

**NICKEL ION EXTRACTION USING LIQUID-
LIQUID EXTRACTION AND SUPPORTED
LIQUID MEMBRANE**

by

AMIR TALEBI

**Thesis submitted in fulfilment of the requirements
for the degree of Doctor of Philosophy**

September 2016

ACKNOWLEDGEMENT

First of all, I am grateful to the GOD Almighty for helping me to complete this thesis. I would like to express my immeasurable appreciation and gratitude to my main supervisor, Prof. Dr. Teng Tjoon Tow, for his excellent and superior supervision and for his wise, enlightening and instructive comments and guidance. I would also like to thank my co-supervisors, Prof. Dr. Norli Ismail and Associate Prof. Dr. Abbas Fadhl Mubarek Al-Karkhi, whom without their supervision, support, inspiration and motivation, this thesis could not be completed. I place on record my sincere gratefulness to my colleagues and friends, specifically Mr. Pazli Ismail and Mr. David Campbell, for their help and for the excitement and joy that they brought to me. I would also like to express my deepest appreciation for Universiti Sains Malaysia and School of Industrial Technology, for giving me this opportunity to use the facilities and equipment and for their financial support via Research University (RU) grant: 1001/PTEKIND/814239. I take this opportunity to thank all the administrative staff of School of Industrial Technology for their help and kind support, especially Madam. Teh Siew Hong, former laboratory manager of the Environmental Technology division, for her priceless support and cooperation. I would also like to thank my family, Mrs. Farideh Hayati Far and Mr. Behrouz Talebi, Mahsa, Michael, Maximilian, Manouchehr Shahverdi, Bahram and my beloved sister in law, Mahsa Ghafouri Nejad, for their most valuable support and enthusiasm.

Last but not least, I wish to express my sincere acknowledgement to the people of Malaysia, whom I lived with them last couple of years and I learned many things from them. I will be always indebted to them and I wish them ever increasing triumph, success and happiness, forever and ever.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	ix
LIST OF FIGURES	xii
LIST OF PLATES	xvi
NOMENCLATURE	xvii
ABSTRAK	xx
ABSTRACT	xxii
CHAPTER 1.0: INTRODUCTION	
1.1 Research Background	1
1.2 Heavy Metals Sources and Treatment Methods	1
1.3 Problem Statement	5
1.4 Research Scope and Hypothesis	8
1.5 Research Objectives	9
1.6 Thesis Outline	10
CHAPTER 2.0: LITERATURE REVIEW	
2.1 Introduction	12
2.2 Industrial Wastewaters Containing Ni(II) Ion	12
2.3 Liquid-Liquid Extraction (LLE)	14
2.4 Liquid Membrane (LM)	15
2.5 Liquid Membrane Classification	16

3.5 Aqueous Feed and Organic Phase Preparation	50
3.6 Equipment and Experimental Procedures	52
3.6.1 Liquid-Liquid Extraction (LLE) System and Procedures	52
3.7 Ni(II) Ion Extraction from Aqueous Solutions using LLE	53
3.7.1 Ni (II) ion extraction from Aqueous Solutions using Palm Oil-based Organic Phase by LLE	53
3.7.1(a) Screening and Optimization of Ni(II) Ion Extraction from Aqueous Solutions using Palm oil-based Organic Phase	54
3.7.2 Ni(II) Ion Extraction from Aqueous Solutions using Ionic-based Organic Phase	56
3.7.2(a) Ni-SDET Complexation and Sodium Ion Measurement	56
3.7.2(b) Effect of SDET Concentration on Nickel Extraction	57
3.7.2(c) Screening and Optimization of Ni(II) Ion Extraction from Aqueous Solutions using Ionic-based Organic Phase	57
3.7.3 Ni(II) Ion Extraction from Aqueous Solutions using Petroleum -based Organic Solvent by LLE	59
3.7.3(a) Preliminary Studies of Ni(II) Ion Extraction by Di(2-Ethyl Hexyl)Phosphoric Acid (D2EHPA) and Kerosene	59
3.7.3(b) Preliminary Studies on the Effect of Phase Modifier TriButylPhosphate (TBP) on Ni(II) Ion Extraction using D2EHPA and Kerosene	59
3.7.3(c) Preliminary Studies on the Effect of Different Organic Solvents on Ni(II) Ion Extraction using D2EHPA and Kerosene	60
3.7.3(d) The Screening Studies of Ni(II) Ion Extraction using D2EHPA, TBP and Kerosene	60

3.7.3(e) Optimization of Ni(II) Ion Extraction using D2EHPA, TBP and Kerosene	61
3.7.3(f) Interaction Between pH and [D2EHPA] Concentration and Effect of pH On Distribution Ratio	62
3.7.4 Determination of Stripping Agent for Ni(II) Stripping from the Organic Phase into the Stripping Phase	64
3.7.4(a) Selection of Suitable Stripping Agent	64
3.7.4(b) Determination of affecting factors on Stripping Process	64
3.8 Ni(II) Ion Extraction from Aqueous Solutions using Petroleum-based Organic Solvent by SLM	65
3.8.1 Supported Liquid Membrane Reactor Design	65
3.8.2 Ni(II) Ion Extraction and Stripping from Aqueous Solutions using Petroleum-based Organic Solvent by SLM	67
3.8.3 Determination of Mass Transfer Coefficient for Ni(II) Ion Extraction by D2EHPA and Kerosene using Supported Liquid Membrane	69
 CHAPTER 4.0: RESULTS AND DISCUSSION	
4.1 Introduction	70
4.2 Ni(II) Ion Extraction from Aqueous Solutions using Palm Oil-based Organic Phase	70
4.2.1 Screening Studies on Ni(II) Ion Extraction from Aqueous Solutions using Palm Oil-based Organic Phase	70
4.2.2 Optimization of Ni(II) Ion Extraction from Aqueous Solutions using Palm Oil-based Organic Phase	72

4.2.3 Effect of TBP on Phase Modification During Ni(II) Ion Extraction using Palm Oil-based Organic Phase	76
4.3 Ni(II) Ion Extraction from Aqueous Solutions using Ionic-based Organic Phase	77
4.3.1 Preliminary Studies on Ni(II) Ion Extraction from Aqueous Solutions using Ionic-based Organic Phase	77
4.3.1(a) Ni-SDET Complexation and Sodium Ion Measurement	77
4.3.1(b) Effect of pH on Ni(II) Ion Extraction using SDET as Carrier and Octanol as Diluent	80
4.3.1(c) Effect of [SDET] and pH on Ni(II) Ion Extraction and Distribution Ratio	81
4.3.2 Screening Studies of Ni(II) Extraction using Ionic-based Organic Phase	83
4.3.3 Optimization of Ni(II) ion Extraction using Ionic-based Organic Phase	86
4.4 Ni(II) Ion Extraction from Aqueous Solutions using Petroleum-based Organic Solvent	87
4.4.1 Preliminary Studies of Ni(II) Ion Extraction by D2EHPA and Kerosene	87
4.4.2 Preliminary Studies on the Effect of Phase Modifier (TBP) on Ni(II) Ion Extraction using D2EHPA and Kerosene	88
4.4.3 Preliminary Studies on the Effect of Organic Solvents on Ni(II) Ion Extraction using D2EHPA and Kerosene	91
4.4.4 Screening Studies of Ni(II) Ion Extraction by LLE using D2EHPA, TBP and Kerosene	92
4.4.5 Optimization of Ni(II) Extraction by LLE using D2EHPA, TBP and Kerosene	94
4.4.6 Interaction Between pH and D2EHPA Concentration	96

4.4.7 Determination of Stripping Agent for Ni(II) Ion Stripping from the Organic Phase into the Stripping Phase	103
4.4.7(a) Selection of the Stripping Agent	103
4.4.7(b) Determination of Affecting Factors on Stripping Process	104
4.5 Optimization of Ni(II) Extraction by D2EHPA and Kerosene using Supported Liquid Membrane	106
4.6 Determination of Mass Transfer Coefficient for Ni(II) Ion Extraction by D2EHPA and Kerosene using Supported Liquid Membrane	108

CHAPTER 5.0: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions	111
5.2 Recommendations	113

REFERENCES	115
-------------------	-----

APPENDICES

Appendix A. Buffer Solution Calculation and Preparation, used in Ni (II) Ion Extraction and Stripping by SLM

Appendix B. The Newly Designed Supported Liquid Membrane

LIST OF PUBLICATIONS

LIST OF TABLES

		Page
Table 1.1	Acceptable conditions for discharge of industrial effluent or mixed effluent of standards A and B	2
Table 1.2	Heavy metals treatment techniques: advantages, disadvantages and removal efficiency	4
Table 2.1	Application of liquid-liquid extraction in metals removal	15
Table 2.2	Metal contaminated wastewater treatment using BLM	19
Table 2.3	Metal contaminated wastewater treatment using ELM	20
Table 2.4	Conventional organic solvents characteristics, used as diluent in LM	29
Table 2.5	Vegetable oils as diluent in LM	30
Table 2.6	Physico-chemical characteristics of conventional vegetable oils used in LM	31
Table 2.7	Nickel ion extraction using ionic as carrier	38
Table 2.8	PTFE membrane physical characteristics for using in SLM	40
Table 2.9	Application of statistical tools in heavy metals removal	43
Table 3.1	Materials list used in the research	45
Table 3.2	List of software programs used in this research	46
Table 3.3	Studied factors on nickel extraction using palm oil-based organic phase	54
Table 3.4	Screening design for nickel extraction using palm oil-based organic phase	55
Table 3.5	Fixed factors for Ni(II) ion extraction	55

Table 3.6	Selected factors used in nickel extraction by SDET as carrier in octanol	58
Table 3.7	Screening for nickel extraction by SDET as carrier in octanol using factorial 2^3 plus 5 center points	58
Table 3.8	Effect of phase modifier (TBP) on nickel ion extraction using petroleum-based organic phase	59
Table 3.9	Selected factors and related ranges for screening of nickel extraction by LLE	60
Table 3.10	Selected factors and related ranges for screening of nickel extraction by LLE	61
Table 3.11	2^3 factorial design of experiments plus 5 centre points, for optimization of nickel extraction using D2EHPA in kerosene	62
Table 3.12	2^3 fractional factorial design of experiments for optimization of nickel stripping using D2EHPA in kerosene in organic phase and sulphuric acid as stripping agent	65
Table 3.13	Studied factors for Ni(II) ion extraction and stripping from aqueous solutions using petroleum-based organic phase by SLM	68
Table 3.14	Studied factors for Ni(II) ion extraction and stripping from aqueous solutions using petroleum-based organic phase by SLM	68
Table 3.15	2^2 factorial design with 4 axial points and 6 centred points; Optimization of Ni(II) ion extraction and stripping, using petroleum-based organic phase by SLM	69
Table 4.1	Studied factors on nickel extraction using palm oil based organic phase	71

Table 4.2	ANOVA for screening of nickel extraction using palm oil-based organic phase	72
Table 4.3	Observed and predicted values of nickel extraction using palm oil-based organic phase. 2^2 factorial design including 4 axial points and 5 centered points	73
Table 4.4	ANOVA for nickel extraction using palm oil-based organic phase	73
Table 4.5	Selected factors used in LLE and the related ranges	83
Table 4.6	Screening studies of Ni(II) extraction using ionic-based organic phase	83
Table 4.7	ANOVA for optimization of selected factorial model, Analysis of variance of screening	85
Table 4.8	ANOVA for optimization of selected factorial model, Analysis of variance	86
Table 4.9	Selected factors and related ranges for screening of nickel extraction by LLE	92
Table 4.10	ANOVA for selected factorial model, Analysis of variance of screening	93
Table 4.11	ANOVA for selected factorial model, Analysis of variance of screening	95
Table 4.12	pH variation after mixing the aqueous feed phase with organic phase; initial aqueous phase pH: 4.5	98
Table 4.13	ANOVA for response surface quadratic model for nickel ions stripping	104
Table 4.14	ANOVA for response surface quadratic model of optimization	105
Table 4.15	Mass transfer coefficient for similar studies	108

LIST OF FIGURES

	Page	
Figure 2.1	Liquid membrane classification based on module design and solute transport mechanism	17
Figure 2.2	A: U-tube BLM reactor for an organic phase with high density solvent; B: H-tube BLM reactor for an organic phase with low density solvent	18
Figure 2.3	Emulsion liquid Membrane (ELM)	19
Figure 2.4	Schematic of a supported liquid membrane (SLM)	22
Figure 2.5	Simple transports of species (S) from feed phase (F), through LM (M) to stripping phase (S)	23
Figure 2.6	Facilitated transport of species “S” through LM	24
Figure 2.7	Solute concentration [S] Vs distance (H) profile from the aqueous feed phase through the LM to the aqueous stripping phase	25
Figure 2.8	Active transport of species “S” through LM	28
Figure 2.9	A: D2EHPA monomer; B: D2EHPA dimer	33
Figure 2.10	A: Metal ion (M^{2+}) complex with carrier ligand (L^-) as an outer sphere (water molecules intervention during metal-carrier complexation) B: Metal ion (M^{2+}) complex with carrier ligand (L^-) as an inner sphere	36
Figure 3.1	A flow chart of the overall experiment	49
Figure 3.2	The scaled schema of the A: SLM profile, B: SLM top view	66

Figure 4.1	Three dimensional response surface of nickel removal as a function of pH and [D2EHPA]	75
Figure 4.2	Interaction plot between pH and D2EHPA during nickel extraction using palm oil-based organic phase	75
Figure 4.3	[Na ⁺] measurements in the aqueous feed phase after extraction of nickel; Initial metal concentration: 100 mg/L, [SDET]: 10 mM	79
Figure 4.4	Effect of pH on nickel extraction; initial metal concentration: 100 mg/L; [SDET]: 10 mM	80
Figure 4.5	Effect pH on nickel extraction using different carrier concentrations; Nickel concentration: 100 mg/L	81
Figure 4.6	Effect of carrier concentration on distribution ratio (pH: 3.5)	82
Figure 4.7	Normal plot of the design for significant factors for nickel extraction	84
Figure 4.8	Three-dimensional response surface for nickel extraction as a function of shaking time and pH	84
Figure 4.9	Three-dimensional response surface for optimum nickel extraction as a function of shaking time and pH obtained by FCCD	87
Figure 4.10	Effect of pH on extraction efficiency. [Ni ²⁺]: 100 mg/L; [D2EHPA]: 50; shaking time: 10 minutes	88
Figure 4.11	Effect of phase modifier on nickel extraction in organic phase (pH: 4.5; [Ni] _{ini} : 100 mg/L; [D2EHPA]: 50 mM; TBP: 5 mM); 1: kerosene; 2: kerosene + D2EHPA; 3: kerosene + D2EHPA + TBP; 4: kerosene+ TBP	89

Figure 4.12	Effect of benzene, kerosene and xylene on nickel extraction ([D2EHPA]: 50 Mm; [Ni] _{ini} : 100 mg/L; TBP: 5 mM)	91
Figure 4.13	Normal plot of the design for significant factors for nickel extraction by LLE	92
Figure 4.14	Three-dimensional response surface for nickel removal as a function of [D2EHPA] and pH	94
Figure 4.15	Optimized three-dimensional response surface for nickel extraction as a function of [D2EHPA] and pH by LLE	95
Figure 4.16	log D versus pH with [D2EHPA]: 150 mM; Initial [Ni ²⁺]: 100 mg/L	97
Figure 4.17	pH variation after mixing the aqueous feed phase with organic phase loaded by 2, 10, 50, 100 and 150 mM of D2EHPA; initial aqueous phase pH of 4.5, initial nickel concentration of 100 mg/L	99
Figure 4.18	log D versus log [(RH) ₂] (pH: 4.7; Initial [Ni ²⁺]: 100 mg/L)	100
Figure 4.19	Nickel complexation with dimeric D2EHPA	101
Figure 4.20	Effect of various pH and carrier concentration on nickel extraction; initial [Ni ²⁺]: 100 mg/L	103
Figure 4.21	Determination of suitable stripping agent; [Ni ²⁺]: 96 mg/L	104
Figure 4.22	Three-dimensional response surface for nickel stripping as a function of [D2EHPA] and [H ₂ SO ₄]	105
Figure 4.23	Three-dimensional optimized response surface for nickel removal as a function of stirring time and stirring speed	108
Figure 4.24	Kinetics plot for nickel ions transport; Initial nickel concentration: 100 mg/L	109

Figure 4.27 Complexation and de-complexation between nickel
and D2EHPA at feed-organic and organic-stripping phase
interfaces

111

LIST OF PLATES

		Page
Plate 4.1	The effect of TBP on phase separation; A: Emulsified organic phase, B: De-emulsified organic phase	76
Plate 4.2	Organic phase color change. A: The organic phase before mixing, B: The organic phase after mixing	78

NOMENCLATURE

A	Membrane surface area (m ²)
<i>a</i>	Metal valence
ANOVA	Analysis of the variation
<i>b</i>	number of D2EHPA molecules
BLM	Bulk liquid membrane
[C]	Carrier concentration (M, mg/L)
CAS	Chemical Abstracts Service
D	Distribution ratio
DF	Degree of freedom
ELM	Emulsion liquid membrane
FAAS	Flame atomic adsorption spectrophotometer
FCCD	Face centered composite design
IUPAC	International union of pure and applied chemistry
J	Diffusion flux (M, g/cm ² /s)
<i>J_f</i>	Diffusion flux in feed phase (M, g/cm ² /s)
<i>J_m</i>	Diffusion flux in membrane phase (M, g/cm ² /s)
<i>J_s</i>	Diffusion flux in stripping phase (M, g/cm ² /s)
<i>K_a</i>	Acid dissociation constant
<i>k_m</i>	Mass transfer coefficient (m/s)
<i>K_c</i>	Equilibrium constants
<i>L⁻</i>	Carrier ligand
LLE	Liquid-liquid extraction
LM	Liquid membrane

M^{2+}	Metal ion
$[M^{2+}]_{ini}$	Initial metal concentration in feed phase (mg/L)
$[M^{2+}]_t$	Metal concentrations at time of sampling (mg/L)
$M(R-RH)$	Metal-carrier complex
MS	Mean square
MgO	Magnesium oxide
n	Number of molecules of carrier in metal-carrier complex, metal valence
Ni(II)	Nickel(II) ion
$[Ni^{2+}]_{ini}$	Nickel initial concentration (M, mg/L)
$[Ni^{2+}]_t$	Nickel concentrations at time of sampling (M, mg/L)
$[Ni^{2+}]_{org, eq}$	Nickel concentrations in organic phase equilibrium (M, mg/L)
$[Ni^{2+}]_{aq, ini}$	Initial nickel concentrations in aqueous phase (M, mg/L)
$[Ni^{2+}]_{aq, eq}$	Nickel concentrations in aqueous phase equilibrium (M, mg/L)
O:A	Organic to aqueous phase ratio
O/W/O	Organic-Water-Organic
PE	Polyethylene
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidenedifluoride
R^2	R squared
$(RH)_2$	D2EHPA dimer
RSD	Relative standard deviations
RSM	Response surface methodology

[S]	Solute concentration
SS	Sum of Squares
[S _f]	Solute concentration in the feed phase
[S _{fm}]	Solute concentration at the feed phase-LM interface
[S _m]	Solute concentration in the membrane phase
[S _{ms1}]	Solute concentration at the LM–stripping phase interface
[S _s]	Solute concentration in the stripping phase
[S=C]	Solute-carrier complex concentration
ΔS	Solute concentration difference between stripping phase and feed phase
SDET	Sodium diethyldithiocarbamate
SO ₄ ²⁻	Sulphate ion
v	Feed phase volume (mL, m ³)
W/O/W	Water-Organic-Water

Greek Letters

μ	Micro
---	-------

PENGEKSTRAKAN ION NIKEL MENGGUNAKAN PENGEKSTRAKAN CECAIR-CECAIR DAN MEMBRAN CECAIR BERSANGGA

ABSTRAK

Pengekstrakan cecair-cecair dan cecair-membran bersangga boleh dianggap sebagai alternatif sesuai untuk teknik-teknik penyingkiran logam berat yang lazim. Kedua-dua teknik mempunyai kebaikan seperti pengekstrakan dan penyingkiran logam berat secara berturut dalam satu unit, penyaluran secara menaik, selektiviti yang tinggi, pemulihan yang tinggi dan penggunaan tenaga yang rendah. Kajian ini bertujuan untuk meneliti kecekapan pengekstrakan cecair-cecair dan menyokong penggunaan teknik membran cecair untuk penyingkiran ion nikel. Tiga fasa organik yang berbeza, termasuk fasa berasaskan minyak sawit, pembawa-ionik dan petroleum dikaji bagi menentukan keadaan optimum untuk pelbagai parameter dalam pengekstrakan ion nikel dan penyingkirannya. Rekabentuk komposit berpusat muka dan kaedah respon permukaan telah digunakan untuk mengoptimumkan dan menentukan kesan impak serentak parameter-parameter yang memberi kesan terhadap pengekstrakan nikel. Keputusan LLE bagi pengekstrakan ion nikel dan proses-proses penyingkirannya yang optimum digunakan dalam penyingkiran ion nikel menerusi SLM. Faktor-faktor yang telah diambil kira dalam rekabentuk adalah pH fasa muatan, kepekatan pembawa, masa pengoncangan, laju pengacauan, kepekatan garam lengai dan kepekatan pengubahsuai fasa. Keputusan pengekstrakan cecair-cecair menunjukkan bahawa kerosin yang dimuat dengan di-2-ethylhexylphosphoric acid dengan kepekatan 0.156 M (sebagai pembawa) dan asid sulfurik dengan kepekatan 1.5 M untuk penyingkiran dan pengekstrakan ion nikel telah membawa kepada penyingkiran nikel sebanyak 95.57%. Apabila minyak sawit digunakan sebagai diluen dan asid di(2-etilhexil) fosforik sebagai pembawa,

pengekstrakan nikel sebanyak 95.57% telah dicapai menerusi keadaan optimum dengan pH: 1.1 dan D2EHPA: 200 mM; manakala kecekapan penyingkiran nikel yang optimum untuk fasa organic berasaskan ion yang mempunyai fasa pemuatan sodium diethylthiokarbamat dengan kepekatan 73.45 mM sebagai pembawa dalam oktanol (diluen) pada pH fasa pemuatan 2.89 menunjukkan kecekapan 94.93%. Keputusan untuk keadaan optimum bagi penyingkiran nikel menggunakan membrane cecair yang disokong ialah pH fasa muatan sebanyak 4.8, [D2EHPA]: 0.156 M, masa pengacauan:450 min dan agen fasa penyingkiran sebanyak 1.5 M H₂SO₄ yang menyebabkan penyingkiran nikel sebanyak 95.38%. Boleh disimpulkan bahawa unit SLM dan keadaan optimum untuk pengeluaran ion nikel dan penyingkirannya yang telah disyorkan boleh dianggap sebagai kaedah pengekstrakan ion nikel yang sesuai.

NICKEL ION EXTRACTION USING LIQUID-LIQUID EXTRACTION AND SUPPORTED LIQUID MEMBRANE

ABSTRACT

Liquid-liquid extraction (LLE) and supported liquid membrane (SLM) can be considered as a suitable alternative for conventional heavy metals removal techniques. Both techniques have interesting advantages such as simultaneous extraction and stripping of heavy metals in a single unit, uphill transport, high selectivity, high recovery, and low energy consumption. This research aims to examine the efficiency of liquid-liquid extraction and supported liquid membrane technique on nickel ion removal. Three different organic phases, including palm oil-based, ionic carrier-based and petroleum-based organic phases were investigated to find out the optimum condition of various effective parameters on nickel ion extraction and stripping. Face centered composite design and response surface methodology were used for optimization and determination of the interactive and simultaneous impact of parameters affecting the nickel extraction. The results of LLE for optimum extraction and stripping processes were applied in nickel ion removal by SLM. The factors considered in the design were feed phase pH, carrier concentration, shaking time, stirring time, stripping agent concentration, stirring speed, inert salt concentration and phase modifier concentration. The liquid-liquid extraction results revealed that kerosene loaded with di-2-ethylhexylphosphoric acid of 0.156 M (as carrier) and sulphuric acid of 1.5 M for nickel ion extraction and stripping, respectively, resulted in 95.1% of nickel removal. In the case of using palm oil as diluent and di(2-ethylhexyl)phosphoric acid as carrier, 95.57% of nickel extraction could be obtained in the optimum condition of pH: 1.1 and D2EHPA: 200 mM; while optimum nickel extraction efficiency for ionic-based organic phase,

containing feed phase 73.45 mM of sodium diethyldithiocarbamate as carrier in octanol (diluent) at the feed phase pH: 3.89, with 94.93% of extraction efficiency. The results of optimum conditions for nickel removal using supported liquid membrane were feed phase pH 4.8, [D2EHPA]: 0.156 M, stirring time: 450 minutes and stripping phase agent of 1.5 M of H₂SO₄ which resulted in 95.38% of nickel removal. It could be concluded that the proposed SLM unit and optimum condition for nickel ion extraction and stripping can be considered as a suitable nickel ion extraction method.

CHAPTER 1

INTRODUCTION

1.1 Research Background

This chapter contains an overview of the research; consists of an initial introduction on heavy metals contamination problem statement and a brief review of various heavy metals treatment techniques and methods. The increasing demands on finding cost effective and environmental friendly methods for removal of heavy metals are discussed along with hypothesis, objectives and main framework of this thesis.

1.2 Heavy Metals Sources and Treatment Methods

Heavy metals contamination of aquatic sources is one of the biggest concerns in developed or developing countries (Sin et al., 2001; Armitage et al., 2007; Yuan et al., 2011). An eager demand of economic growth due to globalization and intensive industrial and agricultural activities to cover up the growing consumption life style, has led to discharge of large quantities of hazardous materials (including heavy metals) into rivers, seas, oceans and underground water resources (Srebotnjak et al., 2012; Su et al., 2013; Islam et al., 2014). Heavy metals are important pollutants with major injurious and harmful effects on terrestrial and aquatic ecosystems (Duruibe et al., 2007; Sanchez, 2008). Many researches have focused on direct negative effects of heavy metals on organisms, from the general toxicity of heavy metals to a variety of biological processes (Boyd, 2010).

Exposure to heavy metals has direct and serious consequences of toxicity on human body and health. It causes serious health disorders such as headache, nausea, vomiting, depression, lethargy, and neurologic signs such as seizures, ataxia, kidney damage, renal disorder, chronic asthma, coughing and many others (Kurniawan et al., 2006; Hamidi et al., 2008). Environmental organizations have set standard thresholds for heavy metal containing wastewater discharge.

In Malaysia, “Environmental Quality (Industrial Effluents) Regulations” guideline for acceptable industrial effluent discharge, include permissible discharge limits of heavy metals under standard A and B (EQA 1974, 2014). Standard A is applicable to discharge into any inland waters within the catchment areas, while Standard B is applicable to any other inland waters or Malaysian waters (Table 1.1).

Table 1.1 Acceptable conditions for discharge of industrial effluent or mixed effluent of standards A and B

Heavy metal (mg/L)	Standard A	Standard B
Boron	1.0	4.0
Cadmium	0.01	0.02
Chromium (III)	0.2	1.0
Chromium (VI)	0.05	0.05
Copper	0.2	1.0
Lead	0.1	0.5
Manganese	0.2	1.0
Mercury	0.005	0.05
Nickel	0.2	1.0
Iron	1.0	5.0
Tin	0.2	1.0
Zinc	2.0	2.0

Most heavy metals removal techniques such as coagulation, precipitation, adsorption, ion exchange, etc., have various advantages and disadvantages. For example, chemical precipitation, coagulation and flocculation despite being cost

effective and simple in operation, provide considerable amount of sludge and hence require extra costs for sludge disposal operations (Shammas, 2005; O'Connell et al., 2008; Pang, et al., 2009; Renault et al., 2009). Heavy metals adsorption as another conventional metal removal method has been found interesting for many researches recently and has shown advantages such as high efficiency and relatively cost effective (Chowdhury et al., 2011; Machida et al., 2012; Li et al., 2013; El-Sadaawy and Abdelwahab, 2014) but low selectivity and waste production are adsorption disadvantages.

Membrane filtration, including ultra-filtration, reverse osmosis and liquid membrane has been investigated vastly by many researches and has shown advantages such as small space requirement, high efficiency, high selectivity and effective metals recovery (Coopera et al., 2004; Vigneswaran et al., 2004; Kurniawan et al., 2006; Leon and Guzman 2008; Liu et al., 2008; Walkowiak and Kozlowski, 2009; Barakat and Schmidt, 2010; Barakat, 2011; Hassaine-Sadi et al., 2012; Al-Rashdi et al., 2013; Lin et al., 2013; Bhatluri et al., 2014) but high power consumption, membrane restoration, high costs of operation, process complexity and membrane fouling are considered as disadvantages of membrane filtration technology (Fu and Wang, 2011).

Table 1.2 summarizes some conventional heavy metals treatment methods, including the removal efficiency, operational conditions, advantages and disadvantages of each technique.

1.3 Problem Statement

Nickel is a hazardous and toxic heavy metal causing serious health disorders (Katsou et al., 2010) which can be found in many industrial wastewaters such as plating, pesticides and Ni-Cd battery manufacturer wastewaters, as the main source of this toxic heavy metal (Ahluwalia and Goyal, 2007). Nickel ions (Ni^{2+}) in wastewater sources are mixture of threat and opportunity and have convinced many researchers to strike out into removal and recovery processes. Apart from negative and hazardous impacts of nickel on living ecosystems as a toxic and hazardous substance, it is considered as a strategic metal in industry due to its toughness, corrosion resistance and as a super alloy (Padmavathy et al., 2003; Villaescusa et al., 2004). Nickel is used in various industries such as electro plating, batteries manufacturing, painting, mineral processing and forging (Dermentzis, 2010; Bhanvase and Deosarkar, 2013).

While ion exchange and adsorption as conventional methods of Ni^{2+} removal have been used for many years, these methods have certain fundamental flaws such as the capacity of exchange or adsorption, which limits the methods to be used for low concentration wastewater treatment, low selectivity potential, or limitation by the saturated adsorbents and ion exchange resins which are still major problems of these methods (Peng et al., 2014).

In recent years, researchers have been working on a method to remove and recover heavy metals species simultaneously, called liquid membrane (LM) technique. Liquid membrane systems are being investigated widely in various fields such as chemistry (organic, inorganic and analytical), biotechnology, biomedical

technology, wastewater treatment, etc. (Muthuraman et al., 2009; Singha et al., 2011). LM can be applied for different purposes including selective separation and recovery of heavy metals, separation of aromatics from hydrocarbons, antibiotics purification, purification of aromatics such as benzene, xylene and toluene, protein extraction using aqueous two-phase systems, dyes and pigments removal, metallurgical purifications, etc. (Chang et al., 2011a).

In conventional heavy metal treatment methods there is little emphasis on the recovery of the removed metals which, if available, is normally carried out in a separate unit by elution with suitable reagents and this incurs additional cost (Kurniawan et al., 2006), while in LM both removal and recovery of the separated species can be combined in one unit. Hence, liquid membranes are more cost effective and environmental friendlier than other conventional heavy metals removal techniques because they need lower volumes of organic reagents (Leon and Guzman, 2005; Keith et al., 2007; Armenta et al., 2008).

The economic comparison between liquid membrane and solvent extraction method has shown 20% to 40% investment saving for using liquid membrane technique (Wasan, 1988). The other advantage of liquid membrane is being highly integrated, which enables the researchers to combine various membrane operations suitable for separation and conversion units. Practically, there are a lot of opportunities for membrane separation processes in all areas of industry (Kislik, 2010).

Three types of LM, namely bulk liquid membrane (BLM), emulsion liquid membrane (ELM) and supported liquid membrane (SLM) have gone under numerous investigations recently (Othman et al., 2004). Extraction and stripping of various heavy metals have been studied using all types of LM but among these different models, SLM has shown a huge potential to be investigated and since the whole system is influenced by various factors and parameters, such as stirring speed, carrier concentration, aqueous phases pH etc., it is necessary to study the simultaneous effect of these parameters on the extraction efficiency.

Successful applications of SLMs are possible due to their advantages compared to other separation methods. The main advantages of SLMs are the small amounts of organic phase and extractant (carrier) used, one-step mass transfer, the possibility of achieving high separation factors, concentration of extracted compound(s) during separation, and low separation costs. Nevertheless, there are some problems limiting the practical application of SLM. The main problem is the stability of the liquid membrane, caused by leakage and/or losses of membrane phase components during transport process. The other reason for the LM instability is due to the elution of the carrier from the membrane to aqueous solutions and formation of [metal ion-carrier] complex on the aqueous/membrane interface (Kamiński and Kwapiński, 2000). However, by proper choice of the micro-porous polymeric support and using organic solvents as a membrane phase and membrane phase components, the instability can be significantly reduced (Dzygiel and Wiczorek 2010).

Apart from membrane stability, it is necessary to take into account the simultaneous interaction effect of those parameters on species extraction during liquid membrane operation. Since various parameters could affect extraction process, it is vital to practically and scientifically monitor, analyze and investigate the effect of each involved factor on the other ones. This so called “simultaneous interaction” effect of the parameters are analyzed and determined using optimization statistical tool such as face centered composite design (FCCD) or response surface methodology (RSM).

1.4 Research Scope and Hypothesis

Metal extraction consists of various parameters and factors engaged. Each factor has a certain and unique impact on metal extraction process. However, a problem that has not been noticed widely is the interaction effect of the studied factors on metal extraction. It is well discussed that common factors such as feed phase pH and carrier concentration have direct effect on the extraction efficiency but to the author best knowledge, the mechanism of co-relation between factors has not been encountered sufficiently.

In this study, first it was hypothesized that during extraction process (at the feed-organic phase interface), nickel cation is replaced by a cation species in the carrier to form nickel-carrier complex and two carriers, Di-(2-ethylhexyl) phosphoric acid (D2EHPA) and sodium diethyldithiocarbamate trihydrate (SDET) were chosen for the extraction facilitation. For D2EHPA it was hypothesized that nickel cation is replaced by H^+ to form Ni-D2EPA complex.

The release of H^+ from D2EHPA into the aqueous feed phase leads to drop of pH value in the aqueous feed phase, which is observed, monitored and confirmed by ΔpH measurement after each extraction run. For SDET it was hypothesized that in aqueous-organic interface, nickel cation is replaced by Na^+ cation to form Ni-SDET complex. For this purpose, the sodium concentration of the aqueous feed phase was measured before and after extraction. To evaluate the interaction effect of different parameters on each other (and on extraction process), face centered composite design of experiments for each phase was introduced and applied, the results of analysis of variance with the evidence of p-value show the significance of each factor (singular or interactive) on extraction process.

A comparison between the suitability of other organic solvents such as benzene and xylene as diluent was made as well. In order to overcome the SLM reactor issue, which is mostly designed as two separated cells and create some performance difficulties during laboratory experiments (such as leakage between the aqueous phases or low membrane surface area), a modification of SLM reactor was designed and used which by using a flange type of membrane container and conical shape cut off wall, eases the installation and performance difficulties.

1.5 Research Objectives

The overall objective of this study is to determine and identify the optimum condition for nickel ion extraction from aqueous solutions using liquid-liquid extraction and supported liquid membrane. For this purpose, the objectives of current research are:

- (a) To determine a suitable diluent, solvent and carrier for nickel extraction from aqueous solutions.
- (b) To identify suitable stripping agent for nickel stripping from the loaded organic phase into the stripping phase.
- (c) To optimize and determine the simultaneous effect of different factors on nickel ion extraction from aqueous solutions and to determine the effect of interaction between factors in nickel extraction process.
- (d) To evaluate the effect of the optimized condition on nickel ion extraction, using a newly-designed SLM.

1.6 Thesis Outline

Chapter one (Introduction) presents a brief preface of heavy metals contamination and pollution created by industrial wastewater, followed by the related difficulties and problems of such an action threatening living ecosystems. A review of different heavy metals treatment methods is presented and problem statement is discussed consequently. Chapter one ends with the thesis objectives.

Chapter two (Literature Review) provides more information about liquid membrane, liquid-liquid extraction and the application of different carriers and diluents on heavy metals removal using liquid membrane. An attempt to describe the mass transfer phenomena of LM is presented in this chapter. Optimization statistical tools such as RSM and CCD are discussed.

Chapter three (Materials and Methods) consists of materials, instruments and equipment which have been used in the current research. Experimental procedures

for liquid-liquid extraction and supported liquid membrane along with the advantages of proposed reactor design are discussed. The research flow chart can be considered as chapter three abstract.

Chapter four (Results and Discussion) elaborates the obtained results of the current research, including preliminary studies and results of nickel ion extraction by liquid-liquid extraction studies, screening experiments, optimization of the data, results of stoichiometry and complexation studies and results of nickel ion extraction and stripping by supported liquid membrane.

Chapter five (Conclusions and Recommendations) as the final chapter, summarizes the highlighted achievements of the current research which were persuaded as the objectives. Overall conclusion of this research is presented and possible recommendations and potential research opportunities related to the presented thesis are suggested.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter starts with a literature review on industrial wastewater containing nickel, followed by an overview on liquid extraction and liquid membrane treatment technique, and a brief review on liquid membrane classification. The role of crucial parameters of a liquid membrane system such as diluents and carriers as well as a review on ionic-based organic phase liquid membrane as potential green carriers have been described and an overview of solute transport properties and mechanism through liquid membrane is presented. A literature survey on extraction of heavy metals by supported liquid membrane technique is presented and finally, statistical methods of design and analysis of the experiments such as face centered composite design and response surface methodology, which have been used in screening and optimization of the experiments, are discussed.

2.2 Industrial Wastewaters Containing Ni(II) Ion

Heavy metals play a major role in industries. There are various methods and techniques for heavy metals removal from industrial wastewater. Reserchers have investigated conventional heavy metals removal on a wide range of heavy metals, such as chemical precipitation for copper, zinc, chromium and lead removal (Guo et al., 2006; Chen et al, 2009), ion exchange for lead and zinc removal (Athanasiadis and Helmreich, 2005; Inglezakis et al., 2007), coagulation and flocculation for cadmium, manganese and copper removal (Charerntanyarak, 1999; Li et al., 2003)

and membrane filtration for cobalt, copper, nickel and cadmium removal (Akita et al., 1999; Qdais and Moussa, 1999; Chaabane et al., 2006).

Among various heavy metals used in industries, nickel is one of the metals that are used in various fields such as, batteries manufacturing, mining, electroplating, metallic plate manufacturers, vitreous enameling, printed circuit board manufacturing, stainless steel, jewelry, coinage, catalyst and paint formulations (Aksu and Dönmez, 2006; Krishnan et al., 2011; Ma et al., 2014; Jeon and Cha, 2015). Among these industrial nickel consumers, nickel-cadmium batteries have numerous applications such as cordless electric utensils, cordless telephones, airplane engine starters, and communicational distribution systems (Matsumiya et al., 2014) and the effluent of nickel-cadmium battery manufacturers are considered as the main source of nickel contaminated wastewaters.

On the other hand, when nickel exists in high concentration of Ni^{2+} in aqueous solution it may cause severe damage to lungs, kidneys, gastrointestinal distress (nausea, vomiting and diarrhea), pulmonary fibrosis, renal edema and skin dermatitis (Malamis and Katsou, 2013). The concentration of nickel ions in wastewaters varies from 0.5 mg/L to 1000 mg/L (Krishnan et al., 2011). However, according to the Department of Environment, Ministry of Natural Resources and Environment in Malaysia, acceptable concentration of nickel discharge for industrial wastewater effluent (standards A and B) is 0.1-0.2 mg/L. In Malaysia, industries dealing in electroplating, electronics, batteries and metal treatment/fabrication are the major sources of heavy metals and specifically nickel contamination. Many of these

industries are located in the western coast of the Malaysia peninsular, which includes Klang Valley, Malacca, Johor Bahru and Penang (Onundi et al., 2010).

2.3 Liquid-Liquid Extraction (LLE)

Liquid-Liquid Extraction (LLE) is the principal and fundamental step for liquid membrane application. LLE is an essential preliminary investigation in order to determine the best and optimum condition of various parameters (such as equilibrium pH, mixing time, carrier concentration, etc.) affecting the solute (metal ion, organic compound, drug, etc.) extraction efficiency. LLE system consists of two phases, named as aqueous phase and organic phase. Aqueous phase refers to the phase of the system which is loaded (contaminated) by a solute (solutes) and the organic phase is an immiscible liquid (diluent) in which based on the liquid extraction classification either contains an extraction facilitator (carrier, extractant) or not (Dean, 1998).

The principle of LLE is based on the distribution of a solute between aqueous phase and organic phase (Thornton, 1992). In other words, LLE is a process where a solute can be distributed into an immiscible solvent and extraction process depends on the solute mass transfer rate (Lee et al., 2000). For this process, the International Union of Pure and Applied Chemistry (IUPAC) recommends the term liquid-liquid extraction (LLE) (Rydberg et al., 2004).

Liquid-liquid extraction has been used in wastewater treatment for many years and many researchers still show interest on this technique.

Table 2.1 summarizes some recent works on this field in which LLE has been used for different heavy metals extraction, using different carriers.

Table 2.1 Application of liquid-liquid extraction in metals removal

Contaminant	Diluent	Carrier	Removal (%)	Reference
Zinc	Kerosene	D2EHPA ^a	97%	Raghuraman et al., 1994
Mercury	Toluene	TOA ^b	98%	Li et al., 1996
Chromium(VI)	Xylene	Cyanex 923	99%	Alguacil et al., 2000
Platinum	Toluene	Cyanex 923	99%	Duche and Dhadke, 2001
Nickel, copper and lead	2-aminothiopheno	1-butyl-3-methylimidazolium hexafluorophosphate	70-80%	Lertlapwasin et al., 2010
Samarium	Kerosene	Cyanex301 and D2EHPA	>95	Torkaman et al., 2012
Vanadium	Kerosene	D2EHPA, TBP ^c	98	Li et al., 2014
Iron, cobalt, nickel, copper, cadmium and lead	2,4,6-tris(2-pyridyl)-1,3,5-triazine	1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)	>96%	Matsumiya et al., 2014

^aDi-(2-ethylhexyl)phosphoric acid; ^bTri-*n*-octylamine; ^cTributyl phosphate.

2.4 Liquid Membrane (LM)

Liquid membrane (LM) consists of an immiscible liquid (named as the solvent, diluent or organic phase) which is separated by two aqueous phases, namely the aqueous feed (donor) and stripping (receiving) phases. Once a specific solute of a mixture, based on chemical potential gradient, moves through the liquid membrane

from the feed phase towards the stripping phase, extraction is achieved (Noble and Way, 1987).

Liquid membrane systems -including bulk liquid membrane (BLM), emulsion liquid membrane (ELM) and supported liquid membrane (SLM)- have been investigated widely in various fields such as pharmaceutical extraction separation of penicillin from broth (the liquid obtained from biological processes) using butyl acetate as diluent, separation of aromatic-ring hydrocarbons (e.g., benzene, toluene) from paraffin using sulpholane as diluent, extraction of vanilla from the oxidized liquors using toluene as diluent, separation of vitamin A from fish-liver oil using propane as diluent, extraction of vitamin E from vegetable oil using propane as diluent (Haan and Bosch, 2013; Eskandari et al., 2011), etc.

Liquid membrane configurations have been used in wastewater treatment for various compound removal and recovery from municipal or industrial wastewaters, such as dye removal (Muthuraman and Teng, 2009), rare earth metals recovery (Wannachod et al., 2014), precious metals recovery (Zaghbani et al., 2007), organic compounds removal (Terry et al., 1982), distillery effluent treatment (Kumaresan et al., 2003), radioactive metals recovery (Panja et al., 2011), toxic metals removal (Alpoguz et al., 2009), etc.

2.5 Liquid Membrane Classification

Liquid membranes can be classified according to:

- 1) Liquid membrane configuration and module design, including BLM, ELM and SLM.

2) Solute transport mechanism from feed phase to stripping phase, including simple transport, facilitated transport and activated transport of the solute from feed to stripping phase. Different types and configurations of liquid membrane are illustrated in Figure. 2.1 (Kislik, 2010).

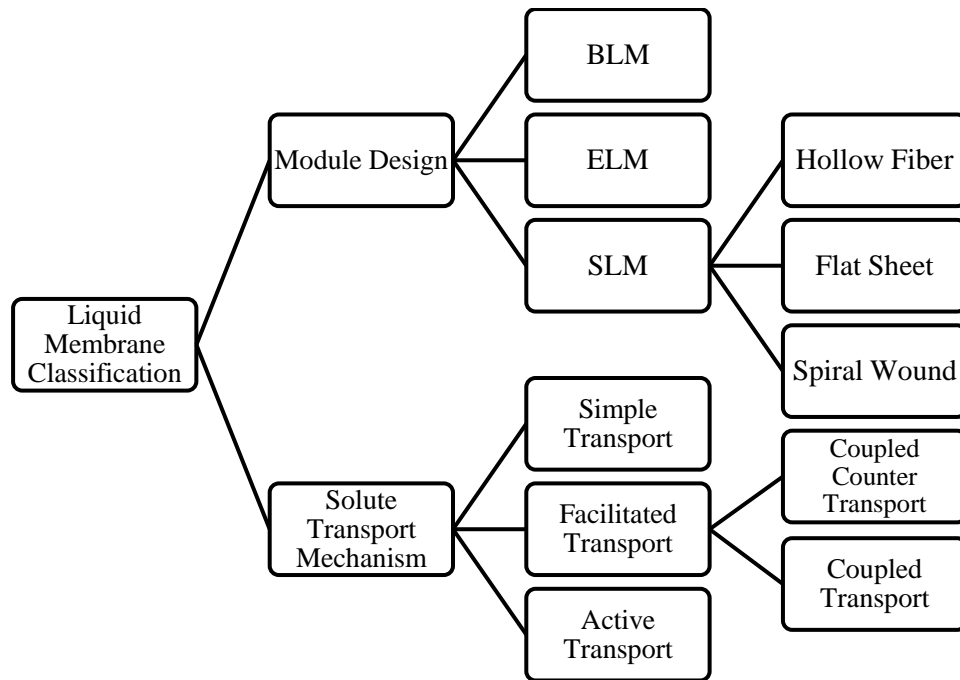


Figure 2.1 Liquid membrane classification based on module design and solute transport mechanism

2.5.1 Liquid Membrane Classifications According to the Design Configuration

Liquid membrane is divided into three major configurations: bulk liquid membrane (BLM), emulsion liquid membrane (ELM) and supported liquid membrane (SLM).

2.5.1(a) Bulk Liquid Membrane (BLM)

Bulk liquid membrane (BLM) contains two bulk aqueous phases (feed and stripping) separated by a bulk organic (immiscible) liquid phase. In its simplest type of design, the solute extraction and partition take place in U-tube (for high density solvent, Figure 2.2 A) or H-tube (for low density solvent, Figure 2.2 B) configurations.

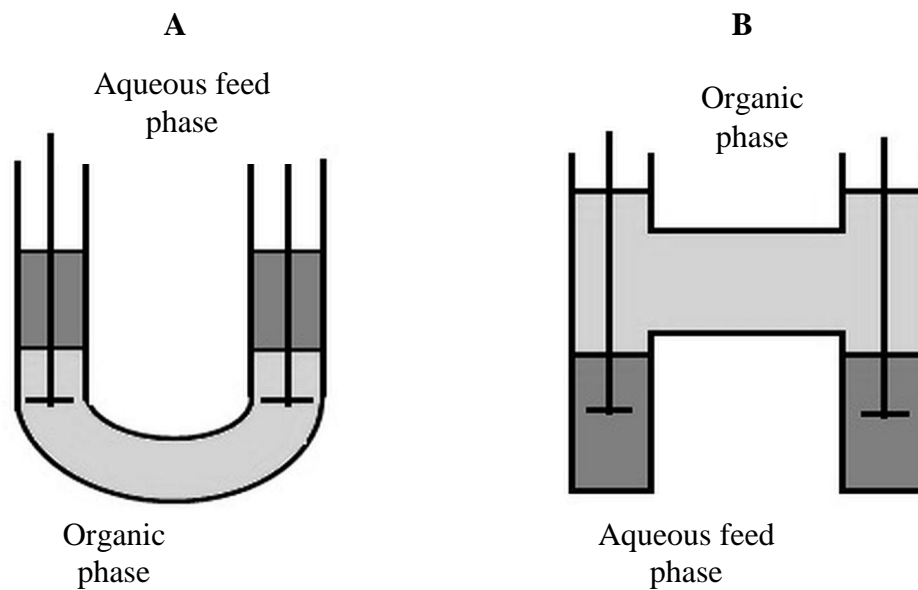


Figure 2.2 A: U-tube BLM reactor for an organic phase with high density solvent;
B: H-tube BLM reactor for an organic phase with low density solvent

Among the liquid membrane configurations, BLM has simple design and ease of operation which make it a great tool for studying the kinetics, transport properties, and reaction mechanisms of various separation processes are the advantages of BLM but relatively low flux rate and high chemical (diluent and carrier) consumption can be counted as the disadvantages of BLM (Boyadzhiev and Lazarova, 1995). Table 2.2 shows a brief review of some BLM applications in wastewater treatment field, specifically heavy metals removal.

Table 2.2 Metal contaminated wastewater treatment using BLM

Contaminant	Diluent	Carrier	Removal (%)	Reference
Chromium (VI)	Hexane	TBP	97	Muthuraman et al., 2009
Copper	Soybean oil	D2EHPA	98	Chang et al., 2011b
Copper, nickel and zinc	Kerosene	D2EHPA	88% of zinc, 95.8% of copper and 95.0% of nickel	Singh et al., 2011

2.5.1(b) Emulsion Liquid Membrane (ELM)

Li (1986) invented a different type of liquid membrane in which the stripping phase was emulsified in an immiscible liquid membrane. ELM may be in the form of water-organic-water (W/O/W) or organic-water-organic (O/W/O). In emulsion liquid membrane (ELM) mass transfer takes place by dispersion of emulsion in the feed solution. ELM extraction ability can be enhanced by using carriers, chemical reagents and electric impulses (Chakraborty et al., 2010). In ELM technique, metal extraction into the membrane phase is highly dependent on the emulsion stability (Ahmad et al., 2012). Figure 2.3 demonstrates a configuration of ELM.

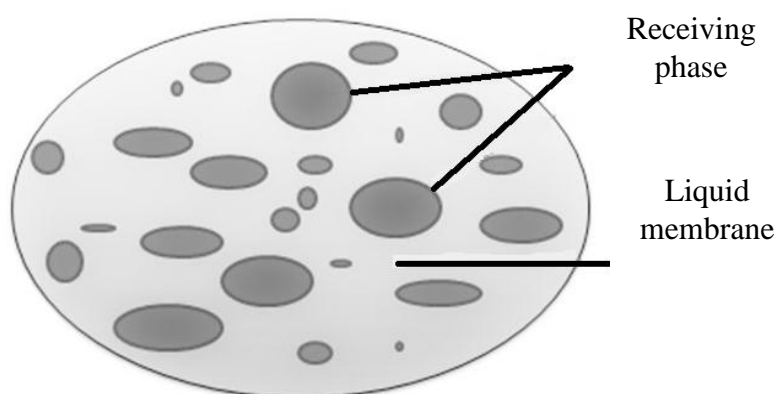


Figure 2.3 Emulsion liquid membrane (ELM)

As the historically first application of liquid membrane in wastewater treatment, ELM has been studied and investigated for many years by numerous researchers and scientists. Table 2.3 summarizes some studies on metal ion treatment using ELM.

Table 2.3 Metal contaminated wastewater treatment using ELM

Contaminant	Diluent	Carrier	Removal (%)	Reference
Gallium	Kerosene	Trioctylphosphine oxide	97%	Kumbasar and Tutkun, 2004
Copper	Kerosene	LIX 984N-C	80	Sengupta et al., 2006
Cadmium	Kerosene	Trioctylamine	98	Ahmad et al., 2011
Chromium (VI)	Kerosene	Cyanex 923	98	Nosrati et al., 2011
Cobalt	Kerosene	Triisooctylamine	99	Kumbasar, 2012
Chromium (III)	Kerosene,	2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester	94	García et al., 2013
Nickel	Kerosene	5,8-diethyl-7-hydroxydodecan-6-one oxime(LIX 63) and 2-bromodecanoic acid(2BDA	>98	Eyupoglu and Kumbasar, 2015
Bismuth	Pentanol	Di(2ethylhexyl)phosphoric	100	Mokhtari and Pourabdollah, 2015

ELM is relatively cheap with high flux rate, high extraction efficiency and environmental-friendly (Ahmad et al., 2013) but coalescence and emulsion swelling resulting in low emulsion stability are considered as its disadvantages (Hu and Wiencek, 1998).

2.5.1(c) Supported Liquid Membrane (SLM)

SLM, in a rather primitive configuration, was reported for the first time by Scholander (1960) who used thin cellulose acetate filters impregnated with an aqueous hemoglobin solution for oxygen transport. A similar system was reported by Wittenberg (1966) for studying the molecular mechanism of oxygen transport.

In supported liquid membrane (SLM) a thin microporous filter is installed as a support between feed and stripping phases. The support is impregnated by an organic carrier (also named as facilitator, modifier or mobilizer) to modify the extraction process. The main advantage of supported liquid membranes is the insignificant amount of organic phase is required for impregnation of the support matrix. For example, 10 cm³ of the organic phase solution are sufficient to impregnate 1 m² of a membrane of 20 µm thickness and 50% porosity, while the main SLM disadvantage is the low stability of the membrane, caused by leakage and/or losses of membrane phase components during transport process.

However, by proper choice of the porous polymeric support, using suitable organic solvents and carriers in the organic phase and proper design of membrane components, the instability can be significantly reduced (Boyadzhiev and Lazarova, 1995). The great potential for energy saving, low capital and operating cost, and the possibility to use expensive extractants due to the low consumption of the membrane phase, make SLM technique noticeable and interesting (Kocherginsky et al., 2007). In addition, supported liquid membrane extraction is the most versatile membrane extraction technique for analytical sample preparation compared with other LM configurations (Jönsson and Mathiasson, 1999).

Configuration-wise, flat sheet SLM is used for laboratory researches (Eyupoglu and Tutkun, 2011) while in industrial applications of SLM, hollow fiber and spiral wound configurations (with higher surface area of aqueous-organic interface compared with flat sheet SLM type) have been used (Venkateswaran and Palanivelu, 2007; Kandwal et al., 2012). Figure 2.4 shows a schematic of a flat sheet SLM reactor in which the LM is sandwiched between feed and stripping phase.

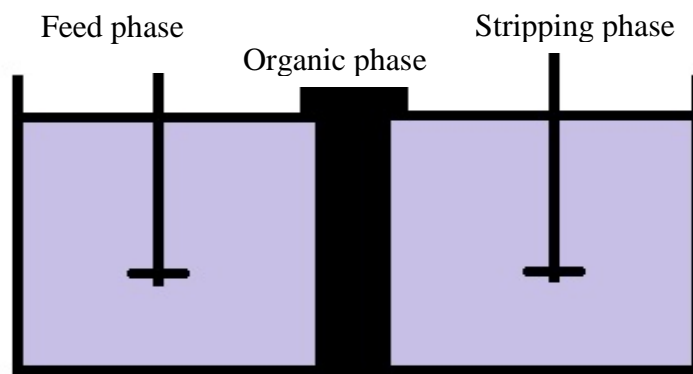


Figure 2.4 Schematic of a supported liquid membrane (SLM)

2.5.2 Liquid Membrane Types Based on Transport Mechanism

The membrane solute diffusion flux can be calculated by Fick's first law:

$$J = k_m ([S_s] - [S_f]) \quad (2.1)$$

where J is diffusion, k_m is mass transfer coefficient, $[S_s]$ is the solute concentration in the stripping phase and $[S_f]$ is the solute concentration in the feed phase.

Liquid membrane, based on the transport mechanism of the solute from the aqueous feed phase, through the membrane (organic phase) to the aqueous stripping

phase, can be divided into three major types: simple transport, facilitated transport and active transport of the solute from the feed to stripping phase.

2.5.2.1 Simple Transport of the Solute from Feed to Stripping Phase

Simple transport of the solute in LM is based on the solute solubility. In this type of solute transport, because the LM is not loaded with any carrier then no chemical reaction occurs between the solute and the LM and hence the solute is in the same form in the stripping phase as it has been in the feed phase and LM. The permeation stops at equilibrium (Schlosser et al., 1993; Boyadzhiev and Lazarova, 1995; Schlosser and Sabolova, 1999; Wodzki and Nowaczyk, 2002). Figure 2.5 illustrates the mechanism of solute transport through the LM in a simple transport configuration; $[S_f]$ is solute concentration in the feed phase, $[S_m]$ is the solute concentration in the liquid membrane and $[S_s]$ is the solute concentration in the stripping phase.

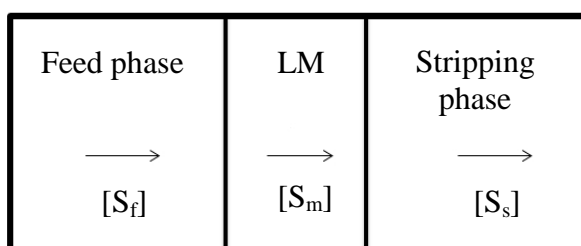


Figure 2.5 Simple transports of species (S) from feed phase (F), through LM (M) to stripping phase (S)

2.5.2.2 Facilitated Transport of the Solute from Feed to Stripping phase

Facilitated transport of the solute from aqueous feed phase, through the membrane, into the stripping is based on the solute partitioning, complexations between the solute and the carrier at the feed-organic interface, the formed complex

diffusion through the membrane (interdiffusion) and the decomplexation and release of the solute into the stripping phase. This type of LM accelerates the flux rate and extraction process. Subsequent mechanisms like coupled counter transport or coupled co-transport can be derived from the facilitated transport mechanism (Szpakowska 1996; Yilmaz et al., 2008; Arslan et al., 2009; Minhas et al., 2013).

Figure 2.6 shows the schematic of the solute facilitated transport through LM. The first stage is the solute (S) partitioning in LM, diffusing from feed phase to feed-LM interface due to chemical potential, then a chemical reaction between the solute and the carrier (C) at the interface occurs to form solute-carrier complex (S=C) and the complex moves through the LM towards the LM-stripping interface (reverse reaction and partitioning of the solute in stripping phase and decomplexation) and stripping in the stripping phase due to different equilibrium conditions at LM-stripping phase interface and diffusion to the stripping phase (SA formation due to chemical reaction with anion (A^-) in stripping phase) (Kislik, 2010).

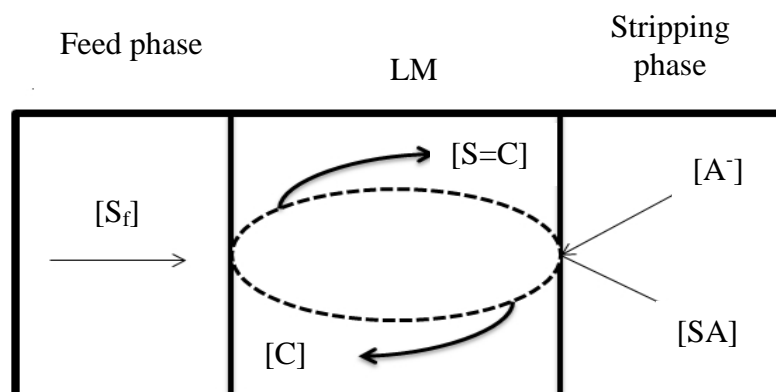


Figure 2.6 Facilitated transport of species “S” through LM