SUPPORTED LIQUID MEMBRANE WITH SELECTIVE STRIPPING FOR SEPARATIVE RECOVERY OF COPPER AND ZINC FROM MULTIMETAL WASTEWATER

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SUPPORTED LIQUID MEMBRANE WITH SELECTIVE STRIPPING FOR SEPARATIVE RECOVERY OF COPPER AND ZINC FROM MULTIMETAL WASTEWATER

by

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$(LH)_2$	Dimeric form of D2EHPA
$[(LH)_2]$	Concentration of free dimeric D2EHPA that is not bounded to any metal ions at equilibrium (mol/L)
$[A^-]$	Acid anion
$[Cu^{2+}]$	Concentration of copper stripped (mol/L)
$[CuL_2(LH)_2]$	Concentration of copper-D2EHPA complex in the organic phase at stripping equilibrium (mol/L)
$[CuL_2(LH)_2]_{init}$	Initial concentration of copper-D2EHPA complex in organic phase before stripping (mol/L)
$[H^+]$	Hydrogen ion concentration (mol/L)
$\mathrm{[LH]tot}$	Total concentration of D2EHPA (mol/L)
$[M^{2+}]$	Concentration of divalent metal ions in aqueous phase (mol/L)
$[ML_2(LH)_x]$	Concentration of metal ions extracted into the organic phase (mol/L)
$[M^{n+}]_{init}$	Initial feed metal ions concentration (ppm)
$[M^{n+}]_t$	Metal ions concentration in feed after a certain elapsed time (ppm)
$[R_3N]_{org}$	Basic carrier concentration in membrane phase
$[RH]_{org}$	Acidic carrier concentration in membrane phase
$[Zn^{2+}]$	Concentration of zinc stripped (mol/L)
$[ZnL_2(LH)_2]$	Concentration of zinc-D2EHPA complex in the organic phase at stripping equilibrium (mol/L)
$[ZnL_2(LH)_2]_{init}$	Initial concentration of zinc-D2EHPA complex in organic phase before stripping (mol/L)
$\sum[M^{n+}]$	Total concentration of all metal ions in the solution (ppm)
A	Effective SLM contact area for transport (m^2)
Ag	Silver
Ag_2SO_4	Silver sulfate

Al	Aluminium
Bi	Bismuth
C	Metal concentration
C_1	Concentration of the source or concentrated solution
C_2	Concentration of diluted solution
Cd	Cadmium
Ce	Cerium
$C_{f(0)}$	Initial metal concentration in feed (mol/L)
$C_{f(t)}$	Concentration of metal ion in feed after elapsed time, t (mol/L)
C_{feed}	Feed metal concentration (mol/L)
Cl^-	Chloride ion
Co	Cobalt
Cr(III)	Chromium(III)
Cr(VI)	Chromium(VI)
$Cr_2O_7^{2-}$	Dichromate ion
Cu	Copper
$CuSO_4.5H_2O$	Copper (II) sulfate pentahydrate
d	Nernst aqueous diffusion layer thickness at the feed-SLM interface (m)
D	Distribution coefficient
D_{aq}	Metal diffusion coefficient in the aqueous feed (m^2/s)
D_m	Effective metal diffusion coefficient in the SLM (m^2/s)
E	Liquid membrane
E	Metal extraction efficiency (%)
Eu	Europium
Fe(III)	Iron(III)
fin	Finish or after extraction

Gd	Gadolinium
H_2CrO_4	Chromic acid
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
$HCrO_4^-$	Hydrogen chromate ion
$HgSO_4$	Mercury (II) sulfate
init	Initial or before extraction
J	Transport flux (mol/m^2.s)
k_1	Pseudo first order metal extraction rate constant (m/s)
$K_2Cr_2O_7$	Potassium dichromate
K_a	Acid dissociation constant
K_D	Distribution coefficient of metal between SLM and feed
K_{ex}	Extraction equilibrium constant
k_i	Wilke-Chang equation constant
$K_{str,Cu}$	Stripping equilibrium constant of copper
$K_{str,Zn}$	Stripping equilibrium constant of zinc
L	Extractant or carrier
l	Membrane thickness (m)
m	Stoichiometric coefficient for carrier in the extraction equation
$M1$	Target metal for recovery
$M2$	Another metal besides M1
M^{2+}	Divalent metal ions
MCl_x	Metal chloride salt
MCl_x^{n-}	Chloridometalates anion
m_M	Mass of metal
$m_{M,org}$	Mass of metal loaded into organic phase before stripping
$m_{M,strip}$	Mass of metal in stripping phase after stripping

Mn	Manganese
M^{n+}	Metal ions
Mo(VI)	Molybdenum
m_{solute}	Mass of solute (g)
n	Stoichiometric coefficient for hydrogen ion in the extraction equation
n	Amount of data
Na_2CO_3	Sodium carbonate
$NaNO_3$	Sodium nitrate
NaOH	Sodium hydroxide
NH_3	Ammonia
Ni	Nickel
n_M	Number of moles of metal
NO_3^-	Nitrate ion
O:A ratio	Organic-to-aqueous volume ratio
org	Organic phase
P	Permeability or permeation coefficient (m/s)
Pb	Lead
Pb(II)	Lead(II)
p_c	Aqueous phase/SLM interface capillary pressure
pH_{eq}	pH at equilibrium
R	Receiving or stripping phase
r	Correlation coefficient
R	Metal recovery efficiency (%)
R1 and R2	Chemical substituents such as hydrocarbon chains
R^2	Coefficient of determination
r_p	Membrane pore radius

S	Solvent
S	Metal stripping efficiency (%)
SCN^-	Thiocyanate
S_{exp}	Experimentally obtained stripping efficiency (%)
S_{mod}	Stripping efficiency calculated using model equations (%)
SO_4^{2-}	Sulfate ion
T	Temperature (°C)
t	Tortuosity
Tm	Thulium
V_1	Volume of the concentrated solution
V_2	Volume of diluted solution
V_f	Volume of feed (m^3)
V_o	Volume of organic phase (mL)
X^{n-}	Counterion in feed
Y	Yttrium
Y^-	Anion of carrier
Zn	Zinc
$ZnSO_4.7H_2O$	Zinc sulfate heptahydrate
γ	Aqueous phase/SLM interfacial tension
$\Delta[M^{2+}]$	Metal concentration (mol/m^3) change in either the feed or stripping phase over elapsed time, Δt
ε	Membrane porosity
η	Membrane viscosity
θ	Advancing contact angle of the aqueous phase on the surface of the membrane support

LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrophotometer
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared spectrometer
CFS	Coagulation-flocculation-sedimentation
CI	Confidence interval
COD	Chemical oxygen demand (mg/L)
D2EHPA	Di-(2-ethylhexyl)phosphoric acid
DBBP	Dibutyl butylphosphonate
DCTA	1,2-diaminocyclohexane--N, N,N', N'-tetraacetic acid
DOE	Department of Environment, Malaysia
DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
FSSLM	Flat sheet supported liquid membrane
HDBP	Di-n-butylphosphoric acid
HFCLM	Hollow fiber contained liquid membrane
HFSLM	Hollow fiber supported liquid membrane
HLB	Hydrophilic-lipophilic balance
Obj 1	Objective 1
Obj 2	Objective 2
Obj 3	Objective 3
Obj 4	Objective 4
PEHFSD	Pseudo-emulsion based hollow fiber strip dispersion
PES	Polyethersulfone
PIM	Polymer inclusion membrane
PP	Polypropylene

PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene difluoride
RMSE	Root mean squared error
SEM	Scanning electron microscope
SF	Separation factor
SLM	Supported liquid membrane
strip	Stripping phase
SX	Solvent extraction
TBP	Tri-n-butyl phosphate
TEA	Triethanolamine
TeOA	Tetraoctylammonium bromide
TOA	Tri-n-octylamine
TOMAC	Tri-n-octylmethylammonium chloride
TOPO	Trioctylphosphine oxide
U.S.	United States of America

LIST OF APPENDICES

MEMBRAN CECAIR BERPENYOKONG DENGAN PENANGGALAN TERPILIH BAGI PEROLEHAN KUPRUM DAN ZINK SECARA BERASINGAN DARIPADA AIR SISA BUANGAN PELBAGAI LOGAM

ABSTRAK

Standard A dan B di bawah Peraturan Kualiti Alam Sekeliling (Efluen Perindustrian) 2009 di Malaysia telah menetapkan syarat-syarat untuk pembuangan efluen perindustrian termasuk had kepekatan logam, bagi mengawal pelepasan logam berbahaya ke dalam air sisa buangan. Proses rawatan adalah penting untuk memenuhi syarat-syarat yang ditetapkan sebelum melepaskan air sisa buangan. Tidak sekadar menyingkirkan logam, usaha perolehan logam untuk tujuan kitar semula juga menawarkan pendekatan yang lebih lestari, selaras dengan inisiatif ekonomi kitaran. Membran cecair berpenyokong (SLM) dilihat sebagai alternatif yang berpotensi untuk usaha ini. Tetapan yang spesifik diperlukan oleh SLM untuk pengangkutan dan perolehan logam secara terpilih. Dalam keadaan tertentu, pengangkutan secara terpilih tidak boleh dilakukan kerana pengekstrakan lebih daripada satu logam oleh pembawa yang digunakan dalam SLM. Sebagai alternatif kepada penggunaan pelbagai tetapan SLM serta untuk mengatasi masalah pengekstrakan lebih daripada satu logam dalam masa yang sama, penyelidikan ini bertujuan untuk mengkaji penggunaan kaedah sebaran dalam fasa penanggalan dengan penanggalan terpilih dalam sistem SLM yang menggunakan pembawa tunggal bagi perolehan kuprum dan zink secara berasingan. Asid di-(2-etilheksil)fosforik (D2EHPA) yang dicairkan dengan kerosin telah digunakan sebagai fasa membran. Faktor-faktor yang mempengaruhi pengekstrakan dan penanggalan kuprum serta zink ditentukan melalui eksperimen pengekstrakan pelarut dan penanggalan. Kajian pengekstrakan pelarut menemui bahawa pH suapan dan kepekatan pembawa mempengaruhi kecekapan dan selektiviti pengekstrakan, serta kestabilan fasa membran. Kompromi juga diperlukan untuk pemilihan tetapan pH dan kepekatan pembawa bagi mencapai kecekapan pengekstrakan kuprum dan zink yang tinggi tanpa menjejaskan kestabilan fasa membran. Dalam kajian tentang penanggalan, model berasaskan teori dihasilkan untuk membantu pemahaman tentang peranan reagen penanggalan dalam penanggalan terpilih. Penemuan menunjukkan bahawa penggunaan reagen dengan kekuatan asid yang lebih rendah dalam kepekatan yang sesuai boleh menanggalkan kuprum yang mempunyai ikatan pembawa logam yang lebih lemah tanpa penanggalan zink yang ketara. Tetapan yang sesuai bagi membolehkan pengasingan logam tanpa menjejaskan kadar pengangkutan dan kestabilan SLM digunakan dalam sistem SLM yang terdiri daripada tiga sel kaca yang dipisahkan oleh dua SLM. Suapan diletakkan di dalam sel pertama manakala 4% (v/v) D2EHPA digunakan dalam fasa membran. Sebaran dalam fasa penanggalan yang mengandungi penimbal sitrat 0.2 mol/L pH 3 menghasilkan keputusan penanggalan terpilih yang terbaik telah digunakan di sel tengah. Asid sulfurik 1 mol/L yang kuat digunakan di dalam sel ketiga untuk menanggalkan zink yang tertinggal di dalam fasa membran. Selepas 30 jam, 94.4% kuprum (ketulenan: 99.4% Cu, 0.6% Zn) dan 93.2% zink (ketulenan: 98.9% Zn, 1.1% Cu) diperolehi secara berasingan daripada suapan sintetik, manakala 83.7% kuprum (ketulenan: 91.0% Cu, 2.9% Zn, 4.6% Ni, 1.4% Mn) dan 85.5% zink (ketulenan: 99.3% Zn, 0.7% Mn) diperolehi secara berasingan daripada air sisa buangan industri. Keputusan ini menunjukkan kebolehlaksanaan sistem SLM yang dikaji. Oleh itu, sistem SLM ini disyorkan untuk dikaji pada skala yang lebih besar untuk tujuan aplikasi praktikal.

SUPPORTED LIQUID MEMBRANE WITH SELECTIVE STRIPPING FOR SEPARATIVE RECOVERY OF COPPER AND ZINC FROM MULTIMETAL WASTEWATER

ABSTRACT

In Malaysia, Standards A and B of the Environmental Quality (Industrial Effluent) Regulations 2009 establish effluent limits, including metal concentration thresholds, to regulate emissions of harmful metal pollutants in wastewaters. Treatment is essential to meet these limits before discharging wastewater. Instead of mere removal, metal recovery for recycling offers a more sustainable approach, aligning with circular economy initiatives. Supported liquid membrane (SLM) has been viewed as a potential alternative. In SLM, specific settings are required for selective metal transport and recovery. Under some conditions, selective transport is not possible due to multiple metal coextraction by the carrier used in SLM. As an alternative to using multiple SLM settings and to overcome metal coextraction, this study aimed to investigate the utilization of strip dispersion with selective stripping in a single-carrier SLM system for separative recovery of copper and zinc. Di-(2-ethylhexyl)phosphoric acid (D2EHPA) diluted by kerosene was used as the membrane phase. The factors that affect extraction and stripping of copper and zinc were determined through solvent extraction and stripping experiments. Solvent extraction studies found that feed pH and carrier concentration affect extraction efficiency, selectivity and membrane phase stability; a compromise in the pH and carrier concentration settings is needed to attain high copper and zinc extraction efficiency without adversely affecting membrane phase stability. In stripping studies, theoretical model was derived to facilitate understanding on the role of stripping reagent in selective stripping. It was found that suitable concentrations of lower acid strength reagents selectively strip copper, which have weaker metal-carrier bond, without significantly stripping zinc. Suitable settings, which enabled separation of the metals without adversely affecting transport rate and stability, were then implemented on the SLM setup comprising three glass cells separated by two SLM. Feed was placed in the first cell while 4% (*v/v*) D2EHPA was applied in the membrane phase. Strip dispersion containing 0.2 mol/L pH 3 citrate buffer, which produced the best selective stripping results, was used in the middle cell. In the third cell, strong 1 mol/L sulfuric acid was used to strip the remaining zinc from the membrane phase. After 30 h, 94.4% copper (purity: 99.4% Cu, 0.6% Zn) and 93.2% zinc (purity: 98.9% Zn, 1.1% Cu) were separately recovered from synthetic feed while 83.7% copper (purity: 91.0% Cu, 2.9% Zn, 4.6% Ni, 1.4% Mn) and 85.5% zinc (purity: 99.3% Zn, 0.7% Mn) were separately recovered from the industrial plating wastewater. These results demonstrate the feasibility of this SLM configuration and thus, it could be recommended for scale-up study for practical application.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Metals have many useful applications in our daily lives. In chemistry, metals are elements which conduct electricity, possess metallic lustre, are malleable and ductile in nature, and form basic oxides (Duffus, 2002). To further improve properties such as strength and corrosion resistance, and to reduce cost, mixing of metal elements to form alloys were carried out (Britannica, n.d.). The diverse use of metals and their alloys includes being utilized for making electrical and electronic products, vehicles, machinery, equipment, construction materials, household products, packaging, armour, weapons, synthetic dyes, fertilizers, pesticides, magnets, jewelleries, coins, catalysts, pharmaceutical products, and auxiliary items (Briffa et al., 2020; Tchounwou et al., 2012).

Metals can be emitted into the environment naturally due to weathering and geogenic activities such as volcanic eruption or because of anthropogenic activities such as mining, metal-based industrial operations, agricultural, pharmaceutical production, and domestic activities (Shazili et al., 2006; Tchounwou et al., 2012). Among the anthropogenic emission routes of metal into aquatic systems include leaching and immobilization of metal pollutants from waste sludge cakes disposed in landfills. Metals may also enter aquatic systems due to accidental process or wastewater spills and unintended run-off from untreated sewage which contains metal pollutants. Worse still, some aquatic systems are possibly contaminated with metal pollutants because of illegally discharged metal-containing waste.

Metals, which enter the soils and aquatic systems, get absorbed by fishes and vegetations and subsequently reach other animals or the human body through food chain (Azimi et al., 2017; Briffa et al., 2020). Metal pollutants have adverse effects on plants, animals and humans. Plants could be negatively affected in several ways such as experiencing decrease in seed germination, lipid content, enzyme activity, growth, chlorophyll production and inhibition of photosynthesis (Akpor et al., 2014). When accumulated in animals or human body, metals lead to undesirable effect ranging from skin irritations and lethargy to very serious health problems such as organ damage, cancer and even death (Akpor et al., 2014; Azimi et al., 2017; Briffa et al., 2020).

Demand for metals is increasing with increasing economic activities and emerging technologies such as solar photovoltaics and electric vehicles (Watari et al., 2020). Supply of various metals is important for the global machinery and equipment industry, which is predicted to be worth RM19.8 trillion by 2023 with a predicted yearly growth rate of 6.4% from 2023 to 2027 (MIDA, 2023). Circular economy and sustainable metal use becomes important. Without the ability to separate metals, conventional treatment methods such as chemical precipitation, ion exchange and adsorption which could only remove metals from wastewater (Barakat, 2011; DOE, 1999), are not sufficient. Recycling and recovering metals from wastewater will be more beneficial in reducing environmental pollution, overcoming short-term waste disposal costs, minimizing long-term liabilities that may surface due to release of hazardous wastes and reducing some raw materials costs because the demand for mined-metals can be replaced with recycled metals (Bless, 2000; Swartzbaugh et al., 1998).

In recent years, studies have been looking into methods of recovery and separation of metals from wastewater. Wastewater generally contains multiple types of metal ions, which needs to be separated when recycling so that the metals can be processed into new products. Plating wastewater is among the wastewater that contains mixture of metal ions. In 2018, about 35,678.23 metric tonne of scheduled waste, which contained metals such as chromium, copper, nickel, zinc and silver, was generated by the metal finishing industry in Malaysia (DOE, 2018). In the electroplating process, plated items need to be rinsed and dried after plating to remove residual plating bath solution (drag-out) on the items. The rinsing process is identified to be the main source of metal-containing wastewater. The wastewater discharged from rinsing could contain about 15 to 100 ppm of the metal used for plating (Al-Shannag et al., 2015; DOE, 1999; Kaya et al., 2016; Rahman et al., 2021), and some works even reported that wastewater from some plating industries had contained metal in the range above 100 ppm (A. Rahman et al., 1994; Tang & Qiu, 2019).

SLM, which could enable selective recovery of metal from wastewater, was identified to be one of the potential methods that is suitable for separating and recovering metals from dilute aqueous solution like plating wastewater. The SLM setup is consist of organic membrane phase embedded in the pores of a thin microporous solid support that becomes a barrier separating the aqueous feed and receiving phase, permitting only selected metal species to be transferred across the membrane via extraction and stripping process as illustrated in Figure 1.1. This research is interested to further explore the use of SLM for separative recovery of metals from wastewater and propose alternatives to overcome challenges associated with the use of SLM.

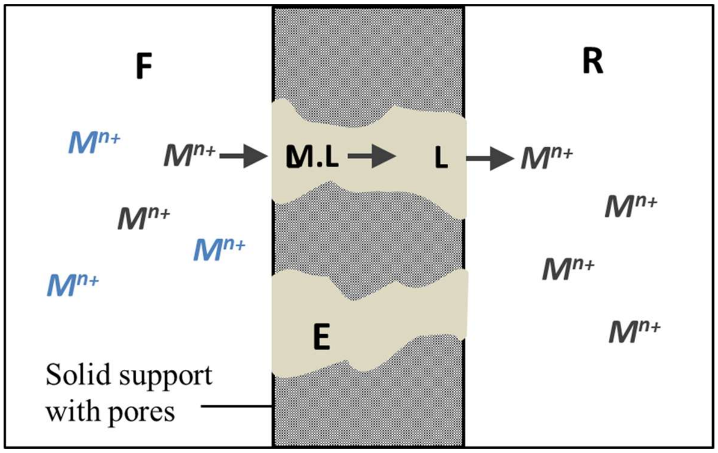

Figure 1.1 Configuration of a SLM (F = aqueous source/feed phase, L = extractant/carrier, E = organic phase comprising extractant in diluent (liquid membrane), R = aqueous receiving/stripping phase, M^{n+} = metal ions). Adapted from Kislik (2010b)

1.2 Problem Statements

Many studies have already been carried out on the use of SLM for various metal recovery and separation (Alguacil & Lopez, 2021; L. Chen et al., 2018; Song et al., 2018; N. Swain & Mishra, 2019), including studies on using SLM for metal recovery from plating wastewater (Kaya et al., 2016; Srirachat et al., 2021; Venkateswaran & Palanivelu, 2005). Available studies have shown that applying suitable carriers and feed chemistry on the SLM system allows selective metal transport but often only focus on transport and recovery of a single metal. However, real wastewater tends to contain more complex mixture of metal ions. This implies that separation and recovery of multiple metals needs to be carried out in a sequential manner by utilization of different selective carriers and feed chemistry adjustments. Recovering multiple metals using this approach is less efficient and will incur increased processing costs, time and complexity.

In the presence of other chemically similar metals in the wastewater, selective transport of target metal became a challenge. Sometimes, more than one metal may be coextracted by the carrier and transported across the SLM in non-negligible amount (de los Ríos et al., 2013; Jean et al., 2018; Srirachat et al., 2021; Xu et al., 2019; Zante et al., 2019). In such cases, selective metal recovery cannot be achieved by relying on carriers alone. Metal coextraction is a common occurrence in solvent extraction. Scrubbing or selective stripping has been utilized to remove and separate the metal that is coextracted by the carrier, but its chemistry is not clearly elucidated.

The applicability of a SLM is mainly dictated by three main aspects, namely its ability to recover metals selectively, its stability and the transport rate it can produce. Studies has shown that certain process parameters affect more than one aspect of the SLM. The same parameter that improves one aspect may degrade another. For example, larger pH gradient improves SLM transport rate but affects selectivity, while higher liquid membrane viscosity is favourable for a better stability but reduces the transport rate. Not considering the effects of the process parameters on the three main aspects when designing a SLM system could negatively impact the performance of the SLM system.

1.3 Research Objectives

As an alternative to using multiple carriers for recovering different metals and overcoming coextraction of chemically similar metals, the idea of a SLM system that utilizes a single carrier together with strip dispersion for selective stripping of coextracted metal ions was proposed for separative recovery of copper and zinc, the two chemically similar metal which are commonly found in plating wastewater. Strip dispersion was shown in other previous studies that it could help to maintain stability of metal transport. On top of the benefit of stability improvement, this study proposed utilization of the organic phase dispersed in the stripping phase to transport the additional coextracted metal into another stripping phase so that the metals could be recovered separately. In line with this idea, the objectives of this research are:

1) to determine the effects of feed pH, buffer and carrier concentration on extraction efficiency of copper and zinc
2) to determine the role of stripping reagent in selective stripping through theoretical modelling and experimental study
3) to design the SLM system and determine the suitable settings to be implemented for separative recovery of copper and zinc
4) to assess the functionality of the SLM system in recovering copper and zinc from real industrial wastewater

1.4 Scope and Limitations of Study

Experiments involving solvent extraction, stripping and metal transport using flat sheet SLM (FSSLM) configuration were performed to meet the research objectives. Solvent extraction and stripping experiments are important to elucidate the chemistry that influence metal transport and recovery selectiveness, which allowed suitable chemical settings to be inferred from the study. The feasibility of the proposed strategy in separative recovery of copper and zinc was then examined through metal transport experiments using FSSLM configuration. Despite being able to recover metals from higher volume of wastewater and produce results that are more representative of an industrial scenario, hollow fiber SLM (HFSLM) configuration was not utilized in this study as HFSLM was not easily available and its cost was much higher. Use of FSSLM configuration is sufficient to address the objectives of this research and its associated cost was within the allocated budget.

In addition to experimental studies, theoretical model on stripping was derived to predict and make sense of stripping selectivity. Because there was hardly any information on stripping mechanisms in existing literature, derivation of model was based on equilibrium constant that relates the distribution of products and reactants at equilibrium given that extraction and stripping are reversible reactions. The equilibrium constant, which arises from law of mass action (Ferner & Aronson, 2016), is well-established and still being applied widely in many solvent extraction studies (Kani et al., 2021; Lei et al., 2022; Shuya et al., 2020).

Another challenge faced in this study was collection of real industrial wastewater. Only one plating company permitted a one-time wastewater sampling after several plating companies within the state were approached. Alternatively, more information on plating wastewater composition and concentration of metals in it was obtained through other journal publications and DOE handbook. Although only being able to obtain a one-time real wastewater sample, the sample was still useful for checking the feasibility of the proposed SLM system.

The carrier is one of the more expensive chemicals required in this study, thus experiments were conducted using relatively small volume of samples whenever possible. As an indication of stability of the SLM, chemical oxygen demand (COD) analysis was used instead of oil and grease analysis to check for loss of membrane phase into the aqueous phase. COD analysis could be performed using much lower sample volume (2 mL) whereas much higher sample volume (350 mL) is required for oil and grease analysis. COD analysis had also been applied and reported by Lee et al. (2011) for checking dissolution of organic phase in aqueous phase.

As resources allowed, experiments were conducted in triplicates to check for results consistency, reliability, variability or any errors that may be incurred. Statistically, the distribution type could not be deduced due to this very small sample size and normality assumption could not be made. Thus, more robust non-parametric methods were used to analyse the results but with less power (confidence less than 95%). In addition to statistical analysis, results obtained were checked against other similar results that were reported in literatures to improve confidence.

1.5 Organization of Thesis

This thesis is organized according to the following order:

Chapter 1 (INTRODUCTION) presents the introduction to this research. General overview about metals and its negative effects as pollutants in aquatic systems, importance of metal recovery, introduction to SLM, problem statements and motivation that inspire this research, the objectives of this research, as well as research scope and limitations are described in this chapter.

Chapter 2 (LITERATURE REVIEW) reviews the literature that are relevant to this research. The content of the literature surveyed are interpreted and summarized to provide deeper and comprehensive understanding of the workings of SLM and the factors that affect its operability. Up to date SLM research studies that had been conducted and gaps in research were mentioned in this chapter.

Chapter 3 (MATERIALS AND METHODS) contains the methodology applied in this research. The research flow is hereby included and explained. The chemicals, materials, equipment needed and experimental methods for solvent extraction, stripping and SLM study and related analysis were specified, and the associated equations were given.

Chapter 4 (RESULTS AND DISCUSSIONS) compiles and discusses all the findings obtained according to the order of the research flow, which include effect of chemical factors on extraction, stripping and organic phase dissolution, effect of stirring on SLM transport and comparison of transport, recovery and selectiveness obtained for synthetic feed and real plating wastewater treated using the proposed SLM system. Theoretical modelling of selective metal stripping from organic phase are also presented and explained in this chapter.

Chapter 5 (CONCLUSIONS AND RECOMMENDATIONS) presents the conclusions that can be drawn from all the findings, including conclusion on the feasibility of the proposed SLM system with selective stripping and provides recommendations on improvements and future study that can be carried out extending from this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In a bid to design practical SLM systems that are capable of selective separation, have reasonable treatment rate, and are stable for long operational lifetime, fundamental understanding and comprehensive consideration of the factors affecting the functionality and quality of the SLM are needed. This chapter describes the basic governing principles of SLM and explains in detail the factors that affect transport selectivity, kinetics and stability of SLM. Studies on SLM improvement strategies were reviewed and gaps in research on SLM were identified.

2.2 Comparing Technologies for Treating Metal-bearing Wastewater

Metal pollutants are globally recognized to be harmful towards the environment. Legislations are put in place by authorities to limit the entry of metal pollutants into the environment. In Malaysia, Environmental Quality Act 1974 specify that industrial facilities, which discharge effluent downstream of any raw water intake, must comply with the maximum effluents limit set by standard B (*Environmental Quality (Industrial Effluent) Regulations 2009 (P.U. (A) 434/2009)*). Table 2.1 lists the permissible concentration limits of metals in wastewater for discharge as set by standard B.

Table 2.1 Acceptable metal concentration limits for discharge of industrial or mixed effluent according to standard B

Metals	**Unit**	**Max. Limits of Effluents**
Mercury	mg/L	0.05
Cadmium	mg/L	0.02
Chromium(VI)	mg/L	0.05
Chromium(III)	mg/L	1.0
Lead	mg/L	0.5
Copper	mg/L	1.0
Manganese	mg/L	1.0
Nickel	mg/L	1.0
Tin	mg/L	1.0
Zinc	mg/L	2.0
Iron	mg/L	5.0
Silver	mg/L	1.0
Aluminium	mg/L	15
Barium	mg/L	2.0

Adapted from Environmental Quality (Industrial Effluent) Regulations 2009 (P.U. (A) 434/2009)

Hence, wastewater treatment for metal removal prior to discharging into the environment is necessary to reduce the metals concentration in the wastewater to below the allowed concentration limit. A brief overview of some of the industrially applied wastewater treatment methods for removing metal pollutants including coagulation-flocculation-sedimentation (CFS), electrochemical treatment, membrane filtration, adsorption, ion exchange and solvent extraction is given in Table 2.2.

Table 2.2 Advantages and disadvantages of common treatment methods for removal/recovery of metals from wastewater

Methods	**Description**	**Advantages**	**Disadvantages**	**Reference**
Coagulation-flocculation-sedimentation (CFS) / chemical precipitation	Utilizes chemical precipitation and/or aggregation to remove soluble metal species	Simple and cost effective	Requires a lot of coagulant, separation system is needed, generation of toxic sludge	Azimi et al., 2017; Barakat, 2011; European Environment Agency, 2019; Mubarak et al., 2015; Ungureanu et al., 2015
Electrochemical	Applies electrical energy to electrodes to either generate coagulants (electrocoagulation), oxygen and hydrogen (electroflotation) or form metal deposition on cathode by reduction (electrowinning)	High removal efficiency, wide range applicability	Other impurities may co-deposit in the cathode metal during electrowinning, high electricity cost	Azimi et al., 2017; Barakat, 2011; Mubarak et al., 2015; Ungureanu et al., 2015; Wang, 2004
Ion exchange	Solid ion exchange resin uptake metal ions from wastewater via complexation while releasing another similar charge ion from the resin in return	Little sludge generation, equipment and operation are relatively simple	Unsuitable for concentrated metal solution, matrix fouls easily, effectiveness could be affected by competing ions	Azimi et al., 2017; Barakat, 2011; Mubarak et al., 2015; Tavlarides et al., 1987; Ungureanu et al., 2015
Membrane filtration	Semi-permeable barrier aided by trans-membrane pressure or physicochemical effects, allows passage of water and/or some solutes while rejecting others mainly based on molecule size	No generation of toxic by-product	High electrical energy is required, high capital and operational costs	Azimi et al., 2017; Barakat, 2011; Mubarak et al., 2015; SUEZ Water Technologies & Solutions., n.d.; Ungureanu et al., 2015

Table 2.2 Continued

Methods	**Description**	**Advantages**	**Disadvantages**	**Reference**
Solvent extraction (liquid-liquid extraction)	Uses extractant dissolved in water-immiscible organic solvent to extract metal ions from wastewater. Metals accumulated in organic solvent is then subsequently recovered by stripping, which also regenerates the extractant for reuse	Higher throughput	Large solvent inventory	Cerná, 1995; Reinhardt and Cox, 2004; Tavlarides et al., 1987; Wang, 2004
Adsorption	Physically or chemically binds metal ions onto surface of solid adsorbents	Cheap and commercially available adsorbents, high removal efficiency	Regeneration and multiple use of adsorbents could be a problem	Azimi et al., 2017; Barakat, 2011; Mubarak et al., 2015; Ungureanu et al., 2015

Since each method has its own advantages and limitations, suitability of treatment method depends on wastewater conditions (i.e. types of metal present and metal concentration) and treatment goals (i.e. discharge metal concentration, removal only, metal recovery). Many conventional treatment methods such as CFS, ion exchange and adsorption are simple to implement but does not allow separative recovery. Membrane filtration, which is a relatively newer technology, was also mainly applied for indiscriminate metal pollutants removal. However, separation is required for metals to be recycled. The electrochemical method, namely electrowinning, is one of the methods that can recover metals from wastewater selectively if the metals have different reduction potential. Nonetheless, electrowinning suffers low current efficiency if used for recovering metals from dilute wastewater. It is recommended to be used with other process such as ion exchange to overcome the problem (Azimi et al., 2017; Bless, 2000). Solvent extraction is another method that can recover metals selectively but this method requires the usage of a considerable amount of solvent. Efforts are ongoing into improving the existing method such as chemical precipitation, adsorption, ion exchange and membrane filtration so that separative recovery of metals can be achieved (Dąbrowski et al., 2004; Huang & Feng, 2019; Krishnan et al., 2021; Lewis, 2010; Tang & Qiu, 2019).

Owing to the need for selective metal recovery and the benefit of process simplification, researchers proposed the idea of liquid membranes, a treatment method combining the concept of solvent extraction and membrane separation. Liquid membrane consists of a liquid immiscible with the source and receiving phase, acting as a separation barrier that allows only certain species of chemical to be transferred from source or feed phase to receiving phase. The selective transport of metal ions, which have low solubility in organic phase, across the liquid membrane can be achieved by reversible binding of desired metal ions with organic soluble complexation agent, also known as carrier or extractant, which is added into the membrane phase (Chakraborty et al., 2010; Kislik, 2010b). The carrier-metal complex then moves across the liquid membrane and the metal ions are eventually released into the receiving phase with the help of stripping agent. This transport cycle repeats until the feed phase is depleted of metal ions or the chemical potentials between the phases are balanced.

By combining the sequential process of extraction and stripping in a single operational unit, liquid membrane separation process requires fewer operating vessels and less energy to operate as compared with treatment methods like CFS, ion exchange, solvent extraction and adsorption. Unlike solvent extraction process, transport of solute across liquid membrane is not confined by the limitation of equilibrium distribution. In solvent extraction, the amount of metal that could be extracted reaches maximum at equilibrium. The metal-loaded organic phase can only be used to extract more metal after stripping away the loaded metal. Otherwise, higher volume of organic phase is required to increase the extraction capacity. In contrast, liquid membrane, which enables transport of metal through repeated cycle of extraction and stripping concurrently in the same operational unit, could increase concentration of recovered metal ions solution and work with significantly less solvent as compared with conventional solvent extraction due to its non-dependence on equilibrium distribution (Parhi, 2013; Tavlarides et al., 1987). Compared with solid polymeric membrane, higher transport flux is expected for liquid membrane owing to the much higher diffusion coefficient of solute in liquids than in solid materials (Kemperman et al., 1996). However, SLM could potentially experience drawbacks similar to drawbacks faced by other polymeric membrane such as integrity issue, which may cause leaking and cross-contamination between the two separated aqueous phases, or fouling, which hampers membrane transport flux (Dżygiel & Wieczorek, 2010).

The beginning of 1980s saw an increase of research interest in SLM as it is easier to implement SLM to a continuous flow system (Dżygiel & Wieczorek, 2010). SLM has the potential for large scale application with improvement in its interfacial contact area to treated volume ratio. Pertaining SLM studies for metal recovery from wastewater, numerous research has since been conducted on the use of SLM for transport and recovery of many different metals including rare earth elements (REEs), use of new carriers such as ionic liquids in SLM to improve transport selectivity, and ways to improve transport rate and stability of SLM. Details of the relevant studies are discussed in the subsequent sections in this chapter.

SLM may be able to be used in place of solvent extraction or ion exchange process for treating and recovering metal selectively from mine waters, dilute waste leachate, and wastewater produced by pickling, etching and plating processes (El-Nadi, 2017; Reinhardt & Cox, 2004). For recovering metals from the wastewater generated by the plating rinsing process, a recovery system using SLM could be implemented as shown in Figure 2.1. After recovery using SLM, the concentrated recovered single metal solution could either proceed for electrowinning or be recycled for use as make-up plating solution. Since concentrated recovered metal solution could be obtained using SLM, the use of evaporator to concentrate the recovered metal solution may become optional. Study by Ho (2003) demonstrated that the pilot size hollow fiber module SLM (HFSLM) (diameter: 10.2 cm, length: 71.1 cm, mass transfer surface area: 19 m^2) was able to treat 121.1 – 129.8 L volume of feed in about 4 hours with resulting recovered solution having concentration up to 20,000 ppm. In addition, Yang et al. (2001) noted that the HFSLM is feasible for recovering metals for electrowinning as recovered solution concentration beyond 40 g/L could be achieved without affecting the transport flux of the HFSLM. Using commercial size HFSLM (diameter: 25.4 cm, length: 71.1 cm, mass transfer surface area: 135 m^2), treatment and recovering metals from wastewater generated by small or medium size plating industries, which typically ranges between 3 – 40 m^3 a day (DOE, 1999), appears to be potentially viable. For recovering metals from larger volume, 50 – 80 m^3 a day of wastewater that is generated from large plating industries, use of larger HFSLM may be considered and evaluated.

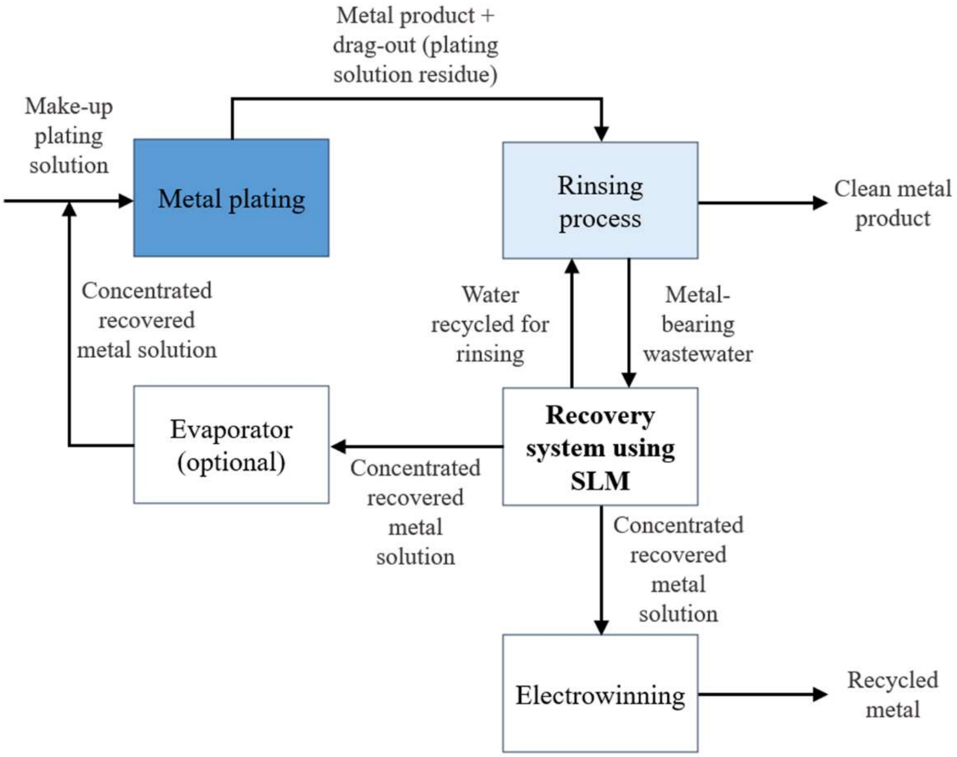

Figure 2.1 Suggested process flow which incorporates SLM recovery system for treating and recovering metals selectively from plating rinse wastewater. Adapted from Bless (2000)

2.3 Basic Governing Principles of SLM

SLM for transport of metal ions essentially consists of mixture of carrier and solvent or diluent embedded in the pores of solid support. Because metal ions are insoluble in the organic membrane phase, the transport of metal ions across SLM requires facilitation by carriers (Kislik, 2010b). The facilitated transport mechanism involved for a metal ion to be transferred from the feed aqueous phase across the SLM to the receiving (or stripping) phase is represented in Figure 2.2.

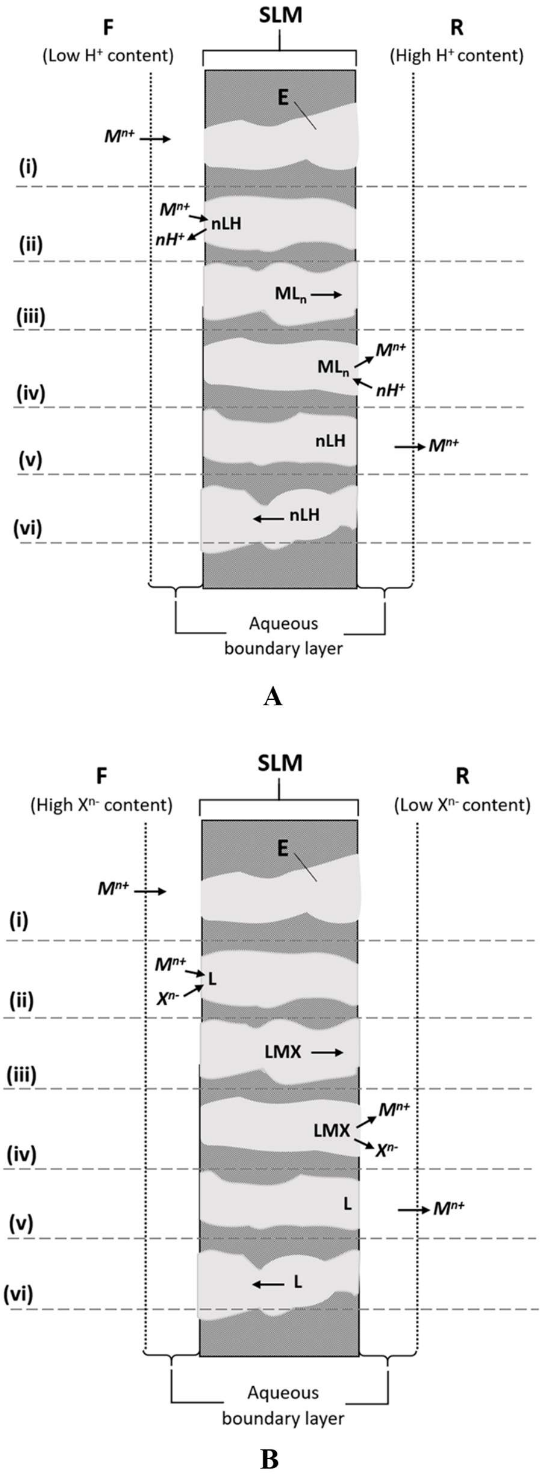

Figure 2.2 Transport mechanism across SLM: (A) Coupled counter transport and (B) Coupled co-transport (F = source/feed phase, E = liquid membrane, R = receiving phase, M^{n+} = metal ions, X^{n-} = counterion, L or LH = carrier). Adapted from Danesi (1984)

Transport of metal ions occurs whether by coupled counter or co-transport mechanism depends on the type of carrier used and the works of carriers will be explained in section 2.3.1. Description of the transport mechanism differ slightly between researchers, but the steps are primarily as follow (Danesi, 1984; X. J. Yang et al., 2003):

(i) Diffusion of metal ion through the feed aqueous boundary layer at feed SLM interface
(ii) Extraction by carrier at the SLM interface by formation of metal ion-carrier complex (hydrogen ions get released into feed for acidic carriers (counter transport); anion from feed get co-extracted by basic or neutral carriers (co-transport))
(iii) Diffusion of metal ion-carrier complex through the SLM phase
(iv) Stripping by dissociation of metal ion-carrier complex to release metal ion at the SLM-stripping solution interface (hydrogen ions replace the metal ions from the acidic carriers (counter transport); co-extracted anions from feed get released together with the metal ions from the basic or neutral carriers into the stripping solution (co-transport))
(v) Diffusion of metal ion through the stripping aqueous phase boundary layer at SLM-stripping solution interface
(vi) Back-diffusion of the uncomplexed carrier across the SLM phase

The transport mechanism depicted in Figure 2.2(A) is known as coupled counter transport because the mechanism involves transport by exchanging one metal ion with another ion such as a hydrogen ion, causing both the ions to be transported in the opposite direction (metal ion moves from feed to stripping phase while hydrogen ion moves from stripping phase to feed). On the other hand, the coupled co-transport occurs when the carrier coextracts a metal ion together with a counterion in feed and transports both the ions in the same direction (from feed to stripping phase) as shown in Figure 2.2(B).

Liquid membrane separation is a rate-governed process, which enables transport of selected metal ions so long as chemical potential gradient (difference in concentration of hydrogen ions or anions between the feed, membrane and receiving phase) exists. In carrier-facilitated transport, chemical potential gradient can be maintained by manipulating feed and receiving phase condition such as maintaining different pHs for the two phases. Therefore, uphill transport of metal ions from lower concentration feed to higher concentration receiving phase is possible, allowing recovery in the form of concentrated metal solution that can then be recycled for other applications such as electroplating without presence of undesirable impurity (Kemperman et al., 1996; Parhi, 2013).

2.3.1 Metal Recovery Efficiency and Selectivity

Since transport of metal ions across the SLM involves extraction by a carrier into the membrane phase at the feed-SLM interface and stripping to release the metal ions from the carrier into the stripping phase, metal recovery is hence, affected by the factors affecting metal extraction and stripping. Factors that affect extraction include type of carrier (carrier is a term widely used in SLM to denote extractant), carrier concentration, counterions present in feed and pH of feed whereas factors that affect stripping include type of stripping reagent and its concentration.

Carriers help to extract and transport metal by replacing the water molecules of the hydrated metal ions and neutralize any ionic charge to enable transfer of metal species from polar aqueous phase to the non-polar organic membrane phase (Cox, 2008). The choice of carrier to be employed for extraction depends on the metal species to be transported and counterion present in feed. Extraction are categorized to work in three ways: metal cation extraction, metalate anion extraction and metal-salt extraction (Wilson et al., 2014), corresponding to acidic or chelating, basic and solvating type carrier respectively (Cox, 2008).

The acidic type carrier is used when the counterion (such as sulfate) present in the aqueous feed is a weak inner sphere ligand. Acidic carriers transport metal cation across SLM via coupled counter transport mechanism as illustrated in Figure 2.2(A). The anion, L of the carrier, LH forms organic-soluble charge-neutral complex with the metal cation, M^{n+} as per equation (2.1) (Wilson et al., 2014).

$$nLH_{(org)} + {M^{n+}}_{(aq)} \rightleftharpoons [ML_n]_{(org)} + {nH^+}_{(aq)} \tag{2.1}$$

As metal cation extraction involves exchange of hydrogen ions into the feed, pH of the aqueous feed has effect on the extend of extraction (Tavlarides et al., 1987). However, it is possible to extract a certain metal even at low pH when the carrier is highly selective towards the metal due to bonding and the structure of the metal-carrier complex formed (Wilson et al., 2014). On the other hand, chelating carriers extract metal cations by forming bidentate complexes with the cations using its electron donor group (Tavlarides et al., 1987). An example of the extraction reaction by chelating carriers and the structure of the metal-carrier complex formed is shown in Figure 2.3.

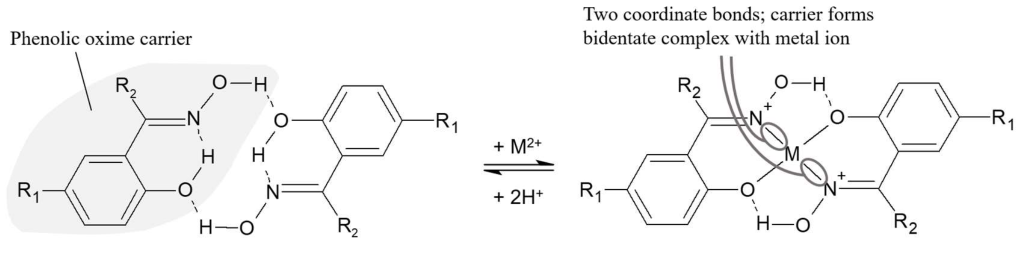

Figure 2.3 Extraction of metal by phenolic oxime extractant, a type of chelating carrier (R_1 and R_2 = chemical substituents such as hydrocarbon chains, M and M^{2+} = metal ion, - - - hydrogen bonding). Adapted from Wilson et al. (2014)

Metalate anion and metal-salt extraction coincides with coupled co-transport mechanism as illustrated in Figure 2.2(B). When a strong inner sphere ligand type counterion (such as chloride) is present in the feed solution instead, metalate anions (chloridometalates MCl_x^{n-} will be used as an example) tend to be formed at higher counterion concentration. In this case, basic carriers, L can be used to bind the metalate anions into the organic membrane phase through ion-pair formation according to equation (2.2). Carriers with permanent positive charge can also be used to extract and transport metalate anions through an anion exchange process as per equation (2.3) but metalate anions will be transported via coupled counter transport mechanism instead (Wilson et al., 2014).

$$nL_{(org)} + nH^+{}_{(aq)} + MCl_x{}^{n-}{}_{(aq)} \rightleftharpoons [(LH)_n MCl_x]_{(org)} \tag{2.2}$$

$$nLY_{(org)} + MCl_x{}^{n-}{}_{(aq)} \rightleftharpoons [L_n MCl_x]_{(org)} + nY^-{}_{(aq)} \tag{2.3}$$

In the presence of strong inner sphere ligand type counterion, neutral carriers extract metal-salt into the organic membrane phase through formation of charge-neutral metal-carrier complexes by contributing lone pair electrons to the metal ions. The carrier "solvates" the metal complex by replacing the water molecules surrounding the metal complex to render it more lipophilic (Cox, 2008). However, this mechanism of solvation can only be achieved through the use of the organophosphorus (phosphorus-oxygen bonding) group of carriers while carriers consisting of carbon-oxygen bonding binds with the metal solute by utilizing water to form hydrogen-bonded bridge between carrier and metal ion, creating hydrated metal complexes in the organic membrane phase (Tavlarides et al., 1987). Equation (2.4) shows the reversible reaction between solvating carrier and the metal salt.

$$nL_{(org)} + MCl_{x\,(aq)} \rightleftharpoons [MCl_x(L)_n]_{(org)} \tag{2.4}$$

Some of the common carriers that had been studied or used in solvent extraction (SX) or SLM are listed in Table 2.3. A desirable carrier is a carrier that can achieve high extraction efficiency but the carrier may extract certain metals more efficiently than other metals, which implies that the carrier exhibit selectivity towards certain metals. For example, a study by Soeezi et al. (2020) showed that oxime type carrier, LIX 984, extracts more than 97% copper but extracts less than 70% nickel even when the same pH and carrier concentration are applied. In contrast, di-2,4,4-trimethylpentylmonothiophosphinic acid, Cyanex 302, could extract up to more than 90% nickel but could only extract about 20% or less of copper. In another study, the extraction efficiencies of chromium(III) differed among the different acidic carriers tested (G. Zhang et al., 2016).

It can be inferred from the extraction equation that the feed conditions/acidity also affects extraction efficiency. In the case of extraction using acidic carriers, a feed condition with lower hydrogen ions concentration (higher pH) is favourable in driving the reaction forward to extract more metals. In many studies which employed acidic type carriers, researchers evaluated effect of pH on extraction by applying pH as low as 1 and up to about 7 so long as the feed pH did not cause metal precipitation. The studies found that extraction of metal cations increased with increase in feed pH (Chang, 2012; Jafari et al., 2018; Mohammadi et al., 2015; B. Swain et al., 2015; G. Zhang et al., 2016).

Table 2.3 Common carriers used/studied for metal ions extraction

Carrier	Carrier trade name	Carrier type	Extracted metal	Anion	Extraction / Removal (%)	Reference
2-ethylhexylphosphonic acid mono-2 ethylhexyl ester	PC-88A	Acidic	Zn	SO_4^{2-}	*no info*	Lee et al., 2004
			Co	NO_3^-	*no info*	Matsuyama et al., 1987
bis-(2,4,4-trimethylpentyl)-phosphinic acid	Cyanex 272	Acidic	Zn	SO_4^{2-}	94.39	Sinha et al., 2011
			Co	SO_4^{2-}	99.99	Swain et al., 2015
Bis(2-ethyl hexyl) di-thiophosphoric acid	-	Acidic	Zn	SO_4^{2-}	99.4	Chakraborty et al., 2010
di(2,4,4-trimethylpentyl) dithiophosphinic acid	Cyanex 301	Acidic	Zn	*no info*	~99.9	Ho, 2003
di-(2-ethylhexyl)phosphoric acid (D2EHPA)	-	Acidic	Cu	SO_4^{2-}	98.17	Chang, 2012
			Y(III), Dy(III)	Cl^-	~100	Mohammadi et al., 2015
			Zn	*no info*	> 99.8	Yang et al., 2001
neodecanoic acid	Versatic 10	Acidic	Ag	SO_4^{2-}	85	Talebi et al., 2018
			Cu	SO_4^{2-}	> 90	
			Pb	SO_4^{2-}	> 75	
(trihexyl-tetradecyl) phosphonium chloride	CYPHOS IL101	Basic	Cr(VI)	Cl^-	> 95	Alguacil et al., 2010
			Zn	Cl^-	> 85	Regel-Rosocka & Wisniewski, 2011
tri-n-octylamine (TOA)	Alamine 300	Basic	Co	SO_4^{2-}	98.4 – 99.9	Surucu et al., 2012
			Cr(VI)	SO_4^{2-}	96.1	Yang et al., 1996