DEVELOPMENT OF SELECTIVE EXTRACTION FOR Cd(II), Cu(II) AND Ni(II) IONS USING DUAL FLAT SHEET SUPPORTED LIQUID MEMBRANE SYSTEM

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by

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A	Effective membrane area
ΔC	Change in concentration of metal ion
C_M	Concentration of M
d	Composite desirability
D	Distribution ratio
D_M	Distribution coefficient of M
D_{M1}	Distribution ratio of metal M_1
D_{M2}	Distribution ratio of metal M_2
%E	Percentage of extraction
F	Value from Fisher-Snedecor distribution
$(HR)_2$	Dimers of D2EHPA
J	Permeation flux
J_M	Diffusive mass transport flux
k	Number of factors studied in central composite design
K_D	Distribution coefficient
K_{eq}	Equilibrium constant
k_M	Mass transport coefficient
m	Valence of metal species
M	Solute
M^{m+}	Metal cation with valency *m*
$MR_m(HR)_n$	Metal-D2EHPA complex
$MSO_4 \cdot nR_4N\text{-}Cl$	Metal-Aliquat 336 complex
$[M]_{aq}$	Total concentration of metal in the aqueous phase
$[M]_{org}$	Total concentration of metal in the organic phase
$[M_I]$	Concentration of metal ion at time, *t*

$[M_I]_{feed}$	Concentration of metal ion after 48 hours in Feed
$[M_I]_{intermediate}$	Concentration of metal ion after 48 hours in Intermediate
$[M_I]_{strip}$	Concentration of metal ion after 48 hours in Strip
$[M_O]$	Initial concentration of metal ion
MN	Compound of solute M and N
MR	Complex of carrier R and solute M
N	Second solute
n	Number of molecules of extractant involved in the reaction
NR	Complex of carrier R and solute N
O:A	Organic to aqueous
p	Probability value
pH_{eq}	Equilibrium pH
PVDF-1	Membrane impregnated with D2EHPA and TBP
PVDF-2	Membrane impregnated with Aliquat 336 and TBP
R	Carrier
R^2	Coefficient of determination
$R_4N–Cl$	Aliquat 336
R_m	Anion of D2EHPA
SD_{coef}	Standard deviation coefficient
SD_{reg}	Standard deviation of regression
$S_{M1/M2}$	Separation factor of metal M_1 and M_2
Δt	Time interval
t-stat	*t*-statistics
V	Volume of feed phase
x	Direction of diffusion
x_i and x_j	Independent variables in coded unit
y	Response/Dependent variable

Greek letters

α	Distance between axial points and central point
β_0	Intercept regression coefficient
β_i	Linear regression coefficient
β_{ii}	Quadratic regression coefficient
β_{ij}	Interaction regression coefficient
δ	Thickness of diffusional layer
ε	Error term

LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
ADMI	American Dye Manufacturer’s Institute
APHA	American Public Health Association
BET	Brunauer-Emmett-Teller
BLM	Bulk liquid membrane
CCD	Central composite design
D2EHPA	Di(2-ethylhexyl) phosphoric acid
DDTP	Ammonium O,O-diethyl dithiophosphate
DF	Degrees of freedom
DFSSLM	Dual flat sheet supported liquid membrane
DOE	Department of Environment
DP8R	Di(2-ethylhexyl) phosphoric acid
DSLM	Dispersion supported liquid membrane
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy dispersive X-ray
ELM	Emulsion liquid membrane
EQA	Environmental Quality Act
FAAS	Flame atomic absorption spectroscopy
FSSLM	Flat sheet supported liquid membrane
FTIR	Fourier transform infrared
FTIR-ATR	Fourier transform infrared-attenuated total reflectance
HFRLM	Hollow fiber renewal liquid membrane
HFSLM	Hollow fiber supported liquid membrane
HLM	Hybrid liquid membrane
IR	Infrared

LIX 84-I	2-hydroxy-5-nonylacetophenone oxime
LIX 860-I	5-dodecylsalicylaldoxime
LIX 973N	5-nonyalicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime
LIX-79	1,3-bis(2-ethylhexyl)guanidine
LLE	Liquid-liquid extraction
LM	Liquid membrane
M2EHPA	Mono-(2-ethylhexyl) phosphoric acid
MDPA	Methylenediphosphonic acid
MIDA	Malaysian Investment Development Authority
MS	Mean of squares
N1923	C19–C23 secondary alkyl primary amine
P507	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester
PC-88A	2-ethylhexylphosphonic mono-2-ethylhexyl ester
PE	Polyethylene
PEHFSD	Pseudo-emulsion-based hollow fiber strip dispersion
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
RSM	Response surface methodology
SEM	Scanning electron microscopy
SEM-EDX	Scanning electron microscopy with energy dispersive X-ray
SLM	Supported liquid membrane
SS	Sum of squares
SWSLM	Spiral-wounded supported liquid membrane
TBP	Tributyl phosphate
TDDA	Tridodecylamine
TEA	Triethanolamine

THF	Tetrahydrofuran
TOA	Trioctylamine
TOMAC	Trioctylmethylammonium chloride
TOPO	Trioctylphosphine oxide
TOPS 99	Di(2-ethylhexyl) phosphoric acid
USEPA	United States Environmental Protection Agency
USM	Universiti Sains Malaysia

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PEMBANGUNAN PENGEKSTRAKAN SELEKTIF ION Cd(II), Cu(II) DAN Ni(II) MENGGUNAKAN SISTEM DWI MEMBRAN CECAIR BERSANGGA

ABSTRAK

Air sisa yang dihasilkan dari pembuangan sisa cucian dan asid terpakai biasanya mempunyai pelbagai ion logam yang berjisim besar. Dalam industri penyaduran, rawatan air sisa logam adalah proses yang kompleks di mana ion logam yang tidak diperlukan akan dibuang dan hanya logam dengan nilai komersial yang tinggi akan dipisahkan untuk pemulihan. Sebenarnya, kebanyakan teknologi rawatan air sisa yang sedia ada bersifat tidak selektif dan terhad khususnya untuk penyingkiran logam tunggal. Oleh sebab persamaan rapat dari segi kandungan kimia, ion-ion logam biasanya wujud bersama dan saling bersaing untuk dipisahkan secara selektif. Hal ini demikian, pelbagai ion logam perlu dipisahkan dan dipulihkan dari efluen industri yang kompleks. Membran cecair bersangga (SLM) membolehkan pemisahan logam berat dengan kelebihannya termasuk pengekstrakan dan pelucutan serentak dalam satu langkah, disokong dengan polimer yang mengandungi pembawa pengekstrakan yang minimum dan kadar penggunaan tenaga yang rendah. Sistem Dwi Membran Bersangga (DFSSLM) menggunakan dua SLM yang dipisahkan untuk memulihkan bukan sahaja satu tetapi tiga jenis ion logam. Penyelidikan ini bertujuan untuk mengkaji kecekapan DFSSLM dalam pengekstrakan selektif ion Cd(II) dan Cu(II) daripada ion Ni(II) dari campuran akues dan air sisa penyaduran. Kesan pH dan kepekatan pembawa ke atas pengekstrakan selektif Cd(II), Cu(II), dan Ni(II) disiasat dan keadaan optimumnya telah dikenalpasti. Kesan pH, kepekatan pembawa dan kepekatan agen pelindung ke atas pemisahan Cd(II) dari Cu(II) juga disiasat dan dioptimumkan. Parameter untuk DFSSLM dipilih berdasarkan eksperimen penyaringan: fasa Penyaluran yang mengandungi 100 mg/L Cd(II), Cu(II) dan Ni(II) dilarutkan dalam natrium sulfat dalam pH_{eq} 4.6, membran pertama direndam dengan 100 mM di(2-etilheksil) asid fosforik dan 50 mM tributil fosfat dalam kerosin, membran kedua direndam dengan 99.64 mM trioktil metilamonium klorida dan 50 mM tributil fosfat dilarutkan dalam toluena, 1 M asid sulfurik dalam fasa Perantaraan dan 48.86 mM asid etilenediaminetetraasetik dalam fasa Penyingkiran. Selepas pengadukan secepat 500 rpm selama 48 jam, terdapat 98.79% Ni(II) dapat dikesan dalam fasa Penyaluran, 91.32% Cu(II) dalam fasa Perantaraan, dan 91.04% Cd(II) dalam fasa Penyingkiran DFSSLM. Pengangkutan kompetitif antara Cd(II) dan Cu(II) dijustifikasikan dengan perubahan fluks dan kajian kinetik Cd(II) dan Cu(II). Rawatan air sisa penyaduran menggunakan DFSSLM menunjukkan nisbah output/input yang tinggi untuk pemulihan Cd(II), Cu(II) dan Ni(II). Sebanyak 89.09% Cd(II) dapat dipulihkan melalui fasa Penyingkiran, 90.87% Cu(II) daripada fasa Perantaraan, 97.61% Ni(II) daripada fasa Penyaluran dan sebahagian besar logam berat lain tidak dijumpai dalam efluen selepas rawatan DFSSLM. Kesimpulannya, kajian ini membuktikan bahawa DFSSLM dapat memisahkan dan memulihkan Cd(II), Cu(II) dan Ni(II) dari campuran kompleks.

DEVELOPMENT OF SELECTIVE EXTRACTION FOR Cd(II), Cu(II) AND Ni(II) IONS USING DUAL FLAT SHEET SUPPORTED LIQUID MEMBRANE SYSTEM

ABSTRACT

Wastewater produced from washing out the mixtures and massive discharge of used acids usually have large mass of diverse metallic ions. In electroplating industry, treating the wastewater with various metals is a complex process whereby unwanted metallic ions are often discarded and only metals with high commercial values are separated for recovery. In fact, most of the existing wastewater treatments are non-selective and some are limited for removal of single metal. Due to close similarities in chemistry, metallic ions usually coexist and compete with each other to be selectively separated. Therefore, multiple metal ions could be separated from industrial effluent. Supported liquid membrane (SLM) allows heavy metals separation with the advantages include simultaneous extraction and stripping in a single step, supported with polymer with minimal usage of extractants and low energy use. Dual Flat Sheet Supported Liquid Membrane (DFSSLM) applies two separated SLMs to selectively recover not just one but three types of metal ions at the end of the system. This research aims to study the efficiency of DFSSLM in selective extraction of Cd(II) and Cu(II) over Ni(II) ions from aqueous mixture and electroplating wastewater. The effects of feed pH and carrier concentration for selective extraction of Cd(II) and Cu(II) over Ni(II) were investigated. The effects of pH, carrier concentration and masking agent concentration for separation of Cd(II) over Cu(II) were optimized. Operating parameters for DFSSLM were selected based on screening experiments: Feed phase containing 100 mg/L of Cd(II), Cu(II) and Ni(II) with pH_{eq} 4.6, first membrane soaked with 100 mM di(2-ethylhexyl) phosphoric acid and 50 mM tributyl phosphate in kerosene, second membrane soaked with 99.64 mM trioctylmethylammonium chloride and 50 mM tributyl phosphate in toluene, and 1 M sulfuric acid in Intermediate phase and 48.86 mM ethylenediaminetetraacetic acid in the Strip phase. After 48 hours of stirring at 500 rpm, 98.79% of Ni(II) were found in Feed, 91.32% of Cu(II) in Intermediate, and 91.04% of Cd(II) in Strip compartment of DFSSLM. Competitive transportation between Cd(II) and Cu(II) was justified with the flux changes and kinetic studies of Cd(II) and Cu(II). Treatment using DFSSLM yielded high output/input ratios for recovered Cd(II), Cu(II) and Ni(II). 89.09% of Cd(II) recovered in Strip, 90.87% of Cu(II) in Intermediate, 97.61% of Ni(II) remained in Feed and most of the other heavy metals were eliminated. This study concluded that DFSSLM is efficient for separation and recovery of Cd(II), Cu(II) and Ni(II) from complex mixture.

CHAPTER 1

INTRODUCTION

1.1 Research background

Selective extraction of heavy metals from wastewater has become a significant issue due to the reduction of world’s high-grade resources, endless demands, metals high prices and environmental pressures. Scheduled wastes containing heavy metals in Malaysia were generated mainly from industries such as electric and electronic (4.23%), metal refinery (3.36%), metal fabrication (2.08%), metal finishing and coating (1.51%), mining (0.19%) and textiles (0.08%) (DOE, 2018). Although heavy metals contribute to small percentage of all waste generated by industrialization, their impact can be detrimental to living things and environment due to their toxicity and nonbiodegradable nature.

Stringent environmental regulations and depletion of world’s mineral resources have urged for the removal and recovery of heavy metals from the metallurgical production wastewaters, hydrometallurgical processing waste and secondary sources in complex leach solutions. Most industries convert their industrial waste stream into sludge and slag form to ease the disposal process. However, not all of the sludge and slag wastes are allowed to be sent to landfill facilities due to leaching test failure. Heavy metal sludge generated in Malaysia was 11.4% of total scheduled wastes of 2,355,085.21 metric tonnes based on the latest Malaysia Environmental Quality Report 2018 (DOE, 2018). Heavy metal sludge produced in 2017 was slightly lesser with 226,747.90 metric tonnes per year or 11.24% of total waste (DOE, 2017).

In most industrial operations, large quantity of water is required for each succeeding process to rinse and remove unwanted chemicals before each processing step. As a result, the wastewater produced from washing out and massive discharge of used acids usually has large mass of diffused metallic ions. However, not many industries in Malaysia have effective wastewater treatment plants and most of the small to medium scale industries opt for low-cost disposal methods by transferring their waste to other treatment facilities for further treatment. Due to lack of sustainable and efficient treatment technologies, most of the wastes are accumulated and stored in their premises prior to disposal and thus, resulted in space-consuming and stockpiling of waste (Plate 1.1).

Plate 1.1 Stockpiling of nickel and copper sludge in electroplating plant

Illegal dumping of heavy metal-bearing sludge and discharge of untreated wastewaters into the natural water streams will definitely cause more harm towards the environment. Therefore, effective wastewater treatments and environmental management systems are needed for minimization of sludge and waste generation. Significant amounts of highly valuable or precious metals could be separated and recovered from wastewaters. Extraction and recovery of a portion or all of such metals will yield a significant income by resale, net saving in chemical costs by recovery-and-recycle, and also eliminate the generation of excessive waste.

Treating the complex mixture with diverse metals is a complicated process due to each waste batch's varying metallic content. As a rule of thumb during the selective extraction operations, only the precious metals of interest are targeted and recovered meanwhile, the irrelevant ones are excluded. Wide variety of techniques have been adapted, mainly on the conventional practices include chemical precipitation (Chen et al., 2018), coagulation-flocculation (Fu and Wang, 2011), ion-exchange (Otrembska and Gega, 2012), membrane filtration (Sum et al., 2019) and solvent extraction (Wilson et al., 2014). These techniques for removing heavy metals are not economical due to the large consumption of energy, solvent, chemical, and space. In the search of alternative technology to overcome the weaknesses of conventional techniques, the development of a cheap and simple liquid membrane technology has led to the advancement in heavy metal separation. Supported liquid membrane technology is one of the configurations in liquid membrane technology which has been reported for its wide range of selectivity, single stage operation of both extraction and stripping, effective utilization of energy and material as compared to many other separation systems.

For this study, the dual flat sheet supported liquid membrane (DFSSLM) system is highlighted as it gives a broader scope of application that involves a single process of concurrently extracting, stripping and selectively separating multiple metal ions from mixture. Therefore, DFSSLM provides a good chance for advancement of metal separation, purification and recovery operation in the future of electroplating wastewater treatment.

1.2 Problem statements

Selective separation and recovery of multiple heavy metals from complex wastewater is a challenging task. Amongst the available techniques, ion exchange, solvent extraction and supported liquid membrane are known to be highly selective for separation and recovery of metals. Ion exchange is extensively employed owing to its rapid kinetics and successful removal rate. However, this method requires high consumption of expensive resins to treat large volume of wastewater with low metal ions concentration. Solvent extraction method is one of the most established approach in extractive metallurgy with its continuous operation, minimal reaction requirement and high recovery of metals (Zhang et al., 2016). Although solvent extraction is highly effective from bench-scale to industrial-scale operations for metal extraction, this method involves more tedious operational procedures (multistep extraction, stripping and scrubbing process), large consumption of solvents and expensive extractants. Apart from solvent extraction, supported liquid membrane (SLM) also demonstrates vast potential for its promising application in purification of metal-bearing wastewater.

In this research, SLM is highlighted since it provides a wider scope in separation technology that involves simultaneous extraction and recovery of metals in a single process with low solvent consumption. The increase number of studies and knowledge in analysis, design and application of SLMs opens new prospects for SLM-based membranes in heavy metals separation and recovery for reuse as valuable by-products. Existing SLM techniques have yet to find commercial applications whereby most applications only focus on the selective separation of one targeted metal ion from a complex mixture. In fact, there are numerous metal ions that could be recovered or separated simultaneously. The existing simultaneous separation and recovery of several heavy metal ions techniques only focused in laboratory scale and are not entirely intensive in covering vast applications (Fang et al., 2018).

The idea of dual flat sheet SLM (DFSSLM) was inspired from Duan et al. (2017) who developed compartmental SLM (sandwich SLM) for the simultaneous separation of copper, cobalt and nickel from ammonia/ammonium chloride solutions using two polyvinylidene difluoride membranes impregnated with Acorga M5640 in kerosene. Along the successful separation of three different metals into three separated compartments simultaneously, SLM with multiple compartments will provide a wider scope in separation technology. To the best of my knowledge, there is no report on the method of using different extractants impregnated into separated membranes of the same SLM. Some metals are transported slowly and others permeate rapidly across the membrane. The difference between permeation rates can be adjusted based on the type of extractant and its concentration. Based on their selectivity preference, incorporation of different extractants onto multiple membranes as separation barriers creates a consolidated multi-compartment system for simultaneous separation of more than two heavy metals.

With the challenges associated with existence of various metal ions in wastewater, selective separation of metals is difficult due to some metal ions with similar physicochemical properties (Zeng et al., 2019). Based on the total permeability and total flux values for various proportion of metals in a mixture, the existence of another metal reduces the overall separation of heavy metals as compared to the separation of individual metal (Bhatluri et al., 2014). Therefore, most researchers faced competitive transportation in the presence of combinatorial transportation of several heavy metal ions in a continuous operation. Since a high degree of selectivity could not be achieved by controlling the pH alone, masking agents were introduced to ensure permeation of selected metals across the membrane and interfering ions were masked to form anionic complex (Ramkumar et al., 1998). Nevertheless, there is still no report on selective separation of metals using masking agent in the stripping process of SLM. Evolution of an integrated DFSSLM system comprising multiple membrane separation stages with the use of selective extractants and masking agent is a novelty for innovation and advancement of separation processes.

1.3 Hypotheses

Based on existing theories, several hypotheses are addressed to cover different aspects of this research:

i. Newly designed dual flat sheets SLM allows selective separation of three types of metal ions at three separated compartments.

ii. Determination of suitable carriers (extractants) allows the selective separation of desired metal ions.

iii. Use of masking agent in stripping process prevents co-transportation of metal ions.

iv. Optimization of operating parameters contributes to the highest selective separation of desired metal ions.

1.4 Objectives of research

The main aim of this research is to study the feasibility of Dual Flat Sheet Supported Liquid Membrane (DFSSLM) to selectively extract Cd(II), Cu(II) over

Ni(II) ions from aqueous mixture. To meet the primary research goal, several specific objectives to be achieved are identified by three stages as follows:

i. Stage 1: Selective extraction of Cd(II), Cu(II) over Ni(II) from synthetic mixture

   a. To investigate the effect of pH and D2EHPA concentration on selective extraction of Cd(II) and Cu(II) over Ni(II)

   b. To screen and optimize the influential operating parameters for selective extraction of Cd(II) and Cu(II) from aqueous mixture

   c. To determine the loading capacity and the Cd(II) and Cu(II) extraction mechanisms in D2EHPA-TBP-kerosene system

ii. Stage 2: Separation of Cd(II) and Cu(II) from Stage 1 mixture

   a. To investigate the effect of pH, Aliquat 336 concentration and EDTA concentration on selective extraction of Cd(II) over Cu(II)

   b. To screen and optimize the influential operating parameters for selective extraction of Cd(II)

   c. To determine the loading capacity and Cd(II) extraction mechanism in Aliquat 336-TBP-toluene system

iii. Stage 3: Selective extraction of Cd(II), Cu(II) over Ni(II) using DFSSLM

   a. To evaluate the effect of optimized conditions on selective extraction of Cd(II), Cu(II) over Ni(II) from synthetic wastewater using DFSSLM

b. To find out the efficiency of DFSSLM in selective extraction of Cd(II), Cu(II) over Ni(II) from real electroplating wastewater

1.5 Research scope

This research was carried out in three stages to formulate the optimum working conditions for DFSSLM system in order to selectively remove and recover three targeted metal ions, Cd(II), Cu(II) and Ni(II) from aqueous mixture. Selective separation of two metals from a mixture of three metals were conducted to achieve objectives in Stage 1, followed by the separation of the remaining two metals to fulfil the objectives in Stage 2, and DFSSLM system was subsequently developed to achieve simultaneous separation and recovery of three targeted metals in Stage 3.

To fulfil the first objective in Stage 1, screening and optimization processes were conducted to determine the influential factors affecting the extraction studies, whereby process variables such as concentration of the selected extractant, di(2-ethylhexyl) phosphoric acid (D2EHPA) (50 to 100 mM), concentration of phase modifier, tributyl phosphate (TBP) (50 to 100 mM), concentration of inert salt, sodium sulphate (200 to 250 mM), organic to aqueous ratio (O:A) (1:1 to 2:1), shaking time (5 to 10 mins), and pH_{eq} (4 to 5) were varied. Other parameters such as the initial concentrations of Cd(II), Cu(II) and Ni(II) in aqueous mixture (100 mg/L), diluent type (kerosene), operating temperature (28±1°C), and shaking speed (150 rpm) were fixed. Further investigations on the effect of influential factors, pH_{eq} (2.0 to 5.5), D2EHPA (50 to 200 mM) and TBP (0 to 100 mM) concentrations on selective extraction of Cd(II) and Cu(II) over Ni(II) were under optimized conditions to achieve the second objective. Under optimized conditions, the maximum loading of D2EHPA-TBP-kerosene system and the extraction mechanisms of Cd(II) and Cu(II) in the system were investigated to meet the third objective in Stage 1.

Screening and optimization studies in Stage 2 were performed on process variables such as concentration of the selected extractant, trioctylmethylammonium chloride (Aliquat 336) (50 to 100 mM), concentration of phase modifier, tributyl phosphate (TBP) (50 to 100 mM), concentration of masking agent, ethylenediaminetetraacetic acid (EDTA) (10 to 50 mM), organic to aqueous ratio (O:A) (1:1 to 2:1), and pH_{eq} (2 to 5) were varied. Other parameters such as the initial concentrations of Cd(II) and Cu(II) in aqueous mixture (100 mg/L), diluent type (toluene), operating temperature (28±1°C), shaking time (10 mins), and shaking speed (150 rpm) were fixed. At the same time when the effect of pH_{eq} (2.0 to 5.5) was investigated, another organophosphorus compound, trioctylphosphine oxide (TOPO) was used to compare its synergistic effect with Aliquat 336 to verify the choice of phase modifier. Further investigations on the effect of influential factors, Aliquat 336 (50 to 200 mM) and EDTA (0 to 100 mM) concentrations on selective extraction of Cd(II) over Cu(II) were under optimized conditions to achieve the second objective in Stage 2. Under optimized conditions, the maximum loading of Aliquat 336-TBP-toluene system and the extraction mechanisms of Cd(II) in the system were investigated to meet the third objective in Stage 2.

As both liquid-liquid extraction and supported liquid membrane processes are associated with similar components such as extractants and diluents, thus, the chemistry of extraction mechanism is more or less identical. Therefore, the optimum operating parameters applied in Stages 1 and 2 were tested and applied on the separation and recovery of Cd(II), Cu(II) and Ni(II) using DFSSLM. Efficiency of

DFSSLM were presented in terms of mass balances and output/input ratio of Cd(II), Cu(II) and Ni(II) to fulfil the first objective of Stage 3. To achieve the second objective in Stage 3, these optimum conditions were tested for the separation and recovery of targeted metals from complex matrices which are electroplating wastewater.

1.6 Research limitations

The use of expensive membranes and extractants, membrane phase instability and clogging of membrane pores are the main limitations of SLM. Proper selection of the components such as, the carriers, diluents and support materials etc. must be carried out to attain a stable SLM with effective transportation of heavy metals. Measurement of in-situ stability is not practical and difficult to do. Hence, stability is often resembled by measuring the average flux of heavy metal ions for a long period of time at different operating conditions. Another limitation of the SLM is the clogging of the micropores in the support membrane. Fouling is found to be at the highest in most SLM applications due to the existence of different chemicals in the real wastewaters or industrial effluents.

Besides, the organic phase starts to diminish at the pores of support due to the high volatility of solvent used and causes direct channelling between the feed and strip aqueous phases across the SLM after operating of SLM at a longer time. Serious leakage of membrane and direct channelling between feed and strip phases will occur and thus, cause a sudden change in the pH of feed phase. The pH of feed solution tends to be as close as to that of strip solution at the point of total loss. Obstacles of SLM to be more economically viable persist as the instability issues have yet to be overcome.

The real industrial wastewater contains not only assorted heavy metals, but also other impurities that will block the pores of membrane interface. The unintended clogging of membrane causes a decrease in transfer flux.

1.7 Organization of thesis

This thesis consists of five chapters. Chapter 1 (Introduction) presents an overview of the background of this research. Critical issues regarding on the extraction and recovery of cadmium, copper and nickel from electroplating wastewater are discussed and compared. Several problem statements related to this research are identified before conducting the experiments. The hypotheses, objectives, scope and limitations of this research are clearly mentioned.

Chapter 2 (Literature Review) explains a general overview of heavy metal pollution caused by industrial effluents and related treatment technologies. Characteristics of electroplating wastewater containing Cd(II), Cu(II) and Ni(II) ions are evaluated. Liquid membrane and its configurations, SLM and its components (extractants, diluents, modifiers, stripping agents and masking agents) for heavy metal separation from aqueous solutions are also reviewed. Multivariate statistical analysis used for this research are discussed in detail.

Chapter 3 (Methodology) shows the overall framework of this research, materials and reagents, analytical equipment, and software programs used throughout the research. The experimental procedures for the preparation of aqueous and organic phases, as well as the extraction of metal in three stages by both liquid-liquid extraction and supported liquid membrane are elaborated. A detailed flow diagram of the overall experimental activities by stages is also presented.

Chapter 4 (Results and Discussion) presents all the results obtained from three stages throughout the research. It covers the findings on the screening and optimization studies of Stage 1 and Stage 2 using liquid-liquid extraction, as well as the extraction studies by DFSSLM for selective separation of Cd(II), Cu(II) and Ni(II) ions from sulphate solution under optimized conditions. Interactions between the extractants and metals are determined by Fourier transform infrared spectroscopy analysis. Efficiency of DFSSLM for separation of metals is tested using synthetic wastewater and real electroplating wastewater. Changes on the surface morphologies and elemental characteristics of support membranes used in DFSSLM are investigated.

Chapter 5 (Conclusions and Recommendations) summarizes all the important findings from this research. Conclusions are specified based on the attainments of the research goals as listed in the first chapter. Lastly, recommendations for future research studies are proposed based on their significance related to the current research.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter covers a brief introduction on heavy metals and the treatment technologies for heavy metal-bearing effluents. Electroplating wastewater containing Cd(II), Cu(II) and Ni(II) ions is specifically elucidated, followed by an overview of liquid membrane and its classifications. Then, supported liquid membrane (SLM) and its modifications, for separation of heavy metals are reviewed extensively. Selection of extractants, diluents, modifiers, stripping agents and the use of masking agents are also highlighted in this chapter. An overview on the fundamental and chemistry of metal extraction by SLM in this research is presented. Selection of significant parameters via screening and multivariate statistical analysis using response surface methodology are explained in the last section of this chapter.

2.2 Heavy metals and their existence in industrial effluent

2.2.1 Heavy metals and their impacts

Heavy metals are generally referring to metallic elements that have atomic densities higher than 4000 kg/m^3 and specific gravities larger than 5 (Alonso-Magdalena et al., 2019; Becker, 2016). Heavy metals are unintentionally or directly discharged into the environment from natural phenomena and anthropogenic sources (Yadav et al., 2019). Most of the heavy metals are essential for survival of living organisms, and they are already present in the human body in trace amounts. Heavy metals unable to degrade like other organic-based pollutants. Furthermore, living organisms are easily exposed to heavy metals via bioaccumulation process. Most heavy metals in dissolved form are harmful and often related to toxicity and pollution issues. Adverse ill effects can occur when humans are exposed to heavy metal concentrations beyond the permissible limits. Due to rapid industrial development, the excessive discharge of heavy metals has caused numerous health and environmental concerns.

Necessity to treat effluent containing heavy metals is an inevitable challenge because of their toxicity and high persistence in the environment. Wide aspects of toxicological effects concerning inorganic contaminants towards the environment and public health are reviewed in many literatures include reduced growth and development, osteoporosis, tumours, gastrointestinal distress, cardiovascular issues, dermatitis, cancer, organ dysfunction, central nervous system damage, and in extreme cases, death (Fu and Wang, 2011; Vardhan et al., 2019). These toxic heavy metals are classified as environmental priority pollutants and discharge of effluents containing these pollutants are strictly regulated by United States Environmental Protection Agency (USEPA).

2.2.2 Heavy metals in industrial effluent

Industrial effluent refers to any waste in the form of liquid or wastewater generated from manufacturing process including the treatment of water for water supply or any activity occurring at any industrial premises (DOE, 2009). Industrial processes utilize a wide variety of chemicals, depending on the types of products that are manufactured and processed. Most of the product parts are typically processed and rinsed in a water-based solution containing combinations of chemicals and heavy metals. Large volume of water in various processing steps is utilized and various heavy metals are often discharged in these processing waters and thus, these metals will find their way into one or more wastewater streams. Large quantity of heavy metal contaminants is found in industrial effluents from metal plating facilities, batteries, textile industries, paper industries, semiconductor manufacturing, metal refining and hydrometallurgical processing (Duruibe et al., 2007; Gumpu et al., 2015; Liu et al., 2019). In most of the industrial effluent treatment, heavy metals of major concern are cadmium, chromium, copper, lead, mercury, nickel and zinc (Fu and Wang, 2011).

2.2.3 Environmental regulations on heavy metal in industrial effluent

Frequent-occurring environmental accidents and illegal dumping are the driving forces for the enforcement of stricter legislation on the discharge of toxic heavy metals. In Malaysia, permissible discharge limits of heavy metals in industrial effluent of Standards A and B, respectively, as specified in the Fifth Schedule by Environmental Quality (Industrial Effluent) Regulations 2009 are given in Table 2.1.

Table 2.1 Acceptable conditions for discharge of industrial effluent of Standard A and B (EQA[a], 2018)

Heavy metals	**Permissible discharge limits (mg/L)**	
	Standard A	**Standard B**
Arsenic	0.05	0.10
Cadmium	0.01	0.02
Chromium, Hexavalent	0.05	0.05
Chromium, Trivalent	0.20	1.0
Copper	0.20	1.0
Lead	0.10	0.50
Manganese	0.20	1.0
Mercury	0.005	0.05
Nickel	0.20	1.0
Tin	0.20	1.0
Zinc	2.0	2.0

[a]EQA: Environmental Quality Act

Discharge of industrial effluent into inlands within the specified catchment areas must not exceed the Standard A limits, whereas the discharge into other inland or Malaysian waters must not exceed the Standard B limits. Industrial effluent which contains two or more metals (copper, manganese, nickel, tin and zinc) as specified in the Fifth Schedule, where Standard A is practiced when the total concentration of these metals is not more than 0.5 mg/L. Standard B is applicable for 3.0 mg/L in total and 1.0 mg/L for soluble forms (EQA, 2018). To comply with these regulations, the development of cost-effective on-site treatment and waste management technologies to control the discharge of heavy metals becomes paramount.

2.2.4 Electroplating effluent containing Cd(II), Cu(II) and Ni(II) ions

2.2.4(a) Electroplating process

As part of the surface engineering industry in Malaysia, there are about 40 prominent companies involve mainly in plating operations to cater the needs of multinationals in the electrical and electronics, automotive, oil and gas, aerospace, medical and solar/photovoltaic industries (MIDA, 2019). More than 300 electroplating small and medium scale industries are also in operations to fulfil the requirements of other manufacturing industries throughout Malaysia (Wangel et al., 2004).

Electroplating involves electrodeposition procedures to form metallic coatings onto solid substrates by electric current, mainly to enhance their properties, appearance and durability. The solid substrates (mainly metals) are electroplated through a series of water-based solutions consisting various chemicals including strong acids, alkaline solutions and complexing agents. Electroplating pretreatment processes involve cleaning (to remove hydrophobic contaminants), acid pickling (to remove surface impurities and inorganic contaminants), acid activation (to remove oxides) prior to subsequent plating. Before drying, passivation process is vital to remove free ions on the surface and to increase corrosion resistance of the metal. Since each processing step uses different specialized chemicals that would react unfavourably with the consecutive process, every processing step is followed with one or two water rinse. Figure 2.1 summarises the process flow of electroplating operations.

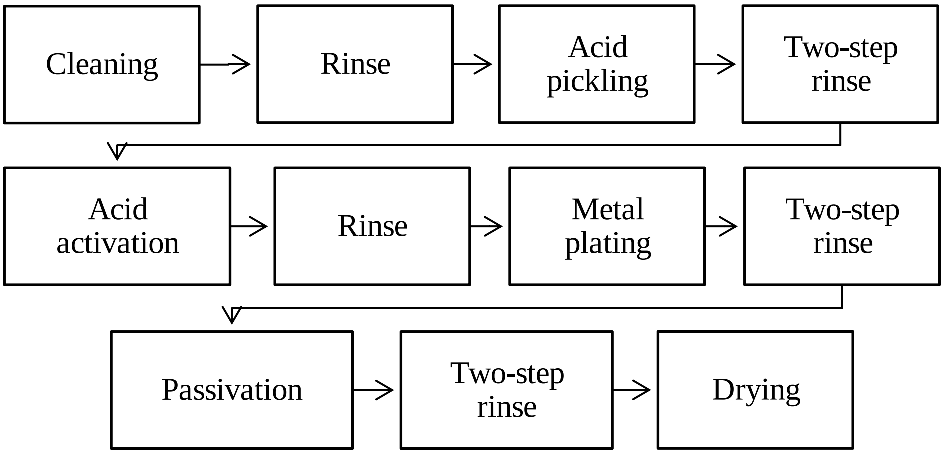

Figure 2.1 Flow diagram of electroplating processes

Large amount of water is needed to rinse off and remove the processing chemicals thus, the rinse water becomes contaminated and needs to be treated prior to discharge. Thus, electroplating effluent generated from rinsing solutions especially, after the plating process often contain high concentrations of dissolved metals especially Cr(III), Cd(II), Cu(II), Ni(II), Fe(III) and Zn(II) (Tang and Qiu, 2019). Most electroplating industries do not practice effective on-the-spot metal extraction and recovery in their own facilities. Recovery of metallic constituents from wastewater is important from the ecological point of view and additionally, these waste streams can be an alternative secondary source of metal ions and beneficial for economic reasons. Therefore, an electroplating wastewater can be one of the potential sources for cadmium, copper and nickel recovery.

2.2.4(b) Characteristics of electroplating effluent

Table 2.2 shows the typical electroplating effluents depending on the types of metal plating industries.

Table 2.2 Heavy metal concentrations in various types of electroplating effluent

	Types of electroplating effluent (mg/L)			
Heavy metals	**Chrome-plating rinse water [a]**	**Copper-plating rinse water [b]**	**Nickel-plating rinse water [c]**	**Zinc-plating rinse water [d]**
Arsenic	0.14	-	-	-
Cadmium	0.04	1	0.05	-
Chromium	540	6	106	15
Copper	-	15560	-	21
Iron	0.8	3.2	5.8	14
Lead	0.4	-	-	-
Nickel	0.01	245	4156	40
Tin	-	1	1	-
Zinc	38.2	13	15	198

Sources: [a]Noah et al., 2018; [b]John et al., 2016; [c]Sulaiman and Othman, 2017; [d]Tang and Qiu, 2019

Chrome, copper, nickel and zinc coatings are the most widely used resistant over-plates. In general, the overall effluent characteristics vary significantly depending on types of metal plating process but are usually composed of significant quantities of heavy metals. The metals used as main element in electroplating (such as chromium, copper, nickel and zinc) are detected with very high concentrations in their respective plating rinse wastewater compared to other metals. Other hazardous metals are also found in these electroplating effluents, resulted from the plating of alloy compounds. Nevertheless, these heavy metals in electroplating effluent often exceed the permissible discharge limits (Table 2.1) and thus, all electroplating industries are required to conduct extensive wastewater treatment to meet the regulatory requirements. In this research, a mixed rinse wastewater containing Cd(II), Cu(II) and Ni(II) from electroplating industry is investigated.

Cadmium coating provides reliable protection to low-alloyed steels since it is more anodic than steel in both galvanic series and electromotive force (Chung et al., 2019). Cadmium plated steel components have excellent corrosion resistance on aircraft engines, bolts and fasteners (Wanhill et al., 2011) and most recently used on cadmium telluride solar panels (Maani et al., 2020). Cadmium plating rinse effluent may hold up to 500 mg/L Cd(II) whereby only 30-40% of the added Cd(II) are fully utilized for plating process (Dermentzis et al., 2011). The use of cadmium has been restricted by the European Restriction of Hazardous Substances due to its toxicity and thus, strict regulations on discharge containing Cd(II) are imposed in most industrial and manufacturing processes (Morrow, 2010). Even at low concentration, cadmium is often found in waste by-products such as cadmium–rich dust, copper-cadmium slag, and also in hydrometallurgical leachates where Cd(II) is present along with other heavy metal ions such as Cu(II), Ni(II), Zn(II), and etc (Bidari et al., 2013).

Nickel electroplating is popular for its corrosion protection, wear resistance, excellent ductility and improved hardness. Therefore, nickel electroplating is broadly used for jewelleries, decorative ornaments, and also nickel alloy film deposition for electronic storage devices (Cattaneo and Riegel, 2009). In plating baths, reducing agents are added together with approximately 5000 mg/L of nickel sulfate (Sulaiman and Othman, 2017). Concentrated rinsing water from nickel electroplating process often contains Ni(II) ranges from 900 to 1583 mg/L (Lu et al., 2015).

Many industries such as automotive, aerospace, electrical and electronics depend on copper plating to enhance a material’s thermal and conductivity properties. For corrosion protection purpose, steel is commonly finished with copper plating as an undercoat prior to nickel plating (Kilany et al., 2020). First and second rinsing bath of electroplating process contain high concentration of Cu(II) in the range of 2513 to 7762 mg/L (Kul and Çetinkaya, 2009).

Despite their toxicity, cadmium, copper and nickel are also used in other industries such as metal refining, mining, manufacturing of alloys and batteries (Vardhan et al., 2019). The demand for copper has increased globally over the medium to long term with green energy policies pointing to more usage of renewable power and electric vehicles, causing an increase of copper prices from RM 19,859 per metric ton in 2015 to RM 29,107 per metric ton in 2020 (Index Mundi, 2020a). Growing demand for nickel from battery manufacturers escalated the prices of nickel from RM 37,9278 per metric ton in 2015 to RM 65,090 per metric ton on in 2020 (Index Mundi, 2020b). Rise in prices for cadmium was recorded from RM 5,890 per metric ton in 2015 to RM 10,410 per metric ton in 2020 due to the growing demand for cadmium in manufacturing of rechargeable batteries and solar panels (Statista, 2020). Thus, separation and recovery of cadmium, copper and nickel from electroplating wastewater is economically interesting due to their high market values with various applications in the industry. It is important to safeguard the environment from heavy metal pollution, as well as to recover to return a portion or all of these metals to the beginning of process cycle. Thus, the significance of the removal and recovery of Cd(II), Cu(II) and Ni(II) ions from electroplating wastewater is highlighted.

2.3 Treatment technologies for heavy metals

Technical innovations and modifications in treatment technologies are highly demanded to develop more reliable and environmentally sound techniques for separation and recovery of heavy metal ions. Selection of treatment techniques for a specific type of wastewater is normally based on the fundamental properties of pollutants in the wastewater, capital investment and operational cost, process flexibility and reliability, and environmental compatibility. Since heavy metals are non-biodegradable, physiochemical treatment methods like adsorption, chemical precipitation, coagulation-flocculation, electrochemical, ion-exchange and membrane filtration are preferable and proven effective with efficiencies of up to 100% provided the equipment used are in good condition and are operated under optimum working conditions (Fu and Wang, 2011). Although these treatment methods are effective to remove heavy metals, the intrinsic benefits and drawbacks of each method are mentioned in numerous literatures and summarized in Table 2.3.

To obtain safe-treated water, most applied methods in Table 2.3 tend to have limitations such as high operational cost, large consumption of energy, chemical and space, non-reusability, infeasibility for scale-up and generation of secondary wastes. Among the various techniques mentioned in Table 2.3, adsorption, ionic exchange and membrane separation have gained popularity in the recent years for their high efficiency and simplicity for implementation in commercial scale.

To date, adsorption with low-cost adsorbents (such as chitosan, clay and natural zeolites) or innovative bio-sorbents (large number of live or dead, dry or wet biomasses) has gained its popularity in removal and degradation of complex pollutants especially in wastewater with low concentration of heavy metals. Agricultural waste materials and industrial by-products have been also studied as potential adsorbents for sequestering heavy metal ions. Among all, activated carbon has been the most used adsorbent, nevertheless it is relatively expensive. Besides generation of sludge, the continuous source and process reproducibility are the main limitation of using adsorbents for heavy metal treatment (Qin et al., 2020).

Table 2.3 The description, benefits and drawbacks of the various treatment methods for removal of heavy metals from industrial wastewater

Treatment methods	**Description**	**Benefits**	**Drawbacks**	**References**
Adsorption	Adsorbents with active functional groups, large surface area and high porosity are used to bind metal ions. Spent adsorbents are removed by filtration and can be regenerated.	• Inexpensive • Availability of wide range of adsorbents (activated carbons, zeolites, polymers, nanomaterials, microflora, plants, agricultural and industrial waste) • Simple operation	• Low selectivity • Complicated post treatment procedures due to generation of by-products	Ihsanullah et al. (2016) Qin et al. (2020)
Chemical precipitation	Metal ions are converted into insoluble solid precipitates by using chemical agents before being removed by filtration process.	• Low operational cost • Simplicity of process control	• High chemical utilization • Generation of low-density toxic sludge • High sludge disposal cost	Chen et al. (2018)
Coagulation-flocculation	Cationic coagulant is introduced to lower particles' surface negative charge. Then, anionic flocculant is added to bind the positively charged aggregates into larger compound before being removed by filtration process.	• Simple operation • Inexpensive coagulant • Reduction in turbidity along with heavy metal removal	• High chemical utilization • Incomplete heavy metals removal • High sludge production	Fu and Wang (2011)

Table 2.3 (Continued)

Treatment methods	**Description**	**Benefits**	**Drawbacks**	**References**
Electrochemical	This process involves the application of electricity to pass a current through effluent, whereby a cathode plate and an insoluble anode are used to separate metal ions.	• Quick and easily controlled treatment • High separation selectivity • Recovery of metal in the elemental state	• High capital investment and operational cost due to energy consumption • Regular need for electrode replacement	Tran et al. (2017)
Ion-exchange	This process involves reversible exchange of ions between solid resins and metal-containing liquid where complexation of metal with free functional group occurs.	• Fast kinetic • Simple operation • Regeneration of resin	• Suitable for effluents with low concentration of metals only • Highly sensitive to pH	Otrembska and Gęga (2012)
Membrane filtration	Membrane acts as a barrier in separation processes such electrodialysis, ultrafiltration, nanofiltration and reverse osmosis depending on the size of target particles and membrane pore size.	• Small space requirement • Various membrane types • High separation selectivity and removal efficiency • High retention rate of metals	• High capital investment and operational cost due to membrane fouling • Lower permeate flux • Complex operation • Involves pressure driven processes	Abdullah et al. (2019) Sum et al. (2019)

Other than that, natural and synthetic resins have been widely applied for removal of dissolved metals from wastewater. Synthetic resins are mostly preferred for their selectivity with cationic forms of metal ions in the wastewater due to the presence of exchangeable ions in the acidic groups of the resins (Kalaivani et al., 2016). Even though the ion-exchange resins have regenerative ability, the chemicals used for the regeneration of resins can cause secondary pollution. To use highly selective resins for industrial applications, ion-exchange process is expensive as it requires a large number of resins to treat large volume of wastewater with low metal ions concentration.

Recent trends of removal of metallic ions from industrial effluent has been focused on the use of membranes with different separation mechanisms (Abdullah et al., 2019). Membrane filtration involves pressure-driven separation process that requires a physical membrane as a barrier for both chemical and mechanical filtering of particles and macromolecules. New breakthroughs in creation of membranes made from less conventional materials have led to greater and cleaner technologies for the selective separation of heavy metal ions. Ultrafiltration (UF) membranes (such as complexation-enhanced UF and micellar-enhanced UF) are suitable for the treatment of effluent containing low concentrations of heavy metals with high separation efficiency. However, post-treatment processes are required due to the generation of ligands/micelles wastes and other harmful by-products. Nanofiltration and reverse osmosis, meanwhile, can potentially be used to treat effluent with high levels of metallic ions and are suitable for large-scale applications. The tendency of membrane fouling is more severe in nanofiltration and reverse osmosis membranes compared to UF membranes due to the requirement of higher operating pressure.

Apart from using polymer-based membranes, immiscible liquids are studied widely as semipermeable phase separators in the treatment of metal-bearing effluents, to urge the replacement of existing separation techniques as listed in Table 2.3. The transport of heavy metal ions from aqueous phase to an organic phase is associated with the concept of solute distribution ratios between two immiscible liquids. In most cases, these immiscible liquids (petroleum-based solvents, vegetable oils and ionic liquids) used comprise of the combination of an extractant for specific metal ions and a diluent (Altin et al., 2010). Separation techniques with these immiscible liquids are known as solvent extraction or liquid-liquid extraction and liquid membrane technology and they have been widely applied for metal ions extraction and recovery.

2.4 Liquid-liquid extraction

Solvent extraction or also known as liquid-liquid extraction (LLE) has been well recognized as an analytical tool for the separation and analysis of elements with identical chemical properties since 1970s. At present, LLE is widely employed in a variety of industries, featuring extensively as selective separation process (Zhang et al., 2018), enhancement and purification of a variety of chemicals and elements (Fleitlikh et al., 2017), and recovery of valuable metal ions (Sinha et al., 2016).

LLE utilizes the principle of solute distribution ratios between two immiscible liquids (generally consist of one organic and one aqueous phase) in contact with each other to achieve separation. The separation procedure is mainly based on the transportation of the solutes, such as metal ions, from the aqueous phase to an organic phase (Teng et al., 2012). Solute M, a heavy metal which is formerly dissolved in one of the phases, gradually distributes itself between the two immiscible liquids with the diffusion/reaction at the interface and finally attains equilibrium, whereby the