that a higher concentration of acid was required in order to achieve a higher stripping rate [5.30]. However, it was not necessary to use a highly concentrated H_2SO_4 as this may bring negative effects to organic phase viscosity and phase separation.

5.4.2.1 Central Composited Design —Nickel Removal

Based on Table 5.10, central composite design tests were performed in a pre-determined order as in stage A. Each test was duplicated in order to confirm the repeatability of the design, the results being averaged and listed in Table 5.11. It should be noted out that all the copper ions remaining in the effluents discharged from stage A were all extracted into ELM in Stage B, thus it was not listed in Table 5.11.

Table 5.11 Central composite design for stage B

Run	**Actual level of factors**				**Response (Average Extraction, %)**	
	X_1	X_2	X_3	X_4	Ni	Ca
1	5	7	25	2.5	63.4%	0.10%
2	7	5	25	2.5	98.0%	0.89%
3	7	5	15	3.5	97.3%	3.46%
4	6	6	20	3	89.0%	4.81%
5	7	7	25	2.5	86.9%	3.27%
6	7	7	15	3.5	83.6%	3.93%
7	7	5	15	2.5	98.3%	1.30%
8	6	6	20	3	95.7%	1.70%
9	6	6	20	2	96.7%	1.99%
10	8	6	20	3	98.8%	0.20%
11	6	6	20	3	97.3%	3.50%
12	7	5	25	3.5	96.7%	2.77%
13	5	5	25	2.5	95.7%	2.78%
14	5	7	25	3.5	59.3%	2.26%
15	5	7	15	2.5	79.6%	3.11%
16	7	7	25	3.5	81.5%	5.61%
17	6	6	10	3	93.0%	6.15%
18	6	6	20	3	95.4%	2.02%
19	6	8	20	3	44.3%	3.32%
20	6	6	20	3	95.3%	4.62%
21	5	5	15	2.5	96.3%	3.48%
22	6	6	20	3	98.9%	1.70%
23	5	5	15	3.5	97.0%	2.44%
24	6	6	20	4	96.3%	2.94%
25	7	7	15	2.5	86.4%	0.78%
26	6	6	30	3	98.5%	0.82%
27	4	6	20	3	94.3%	4.38%
28	5	5	25	3.5	98.1%	2.09%
29	6	4	20	3	99.2%	3.27%
30	6	6	20	3	98.9%	3.23%
31	5	7	15	3.5	68.7%	4.94%

It can be seen from Table 5.11 that the nickel removal ranges from 44.3% to 99.2 % with an average value of 89.6%, while there is a relatively low co-extraction rate of calcium (an average value of 2.83%). This means that ELM can effectively extract and separate nickel from calcium ions under acidic environments. The reason why the mixture extractant has a binding preference for Ni(II) than Ca(II) is that Ca (II) has a closer approach of the p-electrons to the nucleus than Ni(II) with its outermost electrons in the d-orbitals, cancelling a part of the nuclear charge for Ca(II), thus the remaining electrons were less attracted by fewer protons, resulting a higher energy than Ni(II) electrons. [5.63-5.64] Thus, the nickel complexes were more stable than calcium complexes. The second order response model for Ni removal (E_{Ni}) was represented as a function of extractant concentration (X_1), H_2SO_4 concentration (X_2), W/O/W emulsion stirring time (X_3) and synthetic solution/emulsion volume ratio (X_4) in coded units is given in Equation 5.7:

$$E_{Ni}= 95.79 + 6.64X_1 - 23.14X_2 - 1.37X_3 - 1.92X_4 - 1.54X_1^2 - 26.37X_2^2 - 2.35X_3^2 - 1.59X_4^2 + 16.05X_1X_2 + 5.7X_1X_3 + 0.36X_1X_4 - 6.68X_2X_3 - 6.01X_2X_4 + 1.39X_3X_4 \quad \text{Equation 5.7}$$

The regression model for nickel removal in this stage was also given in Table 5.12:

Table 5.12 Regression model for nickel removal in stage B

Term	Coef	T	P
Constant	95.79	52.86	0.000
X_1	6.64	3.39	0.004
X_2	-23.14	-11.82	0.000
X_3	-1.37	-0.7	0.494
X_4	-1.92	-0.98	0.341
X_1^2	-1.54	-0.43	0.673
X_2^2	-26.37	-7.35	0.000
X_3^2	-2.35	-0.66	0.522
X_4^2	-1.59	-0.44	0.664
X_1X_2	16.05	3.35	0.004
X_1X_3	5.7	1.19	0.252
X_1X_4	0.36	0.08	0.941
X_2X_3	-6.68	-1.39	0.183
X_2X_4	-6.01	-1.25	0.228
X_3X_4	1.39	0.29	0.777

The following conclusions can be made from comparing the results in Table 5.12 with Table 5.6 regarding the main effects and the interactions between these four important factors:

1. Based on the signs of the regression coefficient, it can be seen that the coefficient of every single term in Table 5.12 has the same sign as the corresponding term in Table 5.6.
2. For the significance of the main effects, the most significant change from Table 5.6 to Table 5.12 is that the synthetic solution/emulsion volume ratio was no longer statistically significant (p value > 0.05). This means that the change of solution/emulsion volume ratio from 2.0 to 4.0 does not affect the extraction efficiency of nickel ions in stage B. However, it did not mean that the highest value of 4.0 is always preferred since this ratio also affects the stripping efficiency together with H_2SO_4 concentration and W/O/W emulsion stirring time. Thus, careful consideration must be taken while deciding the best ratio here.
3. Out of the four main factors, the most significant factor was still H_2SO_4 concentration based on its t-value in Table 5.6 and Table 5.12, proving that for extraction of both copper and nickel by ELM, the chemical driving force brought by the difference in acidity between the feed solution and internal stripping liquor contributed more to the response than extractant concentration.
4. The numbers of statistically significant quadratic and interactive effects within/between factors also decrease based on the information given in Table 5.6 and Table 5.12, only the quadratic effect of H_2SO_4 concentration and the interactive effect between extractant concentration and H_2SO_4 concentration are still significant. This means that the interactions between these factors will have less influence (if any) on nickel removal.

The summarized ANOVA table (Table 5.13) shows that this model can be accepted from the R^2 value. However, it has a higher standard deviation than that in Table 5.13, which means that this data set was more widely spread and did not provide as much accuracy in variance estimation as the data set in stage A.

Table 5.13 Summarized ANOVA table for nickel removal in stage B

Source	**DF**	**f-value**	**p-value**	**R^2**	**R^2(adj)**	**SD**
Model	14	15.94	0.000	0.933	0.875	4.795

DF: degree of freedom SD: standard deviation adj: adjusted

5.4.2.2 Model Optimization

In order to obtain the optimization parameters for process control, contour plots were generated, and as shown in Figure 5.4.

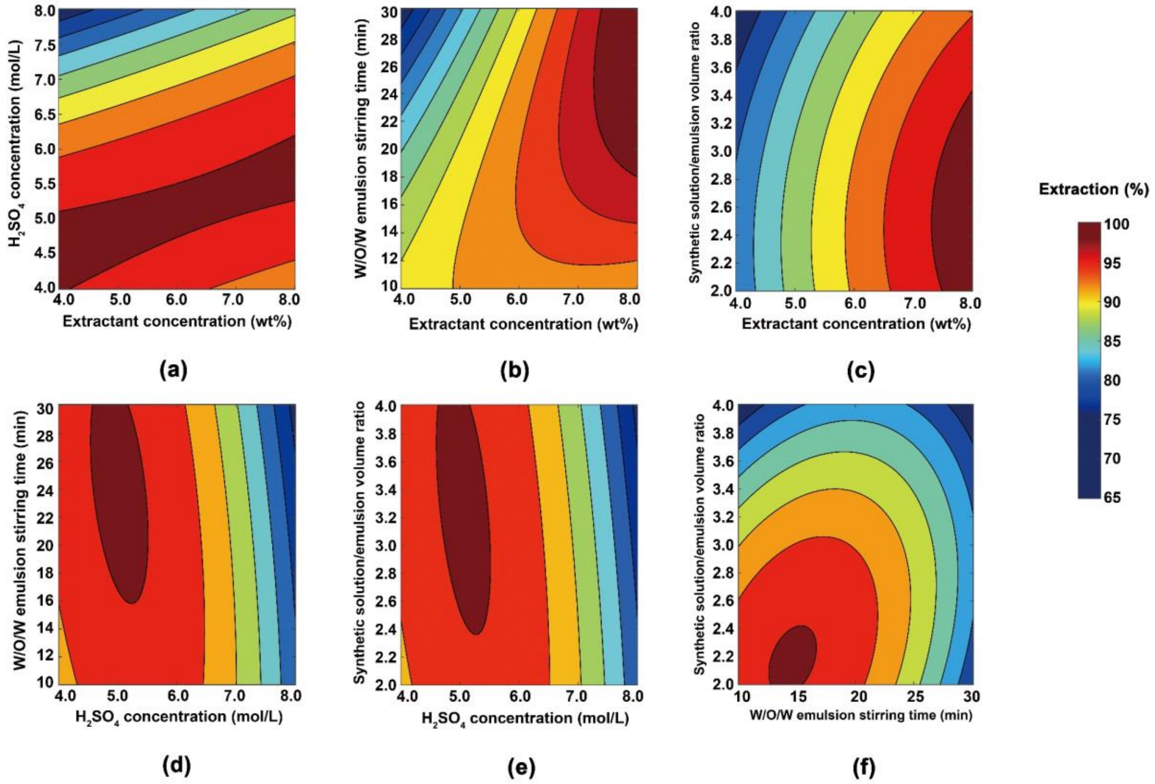

Figure 5.4 Surface contour plots showing the effects of variables on nickel removal in stage B: (a) extractant concentration and H_2SO_4 concentration; (b) extractant concentration and W/O/W emulsion stirring time; (c) extractant concentration and synthetic solution/emulsion volume ratio; (d) H_2SO_4 concentration and W/O/W emulsion stirring time; (e) H_2SO_4 concentration and synthetic solution/emulsion volume ratio; (f) W/O/W emulsion stirring time and synthetic solution/emulsion volume ratio.

In order to reach a nickel removal rate over 95 percent, a few conclusions can be made from Figure 5.4:

1. For extractant concentration, in general a higher concentration is favored, when the value is lower than 6.5 wt%, uncertainty in high nickel removal appears. It was noticed that an increase in extractant concentration (when it is over 6.5%) did not decrease organic viscosity or affect the nickel extraction efficiency [5.31].

2. For H_2SO_4 concentration, it seems that a value of 4.5 to 6.5 mol/L is preferred, a value higher than that may increase the organic viscosity thus depress the nickel extraction; emulsion swelling rate may also increase caused by the increased osmosis pressure between the internal acid phase and aqueous feed phase, which may decrease emulsion stability.
3. For W/O/W emulsion stirring time, a stirring time of 15-22 minutes was ideal, however, a longer time may be needed in real operation for fully strip nickel off its complex.
4. For synthetic solution/emulsion volume ratio, a value of less than 3.0 will secure a high nickel removal.

It can be seen there is a high similarity between the characteristics of these four factors in stage B with that in stage A. While the only exception is the factor of W/O/W emulsion stirring time, where a high value was always acquired in stage A (Figure 5.2). In Figure 5.4 (f), the decrease in nickel removal efficiency with increasing W/O/W emulsion stirring time may be caused by the leakage of H_2SO_4 (breakage of ELM droplets) into the feed solution under a longer stirring time, this increase in feed solution acidity may break the established extraction equilibrium so that nickel ions may be deprived from the formed nickel-extractant complex back in the feed solution rather than the internal droplets. Thus, this may also support the idea of controlling H_2SO_4 concentration within a certain range. Based on the information given, a series of overlaid contour plot (Figure 5.5) were also drawn in order to obtain the optimized process parameters during this process.

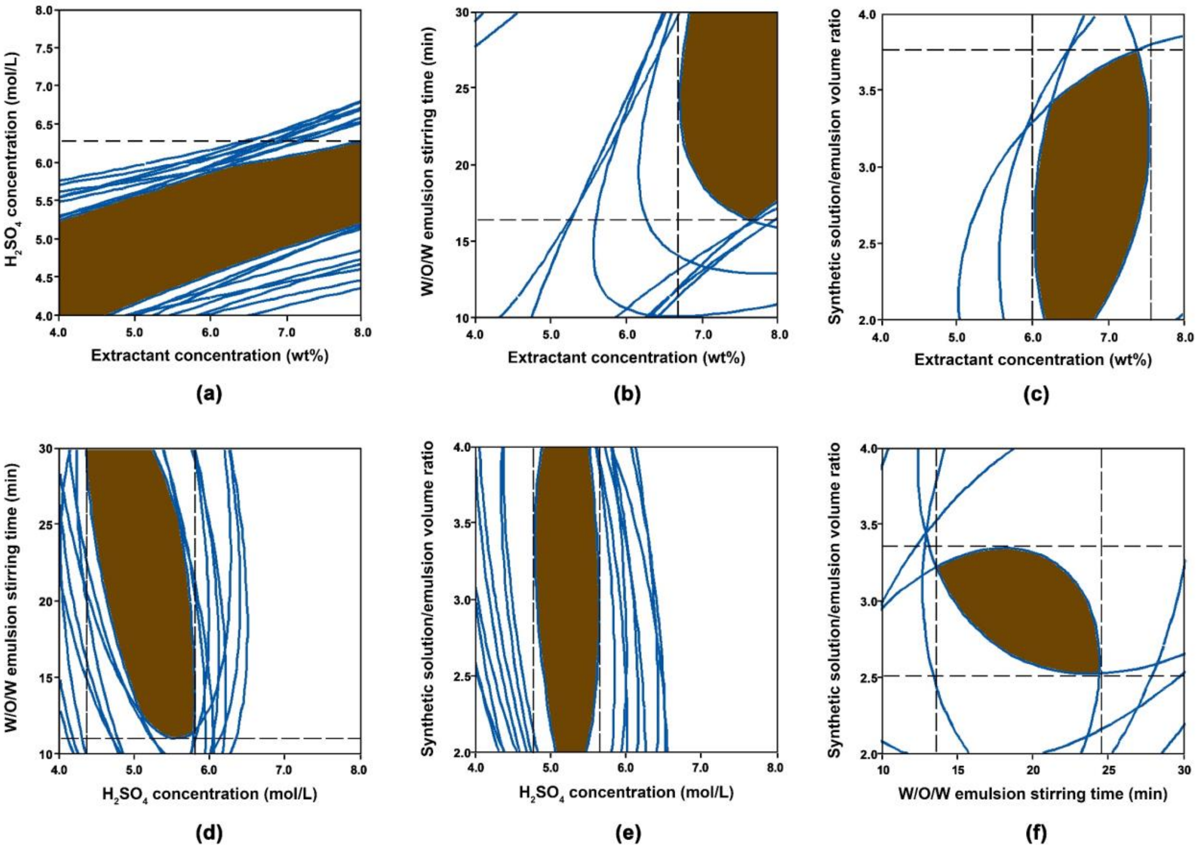

Figure 5.5 Overlaid contour plots showing the effects of variables on nickel removal in stage B: (a) extractant concentration and H_2SO_4 concentration; (b) extractant concentration and W/O/W emulsion stirring time; (c) extractant concentration and synthetic solution/emulsion volume ratio; (d) H_2SO_4 concentration and W/O/W emulsion stirring time; (e) H_2SO_4 concentration and synthetic solution/emulsion volume ratio; (f) W/O/W emulsion stirring time and synthetic solution/emulsion volume ratio.

The shaded area represents operating conditions that result in a nickel removal of 95 percent or higher. Figure 5.5 (a) shows that H_2SO_4 concentration should be limited in the range of 4.0 to 6.3 mol/L while there is no constrain of extractant concentration. The reason why higher H_2SO_4 concentration is not favored has already been discussed previously in Section 5.4.1.1, however, a pattern emerges that in order to achieve a high nickel removal (>95%), a higher concentration of H_2SO_4 concentration is required while increasing the extractant concentration. This can be explained by the fact that it is harder to strip the nickel ions from nickel-extractant complex while the complex is surrounded by more extractant molecules, thus a stronger stripping liquor or a higher concentration of H_2SO_4 is required. This may provide a robust window for the optimum operating conditions for the factors of extractant concentration and H_2SO_4 concentration. Figure 5.5 (b) indicates that it requires an extractant concentration between 6.7 and 8.0 wt% and W/O/W emulsion stirring time of 16 to 30 minutes to achieve a high nickel extraction. Figure 5.5 (c) shows that an extractant concentration of 6.0 to 7.5 % and a synthetic solution/emulsion volume ratio of 2.0 to 3.7 is required. This supports the conclusion above regarding extractant concentration, while the range of synthetic solution/emulsion volume ratio is fairly broad. Figure 5.5 (d) reveals that a H_2SO_4 concentration of 4.3 to 5.8 mol/L and a W/O/W emulsion stirring time of 11 to 30 minutes are safe to operate. This means that the factor of W/O/W emulsion stirring time was not important as H_2SO_4 concentration. However, as discussed, the nickel extraction by ELM process did not only focus on nickel extraction, but also nickel stripping within internal droplets, which means that an extra W/O/W emulsion stirring time may be required. Figure 5.5 (e) supports the idea of the selection of broad range of synthetic solution/emulsion volume ratio (from 2.0 to 4.0) and a narrow range of H_2SO_4 concentration from 4.8 to 5.7 mol/L. Figure 5.5 (f) proves that a suitable range of W/O/W emulsion stirring time being 14 to 25 minutes is preferred while the value of synthetic solution/emulsion volume ratio is from 2.5 to 3.4. Based on the information, a conclusion regarding the optimum range of four factors can be made (Table 5.14)

Table 5.14 Optimum ranges of factors obtained from Figure 5.4 (nickel removal>95%)

Variables	Units	Optimal range
EC	wt %	6.7-7.5
AC	mol/L	4.8-5.7
ST	min	16-25
VR	rpm	2.5-3.4

The optimum condition and corresponding validation test result is listed in Table 5.15, the considerations were as followed: in order to save the cost of raw materials, a minimum extractant concentration of 6.7% was chosen; the H_2SO_4 concentration was determined to be 5.7 mol/L and the W/O/W emulsion stirring time was chosen to be 25 minutes in order to achieve a high nickel stripping rate inside the ELM; the synthetic solution/emulsion volume ratio was set as 3.5 since a higher value will reduce the amount of expensive extractant used in the operating process.

Table 5.15 Optimum point for nickel removal in stage B

Test Condition				Response (Nickel extraction, %)		
				Predicted	**Experimental mean**	**Error (%)**
EC (wt%)	AC (mol/L)	ST (min)	VR			
6.7	5.7	25	3.5	99.7	99.0	0.7%

The percentage calcium extraction rate was also measured to be 0.55 %. This means that the extractant has a very good ability to extract and separate nickel from calcium ions under the experimental conditions tested here. It should also be noted that despite its great extraction efficiency, this mixture was not used in stage A due to that under pH 4.0 it did not reach a good separation between Cu(II) and Ni(II). After the test ended, the emulsion was broken up and an average nickel stripping efficiency of 84.1% was obtained, and the copper ions had been extracted. The average nickel and calcium concentration in the loaded stripping liquor are 293.2 ppm and 0 ppm respectively. This means that the nickel was also concentrated in the stripping solution and calcium was not stripped into the internal H_2SO_4 solution.

5.4.3 Bench Scale Mixer-Settler for Water Processing

Based on the information obtained above, to test the possibility of implementing ELM technique treating semi-batch synthetic process water, a two-stage bench scale mixer-settler has been built using poly (methyl methacrylate) glass. These mixer-settlers (as a whole) in stage A and B are identical in footprint, both having a length of 20 cm and a width of 9.0 cm. However, when talking about the mixer or settler chamber size, due to the difference in optimal operating conditions in stage A & B, the size of the mixer or settler chamber in stage A is slightly different from that in stage B, the volume of each mixer and settler chambers are listed in Table 5.16:

Table 5.16 The volume of the chambers for mixer & settler in both stage A and B

Term	Mixer (ml)	Settler (ml)
Stage A	759	839
Stage B	839	759

For both stages, extraction tests were operated under the optimum operating conditions obtained previously. The total processed synthetic water was 8.0 L and the total experimental time spent was 5.4 hours. In the first stage, the synthetic process water and the emulsion was pumped into the mixer chamber for copper extraction, and during the operation after the mixed water overflows into the settler chamber, there is a fast separation of the loaded emulsion and the water. This water was then sent to the second stage together with emulsion for nickel extraction by the use of a peristaltic pump. The final copper, nickel and calcium removal was 99.7%, 98.2% and 2.2%, respectively. The effluent contained copper, nickel and calcium concentration of 0.03 ppm, 0.36 ppm and 244.5 ppm and a final pH value of 1.1. Then the effluent was neutralized to pH 7.0 by the addition of lime prior to being disposed of. In order to compare ELM with traditional solvent extraction (SX), another test have been performed using organic solvent rather than emulsions. The results are listed in Table 5.17.

Table 5.17 The details and results for ELM and SX in two-stage mixer-settler design

Content	Initial Condition	Stage A		Stage B	
		ELM	SX	ELM	SX
Copper (ppm)	10.0	0.15	3.06	0.03	2.59
Nickel (ppm)	20.0	19.76	19.79	0.36	3.06
Calcium (ppm)	250.0	245.6	243.12	244.4	238.53
pH	4.0	2.4	3.2	1.1	2.7
Water flow rate (ml/min)	/	27.0		27.0	
Extractant flow rate (ml/min)	/	6.7		7.7	

Based on the information above, it was proved that ELM technique was more effective than SX at the bench scale for processing waste water. Further work should include implementing a continuous pilot-scale process to determine the scale-up potential. A schematic process flow using ELM to remove and separate Cu and Ni from Ca ions was given in Figure 5.6.

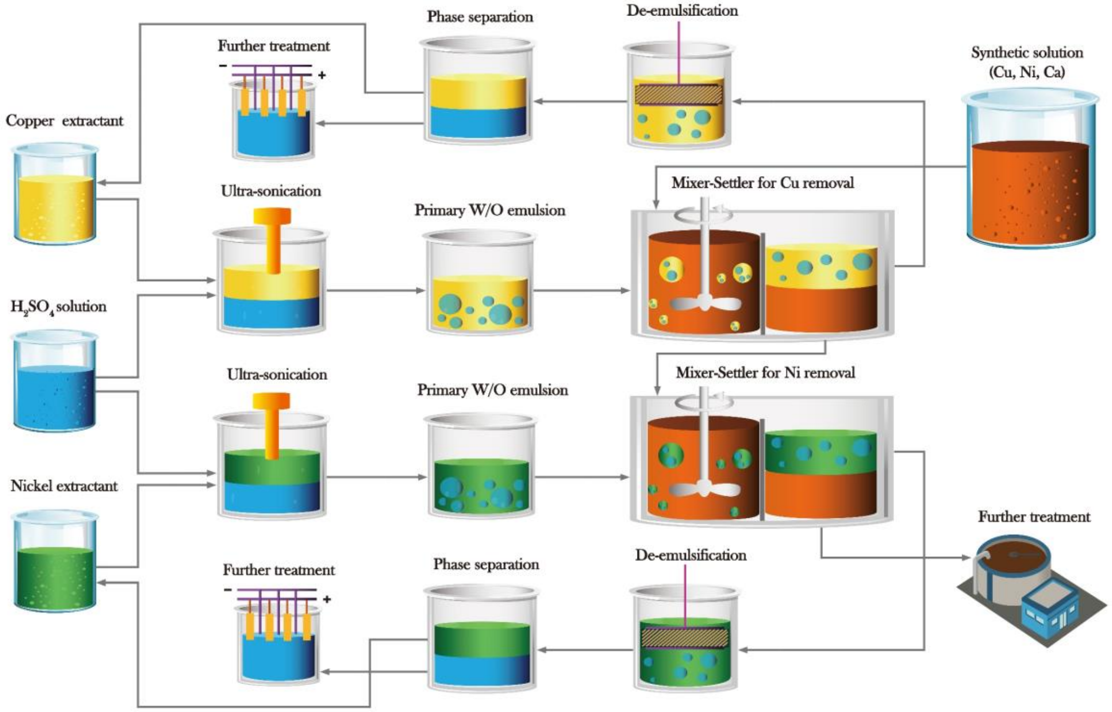

Figure 5.6 A schematic process flow using ELM to remove and separate Cu and Ni from Ca ions

It should be noted that this work was conducted using synthetic water, however, in practical applications, fine particles including clay, kaolinite or resins may exist in the wastewater steam, these solids have a strong tendency to stabilize emulsions. Hydrophilic solids tend to stabilize oil-in-water emulsions by forming a strong, rigid and viscoelastic stagnant film on the oil-water interface that resists droplet coalescence; while hydrophobic solids tend to stabilize water in oil emulsions. This may bring detrimental effect to the extraction efficiency of metal since the diffusion rate of metal ion into the emulsion phase is adversely impacted. Thus, these fine particles need to be removed prior to water treatment by ELMs [5.65-5.67]. The effect of multiple ionic species in solution were discussed in Appendix E.

5.5 CONCLUSIONS

Synthetic process water containing 10 ppm copper, 20 ppm nickel and 250 ppm calcium was treated using a two-stage ELM process. The conclusions for each stage are discussed as follows:

● For stage A, LIX 984N was used as copper extractant and copper ion was effectively separated from nickel and calcium ions. The optimum operating conditions were experimentally determined: extractant concentration of 0.97 wt%, H_2SO_4 concentration of 0.5 mol/L, W/O/W emulsion stirring time of 22.5 minutes and synthetic solution/emulsion volume ratio of 4.0. Under this condition, the copper removal rate was 96.7%, the copper ions were concentrated (187.6 ppm) into the stripping liquor. The separating factor of copper and nickel (β_{Cu}/β_{Ni}); copper and calcium (β_{Cu}/β_{Ca}) was found to be 46.9 and 498.9, respectively.

● For stage B, a mixture of LIX 984N and Cyanex 301 at a volume ratio of 1 to 1 was used as extractant, and the optimum operating conditions were: extractant concentration of 6.7 wt%, H_2SO_4 concentration of 5.7 mol/L, W/O/W emulsion stirring time of 25 minutes and synthetic solution/emulsion volume ratio of 3.5. Under this condition the nickel removal rate was 99.0 % while the nickel ions were concentrated (293.2 ppm) into stripping liquor.

All the results showed that an excellent selective separation of copper and nickel from calcium ions was obtained. Based on the test parameters given, a two-stage mixer-settler was made in order to treat semi-batch synthetic process water and it was proved that ELM method effectively removes and separates copper, nickel from calcium ions. The implementation of this technology in a metallurgical operation can be referred to Appendix F. Whereas a continuous process flowsheet for pilot-scale plant treating wastewater stream using ELMs has been proposed in Appendix G.

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CHAPTER 6. CONCLUSIONS, CONTRIBUTIONS TO ORIGINAL KNOWLEDGE AND RECOMMENDATIONS FOR FUTURE WORK

6.1 CONCLUSIONS

This thesis focused on treating a synthetic waste water stream containing low concentrations of heavy metals ions using the emulsion liquid membrane (ELM) technique. Two steps were involved. In the first step, an investigation of the individual extraction of copper and nickel from single cation solutions was conducted: the important process parameters were determined and the process were optimized. The chemical properties of ELM were also studied. In the second step, the selective extraction and separation of copper and nickel from calcium in a synthetic process wastewater was studied, process optimization have been performed on copper and nickel, respectively. Based on these information, the following conclusions are obtained:

(i) The formed W/O/W emulsion liquid membrane droplets can be observed using optical microscopes: it was noted that all the ELM droplets were in the micrometer size range, mainly distributed from 10-200 μm. The morphology of ELM droplets shows that one or several sulfuric acid droplets are surrounded by an oil droplet and isolated from the external aqueous phase.

(ii) The surfaces of ELM droplets have electric charges and they can be measured using sound. For nickel extraction by Cyanex 301 using ELM, the ELM droplets have the lowest repulsion force under pH value of 2.1, the repulsive force is increasing with the increase of pH, this means that the ELM stability can be predicted depending on the pH that the process was operated under.

(iii) ELM does have a higher metal loading capacity than solvent extraction alone when they contain the same amount of extractant. This is attributed to the stripping process occurred inside ELM that can help extractant regeneration.

(iv) For the tests of heavy metal extraction by ELM technique, design of experiment is an effective tool, fractional factorial design can be used to screen out the important factors while central composite design can be used for process optimization, the validation results always show a good confirmation of the optimized conditions. The followings have been observed during the optimization process:

- Extractant concentration, H_2SO_4 concentration and $CuSO_4$ or $NiSO_4$ solution/emulsion volume ratio are the important factors that affect copper and nickel extraction from single cation bearing solution. Their levels of significance are: extractant concentration > H_2SO_4 concentration > $CuSO_4$ or $NiSO_4$ solution/emulsion volume ratio. This means that the permeation of copper or nickel into the membrane phase is the rate determining step since extractant concentration plays a vital role in this step.
- ELM can remove over 99% of both copper and nickel under optimized conditions. Generally, the reaction is fast and will take 30 minutes or less. During this process, the pH of external solution will be significantly reduced by the H^+ proton released.
- The interactions between the process parameters should not be neglected. For instance, the significant interaction effect between extractant concentration and H_2SO_4 concentration could be understood that higher H_2SO_4 concentration will enhance the speed of extractant regeneration, which may affect the metal extraction as well as metal stripping.
- Compromises are always needed to be made when determining the optimum operating conditions, meaning that a balance of extraction & stripping efficiency and/or materials & energy consumption needs to be obtained. It is a good idea to keep the energy input constant by fixing the emulsion stirring time & speed in order to better evaluate other factors.
- High copper stripping rate from copper-LIX 984N complex is easy to be obtained when using a low concentration H_2SO_4 (0.5M), however, for nickel stripping from nickel-LIX984-Cyanex 301 complex, it requires a much higher H_2SO_4 concentration (5.7M)
- The extraction efficiency of copper & nickel in the ternary system (copper, nickel and calcium) is mostly affected by H_2SO_4 concentration. However, extractant concentration and synthetic solution/emulsion volume ratio also had a significant effect on the copper extraction, while only extractant concentration had a significant effect on the nickel extraction. This means that the difference in acidity between the internal and external phase is critical in reaction rate

determinization, it also supports the Irving-William rules that stability of complexes formed are Ca<Ni<Cu.

- LIX 984N was very effective when treating copper ions in a wide pH range, it also has a preference of copper over nickel and calcium, Cyanex 301 was effective when treating nickel ions solution that has a pH higher than 1. However, when the solution pH is lower than 1, a mixture of LIX 984N and Cyanex 301 at a volume ratio of 1 to 1 was very effective.

(v) ELMs could be regenerated and the oil phase could thus be recycled, however, a slight decrease in extraction efficiency may be seen. This decrease may arise from the additions of new chemicals that are used to break the emulsion chemically.

6.2 CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

This study shows that the ELM technique can be successfully utilized in the extraction of copper and nickel from the wastewater stream. Through this study, it successfully overcomes the drawbacks of using solvent extraction treat wastewater while heavy metal ion concentration is low, and in the meantime, it proves that it inherits the high selectivity, good recyclability and good efficiency of solvent extraction. The process optimization of operating parameters and the exploration of the main effects and interactive effects prove that design of experiment method is very effective and can be used for further ELM extraction tests. Some ELM characteristics have been explored for the first time and comparisons between ELM and conventional solvent extraction were made quantitatively. Chapter 5 also shows that for the first time, a successful extraction and separation of copper and nickel from calcium ions under acid condition can be possible using ELM while having the minimum consumption of materials & energy. All these works expand the current database for metal extraction by ELM and can be used as instructions for comprehensive views of process selection and optimization in the future.

6.3 RECOMMENDATIONS FOR FUTURE WORK

Although this thesis provides a successful application of utilizing ELM technique to extract and separate copper, nickel from calcium ions, some remaining aspects still need to be further investigated. These aspects include:

(i) The extractant used are commercial products from BASF and CYTEC, they may be expensive and they represent a very large proportion of materials cost. Cheaper but effective extractants should be found and tested.

(ii) The ternary Cu-Ni-Ca system is still too limited for most mining effluents, more kinds of heavy metal ions (such as Fe, Cr and Cd) should be added to the current system and tested.

(iii) Emulsion stability could be further studied for bringing up a better way in breaking up the emulsion droplets and recycling the oil phase.

(iv) Pilot-scale continuous water processing plant should be developed in order to test the current ELM technique.

(v) The metal stripping efficiency should be considered as the second response rather than having metal removal as the sole response to the system.

Appendix A: The optical microscopy images of organic and ELM phase droplets under different conditions

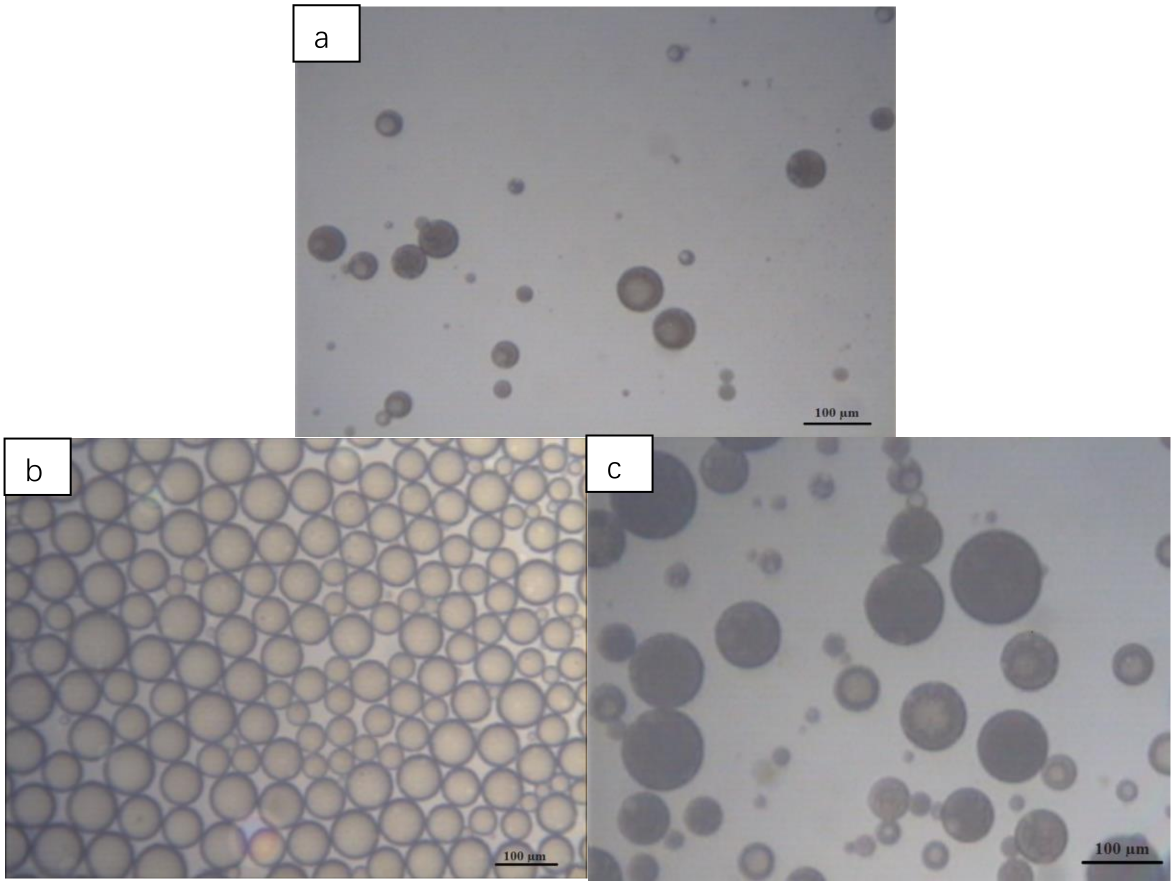

Figure A1 Examples showing the optical microscopy image of (a) ELM droplets during zeta potential measurement; (b) organic phase droplets and (c) ELM droplets during the kinetics study.

Appendix B: Derivation procedures of the diffusion transport model

Fick’s first law was introduced for the diffusion transport model of nickel ions into the ELMs assuming the droplets formed are stable and constant. The transfer rate of Ni(II) ion per unit surface area of emulsion droplet, J_{Ni}, can be expressed as:

$$J_{Ni} = -\frac{V_{aq}}{A_{em}}\frac{d[Ni^{2+}]_t}{dt} \text{ (mol/cm}^2\text{s)} \quad \text{B.1}$$

Where J_{Ni} is the flux of Ni^{2+} ions, V_{aq} is the volume of aqueous solution and A_{em} is the surface area of emulsion droplets, $d[Ni^{2+}]_t/dt$ represents the change of Ni^{2+} ion concentration with time. A_{em} can be estimated from the total volume of emulsion droplets V_{em}, and the surface area and volume of each droplet, S_{drop} and V_{drop} as follows

$$A_{em} = V_{em}\frac{S_{drop}}{V_{drop}} \quad \text{(cm}^2\text{)} \quad \text{B.2}$$

Thus, the flux of Ni^{2+} can be rewritten as:

$$J_{Ni} = -\frac{V_{aq}}{V_{em}}\frac{D_{drop}}{6}\frac{d[Ni^{2+}]_t}{dt} \quad \text{B.3}$$

Where D_{drop} represents the average droplets size. With further developing of the equation:

$$\frac{J_{Ni}}{[Ni^{2+}]_t} = k = -\frac{d[Ni^{2+}]_t}{[Ni^{2+}]_t dt}\frac{D_{drop}}{6}\frac{V_{aq}}{V_{em}} \quad \text{B.4}$$

Where $J_{Ni}/[Ni^{2+}]_t$ represents the mass transfer rate of Ni^{2+} to ELMs (k). The equation can be rewritten as:

$$-k\frac{V_{em}}{V_{aq}}\frac{6}{D_{drop}} = \frac{d[Ni^{2+}]_t}{[Ni^{2+}]_t dt} \quad \text{B.5}$$

Then it can be integrated into the following equation:

$$-k\frac{V_{em}}{V_{aq}}\frac{6}{D_{drop}}dt = dln[Ni^{2+}]_t \quad \text{B.6}$$

Then:

$$-k\frac{V_{em}}{V_{aq}}\frac{6}{D_{drop}}t = ln[Ni^{2+}]_t/[Ni^{2+}]_{ini} \quad \text{B.7}$$

Initially, k can be calculated using the following equation:

$$k = -\frac{ln[Ni^{2+}]_t/[Ni^{2+}]_{ini}}{t}\frac{V_{aq}}{V_{em}}\frac{D_{drop}}{6} \qquad \text{B.8}$$

The following equation (integrated form) was then employed for better parameter estimation:

$$[Ni^{2+}]_t/[Ni^{2+}]_{ini}{=}exp^{\left(-k\frac{V_{em}}{V_{aq}}\frac{6}{D_{drop}}t\right)} \qquad \text{B.9}$$

kinetics tests were repeated 3 times for both the organic and emulsion phase, non-linear regression model based on Equation B.9 was employed (Figure 4.7 (a) and (b) in Chapter 4) since statistical analysis showed that it was more accuracy in parameter estimations. The ratio of V_{aq}/V_{em} was known to be 3.5 and D_{drop} was measured with the help of optical microscope and analysed by software “imageJ”, which gave the diameters of 72 µm and 103 µm for organic and emulsion droplets (Examples were given in Figure A1 (b) and (c), Appendix A). k (m/s) was thus calculated.

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Appendix C: A detailed comparison between ELM and SX technique.

When compared with solvent extraction technique, ELM has the following advantages:

1. The ELM process has a higher surface area to contact with metal ions than SX process, bringing a relatively high efficiency.
2. The ELM process combines solvent extraction and stripping in a single unit, the extractant can be regenerated thus eliminating the equilibrium constraints and bringing a higher loading capacity.
3. The ELM process can be used to treat solution with a much lower solute concentration than SX process, the metal ions can be highly concentrated since the volume of the stripping phase is much lower than the external phase.
4. The combination of solvent extraction and stripping in a single unit will bring a higher acidic concentration gradient, thus enhancing the extraction kinetics.
5. The ELM process generally requires a lower organic extractant than SX process, lowering the materials cost since commercial solvent extractants are generally very expensive.

However, in the meantime, ELM also has several disadvantages:

1. The emulsion stability (including membrane leakage, swelling, breaking) is an issue that prevents the ELM technique from being industrialized on a large scale.
2. The external phase pH was more difficult to control than SX process since membrane leakage of the acid into the external phase is inevitable during the process. This affects the process selectivity.
3. The emulsion needs to be broken afterwards to release the organic and acid.

Also, when compared with SX from the economical perspective, ELM technique generally has a lower investment cost, the amount and size of the equipment are smaller than that in SX process since ELM combines extraction and stripping in one step. It also requires a smaller organic extractant input than SX since the extractant can be regenerated and reused within the membrane phase, this could save a considerable materials cost. In the ELM process, the operating costs were generally considered to be equal or lower than SX despite the fact it requires a certain energy input during the de-emulsification process. Frankenfeld et al. performed an economic evaluation based on bench-scale pilot plant runs, showing that ELM process was 40% cheaper than SX, where the major savings in cost arise from the reduction of processing stages and organic inventory. It should be noted that although the elimination of scrubbings stages and pH regulations during ELM process can significantly save the operating cost, the applications of ELM process are restricted. Thus, ELM process can never be able to completely replace SX process.

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Appendix D: The reaction mechanisms between LIX 984N & Cyanex 301 and copper & nickel ions

1. For copper ion extraction:

LIX 984N was used as the extractant, it is a 1:1 volume blend of 5-nonylsalicylaldoxime (LIX 860N) and 2-hydroxy-5-nonylacetophenone oxime (LIX84) in a high flash point hydrocarbon diluent, the reaction between LIX 984N and copper is shown in Figure D1:

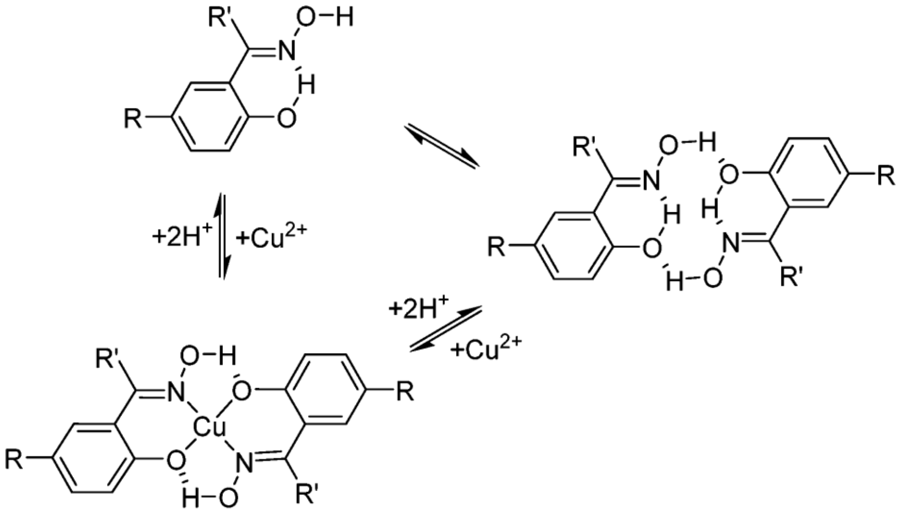

Figure D1 The chemical reaction between copper and LIX 984N, where R and R' represents C_9H_{19}, H or $C_{12}H_{25}$, CH_3.

It can be seen that as phenolic oximes, LIX984N complexes with copper show a square planar coordination environment with a pseudo-macrocyclic structure. The inter-ligand H-bonds between the oxime hydrogen and phenolic oxygen atoms bring a planar donor set and a good cavity size specially for Cu(II) ion.

2. For nickel ion extraction:

Cyanex 301 was used for nickel extraction when pH is over 2.0. According to the hard and soft acids theory, the thio-substituted organic reagents can easily bind to soft to intermediate Lewis acids, such as Ni(II), and Co(II). Depending on the concentration, Cyanex 301 can be monomeric or dimeric. The extraction of nickel with the monomeric form of Cyanex 301 can be described:

$$Ni^{2+} + 2HR + qH_2O \leftrightarrow NiR_2 \cdot qH_2O + 2H^+ \quad D.1$$

It can be seen that this reaction is highly pH dependent. Since Cyanex 301 has a pKa of approximately 1.7, when pH is less than 2.0, it will have difficulty in achieving a very high nickel extraction efficiency, it was found in this work that a 1:1 volume ratio of LIX984N and Cyanex 301 was very effective for nickel extraction when pH is less than 2.0, this was attributed to the neutralization of metal ion charges by the chelating extractant (LIX 984N) and the replacement of residual water from the inner coordination sphere by the other extractant (Cyanex 301), this could render the nickel-LIX984N-Cyanex 301 complex more hydrophobic. The reaction between Ni(II) with 1:1 volume ratio of monomeric LIX984N and Cyanex 301 is shown in Figure D2:

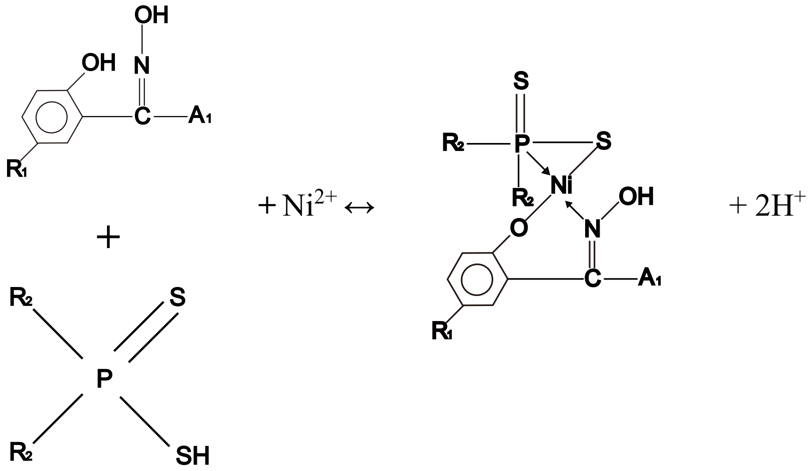

Figure D2 The reaction between Ni(II) with 1:1 volume ratio of LIX984N and Cyanex 301, A_1, R_1 represents H, $C_{12}H_{25}$ or CH_3, C_9H_{19}; R_2 represents C_8H_{17}.

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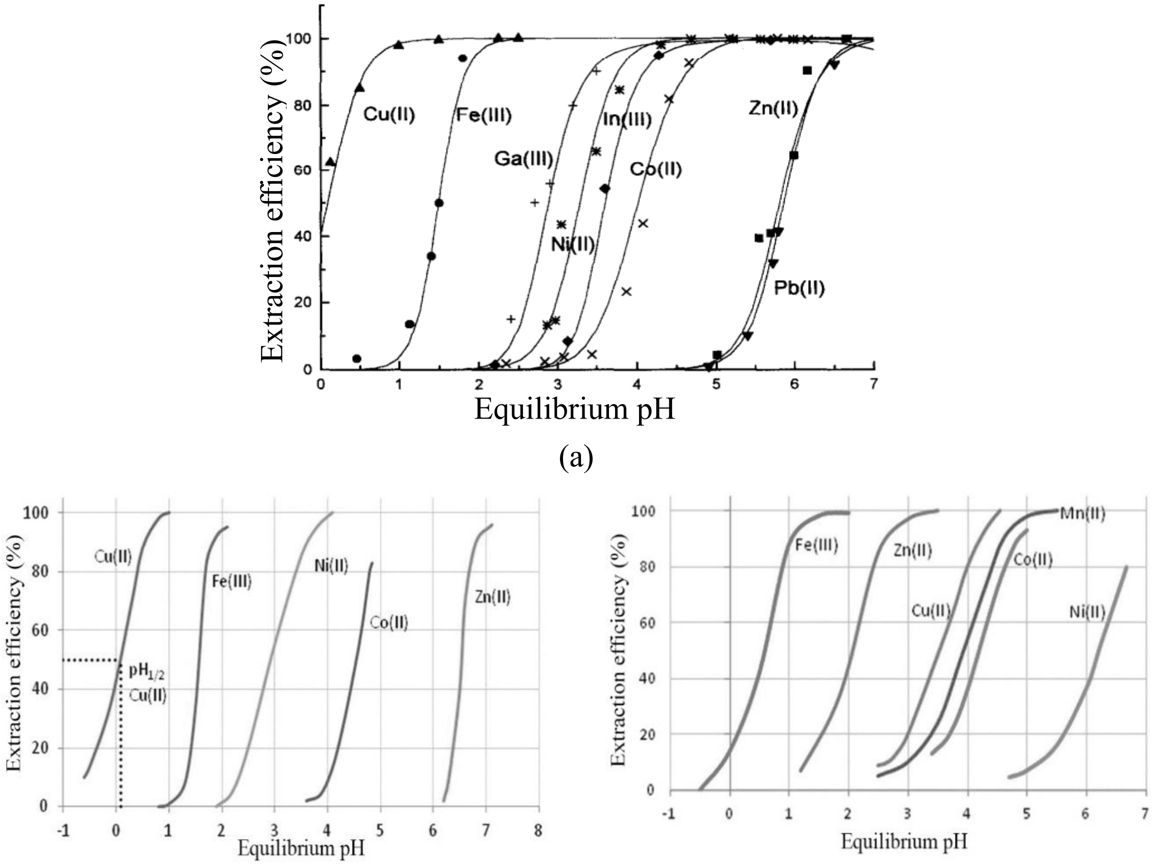
Appendix E: The effect of multiple ionic species in solution

The extraction of multiples ionic metal species has been conducted in various studies, in general, the membrane selectivity needs to be compromised. For example, in Kumbasar’s research, a selective separation of chromium (VI) from acidic solutions containing various metal ions was performed through emulsion liquid membrane using trioctylamine as extractant, it was found that under the optimum testing conditions, over 99% Cr (VI) was removed while the removal percentages for Co, Ni, Cu, Zn and Cd are 2.0%, 1.0%, 3.0%, 8.0% and 13.0%, respectively (initial concentration of all metal ions: 600 ppm); Draxler et al. had performed a study of separation of various metal ions using emulsion liquid membrane through a pilot plant, it was found that zinc, copper, cadmium and lead can easily be separated down to concentrations which are below the limits of most environmental protection agencies. However, for nickel and Cr (VI), a complete separation was not possible, they believed the residence time was not long enough for nickel separation while the co-transport of sulphate ions impeded the Cr(VI) separation.

It should also be noted that the membrane selectivity is affected by many factors, including the feed solution pH, extractant types and compositions. Thus, an improvement of membrane selectivity can be obtained by controlling these factors such as feed solution pH. For instance, as reported by Asghari et al. and Wilson et al., the order of extraction for different ions against equilibrium pH using LIX 984N, AcorgaP50 and Cyanex 272 can be seen in Figure E1. Although it is more difficult to maintain the equilibrium pH in the process of emulsion liquid membrane than solvent extraction, this could provide us prospect towards a better path to improve the separation of multiple ionic species by emulsion liquid membranes.



(a)

(b)

(c)

Figure E1 The order of extraction for different ions against equilibrium pH using LIX 984N (a), AcorgaP50 (b) and Cyanex 272 (c).

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Appendix F: The implementation of ELM technology in a metallurgical operation

Examples of the implementation of emulsion liquid membranes (ELM) technique have been reported by different researchers. Generally, two types of solutions were investigated including heap-leach solutions and waste streams containing much lower levels of metal ions. For the former case, it was reported by Ruppert et al. (1986), a pilot-scale plant using ELM was built by Lenzing AG in Austria for the recovery of zinc from spin baths in viscose production. This technique replaced the traditional solvent extraction and stripping processes and the concentrated zinc solution was then sent for electrowinning to recover the zinc. For the latter case, Wright et al. performed the field tests of the removal of copper ions from mining tailing waste stream at a copper mine in Arizona in 1993.

In some cases where there exists a solution with higher copper ion concentration, it should be noted that the internal stripping liquor concentration may also need to be increased as well as extractant concentration. Unlike traditional solvent extraction process, the ELM process combines the solvent extraction and stripping in a single unit, the acid concentration in the internal phase plays a very important role for copper extraction process. Since the volume of the internal stripping liquor is much lower than the external phase, meaning that fraction of internal phase to external phase can be very high (1:20). Thus, with an increase in copper concentration, in order to strip all the copper from copper-extractant complex and regenerate the extractant to maintain a higher extraction efficiency, the internal stripping liquor may need to be increased to bring sufficient stripping acidity.

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Appendix G: The proposed continuous process flowsheet for pilot-scale plant treating wastewater stream using ELMs