COPPER RECOVERY AND SPENT ETCHANT REGENERATION BASED ON SUPPORTED LIQUID MEMBRANE TECHNOLOGY

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS .................................................................................................................I

TABLE OF CONTENTS ..................................................................................................................III

SUMMARY ........................................................................................................................................X

NOMENCLATURE ..........................................................................................................................XIV

LIST OF TABLES ........................................................................................................................... XVII

LIST OF FIGURES ..........................................................................................................................XIX

LIST OF FIGURES ..........................................................................................................................XIX

1.  CHAPTER ONE: INTRODUCTION .......................................................................................... 1

1.1 General Background Information .......................................................................................... 1

1.2 General Information on Membranes ..................................................................................... 6

1.3 Membrane Fabrication, Characterization and Evaluation ..................................................... 7

1.4 Liquid Membranes (LM) ........................................................................................................... 8

1.5 Supported Liquid Membranes (SLM) ...................................................................................... 11

1.6 Research Objectives and Outline of the Thesis ..................................................................... 13

References ...................................................................................................................................... 17

2.  CHAPTER TWO: LITERATURE REVIEW .............................................................................. 22

2.1 Recent Advances in Supported Liquid Membranes ............................................................... 22

2.1.1 Overview .......................................................................................................................... 22

2.1.2 Mechanistic and Kinetic Studies of SLM Based Separations ............................................. 27

2.1.3 New Applications of SLM ............................................................................................... 32

2.2 Stability of Supported Liquid Membranes ............................................................................. 34

2.2.1 Mechanisms of SLM Instability ....................................................................................... 35
2.2.1.1 Chemical Bonding Effect ................................................................. 36
2.2.1.2 Osmotic Pressure Model ................................................................. 36
2.2.1.3 Pressure Difference Mechanism ..................................................... 38
2.2.1.4 Mutual Solubility Effect ................................................................. 39
2.2.1.5 Pore Blocking Mechanism .............................................................. 41
2.2.1.6 Shear Induced Emulsion Mechanism .............................................. 42

2.2.2 SLM Stability Performance Optimization ............................................. 45
2.2.2.1 Optimal Membrane Preparation ..................................................... 45
2.2.2.2 Optimal Operation Conditions ....................................................... 46
2.2.2.3 Liquid Membrane Reimpregnation .................................................. 47
2.2.2.4 Formation of Gel Structures of SLM .............................................. 48
2.2.2.5 Formation of Barrier Layers on Substrate Membrane Surfaces ........ 49

2.3 Summary ............................................................................................... 51
References .................................................................................................... 53

3. CHAPTER THREE: SCREENING OF CARRIER IN SUPPORTED LIQUID MEMBRANE SYSTEM FOR MEMBRANE EXTRACTION OF Cu(II) FROM AMMONIACAL SOLUTIONS ......................................................... 68
3.1 Introduction ............................................................................................ 68
3.2 Experimental .......................................................................................... 69
3.2.1 Reagents ............................................................................................ 69
3.2.2 Analytical Methods .......................................................................... 70
3.2.3 SLM Setup ........................................................................................ 71
3.2.3.1 Flat Sheet Supported Liquid Membrane (FSSLM) ......................... 71
3.2.3.2 Hollow Fiber Supported Liquid Membrane (HFSLM) ....................... 73

3.2.4 Characterization of LIx54, LIx84 and Their Complexes with Ammoniacal
Copper Solutions ............................................................................................. 74

3.2.4.1 Experimental Methodology ................................................................. 74

3.2.4.2 Computational Methodology ................................................................. 75

3.2.5 Selective Separation of Copper over Other Cations in Ammoniacal Waste
Solutions Using HFSLM system ....................................................................... 76

3.2.6 Comparative Study of Long Term Stability of FSSLM to Treat Ammoniacal
Waste Solutions Using LIx54 and LIx84 as the Carrier .................................... 77

3.3 Results and Discussion ............................................................................... 79

3.3.1 Copper Complexes Formation with LIx54 and LIx84 .............................. 79

3.3.2 Effect of the Feed pH on Copper Transmembrane Flux with LIx54 and LIx84
as the Carrier ................................................................................................... 85

3.3.3 Effect of Carrier LIx54 or LIx84 Concentration on Copper Transmembrane
Flux .................................................................................................................... 87

3.3.4 Selective Separation of Copper over Other Cations Contaminants by Once-
through Transport in HFSLM Modules Using LIx54 or LIx84 as the Carrier 89

3.3.5 Long Term Stability of Vertical Flat Membrane System to Treat Ammoniacal
Wastewater Using LIx54 or LIx84 as the Carrier ............................................. 91

3.4 Summary .................................................................................................... 96

References ..................................................................................................... 98
4. CHAPTER FOUR: KINETICS AND MECHANISM OF COPPER REMOVAL
FROM AMMONIACAL WASTEWATER THROUGH FLAT SHEET SUPPORTED LIQUID MEMBRANES ..................................................................... 106

4.1 Introduction ............................................................................................................... 106

4.2 Experimental ............................................................................................................. 109

4.3 Results ....................................................................................................................... 109

  4.3.1 The Influence of Carrier Concentration on Cu(II) Transmembrane Flux ...... 109
  4.3.2 The Influence of Feed Cu(II) Concentration on Cu(II) Transmembrane Flux 110
  4.3.3 The Influence of pH in Feed Solution on Copper Transmembrane Flux ...... 113

4.4 Discussion ................................................................................................................. 115

  4.4.1 Description of Transmembrane Cu Transport Based on Facilitated “Small
        Carrousel” Mechanism........................................................................ 115

  4.4.2 Description of Transmembrane Cu Transport Based on Facilitated “Big
        Carrousel” Mechanism .................................................................................... 127

4.5 Summary ................................................................................................................... 133

References ....................................................................................................................... 135

5. CHAPTER FIVE: TREATMENT OF SPENT AMMONIACAL ETCHING
SOLUTION WITH HOLLOW FIBER SUPPORTED LIQUID MEMBRANES:
FROM BENCH-SCALE TO THE PILOT-SCALE TESTS..................................... 141

5.1 Introduction ............................................................................................................... 141

5.2 Experimental ............................................................................................................. 143

  5.2.1 Regents ............................................................................................................ 143
  5.2.2 SLM Setups ..................................................................................................... 143
7. CHAPTER SEVEN: THE DEVELOPMENT OF CHEMICALLY MODIFIED P84 CO-POLYIMIDE MEMBRANES AS SUPPORTED LIQUID MEMBRANE MATRIX FOR Cu(II) REMOVAL WITH PROLONGED STABILITY .......... 193

7.1 Introduction ............................................................................................................... 193

7.2 Experimental ............................................................................................................. 197

7.2.1 Materials .......................................................................................................... 197

7.2.2 Preparation of Asymmetric Membranes .......................................................... 197

7.2.3 Preparation of Symmetric Membrane .............................................................. 199

7.2.4 Membrane Modification by Chemical Cross-linking ...................................... 200

7.2.5 Membrane Characterizations ........................................................................... 201

7.2.6 SLM Preparation and Stability Characterization ............................................. 202

7.3 Results and Discussion .............................................................................................. 204

7.3.1 Characterization of the Original and Chemical Cross-linked Asymmetric Flat Membranes ................................................................. 204

7.3.2 Fabrication of Symmetric Flat P84 Membrane and Characterization of the Cross-linked P84 Membrane ...................................................... 205

7.3.3 Stability Characterization of SLMs with Unmodified and Chemical Crosslinked Membrane Support Matrixes .................................................. 208

7.3.3.1 Asymmetric Flat P84 Membrane ........................................................... 208

7.3.3.2 Symmetric Flat P84 Membrane ........................................................... 213

7.4 Summary ................................................................................................................... 215

References ....................................................................................................................... 217

8. CHAPTER EIGHT: CONCLUSIONS AND RECOMMENDATIONS .......... 221
8.1 Conclusions ............................................................................................................... 221

8.1.1 Screening of Carrier in Supported Liquid Membrane System for Membrane
Extraction of Cu(II) from Ammoniacal Solutions....................................................... 222

8.1.2 Kinetics and Mechanism of Copper Removal from Ammoniacal Wastewater
through Flat Sheet Supported Liquid Membrane (FSSLM) System ..................... 222

8.1.3 Treatment of Spent Ammoniacal Etching Solution with Hollow Fiber Supported
Liquid Membrane (HFSLM) System: From Bench-scale to the Pilot-scale Tests
.............................................................................................................................. 223

8.1.4 The Development of Chemically Modified P84 Co-Polyimide Membranes as
Supported Liquid Membrane Matrix for Cu(II) Removal with Prolonged
Stability............................................................................................................ 225

8.2 Recommendations ..................................................................................................... 226

8.2.1 Other Metals Removal, Recovery, Separation and Purification....................... 226

8.2.2 Desalination ..................................................................................................... 227

8.2.3 Recovery and Separation of Organic Acids..................................................... 228

8.2.4 Separation of Amino Acid Enantiomers......................................................... 229

References ....................................................................................................................... 231

LIST OF PUBLICATIONS ........................................................................................................ 232
SUMMARY

The purpose of this PhD research work is to develop a novel and more efficient supported liquid membrane (SLM) based process to recover copper and regenerate spent ammoniacal etchant solution with low operation cost and without generating secondary waste for Printed Circuit Board (PCB) manufacturers. A comprehensive study, which covers a state of review on the recent advances in SLM technology, the screening of proper carrier for Cu(II) extraction in SLM system, the fundamental kinetics and mechanism of Cu(II) transport through flat sheet supported liquid membrane (FSSLM) in ammoniacal solution, from lab-scale to pilot-scale spent etchant treatment processes using hollow fiber supported liquid membrane (HFSLM) system, is presented in this thesis. Despite their promising properties, SLMs are not widely used in an industrial scale mainly due to their instability and short life-time. In this study, the backgrounds and mechanisms of SLM instability and stability improvement methods are reviewed. In addition, a low cost and promising room-temperature chemical surface crosslinking was firstly developed in this research work to improve the stability of SLM with polyimide as the support matrix.

Firstly, the screening of carrier in SLM system for Cu(II) extraction from ammoniacal solution was investigated. A comparative study of two widely used copper extractants, namely LIX54 and LIX84, and their impregnated supported liquid membrane (SLM) systems was carried out in this work. Experimental and computational characterization of LIX54/Cu(II) and LIX84/Cu(II) complexes were investigated and the results agreed well
in the reaction mechanisms, complexes geometries and copper extraction strengths of these two carriers. Copper transmembrane fluxes at different conditions were compared and the results showed that LIX54 had slightly higher copper removal rate in ammoniacal solution but much poorer copper loading in acidic media. Much higher selective separation performances of Cu(II) over Zn(II) and Cd(II) and no ammonia carry-over provide LIX54 significant advantages over LIX84 for ammoniacal solutions treatment. In this work, impedance spectroscopy technique and initial flux measurement were employed to study the long term stabilities of both LIX54 and LIX84 impregnated vertical flat membrane system. The results show that the membrane stability is promising for practical industrial applications.

Subsequently, copper recovery from industrial ammoniacal wastewater using flat sheet supported liquid membranes system (FSSLM) was investigated. LIX54 in kerosene was used as a carrier in the liquid membrane phase to extract and transfer copper. Detailed theoretical model for facilitated transport through flat membrane was developed, where diffusion of copper complex with ammonia in aqueous stagnant layer and fast reactions of the carrier and copper species in aqueous reaction layer have been taken into account. This model, where the carrier moves slightly out from the membrane in the reaction layer, then transfers from one aqueous phase to another through the membrane, and finally moves back, is called “Big Carrousel”. Mathematical model simulation demonstrated that only “Big Carrousel” model, based on the ability of the carrier to leave the membrane and to react with copper ammonia complexes in aqueous solutions, gives satisfactory quantitative description of all experimental results, including the flux plateau at high feed
copper concentrations and the decrease of copper flux at lower pH of the feed solutions.

Based on the understandings of kinetics and mechanism of Cu(II) transport through FSSLM, a bench scale hollow fiber supported liquid membrane (HFSLM) system was further studied to find optimal hydrodynamic and other conditions for spent ammoniacal etching solutions treatment. It was found that the excess of ammonia in spent etching solutions had negative effect on copper transfer, especially when copper concentration as the result of treatment became low. Different methods were used to control the ammonia level and their efficiency was compared. A pilot scale HFSLM was setup based on bench scale experiment results and successful pilot scale experiments were conducted. The process resulted in Cu removal from spent etching solution through the membrane and formation of saturated copper sulfate solution in sulfuric acid, used as a striping phase. Composition of the regenerated etching solution and purity of CuSO$_4$$\cdot$5H$_2$O crystals formed in the striping phase were comparable or even better than their commercial analogues.

A prototype of Etchant Regeneration System (ERS) based on SLM technology was assembled. Preliminary economic evaluation shows that ERS enjoys much shorter payback time and lower spent etchant treatment cost compared to Mecer®, currently existing most successful spent etchant treatment process.

Lastly, fabrications of asymmetric and symmetric polyimide P84 flat microporous membranes via phase inversion for supported liquid membrane (SLM) applications were
investigated in this work. It was found that the SLM with symmetric support matrix is much more stable than that with asymmetric matrix. This is attributed to the force balance exerted at two interfaces besides the SLM, that is, feed/membrane and strip/membrane interfaces, and proposed formation of stagnant layer in the SLM system with symmetric matrix. Furthermore, a simple room-temperature chemical cross-linking technology was applied to do surface modification and shown to be an effective method for improving the stability of SLM containing LIX54 as the carrier for Cu(II) transport. The SLM after chemical cross-linking can reduce the size of surface pores without changing the membrane cross-section and without producing a skin layer with significant mass transfer resistance. In addition, the SLM after cross-linking was harder for the impregnating carriers to move out from the mouths of the membrane pores. All these favor to form the more stable SLM system.
**NOMENCLATURE**

- $CuR_2$: Copper carrier complex
- $Cu(NH_3)_4^{2+}$: Copper-ammonia complex
- $D$: Diffusion coefficient (cm$^2$/s)
- $d_o$: Effective module outer diameter (cm)
- $d_i$: Effective module inner diameter (cm)
- $EF$: Enrichment factor
- FSSLM: Flat sheet supported liquid membrane
- HFSLM: Hollow fiber supported liquid membrane
- $G_z$: Graetz number
- $HR$: Extractant/carrier LIX 54
- $J$: Transmembrane flux (mol·cm$^{-2}$·s$^{-1}$)
- $K_d$: Dissociation constant of NH$_4^+$ (M or mole/cm$^3$)
- $K_{ex,f}$: Extraction equilibrium constant for $Cu(NH_3)_4^{2+}$/LIX54 system (M$^2$)
- $K_{ex,s}$: Extraction equilibrium constant for Cu$^{2+}$/LIX54 system
- $K_F$: Formation constant of the complex CuR$_2$ in LIX54/Cu(NH$_3)_4^{2+}$ system in the area of contact stagnant/reaction layer (M$^2$)
- $K_f$: Formation constant of the complex CuR$_2$ in LIX54/Cu$^{2+}$ system in the area of contact stagnant/reaction layer
- $K_s$: Stability constant for copper ammonia complex (M$^4$)
- $K$: Experimental overall mass transfer coefficient (cm/s)
- $K'$: Theoretical overall mass transfer coefficient (cm/s)
- $k_f$: Forward reaction rate constant for $Cu(NH_3)_4^{2+}$/LIX54
system (cm\(^7\)·mole\(^{-2}\)·s\(^{-1}\))

\(k_f\) Forward reaction rate constant for Cu\(^{2+}\)/LIX54 system (cm\(^7\)·mole\(^{-2}\)·s\(^{-1}\))

\(k_r\) Reverse reaction rate constant for Cu(NH\(_3\))\(_4\)^{2+}/LIX54 system (cm\(^7\)·mole\(^{-2}\)·s\(^{-1}\))

\(k_{r'}\) Reverse reaction rate constant for Cu\(^{2+}\)/LIX54 system (cm\(^7\)·mole\(^{-2}\)·s\(^{-1}\))

\(k_m\) Mass transfer coefficient in the organic membrane phase (cm/s)

\(k_R\) Mass transfer coefficient for chemical reaction (cm/s)

\(k_s\) Mass transfer coefficient in the shell side of membrane module (cm/s)

\(k_t\) Mass transfer coefficient in the tube side of membrane module (cm/s)

\(L\) Effective length of the hollow fiber membrane (cm)

\(m\) the coefficient as a function of packing density in membrane module

\(m_{CuR2}\) Effective distribution coefficient of copper-carrier complex

\(m_{HR}\) Effective distribution coefficient of the carrier

\(N\) Number of fibers in the membrane module

\(n\) an indicator of hydrodynamics developed in the membrane module

\(Q\) Volumetric flow rate (cm\(^3\)/s)

\(Re\) Reynolds number

\(R_m\) Mass transfer resistance in the organic membrane phase (s/cm)

\(R_r\) Mass transfer resistance for chemical reaction (s/cm)

\(R_s\) Mass transfer Resistance in the shell side of membrane module (s/cm)

\(R_t\) Mass transfer Resistance in the tube side of membrane module (s/cm)

\(r_i\) Fiber inner radius (cm)

\(r_o\) Fiber outer radius (cm)
\( r_p \) Effective pore size
\( Sc \) Schmidt number
\( Sh \) Sherwood number
SLM Supported Liquid Membrane
\( S_m \) Membrane surface area (cm\(^2\))
\( SF \) Separation factor
\( v_t \) Linear velocity in the tube side of membrane module (cm/s)
\( v_s \) Average superficial velocity in the shell side of membrane module (cm/s)

**Greek Symbols:**

\( \epsilon \) Porosity
\( \eta \) Dynamic viscosity
\( \rho \) Density
\( \tau \) Tortuosity

**Subscripts:**

\( a \) Aqueous phase
\( f \) Feed phase
\( i \) Inter phase
\( m \) Membrane phase
\( r \) Reaction zone
\( s \) Strip phase
LIST OF TABLES

Table 1.1: Development of membrane processes market .............................................................. 7
Table 1.2: Features and advantages of hollow fiber membrane contactor ............................... 12
Table 3.1: Typical compositions of copper containing ammoniacal solutions ....................... 70
Table 3.2: Liqui-cell® Extra-flow membrane contactor (2.5”×8”) specifications .................. 74
Table 3.3: Quantum chemical computation results of LIXs/Cu(II) complexes .................. 85
Table 3.4: Once-through selective separation of copper over other cations contaminants by HFSLM using LIX54 and LIX84 as the carrier ........................................... 91
Table 4.1: Comparisons on $J/J_{\text{max},a}$ and $J/J_{\text{max},m}$ with different feed copper concentrations in the feed ................................................................. 111
Table 4.2: Parameters necessary for theoretical simulation .................................................. 126
Table 5.1: Properties of hollow fiber membrane module for pilot plant test ...................... 145
Table 5.2: The influence of tube flow rate on the overall mass transfer coefficient and relative resistance to Cu(II) mass transfer ...................................................... 166
Table 5.3: Separation of Cu(II) over other metals in ammoniacal wastewater treatment .................................................................................................................. 167
Table 5.4: Initial copper flux and apparent mass transfer coefficient for three different spent etchant treatment processes .............................................................. 170
Table 5.5: Rate constants of different spent etchant treatment processes .......................... 172
Table 5.6: Mass balance for spent ammoniacal etchant treatment .................................. 173
Table 5.7: Comparison of treated spent etchant with commercial replenisher ............... 175
Table 5.8: Purity comparison of pilot test CuSO$_4$·5H$_2$O crystals and commercial product. .................................................................................................................. 176
Table 6.1: The economic comparison of two systems for spent ammoniacal etchant treatment .......................................................................................................................... 189

Table 6.2: The economic evaluation of ERS to reduce copper less than 5 ppm in spent etchant treatment process ............................................................................. 190

Table 7.1: Contact angle changes with different chemical cross-linking time .......... 205

Table 7.2: BET measurements of unmodified and chemical cross-linked P84 symmetric membrane.................................................................................................................. 207
LIST OF FIGURES

Figure 1.1: A general etching process to remove unwanted copper from PCBs board ...... 2
Figure 1.2: Diffusion modes in liquid membranes ............................................................. 9
Figure 1.3: Schematic drawings of (A) BLM; (B) ELM; (C) SLM................................. 10
Figure 2.1: Facilitated coupled transport of ions through liquid membranes (LM) ....... 25
Figure 3.1: A horizontal flat membrane system............................................................. 72
Figure 3.2: A vertical flat membrane system.................................................................. 73
Figure 3.3: Proposed reaction mechanism between (A) Cu(NH₃)₄²⁺/LIX54 and (B) Cu(NH₃)₄²⁺/LIX84 ......................................................................................... 79
Figure 3.4: FTIR spectra of extractants and their complexes with spent etchant solutions ....................................................................................................................... 81
Figure 3.5: EPR spectra of LIX54/Cu(II) and LIX74/Cu(II) complexes at 77K.......... 82
Figure 3.6: Molecular model of the optimized geometry of LIX54/Cu(II) complex with mapped electrostatic potential (ESP) using B3LYP/6-31g level of theory ... 84
Figure 3.7: Molecular model of the optimized geometry of LIX84/Cu(II) complex with mapped electrostatic potential (ESP) using B3LYP/6-31g level of theory ... 85
Figure 3.8: Cu(II) flux as a function of pH in the feed solution ....................................... 86
Figure 3.9: Cu(II) flux as a function of carrier concentrations in SLM......................... 89
Figure 3.10: Schematic descriptions and representative equivalent circuits of (A) intact SLM and (B) partially degraded SLM in vertical flat membrane setup ....... 93
Figure 3.11: Electrical capacitance and resistance changes of the vertical flat membranes ....................................................................................................................... 95
Figure 3.12: Initial copper transmembrane flux measurement of SLMs immobilized with LIX54 or LIX84 over extended periods of time ............................................ 96

Figure 4.1: Kinetics of pH and copper concentration changes in feed solution. ........... 107

Figure 4.2: Copper removal rate as a function of carrier concentration. .................... 110

Figure 4.3: Influence of the feed Cu(II) concentration on flux ..................................... 111

Figure 4.4: Copper flux as a function of pH in the feed ................................................. 114

Figure 4.5: Schematic description of copper transport through SLM with “Small Carrousel” model ................................................................................................. 116

Figure 4.6: Schematic description of copper transport through SLM with “Big Carrousel” model shown for the feed solution ..................................................... 127

Figure 5.1: Lab experimental setup for spent etchant treatment ................................... 144

Figure 5.2: Schematic diagram of Liqui-Cel® 10×28 Extra-Flow hollow fiber membrane contactor ........................................................................................................ 145

Figure 5.3: Recycling operation mode used for spent ammoniacal etchant treatment in pilot tests ............................................................................................................ 145

Figure 5.4: Schematic description of copper transport through HFSLM ........................ 148

Figure 5.5: Effect of volume of the stripping solution on copper removal rate from the bench-scale experiments ................................................................. 155

Figure 5.6: Effect of H₂SO₄ molarity on initial copper transfer flux from the bench-scale experiments ........................................................................................................ 157

Figure 5.7: Effect of volumetric flow rate on copper flux from the bench-scale experiments ..................................................................................................................... 159

Figure 5.8: Cross-flow pattern in shell side of Liqui-Cel® membrane contactor .......... 163
Figure 5.9: Comparison of the methods to control ammonia in spent ammoniacal etchant treatment from the bench-scale experiments ................................................................. 170
Figure 5.10: Kinetic analysis of Cu transport based on Figure 5.9........................................ 171
Figure 5.11: Cu removal kinetics in pilot tests ..................................................................... 174
Figure 5.12: XRD spectra of CuSO₄·5H₂O crystals from pilot test and commercial..... 176
Figure 6.1: Prototype of etchant regeneration system (ERS) based on SLM technology ................................................................................................................................. 186
Figure 6.2: Mecer process..................................................................................................... 187
Figure 7.1: The chemical structure of P84 co-polyimide ..................................................... 197
Figure 7.2: Knife casting of asymmetric flat membrane ........................................................ 199
Figure 7.3: The fabrication of the symmetric flat membrane via film die extrusion...... 200
Figure 7.4: FESEM images of P84 (A) asymmetric and (B) symmetric flat membrane after chemical cross-linking in p-xylendiamine/water for 24 hr............... 205
Figure 7.5: FESEM images of (A) surface morphologies of as-spun symmetric P84 membrane; surface morphology after chemical cross-linking for (B) 10 min; (C) 30 min; (D) 24 hr....................................................................................... 206
Figure 7.6: FTIR spectra of unmodified and cross-linked symmetric flat P84 membrane ................................................................................................................................. 208
Figure 7.7: Cu(II) flux as a function of time for asymmetric membranes in long term stability studies (A) Top surface faces to the feed (B) Bottom surface faces to the feed......................................................................................................................... 209
Figure 7.8: Schematic description of longer stability of SLM with (A) asymmetric microporous support matrix than (B) symmetric support matrix .............. 211
Figure 7.9: Fluxes changes with time of the original and modified symmetric P84 membrane for 10 min cross-linking............................................................. 214

Figure 7.10: Effect of the immersion time on Cu(II) transmembrane fluxes .................. 215
1.  CHAPTER ONE

INTRODUCTION

1.1 General Background Information

Printed circuit boards (PCBs) are important components of modern electronic products, which have generated billions of US dollars globally [1]. The manufacture of PCBs involves several technical processes and etching is one of the most important steps. According to PCBs’ design [2], part of the copper thin layer on the silicon base surface is first covered with photo resistant plastics. This permits the unmasked copper to be dissolved chemically into the etchant and the desired circuit pattern is produced. The general etching process involved in PCBs manufacture can be simply illustrated by Figure 1.1. Either alkaline or acidic etchant could be used depending on the actual production conditions [3, 4]. The ammoniacal (alkaline) etchant has relatively high etching speed, while the acidic etchant can achieve fine line width etching although it typically has a slower etch rate than the ammoniacal etchant. After that, the plastic mask is removed from the top of the remaining copper, allowing the PCBs to be conveyed into the next step. Approximately 60% of the copper on the board is removed by the etchant [5], implying that a lot of copper containing etchant could be generated during PCBs manufacturing.
Generally, the alkali etching process using ammoniacal etchant can be formulated using the following equations [3]:

Initiation: \[ Cu + Cu(NH_3)_2Cl_2 \rightarrow 2Cu(NH_3)_2Cl \] (1.1)

Propagation: \[ \frac{1}{2}O_2 + 2Cu(NH_3)_2Cl + 2NH_4Cl + 2NH_4OH \rightarrow 2Cu(NH_3)_4Cl_2 + 3H_2O \] (1.2)

From above equations, it can be found that copper is firstly dissolved as cuprous diamine complex. This complex does not have any etching effect; therefore, a regeneration reaction is required to get cupric tetra-amine again. The regeneration reaction permits the etching process to run continuously. As more and more copper dissolves into etchant, the specific gravity of etchant increases, resulting in a lower etching speed. In the mean time, ammonium chloride concentration decreases and this slows down the regeneration reaction. In order to achieve a stable etching operation, replenishment of fresh etchant is necessary. A typical fresh alkaline etchant is the one that can be purchased from MacDermid Inc., USA. Its main components are ammonia (8.5 wt%) and ammonium chloride (28.3 wt%). The replenishment of fresh etchant could maintain the concentration level of ammonium chloride but also help to keep a constant specific gravity of etching solution. As such, a stable operation condition could be achieved. The side effect of this replenishment is also obvious. The total volume of etching solution will increase with time. Practically, the excess solution is discharged from the process equipment as spent.
etchant and shipped out for off-site treatment.

With the rapid growth of PCBs industry, the total volume of generated spent etchant keeps increasing. Based on market analysis in Singapore conducted by MacDermid in 2002 [4], it is estimated that 70,000L of spent ammoniacal etchant are produced every month by local PCBs plants. These spent etchant are usually stored in drums or tanks and are ultimately shipped to an off site treatment plant for copper recovery before disposal. Although the spent etchant is treated by the waste haulier, this waste stream may still be an environmental hazard. Transportation of the spent etchant and its ultimate disposition may pose environmental risks and result in increased liability for PCBs manufacturers [5].

Currently, the main problems in the area of spent etchant treatment are:

- High cost associated with current spent etchant regeneration and copper recovery techniques
- Regeneration of spent etchant for further reuse
- Recovery of copper as a value added product

Numerous methods for the removal of copper from process streams have been proposed in the literatures and patents, such as chemical precipitation, cementation and sedimentation [6, 7], flotation [8], adsorption [9], evaporation [10], ion exchange [11, 12], electrolysis [13], electrodialysis [14-16], solvent extraction [17], membrane filtration [18, 19], membrane bioreactors [20] and biological methods:

- Chemical precipitation, cementation and sedimentation: By addition of hydroxides, sulfides or other reagents, the copper falls out as a solid. With this
method, copper is hard to be recovered due to contamination by other metal ions. It also generates large volume of waste sludge.

- **Evaporation:** Water is evaporated from the waste and a concentrate remains. Obviously, this method is completely non-selective.

- **Solvent extraction:** An extractant dissolved in an organic phase binds the copper in the waste stream. The organic phase is then separated from the effluent and regenerated in the stripping solution. The selectivity of copper over other ions can be high. However, phase disengagement difficulty, loss of organic reagents leading to the contamination of aqueous phases and labor- and time-intensiveness of operation are the main drawbacks of this technology.

- **Electrochemical processes:** In electrolysis, copper ions in solution are reduced to copper metal. The selectivity of this method is limited because other cations are also electrolyzed. Electrodialysis, another electrochemical process, is a membrane based process in which a potential gradient over cation and anion selective membrane is used to produce an acid and a hydroxide. The inherent membrane fouling and high energy consumption can be major problems when this method is used.

- **Adsorptive techniques:** Ion exchange resins that contain chelating agents bind copper from the solution. Therefore, regeneration of the resin after fully loading with copper is needed. Other adsorptive agents are zeolite and activated carbon which have lower selectivities.

- **Membrane filtration:** By nanofiltration or reverse osmosis, the impurities are concentrated in a retentate system, while the larger part of the process water
forms a high quality permeate. The fouling of membrane and high energy requirement retard the feasibility of this method to recover copper.

Nowadays, two commonly used copper recovery methods employed by PCBs industry are neutralization and solvent extraction. In neutralization, acid and alkaline spent etchant are mixed together to form Cu(OH)$_2$, which can be decomposed to CuO upon heating. The drawbacks of this method are:

- CuO is a low value added product.
- Resulting waste water contains more than 100ppm of Cu and requires further treatment before disposal.
- Spent etchant treated by this method is not reusable.

To date, the most effective method for regeneration of spent etchant is the MECER$^\text{®}$ system, developed by Sigma Metalleextraktion AB, Sweden [21]. This method is based on solvent extraction and uses a patented organic extractant, which extracts copper dissolved in spent etchant. Since this organic extractant is immiscible with etchant, treated etchant can be reused when copper is removed. The copper rich organic layer is then transferred into a sulphuric acid electrolyte, in which electro-winning is performed to obtain pure copper sheets. The main drawbacks associated with this system are high running costs and long pay back time. Expensive extractants, coupled with expensive equipments are greatly hindering the prevalence of this method.

Therefore, a low cost and efficient on–site process for spent etchant treatment is desired.
Membrane separation technology is becoming increasingly attractive as a low cost separation technique for volume reduction, purification of the liquid phase and recovery of the contaminants or solutes. It would offers outstanding future potential in the reduction and recycling of hazardous pollutants from waste streams [22-24].

1.2 General Information on Membranes

A membrane can be defined as a barrier which separates two phases and restricts transport of some kinds of chemicals in a selective manner. A membrane process requires two bulk phases physically separated by a third phase-the membrane [22]. The membrane phase may be any one or a combination of nonporous solid, microporous or macroporous solid with a liquid or gas in the pores, a liquid phase with or without second phase or a gel.

Membranes are primarily used for separation processes. Over the last 40 years, membrane process has been developed and widely adopted by processes industries. Large-scale commercial uses of membrane separation processes have displaced conventional separation processes such as distillation, absorption, adsorption, solvent exchange, crystallization, etc. Compared to other conventional mass separation technologies, the membrane process is relatively new unit operation and is often more capital and energy efficient. Membrane devices and systems are always compact and modular which is easier to further scale-up [22].
Membrane technology for the separation of liquid/liquid and liquid/solid streams has been practiced in industry for many years in reverse osmosis (RO), ultrafiltration (UF), microfiltration (MF), nanofiltration (NF), pervaporation (PV), hemodialysis, electrodialysis, controlled release of drugs, gas separation and so on. In the worldwide membrane market in 1988, the sales of membranes and modules reached US$ 4.4 billion and sales of membrane systems were more than US$ 15 billion. The development of membrane market in the end of century is reviewed and tabulated as shown in Table 1.1 [25].

Table 1.1: Development of membrane processes market

<table>
<thead>
<tr>
<th>Membrane Process</th>
<th>Sales (US$ Million) in 1998</th>
<th>Growth per year (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dialysis</td>
<td>1,900</td>
<td>10</td>
</tr>
<tr>
<td>Microfiltration</td>
<td>900</td>
<td>8</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>500</td>
<td>10</td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>400</td>
<td>10</td>
</tr>
<tr>
<td>Gas Exchange</td>
<td>250</td>
<td>2</td>
</tr>
<tr>
<td>Gas Separation</td>
<td>230</td>
<td>15</td>
</tr>
<tr>
<td>Electrodialysis</td>
<td>110</td>
<td>5</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>70</td>
<td>5</td>
</tr>
<tr>
<td>Pervaporation</td>
<td>&gt;10</td>
<td>...</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>4400</strong></td>
<td><strong>&gt;8</strong></td>
</tr>
</tbody>
</table>

1.3 Membrane Fabrication, Characterization and Evaluation

The morphology and physical properties of membranes significantly affect the permeation properties of a membrane. The challenge for industrial application of the membrane process is the fabrication of membranes having both economically high permeability and high durability in specific separation processes. Membrane fabrication is important to pattern the materials with appropriate technique to obtain membranes with suitable morphology. Numbers of different techniques such as stretching, sintering, track-
etching, compression molding, sol-gel process, metal extrusion, vapor deposition, solution casting, phase inversion, etc. are developed to manufacture organic and inorganic membranes.

Membrane characterization and evaluation is an important step in membranes engineering to characterize the morphology, physical and chemical properties. The intrinsic properties of membranes (permeability, selectivity, solubility, diffusivity, etc.) are also extremely important in determining the ability of a membrane under prevailing conditions to achieve a designed function for a specific application.

1.4 Liquid Membranes (LM)

Membrane may be classified into two categories, namely (1) polymeric membrane and (2) liquid membranes (LM). Polymeric membrane separation processes are usually size-exclusion-based pressure-driven membrane separation processes and have generally suffered from inherent drawbacks such as low transmembrane flux, membrane fouling and insufficient selectivity. Recently developed liquid membrane has been recognized a promising technology to overcome these shortcomings. Unlike traditional membranes, liquid membrane extracts target pollutants from bulk solutions by chemical potential rather than by size. Thus, liquid membrane technology is somehow similar to solvent extraction process but with extraction and back extraction performed just in one technical step. The so-called liquid membrane is formed by a thin layer of organic phase that separates the aqueous process stream from the aqueous receiving phase. Liquid
membrane provides relatively higher flux than that of solid polymeric membranes due to its higher diffusivity and thinner thickness. In addition, transport through the liquid membrane can be facilitated with appropriate carrier which presents in the membrane phase and binds selectively with targeted species in the feed phase and transports it into the stripping phase. Bloch was probably the first to use extraction reagents dissolved in an organic solution and immobilized on microporous inert supports for removal of metal ions from a mixture [26].

Liquid membranes are media consisting of liquid films through which selective mass transfers of gases, ions and molecules occur via permeation and transport processes [27]. The four main types of diffusion that can occur through liquid membranes are illustrated in Figure 1.2.

![Diffusion modes in liquid membranes](image)
Liquid membranes can be divided into three different types: Bulk Liquid Membranes (BLM), Emulsion Liquid Membranes (ELM) and Supported Liquid Membranes (SLM). All these three kinds of LMs are schematically described in Figure 1.3:

![Schematic drawings of (A) BLM; (B) ELM; (C) SLM](image)

Bulk liquid membranes usually consist of an aqueous feed and stripping phase, separated by a water-immiscible liquid membrane phase in a U-tube. BLMs are often used to study the transport properties of novel carriers. ELMs consist of a dispersion of water containing oil droplets in a bulk aqueous feed phase. The volume of the stripping phase inside the oil droplets is at least ten times smaller than that of the feed phase. The thickness of the liquid membrane film is very small, while the surface area is large. Subsequently, the emulsion droplets have to be separated from the feed phase and broken up to recuperate the stripping phase. A small membrane surface area of BLM and the
labor intensive operations of ELM make them technologically not very attractive. Therefore, there have been very few large scale applications of these two liquid membrane systems.

1.5 Supported Liquid Membranes (SLM)

A typical SLM consists of a polymeric microporous support in which the liquid membrane (LM) phase is immobilized by capillary forces. The LM phase usually contains the extractant or carrier with the organic solvent as the diluent to reduce the viscosity and increase diffusivity of the LM phase. Sometimes the LM contains another component called the modifier which is added to favor the extraction of a selected species in a synergetic way or to avoid microemulsion or third phase formations. Flat sheet supported liquid membrane (FSSLM) which is used mainly for fundamental studies but is not practical for industrial application and hollow fiber supported liquid membranes (HFSLM) in which the organic liquid membrane phase is impregnated into the pores of a hollow fiber membrane module (HFM) are two commonly used SLM configurations.

In the case of FSSLM, the support is generally a sheet-form inert porous material. The solute in the aqueous feed solution permeates selectively through the membrane by interacting with the specific carrier contained in the LM phase. On the opposite side of the membrane the carrier-solute is back-extracted, the solute transports into the strip solution and the carrier stays in the SLM to repeat the cycle.
In HFSLMs, the carrier is usually immobilized in the microporous walls of tiny hollow fibers and two aqueous solutions flow continuously in the tube and shell side, respectively. In such a case extraction and re-extraction take place simultaneously. In some case, aqueous and organic solutions recirculate in the shell and tube side respectively with both phases contacting at the pores of fiber wall. In this case, only extraction or re-extraction is realized in a single membrane module. HFSLMs have the greatest surface area per unit volume among the configurations and present an effective solution to the need for operating membrane modules with high throughputs [28]. Usually hollow fiber membrane contactor (HFM) is widely used to serve as the support matrix for HFSLM system. The features and advantages of using a HFM [29] are presented in Table 1.2.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Advantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large surface area per volume (~1000 m²/m³).</td>
<td>Efficient membrane separation with rapid transportation. Allows for smaller design.</td>
</tr>
<tr>
<td>Interfacial area is known and constant.</td>
<td>Performance can be predicted easily.</td>
</tr>
<tr>
<td>Scale up is more straight-forward, usually scales up linearly.</td>
<td>Easy scaling up to industrial use.</td>
</tr>
<tr>
<td>Membrane contactors are modular.</td>
<td>Allows scaling up using larger or more modules.</td>
</tr>
<tr>
<td>No fluid/fluid dispersion or emulsion formation.</td>
<td>Feed and stripping phases can be easily recovered.</td>
</tr>
<tr>
<td>Membrane contactors are not sensitive to flooding, channeling, or back-mixing.</td>
<td>Can be operated over a wide range of flow rates.</td>
</tr>
<tr>
<td>Solvent hold-up is low.</td>
<td>Less solvent required resulting in cost savings when expensive solvents are used.</td>
</tr>
<tr>
<td>No density difference is required between fluids.</td>
<td>Can accommodate fluids of identical density and be operated in any orientation.</td>
</tr>
</tbody>
</table>
1.6 Research Objectives and Outline of the Thesis

The feasibility of Supported Liquid Membrane for selective and recovery of copper was probably first studied by Kim [30]. Prasad and Sirkar [31] provided an overview for successful applications of SLM for metal removal. Nevertheless, the previous researches were mostly focused on treatment of model copper solution (copper species existed as the form of $\text{Cu}^{2+}$) with low concentration based on SLM and constrained in the lab scale. To date, pilot scale treatment of real industry wastewater from PCBs industry with very high copper concentration around 200 g/L (copper species existed as the form of $\text{Cu(NH}_3\text{)}_4^{2+}$) is never carried out. In addition, little information is available on detailed and comprehensive kinetics and mechanism of copper species as the form of $\text{Cu(NH}_3\text{)}_4^{2+}$ transport through SLM. Despite their promising properties, SLMs are not widely used in an industrial scale mainly due to their instability and short life-time. The main reason for the instability is the loss of carrier out of the LM phases into surrounding bulk aqueous solutions. Several research groups have made efforts to improve the life-time of SLMs [32-36] but most of their solutions to improve SLM stability are not suitable for large scale applications.

The main objective of this research was to develop a novel and more efficient SLM based process to recover copper and regenerate spent ammoniacal etchant solution with low operation cost and without generating secondary waste for PCB manufacturers. In addition, a low cost and promising room-temperature chemical surface crosslinking was developed to improve the stability of SLM with polyimide as the support matrix. In order
to achieve the objectives, the scopes of this PhD work have been drawn as follows:

- Screening of proper carrier for SLM system preparation to extract copper species (\(\text{Cu}(\text{NH}_3)_4^{2+}\)) from ammoniacal wastewater and spent ammoniacal etchant.
- Fundamental kinetics and mechanistic study of Cu(\(\text{NH}_3)_4^{2+}\) transfer through SLM system.
- Spent etchant solutions regeneration and copper recovery using HFSLM system.
- Investigation and improvement of the stability of SLM.

This thesis is organized into eight chapters. Chapter One is an introductory part of this thesis. It provides general background information about PCBs etching processes and status quo & problem encountered in spent etchant treatment. The brief introductory descriptions of the membrane and membrane processes, membrane market, membrane fabrication and characterization, liquid membranes especially supported liquid membranes are presented. The research objective and outline of this thesis are also provided in this chapter.

A literature review on recent advances in supported liquid membrane technology as well as the stability issue of supported liquid membrane is given in Chapter Two. This chapter provides the overview of a mechanism and kinetic study of SLM based separations and highlights the possible applications of SLM. The causes of SLM instability and possible solutions are also discussed and reviewed in this chapter.

Chapter Three describes a comparative study of membrane extraction of copper from
industrial waste solutions using LIX54 and LIX84 impregnated supported liquid membrane systems. Experimental and computational characterization of LIX54/Cu(II) and LIX84/Cu(II) complexes are investigated. Cu(II) transmembrane fluxes at different conditions together with selectivities of Cu(II) over other cations contaminants are compared and the results show that LIX54 has significant advantages over LIX84 for ammoniacal copper solutions treatment.

Copper recovery from industrial ammoniacal wastewater using FSSLM has been investigated in Chapter Four. A detailed theoretical model for facilitated transport through flat membrane have been developed, where diffusion of copper complex with ammonia in aqueous stagnant layer and fast reactions of the carrier and copper species in aqueous reaction layer have been taken into account. This model, where the carrier moves slightly out from the membrane in the reaction layer, then transfers from one aqueous phase to another through the membrane, and finally moves back, is called “Big Carrousel”. Mathematical model simulation based on “Big Carrousel” model gives satisfactory quantitative description of all experimental results, including the flux plateau at high feed copper concentrations and the decrease of copper flux at lower pH of the feed solutions.

Chapter Five explores a bench scale hollow fiber supported liquid membrane (HFSLM) system to investigate the optimal hydrodynamic and other operation conditions for spent ammoniacal etching solutions treatment. Successful pilot scale experiments are conducted on a hollow fiber membrane module with surface area 130 m². The process
results in Cu removal from spent etching solution through the membrane and formation of saturated copper sulfate solution in sulfuric acid, used as a striping phase. Composition of the regenerated etching solution and purity of CuSO₄·5H₂O crystals formed in the striping phase are comparable or even better than their commercial analogues.

After thoroughly studying the kinetics and mechanism of copper transport through SLM at different experimental and hydrodynamic conditions together with the results from bench-scale and pilot-scale tests, we set up a prototype of Etchant Regeneration System (ERS) and present it in Chapter Six. A detailed economic evaluation and feasible study of this ERS is conducted and compared with a commercial competitor.

We have demonstrated in Chapter Seven, for the first time, P84 co-polyimide with novel chemical cross-linking modification can be effectively used as the polymeric microporous matrix for SLM applications. It is found that the symmetric membrane outperforms the asymmetric one. However, the performance of both unmodified asymmetric and symmetric flat membranes deteriorates severely after use for 20-30 hours. The newly developed chemically modified SLM has a similar life time compared with other SLM systems using commercial PTFE as the support matrix.

General conclusions drawn from this PhD thesis are summarized in Chapter Eight. Inclusive in this ending chapter are some recommendations and suggestions for future research.
References


[4] Personal communication with Mr. Robert E.S. Jr., Electronics business manager of MacDermid, 2002


2. CHAPTER TWO
LITERATURE REVIEW

2.1 Recent Advances in Supported Liquid Membranes

2.1.1 Overview

Membranes are not only more and more widely used in different new chemical engineering separation processes, they are also able to substitute existing separation and purification technologies. Well known examples are pressure driven different types of filtration and reverse osmosis, electrical field driven electrodialysis and its new modification, continuous deionization, and finally gas and vapor separation processes where the driving factor often is a combination of pressure, concentration difference and also temperature. Using linear thermodynamics it is possible to demonstrate that external pressure is much less efficient driving factor in the case of liquid/liquid separations on a molecular level. It is also well known that transport through biomembranes is usually driven by concentration difference and transmembrane voltage.

If the process is based on diffusion, the membrane permeability for the transported species, which has to be as high as possible, is determined by the expression $KD_m/L$, and to increase permeability and selectivity one has to use chemical affinity (change distribution coefficient $K$), decrease membrane thickness $L$ (biomembranes have the thickness of only two lipid molecules) and finally to increase diffusion coefficient in the membrane $D_m$. The idea to use thin organic liquid layer separating two aqueous phases
seems very attractive from this point of view simply because the $D_m$ value in liquids is at least three- four orders of value higher than in solid polymer and inorganic membranes [1, 2]. Besides that it is possible to dissolve some hydrophobic chemicals in the organic liquid, so that they will be able to interact with the transported hydrophilic species. This process would remind extraction and can be highly specific based on fine chemical interactions. Then the complex could easily diffuse through the organic liquid. Though the value of $D$ for the complex is slightly less than that for smaller species penetrating directly, the value of $K$ can be increased by many orders of value, which results in so called facilitated transport and much higher rates of process. Bloch was probably the first who has proposed to use extraction reagents dissolved in an organic solution and immobilized on microporous inert supports for removal of metal ions from a mixture [3].

Liquid membranes may be broadly classified into three types: bulk liquid membranes (BLM), emulsion liquid membranes (ELM) and supported liquid membranes (SLM). Emulsion Liquid Membranes suggested by Li [4] have a very high surface area per unit of volume and low thickness and it means the separation process and accumulation inside the emulsion vehicle is fast. The problem is that the vehicles have to be produced before the process; they have to be stable enough so that leakage is reduced to minimum, but still not very stable so that they could be destroyed after the separation, thus allowing the removal of the transported species. As the result the process has to use several unit operations and becomes technologically not very attractive.

In SLM usually organic liquid is imbedded in small pores of a polymer support and is
kept there by capillary forces. If the organic liquid is immiscible with the aqueous feed and strip streams, SLM can be used to separate the two aqueous phases. It may also contain an extractant, a diluent which is generally an inert organic solvent to adjust viscosity and sometimes also a modifier to avoid so called third phase formation. Relatively small volume of organic components in the membrane and simultaneous extraction and re-extraction in one technological step offers the advantages of possible usage of expensive carriers, high separation factors, easy scale-up, low energy requirements, low capital and operating costs, etc.

Figure 2.1 shows the mechanism of SLM based separation of ions. In this case charged species A from the feed solution are selectively extracted by the carrier through organic membrane/feed interface. The carrier picks up A, moves across the membrane as a complex and finally exchanges A with the charged species C on the other side of membrane. In this case C has the same charge as A. To preserve electrical neutrality the carrier acts as a shuttle carrying A and C in the opposite directions. That is why the process is called facilitated coupled counter-transport. The most typical example of this process is metal cation exchange with $H^+$ ions, facilitated by acidic carriers. Basic carriers, like amines, can be used to carry $H^+$ ions together with negatively charged ions such as $Cl^-$ in the same direction. This process is called facilitated coupled co-transport (Refer to Figure 2.1-B).
Figure 2.1: Facilitated coupled transport of ions through liquid membranes (LM)

It is easy to make the feed and strip solutions with different pH, so that ion exchange processes on the two membrane surfaces will be shifted in opposite directions. This creates a concentration gradient of different forms of the carrier (with and without ions) in the membrane, and results in the directed ion flux through the membrane. Evidently the process leads to the transport of targeted ionic species across the membrane against their concentration gradient. This type of so-called “uphill” or active transport will continue until one driving factor (difference of chemical potentials of H⁺ ions) is balanced by difference of chemical potentials of another transported ion. If the carrier selectively extracts A in the presence of B, A in the feed mixture will be finally separated from B, and then purified and concentrated in the strip solution. It is important that the process is using only chemical energy as a driving factor, and does not need transmembrane pressure or voltage.
Common configurations of SLM are flat sheet supported liquid membrane (FSSLM) and hollow fiber supported liquid membrane (HFSLM). Small experimental laboratory setup usually consists of a two-compartment cell, separated by a flat membrane. If the SLM is not stable and organic liquid does not stay in the pores, it is possible to use cells with three compartments where two porous supports of same [5] or different nature [6] are used to separate the organic and aqueous phases. The support in this case often is hydrophilic and is filled with aqueous solutions. The organic solution with the carrier can be stirred or circulated in the middle compartment to decrease mass transfer resistance.

Hollow fiber modules are usually more expensive but they offer much higher surface area per unit of module volume up to 500 m$^{-1}$. Commercially available modules can be big enough and have up to 220 m$^{2}$ area. In the case of HFSLM there are several modes of operation [7]. In the simplest case the organic solvent with a carrier is filling the pores of the microporous walls of hollow tubes. Usually the feed solution is circulated through the lumen and the strip solution on the shell side of the hollow fibers to make the back-extraction faster. To avoid the problems due to low stability of organic liquid phase in the pores, in another mode aqueous and organic solutions flow continuously with both phases coming into contact through the pores of the fiber wall. In such a case, only one unit operation, either extraction or back-extraction, is realized in one module and it is necessary to use two modules for the whole process. Pressure difference (higher in the non-wetting liquid) is applied to avoid phase entrainment. To carry out these two separation operations simultaneously, contained liquid membranes (CLM) can be used. In
this case the extracting organic solvent is contained in the interstices of two sets of microporous hollow fibers [8]. The feed solution passes through the lumen of one set. The strip solution flows in the lumen of the other set. Each aqueous-organic interface is immobilized at the respective fiber by applying the correct pressure difference. Modules with three sets of hollow fibers were introduced to conduct simultaneous separation of cations and anions using two different carriers and two different stripping solutions [9]. The synergistic extraction for individual extraction, recovery and separation of heavy metals can be achieved in this HFCLM system with a two-separate-fiber-set based membrane extractor [10].

Usually SLMs are based on organic solvent separating two aqueous solutions, but in some cases the arrangements were opposite, and the pores in the polymer support separating two nonaqueous phases were impregnated by water [11]. The problem with this arrangement is that water has relatively high volatility and the membrane is not stable. It seems that this problem can be solved using relatively new materials, so called ionic liquids. In this case a bulk organic cation, being apart from its anion is chemically more active and able to form complexes with olefins [12, 13], thus facilitating their separation from saturated hydrocarbons through the membrane.

2.1.2 Mechanistic and Kinetic Studies of SLM Based Separations

It is important that using simple H⁺ concentration difference it is possible to shift equilibrium of metal ion exchange in the donor and acceptor phases in different

27
directions [14]. This creates concentration gradients of the ion-carrier complexes in the membrane and results in the directed transport of a metal from, for example, alkaline feed to a more acidic strip solution. After an ion exchange on another side of the membrane the carrier becomes protonated and diffuses back towards the donor phase. Evidently this simple cyclic mechanism can be used for active transport of a metal ion against concentration gradient.

When the extractant exhibits acidic properties, coupled counter-transport takes place and the extraction reaction proceeds in the donor and acceptor phases according to the following equations:

\[ M^{n+}(aq) + nHR(\text{org}) \rightleftharpoons MR_n(\text{org}) + nH^+(aq) \]  
\[ MR_n(\text{org}) + nH^+(aq) \rightleftharpoons M^{n+}(aq) + nHR(\text{org}) \]

(2.1) \hspace{1cm} (2.2)

However, when basic or neutral extractants are used, coupled co-extraction takes place according to:

\[ M^{n+}(aq) + nX^-(aq) + E(\text{org}) \rightleftharpoons EMX_n(\text{org}) \]

(2.3)

The transport process can be described as a pseudo chemical reaction. For example for counter-transport of species A and B from the feed phase f to the strip phase s if they have different charges of the same sign we may write:

\[ nA_f + mB_f \rightleftharpoons nA_s + mB_s \]

(2.4)

At an equilibrium we have

\[ \mu_0(A) + nRT \ln a_{A_f} + \mu_0(B) + nRT \ln a_{B_f} = \mu_0(A) + nRT \ln a_{A_s} + \mu_0(B) + nRT \ln a_{B_s} \]

(2.5)
This equation can be rewritten as:

\[
\left( \frac{[A]_r}{[A]_i} \right)^n = \left( \frac{[B]_r}{[B]_i} \right)^m
\]  \hspace{1cm} (2.6)

It means for example that in the case of copper transfer in exchange for two H\(^+\) ions the separation or concentration factor of Cu\(^{2+}\) can reach 10\(^{20}\) if pH in feed and strip solutions are 10 and 0, respectively.

Separation and recovery of copper [15-19], zinc [20-22], nickel [23-25], alkali metals [26], precious metals [27-30], rare earth metals [31-35], etc. from aqueous technological solutions and wastewater purification based on supported liquid membranes has long been studied. One of the problems is that when H\(^+\) concentration difference is used as a driving factor to transfer metal ions, with time this difference decreases and the process stops. One of the possible ways to intensify the process is to conduct it in the presence of ammonia in the feed solution. In this case a metal like Cu is extracted and transferred through the membrane from the complex with ammonia. The released NH\(_3\) reacts with counter transported H\(^+\) and keeps pH in the feed practically constant [36]. As the result it is possible to remove practically all Cu ions from the feed even if the initial concentration is as high as 160 g/L. If sulfuric acid is used as the striping agent, with time Cu\(^{2+}\) concentration in it reaches solubility level and copper sulfate pentahydrate crystals are formed. The process can be used for regeneration of spent alkaline etching solutions, formed in big volumes as the result of printed circuit board production in microelectronic industry. Simultaneously copper sulfate crystals have quality comparable to a commercial chemical grade product. Stability of the membrane and the rates of Cu removal are high.
enough to make a process commercially feasible. Swedish company Mecer-Sigma is planning to manufacture industrial plants for this process, which does not form secondary waste and can be considered as a green chemistry process.

Rate of mass transfer in the case of HFSLM is controlled by three individual resistances, which are the resistance in a solution inside the fiber, across the membrane and outside the fiber. Often one of the three individual resistances will dominate the overall resistance. Normally, the flow through the tube side of hollow fibers is laminar and mass transfer coefficient \( (k_i) \) in the tube side could be estimated based on the Sherwood-Graetz correlation [17, 37-43]:

\[
Sh = m \cdot Gz^n
\]  

\( Sh \) and \( Gz \) are Sherwood number and Graetz number, respectively.

\[
Sh = \frac{k_i \cdot d_i}{D} \quad \text{(2.8)}
\]

\[
Gz = \frac{d_i^2 \cdot v}{H \cdot D} \quad \text{(2.9)}
\]

where \( d_i \), \( H \), \( D \) and \( v \) are inner diameter and the length of hollow fiber, diffusivity of interested species in the aqueous solution and linear velocity of the feed solution in the tube side, respectively.

Theoretically, for a diffusion process with fast chemical reaction, \( m \) can be from 1.62 [44] to 1.86 [45] and \( n=0.33 \). Slow chemical reactions with the carrier, membrane pore and module geometries could be potential factors responsible for the deviation of theoretical
mass transfer coefficient from an experimental one. Modified correlations were proposed to overcome the deviations [38, 40, 46]. Typical values of \( k_i \) based on these correlations are in the range of \( 10^{-4} \) cm/s to \( 10^{-3} \) cm/s [43, 47, 48].

The diffusion of species through the membrane can be approximated by diffusion through a cylindrical wall. The individual mass transfer coefficient \( k_m \) can be expressed as [49, 50]:

\[
k_m = \frac{\varepsilon \cdot D_m}{\tau^2 \cdot R_i \cdot \ln \left( \frac{R_o}{R_i} \right)}
\]

(2.10)

where \( \varepsilon \) is the porosity of the hollow fiber membrane, \( \tau \) is the tortuosity of the hollow fiber membrane, \( R_o \) and \( R_i \) are the outer and inner radius of the hollow fiber membrane and \( D_m \) is the diffusivity of the carrier complexes in the liquid membrane. Typical \( k_m \) in this case is in the range of \( 10^{-5} - 10^{-4} \) cm/s [39, 51].

Mass transfer coefficient (\( k_o \)) in the shell side of hollow fiber module is described by various empirical correlations [37, 41-43, 48, 52-56]. Results of these studies varied significantly due to more complex geometry of the system, the influence of module wall, the irregularity of fiber spacing and diameters, the fiber movement during operation, the inlet and outlet effects [53], possible channeling between fibers [55] and deformation of fibers during process. Nevertheless the value of \( k_o \) in the shell side is around \( 10^{-3} \) cm/s [39, 50, 52, 53] and can be additionally improved by a more efficient fiber arrangement and improved liquid flow patterns inside the module.
These estimated mass transfer coefficients based on empirical correlations together with experimentally determined values provide a useful tool for system modeling and scale-up of the corresponding membrane contactor process.

The theoretical description of facilitated transport across liquid membrane can be based on the assumption that the reactions of species with a carrier take place only on the membrane surface [57]. However, if the carrier is not very hydrophobic, it can leave the interior of membrane. In this case the reactions take place mainly in the aqueous phase. Transport mechanisms in the two cases were called “small and big carrousel”, respectively [57]. Equations for this situation without stirring and with stirring have been proposed [58]. It was also shown that the equations for the so-called “big carrousel” may be simplified to the well-known transport equations with the reaction at the membrane /water interface, when the chemical reactions in the stagnant aqueous layers near the membrane surface are fast, and diffusion through the membrane or stagnant aqueous layer becomes the flux controlling processes.

2.1.3 New Applications of SLM

There are a larger number of reviews describing many experimental works dealing with SLMs since 1970 until now [3, 59]. After our general analysis we would like to mention that during the last several years more and more papers have described SLM based processes applicable for fine chemicals and even drugs. Evidently the possibility to produce value added products in relatively small volumes makes the SLM technology
even more attractive for chemical and pharmaceutical industry.

As an illustration only a few examples are given in this thesis. SLM can be used for the separation of citric and lactic acids in aqueous solutions [60]. The pores in the membrane support were filled with tri-n-octyl amine (TOA) and sodium carbonate was used as a strip solution. The feasibility of using SLM with hydrophobic liquid polyorganosiloxanes functionalized with amine, ether, ester and alkyl organo-functional groups in transport of lactic acid and ethyl lactate between aqueous phases was also reported [61]. The pH driven facilitated transport through both ether and amine functionalized polyorganosiloxane/celgard K-273 SLMs results in a dramatic permeability enhancement compared with that displayed by the free organic acid. The value of flux for an initial feed concentration of 10 g/l was $1.4 \times 10^{-7}$ mol/cm$^2$s. Both amine and ether functionalized polyorganosiloxane based SLMs were stable for about 100 hours. Valeric (n-pentanoic) acid extraction with Amberlite LA-2 (10 v%) in toluene (90 v%) is also possible [62]. Transport of aminoacids like phenylalanine through a SLM containing di-2-ethylhexylphosphoric acid (DEPHA) as a carrier in a spiral-channel module was studied and the effects of velocity of feed phase, initial feed concentration and the carrier concentration on the flux were determined [63]. Extraction of Penicillin G was carried out using two hollow fiber modules with organic phase containing a secondary amine Amberlite LA-2 as a carrier, 10% isodecanol as a modifier and kerosene as a diluent. The effects of initial feed concentration and carrier concentration on the kinetics of the complex mass transfer process were examined [64].
SLM can be used also for an increase of a concentration in analytical chemistry [65, 66]. The advantages of SLM extraction over other methods for drugs and other substances determination are small sample volumes, short analysis time, low consumption of organic solvents for extraction, possibilities to work under physiological conditions and an excellent possibility for connection with various analytical instruments, possibly with automation of the whole process [67]. A technique based on a membrane extraction can be used for determination of drug–protein binding and was termed as “equilibrium sampling through membrane (ESTM)”. A basic solution of opipramol, noxiptyline, amitriptyline and diethazine was passed over the membrane and after enrichment the acceptor solution was analyzed by reversed-phase high-performance liquid chromatography with UV detector. A porous PTFE membrane from Millipore with polyethylene backing was used with TOPO (Trioctylphosphine oxide) as a carrier and with n-undecane and di-n-hexyl ether as organic solvents.

2.2 Stability of Supported Liquid Membranes

Although SLMs have been widely studied for the separation and concentration of a variety of compounds and present many potential advantages over other separation methods, there have been very few large scale applications of SLM due to insufficient membrane stability. Various mechanisms have been proposed for SLM instability: loss of organic phase (carrier and/or solvent) from the membrane phase by dissolution, progressive wetting of the support pores, pressure difference or osmotic pressure gradient over the membrane [68-71], and emulsion formation [71] or attrition of the organic film.
due to lateral shear forces. The time periods of instability observed vary from few hours to several months depending on the system.

Different approaches were used to determine SLM (in)stability: measuring membrane liquid loss by weighing methods; determining water content within the decayed SLM; measuring flux or permeability coefficients over extended periods of time; comparing counter transport factor over experimental time course; measuring physico-chemical properties of the organic phase (interfacial tensions, viscosities, contact angles and water solubilities); using a non-invasive technique such as impedance spectroscopy etc.

2.2.1 Mechanisms of SLM Instability

Instability of SLM can be due to the loss of the carrier and/or solvent out of the membrane pores, which has an influence on both flux and selectivity of the membrane. This loss of carrier and/or membrane solvent can be due to:

- Absence of any chemical bonding of the carrier and/or solvent to the substrate matrix
- Presence of osmotic pressure gradient
- Pressure difference over SLM
- Mutual solubility of species from the aqueous phase and liquid support membrane phase
- Blockage of membrane pores by precipitation of a carrier complex at the surface [70, 86]
- Emulsion formation by and in the liquid membrane phase [70, 76, 77]

SLM stability can also be affected by the type of polymeric support and its pore radius [87], organic solvent used in the liquid membrane, interfacial tension between the aqueous and membrane phase, flow velocity of the aqueous phases [77], and method of preparation [88].

2.2.1.1 Chemical Bonding Effect

In SLM, the carrier and solvent is immobilized in the pores of a microporous support. The organic phase is sustained in the micropores by capillary force only. Without chemical bonding of the organic phases to the substrate matrix, it is easy for the organic phases be “kicked” out of the pores of membrane support. The obvious way to improve membrane stability is to chemically bind the mobile carrier with the membranes. Cussler et al. [89] developed a theory for “chained carrier” which provides both the selectivity of liquid membranes and the stability of solid membranes.

2.2.1.2 Osmotic Pressure Model

Danesi et al. [79] and Fabiani et al. [83] developed the effect of osmotic pressure as a mechanism of SLM instability independently. Danesi et al [79] carried out lots of work
dealing with the stability of several SLM for metal ions transport, especially the influence of osmotic pressure differences on SLM stability. In their work, an SLM was considered to be stable when it showed a constant flux and water transport over extended time periods. The results of long term operation of several types of SLMs indicate that they are relatively stable when the osmotic pressure between feed and strip solutions are approximately the same, but become increasingly unstable as the osmotic pressure gradient increases. The increased water transportation rate through the SLMs under the influence of a given osmotic pressure difference results to the decreased membrane lifetime. In presence of an osmotic pressure difference water tends to flow through the organic filled pores. This initial water flow can be imagined as the diffusion of water through stagnant organic layer stayed within the membrane wall. When the amount of flowing water becomes significant and SLM is easily wetted by the aqueous phases, the organic phase in the support pores is eventually displaced by water. The ability to perform carrier-facilitated and selective coupled transport is completely lost when the membrane pores are totally water filled.

Fabiani et al. [83] measured water flows and salt fluxes through SLMs separating two LiCl solutions at difference concentrations. When the osmotic pressure increased (without hydrostatic pressure gradient) over membrane, water transport increased and membrane appeared to be unstable. The organic phase was dragged out of the pores of membrane support as a consequence of the volume flux across the membrane.

Several research groups objections against the “osmotic pressure model”. Neplenbroek et
al. showed that in the absence of osmotic pressure difference by using equal slat concentration in the feed and strip solutions, their SLMs still showed a considerable loss of organic phase [69, 76]. In contradiction with the proposed theory of the osmotic pressure effect, SLM stability increases with an increase in osmotic pressure induced by an increase in slat concentration in the strip solutions. Zha et al. [70] obtained the similar results from phenol transport through SLM. They also drew the conclusion that the osmotic pressure difference was not the cause of SLM degradation. In Kemperman et al. [71] review paper, they concluded that an osmotic water flow might be an additional reason of SLM degradation, but this depends on the solubility of water in the liquid membrane phase. Not all effects can be explained when the osmotic pressure is the only cause of SLM instability.

2.2.1.3 Pressure Difference Mechanism

One of the probable causes of membrane instability is the transmembrane pressure induced by streaming of solutions across the membrane, especially when hollow fiber SLM is used or when the liquid contains surfactants [84]. The minimum transmembrane pressure defined as critical displacement pressure by Zha et al. [70] required to push the impregnating phase out of the largest pores can be calculated using Laplace equation:

$$P_c = \frac{2\gamma \cos \theta}{r}$$  \hspace{1cm} (2.11)

where $\gamma$ is the interfacial tension between strip or feed solution and LM phase, $\theta$ is the contact angle between the membrane pores and the impregnating liquid, and $r$ is the pores radius.
Usually for commercial hollow fiber membrane contactors and hydrocarbon solvents $P_c$ is much larger than transmembrane pressure, which indicates that pressure difference is not the main cause of SLM degradation [71]. However, Eq. 2.11 is only valid for cylindrical capillaries while SLM supports usually are highly irregular in geometry. Zha et al. [70] also derived an equation for the estimation of the critical displacement pressure for SLM in such case. Pulsations of the feed and strip fluxes, in addition to transmembrane pressure, will also effect membrane stability. In order to obtain a stable liquid membrane, transmembrane pressure together with fluctuations should be minimized.

### 2.2.1.4 Mutual Solubility Effect

Danesi [68] was first proposed this mechanism as the effect of membrane instability. Takeuchi et al. developed this mechanism in detail and found that both the interfacial tension and the contact angle might decrease with time because of the formation of metal complexes, contamination of the interface between membrane and the aqueous solutions, dissociation of the chelating agents or other factors [70, 90, 91], although the effect was small. The local wetting of SLM by water will progressively spread throughout the membrane in accordance with buoyancy, capillary action and pressure forces. Imbibitions of water into SLM can also be brought about by forcing out or dissolution of the organic phases. Furthermore, the applied pressure would facilitate the advance of the water-organic boundary in the pores [91]. In case a chemical potential difference between the
liquid membrane and the aqueous phases is present, there is a driving force for the liquid membrane components to dissolve in the aqueous phases, which is the case in many actual operation conditions. The solubility greatly influences membrane lifetime when carrier or membrane solvent has a significant solubility in the adjacent aqueous phases, and vice versa [71]. Furthermore, the higher the partition coefficient toward the aqueous phases, the shorter the membrane lifetime [68, 69, 76, 86, 87, 91-93]. Deblay et al. [92] and Lamb et al. [93] observed that the membrane stability increased as the boiling point of the solvent increased or water solubility decreased.

Pre-saturation of the aqueous feed and strip phases with the organic phase improved membrane lifetime [75, 94]. Takeuchi et al. [91] and Neplenbroek et al. [69] found no or little effect on SLM lifetime when the aqueous phases were pre-saturated with the membrane solvent. However, the solubility in their system is probably not the most important mechanism, but in other systems the solubility may play an important role.

To obtain stable SLM, it is possible to select a combination of solid support and membrane solvent taking into consideration of the force holding the organic within the membrane pores and the imbibitions rate if water into organic filled pores. With regard to the former, small contact angle, small pore size and high interfacial tension of an SLM system should be selected. As regard the latter, a system which has low interfacial tension, large viscosity and large contact angle as well as small pore size should be preferred [91]. Dreher and Stevens [72] gave quantitative correlation of membrane lifetime increases with membrane liquid viscosity to the power of 0.64.
2.2.1.5 Pore Blocking Mechanism

This mechanism was first proposed by Babcock et al. [78]. The membrane pores are blocked by precipitates or by water droplets. The formation of solid or gelatinous precipitates in the pores, beyond the saturation limit in the liquid membrane phase, slows down the diffusion rate of the permeate species, but might have a positive effect on the prevention of membrane leakage [78, 87] and by preventing the formation of emulsions with the aqueous phases [71].

In most case, the blockage of membrane pores by water droplets is an important phenomenon. It was thought that water could enter the organic phase at the surface of membrane and replace the organic phase. It considers that water enters the organic filled pores in micelles. The formation of micelles by the carrier solubilized water and resulted in the imbibitions of water into the organic phase [70, 71]. However, there is no experimental proof for the existence of these micelles and such micelles are small. It is therefore doubtful whether sufficient large quantities of water can be introduced into the organic phase. Zha et al. [70] detected there were no water droplets or micelles with solubilized water in decayed SLM with the help of gas chromatography and objected the pore block mechanism.

It is very doubtful that organic droplets formed when the micelles break up or when the organic phase pushes out from the membrane pores. There is no clear explanation how
the micelles break up spontaneously. Furthermore, there will always be a driving force to minimize the surface area, and without the supply of extra energy it is not likely that an extra area is created to form small droplets [71]. It also fails to explain why the ratio of carrier to organic solvent loss in the adjacent aqueous solutions was different from that in the initial liquid membrane, as found in the experiments by Babcock et al. [78] and Neplenbroek et al. [69].

2.2.1.6 Shear Induced Emulsion Mechanism

Shear forces across a membrane can lead to instabilities at the fluid interface, resulting in membrane degradation. Fluids in motion are influenced by the capillary ripples due to pulsation of the aqueous solutions, the Tollmien-Schlichting instabilities due to laminar-turbulent transition and the Kelvin-Helmholtz instabilities due to movement of two phases at different velocities, whereas the Rayleigh-Taylor instabilities due to acceleration of the interface perpendicular to its plane and direction from the lighter to the heavier phase and the Benard instabilities due to density difference can occur in fluids at rest [71, 95]. For the case of SLM the aqueous fluids are always under forced flow across the membrane by stirring or pumping. Therefore, it is to be expected that capillary ripples and the Kelvin-Helmholtz instability will have an important role on the integrity of the aqueous-organic fluid interface. Due to the gravitation force acts parallel to the interface, the Benard instability is not likely to have significant influence on the membrane stability. Chandrasekhar provided the conditions to suppress the perturbation as well as the conditions for the interfacial tension to suppress Kelvin-Helmholtz
instability [96]. According to Chandrasekhar’s work [96], the organic/aqueous interface will be stable if the velocity difference between the two phases is less than 0.16 m/s which corresponds to the wave number of 353 m\(^{-1}\). The tip velocity of the stirrer moved at 0.8 m/s will give a velocity difference in this order. There are two regions of membrane liquid loss: quickly removal from the film surface and the loss from the support pores [72]. The loss from the surface is probably due to hydrodynamic instabilities, in particular the Kelvin-Helmholtz instability. Once the organic on the membrane surface has been removed, the membrane liquid resides in the pores of the membrane support. The relative small pore size of membrane support makes it only possible for wavelength much lower than that required for instability to exist. Dreher and Stevens [72] thought hydrodynamic instabilities could unlikely to be the cause of further membrane liquid loss.

Kelvin-Helmholtz instabilities and membrane vibrations are the main causes for liquid membrane meniscus deformations. The commencement of the deformation of liquid membrane meniscus results to the formation of emulsion droplets by Marangoni effects. The deformed meniscuses become unstable and produce droplet shredding and emulsion formation [76]. Eventually, the new meniscus with partial water filled up the membrane pores will reinforce itself and stays at one of the boundaries of the membrane since the smallest pores are present at the membrane surface [70]. The higher the flow velocity, the more meniscus instabilities, and the more possibilities of emulsion formation [76].

Neplenbroek et al. [76, 97] proposed the instability of SLM was emulsion formation
induced by lateral shear forces. They found the relation between the removals of the liquid membrane phase from membrane pores as a function of the carrier molecular structure, the type of liquid membrane solvent and the formation of emulsions. Zha et al. [70, 81] further developed and extended and confirm this hypothesis. From a thermodynamic point of view, a system prefers a surface area as small as possible. Emulsions are therefore thermodynamically unstable. Although emulsification of the liquid membrane phase can explain all observed instability phenomena, it is doubtful whether enough energy can be supplied to the liquid membrane interface to cause droplet shredding [71]. Dreher and Stevens [72] found that mass transfer caused turbulence at an interface termed as the Marangoni effect has a destabilization effect on the membrane. In general, drops of feed solution were observed to “kick” slightly when it contacted with a membrane solution. It was not the case for strip solution.

In summary, the instability of SLM is a complicated process and several mechanisms are attributed to the instability of SLM. Many factors can influence the stability or lifetime of SLM. Chemically bind the mobile carrier with the membranes will improve the stability of SLM. The osmotic pressure gradient might have an influence on the instability of SLM provided that the liquid membrane phases can accommodate enough water. A pressure difference over the membrane might have an effect on SLM instability but not the major cause. The mechanism of mutual solubility of species from the aqueous phase and liquid support membrane phase is also doubtful. The most likely mechanisms of membrane instability are emulsification of the liquid membrane due to lateral shear forces, Kelvin-Helmholtz instabilities and membrane vibrations.
2.2.2 SLM Stability Performance Optimization

2.2.2.1 Optimal Membrane Preparation

Proper preparation of SLM has a significant influence on its stability and lifetime. The SLM materials include the carrier, the solvent for the carrier and the membrane support. The carrier high hydrophobicity, low surface activity and low solubility in adjacent aqueous solutions are important factor for the stability of SLM. It is believed that the organic solvent has also a significant effect on membrane stability. In order to obtain good lifetime of SLM, the organic solvent should have 1) a low solubility in water [92, 94] and vice versa [79, 86, 92, 93]; 2) a high interfacial tension between organic and aqueous phases [76, 79, 90-92] and 3) a high boiling point [92, 93]. The loss of liquid membrane (carrier together with solvent) reduces the membrane thickness results in the decreased membrane resistance and the increased transmembrane flux. However, the loss of liquid membrane leads to the smaller availability of carrier for transporting targeted species. An increase of flux due to the combined effect suggests that the membrane geometry factor is dominant than the carrier concentration factor [98]. Increasing liquid membrane viscosity will improve SLM stability, but it will also lead to lower diffusion coefficient of the liquid membrane phase and hinder mass transfer.

The pore size, thickness and hydrophobicity of the membrane support will influences SLM stability. Membrane support with smaller pore size is more stable than those with a larger pore size. Zha et al. [84] recommended the use of supports with sharp pore edges.
and less connected network in morphology to get stable SLM. Neplenbroek et al. [76] suggested the usage of larger membrane thickness and interconnected pore structure. In general, the higher the membrane thickness, the more stable the SLM since more liquid membrane phases are filled in the membrane support and therefore it will take longer before SLM completely break down. Hydrophobic supports are generally better from the stability point of view than hydrophilic one. Takeuchi et al. [91] found that the organic liquid membrane should have a surface tension smaller than the critical surface tension of the support in order to get a good stable SLM system.

2.2.2.2 Optimal Operation Conditions

In practice, stirring or pumping velocity, carrier concentration, aqueous solution concentration and temperature also influence membrane stability. Zha et al. [70] found that an increase in stirring rate would result both carrier and solvent loss for flat sheet SLM. The increased pumping velocity in hollow fiber SLM increase pressure drop over the membrane, which may results in a large loss of liquid membrane phase when the transmembrane pressure exceeds the critical displacement pressure. Danesi et al. [68] observed a constant flux over two months when tube and shell side hydraulic pressure were balanced in a hollow fiber SLM.

Chiarizia [87] observed that the solid or gelatinous precipitates formed in the membrane pores when the carrier concentration reached the saturation with targeted species. The mechanism of precipitation to enhance membrane stability by preventing emulsification
and by preventing water bridging in semi-devoid pores is not elucidated [71]. When the
carrier is surface active, a higher carrier concentration will decrease the interfacial
tension of the organic phase which leads to less stable SLM.

Neplenbroek et al. [69, 76, 97] observed that the decrease of solute concentration in
either feed or strip resulted in the decrease of SLM lifetime. In contrary, Szpakowska and
Nagy [98] found the membrane lifetime decrease with increasing initial feed copper
concentration and increasing acceptor phase acidity. Zha et al. [70] also observed that
SLM was more stable at higher salt concentration in either feed or strip aqueous solutions.
The mechanism of aqueous solution concentration influence on membrane stability need
further studies.

It was found the membrane life time decrease with the increasing operation temperature
due to an increased solubility of both carrier and membrane solvent in the aqueous phase
at higher temperatures [99]. It is true that the water solubility in liquid membrane phase
increases at elevated operation temperatures which also lead to less stable SLM.

2.2.2.3 Liquid Membrane Reimpregnation

One effective method for SLM continuous use is the regeneration of liquid membrane.
Different methods of regeneration techniques were adopted to stable the SLM worldwide.
Makoto et al. [85] reviewed several methods for continuous regeneration of SLMs:
solvent continuously soaked into the pores of porous support by capillary action with a
reservoir for liquid membrane at the top of module; pressure flow of membrane solvents sucking at one end of SLM and soaking into it at the other end; utilization the capillary and buoyant forces to continuously regenerate SLM with membrane liquid pool. Babcock et al. [100] regenerated both flat sheet and hollow fiber SLM with fresh liquid membrane solution after membrane degradation and recovered the flux after reimpregnation. Teramoto and Tanimoto [101] simply regenerated hollow fiber liquid membranes by reimpregnating with the original liquid membrane within the tube side of the membrane. Ho [102] proposed SLM with strip dispersion to remove and recover metals and other materials. An aqueous solution is dispersed in an organic membrane solution and the formed water in oil dispersion is pumped into one side of a membrane module. The continuous organic phase refills the membrane pores continuously and provides a stale SLM.

Continuous regeneration of liquid membranes provide fairly good stability, but it causes the contamination of feed or strip solution with liquid membrane solutions which is certainly not desirable in large scale application.

2.2.2.4 Formation of Gel Structures of SLM

Bloch et al. [103] first proposed the idea of gelation to improve SLM stability. The lifetime of these membranes was insufficient as a result of loss of plasticizer, resulting incompletely impermeable and hard films. The idea to apply “solvent polymer membranes” to improve membrane stability was provided by Sugiura et al. [104, 105].
Relative high polymer contents and rather thick membranes caused a small flux far from practical value of using above mentioned “solvent polymer membranes”.

Instead of gelling the wall of membrane support, gelation in the pores of support was first suggested by Neplenbroek et al. [74, 80]. The inert support does not only immobilize the liquid membrane but also provides mechanical strength to the gel. It also leads to a much more difficult formation of emulsion droplet and results to a higher stability of SLM. Only a small amount of polymer is required without risking of deformation of the membrane. The diffusion rate of the species through this gel network is diminished insignificantly. Promising results were obtained using PVC as a thin layer on the feed side of the support and crosslinked after preparation [74, 80]. A membrane lifetime far over one year under normal circumstances was predicted [74, 97]. The major disadvantage of this technique is the bad reproducibility and the coating technique of the membrane with gel layer seems hard for hollow fibers and not suitable for large scale applications [71].

2.2.2.5 Formation of Barrier Layers on Substrate Membrane Surfaces

An alternative approach to stabilize the SLM is to use interfacial polymerization, that is, the formation of a condensation polymer at the interface of two non-or slightly miscible phases each containing one type of monomer. Wijers et al. [106] developed a new type of composite membrane using sulphonated poly ether ether ketone (SPEEK) as material for the stabilization layer. It was shown that the lifetime of the SLM is significantly
improved when one stabilization layer was applied at the strip side or two stabilization layers at both sides of the SLM. The composite membrane also provided an increase in species transport rate by a decrease in thickness of liquid membrane phase. The disadvantage of this composite membrane was the selectivity would be lost if SPEEK bridged through the entire membrane support.

Besides the formation of barrier layers by physical deposition, interfacial polymerization was also adopted [107-109]. Kemperman et al. [107] found the modified supports with a number of top layers by interfacial polymerization increased the stability of SLM and did not hinder transport rate of targeted species. Top layers of piperazine and trimesoyl chloride showed the most promising. In Wang’s group [108, 109], they explored different monomers systematically to make interfacial polymerization on top of membrane support. They found the membrane was more stabilized with semi-permeable polyamide [108] and epoxy [109] skin layers deposited on SLM.

It is evident that the reproducibility of SLM coated with an interfacial polymerization film is poor, the adhesion to the substrate is not strong and the coating probably impairs the separation. Yang et al. [110] proposed plasma polymerization as a highly effective technique for the formation of ultra-thin membranes and surface modification of polymer substrate. It is a promising technique for improving membrane stability by reducing the pore size of the membrane support and reducing contact angle of membrane surface. Advantages of this technology are the good chemical and thermal stability of the coatings and the strong adhesion to the substrate. Moreover, almost all volatile organic compounds
can be used as monomers, and even air can be used for the surface modification [111, 112].

2.3 Summary

The SLM technology theoretically is one of the most efficient membrane based methods of separation. It does not use pressure or voltage but is based on difference of chemical energy as a driving factor of the process, for example it can use simple $\text{H}^+$ concentration difference. Coupled co- or counter-ion transport allows to get an active transport of the targeted species from diluted solutions into more concentrated and to collect toxic or precious species in a small volume of the acceptor solution. Sometimes it is even possible to reach saturation of the strip solutions and finally precipitation of the product. Modern extractants make separation much faster due to facilitated transport and more selective due to their chemical specificity. Small volumes of extractant solutions and possibility to conduct continuous process make the SLM more attractive than classical ion exchange and solvent extraction technologies. Due to high diffusion coefficients in SLM it is possible to have ion extraction, transport and re-extraction in one continuous technological step. Recent development and commercialization of hydrophobic hollow fiber membranes makes it possible to use them as a porous support and to reach high membrane surface per unit of volume with satisfactory membrane stability. High surface area of these systems gives the separation rates sufficient for industrial purposes. One can expect that SLM technology will find a lot of industrial applications in the near future.
The degradation of SLM is a complicated process and different mechanisms are attributed to the instability of SLM. The solubility of the liquid membrane components in the adjacent feed and strip solutions as well as an emulsification induced by lateral shearing forces are the most possible reason for membrane instability. Proper SLM preparation, careful choice of carrier, membrane solvent and operation conditions is paramount important for a stable SLM system. Recent developments in forming stable liquid membranes are promising although these approaches suffer from several limitations and did not result in commercialization yet. Research activity should include more efforts in fundamental understanding of the role of a substrate for SLM preparation, and development of new solvents and carriers for SLM preparation [82].
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3. CHAPTER THREE

SCREENING OF CARRIER IN SUPPORTED LIQUID MEMBRANE SYSTEM FOR MEMBRANE EXTRACTION OF Cu(II) FROM AMMONIACAL SOLUTIONS

3.1 Introduction

The recovery of copper from ammoniacal etching solutions generated by print circuit board (PCB) manufacturing in microelectronic industry has become an important process and a large number of studies have been reported towards this end [1-7]. Supported liquid membrane (SLM) based separation and concentration of copper has received considerable attention through past decades [8-13] due to its low operation and capital cost, easy of operation, low energy consumption and high selectivity advantages. Unlike traditional membranes, liquid membrane extraction targets and removes the solute from bulk solutions based on chemical potential rather than by size difference. SLM technology is somehow similar to the solvent extraction process but with extraction and back-extraction performed just in one technological step. Liquid membrane provides relatively higher flux than that of solid polymeric membranes due to its higher diffusivity and thinner thickness. In addition, transport through the liquid membrane can be facilitated with appropriate carrier which presents in the membrane phase and binds selectively with targeted species in the feed phase and transports it into the strip phase.

Since Cognis Corporation (formerly Henkel KGaA) developed extractants for solvent
extraction process, a few of her materials have found broad applications in metals recovery and purification. The LIX® reagents have been used by numerous metal recovery operations around the world. Among them, LIX54 and LIX84 are well established copper extractants [14, 15]. It is commonly accepted that a weak β-diketone extractant LIX54 should be used for copper recovery from ammoniacal solutions, whereas a strong hydroxyoxime extractant LIX84 is utilized for copper recovery from acidic sulfate solutions [2, 10, 16-21]. However, to our best knowledge, no reasonably theoretical explanations for the above empirical statement have been given in any literatures. In this work, efforts were made to illustrate the different copper extraction capabilities by these two extractants both experimentally and computationally. The results can be utilized to screen other potential carriers in SLM system for Cu(II) extraction from different aqueous acidic or alkaline media. In addition, the scarce information regarding the selectivity of copper over other cation contaminants as well as ammonia in SLM system also fueled our intentions to conduct investigations in this area from a molecular level. Furthermore, in this work the stabilities of immobilized SLMs with LIX54 and LIX84 were monitored with impedance spectroscopy together with the flux observations over extended periods of time and the mechanisms of instabilities of SLM were proposed.

3.2 Experimental

3.2.1 Reagents

LIX54 and LIX84 were supplied by Cognis Corporation, USA and were diluted in
kerosene (Aldrich, Singapore) as the carrier in the liquid membrane phase. Reagent grade sulfuric acid (Merck, Singapore) was diluted with de-ionized water and used as the strip solution. All chemicals were used as received without any further purification.

Two kinds of copper-containing ammoniacal solutions free of solids and precipitations were kindly supplied by a PCB producing company in Singapore. Spent etching solution with a high content of both ammonia and copper is formed after PCB etching with ammoniacal etching solutions. The spent solution is then treated with an acid (usually HCl) so that the main part of copper precipitates as copper oxide and hydroxide. After this treatment the spent solution still contains some copper. This solution and also solution after washing of PCBs form the industrial ammoniacal wastewater. Typically, the Cu(II) concentration in the ammoniacal wastewater generated in this company was in the range of 100–1400 ppm (1.5×10⁻³ ~ 0.021 M), together with other trace amounts of impurities.

| Table 3.1: Typical compositions of copper containing ammoniacal solutions |
|-------------------------------------------------|-----------------|
| Ammoniacal waste solution                       | Spent ammoniacal etchant solution |
| Cu(II) 5.6×10⁻³ M                               | 2.5 M           |
| Total NH₃ 0.4 M                                 | 11 M            |
| Cl⁻ 0.5 M                                      | 5 M             |
| Zn(II) 5.5×10⁻³ M                              | 1.7×10⁻³ M      |
| Ni(II) 0.37×10⁻³ M                             | 0.34×10⁻³ M     |
| Cd(II) 1.8×10⁻⁶ M                              | 1.8×10⁻⁶ M      |
| pH ~7.25                                       | ~10             |

3.2.2 Analytical Methods

Metal concentrations in the aqueous solutions were measured by an inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Perkin Elmer, USA). In some cases
solutions in the feed and strip were diluted so as to coincide with the measuring range. Values of pH were measured with a digital pH meter (Horiba F-23, Japan) and combined pH glass electrode. The density of the interested liquid solution was measured by a specific gravity bottle. The dynamic viscosity was measured by a capillary viscometer. The interfacial tension between aqueous/organic solutions was determined by a First Ten Angstrom® instrument (Model: FTA125, USA) using the drop shape method.

3.2.3 SLM Setup

3.2.3.1 Flat Sheet Supported Liquid Membrane (FSSLM)

Two kinds of flat membrane systems, namely, horizontal and vertical setups were used in this work. Effective membrane surface area in the horizontal flat membrane system (Figure 3.1) was 10 cm². Volumes of the strip solution and feed solution were 20 ml and 100 ml, respectively. Both aqueous phases were mechanically stirred with magnetic stirrers at 250 rpm. The smaller strip volume compared to that of the feed can provide a faster accumulation of targeted species in the strip (acceptor) solution. Sometimes it is even possible to reach saturation of the strip solutions and finally precipitation of the product. These two factors provided attractiveness for using horizontal setup to conduct tests. The stirring of both aqueous solutions was aimed to reduce the mass transfer resistances in the aqueous un-stirring layers and also provide homogeneous environments in both feed and strip solutions when sampling. The polymer porous support used for the horizontal flat membrane system was a fluoropore (PTFE) membrane filter (Millipore, USA) with an average thickness of 50 μm, 70% porosity and average pore size of 0.2 μm.
The horizontal flat membrane system was used to study the effects of feed pH and membrane carrier concentration on Cu(II) transmembrane flux so as to determine the optimal conditions for SLM based copper recovery process using LIX54 and LIX84 as the carrier.

In the vertical flat membrane system (Figure 3.2), effective membrane surface area was 4.9 cm². It had two Teflon chambers holding the feed and strip solutions with volume of 37 ml each. Both aqueous phases were mechanically stirred with Teflon impellers in connection with an overhead mixer (CAT R18, M. Zipperer, GmbH, Germany) at 200 rpm. A PTFE membrane filter (Whatman®, England) was used as a membrane support. It has a diameter of 4.7 cm and a thickness of 150 μm with ~ 80% porosity and an average pore size of 0.2 μm. At top of each Teflon chamber there were opening holes designed for electrodes insert. The electrodes connected to analytical equipments were utilized for real time monitoring of physicochemical conditions of liquid membrane impregnated membrane filter, which was specifically designed for long term stability studies and real-time monitoring of the physicochemical properties of impregnated membranes.
To prepare supported liquid membrane, the membrane filter was immersed into organic solution (LIX54 in kerosene under predetermined ratio). After fully wetted by the organic solution, membrane filter was then taken out and extra oil on the membrane surface was blotted by tissue paper. Then the impregnated filter was fixed in the membrane module. If the weight gain in membrane after impregnation was close to what could be expected based on the known porosity and the density of carrier, the membrane pores were considered to be fully impregnated by the organic carrier.

### 3.2.3.2 Hollow Fiber Supported Liquid Membrane (HFSLM)

A laboratory scale microporous polypropylene hollow fiber module (Liqui-Cel® Extra-Flow 2.5”×8” membrane contactor, Hoechst Celanese, USA) was employed to prepare HFSLM. Detailed specification of the hollow fiber membrane module was given in Table 3.2 [22, 23, 24]. The liquid membrane phase was impregnated in fiber wall by pumping
organic membrane phase through the contactor using a peristaltic pump (Cole-Parmer, USA) in a recycling mode for about one hour. The extra oil was washed out with de-ionized water.

Table 3.2: Liqui-cel® Extra-flow membrane contactor (2.5”×8”) specifications

<table>
<thead>
<tr>
<th>Fiber Specifications</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber Type</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>Number of Fibers (N)</td>
<td>9950</td>
</tr>
<tr>
<td>Fiber Internal Radius (ri)</td>
<td>120 μm</td>
</tr>
<tr>
<td>Fiber Outer Radius (ro)</td>
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</tr>
<tr>
<td>Effective Pore Size (rp)</td>
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</tr>
<tr>
<td>Porosity (ε)</td>
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<tr>
<td>Tortuosity (τ)</td>
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</tr>
<tr>
<td>Effective Fiber Length (L)</td>
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</tr>
<tr>
<td>Effective Surface Area (Sm)</td>
<td>1.4 m² (15.1 ft²)</td>
</tr>
<tr>
<td>Fiber Potting Material</td>
<td>Polyethylene</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Module Specifications</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Case Material</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>Effective module outer diameter (dₑ)</td>
<td>4.67 cm</td>
</tr>
<tr>
<td>Effective module inner diameter (dᵢ)</td>
<td>2.2 cm</td>
</tr>
<tr>
<td>Case Diameter</td>
<td>6.3 cm</td>
</tr>
<tr>
<td>Case Length</td>
<td>20.3 cm</td>
</tr>
<tr>
<td>Shell Side Connections</td>
<td>¼” NPT female</td>
</tr>
<tr>
<td>Tube Side Connections</td>
<td>¼” NPT female</td>
</tr>
<tr>
<td>Maximum Operating Pressure</td>
<td>3.06 bar (45 psig)</td>
</tr>
<tr>
<td>Operating Temperature Range</td>
<td>10 – 40 °C</td>
</tr>
<tr>
<td>Priming Volume (Tube Side)</td>
<td>150 cm³</td>
</tr>
</tbody>
</table>

3.2.4 Characterization of LIX54, LIX84 and Their Complexes with Ammoniacal Copper Solutions

3.2.4.1 Experimental Methodology

The β-diketone LIX54 and hydroxyoxime LIX84 extractants and their complexes formed after reaction with spent etchant solution (Table 3.1) were analyzed by an FT-IR spectrometer (Bio-Rad, USA) to study the reaction mechanisms of the extractants with
Cu(NH$_3$)$_4^{2+}$.

Electron Paramagnetic Resonance (EPR) spectra of two types extractant-Cu complexes were also investigated at low temperature of 77K with an Elexsys Series E500 CWEPR X-band spectrometer (Bruker, BioSpin GmbH, Rheinstetten/Karlsruhe, Germany). The Spin Hamiltonian parameters were got from simulation results using WINEPR Simfonia software (Bruker Biospin GmbH, Germany) to fit experimental EPR spectra.

### 3.2.4.2 Computational Methodology

With recent advance in computer resources and the development of sophisticated algorithms, quantum chemical computations are playing increasingly important role in chemical science and engineering. The objective of computational chemistry is to mathematically reveal molecular structure-property relation. In the current work, the reaction processes of carriers LIXs with Cu(NH$_3$)$_4^{2+}$ were analyzed from the first-principles density functional theory (DFT) calculations. It is well recognized that DFT generally performs well for the organometallic compounds [25]. The geometries of the related reactants and products in Cu(NH$_3$)$_4^{2+}$/LIXs reaction processes were fully optimized with the Becke’s three-parameter hybrid functional coupled with the Lee-Yang-Parr correlation functional (B3LYP) level of theory at 6-31g basis set. One of the most important properties of a molecule is its orbitals, which can be approximated by additive basis sets. The split-valence basis set 6-31g used here means that the inner shell orbitals are represented by six gaussians, and the valence orbitals by three gaussians for
the first Slater Type Orbital (STO) and by one gaussian for the second STO.

To provide good starting coordinates for DFT optimization, the geometries of the carriers and copper-carrier complexes were energy mechanically minimized using AMBER 8 with the general Amber force field [26]. There were 5000 steps in the minimization, in which the first 1000 steps used the steepest descent method, while the second 4000 steps used conjugate gradient method. The single point energies of these fully optimized geometries were calculated using B3LYP at 6-31+g(d) basis set. Here the ‘+’ sign means 6-31g basis set is supplemented by a diffuse function. Normally a basis set is centered in the inner shell. However, the incorporation of diffusion function can account for electron at large distance from nuclei. The ‘d’ means single polarization function is added to 6-31g basis set which results in the addition of one d function to the first and second row atoms and one f function to the first transition row atoms. All the first-principles DFT calculations were performed using the GAUSSIAN 03 program suite [27]. The energy changes in complex formation processes were estimated by $\Delta E = \sum E_{\text{Products}} - \sum E_{\text{Reactants}}$.

3.2.5 Selective Separation of Copper over Other Cations in Ammoniacal Waste Solutions Using HFSLM system

Although it is useful for the fundamental mechanism studies, the flat sheet SLM system is not suitable for practical application of SLM technology due to its small membrane surface area. In contrary, hollow fiber SLM represents a very attractive solution to the need of applying SLM with very high throughputs. In addition, the hollow fiber SLM
system has following advantages such as high membrane surface area per unit volume, favorable hydrodynamics which minimizes aqueous concentration polarization and membrane fouling problems.

Therefore, the treatment of industrial ammoniacal wastewater with typical compositions shown in Table 3.1 by LIX54 or LIX84 as the carrier was conducted in the hollow fiber SLM system. After liquid membrane preparation, the ammoniacal waste solution was pumped through the lumen side of hollow fiber membrane contactor, whereas the strip solution co-currently was fed in the shell side. The feed and strip solutions were pumped at same volumetric flow rates. The co-current flow mode and the same volumetric flow rates were adopted in order to provide a stable SLM system and forbid the Kelvin-Helmholtz instability caused by the hydrodynamic velocity difference between tube and shell sides of hollow fiber membrane contactor.

The effect of feed and strip volumetric flow rates on copper selectivity performances was also studied. Before the experiment was carried out with another different volumetric flow rate, the lumen and shell side of the hollow fiber membrane contactor were thoroughly cleaned up with de-ionized water and any remaining solutions in the module were pumped out.

3.2.6 Comparative Study of Long Term Stability of FSSLM to Treat Ammoniacal Waste Solutions Using LIX54 and LIX84 as the Carrier
The liquid membrane stability was investigated by monitoring copper transmembrane flux using the vertical flat membrane system. The strip solutions were pumped through a quartz flow-cell (Hellma, Germany) with optical window of 1 cm (H) × 0.1 cm (W) where the copper concentration in the strip side was real-time monitored using a UV-VIS scanning spectrophotometer (Libra S32, Biochrom Ltd., England) at a wavelength of 780 nm. A calibration of the system was performed by diluting a standardized CuSO$_4$ solution with 2M H$_2$SO$_4$, and then the optical absorbance of the diluted Cu$^{2+}$ solutions at 780 nm were plotted as a function of concentrations. A 37 ml feed ammoniacal solutions containing 2.5 mM Cu(NH$_3$)$_4$$^{2+}$ and a 42 ml 2M H$_2$SO$_4$ as strip solutions (additional volumes of 5 ml were used to fill up the tubing and quartz cell) were homogeneously stirred at 200 rpm in the two Teflon chambers of vertical flat membrane setup. After preset time intervals (one day) the feed and strip solutions were replaced by fresh ones with the same compositions so as to forbid the variation of flux due to composition differences. The plot of optical absorbance versus time was always a straight line over a long period of time in each run.

Membrane stability of the vertical flat membrane setup was also monitored by measuring the electrical resistance and capacitance of the Whatman® PTFE membrane impregnated by 33 v/v% LIX54 or LIX84. The electrical characteristics of liquid membrane were measured by an impedance spectroscopy (Autolab, PGSTAT20, Eco Chemie BV, Netherlands) and four electrodes (two platinum and two Ag/AgCl) electrochemical system. When the impedance measurement was carried out, the aqueous solutions were not stirred so as to forbid the interference caused by mechanical stirring.
3.3 Results and Discussion

3.3.1 Copper Complexes Formation with LIX54 and LIX84

The active ingredients of LIX54 and LIX84 are 1-phenyl-1, 3-decanedione and 2-hydroxy-5-nonylacetoephone oxime, respectively. For LIX54, it exists as an equilibrium mixture of enol and keto forms. The mixture of keto and enol are involved in valence and co-ordination bonding with copper [14, 28]. The general reaction mechanisms involving Cu(NH3)4^{2+}/LIX54 and Cu(NH3)4^{2+}/LIX84 are described in Figure 3.3 and both the reactions can be described as:

\[ Cu(NH_3)_4^{2+} + 2HR \Leftrightarrow CuR_2 + 2NH_3 + 2NH_4^+ \]  \hspace{1cm} (3.1)

where HR represents the carrier LIX54 or LIX84; CuR_2 represents the copper-carrier complexes.

![Figure 3.3: Proposed reaction mechanism between (A) Cu(NH3)_4^{2+}/LIX54 and (B) Cu(NH3)_4^{2+}/LIX84](image-url)
It is well known that Cu$^{2+}$ in aqueous solutions with ammonia forms octahedral complexes from Cu(NH$_3$)(H$_2$O)$_5^{2-}$ to Cu(NH$_3$)$_4$(H$_2$O)$_2^{2-}$ and the fifth and sixth ammonia do not bind strongly with Cu$^{2+}$ because of Jahn-Teller effect [29, 30]. Recently, it has been demonstrated that Cu complex with four NH$_3$ is the predominate form in ammoniacal solutions containing an excess of NH$_3$ in comparison to Cu [18]. The complex is characterized by high value of stability constant $K_s$=10$^{12.46}$ M$^{-4}$ of copper-tetra ammonia complex [31]. Evidently, Cu(NH$_3$)$_4$$^{2+}$ is the dominant species in the ammoniacal waste water and spent ammoniacal etchant solution used in our experiments.

Figure 3.4 shows the IR spectra of extractants and their complexes after extraction with spent etching solutions. All the spectra have strong peaks around 3200-2500 cm$^{-1}$ which are the characteristic peaks of chelated O-H groups referred to [32, 33]. The IR spectrum of LIX54 shows a strong band in the region around 1610 cm$^{-1}$ which represents the existence of β-diketone fragment. However, the vibration bands between 1520-1400 cm$^{-1}$ of LIX54 complex with copper indicate the C=C stretching vibrations. This proves the chelation reaction between carbonyl groups of LIX54 with Cu(NH$_3$)$_4$$^{2+}$ (Figure 3.3. A).

For aromatic oxime, the R$_2$C=N-OH stretching band occurring in the region 1670-1620 cm$^{-1}$ appears both in the spectra of LIX84 and its complex with Cu(II). The oxime with intramolecular hydrogen bond has characteristic stretching vibrations in the region 3400-3200 cm$^{-1}$, which appear both in the spectra of LIX84 (O-H···N) and LIX84/Cu(II) complex (O-H···O). The N-H stretching vibrations in high wave number area occurring in the LIX84 spectra confirm its intra-molecular hydrogen bond (O-H···N), whereas this is not the case for LIX84 complex with copper.
Notice should be taken that there are small peaks at 1067 and 1176 cm\(^{-1}\) in LIX84/Cu(II) complex spectrum. The presence of NH\(_3\) in the extracted organic solution will result in peaks at these ranges [34]. It was also mentioned in [14, 35] that nonylphenol used in the synthesis of hydroxyoxime was found to extract ammonia quite strongly at high pH. The appreciable ammonia carry-over from the feed to the strip by the organic carrier over long periods is deleterious to the subsequent performance of electrowinning step; While it has been discovered that the use of diketone having very high steric hindrance will provide a further improved process in which the strip kinetics remains rapid and substantially reduced co-extraction of ammonia occurs during loading with copper [36] which is also confirmed in our IR spectrum of LIX54/Cu(II) complex. The low or no extraction of ammonia provides a significant advantage for LIX54 over other copper extractants in the ammoniacal copper solution treatment [14, 15].

Figure 3.4: FTIR spectra of extractants and their complexes with spent etchant solutions
Figure 3.5 displays the EPR spectra of LIX54/Cu(II) and LIX84/Cu(II) at 77K. Typical spectra with axial symmetry consist an intense (perpendicular) absorption in the high-field range and a weaker (parallel) signal in the low-field side, which usually splits into four equally spaced hyperfine lines and shows the shifts depending on the nature of the copper complex [37].

![EPR spectra of LIX54/Cu(II) and LIX74/Cu(II) complexes at 77K.](image)

**Figure 3.5: EPR spectra of LIX54/Cu(II) and LIX74/Cu(II) complexes at 77K.**

Spin Hamiltonian parameters are: $g_\perp = 2.053, g_\parallel = 2.277, A_\perp^{Cu} = 22, A_\parallel^{Cu} = 170$ for LIX54/Cu(II) complex and $g_\perp = 2.053, g_\parallel = 2.196, A_\perp^{Cu} = 18.7, A_\parallel^{Cu} = 207, A_\perp^{N} = 23, A_\parallel^{N} = 10$ for LIX84/Cu(II) complex.

The spectrum of LIX54/Cu(II) complex demonstrates the Cu$^{2+}$ as a magnetic nuclear center surrounded by a symmetric square planar arrangement of four ligating ligands e.g. 4O, which corresponds to the super-hyperfine splitting structure in the high-field range. When two ligands are of one type and the other two of another type, e.g. 2N and 2O in LIX84/Cu(II) complex, the symmetry will be orthorhombic for a square planar trans-configuration [38]. The more super-hyperfine splitting lines in the high-field range illustrates the Cu$^{2+}$ nuclear center are surrounded by both O and N ligands in LIX84/Cu(II) complexes. Considered the naturally abundant O$^{16}$ has no nuclear spin, the
naturally scarce O\textsuperscript{17} with nuclear spin 5/2 has little contribution to both LIX54/Cu(II) and LIX84/Cu(II) EPR spectra. While for N\textsuperscript{14} with nuclear spin 1 and natural abundance of 99.63\%, its contribution to the EPR spectrum of LIX84/Cu(II) complex has to be taken into consideration.

It was suggested the most reliable information from the observed Cu(II) complex EPR spectra was derived from the $g_\perp$ and $A_\perp$ values \[38\]. The $A$ value further provides a very good indication of the extent to which electrons have migrated from the central Cu to the surrounding ligands \[39\]. For the LIX84/Cu(II) complex, the hyperfine splitting constant $CuA_\perp$ of the Cu nucleus surrounded by 2N and 2O is 18.7, which is smaller than $CuA_\perp=22$ in the LIX54/Cu(II) complex. According to \[39\], the higher value of the hyperfine splitting constant indicates that the orbital occupied by the unpaired electron in LIX54/Cu(II) complex becomes more ligand-like and interacts more weakly with the Cu(II) nucleus.

Furthermore, the quantum chemical calculation results agree well with the experimental characterization results and support the proposed reaction mechanisms. From the optimized LIXs/Cu(II) geometries (Figure 3.6 and Figure 3.7), Cu\textsuperscript{2+} as a center is surrounded by a square planar arrangement of four oxygen ligands in the LIX54/Cu(II) complex, while in the LIX84/Cu(II) complex it is surrounded by an orthorhombic arrangement of two oxygen ligands and two nitrogen ligands. This is confirmed by all the same distances between copper and four oxygen atoms in LIX54/Cu(II) complex and different distances between Cu-O and Cu-N in LIX84/Cu(II) complex. In addition, there
are intra-molecular hydrogen bonds between O$^1$···H$^2$ and O$^2$···H$^1$ with a bond length of 1.65 Å in the optimized LIX84/Cu(II) complex geometry, which evidently support the reaction mechanism proposed in Figure 3.3. The single point energy calculation using B3LYP/6-31+g(d) shows that LIX84/Cu(II) complex formation is more favorable than LIX54/Cu(II) complex, with a more negative energy change in the complex formation process (Table 3.3). The computational results also show that LIX84 is a stronger extractant for copper than LIX54, which is in accordance with [14] and our EPR results.
Figure 3.7: Molecular model of the optimized geometry of LIX84/Cu(II) complex with mapped electrostatic potential (ESP) using B3LYP/6-31g level of theory

Table 3.3: Quantum chemical computation results of LIXs/Cu(II) complexes

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
<th>LIX54/Cu(II) complex</th>
<th>LIX84/Cu(II) complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-O(^1)</td>
<td>1.91</td>
<td>1.91</td>
</tr>
<tr>
<td>Cu-O(^2)</td>
<td>1.91</td>
<td>1.91</td>
</tr>
<tr>
<td>Cu-O(^3)</td>
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<td>1.91</td>
</tr>
<tr>
<td>Cu-O(^4)</td>
<td>1.89</td>
<td>1.89</td>
</tr>
<tr>
<td>Cu-N(^1)</td>
<td>1.95</td>
<td>1.95</td>
</tr>
<tr>
<td>Cu-N(^2)</td>
<td>1.95</td>
<td>1.95</td>
</tr>
<tr>
<td>ΔE (kJ/mole)</td>
<td>-99.33</td>
<td>-114.61</td>
</tr>
</tbody>
</table>

3.3.2 Effect of the Feed pH on Copper Transmembrane Flux with LIX54 and LIX84 as the Carrier

It is well-known that carrier for copper extraction from alkaline solutions and the equilibrium distribution of copper between the aqueous and organic phases depends on pH of the feed solution [2, 14, 28]. In experiments the feed pH was adjusted by the addition of HCl and aqueous NH\(_3\)·H\(_2\)O solutions. The transmembrane flux is determined
according to the expression:

$$J = \frac{dC}{dt} \cdot \frac{V}{S_m}$$ (3.2)

Where $dC$ is the change in concentration in the strip over time interval $dt$, $V$ is the strip solution volume and $S_m$ is the effective membrane surface area.

Figure 3.8 shows LIX54 has a very low copper transport rate through SLM at pH lesser than 3 and copper is transported through SLM fairly well at pH values above 3 and the rate increases gradually with increasing pH, reaching a plateau at pH around 6. The results are quantitatively similar to the data by Alguacil et al. [16], who has conducted detailed liquid-liquid copper extraction experiments at various pH using LIX54. There is slightly decrease of flux in more alkaline solution ($1.46 \times 10^{-8}$ mol/cm$^2$/s at pH 8.66 versus $1.48 \times 10^{-8}$ mol/cm$^2$/s at pH 7) which is due to higher NH$_3$ content at higher feed pH solutions. This makes it more difficult for the extractant to compete with NH$_3$ for copper. The effect is especially strong at low copper concentration when a significant excess of
ammonia is present in the feed solution [14].

In comparison, LIX84 can transfer copper fairly well through SLM even at pH lesser than 1. The maximum copper transmembrane fluxes are reached at pH around 2 and the fluxes are then almost constant at pH higher than 2 due to possibly saturation of LIX84 by Cu at the feed/membrane which was very rapid observed in [20]. The high copper loading capacity in acidic copper solution provides LIX84 as a good candidate for copper recovery from acidic media. However, the compromise between higher copper loading and slower strip kinetics in ammoniacal copper solutions treatment makes copper transmembrane fluxes in an SLM system with LIX84 as the carrier slightly lower than that of LIX54: At pH around 7, the flux of SLM system with LIX54 as the carrier is $1.48 \times 10^{-8}$ mol/cm$^2$s and that is $1.35 \times 10^{-8}$ mol/cm$^2$s for LIX84. The lower flux together with its significant ammonia carry-over in extended periods of process time makes LIX84 incompetent to treat ammoniacal copper solutions.

### 3.3.3 Effect of Carrier LIX54 or LIX84 Concentration on Copper Transmembrane Flux

As recommend by the LIx supplier and also from our observations, β-diketone extractant LIX54 should be used for copper recovery from ammoniacal solutions, whereas a strong hydroxyoxime extractant LIX84 is utilized for copper recovery from acidic sulfate solutions. In this work we also tried to figure out the optimal carrier concentrations for SLM based ammoniacal or acidic copper solutions treatment using
LIX54 or LIX84, respectively. Both Cu(II) concentration in ammoniacal and acidic solutions was the same (0.021 M) but pH were adjusted differently at pH 3 for acidic solution and pH 7.25 for ammoniacal solution. Figure 3.9 shows that Cu(II) transmembrane fluxes using LIX54 as the carrier are higher than that of LIX84 at the corresponding same volume ratio. This is consistent with the results shown in Figure 3.8. It also shows that an increase in the carrier concentration results in an increase in the copper transmembrane flux for both LIX54 and LIX84 system and flux reaches the maximum at a carrier concentration of approximately 33 v/v%. Further increase of the copper removal rate is hindered probably by the reduced copper-carrier diffusion coefficient in the membrane phase. A decreasing copper-carrier diffusion coefficient at higher carrier concentrations is attributed to the increasing membrane phase viscosity [40-43] for both carriers or because of the dimerization of the extractant LIX84 in more concentrated extractants [35, 41]. For readers’ information, the LIX54/kerosene viscosity increases from 2.28 cP (33.3 v/v%) to 2.77 cP (50 v/v%); while for LIX84/kerosene system, the viscosity increases from 4.04 cP (33.3 v/v%) to 8.51 cP (50 v/v%). The drastic increment of viscosity in LIX84/kerosene system could be the cause of slightly lower flux at higher LIX84 volume ratio in kerosene.
3.3.4 Selective Separation of Copper over Other Cations Contaminants by Once-through Transport in HFSLM Modules Using LIX54 or LIX84 as the Carrier

In selectivity studies both inlet and outlet concentrations of targeted metal species (Cu(II), Zn(II), Ni(II), Cd(II)) in aqueous solutions were measured to get corresponding metal ions tube side mass transfer coefficient \( K \) according to:

\[
K = \frac{Q}{S_m} \ln \frac{C_m}{C_{out}}
\]

(3.3)

Where \( C_m \) and \( C_{out} \) is the inlet and outlet concentrations of metal ions, respectively; \( Q \) is the volumetric flow rate in the tube side.

The separation factor (SF) of copper over other cation contaminants (M) is defined as:
Table 3.4 shows the comparative results of selective separation of Cu(II) over Zn(II), Ni(II) and Cd(II) with LIX54 and LIX84 impregnated HFSLM. Obviously, LIX54 enjoys much higher selective separations of Cu(II) over Zn(II) and Cd(II) than LIX84. However, selective separation of Cu(II) over Ni(II) is almost the same for LIX54 and LIX84. The same results are obtained in solvent extraction experiments: LIX54 can extract both Cu(II) and Ni(II) very well at pH around 7.25, but it has low Zn(II) loading capacity [43, 44]; LIX84 can co-extract Cu(II) and Ni(II) from alkaline conditions [45]. At equilibrium pH around 7.25, all Cu(II), Zn(II) and Ni(II) are well extracted by LIX84 [46]. It is a practical way in solvent extraction that the recovery and separation of specific cation from the mixtures after co-extraction can be achieved by a selective stripping process [45, 47]. Similarly to the solvent extraction method, the SLM based membrane extraction technology performs extraction and back-extraction in one technological step. The co-extraction of cations by carrier can be separated and purified in strip solutions with different strip concentrations or even in different strip solutions. Nevertheless this operation makes SLM based membrane extraction not economically and practically attractive because more membrane contactors are needed in the selective stripping process and also the operation becomes more complicated. The high selectivity of Cu(II) over Zn(II) and Cd(II) provides another significant advantage for LIX54 over other copper extractants such as LIX84 to treat copper-containing ammoniacal solutions using HFSLM.
Table 3.4: Once-through selective separation of copper over other cations contaminants by HFSLM using LIX54 and LIX84 as the carrier

<table>
<thead>
<tr>
<th>Flow rate</th>
<th>55 ml/min</th>
<th>140 ml/min</th>
<th>210 ml/min</th>
<th>390 ml/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF</td>
<td>Cu/Zn</td>
<td>Cu/Ni</td>
<td>Cu/Cd</td>
<td>Cu/Zn</td>
</tr>
<tr>
<td>LIX54</td>
<td>17.05</td>
<td>3.77</td>
<td>103.26</td>
<td>21.25</td>
</tr>
<tr>
<td>LIX84</td>
<td>1.08</td>
<td>1.51</td>
<td>0.49</td>
<td>1.21</td>
</tr>
</tbody>
</table>

It is worth noting that the light blue ammoniacal waste solution with 5.6 mM Cu(II) became colorless (outlet Cu(II) concentration measured was less than 5 ppm) when it was pumped through the LIX54 or LIX84 impregnated HFSLM once through at low volumetric flow rate of 55 ml/min. This means the ammoniacal copper solutions after the HFSLM single pass through treatment can be reused as the rise water or be discharged directly in compliance with the environmental regulations. The ammoniacal wastewater treatment capacity of one membrane contactor with 1.4 m² membrane area is around 3.5 L/hr. In addition, Table 3.4 shows that selective separation of copper with LIX54 will be somehow decreased with increasing flow rate, which maybe due to the decreasing “residence time” of cations contacted with this highly selective extractant of copper over other cations contaminants. However, the selective separation of copper over other cations using LIX84 impregnated HFSLM did not change significantly at various flow rates. This is mostly due to the co-extraction of copper with other cations at pH 7.25 of the ammoniacal solutions by LIX84.

3.3.5 Long Term Stability of Vertical Flat Membrane System to Treat Ammoniacal Wastewater Using LIX54 or LIX84 as the Carrier
Although SLMs have been widely studied for the separation and concentration of a variety of compounds and present many potential advantages over other separation methods, there have been very few large scale applications of SLM due to insufficient membrane stability. Various mechanisms have been proposed for SLM instability: loss of organic phase (carrier and/or solvent) from the membrane phase by dissolution, progressive wetting of the support pores, pressure difference or osmotic pressure gradient over the membrane [48-51], and emulsion formation [51] or attrition of the organic film [52] due to lateral shear forces. The time period of instability observed varies from few hours to several months [53-55] depending on the system.

Different approaches were used to determine SLM (in)stability: measuring membrane liquid loss by weighing methods [50, 56, 57]; determining water content within the decayed SLM [58], measuring physico-chemical properties of the organic phase (interfacial tensions, viscosities, contact angles and water solubilities) [59]. All the above mentioned techniques are membrane-destructive methods, that is, the experiments have to be terminated and the membrane cannot be used again after analysis.

Membrane stability measurement using impedance spectroscopy was first proposed by Zha et al. [60]. It is based on the idea that the effective area and thickness of an SLM would change as the membrane liquid is lost to the adjacent aqueous solutions and subsequently the empty parts of SLM would be occupied by aqueous solutions. The sufficiently different dielectric and conductance properties of the individual sub-structural layers within the SLM would result in a significant difference in the
capacitance and resistance of the decayed membrane (Figure 3.10-B) from that of the original and intact SLM (Figure 3.10-A). Therefore, based on measurements of the changes of the capacitance or the resistance of an SLM with time, it should be possible to characterize the process of the membrane liquid loss.

![Schematic descriptions and representative equivalent circuits of (A) intact SLM and (B) partially degraded SLM in vertical flat membrane setup](image)

Figure 3.10: Schematic descriptions and representative equivalent circuits of (A) intact SLM and (B) partially degraded SLM in vertical flat membrane setup

In this work for liquid membrane stability studies, non-invasive impedance spectroscopy technique and initial flux measurement over extended periods of time described in section 3.2.6 were used to compare SLM stabilities using LIX54 and LIX84 as the carrier. Figure 3.11 shows that the resistances of both LIX54 and LIX84 impregnated SLM in the first two days dropped a lot. For LIX54 impregnated SLM, the resistance decreased from 5 MOhm on the first day to 2 MOhm on the second day, whereas for LIX84, the resistance decreased from 1.88 MOhm to 0.78 MOhm. This resistance decrease is probably due to the partial dissolution of membrane solvent-kerosene into the adjacent aqueous phases. It can be confirmed by the same transmembrane flux on the first two days (Figure 3.12) which indicates the effective carrier in the membrane phase did not change a lot. The resistances and capacitances of the LIX54 impregnated membrane then were kept almost
the same for next 280 hours, whereas for LIX84 impregnated membrane the period was about 230 hours. After that the resistances of both membranes strongly decreased and the capacitances increased. The significant decrease of membrane resistances from several MOhm to several KOhm indicates that liquid membranes are under degradation and microporous of membrane support are gradually occupied by the adjacent aqueous solutions. Degraded SLM has the equivalent circuit as shown in Figure 3.10-B which is a combination of two aqueous layers in feed and strip sides in series with one organic membrane layers. As long as the effective surface area of the capacitance double plates during the experiment is constant, probably change in the capacitance is due to the changes of SLM thickness as the membrane liquid is lost with time. The dielectric constant (or permittivity) of water is much larger than that of organic carrier and solvent which results in the much larger membrane capacitance of the degraded membrane than the original or intact one. This conclusion is based on the equation:

\[
\frac{1}{C_{m'}} = \frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} = \frac{\delta_1}{\varepsilon_0 A \varepsilon_1} + \frac{\delta_2}{\varepsilon_0 A \varepsilon_2} + \frac{\delta_3}{\varepsilon_0 A \varepsilon_3} = \frac{1}{\varepsilon_0 A} \left( \frac{\delta_1}{\varepsilon_1} + \frac{\delta_2}{\varepsilon_2} + \frac{\delta_3}{\varepsilon_3} \right) < \frac{1}{\varepsilon_0 A \varepsilon_m} = \frac{1}{C_{m0}} \tag{3.5}
\]

Where \( C \) is the capacitance; \( \delta \) is the thickness; \( A \) is the surface area of capacitance double plates; \( \varepsilon_0 \) is the permittivity of vacuum space; \( \varepsilon \) is the dielectric constant (or permittivity); Subscripts \( m' \) and \( m0 \) represent the degraded SLM and the intact or original one, respectively; subscripts 1, 2 and 3 represent the feed aqueous solution into the microporous support, remaining liquid membrane and strip aqueous solution into the microporous support. The effective membrane capacitance of the degraded SLM is just the combination of these three capacitances in series.
Figure 3.11: Electrical capacitance and resistance changes of the vertical flat membranes impregnated by 33 v/v% LIX54 or LIX84 with time

The initial flux measurement over extended periods of time (Figure 3.12) also shows similar time dependence of membrane stabilities as impedance spectroscopy technique. SLM with LIX54 as carrier has slightly higher transmembrane flux than LIX84, which is consistent with the results found in section 3.3. Furthermore, LIX54 impregnated SLM also has slightly higher stability than LIX84. After 15 days treatment, the copper transmembrane flux through LIX54 impregnated SLM decreases by 28.9% from $1.24 \times 10^{-9}$ mol/cm$^2$·s to $8.82 \times 10^{-10}$ mol/cm$^2$·s, whereas for LIX84 impregnated SLM, its transmembrane flux is decreased by half from $1.07 \times 10^{-9}$ mol/cm$^2$·s to $5.28 \times 10^{-10}$ mol/cm$^2$·s after 13 days treatment. For LIX84, its active substance losses during metal extraction from ammoniacal solutions maybe happened as the result of enhanced hydrophilicity of the carrier due to its phenolic group dissociation [35]. Nevertheless the carrier is not fully leaking from membrane support and you can still see active/facilitated transport. For readers’ information, the measured interfacial tensions between
feed/organic and strip/organic phases are around 26.5 mN/m. The corresponding critical
displacement pressures according to Eq. 2.10 are equal to 2.3 atm, which is much larger
than the hydrodynamic pressure caused by the continuous stirring. This ensures the
carrier not fully leaking from the membrane support. The control experiment with only
kerosene impregnated membrane shows no copper transport at all over a long time span.
Stability of supported liquid membrane in ammoniacal copper solutions treatment is
promising for practical industrial applications.

![Figure 3.12: Initial copper transmembrane flux measurement of SLMs immobilized with
LIX54 or LIX84 over extended periods of time](image)

Feed: 37 ml ammoniacal solutions with 2.5 mM Cu(NH₃)₄²⁺; Strip: 42 ml 2M H₂SO₄
SLM: Vertical flat membrane impregnated with 33 v/v% LIX54 or LIX84

3.4 Summary

In this work, two well-established copper extractants LIX54 and LIX84 commonly used
in solvent extraction process were chosen as the carrier candidates in supported liquid
membrane system to remove copper from ammoniacal wastewater. The comparative
studies in membrane flux, selectivity and stability by these two carriers were carried out.
The geometries of LIXs/Cu(II) complexes and the energy changes in these complexes formation processes were studied first time by the sophisticated quantum chemical computations to prove the experimental results. Experimental characterization results on LIX54/Cu(II) and LIX84/Cu(II) complex geometries, reaction mechanisms are in accordance with the quantum chemical computations results. The EPR results together with the computational results show that LIX84 is a stronger extractant for Cu(II) than LIX54. However, the compromise between higher copper loading and slower strip kinetics in ammoniacal copper solutions treatment makes copper transmembrane fluxes in an SLM system with LIX84 as the carrier slightly lower than that of LIX54. The high selectivity of copper over other cation contaminants and low or no ammonia carry-over provide significant advantages for LIX54 as a better candidate over LIX84 for SLM based ammoniacal copper solutions treatment. As a modern strong extractant, LIX84 can be used for copper recovery from acidic solutions. The hydrophilic nonylphenol group makes LIX84 impregnated SLM stability slightly shorter than LIX54 impregnated one. However, the stability of both LIX54 and LIX84 impregnated SLM in ammoniacal copper solutions treatment process is promising for practical industrial applications.
References


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4. CHAPTER FOUR

KINETICS AND MECHANISM OF COPPER REMOVAL FROM AMMONIACAL WASTEWATER THROUGH FLAT SHEET SUPPORTED LIQUID MEMBRANES

4.1 Introduction

Compared with conventional separation process such as solvent extraction, supported liquid membranes (SLM) have dramatic advantages, including the possibility to conduct both processes of extraction and re-extraction in one technological step, relatively high membrane surface area per unit volume, complete loading, no flooding, low organic species (extractant and solvent) usage, etc. [1]. Recent studies have demonstrated that SLM can be an effective tool for metal ions reclamation [2-5], pharmaceutical product recovery [6, 7], removal of organics [8, 9], sea water desalination [10], etc. Feasibility studies of copper separation from aqueous solutions by SLM have also been conducted worldwide [11-16], which is determined both by simplicity of the process and its practical potential and importance for microelectronic industry, generating a lot of waste water and spent etching solutions with high copper contents.

Copper-containing wastewater is formed in big volumes as rinsing water after etching process during printed circuit board (PCB) manufacturing or as the effluent generated after spent etchant treatment. Generally, copper concentration in this wastewater is around several hundred ppm. It has to be reduced to less than 5 ppm before the solution
can be reused or discharged safely. Removal of copper ions through SLM is possible due to chemical potential difference for $\text{H}^+$ ions in the feed and strip solutions. In this case initial pH of the feed copper solution is less acidic and it decreases with time due to electroneutral $2\text{H}^+/\text{Cu}^{2+}$ exchange through the liquid membrane. The problem is that copper transfer process stops because the chemical potential difference of $\text{H}^+$ ions decreases. The pH value in the feed becomes more acidic in this process and final $\text{Cu}^{2+}$ concentration in this solution is not low enough because at equilibrium chemical potential difference of copper ions is balanced by chemical potential difference of $\text{H}^+$ ions.

We have demonstrated that in contrast to usual aqueous solutions with simple $\text{Cu}^{2+}$ ions, during treatment of copper-containing ammoniacal solutions pH of the feed does not decrease but can even slightly increase [17]. Then it stays almost constant due to the buffer effect of $\text{NH}_3/\text{NH}_4^+$. As a result it was not necessary to adjust the pH in the feed side to keep large $\text{H}^+$ gradient and the process could be conducted till very low copper content in the treated water. Comparison of these two processes is given in the Figure 4.1.

Figure 4.1: Kinetics of pH and copper concentration changes in feed solution. Strip: 2M $\text{H}_2\text{SO}_4$. Organic membrane phase: 33 v/v% LIX54 in kerosene.
A: Copper solution without ammonia, initial pH 4.2.
B: Copper-containing ammoniacal solution, initial pH 6.95.
Usually facilitated ion transport through SLM is described based on the idea that ions in aqueous solutions are reacting through the interface with the chelating agent (carrier) located in the organic membrane phase. Physico-chemical mechanism of the reaction between the two species located in different phases and separated by liquid/liquid interface stays behind the scene. In this chapter we demonstrate that this simple mechanism and the same set of basic parameters can not systematically explain the totality of experimental results and we suggest more detailed and physically reasonable mechanism of copper removal from typical ammoniacal waste aqueous solutions, based on the idea that chelating agent is able to diffuse from organic into the aqueous phase where ion exchange reactions are taking place. The mechanism where the carrier is moving from one aqueous phase through the membrane into another then back and forming the cycle is called “Big Carrousel”, while the simpler mechanism where the carrier stays in the membrane and two ion exchange reactions take place on the water/membrane interfaces corresponds to the term “Small Carrousel” [18]. Although “Big Carrousel” mechanism was suggested long time ago [19], there was no experimental work demonstrating its applicability. In this work, copper recovery from industrial ammoniacal wastewater using flat supported liquid membranes (SLM) was chosen as one of the most well known and practically important examples to first time demonstrate the validity of “Big Carrousel” mechanism to describe facilitated ion transport through SLM. The thickness of aqueous reaction layer where interactions of LIX 54 and copper are taking place is near 5×10⁻⁶ cm at neutral pH and decreases at pH below 5.
4.2 Experimental

Sulfuric acid, hydrochloric acid and sodium hydroxide (Merck, USA) were all of Reagent grade. LIX54 was supplied by Cognis Corporation, USA and was diluted in kerosene (Aldrich, USA) as a carrier in liquid membrane phase. All chemicals were used as received without any further purification. The ammoniacal wastewater and spent ammoniacal etchant solution described in Chapter Three were used as model solutions to carry out the experiments.

Horizontal flat membrane system described in Chapter Three was used in this chapter. Copper concentration was measured by inductively coupled plasma spectroscopy (ICP-AES, Perkin Elmer, USA). In some cases copper solutions were diluted so as to coincide with the measuring range. Values of pH were measured with a Cyberscan 200 digital pH meter and combined pH glass electrode.

Total NH₃ concentration in the ammoniacal copper solution was determined by Kjeldahl method [20], based on ammonia removal from the sample distillation, addition of predetermined amount of sulfuric acid and its back titration with the standard concentration of sodium hydroxide.

4.3 Results

4.3.1 The Influence of Carrier Concentration on Cu(II) Transmembrane Flux
Figure 4.2 shows that the rate of copper transfer through the membrane increased gradually with increase of the carrier concentration, reaching a maximum above 20 v/v% in kerosene. Further increase of the flux was hindered by reduced copper-carrier diffusion coefficient $D_{Cu,R,m}$ due to an increase of membrane viscosity [11, 21]. In the subsequent experiments, 33 v/v% LIX54 in kerosene was used as the organic membrane phase.

Figure 4.2: Copper removal rate as a function of carrier concentration.
Feed: ammoniacal wastewater with 0.021 M Cu(II) at pH ~7
Strip: 2M H2SO4; Horizontal SLM with different volume ratios of LIX54 in kerosene (Simulation based on Eq. 4.24 and Eq. 4.37, simulation parameters are given in Table 4.2)

4.3.2 The Influence of Feed Cu(II) Concentration on Cu(II) Transmembrane Flux

Figure 4.3 shows experimentally the relationship between copper flux and its concentration (range from $2.3 \times 10^{-4}$ to 0.4 M) in the ammoniacal feed solution as well as its simulation (see later). The different concentrations of feed copper solutions were prepared by diluting spent ammoniacal etchant solution or ammoniacal wastewater and the pHs were all controlled at 7.25±0.2. The experimental results show that when copper concentration is lower than 0.1 M, the flux is 1st order with respect to copper
concentration and the rate limiting step is determined by processes in stagnant aqueous layers [13, 15, 22, 23]. When copper concentration is higher than 0.1 M, the flux reaches plateau. The carrier on the feed side of the membrane in this case is saturated with copper [11, 15, 22] and transport is limited by diffusion through the membrane phase.

![Figure 4.3: Influence of the feed Cu(II) concentration on flux.](image)

Strip: 2M H₂SO₄; Horizontal SLM with 33 v/v% LIX54 in kerosene.
(Simulation based on Eq. 4.24 and Eq. 4.37, simulation parameters are given in Table 4.2)

<table>
<thead>
<tr>
<th>Feed Cu(II) conc., M</th>
<th>( J/J_{\text{max},a} )</th>
<th>( J/J_{\text{max},m} )</th>
<th>Rate-limiting step</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2.30 \times 10^{-4} )</td>
<td>1.00</td>
<td></td>
<td>Diffusion in the stagnant layer of aqueous phase</td>
</tr>
<tr>
<td>( 2.30 \times 10^{-2} )</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 5.00 \times 10^{-2} )</td>
<td>0.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 1.00 \times 10^{-1} )</td>
<td>0.98</td>
<td></td>
<td>Diffusion in membrane phase</td>
</tr>
<tr>
<td>( 2.00 \times 10^{-1} )</td>
<td>0.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 4.00 \times 10^{-1} )</td>
<td>0.99</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( J_{\text{max},m} \) and \( J_{\text{max},a} \) are the maximum possible copper fluxes through the membrane and stagnant aqueous layer with given copper concentration in the feed solution, respectively.
They are defined as:

\[ J_{\text{max},m} = \frac{D_{\text{CuR}_{2,m}}}{\delta_m} \frac{[HR]_m^0}{2} \]  

\[ J_{\text{max},a} = \frac{D_{\text{CuR}_{2,a}}}{\delta_a} [Cu(NH_3)_2^+]_a \]  

The maximum flux \( J_{\text{max},m} \) is \( 4.9 \times 10^{-8} \) mol/cm\(^2\)s (Ref. to Figure 4.3). This value was determined by diffusion through the membrane. The membrane thickness in this case was 50 µm and the carrier concentration was 0.55 M as 33 v/v% LIX54 in kerosene, which gave the value of diffusion coefficient for copper-carrier complex \( D_{\text{CuR}_{2,m}} \) in the membrane phase near \( 8.9 \times 10^{-7} \) cm\(^2\)/s.

The \( D_{\text{CuR}_{2,m}} \) value calculated based on Wilke-Chang estimation method (Ref. to Eq. 4-3) for monomeric form is slightly higher (\( 2.8 \times 10^{-6} \) cm\(^2\)/s) [24]. Taking into consideration the tortuosity 2.5 and porosity 0.8 of the membrane filter, the effective diffusion coefficient of the copper-carrier complex in the membrane phase is \( 9.0 \times 10^{-7} \) cm\(^2\)/s, in consonance with the experimental values got from both horizontal and vertical flat membrane system.

\[ D_{AB}^0 = \frac{7.4 \times 10^{-8} \times (M_B)^{0.5} T}{\eta \times V_A^{0.6}} \]  

(4.3)

where \( D_{AB}^0 \) is the diffusion coefficient of solute A (CuR\(_2\)) in solvent B (kerosene), \( M_B \) is the molecular weight of solvent B (\( \sim 200 \) g/mole), T-temperature (299 K), \( \eta \) - viscosity of 33 v/v% LIX54 in kerosene organic solution (2.28 cP), \( V_A \) (666.6 cm\(^3\)/mole) is the molar volume of solute A at its normal boiling temperature according to LeBas method [25].
Further we assumed that in stagnant aqueous solution diffusion coefficients of copper-ammonia complex and copper-water complex were approximately the same, and equal to $6.5 \times 10^{-6}$ cm$^2$/s [25]. Based on the experimental mass transfer coefficient, equal to $8.37 \times 10^{-4}$ cm/s (slope of the insert in the Figure 4.3) we estimated the thickness of this stagnant aqueous layer $\delta$ equal to 77 µm, which is comparable to 110 µm at stirring 400 rpm [26] and 26µm at stirring 1200 rpm [27].

From Table 4.1, we can find that when diffusion in the stagnant layer of aqueous phase is the rate-limiting step, $J/J_{\text{max,a}} \approx 1$; meanwhile, when membrane resistance dominate the mass transfer process, $J/J_{\text{max,m}} \approx 1$. Therefore, comparisons on these two ratios could show us the rate-limiting region under different conditions.

### 4.3.3 The Influence of pH in Feed Solution on Copper Transmembrane Flux

Equilibrium distribution of copper between aqueous solution with ammonia and organic phase with LIX54 depends on pH in the feed [15, 28-31]. Zapatero et al. [32] have found that copper extraction with LIX54 was near 100% at alkaline pH and decreased at pH lesser than 6. Alguacil et al. [28] have found that copper extraction by 1% and 10% (v/v) LIX54 both increases gradually from pH 3 to pH 8.5, and only slightly decreases at higher pH values. Figure 4.4 demonstrates qualitatively similar behavior for transmembrane Cu(II) transport from the ammoniacal wastewater with pH adjusted by HCl or ammonia aqueous solution.
Summarizing this section, we were able to reproduce main published results, such as the effects of carrier, pH and Cu(II) concentration in the feed on copper transmembrane flux. Figure 4.3 and Table 4.1 demonstrate that when copper concentration in the feeding solution is lower than 0.1 M, the rate-limiting step is the diffusion of copper-ammonia complexes through aqueous stagnant layer. When copper concentration is higher than 0.1 M, diffusion of copper-carrier complex in the membrane phase becomes the rate-limiting step. Our experimental values of diffusion coefficient in the membrane and thickness of aqueous unstirred layer are used later in detailed simulation of all results.
4.4 Discussion

4.4.1 Description of Transmembrane Cu Transport Based on Facilitated “Small Carrousel” Mechanism

It is usually assumed that the heterogeneous reaction of an ion with a carrier takes place only on/at the membrane surface. The ion-carrier complex moves through the membrane, and then participates in the ion-exchange reaction with $\text{H}^+$ on another surface. Finally the protonated carrier comes back. This process of facilitated counter-transport is based on the idea that the carrier and metal ion are in different phases but still they react. This simplified model may be termed a “Small Carrousel” and is different in comparison to the more detailed mechanism where the carrier exits the membrane, reacts with ions while diffusing in an aqueous solution and then is transported back into and through the membrane. Same sequence of elementary steps takes place near the opposite interface, and the whole process was called by us “Big Carrousel” [18]. The “Big Carrousel” mechanism was firstly proposed for the description of facilitated transportation through the lipid membranes in early 1970’s [19].
To model the mass transfer of copper in the “Small Carrousel” process, we assume that the system is in a steady state and it means that:

1. Linear concentration gradients of copper-ammonia complexes and copper-carrier complexes exist through an aqueous stagnant layer and through the membrane phase (Figure 4.5), respectively [13, 30, 33-36].

2. Chemical reaction with the carrier on the aqueous/membrane interface is fast in comparison to the diffusion process [37], so that it is possible to assume the existence of extraction equilibrium at the interface [11].

3. H⁺ ions transferred from the strip to the feed solution are bound by ammonia and as the result feed pH practically does not change in the process (Figure 4.1-B).
Specifics of the system described in this work is that copper ions in the feed ammoniacal solutions are in the complex with four ammonia molecules, while in the strip phase they are in a complex with water. This asymmetry of the system was not considered in the previous papers [21, 27, 30] on membrane transport, but it is because of this asymmetry it is possible to conduct the process and decrease Cu content in the feed practically to zero (Figure 4.1-B). To simplify the equations we assume that diffusion coefficients of copper-ammonia complex and hydrated copper ions are approximately the same, and equal to $D_{Cu,a}$.

Earlier we have mentioned that speciation of Cu(II) in solution depends on pH, concentrations of ammonia and Cl$^-$, etc. Cu(NH$_3$)$_4$(H$_2$O)$_2$$^{2+}$ is an important component in the ammoniacal waste water used in our experiments, at least at pH 8-9. EPR spectra also support this interpretation. Additional equilibrium processes with the formation of copper complex with three ammonia molecules at pH near 7 and also different mixed copper complexes with ammonia, OH$^-$ and chloride are possible at lower pH. It is important that these complexes are much less stable than Cu(NH$_3$)$_4$$^{2+}$ and are at equilibrium with it. If we accept that LIX54 reacts mainly with Cu(NH$_3$)$_4$$^{2+}$, it would mean that other complexes are transformed in Cu(NH$_3$)$_4$$^{2+}$ and thus do not change the total kinetics. Further for the sake of simplicity and also because the extraction constants of Cu(II) with LIX54 are known only for Cu(NH$_3$)$_4$$^{2+}$ and Cu$^{2+}$ species, we will present the mechanism based on existence of Cu(NH$_3$)$_4$$^{2+}$ species in the feed and Cu$^{2+}$ in the highly acidic strip solution. This simplification is certainly correct at pH above 8, where Cu(NH$_3$)$_4$$^{2+}$ becomes the dominant species.
In this case we can suggest the following description:

1. The flux of copper in the stagnant layer of aqueous feed solution is:

$$J_1 = \frac{D_{Cu,a}}{\delta_a} ([Cu(NH_3)_4^{2+}]_f - [Cu(NH_3)_4^{2+}]_i)$$  (4.4)

where $D_{Cu,a}$ is the diffusion coefficient of copper-ammonia complex in the aqueous solution; subscript $a$ indicates species in the aqueous phase; subscripts $f$ and $fi$ indicate species in the bulk feed solution and near the feed/membrane interface; $\delta_a$ is the effective thickness of aqueous stagnant layer.

2. Copper extraction with LIX54 at the feed/membrane interface:

$$Cu(NH_3)_4^{2+} + 2HR \leftrightarrow CuHR_2 + 2NH_4^+ + 2NH_3$$

$$K_{ex,f} = \frac{[CuR_2]_i \cdot [NH_3]^2_4 \cdot [NH_4]^2_4}{[Cu(NH_3)_4^{2+}]_f \cdot [HR]^2_i}$$  (4.5)

where $K_{ex,f}$ (M$^2$) represents the effective equilibrium constant for extraction of copper from tetra ammonia complex at the feed/membrane interface; subscript $i$ indicates species in the membrane near aqueous/membrane interface; overbar indicates species in the organic phase.

Equilibrium between NH$_3$ and NH$_4^+$ is described by the following dissociation constant $K_d$(M) [25]:

$$K_d = \frac{[NH_4][H^+]}{[NH_3]} = 5.56 \times 10^{-10}$$  (4.6)
The stability constant $K_s$ (M$^{-4}$) of copper-tetra ammonia complex is [38]:

$$K_s = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = 10^{12.46} \quad (4.7)$$

The values of stability constants for Cu (II) complexes with one, two and three ammonia are $10^{4.14}$, $10^{7.61}$ and $10^{10.48}$, respectively [38]. High value of this constant evidently demonstrates that practically all copper in ammoniacal solutions is predominant in the complex with ammonia.

Earlier Lazarova [30] has studied the kinetics of copper extraction with LIX54 from aqueous ammonia solutions using a rotating diffusion cell and published the value of the extraction equilibrium constant equal to $8 \times 10^{-10}$. Alguacil et al. [15, 28] also studied copper recovery from ammoniacal/ammonium sulphate medium by LIX54, but according to this group extraction equilibrium constant was $7 \times 10^{-7}$. In both papers copper extraction from the ammoniacal solution was described based on simple extraction of copper ions:

$$K_{ex, f} = \frac{[CuR_f][H^+]^2}{[Cu^{2+}][HR]^2} \quad (4.8)$$

Three orders of value difference in these two groups can be explained based on more accurate description, taking into account the fact that practically all copper in the ammoniacal solutions is in the form of copper-tetra ammonia complex:

$$K_{ex, f} = \frac{[CuR_f][H^+]^2}{[Cu(NH_3)_4^{2+}][HR]^2} \cdot \frac{[NH_3]^4}{K_d^2} = K_{ex, f} \cdot \frac{[NH_3]^4}{K_d^2} \quad (4.9)$$

Evidently, $K_{ex, f}$ is only an effective constant and its value should strongly depend on
ammonia content. Recently, Ismael et al. [39] reported that the extraction constant for copper extraction from Cu(NH$_3$)$_4^{2+}$ in ammoniacal media with LIX54 is $10^{2.89}$ M$^2$. The non-ideality of the aqueous phase was taken into consideration by applying the Pitzer model and the extended Debye-Huckel equation and the use of the thermodynamic equilibrium constant got in this paper allowed the satisfactory prediction of isotherms for copper extraction from ammoniacal media with LIX54. This more accurate value of extraction constant for Cu(NH$_3$)$_4^{2+}$/LIX54 system is used further in our work for simulation.

3. The complex LIX54-copper formed at the feed/membrane interface diffuses through the membrane:

$$J_2 = \frac{D_{CuR_{m,m}}}{\delta_m} ([CuR_2]_{fi} - [CuR_2]_{si})$$

(4.10)

where $D_{CuR_{m,m}}$ is the diffusion coefficient of copper-carrier complex in the membrane; subscript $m$ indicates species in the membrane phase; $\delta_m$ is the thickness of liquid membrane and subscript $si$ indicates species in the membrane near membrane/strip interface.

4. Copper ions are re-extracted at the interface membrane/acidic strip phase without ammonia:

$$CuR_2 + H_2SO_4 \Leftrightarrow CuSO_4 + 2HR$$

$$K_{ex.f} = \frac{[CuR_2]_{fi} \cdot [H^+]_{fi}^2}{[Cu^{2+}]_{si} \cdot [HR]_{si}^2} = K_{ex.f} \cdot K_s \cdot K_d^2$$

(4.11)
where $K_{ex,s}$ is the extraction equilibrium constant for copper ion in $\text{H}_2\text{SO}_4$/LIX54 system; subscript $s$ indicates species in the strip solution.

5. The carrier at the strip/membrane interface diffuses back to the membrane/feed interface:

$$J_3 = \frac{D_{HR,m}}{\delta_m} ([\text{HR}]_s - [\text{HR}]_f)$$

(4.12)

where $D_{HR,m}$ is the diffusion coefficient of carrier in the organic liquid membrane phase.

6. The stripped copper ions permeate through an aqueous stagnant layer and enter the volume of stripping phase. Diffusion coefficient of copper species in this case is the one for an aqueous complex:

$$J_4 = \frac{D_{Cu,a}}{\delta_a} ([\text{Cu}^{2+}]_s - [\text{Cu}^{2+}]_i)$$

(4.13)

Based on the steady state assumption we have:

$$J_1 = J_2 = \frac{J_3}{2} = J_4 = J$$

(4.14)

Also there is a mass balance in the liquid membrane phase between HR and CuR$_2$:

$$2[\text{CuR}_2]_f + [\text{HR}]_s = 2[\text{CuR}_2]_m + [\text{HR}]_s = [\text{HR}]_m^0$$

(4.15)

From Eq. 4.4, Eq. 4.5, Eq. 4.14 and Eq. 4.15, we can get:

$$[\text{CuR}_2]_f = ([\text{Cu}(\text{NH}_3)_4]^{2+})_f - \frac{J \cdot \delta_a}{D_{Cu,a}} \cdot K_{ex,f} \cdot K_a^2 \cdot [\text{HR}]_s^2 \cdot \frac{[\text{NH}_3]^4_4 \cdot [H^+]^2}{[\text{NH}_3]^4_4}$$

(4.16)
For the strip side we have slightly simpler expression:

$$[\text{CuR}_2]_{sl} = ([\text{Cu}^{2+}]_s + \frac{J \cdot \delta}{D_{\text{Cu},a}} \frac{K_{\text{ex,sl}}[\text{HR}]_{sl}^2}{[H^+]_{sl}^2})$$ (4.17)

Substituting Eq. 4.16 and Eq. 4.17 into Eq. 4.10, we finally have:

$$J = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]_f \cdot [\text{HR}]_{fi}^2 - K_f [\text{Cu}^{2+}]_i [\text{HR}]_{sl}^2}{\delta_a \frac{1}{D_{\text{CuR,sl}}} K_{\text{ex,sl}} \cdot K_f^2 + \delta_a \frac{[\text{HR}]_{fi}^2}{[\text{NH}_3]^4_f[H^+]^4_f} - K_f \frac{[\text{HR}]_{sl}^2}{[H^+]_{sl}^2}}$$ (4.18)

At equilibrium, when $[\text{HR}]_{fi} = [\text{HR}]_{sl}$ and $J = 0$, Eq 4.18 gives:

$$\frac{[\text{Cu}(\text{NH}_3)_4^{2+}]_f}{[\text{Cu}^{2+}]_i} = K_s \left(\frac{[H^+]_f}{[H^+]_i}\right)^2 \cdot [\text{NH}_3]^4_f = \frac{1}{EF}$$ (4.19)

where $EF$ indicates enrichment factor.

This important relationship can also be derived based on thermodynamic considerations. Total transport process for ammoniacal wastewater treatment can be described as a simple pseudo-chemical reaction:

$$[\text{Cu}(\text{NH}_3)_4^{2+}]_f + 2[H^+]_i \Leftrightarrow [\text{Cu}^{2+}]_i + 2[\text{NH}_3]_f + 2[H^+]_f$$

We can consider the next cycle:
Equilibrium between the second and the fourth states can be easily described based on chemical potentials:

\[
\begin{align*}
\mu^{0}_{Cu^{2+}} + RT \ln[Cu^{2+}]_{f} + \mu^{0}_{NH_3} + 4RT \ln[NH_3]_{f} + \mu^{0}_{H^+} + 2RT \ln[H^+]_{s} &= \mu^{0}_{Cu^{2+}} + RT \ln[Cu^{2+}]_{s} + \mu^{0}_{NH_3} + 4RT \ln[NH_3]_{f} + \mu^{0}_{H^+} + 2RT \ln[H^+]_{f} \\
\end{align*}
\]

(4.20)

It means that

\[
\left(\frac{[Cu^{2+}]_{f}}{[Cu^{2+}]_{s}}\right)^2 = \left(\frac{[H^+]_{f}}{[H^+]_{s}}\right)
\]

(4.21)

And finally for copper-ammonia complex we have the same equilibrium condition as shown in Eq. 4.19

Both kinetic and thermodynamic analyses give the same equation for equilibrium. It demonstrates that it is possible to transfer copper from ammoniacal solutions against of its concentration gradient and thus to have an active transport. The simplest way to accumulate copper in the strip solution is due to higher H\(^+\) concentration in the strip, but an increase of ammonia concentration in the feed makes this process less favorable.

As an example for \(~1\text{ M NH}_3\) and pH\(_f=10\) in the feed and pH\(_s= 0\) in the strip solutions enrichment factor EF can be higher than \(10^4\). Too high ammonia concentration in the
feed solution will decrease enrichment and hinder copper transfer from the feed to the strip side, which was confirmed in our separate experiments. Earlier Kyuchoukov et al. [31] have found that ammonia depresses the extraction of copper with LIX54 when a significant excess of ammonia is present in the aqueous solutions.

If the stripping pH is low enough, effective distribution coefficient of copper between the strip phase and membrane is much lower than that between the feed phase and the membrane [40]. In this case only one way transport from the feed solution through the membrane phase is important and Eq. 4.18 can be simplified to the Eq. 4.22:

\[
J_a = \frac{[Cu(NH_3)_2]_f}{\delta_a + \frac{1}{\delta_m} \left( \frac{[NH_3]^4_f [H^+]_f}{D_{Cu,a} K_{ext} D_{Cu,R,m} K_g^2 ([HR]_f^0)^2} \right)}
\]  

(4.22)

\[J_a\] is determined by total of two resistances, i.e. that of aqueous stagnant layer and membrane phase. The difference of \(J\) and \(J_a\) describes the role of the process reversibility.

Combination of Eq. 4.1, Eq. 4.10 and Eq. 4.15 gives:

\[\left[\frac{HR}{\beta}\right] = \left[\frac{HR}{\beta}\right]_m^0 (1 - \frac{J}{J_{max,m}})
\]  

(4.23)

and then:

\[
J_a = \frac{[Cu(NH_3)_2]_f}{\delta_a + \frac{1}{\delta_m} \left( \frac{[NH_3]^4_f [H^+]_f^2}{D_{Cu,a} D_{Cu,R,m} K_{ext} D_{Cu,R,m} K_g^2 ([HR]_m^0)^2 \left(1 - \frac{J_a}{J_{max,m}}\right)^2} \right)}
\]  

(4.24)

It is easy to show that if no ammonia is presented or pH of the solution is relatively low,
which corresponds to the transport of Cu$^{2+}$ ions from acidic phase, mono-directional copper flux is described by slightly simpler Eq. 4.25:

$$J_a = \frac{[Cu^{2+}]_f}{\delta_a + \frac{\delta_m}{D_{Cu,a}} \cdot \frac{[H^+]_f^2}{[H^+]_m^2 \cdot K_{ext} \cdot (\frac{J_a}{J_{max,m}})^2}}$$  \hspace{1cm} (4.25)

Similar equation can be easily derived based on expressions presented in [40]. According to Eq. 4.24, when the aqueous stagnant layer resistance is dominant and the membrane role can be neglected, copper flux $J_a$ is first order with respect to the feed concentration of copper- tetra ammonia complex, and is described by Eq. 4.2.

In slightly more general case when copper concentration in the feed solution is low and $J_a < J_{max,m}$ we have:

$$J_a = \frac{[Cu(NH_3)_4^{2+}]_f}{\delta_a + \frac{\delta_m}{D_{Cu,a}} \cdot \frac{[NH_3]^2 \cdot [H^+]_f^2}{K_{ext} \cdot K^+_d \cdot ([HR]_m^0)^2}}$$  \hspace{1cm} (4.26)

Here $k$ is the overall mass transfer coefficient, which depends on pH and ammonia content in the feed solution as well as the carrier concentration.

In the opposite situation when the feed copper concentration is high, the carrier is fully loaded with copper. In these conditions $[HR]_f / [HR]_m^0 \approx 0$ and $[CuR_2]_f \approx [HR]_m^0 / 2$. Using Eq. 4.4 and 4.5, after transformation of Eq. 4.24 we can show that the flux is now described by Eq. 4.1.
As it should be expected, the rate of copper transfer reaches maximum and is independent on the feed copper concentration.

Figure 4.2 shows that the experimental flux dependence on carrier concentration can be satisfactory simulated by this model based on the set of parameters given in Table 4.2. Nevertheless one can see that copper flux dependences on feed copper concentration (Figure 4.3) and on feed pH (Figure 4.4) can not be described by this model. Using the same values of parameters we have the first term in the denominator of Eq. 4.24 always much larger than the second term, which cannot explain the flux plateau at high copper concentrations. The “Small Carrousel” model also cannot predict the flux decrease in more acidic feed solutions (Figure 4.4). To do this we have to use more complex “Big Carrousel” model presented below.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{Cu,a}$</td>
<td>$6.5 \times 10^{-6}$ cm$^2$/s</td>
<td>[26]</td>
</tr>
<tr>
<td>$D_{HR,r}$</td>
<td>$5.35 \times 10^{-6}$ cm$^2$/s</td>
<td>[25]</td>
</tr>
<tr>
<td>$D_{CuR,r}$</td>
<td>$3.58 \times 10^{-6}$ cm$^2$/s</td>
<td>[25]</td>
</tr>
<tr>
<td>$D_{CuR,m}$</td>
<td>$8.9 \times 10^{-7}$ cm$^2$/s</td>
<td>This work</td>
</tr>
<tr>
<td>$K_{ext}$</td>
<td>$7 \times 10^{-9}$</td>
<td>[15, 28]</td>
</tr>
<tr>
<td>$K_{ext}$</td>
<td>$10^{-15}$ M$^{-2}$</td>
<td>[39]</td>
</tr>
<tr>
<td>$K_d$</td>
<td>$5.56 \times 10^{-10}$ M</td>
<td>[25]</td>
</tr>
<tr>
<td>$K_s$</td>
<td>$10^{12.46}$ M$^{-4}$</td>
<td>[38]</td>
</tr>
<tr>
<td>$\delta_m$</td>
<td>50 $\mu$m</td>
<td>Supplier</td>
</tr>
<tr>
<td>$\delta_n$</td>
<td>77 $\mu$m at 250 rpm</td>
<td>This work</td>
</tr>
<tr>
<td>$\delta_r$</td>
<td>$10^{-6}$-10^{-5}$ cm</td>
<td>This work</td>
</tr>
<tr>
<td>$\log m_{CuR}$</td>
<td>-0.46pH+7.95</td>
<td>[41]</td>
</tr>
<tr>
<td>$\log m_{HR}$</td>
<td>-0.27pH+6.06</td>
<td>[41]</td>
</tr>
</tbody>
</table>
4.4.2 Description of Transmembrane Cu Transport Based on Facilitated “Big Carrousel” Mechanism

If the carrier is not very hydrophobic, it can leave the interior of the membrane. This implies that both metal ions and chelating agents are in the same aqueous phase where chemical reactions take place and transport through the membrane proceeds by a mechanism, which may be called “Big Carrousel” (Figure 4.6) [18]. This type of the description is based on common ideas for the reactions of the substances in the same phase and does not need introduction of the effective parameters like interface rate constants for the processes between substances located in two different liquid phases. Very low concentrations of the carrier and corresponding complex with the metal ion in the aqueous phase mean high transport resistance of this elementary step, playing an important role in the actual mass transfer process.

![Figure 4.6: Schematic description of copper transport through SLM with “Big Carrousel” model shown for the feed solution](image)

According to usual macro-kinetics ideas the location of the chemical reaction should be
in the vicinity of membrane/water interface because of high distribution coefficients of organic species, their slow diffusion and fast reactions. The strip pH is low enough in membrane experiments and the effective distribution coefficient of copper between the membrane phase and the stripping phase is much lower than that between the feed phase and the membrane, thus, the concentration of the copper extracted complex in the membrane phase at the stripping side may be considered negligible compared to that at the feed side [40, 42]. To simplify the kinetic model, the description below is only for mono-directional transport from the feed solution through the membrane phase. We will also use classical two-film model [43], assuming that the reaction of LIX54 and copper-ammonia complex is instantaneous. It means when they meet each other in the area of contact stagnant/reaction layer, formation of the complex CuR$_2$ can be described by the equilibrium constant $K_F$:

$$K_F = \frac{[\text{NH}_3]^2 \cdot [\text{CuR}_2] \cdot [\text{NH}_4^+]^2}{[\text{Cu(NH}_3)_2^{3+}] \cdot [\text{HR}]^2} = \frac{[\text{NH}_4^+]^4 \cdot [\text{CuR}_2] \cdot [\text{H}^+]^2}{[\text{Cu(NH}_3)_2^{3+}] \cdot [\text{HR}]^2 \cdot K_d^2} \quad (4.27)$$

Based on Eq. 4.5 the relationship between $K_{ex,f}$ and $K_F$ can be described as:

$$K_{ex,f} = \frac{m_{\text{CuR}_2}}{m_{HR}^2} \cdot K_F \quad (4.28)$$

Where $m_{HR}$ and $m_{\text{CuR}_2}$ are effective distribution coefficients of the carrier and copper-carrier complex, respectively. It was demonstrated that both LIX54 and its copper complex are partially soluble in aqueous solutions [30, 41].

In diluted acidic copper solutions without ammonia
\[ K_f = \frac{[CuR_2][H^+]^2}{[Cu^{2+}][HR]^2} \]  
\[ \text{and } K_{ex,s} = \frac{m_{CuR_2}}{m_{HR}} K_f \]  

where \( K_f \) is the formation constant of the complex \( CuR_2 \) in LIX54/Cu\(^{2+}\) system in the area of contact stagnant/reaction layer.

The corresponding equations for flux are:

\[ J_1 = \frac{D_{Cu,R,a}}{\delta_a} ([Cu(NH_3)_2^{2+}]_a - [Cu(NH_3)_2^{2+}]_r) \]  
\[ J_2 = \frac{D_{HR,r}}{\delta_r} ([HR]_a - [HR]_r) = \frac{D_{HR,r}}{\delta_r} \left( \frac{[HR]}{m_{HR}} - [HR]_r \right) \]  
\[ J_3 = \frac{D_{CuR_2,r}}{\delta_r} ([CuR_2]_r - [CuR_2]_a) = \frac{D_{CuR_2,r}}{\delta_r} \left( [CuR_2]_r - \frac{[CuR_2]}{m_{CuR_2}} \right) \]  
\[ J_4 = \frac{D_{CuR_2,m}}{\delta_m} [CuR_2]_m \]  

where subscript \( r \) indicates species at the aqueous/reaction layer interface; \( \delta_r \) is the thickness of reaction layer.

At the steady state:

\[ J_1 = \frac{1}{2} J_2 = J_3 = J_4 = J \]  

Similar to the “Small Carrousel” kinetic model (Eq. 4.23 and Eq. 4.24), we can show that:

\[ [HR]_r = \frac{[HR]_m^{\delta_r}}{m_{HR}} \left[ 1 - \left( \frac{1}{J_{max,m}} + \frac{2\delta_r}{D_{HR,r}[HR]_m^{\delta_r}} \right) \cdot J \right] \]
Further, similar to the Eq. 4.25 for transport from acidic copper solution without ammonia, copper flux is:

\[
J = \frac{\delta_a}{D_{Cu,a}} + \left( \frac{\delta_r}{D_{Cu,b,r}} + \frac{\delta_m}{D_{Cu,b,m} \cdot m_{Cu,b}} \right) \cdot \frac{[Cu(NH_3)_2]^+}{[NH_3]^+ \cdot [H^+]^2} \cdot \frac{K_F \cdot K_\gamma \cdot \left( \frac{HR^\gamma}{m_{HR}} \right)^2 \left( 1 - \left( \frac{1}{J_{max,m}} + \frac{2 \delta_r \cdot m_{HR}}{HR^\gamma \cdot D_{HR,r}} \right) \cdot J \right)}{(4.37)}
\]

One can see that in the case of “Big Carrousel” model the denominator has two additional terms, related to the reaction layer thickness \( \delta_r \). At low copper concentrations, the second term in the denominator of Eq. 4.37 is much less than the first term and the calculated flux is first order with copper concentration. The two additional terms make the “Big Carrousel” model able to predict flux plateau at high copper concentrations (Figure 4.3).

In these conditions when \( J = J_{max,m} \), the existence of \( \delta_r \) makes the value of second term in the denominator comparable to first one, which results in flux saturation at high copper concentrations. In comparison, in the “Small Carrousel” model though it is possible to get simulated flux \( J_a \) very close to the experimental \( J_{max,m} \) at high copper concentrations, the second term of the denominator of Eq. 4.24 is still negligible compared to the first one, which leads to the proportionality of the flux to copper concentration.

In addition, Eq. 4.37 has three additional parameters in the denominator, \( \delta_r \), \( m_{HR} \) and
which make the model much more sensitive to pH changes in the feed (Figure 4.4) than it was in the case of “Small carousel”. It is well known that the distribution of species in aqueous and/or organic phases is varied with pH changes. According to Boyadzhiev and Alexandrorva [41], the correlation between feed aqueous pH and distribution coefficients is 

\[
\log m_{\text{CuR}_2} = -0.48\,pH + 7.94 \quad \text{and} \quad \log m_{\text{HR}} = -0.27\,pH + 6.06.
\]

Experimental value of the flux \(J_{\text{exp}}\) and published correlations for distribution coefficients of LIX54 and its complex with Cu as a function of pH were used as starting values in right hand side of Eq. 4.37 for simulation. Optimization of parameters \(\delta_r\) was conducted to fit the simulated flux to experimental one using Microsoft Excel built-in “solver” function. After optimization, the range of reaction layer thickness is between \(10^{-6}-10^{-5}\) cm at the experimental feed pHs from 4 to 9. Using these optimized values at different feed pHs in “Big Carrousel” model, we are able to give satisfactory quantitative description of pH dependence presented in Figure 4.4.

According to the developed model when the reaction is much faster compared to the diffusion, the resistance of the reaction layer could be negligible and the “Big Carrousel” model (Eq. 4.37) is reduced to the “Small Carrousel” (Eq. 4.24). In this case

\[
\frac{\delta_r^c}{D_{\text{CuR}_2,r}} \ll \frac{\delta_m}{D_{\text{CuR}_2,m} \cdot m_{\text{CuR}_2}} \quad (4.39)
\]

and

\[
\frac{2\delta_r^c \cdot m_{HR}}{[HR]^m \cdot D_{HR,r}} \ll \frac{1}{J_{\text{max,m}}} \quad (4.40)
\]

where \(\delta_r^c\) is the critical thickness of reaction layer.
Substituting kinetic parameters from Table 4.2 into expressions Eq. 4.39 and Eq. 4.40, we have for example that at pH around 7 and if also $\delta_r^c << 3.7$ nm the “Big Carrousel” can be reduced to the “Small Carrousel” model. In addition $\delta_r^c$ is inversely proportional to $m_{HR}$ and $m_{CuR}$, both of which increase at lower pH, resulting in even smaller $\delta_r^c$ value at more acidic feed solutions.

On the contrary, when the reaction layer thickness is much larger than the critical value, the chemical reaction developed in the chemical reaction layer cannot be neglected. Therefore, the “Big Carrousel” model in this case is superior to describe the actual mass transfer process. For example, as the result of parameters optimization to fit the experimental data, the calculated reaction layer thickness was much higher. It was practically constant and equal to $\sim 5 \times 10^{-6}$ cm at pH from 8.6 to 5 and only then it decreased to $1 \times 10^{-6}$ cm at pH 4. That is why only “Big Carrousel” model is able to describe the experimental decrease of the flux in the more acidic feed solutions.

Earlier it was demonstrated that the thickness of reaction layer for simple reversible ion exchange reactions should be determined by the square root of the ratio $D/(k_c+/k_c-)$, where subscripts $+$ and $-$ mean the forward and reversed reaction, respectively and $k$ is the rate constant [18, 44]. When concentration of $H^+$ is too small the thickness of reaction layer should be constant, and then it should start decreasing at lower pH, which agrees well with our simulation results.

The reaction layer plays an important role in the actual mass transfer process through
SLM, which was discussed in a recent review regarding interfacial aspects of metal extraction in liquid-liquid system [45]. In some cases to describe kinetics of metal extraction facilitated by ligands it is necessary to assume that the extraction is possible due to diffusion of the extractant into the aqueous phase where it reacts with metal ion and then the complex transfers back into the organic phase. Evidently this mechanism is similar to the statements of “Big Carrousel” model developed for the carrier in this paper.

4.5 Summary

Facilitated active copper transport through the flat supported liquid membrane from aqueous ammoniacal solution in exchange to two H\(^+\) ions has been investigated. Copper concentration in wastewater can be reduced by several orders of value. Due to the buffer effect of NH\(_3\)/NH\(_4^+\) in the copper containing ammoniacal wastewater, it is not necessary to adjust pH in it to keep large H\(^+\) gradient. Copper forms complexes with ammonia and if the ammonia concentration in the feed solution is too high, it hinders copper transfer from feed to strip side. Simple thermodynamic description of enrichment and role of ammonia is presented.

To describe kinetics of the process a new “Big Carrousel” model was developed and compared with usually assumed mechanism of facilitated transport, which does not consider the ability of the carrier to leave the membrane. Mathematical model simulation demonstrated that only “Big Carrousel” model, based on the ability of the carrier to leave the membrane and to react with copper ammonia complexes in aqueous solutions, gives
satisfactory quantitative description of all experimental results, including the flux plateau at high feed copper concentrations and the decrease of copper flux at lower pH of the feed solutions.
References


5. CHAPTER FIVE

TREATMENT OF SPENT AMMONIACAL ETCHING SOLUTION WITH HOLLOW FIBER SUPPORTED LIQUID MEMBRANES: FROM BENCH-SCALE TO THE PILOT-SCALE TESTS.

5.1 Introduction

Big volumes of spent copper-containing ammoniacal etching solutions are generated by PCB production industry annually. These spent etchants are usually stored in drums or tanks and are ultimately shipped to an off-site treatment plant for copper recovery before disposal. Although the spent etchant is treated by the waste haulers, this waste stream may still be an environmental hazard. Transportation of the spent etchant and its ultimate disposition may pose environmental risks and result in increased liability for PCBs manufacturers. Because of this, it is necessary to develop a low cost and efficient process for spent etchant treatment.

One of possible approaches to treat this waste is to use supported liquid membrane (SLM) system. A carrier molecule dissolved in organic solution is generally used as a liquid membrane phase for copper transfer. It has been found that LIX54, a commercial product from Cognis Corp., could be used as a carrier for selective removal of copper from alkaline solutions. LIX54 is a β-diketone extractant with an active ingredient 1-phenyl-1, 3-decanedione. In recent 10 years [1-7] it has been proved that LIX54 is an excellent extractant for copper recovery from ammoniacal solutions due to ease of stripping, low or
no ammonia loading capacity, high selectivity of Cu$^{2+}$ over Zn$^{2+}$ and Ni$^{2+}$, fast transfer kinetics, good stability, etc [8].

Removal of copper ions through liquid membranes is possible due to H$^+$ chemical potential difference in the feed and strip solutions. The common problem is that pH of the feed copper solution is initially much less acidic but it decreases with time due to electroneutral 2H$^+$/Cu$^{2+}$ exchange through the liquid membrane. Usually copper transfer process stops when the H$^+$ gradient between donor (feed) and acceptor (strip) phase decreases and is balanced by Cu$^{2+}$ concentration gradient. In contrast to this situation we have demonstrated that in copper-containing ammoniacal solutions during their treatment pH was almost constant due to the buffer effect of NH$_3$/NH$_4^+$. It is not necessary to adjust pH in the feed side to keep large H$^+$ gradient and the process can be conducted till very low copper concentrations in the feed waste water.

In Chapter Four and also in our published work [9] copper recovery from ammoniacal wastewater by SLM has been investigated and the dependences of Cu removal rate on the Cu concentration, pH of feeding solution and the carrier (LIX54) concentration in liquid membrane phase have been described using Flat Sheet Supported Liquid Membrane (FSSLM) system. In this chapter an effective hollow fiber supported liquid membrane (HFSLM) system developed from bench-scale to pilot-scale for copper recovery and spent etchant regeneration is described and optimal hydrodynamic and other operation conditions for spent ammoniacal etching solutions treatment are presented. In this case copper is present as Cu(NH$_3$)$_4^{2+}$ complex at concentration as high as 160 g Cu(II) per liter.
5.2 Experimental

5.2.1 Regents

LIX54 was kindly supplied by Cognis Corporation, USA. It was diluted in kerosene (Aldrich, USA) and used for preparation of liquid membrane phase. Copper sulfate pentahydrate (Nacalai Tesque, Japan), sulfuric and hydrochloric acids (Merck) were of reagent grade. All chemicals were used as received without any further purification. Two kinds of copper-containing ammoniacal solutions were kindly supplied by local PCB companies in Singapore. Their typical compositions are given in Table 3.1.

5.2.2 SLM Setups

5.2.2.1 Bench Scale HFSLM System

Detailed specification of the hollow fiber membrane module (Liqui-Cel® 2.5×8 Extra-Flow hollow fiber membrane contactor) is given in Table 3.2. The membrane module was operated in the cross flow mode. Fiber walls were impregnated with liquid membrane phase by pumping LIX54 33 v/v% in kerosene through the module in a recycling mode using a peristaltic pump (Cole-Parmer, US) for about one hour. The extra oil was washed out with water.

In the subsequent experiments, feed etchant solutions were pumped through the tube (lumen) side of hollow fiber membrane module and acidic stripping solutions were
pumped in the shell side. The hollow fiber with micropores impregnated by organic solutions (LIX54 in kerosene) acts as a barrier to forbid the direct contact of the feed etchant solutions and the stripping acid. Unless otherwise specified only one hollow fiber membrane module was used. In the case of spent etchant treatment with additional control of NH$_3$ content the second hollow fiber module was used for this purpose (Figure 5.1).

![Figure 5.1: Lab experimental setup for spent etchant treatment](the grey part is only for NH$_3$ control with another hollow fiber module)

### 5.2.2.2 Pilot Scale Setup

For a pilot test, a bigger membrane module, Liqui-Cel® 10×28 Extra-Flow hollow fiber membrane contactor with 130 m$^2$ effective surface area, was used (Figure 5.2). Table 5.1 lists its properties and the assembled pilot scale setup is schematically depicted in Figure 5.3.
Table 5.1: Properties of hollow fiber membrane module for pilot plant test

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water flow range</td>
<td>10 ~ 57 m³/hr</td>
</tr>
<tr>
<td>Housing characteristics</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>316 SS; FRP &amp; PVDF</td>
</tr>
<tr>
<td>Connections</td>
<td>Shellside: 3” class 150 raised</td>
</tr>
<tr>
<td></td>
<td>Lumenside: 1” class 150 raised</td>
</tr>
<tr>
<td>Priming volume</td>
<td>Shellside: 26.1 L; Lumenside: 10.6 L</td>
</tr>
<tr>
<td>Weight (liquid full in shell side)</td>
<td>316 SS: 137Kg; FRP &amp; PVDF: 57Kg</td>
</tr>
<tr>
<td>Seal material</td>
<td>EPDM</td>
</tr>
<tr>
<td>Cartridge characteristics</td>
<td></td>
</tr>
<tr>
<td>Membrane</td>
<td>Material: polypropylene; Porosity: ~ 40%</td>
</tr>
<tr>
<td></td>
<td>OD/ID: 300/220μm; Surface area: 130m²</td>
</tr>
<tr>
<td>Potting material</td>
<td>Epoxy</td>
</tr>
<tr>
<td>Shell side pressure drop</td>
<td>6.0 psi max. at water flow rate: 37m³/hr, 20°C</td>
</tr>
</tbody>
</table>

Figure 5.2: Schematic diagram of Liqui-Cel® 10×28 Extra-Flow hollow fiber membrane contactor [10]

Figure 5.3: Recycling operation mode used for spent ammoniacal etchant treatment in pilot tests
5.2.3 Analytical Methods

Samples of the bulk feed and strip solutions were collected at predetermined time intervals and concentrations of metal ions were measured using an inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Perkin Elmer, USA). In the case of once-through experiments the inlet and outlet concentrations of Cu(II) were measured before the mixing with the bulk feed volume. pH value of the solutions was measured with a Cyberscan 200 digit pH meter and combined pH glass electrode.

Total NH$_3$ in the feed was found by back titration using H$_2$SO$_4$ to convert all NH$_3$ into NH$_4^+$ in the solution before titration with NaOH. Chloride concentration was measured with Cl$^-$ ion-selective electrode (Metrohm, Singapore). The specific gravity was measured using a hydrometer. These parameters of the regenerated etchant were analyzed and compared with the production specification for the commercial replenisher Plus-Cu-Etch (Plaschem, Singapore).

The purity of CuSO$_4$·5H$_2$O crystals formed after the pilot tests was characterized using ICP-AES and concentration of various possible contaminants was compared with CuSO$_4$·5H$_2$O purchased from Nacalai Tesque, Japan. Wide-angle X-ray diffraction (XRD) measurements of these crystals were carried out on a Shimadzu XRD-6000 X-Ray Diffractometer at 40 kV and 30 mA and at a scan speed of two degrees per minute.
5.3 Modeling of Mass Transfer Process through Hollow Fiber Supported Liquid Membrane (HFSLM) System

In Chapter Four we have demonstrated that the concentration and recovery of copper from these complexes is possible through a flat sheet supported liquid membrane (FSSLM) system with LIX54 as the carrier. However, small surface area of this membrane system did not allow it for any practical applications. Now we are describing an effective hollow fiber supported liquid membrane (HFSLM) technology, a feasible way for copper removal from industrial ammoniacal wastewater. Because copper in ammoniacal solution is in the form of relatively stable complexes with ammonia, the reactions between this species and the carrier can be the rate limiting step, which makes it necessary to apply more advanced “Big carrousel” mechanism to describe the kinetic process. The cylindrical form of a membrane in our HFSLM system changes only the quantitative values of mass transfer but does not influence on the mechanism of facilitated transportation. However, the inherent hydrodynamic conditions developed in the HFSLM system make it a much more complex system. To our best knowledge, this is the first time that the “Big carrousel” mechanism is developed to describe the experiment results in the HFSLM systems.

In this chapter it will be further shown that Cu(II) transport through HFSLM can also be described based on the “Big Carrousel” mechanism where the following assumptions are made:
1. The diffusion of H\(^+\) ions is much faster compared to that of Cu(II) ions.

2. The chemical reactions (formation of copper-carrier complexes and their decomposition) take place in thin aqueous reaction zones, which are located in the aqueous unstirred diffusion film (Nernst layer) near the organic membrane phase (Ref. to Figure 5.4)

![Figure 5.4: Schematic description of copper transport through HFSLM](image)

The process therefore can be described as the following:

Step 1: Due to the driving force of the concentration gradient, the Cu(II) ions in the aqueous feed ammoniacal solution as the predominant form of \([\text{Cu(NH}_3\text{)}_4]^2+\) permeate
through a diffusion aqueous feed film formed along the hollow fiber wall:

$$J_1 = k_i([Cu(NH_3)_4]_{f}^{2+}) - [Cu(NH_3)_4]_{p}^{2+})$$

(5.1)

Where $k_i$ is the mass transfer coefficient in tube side of hollow fiber membrane contactor; subscripts $f$ and $fi$ indicate substances in the feed phase and interface between internal diffusion layer and reaction zone, respectively.

Step 2: On reaching the aqueous reaction zone $Cu(NH_3)_4^{2+}$ ions react homogeneously with the carrier dissolution from the membrane wall to form copper carrier complexes:

$$Cu(NH_3)_4^{2+} + 2HR \leftrightarrow \frac{k_i}{k_r} CuR_2 + 2NH_4^+ + 2NH_3$$

The process for simplicity is characterized by Eq. 5.2 (equilibrium state) or Eq. 5.3 (rate of copper-carrier complex formation):

$$K_{ex,f} = \frac{k_f}{k_r} = \frac{[CuR_2]_{fi}[NH_3]^2[2NH_4^+]^2}{[Cu(NH_3)_4]^{2+}_{fi}[HR]^2_{fi}}$$

(5.2)

$$R_2 = k_f([Cu(NH_3)_4]^{2+}_{fi}[HR]^2_{fi} - k_r[CuR_2]_{fi}[2NH_4^+]^2[NH_3]^2)$$

(5.3)

Where $k_f$ and $k_r$ represent forward and reverse reaction constants in copper extraction process, respectively; $K_{ex,f}$ is the extraction equilibrium constant in $Cu(NH_3)_4^{2+}$/LIX54 system.

The distribution of the copper-carrier complexes and the carrier between the organic membrane phase and internal reaction zone can be described by distribution coefficients $m_{CuR}$ and $m_{HR}$.
\begin{align*}
    m_{CuR_2} &= \frac{[CuR_2]_{fm}}{[CuR_2]_{fi}} \\
    m_{HR} &= \frac{[HR]_{fm}}{[HR]_{fi}}
\end{align*}

Here overbar means species in the organic phase, subscript fm indicates species at the internal reaction zone/membrane interface.

In Chapter Four, we found the feed pH stays almost constant due to the buffer effect of \(NH_3/NH_4^+\) during the treatment of copper-containing ammoniacal solutions. Therefore, we assumed the equilibrium distributions of free carrier and copper-carrier complex do not change.

Step 3: The complexes formed in the reaction zone and extracted into the membrane, permeate through the membrane toward the outer side of the hollow fibers:

\[ J_3 = k_m ([CuR_2]_{fm} - [CuR_2]_{sm}) \]  

(5.6)

Where \(k_m\) is the mass transfer coefficient in the membrane phase; subscripts \(fm\) and \(sm\) indicate species in the internal and external reaction zone/membrane interface, respectively.

Step 4: After transmembrane transport and back-extraction into the external reaction zone the copper ions are stripped off from the copper-carrier complexes by strong acid present in the shell side of hollow fiber membrane module:

\[ CuR_2 + 2H^+ \xrightleftharpoons[k_f/k_r]{k_f} Cu^{2+} + 2HR \]
Similar to the step 2, the process is characterized by Eq. 5.7 (equilibrium state) or Eq. 5.8 (dissociation rate of copper-carrier complex):

\[
K_{ex,s} = \frac{k'_f}{k'_r} = \frac{[CuR_2]^s[H^+]^2_s}{[Cu^{2+}]_s[HR]^2_s} \tag{5.7}
\]

\[
R_s = k'_f[CuR_2]^s[H^+]^2_s - k'_r[Cu^{2+}]_s[HR]^2_s \tag{5.8}
\]

Where \(k'_f\) and \(k'_r\) represent the forward and reverse reaction constants in stripping process, respectively; \(K_{ex,s}\) is the extraction equilibrium constant in LIX54/Cu\(^{2+}\) system; Subscripts \(s\) and \(si\) indicate substances in the stripping solution and in the boundary of external reaction zone in the diffusion layer.

Both NH\(_3\) concentration in the bulk feed and reaction zone and also H\(^+\) concentration in the bulk strip and reaction zone are assumed constant which is a good approximations if both NH\(_3\) concentration and buffer capacity are high enough.

Similar to Eq. 5.4 and Eq. 5.5, we can get:

\[
m_{CuR_2} = \frac{[CuR_2]^m}{[CuR_2]^i} \tag{5.9}
\]

\[
m_{HR} = \frac{[HR]^m}{[HR]^i} \tag{5.10}
\]

The excess amount of H\(^+\) ions present provides also a constant pH environment in the strip solution. Therefore, the equilibrium distributions of free carrier and copper-carrier complex in the strip side do not change with time.

In Chapter Four, we derived the relationship between \(K_{ex,f}\) and \(K_{ex,s}\):
\[ K_{ex,s} = K_{ex,f} \cdot K_s \cdot K_d^2 \]  

(5.11)

Where \( K_s \) is the stability constant of \( Cu(NH_3)_4^{2+} \); \( K_d \) is the dissociation constant of \( NH_4^+/NH_3 \) system.

Step 5: The stripped copper ions diffuse through the external aqueous film and enter the stripping solution.

\[ J_5 = k_s ([Cu^{2+}]_s - [Cu^{2+}]_f) \]  

(5.12)

Where \( k_s \) is the mass transfer coefficient in the shell side of hollow fiber membrane module;

At the steady state all elementary rates are equal:

\[ J_1 = R_2 = J_3 = R_4 = J_5 = J \]  

(5.13)

Based on Eq. 5.1 to Eq. 5.13, we can get:

\[ J = \frac{K_{ex,f} [Cu(NH_3)_4^{2+}]_f [HR]_{jm}}{[NH_4^+]_f [NH_3]_f^2} - \frac{K_{ex,s} [Cu^{2+}]_s [HR]_{jm}}{[H^+]_s^2} \]

\[ \frac{K_{ex,f} [HR]_{jm}^2}{k_s [NH_4^+]_f [NH_3]_f^2} + \frac{K_{ex,s} [HR]_{jm}^2}{k_s [H^+]_s^2} + \frac{m_{HR}^2}{k_{s,m} \cdot m_{Cu_{ex}}} + \frac{m_{HR}^2}{k_s [NH_4^+]_f [NH_3]_f^2} + \frac{m_{HR}^2}{k_s [H^+]_s^2} \]  

(5.14)

Eq. 5.14 demonstrates that copper transfer from ammoniacal solution through hollow fiber supported liquid membrane is determined by total of four resistances, those in the tube side, shell side, membrane phase and chemical reactions. This last factor usually was neglected when dealing with transmembrane facilitated transport of metals. In the case of copper transport from ammoniacal solutions it becomes important and can not be
neglected. This is because the copper-ammonia complexes are very stable and their reaction with the carrier cannot be considered as an instantaneous step in comparison to the elementary transport processes.

As demonstrated in Chapter Four, when the reaction layer is thin and the distribution coefficients for the carrier \( (m_{HR}) \) and copper-carrier complex \( (m_{CuR_2}) \) are big, the amount of the carrier \( ([HR]_i) \) and copper-carrier complex \( ([CuR_2]_i) \) in the reaction layers can be neglected. In this case, total of free carrier and copper-carrier complex concentrations at each side of the membrane is equal to initially total concentration of the carrier in the membrane, which is constant everywhere in the membrane and is not dependent on the coordinate.

\[
[HR]_{jm} + 2[CuR_2]_{jm} = [HR]_{sm} + 2[CuR_2]_{sm} = [HR]_0 \tag{5.15}
\]

In the other hand, the fast strip kinetics of LIX54 as the excellent extractant in ammoniacal copper solution treatment ensures the complete and instantaneous dissociation of copper-carrier complexes at the interface between membrane and the external reaction layer, that is, \( [CuR_2]_{jm} = 0 \). In addition, the relative dilute feed ammoniacal wastewater (with Cu(II) concentration around 5.6 mM) in comparison to the carrier concentration (For readers’ information, 33 v/v% LIX54 in kerosene corresponds to the mole concentration of 0.55 M) makes copper-carrier complex concentration at the internal reaction zone/membrane interface can be negligible. In this case, Eq. 5.14 can be simplified as:
When the whole transport process through HFSLM reaches equilibrium, that is, \( J = 0 \), we can get:

\[
J = \frac{K_{ex,f}[Cu(NH_3)_4]^{2+}}{[NH_4]^+}[NH_4]_i^2[H^+]_i^2 - \frac{K_{ex,d}[Cu^{2+}]}{[H^+]_i^2} + \frac{K_{ex,f}}{k_f[NH_4]^+\cdot[NH_3]_i^2[H^+]_i^2} + m_{ia}^R + \left( \frac{m_{ia}^R}{k_r[NH_4]^+\cdot[NH_3]_i^2[H^+]_i^2} \right) \]

(5.16)

We have derived the same equation for equilibrium with a flat sheet supported liquid membrane system in Chapter Four. This demonstrates that it is possible to transfer copper from ammoniacal solutions against of its concentration and thus to have an active transport. In addition, the competition between ammonia and carrier for copper will decrease enrichment and hinder copper transfer from the feed to the strip side. However, in most previous paper it was assumed that simple copper ion (Cu\(^{2+}\)) alone is transported through the membrane in exchange to two H\(^+\) ions and the role of ammonia was not considered.

In a more specific condition when feed copper concentration is low and the stripping pH is low enough, effective distribution coefficient of copper between the stripping phase and membrane is much lower than that between the feed phase and the membrane [11]. In this case only transport from the feeding solution through the membrane phase is important. The reactions in the external reaction zone and the diffusion to the bulk of the stripping solution are not rate limiting step. Copper flux is described by slightly simpler Eq. 5.18. Similar equation can be derived also based on the analysis presented in [12, 13].

\[
\frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}]}_f = \frac{K_{ex,d}[NH_4]^+\cdot[NH_3]_f^2[H^+]_f^2}{[H^+]_i^2} = \frac{[H^+]_f^2}{[H^+]_i^2} \cdot K_f \cdot [NH_3]_f^4
\]

(5.17)
\[ J = \frac{[Cu(NH_3)_4]^{2+}}{1 + \frac{m_{HR}^2}{k_i} \cdot \left[ H^+ \right] f \cdot [NH_3]_f \cdot \frac{1}{K_{ex,f}} \cdot \frac{1}{K_{r}^2} \cdot \frac{1}{[HR]_0} + \frac{m_{HR}^2}{k_i} \cdot \frac{1}{[HR]_0} \cdot \frac{1}{k_r} \cdot \frac{1}{[HR]_0} } \]  

(5.18)

5.4 Results and Discussion

5.4.1 The Effect of Stripping Acid Solution on Copper Removal

LIX54 is a weak $\beta$-diketone extractant and the active ingredient of LIX54 is 1-phenyl-1, 3-decanedione. $pK_a$ for the acid-base equilibrium of LIX54 is 9.73 [2] and acidic stripping is easy with this chelating extractant. Kinetics of Cu transfer from spent etchant for two different volumes of 1M H$_2$SO$_4$ used as striping solution is shown in the Figure 5.5.

![Figure 5.5: Effect of volume of the stripping solution on copper removal rate from the bench-scale experiments.](image)

Feed: 600 ml spent etchant; Flow rate 70 ml/min both in tube and shell side
Exp. I: Strip: 0.6L 2M 2M H$_2$SO$_4$; Exp. II: Strip: 3L 2M H$_2$SO$_4$
Though initial rate of Cu transfer was practically the same, when 3L 1M H₂SO₄ was used as stripping solution, after half an hour it resulted in a faster copper removal than 0.6L 1M H₂SO₄. When smaller volume of stripping acid solution with the same molarity was used to treat spent etchant solutions, due to exchange Cu²⁺-2H⁺ an acid concentration in the strip decreased with the time faster than in the case of larger strip volume. Simultaneously, increase of copper concentration in the stripping solution was higher than that for the larger strip volume. Both these factors shift the copper extraction reaction backward and make the whole transmembrane transport process slower.

Figure 5.5 shows that with time copper concentration in the feed could be lower than that in the strip, which evidently demonstrates the possibility of the carrier-facilitated active transport [9]. Usually decrease of Cu mass in the feed side in the time interval $dt$ is slightly larger than corresponding increase in the strip side. This can be understood based on the fact that most of Cu is transferred from feed to strip phases but some still stays in the complex with carrier in the membrane phase.

The initial copper flux can be calculated based on the linear part of copper concentration changes over time in the initial stage in feed or strip solution:

$$J = \frac{dC}{dt} \frac{V}{S_m}$$

(5.19)

where $dC$ is the change in concentration in the feed or strip over time interval $dt$, $V$ is the feed or strip solution volume and $S_m$ is the effective membrane surface area.
Figure 5.6 shows that an increase of an acid concentration in the stripping phase facilitates initial copper transfer flux. However, an increase from 2M to 3M results only in 20% increase of the flux and higher SO$_4^{2-}$ reduces the level of copper concentration in the saturated stripping solution. If the experiment was long enough it was possible to reach saturation of the strip solution where blue crystals of copper sulfate were formed. Trying to avoid this effect at least in the first part of kinetic experiment usually 2M H$_2$SO$_4$ was used as the stripping phase.

![Plot showing effect of H$_2$SO$_4$ molarity on initial copper transfer flux from bench-scale experiments.](image)

Feed: 1L spent ammoniacal etchant; Strip: 3L different concentrations of H$_2$SO$_4$
Flow rate: 70 ml/min in both tube and shell side

5.4.2 The Effect of Hydrodynamic Flow Rates on Copper Removal

It is very important to find the optimal hydrodynamic conditions in HFSLM system for better copper recovery and further scaling-up of the process. In Chapter Four and also in our published work [9], we found that Cu(II) transmembrane flux is constant at high Cu(II) concentration and is 1st order with Cu(II) concentration at low concentrations. In this Chapter, optimal hydrodynamic conditions for these two stages were therefore investigated respectively.
At high Cu(II) concentration, the carrier is fully saturated and the copper transmembrane flux is zero order with respect to copper. In these experiments volumetric flow rate of one stream was varied while the other was kept fixed at 70 ml/min and the initial flux was calculated based on the increase of copper concentration in the strip solution. The lineal velocity in the tube (\(v_t\)) and the average superficial velocity in the shell side (\(v_s\)) of the membrane module [14] can be described as:

\[
v_t = \frac{Q_t}{N \pi r_i^2} \tag{5.20}
\]

\[
v_s = \frac{2Q_s}{\pi L} \frac{\ln(d_a/d_i)}{d_a - d_i} \tag{5.21}
\]

Where \(Q\) is the volumetric flow rate in the tube or shell side.

Volumetric flow rates of 50, 70, 150, 200 ml/min correspond with a linear velocity of 0.18, 0.25, 0.54 and 0.75 cm/s, respectively through the fibers in the tube side of membrane module and correspond with a superficial velocity of 0.62, 0.87, 1.87 and 2.49 cm/min, respectively across the fibers in the shell side of membrane module.
Figure 5.7 demonstrates that an optimal flow rate exists both for the feed and strip streams and its value in both cases is around 70 ml/min. This value was used for subsequent experiments. Volumetric flow rates lower than 50 ml/min were not used because of too low etchant volume purified in the unit of time. On the opposite side with the flow rates higher than 200 ml/min the supported liquid membrane could be unstable. When the solutions in the tube and shell sides were swapped, the results were practically the same, probably because the rate determining step is not the transport in both aqueous solutions but in the liquid membrane phase.

When ammoniacal wastewater (Cu(II)=5.6 mM, Ref. to Table 5.1) was used to investigate the hydrodynamic conditions for low copper solution treatment. The feed ammoniacal wastewater was pumped through the tube side of membrane module at different volumetric flow rates, while 2M H₂SO₄ was recirculated in the shell side at
same flow rate 70 ml/min. Before the experiment was conducted at a different feed flow rate, the lumen and shell side of the hollow fiber membrane contactor were thoroughly cleaned with de-ionized water and any remaining solutions in the membrane contactor were pumped out. The experiments were conducted thrice for each feed flow rate. It was found that the measured outlet metal concentrations’ deviations were all less than 1%. It could be found that even at the highest volumetric flow rate of 300 cm³/min, the Reynolds number is still very low (~3), which means that the flow through the tube side of the hollow fibers stays laminar.

In the once-through operation mode and with carrier concentration much less than saturation level, the overall mass transfer coefficient \( K \) can be defined considering an overall mass balance around the membrane module:

\[
Q_f dC(x) = KC(x)dS_m
\]  

where \( C(x) \) is the axial distribution of copper concentration.

In this case, the experimental overall mass transfer coefficients can be described as:

\[
K = \frac{Q}{S_m} \ln \left( \frac{C_{in}}{C_{out}} \right)
\]  

Where \( C_{in} \) and \( C_{out} \) are Cu concentrations at the inlet and outlet of the hollow fiber tube, respectively.

Assuming steady state is reached for mass transfer through the HFSLM, We can describe
the Cu(II) flux from feed to strip per unit fiber length in terms of individual mass transfer coefficients [15] by:

\[ k_t \pi r_i ([Cu(NH_3)_4]^{2+}_f - [Cu(NH_3)_4]^{2+}_fi) = k_m \pi r_i \ln \frac{r_o}{r_i} ([CuR_2]_{fm} - [CuR_2]_{sm}) \]

\[ = k_s \pi r_o ([Cu^{2+}]_{si} - [Cu^{2+}]_s) = K'_r \pi r_i ([Cu(NH_3)_4]^{2+}_f - [Cu^{2+}]_s) \]  

(5.24)

Where \( k_t, k_m, k_s, K' \) are the mass transfer coefficients in the tube side, in the organic membrane phase, in the shell side and theoretical overall mass transfer coefficient, respectively. Subscripts \( f, fi, s \) and \( si \) indicates species at bulky feed, feed/membrane interface, bulky strip and strip/membrane interfaces, respectively. The copper species in both aqueous/membrane interfaces and in the membrane phase can be correlated by a solute distribution coefficient \( m \) which are assumed to be the same in feed/membrane and membrane/strip interfaces for simplicity. The value of \( m \) was experimentally determined as 143.1:

\[ m = \frac{C_{fi}}{C_{fi}} = \frac{C_{si}}{C_{si}} \]  

(5.25)

Therefore mass transfer in a hollow fiber membrane module can be described using a conventional resistance-in-series model:

\[ \frac{1}{K} = \frac{1}{k_t} + \frac{1}{k_m \cdot m \cdot \ln \frac{r_o}{r_i}} + \frac{r_i}{m \cdot k_s \cdot r_o} \]  

(5.26)

Where \( r_i \) and \( r_o \) is the fiber inner and outer radius, respectively.

Generally for laminar flow in the tube side of membrane module, the tube side mass transfer coefficient can be estimated based on the Sherwood-Graetz correlation [12, 16-
Here $Sh$ and $Gz$ are Sherwood and Graetz numbers, respectively; $D_{Cu,a}$ is the diffusion coefficient of $\text{Cu(NH}_3)_4^{2+}$ in aqueous solution. Its value is $6.5 \times 10^{-6}$ cm$^2$/s [9]. The empirical coefficients $m$ and $n$ are usually determined from experimental results. The coefficient $m$ is a function of the packing density, $n$ is an indicator of the hydrodynamic conditions related to the mass transfer regime together with development of concentration profiles down the module [21]. Theoretically, for a diffusion process with fast chemical reaction $m=1.62$, $n=0.33$ according to Leveque approximation [21]. It could be found that even at the highest volumetric flow rate of 390 cm$^3$/min used in our experiments, the Reynolds number in the tube side of the hollow fibers is still very low, which means that the flow stays laminar. The values of $k_t$ at different feed flow rates based on the above empirical correlations are tabulated in Table 5.2.

Mass transfer coefficient in the shell side of hollow fiber module is described by various empirical correlations [17, 18, 20, 22-24]. However, the results are not very accurate probably due to the influence of module wall, the irregularity of fiber spacing, the deformation and movement of fibers during process, poly-dispersity of fiber diameters, the inlet and outlet effects, possible channeling between fibers. In the Liqui-Cel® Extra-Flow Membrane contactor, the hollow fiber fabrics were wrapped around a center tube in
the membrane module. The central baffle plate was created in the middle of module to provide the maximum mass transfer efficiency. The sulfuric acid was pumped into the distribution tube from the shell side port and then forced radially over the fibers on each side of the central baffle plate and finally exited through the collection tube to the second shell side port (Ref. to Figure 5.8). Schoner et al. [14] developed a modified approach to describe the shell side mass transfer correlations in cross-flow module:

\[
\text{Re} = \frac{Q \rho (d_x + d_i) \ln(d_x / d_i)}{\pi \eta L N r_o} \quad (5.30)
\]

\[
Sh = 1.76 \text{Re}^{0.82} \text{Sc}^{0.33} \quad (5.32)
\]

\[
Sh = \frac{k_o (d_x^2 - d_i^2 - 4N r_o^2)}{2D_{Cu,a} N r_o} \quad (5.33)
\]

where \( Sc \) is Schmidt number; \( \eta \) and \( \rho \) is the dynamic viscosity and density of aqueous solution in the shell side, respectively. Based on the above correlations the shell side mass transfer coefficient at 70 ml/min is \( 6.57 \times 10^{-4} \) cm/s and evidently this step is not the rate limiting step in the whole Cu removal process.
The diffusion of copper-carrier complexes species through the membrane support can be approximated by diffusion through a cylindrical wall. The individual mass transfer coefficient in the membrane phase \( k_m \) can be expressed as [12]:

\[
k_m = \frac{\varepsilon \cdot D_{\text{CuR},m}}{\tau \cdot r_i \cdot \ln \left( \frac{r_o}{r_i} \right)}
\]

(5.34)

where \( D_{\text{CuR},m} \) is the diffusivity of the Cu(II)/LIX54 complex in membrane phase with the value of \( 8.9 \times 10^{-7} \) cm\(^2\)/s [9]. The calculated \( k_m \) is \( 5.32 \times 10^{-5} \) cm/s, which is much less than the mass transfer coefficients in tube and shell side. Probably it is a rate limiting step (Ref. to Table 5.2).

Table 5.2 shows that the theoretical \( K' \) values are well above those experimental overall mass transfer coefficients \( K \). In Chapter Four, we developed a “Big Carrousel” model to describe ammoniacal copper transfer through SLM where diffusion of copper complex with ammonia in aqueous stagnant layer and reactions of the carrier and copper in aqueous reaction layer have been taken into account. The reaction layer plays an important role in the actual mass transfer process, especially when feed copper concentration is low. Therefore we can conclude that the difference between experimental and predicted mass transfer coefficients is due to the contribution of chemical reaction kinetics to the overall resistance to mass transfer. In this case the overall mass transfer coefficient can be described as

\[
\frac{1}{K} = \frac{1}{k_t} + \frac{1}{mk_m \ln \frac{r_o}{r_i}} + \frac{r_i}{r_o k_s} + \frac{1}{k_R} + \frac{1}{R_t} + \frac{1}{R_m} + \frac{1}{R_s} + \frac{1}{R_r}
\]

(5.35)
Where $k_R$ is the mass transfer coefficient due to chemical reaction happened in aqueous reaction layer. $R_b$, $R_s$, $R_m$ and $R_r$ represent the mass transfer resistances due to diffusion inside the fiber, in the shell, across the membrane and the chemical reaction kinetics, respectively.

The relative contribution of each resistance can be estimated by the fractional resistance ($\Delta_i$) with respect to the total resistance as shown in Table 5.2. The results show that with relative dilute copper concentration in the feed, the resistance due to chemical reaction is significant and cannot be neglected and this is in line with our developed “Big Carrousel” model. The significant contribution of reaction kinetics to mass transfer in hollow fibers for metal extraction has also been discussed by other groups. Lin and Juang [25] reported that Cu$^{2+}$ extraction with LIX64N was governed by combined aqueous diffusion and chemical reaction resistance. Kumar et al. [26] studied gold extraction from cyanide with LIX79 using hollow fiber modules and concluded that resistance due to chemical reaction was important under all conditions studied.
Table 5.2: The influence of tube flow rate on the overall mass transfer coefficient and relative resistance to Cu(II) mass transfer
(Strip at 70 ml/min)

<table>
<thead>
<tr>
<th>Flow rate/ml/min</th>
<th>Experimental</th>
<th>Tube side</th>
<th>Shell side</th>
<th>Membrane</th>
<th>Theoretical</th>
<th>Chemical reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K$, cm/s</td>
<td>$k_t$, cm/s</td>
<td>$\Delta_t$, %</td>
<td>$k_s$, cm/s</td>
<td>$\Delta_s$, %</td>
<td>$k_m$, cm/s</td>
</tr>
<tr>
<td>70</td>
<td>1.93×10^{-4}</td>
<td>4.70×10^{-4}</td>
<td>41.09</td>
<td>6.57×10^{-4}</td>
<td>0.16</td>
<td>5.32×10^{-3}</td>
</tr>
<tr>
<td>140</td>
<td>1.99×10^{-4}</td>
<td>5.91×10^{-4}</td>
<td>33.64</td>
<td>6.57×10^{-4}</td>
<td>0.17</td>
<td>5.32×10^{-3}</td>
</tr>
<tr>
<td>210</td>
<td>1.65×10^{-4}</td>
<td>6.75×10^{-4}</td>
<td>24.37</td>
<td>6.57×10^{-4}</td>
<td>0.14</td>
<td>5.32×10^{-3}</td>
</tr>
<tr>
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<td>1.84×10^{-4}</td>
<td>7.68×10^{-4}</td>
<td>23.98</td>
<td>6.57×10^{-4}</td>
<td>0.16</td>
<td>5.32×10^{-3}</td>
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<tr>
<td>390</td>
<td>1.92×10^{-4}</td>
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<td>23.23</td>
<td>6.57×10^{-4}</td>
<td>0.16</td>
<td>5.32×10^{-3}</td>
</tr>
</tbody>
</table>
5.4.3 The Selective Separation of Copper in the Presence of Other Cations in the Ammoniacal Wastewater.

Copper/ion selectivity of the process was determined in the experiment where ammoniacal wastewater (Table 3.1) was pumped through the tube side of the bench scale hollow fiber membrane module “once-through” and 2M stripping H₂SO₄ was recycled through shell side at 70 ml/min. The inlet and outlet concentrations of cations were measured by ICP-AES and the experimental overall mass transfer coefficients for different metals were calculated based on Eq. 5.23 and the selectivity (S) was defined as the experimental overall mass transfer coefficient of copper over that of other metal species in these conditions.

Table 5.3: Separation of Cu(II) over other metals in ammoniacal wastewater treatment

<table>
<thead>
<tr>
<th>Flow rate, ml/min</th>
<th>S&lt;sub&gt;Cu/Zn&lt;/sub&gt;</th>
<th>S&lt;sub&gt;Cu/Ni&lt;/sub&gt;</th>
<th>S&lt;sub&gt;Cu/Cd&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>17</td>
<td>3.8</td>
<td>103</td>
</tr>
<tr>
<td>140</td>
<td>21</td>
<td>1.7</td>
<td>35</td>
</tr>
<tr>
<td>210</td>
<td>11</td>
<td>0.7</td>
<td>12</td>
</tr>
<tr>
<td>310</td>
<td>13</td>
<td>0.5</td>
<td>7.2</td>
</tr>
<tr>
<td>390</td>
<td>11</td>
<td>0.4</td>
<td>5.5</td>
</tr>
</tbody>
</table>

The experiment results show high separation factors of copper over zinc and cadmium. Selectivity for copper over nickel is not very high which indicates LIX54 can extract both metal ions well in ammoniacal solution [8, 27]. High separation factors for copper over other metals guarantees the high purity of copper sulphate recovered in the strip solution.
5.4.4 The Effect of Feed Ammonia and A Comparison of Different Methods To Control Ammonia Level in the Feed Solution

From Chapter Four together with the mass transfer model derived for HFSLM system in this chapter, we got the same equilibrium condition (Eq. 5.17) for ammoniacal copper transport through SLM both from kinetic and thermodynamic analyses. This condition demonstrates that it is possible to transfer copper from ammoniacal solutions against copper concentration gradient and thus to have an active transport. The simplest way to accumulate copper in the strip solution is due to higher H\(^+\) concentration gradient of strip acid over feed ammoniacal solution. But an increase of ammonia concentration in the feed makes this process less favorable. Increase of ammonia in the feed solution could lead to the formation of higher order copper-ammonia complexes and thus depress the extraction of copper. In the beginning of the process, at high copper concentration the carrier is fully loaded with copper and the hindrance effect of ammonia on copper removal should not be significant. Later, at low copper concentrations when a significant excess of ammonia is present in the etchant the ammonia effect can become stronger [6]. It can change both the rates and final equilibrium state.

Below we show that excessive NH\(_3\) accumulation in the feed hinders the forward copper extraction and reduces the copper transfer flux. The experiment results prove the competition of NH\(_3\) with extractant over copper. Several methods were investigated to reduce free ammonia concentration in the feed etchant solution. One way to reduce ammonia concentration was to add HCl into the feed. Either concentrated HCl (37%) or 5M HCl solution was used for this purpose. The addition
was carried out step by step within the whole experiment in order to keep pH of feed solution around 8. When concentrated HCl was used, needle shape crystals of NH₄Cl were found in the feed solution. To avoid this, in further experiments 5M HCl was used to control ammonia level in the feed. Figure 5.8 shows that HCl addition at initial stage with high copper concentration has no significant effect. However, at low copper concentrations faster removal rate could be obtained by this method. However, HCl addition would decrease NH₃ content in the feed solution due to its conversion to NH₄Cl, thus decreasing the efficiency of the etchant after its regeneration. NH₃ should be added to reuse the regenerated etchant in PCB production again.

Recently, it was reported that membrane modules can be used to remove 95% of ammonia with concentration of 1100 mg/L [28]. This information ignited the idea to use hollow fiber membrane method to sweep NH₃ out from etchant treatment process. The swept NH₃ can be adsorbed by conventional methods and the absorbed NH₃ then can be re-used to top up ammonia level in the treated etchant. Therefore, additional hollow fiber membrane module was used in our experiments to sweep free ammonia dissolved in spent ammoniacal etchant solution which was recirculated in the shell side in this process. Ammonia can diffuse through the gas-filled membrane pores, while aqueous solution cannot penetrate through the pores due to the hydrophobicity of the polypropylene membrane and higher pressure applied in the tube side of hollow fiber membrane module (grey part of the experimental setup on Figure 5.1).
Figure 5.9: Comparison of the methods to control ammonia in spent ammoniacal etchant treatment from the bench-scale experiments
Feed: 1L spent ammoniacal etchant solution; Strip: 4L 2M H₂SO₄

Figure 5.9 demonstrates clearly that there is no significant difference in copper removal rate in first 10 hours when feed copper concentration is high. Later, when copper concentration in the feed is low, controlling of NH₃ level in feed etchant solution greatly facilitates copper removal (insert in Figure 5.9). Initial copper flux $J$ obtained from the linear part of concentration dependence versus time and also apparent copper mass transfer coefficient $K_a$ for low Cu concentration stage are listed in Table 5.4. The apparent mass transfer coefficient was calculated based on Eq. 5.23 where $C_{in}$ and $C_{out}$ were replaced by copper concentration at time $t$ and $t+\Delta t$ in the feed etchant solution at low copper concentration stage.

Table 5.4: Initial copper flux and apparent mass transfer coefficient for three different spent etchant treatment processes

<table>
<thead>
<tr>
<th></th>
<th>HCl addition</th>
<th>Hollow fiber membrane</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J,(mol/cm^2s)$</td>
<td>5.19×10⁻⁹</td>
<td>5.07×10⁻⁹</td>
<td>4.98×10⁻⁹</td>
</tr>
<tr>
<td>$K_a,(cm/s)$</td>
<td>1.27×10⁻⁵</td>
<td>1.45×10⁻⁵</td>
<td>7.23×10⁻⁶</td>
</tr>
</tbody>
</table>

It was found the experiment data of feed solutions can be well described by shift order reaction [29]:

170
\[ -r = - \frac{dC}{dt} = \frac{k_1C}{1 + k_2C} \]  

(5.36)

From this rate equation we can see that at high \( C \) (or \( k_2C \gg 1 \)), the reaction is of zero order with rate constant \( k_1/k_2 \); at low \( C \) (or \( k_2C \ll 1 \)), the reaction is of first order with rate constant \( k_1 \). This was also observed in copper transfer through flat sheet supported liquid membrane system [9]. After integration it gives:

\[
\frac{\ln(C_0 / C)}{C_0 - C} = -k_2 + \frac{k_1t}{C_0 - C} \]  

(5.37)

Both Table 5.4 and Table 5.5 show that the initial fluxes are almost the same in each experiment when copper concentration in feed solution is high, while control of NH\textsubscript{3} level in feed etchant solution in low concentration stage facilitates copper removal. Removal of excess ammonia at the later stages of the process really helps further copper removal and can be characterized by the higher apparent mass transfer coefficients \( K_a \) and first order rate constants \( k_j \).

![Figure 5.10: Kinetic analysis of Cu transport based on Figure 5.9.](image)
Table 5.5: Rate constants of different spent etchant treatment processes

<table>
<thead>
<tr>
<th></th>
<th>HCl addition</th>
<th>Hollow fiber membrane</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$ (s$^{-1}$)</td>
<td>$1.07 \times 10^{-4}$</td>
<td>$9.73 \times 10^{-5}$</td>
<td>$7.21 \times 10^{-5}$</td>
</tr>
<tr>
<td>$k_2$ (M$^{-1}$)</td>
<td>1.08</td>
<td>1.03</td>
<td>0.73</td>
</tr>
<tr>
<td>$k_1/k_2$ (M/s)</td>
<td>$9.91 \times 10^{-5}$</td>
<td>$9.45 \times 10^{-5}$</td>
<td>$9.87 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Role of ammonia probably is not only reduced to complex formation with copper in the feed and also to the shift of extraction equilibrium. It is also necessary to investigate if ammonia can penetrate through the membrane into the acidic media. Simultaneously with Cu/2H$^+$ exchange and ammonia transport there is also a chance that H$^+$ can go directly through the membrane due to high pH difference. It was found that LIX54 did not extract ammonia in appreciable quantities in the absence of copper in aqueous solution, while copper loading led to an increase in ammonia content in the organic phase. The quantities of ammonia carry-over from feed to strip solutions could be significant over long periods and is deleterious to the subsequent performance of electrowinning or crystallization steps. To characterize relative role of these three processes we have measured the concentrations of H$^+$ in the stripping sulfuric acid and also ammonia and alkalinites of feed etchant solution at the beginning and end of each treatment process and compared them with the amount of copper transferred through the membrane.

For example in the control experiment (refer to Table 5.6), when amount of copper in the feed phase is decreased by 2.54 moles in whole treatment process, content of ammonia measured in the feed is decreased by 8.62 moles. Only part of it (5.08 moles) can be explained by its conversion into NH$_4^+$. Total consumption of H$^+$ was also much higher (6.83 moles) than theoretical consumption (5.08 moles). The difference of 1.75 moles is probably due to direct ammonia diffusion through the organic membrane phase and neutralization of the acid in stripping side. The rest of ammonia decrease
(1.79 moles) could be due to simple loss to an air.

<table>
<thead>
<tr>
<th>Feed side</th>
<th>control mole %</th>
<th>HCl addition mole %</th>
<th>Air stripping mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Total Cu(II) removal</td>
<td>2.54 2.49</td>
<td>2.43</td>
<td></td>
</tr>
<tr>
<td>B. Total NH₃ loss</td>
<td>8.62 100</td>
<td>9.14 100.0</td>
<td>9.25 100</td>
</tr>
<tr>
<td>C. Conversion to NH₄⁺</td>
<td>5.08 58.93</td>
<td>4.98 54.49</td>
<td>4.86 52.54</td>
</tr>
<tr>
<td>D. Moved to stripping (=J)</td>
<td>1.75 20.30</td>
<td>0.19 2.08</td>
<td>0.12 1.30</td>
</tr>
<tr>
<td>E. Due to HCl neutralization</td>
<td>- -</td>
<td>3.60 39.39</td>
<td>- -</td>
</tr>
<tr>
<td>F. Due to air stripping</td>
<td>- -</td>
<td>- 4.27</td>
<td>- 46.16</td>
</tr>
<tr>
<td>G. Evaporated to air</td>
<td>1.79 20.77</td>
<td>0.37 4.05</td>
<td>- -</td>
</tr>
</tbody>
</table>

| Stripping side          |                |                    |                    |
| H. Total H⁺ consumption | 6.83 100       | 5.17 100           | 4.98 100           |
| I. H⁺ consumption due to Cu/2H⁺ exchange | 5.08 74.38 | 4.98 96.32 | 4.86 97.60 |
| J. Discrepancy (=H-I)   | 1.75 25.62     | 0.19 3.68          | 0.12 2.40          |

As mentioned before there is also a possibility of H⁺ direct transport from the stripping acid to feed etchant which could be accounted for the discrepancy between theoretical H⁺ consumption and experimental determination in the whole etchant treatment process. If it is the truth, the amount of H⁺ direct transportation over long periods of treatment should be almost the same for these three experimental runs. However, this is contradictory to the fact that when measures are taken to control and decrease feed NH₃ level, total H⁺ consumption in the stripping is much less. Both with HCl addition and air stripping using second membrane contactor less NH₃ was transferred directly into the stripping sulfuric acid. This is very important for the downstream electrowinning or crystallization unit operations. In large scale treatment process, the stripping acidic solution has to be reused as long as possible and carry-over of ammonia through the organic phase should be avoided or at least minimized.
5.4.5 Pilot-scale HFSLM System for Regeneration of Spent Etchant

Pilot plant experiments were carried out two separate runs with the setup shown in Figure 5.3. In the 1st run 120L spent etchant was treated. The Cu concentration was reduced from 150 g/L to 50 ppm within 35 hours. During this period, 15% HCl was periodically added into the stripping solution to maintain feed pH around 8. In the 2nd run, 80L spent etchant was treated within 20 hours to reduce copper from 110 g/L to less than 50 ppm.

Meanwhile in the stripping side, when Cu$^{2+}$ in stripping was reached at ~1M (60-70g/L), the saturated solution was pumped into another storage drum and fresh H$_2$SO$_4$ solution was pumped into the system. Within the 55 hours’ operation, nearly half a ton of saturated copper sulphate in sulfuric acid solution was formed.

It was reported maximum etching efficiency is obtained when ammoniacal solution contains 110-130 g/L copper and gradually disappears when the copper concentration is 150-170 g/L [6]. Thus to keep the etching efficiency constant and optimal, the etching solution must be continuously removed and regenerated. If a HFSLM system
is used for copper reduction in spent etchant solutions to 110-130 g/L, the volume treated and the yield of copper sulphate pentahydrate crystals would be even much higher.

Comparison of the regenerated etchant and the commercial replenisher which is used as an additive to dilute spent etchant demonstrates that NH₄Cl concentration is within limits necessary for the replenisher. Simultaneously total alkalinity and ammonia content after the treatment were very low compared to the replenisher. Therefore it is necessary to add NH₃ in order for it to be used as a replacement for the replenisher. The treated etchant after addition of NH₃ is similar to the commercial etchant and is ready for reuse at PCB production.

| Table 5.7: Comparison of treated spent etchant with commercial replenisher |
|--------------------------------------------------|------------------|--------------------|
|                                    | Treated etchant | Regenerated Etchant after NH₃ top-up | Commercial replenisher |
| Cu conc. (ppm)                  | 47              | 50                  | -                  |
| NH₄Cl conc. (g/L)             | 276             | 271                 | 250-270            |
| Total alkalinity (g/L)        | 18              | 346                 | 310-370            |
| pH                              | 8.15            | 9.68                | 9.5-9.9            |
| Specific gravity              | 1.070           | 1.02                | 1.020-1.040        |

Crystallization of CuSO₄·5H₂O was conducted by refrigeration of stripping acidic solution with concentration of copper sulphate near saturation. The crystals in terms of cation composition as well as the crystal size were similar to commercial analogues (Table 5.8). The X-Ray diffraction (XRD) spectra of the produced crystals is also similar to that of commercial crystals and both have the peaks at the principle scattering angles (2θ) correspond to the typical occurrence of CuSO₄·5H₂O crystal structure [30]: Four of the waters are arranged in squares around the copper, and two oxygens make with these approximately octahedron. The fifth water is not
coordinated but is in contact with two oxygens and two waters [31].

Figure 5.12: XRD spectra of CuSO₄·5H₂O crystals from pilot test and commercial product.

Table 5.8: Purity comparison of pilot test CuSO₄·5H₂O crystals and commercial product.

<table>
<thead>
<tr>
<th>Element</th>
<th>Pilot test crystals (%)</th>
<th>Commercial crystals (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al</td>
<td>0.36</td>
<td>0.858</td>
</tr>
<tr>
<td>Cd</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cr</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fe</td>
<td>0.004</td>
<td>0</td>
</tr>
<tr>
<td>K</td>
<td>0.23</td>
<td>0.17</td>
</tr>
<tr>
<td>Mg</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Pb</td>
<td>1.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Zn</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

5.5 Summary

The HFSLM method is an effective way to recover copper and to regenerate spent ammoniacal etching solution. Kinetics of the process in the hollow fibre membrane module was studied and optimized. Copper can be easily removed from spent ammoniacal etching solution due to active transport using pH gradient as a driving factor. Treated solution with very low Cu concentration has chemical and physical properties, satisfying the specification of commercially available replenisher. Copper is recovered in the form of CuSO₄·5H₂O, a value added product with high purity.
Accumulation of excess ammonia in the feed solution has negative effect on the copper removal. The effect is more significant at low copper concentration stage. Ammonia removal from the feed improves the copper removal and reduces the ammonia transfer to the acidic stripping solution. Both sweeping gas in the additional hollow fiber membrane module and addition of HCl to the etchant can be used to decrease NH$_3$ concentration. The high selectivity of copper over other cations and the stability of supported liquid membrane are promising for practical industrial application.
References


6. CHAPTER SIX

PROCESS DESIGN AND ECONOMIC EVALUATION FOR THE PROTOTYPE OF ETCHANT REGENERATION SYSTEM (ERS) BASED ON HOLLOW FIBER SUPPORTED LIQUID MEMBRANE SYSTEM

6.1 Introduction

 Manufacture and applications of membrane products are becoming one of contemporary advanced industries. Prosperity of membrane production has contributed to the overall well-being of the global economy and created great business opportunity. Principally, membrane products could find applications in almost every industry, even though the majorities of current applications are in filtration and separation. Elsevier [1] has claimed that the value of worldwide membrane market in filtration and separation is US$2.7 billion in 1995, with an estimated average 7% annual increment globally. In Singapore, the increment ratio could be 10% as the estimation by Elsevier in 1996. Now, with the implementation of new environmental regulations and the increasing demand for “Newater”, a quick growth in membrane application in Singapore could be expected.

 One of this work’s targets is to recover copper from spent ammoniacal etchant and to regenerate the etchant from waste. Development of semiconductor industry has generated a huge business globally. One of the branches in this area is printed circuit boards (PCB) production, which has generated billions of US dollars market globally [2]. All of these
provide a good opportunity to apply our technology.

Currently, the main competitor in the area of spent ammoniacal etchant treatment is a Swedish company Metallextraktion AB. It has developed a Mecer system to regenerate ammonium chloride, recycle rinse water and recovers copper using a process of solvent extraction and electrowinning [3, 4]. The Mecer system is available in different sizes to suit different consumption rate of replenisher in PCB producing companies. It has built the first prototype with copper productivity of 1.2 tons/year in 1978. In the following years, the company has developed its business quite well and since that it has sold its system to more than 80 PCB manufacturers in America, Europe, East Asia, Australia and Africa. Its customer list includes several famous companies such as Siemens, Nokia, Hewlett Packard, Ericsson, AT&S, etc. But a market survey conducted in 2001 has revealed that the sales record of Mecer system is becoming worse. It has been evaluated that the payback time of Mecer system is 2.5 ~ 3 years [4]. As we know nowadays the economic recycle time is becoming shorter and no PCB manufacturer would like to accept a system with a payback time more than 2 years, especially the system was used only for waste treatment. Another drawback of the system is that it uses a complex system with extraction and re-extraction in different unit operations, used a lot of organic solvent and can remove only 33% of the copper before the regenerated etchant being returned back to etching process. Therefore, it is quite clear that the current market needs technology breakthrough to supply a more effective spent etchant treatment system.

Supported Liquid Membrane (SLM) is a new generation of separation technology. Its
unbeaten features, compared with the conventional solvent extraction process, are small equipment size, low organic solvent usage, simple operation procedure, less maintenance, low investment, low energy consumption, short pay-back time, high versatility, etc. With SLM technology to treat spent ammoniacal etchant, the main chemicals in the etchant can be reused. Meanwhile, copper is recovered in the value-added form as copper sulfate pentahydrate crystal, which is higher value and bigger molecular weight product than simple copper metal.

6.2 Process Design

After thoroughly studying the kinetics and mechanism of copper transport through SLM at different experimental and hydrodynamic conditions together with the results we got from bench-scale and pilot-scale tests, we set up a prototype of Etchant Regeneration System (ERS) based on hollow fiber supported liquid membrane (HFSLM) system as shown in Figure 6.1. In this prototype, two 10”×28” Liqui-Cel® Extra Flow contactors with 130m² membrane surface area each is employed in parallel for copper removal and another 4”×28” Liqui-Cel® Extra Flow contactor with 20m² membrane surface area is used to control ammonia in etchant stream. The membrane contactors were mounted to the movable skid horizontally to avoid the pressure drop across the membrane contactor placed in vertical way. The feed and strip solutions were pumped at the almost same volumetric flow rate in a concurrent mode. The concurrent flow mode and the same flow rates were adopted to provide a stable SLM system and prevent the Kelvin-Helmholtz instability caused by the hydrodynamic velocity difference between tube and shell side of
hollow fiber membrane contactor. Two polypropylene flexible liner pumps are used to recirculate feed and strip solutions. This liner pump can fulfill our requirements for ERS very well:

- Flow rate range from 1 GPM (gallon per minute) to 3GPM
- Low fluid pressure
- Pulseless flow pattern to forbid pushing the liquid membrane phase from membrane pores by pulsation
- Self-priming and dry-run properties
- Reversible flow which is critically important for the flexible operation of ERS
- Good chemical resistance to kerosene, sulfuric acid and alkaline solution

The in-line filters are installed before membrane modules to forbid particles and precipitates blocking the membrane fiber. This filter has a maxim flow rate 20 GPM, low pressure drop and good chemical compatibilities to organic solvents, alkaline and inorganic acids.

One additional oil separation tank is connected to the feed etchant reservoir to collect the organic membrane phase that could probably be out of membrane pores after extended period of operations, if any. Transmitters, indicators, sensors and controllers are employed in ERS to make the process automatic and less labor-requirement. All these will be monitored and controlled by a central programmer logic controller (PLC).
6.3 Economic Evaluation of ERS to Treat Spent Ammoniacal Etchant

In this chapter, the economic evaluation was conducted based on this prototype. Because low profit is obtained to treat ammoniacal wastewater with low copper content, the evaluation was focused on spent etchant treatment. It was reported maximum etching efficiency is obtained when ammoniacal solution contains 110-130 g/L copper and gradually disappears when the copper concentration is 150-170 g/L [5]. Thus to keep the etching efficiency constant and optimal, the etching solution must be continuously removed and regenerated, which is usually employed by Mecer system. For comparison, Mecer SX100-15 system with regeneration of 100 liters spent etchant and recovery of 15 kg copper metal per hour was compared with our ERS due to their similar productivity.
In Mecer system, the solvent extraction process requires complex chemistry as shown in Figure 6.2 and requires large space area to operate. Only 33% of copper in the spent etchant is extracted. The copper in the spent etchant is recovered as copper metal by electrowinning which is an intensive energy consumption process. In addition, the probable ammonia carry-over to the stripping acid is deleterious to the electrowinning step. In comparison, ERS based on SLM technology combines extraction and back-extraction just in one technological step and needs much smaller space to operate. It is a continuous process which can be connected to the etching process and can provide a secured etching operation; that is, in case ERS fails it can be totally cut off from the etching process and allows etching operation to continue. Hollow fiber membrane module as the main component of ERS is allowed to do system scale-up easily.
addition, the regeneration of hollow fiber membrane modules after extended period of operation can be easily carried out offline in an alternative mode, that is, the deteriorated membrane module with much lower flux can be dismantled from ERS while the other membrane modules are still in operation. The wash, dry and liquid membrane refill can be carried out in another skid. Therefore the down-time of ERS can be neglected. In addition, the copper can be collected as copper sulphate pentahydrate crystal in stripping acidic solution with concentration of copper sulphate near saturation using a simple and cheap chiller. Four times weight increment of product can be achieved form the Cu by electrowinning to CuSO₄·5H₂O, which is also more expensive than Cu metal.

Table 6.1 shows that the treatment cost of per liter spent etchant is half by using our ERS with respect to Mecer system to reduce copper content to 100 g/L level. The payback time is much shorter using our ERS. Furthermore, as the rule of thumb the larger our ERS’ operation capacity by adding more membrane modules, the even shorter payback time for implementing our membrane technology for etchant regeneration.

In addition, our ERS can also be used to reduce copper content to less than 5 ppm. The treated etchant after ammonia top-up has the similar physical and chemical properties with the commercial replenisher and is ready to be used for etching by our potential PCB manufacturers. The economic estimation of this treatment process is tabulated in Table 6.2.
Table 6.1: The economic comparison of two systems for spent ammoniacal etchant treatment [4]

<table>
<thead>
<tr>
<th>Items</th>
<th>Unit</th>
<th>Quantity</th>
<th>Unit Price, US$</th>
<th>Value, US$</th>
<th>Total Value, US$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mecer</td>
<td>ERS</td>
<td>Mecer</td>
<td>ERS</td>
<td>Mecer</td>
</tr>
<tr>
<td>Operation time</td>
<td>Hr/y</td>
<td>6,000</td>
<td>6,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A. TOTAL INVESTMENT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B. ANNUAL BALANCED COST</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1. Annual revenue</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saving replenisher cost</td>
<td>L/y</td>
<td>635,880</td>
<td>420,000</td>
<td>0.14</td>
<td>89,100</td>
</tr>
<tr>
<td>Recovered copper value</td>
<td>Kg/y</td>
<td>95,382</td>
<td>1.6</td>
<td></td>
<td>152,700</td>
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<tr>
<td>Recovered CuSO₄·5H₂O value</td>
<td>Kg/y</td>
<td>100,000</td>
<td>4.0</td>
<td></td>
<td>400,000</td>
</tr>
<tr>
<td>Savings in wastewater treatment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Annual Revenue</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B2. Annual consumption cost</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ammonia top-up</td>
<td>Kg/y</td>
<td>11,446</td>
<td>2,000</td>
<td>1.1</td>
<td>12,600</td>
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<tr>
<td>Replenisher make-up</td>
<td>L/y</td>
<td>3,815</td>
<td>2,000</td>
<td>9.8</td>
<td>37,400</td>
</tr>
<tr>
<td>Reagent make-up</td>
<td>L/y</td>
<td>325</td>
<td>214</td>
<td>63</td>
<td>20,500</td>
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<tr>
<td>Sulfuric acid, 96%</td>
<td>Kg/y</td>
<td>2,100</td>
<td>10,000</td>
<td>1.5</td>
<td>3,150</td>
</tr>
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<td>Deionized Water</td>
<td>Ton/ y</td>
<td>48</td>
<td>30</td>
<td>86</td>
<td>4,128</td>
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<tr>
<td>Change of anodes</td>
<td>Pcs/5y</td>
<td>42</td>
<td>1448</td>
<td></td>
<td>12,200</td>
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<tr>
<td>Copper starter-sheets</td>
<td>Pcs/y</td>
<td>763</td>
<td>62</td>
<td></td>
<td>47,500</td>
</tr>
<tr>
<td>Carrier reimpregnation</td>
<td>L/y</td>
<td>500</td>
<td>1.00</td>
<td></td>
<td>500</td>
</tr>
<tr>
<td>Consumption of electricity</td>
<td>Kw/y</td>
<td>230,000</td>
<td>20,000</td>
<td>0.05</td>
<td>11,600</td>
</tr>
<tr>
<td>Labor and maintenance</td>
<td>Hr/y</td>
<td>225</td>
<td>225</td>
<td>19</td>
<td>4,300</td>
</tr>
<tr>
<td>Total Annual Consumption cost</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL ANNUAL PROFIT (B1-B2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Payback Time (Total Invest./Annual Profit)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spent etchant treatment cost</td>
<td>US$/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6.2: The economic evaluation of ERS to reduce copper less than 5 ppm in spent etchant treatment process

<table>
<thead>
<tr>
<th>Items</th>
<th>Unit</th>
<th>Quantity</th>
<th>Unit Price</th>
<th>Value, US$</th>
<th>Total Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operation time</td>
<td>Hr/y</td>
<td>6,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A. INVESTMENT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane contactors (130 m²)</td>
<td>2</td>
<td>8,000</td>
<td>16,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane contactors (20 m²)</td>
<td>1</td>
<td>2,000</td>
<td>2,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Design, fabricate and assemble</td>
<td></td>
<td>50,000</td>
<td>10,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chiller</td>
<td>1</td>
<td>2,000</td>
<td>2,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Investment</td>
<td></td>
<td></td>
<td></td>
<td>30,000</td>
<td></td>
</tr>
<tr>
<td>B. ANNUAL BALANCED COST</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1. Annual revenue</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saving replenisher cost</td>
<td>L/y</td>
<td>60,000</td>
<td>0.14</td>
<td>8,400</td>
<td></td>
</tr>
<tr>
<td>Recovered CuSO₄·5H₂O value</td>
<td>Kg/y</td>
<td>37,500</td>
<td>4.00</td>
<td>150,000</td>
<td></td>
</tr>
<tr>
<td>Savings in wastewater treatment</td>
<td>L/y</td>
<td>60,000</td>
<td>0.1</td>
<td>5,500</td>
<td></td>
</tr>
<tr>
<td>Total Annual Revenue</td>
<td></td>
<td></td>
<td></td>
<td>164,000</td>
<td></td>
</tr>
<tr>
<td>B2. Annual consumption cost</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia top-up</td>
<td>Kg/y</td>
<td>2,000</td>
<td>1.1</td>
<td>2,200</td>
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<tr>
<td>Sulfuric acid, 96%</td>
<td>L/y</td>
<td>4,000</td>
<td>1.50</td>
<td>6,000</td>
<td></td>
</tr>
<tr>
<td>Deionized water</td>
<td>Ton/y</td>
<td>15</td>
<td>86.0</td>
<td>1,300</td>
<td></td>
</tr>
<tr>
<td>Labor and maintenance</td>
<td>Hr/y</td>
<td>225</td>
<td>19</td>
<td>4,300</td>
<td></td>
</tr>
<tr>
<td>Carrier reimpregnation</td>
<td>L/y</td>
<td>500</td>
<td>1.00</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>Consumption of electricity</td>
<td>Kw/y</td>
<td></td>
<td>0.05</td>
<td>1,000</td>
<td></td>
</tr>
<tr>
<td>Total Annual Consumption cost</td>
<td></td>
<td></td>
<td></td>
<td>15,000</td>
<td></td>
</tr>
<tr>
<td>Annual Profit (B1-B2)</td>
<td></td>
<td></td>
<td></td>
<td>149,000</td>
<td></td>
</tr>
<tr>
<td>Payback Time (Total Investment/Annual Profit): 2.5 Months</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Treatment cost of spent etchant without labor cost: 25 cents/L</td>
<td></td>
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</table>

### 6.4 Summary

The advantages of our Etchant Regeneration System (ERS) can be summarized as below:

- Extraction and re-extraction in one technological step
- Exchange of Cu(II) per two H⁺ ions allowing to remove practically 100% of the Cu(II) if necessary
- Continuous operation- can be connected to the etching system
- Small volume of organic phase - safe, nonflammable
- Two possible products: Cu sulfate pentahydrate (crystallization) and also usual Cu metal (electrowinning).
- Less space demand
- Less power consumption
- Green chemistry process. No secondary waste generated.
- Easy scale-up.
- Short payback time even on existing system it is less than one year.
References


7. CHAPTER SEVEN
THE DEVELOPMENT OF CHEMICALLY MODIFIED P84 CO-POLYIMIDE MEMBRANES AS SUPPORTED LIQUID MEMBRANE MATRIX FOR Cu(II) REMOVAL WITH PROLONGED STABILITY

7.1 Introduction

The use of supported liquid membrane (SLM) for the removal of metal ions from aqueous solutions is a promising separation technique which offers an attractive alternative to conventional solvent extraction and ion exchange processes. The SLM based separation process has enjoyed many inherent advantages such as the high selectivity, the possibility to concentrate ions by coupled transport with relatively high mass transfer rates, smaller quantity of expensive extractants or solvents required, and the ability of extracting all of the solute and concentrating the extracted species in the stripping solution, which is especially economically and practically attractive when large volumes of solutions require treatment.

Although SLMs have been widely studied for the separation and concentration of a variety of compounds and present many potential advantages over other separation methods, there have been very few large scale applications of SLM due to insufficient membrane stability. Various mechanisms have been proposed for SLM instability: lose of organic phase (carrier and/or solvent) from the membrane phase by dissolution,
progressive wetting of the support pores, pressure difference or osmotic pressure gradient over the membrane [1-3], and emulsion formation [4] or attrition of the organic film [4, 5] due to lateral shear forces. SLM stability can also be affected by the type of polymeric support and its pore radius [6], organic solvent used in the liquid membranes, method of preparation [7], etc. The time periods of initiating instability are observed varies from few hours to several months depending on the systems [1, 3].

One effective method for SLM continuous use is the regeneration of liquid membranes. Different methods of regeneration techniques have been reviewed and adopted to stable the SLMs [8]. Ho proposed SLM with strip dispersion to remove and recover metals and other materials. The continuous organic phase refilled the membrane pores constantly and provided a stable SLM [9]. Continuous regeneration of liquid membranes provides fairly good stability, but it causes the contamination of feed or strip solution with liquid membrane solutions, which is certainly not desirable in large scale application. Prof. Sirkar’s group had developed novel hollow-fiber-contained liquid membrane (HFCLM) systems in which the organic phase is contained in the interstices of two well packed sets of hollow fibers [10, 11]. The aqueous feed and strip solution flows in the lumen sides of these two separate hollow fiber sets, while the bulky volume of extracting organic phase in the shell side continuously immobilize and regenerate at the mouths of the respective fiber with proper pressures applied.

Bloch et al. [12] first proposed the idea of gelation to improve SLM stability. The lifetime of these membranes was insufficient as a result of loss of plasticizer, resulting
incompletely impermeable and hard films. Instead of gelling the wall of membrane support, gelation in the pores of support was also suggested [13, 14]. Not only did the inert support immobilize the liquid membranes but also provided mechanical strength to the gel. The major disadvantage of this technique is the poor reproducibility. In addition, the coating technique of the membrane with gel layer seems hard for hollow fibers and not suitable for practical applications [3].

Besides the formation of barrier layers by physical deposition, interfacial polymerization was also adopted [15-17]. Wijers et al. [15] developed a new type of composite membrane using sulphonated poly ether ether ketone (SPEEK) as material for the stabilization layer and found that the lifetime of the SLM was significantly improved when one stabilization layer was applied at the strip side or two stabilization layers at both sides of the SLM. The disadvantage of this composite membrane was the potential loss in selectivity if SPEEK bridged through the entire membrane support. Wang et al. [16, 17] explored different monomers systematically for interfacial polymerization on top of the membrane support. They found the membrane was more stabilized with semi-permeable polyamide [16] and epoxy [17] skin layers deposited on SLM. However, the reproducibility of SLM coated with an interfacial polymerization film is poor. In addition, the adhesion to the substrate is not strong and the coating probably impairs the separation. Yang et al. [18] proposed plasma polymerization for the formation of ultra-thin membranes and surface modification of polymer substrate. Advantages of this technology are the good chemical and thermal stability of the coatings and the strong adhesion to the substrate. However, the plasma polymerization method is too expensive to fulfill the
In this chapter, P84 (BTDA-TDI/MDI, co-polyimide of 3,3’,4,4’-benzophenone tetracarboxylic dianhydride and 80% methylphenylene diamine+20% methylene diamine), a most recent commercially available polyimide, has been the first time used as the polymeric microporous support for SLM preparation. This aromatic polyimide was chosen because it possesses a number of attractive mechanical and physicochemical properties [19, 20]. Because of its superior chemical resistance, it may have potential to serve as the polymeric support matrix for organic carrier immobilization and then to separate two aqueous solutions in harsh chemical environments. We have proposed, for the first time, P84 co-polyimide with novel chemical cross-linking modification can be effectively used as the polymeric microporous matrix for supported liquid applications. To prove our hypothesis, both symmetric and asymmetric membranes were fabricated by both casting and solution spinning using the phase inversion method. Chemical modifications with the aid of p-xylenediamine were conducted in order to enhance chemical resistance, surface hydrophobicity and SLM stability. It was found that the SLM with symmetric membrane support had much higher stability than that of the asymmetric one. Therefore, the objectives of this paper aim to summarize our studies on 1) the science and engineering of solution spinning of flat P84 microporous membranes, 2) the effects of p-xylenediamine chemical modification on P84 membranes stability and their separation performance for SLM applications.
7.2 Experimental

7.2.1 Materials

Figure 7.1 shows the chemical structure of P84. It was purchased from HP Polymer GmbH, Austria. The polymer was dried at 120 °C in a vacuum oven overnight before use. The solvent for P84 was N-methyl-2-pyrrolidinone (NMP) purchased from Merck. Non-solvent ethanol was purchased from Fisher Scientific. Methanol and n-hexane from Merck were used to conduct solvent exchange. P-xylenediamine purchased from Tokyo Kasei Kogyo Co. Ltd., Japan was employed as the crosslink agent. All these chemicals were used as received without further purification. Technical grade isopropanol purchased locally after filtration was mixed with NMP as the coagulation bath for symmetric membrane spinning. LIX54 was supplied by Cognis Corporation, USA and was diluted in kerosene from Aldrich in 33 v/v% as a carrier in liquid membrane phase.

![Figure 7.1: The chemical structure of P84 co-polyimide](image)

7.2.2 Preparation of Asymmetric Membranes

The dried P84 powder was dispersed slowly into a chilled NMP and ethanol mixture at predetermined weight ratio of P84/NMP/ethanol (25/65/10). According to the phase
diagram of this ternary system [20], this composition may produce membranes with reasonably high porosity. The mixture solution was stirred until it became homogeneous, then it was cast onto a glass plate with a casting knife at a thickness about 200 µm. The nascent films were immediately immersed into a coagulation bath of 60/40 wt% NMP/ethanol at 60 °C for half an hour. The specific composition of the coagulant was chosen to reduce the difference in solubility parameter between the polymer solution and the coagulant, thus slowing down the precipitation rate in a hot bath and form spongy-like cross-section morphology.

The as-cast asymmetric polyimide membranes were solvent exchanged and dried according to the following procedure: The membranes were immersed into water overnight. Low surface tension liquids (methanol and followed by hexane) were employed to remove water and residual solvents. The membranes were immersed in methanol three times then hexane three times both with magnetic stirring, each time for half hour. After solvent exchange, the membranes were dried naturally at room temperature. The schematic diagram of asymmetric flat membrane fabrication is described in Figure. 7.2.
7.2.3 Preparation of Symmetric Membrane

The same dope formulation was utilized for solution spinning. Fig. 7.3 illustrates the schematic process of symmetric flat membrane fabrication. The specifically designed film die has two half cells with similar shape and geometry. The flat membrane was extruded through the interstice between these two cells and the membrane thickness can be adjusted by changing the thickness of the Teflon gasket. The homogeneous solution was degassed before spinning and filtered by a metal filter with the pore size of 15 µm. The film die was immersed horizontally in the coagulation bath containing 20/80 wt% NMP/isopropanol and the dope solution was fed into the film die by an ISCO syringe pump. To avoid heating the coagulation bath as adopted in the asymmetric membranes casting, more NMP weight ratio and a weaker coagulant of isopropanol than ethanol were used as the coagulation bath in order to form spongy-like cross-section morphology. Horizontal extrusion is preferred so as to reduce the effect of gravity force on membrane morphology. The nascent symmetric flat membranes were collected by a rotator. The as-
spun symmetric flat membranes were post-treated to remove residual solvent and non-solvent as the same procedures described in section 7.2.2.

![Figure 7.3: The fabrication of the symmetric flat membrane via film die extrusion](image)

**7.2.4 Membrane Modification by Chemical Cross-linking**

The cross-linking modification was carried out by immersing the membranes into 10 wt% P-xylenediamine in deionized water for certain period of time, after which the membrane was taken out followed by washing with fresh deionized water and drying at ambient temperature. For stability tests, the membrane was first fully impregnated with the liquid membrane phase (33 v/v% LIX54 in kerosene) and then immersed into 10/90 wt% p-xylenediamine/water solution for preset time periods.

Previous studies on surface modification of polyimides using p-xylenediamine/methanol solutions were based on the fact that methanol swollen up the dense polymeric chains,
facilitated the diffusion of p-xylenediamine molecules into interstitial space among intra- and inter-chain segments, and induced cross-linking reactions with polyimides [21]. However, the functions of the current p-xylenediamine/water solution are to induce chemical cross-linking reaction upon pore surface and reduce the pore size but without much changing the membrane cross-section and without producing a thin skin layer with significant mass transfer resistance. Water is purposely chosen because of its immiscibility and immobility with kerosene and LIX54. As a result, the cross-linking reaction can take place very locally and specifically near the outer surface pore. For readers’ information, the p-xylenediamine/methanol mixture does not work in this case as the cross-linking agent because of the miscibility of methanol and carrier and/or kerosene. As a result, the weights of impregnated membranes were even decreased after cross-linking when p-xylenediamine/methanol was employed as the cross-linking agent.

7.2.5 Membrane Characterizations

The membrane thickness was measured by a micrometer and only the membranes with about 150 µm thickness were used in our experiments. Each membrane thickness value with deviation less than 10% was determined by an average of 10 measurements in different places of one membrane piece. The contact angle measurements were performed by a contact angle and surface tension instrument (First Ten Ångstroms, USA, model FTÅ125) at room temperature. Deionized water droplets were introduced by a Hamilton microsyringe (Gastight® 1750, Hamilton Company, USA) onto the membrane surface. At least 8 droplets were introduced and the average contact angle data was taken for each
membrane with deviation less than 5%.

The porosity ($\varepsilon$) of the symmetric membrane was estimated by the ratio of empty voids to total volume of the membrane sample [22]. The total geometrical volume of the membrane was approximately calculated by the product of the membrane length, width and thickness. After the membrane sample was fully impregnated by 33% LIX54 in kerosene solution, we assumed all the empty voids were filled with the liquid membrane phase. Therefore, the empty volume could be calculated by the weight gain of the membrane sample divided by the known density of the liquid membrane phase. Four pieces of symmetric membranes were used to estimate the porosity and the results were found to be reproducible with less than 1% deviation. The total pore volume and mean pore size of the symmetric membranes were also measured by a Brunauer-Emmett-Teller (BET) analyzer (Nova 3000 series, Quantachrome Corp., Germany) based on Barrett, Joyner and Halenda (BJH) method [23].

The morphology of membranes was observed by using a JSM-6700F field emission scanning electron microscope (FESEM) (JSM-6700F, JEOL, Japan). All dried membrane samples were prepared by fracturing them in liquid nitrogen then coated with platinum. FTIR-ATR measurements were carried out using a Perkin-Elmer FTIR microscope (Spectrum 2000, Perkin-Elmer, USA).

### 7.2.6 SLM Preparation and Stability Characterization
The dried membrane after solvent exchange was immersed into a 33/67 v/v% LIX54/kerosene solution. It was found that two days impregnation was long enough to get the fully impregnated membrane which was confirmed by showing no further weight gain. The extra organic phase upon the membrane surface was wiped off with the tissue paper. The chemical cross-linking modification was further carried out by immersing the fully impregnated SLM into the 10/90 wt% p-xylenediamine/water solution in predetermined time periods. The impregnated SLM or the impregnated membrane after chemical cross-linking modification was clamped into the vertical flat membrane setup with effective membrane surface area 4.9 cm² described in Chapter Three to carry out the SLM stability study.

The SLM stability was characterized by monitoring copper transmembrane flux which was experimentally determined based on copper transfer rate in the strip solution per unit of membrane surface area. The strip solution was pumped through a quartz flow-cell (Hellma, Germany) with an optical window of 1 cm (H) ×0.1 cm (W) where the copper concentration in the strip side was real-time monitored using a UV-VIS scanning spectrophotometer (Libra S32, Biochrom Ltd., England) at a wavelength of 780 nm. A calibration of the system was performed by diluting a standardized CuSO₄ solution with 2M H₂SO₄ and then the optical absorbance of the diluted Cu²⁺ solutions at 780 nm were plotted against their concentrations. 37 ml feed ammoniacal solutions containing 5.6 mM Cu(II) at pH 8.72 and 42 ml 2M H₂SO₄ as strip solutions (additional volumes of 5 ml were used to fill up the tubing and quartz cell) were homogeneously stirred at 200 rpm in the two Teflon chambers of the vertical flat membrane setup. After preset time intervals
the feed and strip solutions were replaced by fresh ones with the same compositions so as to avoid the variation of flux due to composition differences. The optical absorbance vs. time plot was always a straight line over a long period of time in each run.

7.3 Results and Discussion

7.3.1 Characterization of the Original and Chemical Cross-linked Asymmetric Flat Membranes

Figure 7.4 (A1-A4) shows FESEM images of the morphology of the as-cast asymmetric membrane. The top surface (which is exposure to the air when the membrane is casting) has a more porous structure, while the bottom surface (which is attached to the glass plate) has a less porous morphology.

After immersing in the chemical cross-linking solution for 24 hours, the P84 asymmetric membrane shows that both top and bottom surfaces are partially covered (Figure 7.4 B1-B2). However, no visible changes can be observed in the cross-section morphology even after 24-hour immersion (Figure 7.4 B3-B4). The contact angle measurements show that the hydrophobicity of both surfaces after chemical cross-linking is increased (Table 7.1).
Figure 7.4: FESEM images of P84 (A) asymmetric and (B) symmetric flat membrane after chemical cross-linking in p-xylenediamine/water for 24 hr

Table 7.1: Contact angle changes with different chemical cross-linking time
(T-Top surface exposed to air when membrane is casting;
B- Bottom surface attached to the glass plate)

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>10 min</th>
<th>30 min</th>
<th>24 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asymmetric P84</td>
<td>55.86 (T)</td>
<td>44.16 (B)</td>
<td>--</td>
<td>79.87 (T)</td>
</tr>
<tr>
<td>Symmetric P84</td>
<td>67.98</td>
<td>72.79</td>
<td>72.04</td>
<td>65.83</td>
</tr>
</tbody>
</table>

7.3.2 Fabrication of Symmetric Flat P84 Membrane and Characterization of the Cross-linked P84 Membrane

Compared with symmetric micro-filtration membranes prepared by the track-etch and sintering methods, the phase inversion method tends to fabricate symmetric membranes with a high degree of tortuosity. High tortuosity of membrane matrix may help hold the liquid membrane phase in the pores tighter and also improve the stability of SLM system, but prolong the length of diffusion path. Fig. 7.5A shows the two membrane surfaces share the similar structure because they are encountered the same hydrodynamic and chemical conditions in the spinning process. FESEM images show that both surfaces
have slit-shaped pores and the cross-section is in an open cell structure. The membrane porosity estimated based on the method described in section 2.5 is around 0.58.

Figure 7.5: FESEM images of (A) surface morphologies of as-spun symmetric P84 membrane; surface morphology after chemical cross-linking for (B) 10 min; (C) 30 min; (D) 24 hr

Figure 7.5 (A-D) shows a comparison of morphological changes before and after chemical cross-linking at different immersion times. The longer the immersion time, the more crosslink agent deposits on the membrane surface. There is no much visible change in the cross-section morphology after cross-linking modification (therefore, no FESEM picture on cross-section is shown). The contact angle measurements indicate that the chemical cross-linking treatment increases hydrophobicity of the symmetric flat membrane surface slightly. Notice should be taken that for a long term cross-linking reaction; for example 24 hours, the contact angle of the chemically modified symmetric P84 membrane is less than the original one. This may be attributed to the depositions of
un-reacted P-xylenediamine with hydrophilic amine groups on the membrane surfaces, which could be not completely removed by washing with water. In addition, the BET results show that total pore volume and average pore diameter decrease with an increase in the immersion time (Table 7.2).

<table>
<thead>
<tr>
<th>Immersion time</th>
<th>Total pore volume, cm$^3$/g</th>
<th>Average pore diameter, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.07639</td>
<td>391.702</td>
</tr>
<tr>
<td>10 min</td>
<td>0.06239</td>
<td>164.996</td>
</tr>
<tr>
<td>30 min</td>
<td>0.05712</td>
<td>181.286</td>
</tr>
<tr>
<td>24 hr</td>
<td>0.03728</td>
<td>77.523</td>
</tr>
</tbody>
</table>

The chemical structure changes during the cross-linking process are also monitored by FTIR-ATR and the results are illustrated in Fig. 7.6. With the progress of chemical cross-linking reaction, the intensities of the characteristic peaks of the imide group at 1780, 1728 and 1380 cm$^{-1}$ decrease with increasing immersion time. Meanwhile, the characteristic peaks of amide groups at 1656, 1550 and 3300 cm$^{-1}$ appear and become stronger. These prove the reaction between p-xylenediamine and imide groups of P84 produces amide groups and forms the chemical cross-links.
7.3.3 Stability Characterization of SLMs with Unmodified and Chemical Crosslinked Membrane Support Matrixes

7.3.3.1 Asymmetric Flat P84 Membrane

In the Cu(II) transport through SLM studies, the fully impregnated P84 asymmetric membrane was clamped into the vertical flat membrane setup. The top or bottom surface was intentionally faced to the feed ammoniacal copper solution respectively in order to compare the Cu(II) transmembrane flux as a function of membrane assembly. When the top surface with more porous structure faces to the feed solution, it shows much higher initial Cu(II) flux (Figure 7.7) at $1.33 \times 10^{-9}$ mol/cm$^2$.s, while the value is reduced to $2.99 \times 10^{-10}$ mol/cm$^2$.s for the bottom surface with less porous structure facing to the feed solution. This is due to the fact that the effective membrane carrier concentration is higher in the top surface due to its larger effective membrane area than in the bottom surface.
Figure 7.7: Cu(II) flux as a function of time for asymmetric membranes in long term stability studies (A) Top surface faces to the feed (B) Bottom surface faces to the feed

In both case, the flux drops drastically in the first day due to the loss of carrier and/or solvent to the bulky aqueous solutions: after 28 hours operation, flux is reduced 99% to $9.88 \times 10^{-12}$ mol/cm$^2$.s and $9.20 \times 10^{-13}$ mol/cm$^2$.s for the asymmetric membranes with top and bottom surface facing to the feed solution, respectively. The most acceptable
mechanism to describe the instability of SLM is that local deformations of the meniscus in the pores of the membrane support lead to the splitting off emulsion droplets induced by lateral shear forces [24]. Figure 7.8 schematically describes the evolution of meniscus stability in SLM. Once the liquid membrane phase is lost from the membrane pores to the aqueous bulk solutions in the form of emulsion droplets in both sides of membrane (Figure 7.8-A1), the empty spaces could be filled with the aqueous solutions (Figure 7.8-A2). Mathematically, the forces exerted per unit area of the interfaces between the bulk aqueous solutions and the supported liquid membrane phase can be described as [2]:

$$\sum F = P - p_c$$

(7.1)

Here $P$ is the hydraulic pressure including exerted pressure, the atmosphere pressure and hydrostatic pressure. $p_c$ means the capillary pressure at the interface of aqueous/organic phases and can be expressed by the Laplace-Young equation:

$$p_c = \frac{2\gamma \cos \theta}{r_p}$$

(7.2)

Where $\gamma$ is the interfacial tension between aqueous/membrane interface, $\theta$ is the advancing contact angle of the aqueous solution on the membrane support surface and $r_p$ is the radius of membrane pore.
Figure 7.8: Schematic description of longer stability of SLM with (A) asymmetric microporous support matrix than (B) symmetric support matrix

For an SLM with an asymmetric membrane as the support matrix, its pores may be considered to have trapezoid geometry. Assuming $\gamma$ and $\theta$ are comparably the same on both sides of the membrane, Eq (7.2) implies that a bigger pore size (i.e., $r_p$) would result in a lower $p_c$. Thus, the total force per unit of area (i.e., $P_{-p_c}$) in the left-hand side of the membrane, as shown in Figure 7.8-A2, is greater than that (i.e., $P_{-p_c}$) in the right-hand side. The net unbalance force [i.e., $(P_{-p_c})_1 - (P_{-p_c})_2$] across the SLM membrane would continuously help push the liquid membrane phase out of the membrane pores. In addition to the inherent instability of SLM caused by the convective flows and lateral shear forces, the extraction and back extraction of Cu(II) in these two moving aqueous/membrane interfaces, the net unbalance force cross the membrane may further contribute to an unstable SLM system and shorten its life time. This hypothetic mechanism is confirmed by the experimental results shown in Figure 7.7: no matter
whether top or bottom surface is faced to the feed ammoniacal copper solution, there is continuously decreasing in Cu(II) flux.

Recently, the unusual transport characteristics of stacking several asymmetric membranes into a multilayer structure have been adopted for protein purification [25, 26]. This ignited our intention to stack two pieces of asymmetric membranes together and mount to the vertical flat membrane setup for stability studies. In the trial, the top or the bottom surface from the first membrane faces the same top or the bottom surface of the second membrane without any artificial spacer, gaskets or adhesives in between. In this case, the forces exerted are even for both membrane surfaces in the SLM system. Unfortunately, there was no copper transmembrane flux detected over an extended period of time for several days. This is mostly because the extraction in the feed-membrane interface and back-extraction in the membrane-strip interface are low when less porous surfaces face the aqueous solutions, and because there are transportation gaps or un-matched pores in between when less porous structures face each other.

To validate the hypothesis that the even forces exerted at both membrane-aqueous interfaces will favor a stable SLM system, we firstly cross-linked the asymmetric flat membranes. Figure 7.7 shows much improved stabilities but slightly decreased fluxes for the chemical cross-linked asymmetric P84 membranes. The increased membrane hydrophobicity after chemical cross-linking may be the causes for the prolonged stability. The lower initial flux after cross-linking modification is mostly attributed to the smaller pore size and partially covered membrane surface. Because the bottom surface has less
numbers of pores than the top surface, the amount of initial flux decline after cross-linking modification is more severe if the former faces the feed stream. The stability improvement and lower flux is mostly attributed to the smaller pore size and partially covered membrane surface. Based on Eq (7.2), the smaller pore size can also leads to a higher critical displacement pressure for the SLM system. As a consequence, the critical displacement pressure defined as the minimum transmembrane pressure required to displace the impregnating phase out of the largest pores is increased and therefore improves SLM stability.

7.3.3.2 Symmetric Flat P84 Membrane

The SLM system using the symmetric P84 membrane as the support matrix shows much higher stability than the asymmetric P84 membrane. As shown in Figure 7.9, the flux decline of the un-modified P84 membrane mostly happens in the first 100 hours, then the slope of flux decrease becomes slower in the subsequent 200 hours. The SLM system with a symmetric membrane support matrix can be assumed to have the same pore sizes in both membrane surfaces and the pores may be assumed to be in a cylindrical structure. As illustrated in Figure 7.8B series, the forces exert at the two membrane/aqueous interfaces may be almost the same, thus resulting in the improvement of SLM stability. This is another separate experiment to verify our hypothesis that the even forces exerted at both membrane surfaces will favor a stable SLM system. In addition, further loss of liquid membrane phase could be stopped when stagnant layers are formed inside the pores of the polymeric support (Figure 7.8-B3) where hydrodynamic stability is reached.
and no further emulsion formation is created by the lateral shear forces.

![Graph showing flux changes with time](image)

**Figure 7.9: Flux changes with time of the original and modified symmetric P84 membrane for 10 min cross-linking**

The effect of p-xylenediamine immersion time on SLM performance is also studied. Fig. 7.10 shows the fluxes decline with an increase in immersion time. The flux decline is a result of the smaller effective contact area which leads to the less chances for Cu(II) extracted and back-extracted at the feed/membrane and membrane/strip interfaces, respectively. Nevertheless, the SLM with 10-min chemical cross-linking shows a slightly decreased but acceptable flux. In addition, it is excited to find that the symmetric P84 membrane after 10-min room-temperature chemical cross-linking modification is much more stable than the unmodified one and the stability is comparable to our previous SLM systems using commercial PTFE membrane described in Chapter Three [27]. As shown in Figure 7.9, after 100-hour operation, the flux is decreased by 52% for the original membrane, but only by 10% for the modified one; after 280-hour, the fluxes are decreased by 74% and 34% for the original and modified membrane, respectively. It proves the reduced surface pore sizes, increased membrane surface hydrophobicity and
improved chemical resistance can improve SLM stability.

Figure 7.10: Effect of the immersion time on Cu(II) transmembrane fluxes

7.4 Summary

The fabrication of asymmetric and symmetric co-polyimide P84 flat membranes via the phase inversion method for supported liquid membrane (SLM) applications was investigated in this work. The following conclusions were summarized:

1. SLM with symmetric support matrix is much more stable than that with asymmetric matrix. This is attributed to the proposed force balance exerted at two aqueous/membrane interfaces and the formation of stagnant layers in SLM system.

2. SLM after chemical modification with novel p-xylenediamine/water as the cross-linked agent can reduce the size of surface pores without changing the membrane cross-section and without producing a skin layer with significant mass transfer resistance. The chemically modified SLM has similar life time with other SLM systems using commercial PTFE as the support matrix.

3. The room-temperature chemical cross-linking technology is an economic and
feasible way to improve the stability of SLM.

4. High tortuosity, high hydrophobicity, good chemical resistance, symmetric structure, small pore size of the membrane matrix are all favorable to form a stable SLM system.
References


8. CHAPTER EIGHT
CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

With the rapid growth of PCBs industry, the total volume of high copper-containing spent etchant solutions keeps growing. Current existing technology for spent etchant treatment was suffered from the complex process operation and long payback time problems. Therefore, a low cost and efficient Supported Liquid Membrane (SLM) process is developed in this PhD work to recovery copper and regenerate spent etchant solutions. This PhD research study consists of four major aspects:

- Screening of carrier in SLM system for membrane extraction of Cu(II) from ammoniacal solutions.
- Kinetics and mechanism of copper removal from ammoniacal wastewater through flat sheet supported liquid membrane (FSSLM) system.
- From bench-scale to pilot-scale treatment of spent ammoniacal etching solution with hollow fiber supported liquid membrane (HFSLM) system.
- Stability improvement of SLM system for Cu(II) removal.

The important findings, results and conclusions for different aspects of this study are derived and summarized below.
8.1.1 Screening of Carrier in Supported Liquid Membrane System for Membrane Extraction of Cu(II) from Ammoniacal Solutions.

Among the most widely used carrier for copper extraction, β-diketone LIX54 shows higher copper transmembrane flux than hydroxyoxime LIX84 at same volume ratio of the extractant in the membrane phase. Furthermore, the high selectivity of copper over other cation contaminants and low or no ammonia carry-over provide significant advantages for LIX54 as a better candidate over LIX84 for SLM based ammoniacal copper solutions treatment. LIX84 is a modern strong extractant used for copper recovery from acidic solutions. The hydrophilic nonylphenol group makes LIX84 impregnated SLM stability slightly shorter than LIX54 impregnated one. However, stability of both LIX54 and LIX84 impregnated SLM in ammoniacal copper solutions treatment process is promising for practical industrial applications.

8.1.2 Kinetics and Mechanism of Copper Removal from Ammoniacal Wastewater through Flat Sheet Supported Liquid Membrane (FSSLM) System

Facilitated active copper transport through the FSSLM from aqueous ammoniacal solution in exchange to two H\(^+\) ions has been investigated. Copper concentration in wastewater can be reduced by several orders of value. Due to the buffer effect of NH\(_3\)/NH\(_4^+\) in the copper containing ammoniacal wastewater, it is not necessary to adjust pH in it to keep large H\(^+\) gradient. Copper forms complexes with ammonia and if the ammonia concentration in the feed solution is too high, it hinders copper transfer from
To describe kinetics of the process a new “Big Carrousel” model was developed and compared with usually assumed mechanism of facilitated transport, which does not consider the ability of the carrier to leave the membrane. Mathematical model simulation demonstrated that only “Big Carrousel” model, based on the ability of the carrier to leave the membrane and to react with copper ammonia complexes in aqueous solutions, gives satisfactory quantitative description of all experimental results, including the flux plateau at high feed copper concentrations and the decrease of copper flux at lower pH of the feed solutions. Stability of supported liquid membrane is promising for practical industrial applications.

8.1.3 Treatment of Spent Ammoniacal Etching Solution with Hollow Fiber Supported Liquid Membrane (HFSLM) System: From Bench-scale to the Pilot-scale Tests

The HFSLM method is an effective way to recover copper and to regenerate spent ammoniacal etching solution. Kinetics of the process in the hollow fibre membrane module was studied and optimized. Copper can be easily removed from spent ammoniacal etching solution due to active transport using pH gradient as a driving factor. Accumulation of excess ammonia in the feed solution has negative effect on the copper removal. The effect is more significant at low copper concentration stage. Ammonia removal from the feed improves the copper removal and reduces the ammonia transfer to
the acidic stripping solution. Both sweeping gas in the additional hollow fiber membrane module and addition of HCl to the etchant can be used to decrease NH₃ concentration. The high selectivity of copper over other cations and the stability of supported liquid membrane are promising for practical industrial application.

Treated etchant solution with very low Cu concentration has chemical and physical properties, satisfying the specification of commercially available replenisher. Copper is recovered in the form of CuSO₄·5H₂O, a value added product with high purity. Furthermore, the economic evaluation and comparison with commercial Mecer® system demonstrate our Etchant Regeneration System (ERS) is both technical and economic attractive method for spent etchant treatment.

Compared with current existing Mecer system for spent ammoniacal etchant treatment, the advantages of our ERS based on SLM technology can be summarized as below:

- Extraction and re-extraction in one technological step
- Exchange of Cu(II) per two H⁺ ions allowing to remove practically 100% of the Cu(II) if necessary
- Continuous operation- can be connected to the etching system
- Small volume of organic phase- safe, nonflammable
- Two possible products: Cu sulfate pentahydrate (crystallization) and also usual Cu metal (electrowinning).
- Less space demand and less power consumption
- Green chemistry process. No secondary waste generated.
• Easy scale-up.
• Short payback time even on existing system it is less than one year.
• Protected with the US and Singapore patents.

8.1.4 The Development of Chemically Modified P84 Co-Polyimide Membranes as Supported Liquid Membrane Matrix for Cu(II) Removal with Prolonged Stability

In the SLM stability improvement studies, we investigated the engineering and science of fabricating both asymmetric and symmetric polyimide flat membrane via traditional phase inversion method. The SLM with symmetric membrane support matrix is found to be more stable than the SLM with asymmetric matrix due to its balanced force exerted at both aqueous/membrane interfaces. The proposed stagnant layers formed in the symmetric membrane pores could lead to long term stability of SLM. Room temperature and low cost chemical cross-linking modification has been demonstrated to further improve SLM stability by reducing the surface pore size of the membrane support without forming thin skin layers with significant mass transfer resistance. It could be a promising and feasible technique to improve SLMs’ stability. The surface chemical cross-linking could also “lock” the impregnating carriers inside the membrane pores. This is also favorable to form a stable SLM system.
8.2 Recommendations

Based on the experimental results obtained, discussions presented and conclusions drew from this research study, the following recommendations and suggestions given may provide further insight for future investigations related to SLM applications.

8.2.1 Other Metals Removal, Recovery, Separation and Purification

An increasing demand for metals in general and high purity metals in particular, decreasing ore grades and more stringent environmental regulations have driven researches into finding more effective and efficient methods for recycling previously used metals. Several advantages of using SLM can fulfill the above-mentioned demands. It is estimated that most of the metal elements in the periodic table can be recovered and purified based on SLM technology with proper choices of polymer membrane support matrix, organic carrier, solvent and diluent for SLM preparation and receptor solutions. The investigations can be conducted on the mass transfer mechanism and the factors that influence the liquid membrane mass transfer rates and membrane stability. The study of hydrodynamic conditions in separation process is also important for achieving optimal membrane separation effects. To make meaningful interpretation of experimental results using SLM to removal, recovery, separate and purify metals, mathematical modeling can also be carried out in future work to acquire a deeper understanding of mechanism and kinetics of mass transfer process among various process parameters. The mathematic modeling will also be utilized to engineering design of SLM separation process.
Present technologies for desalination maybe generally classified into thermal and Reverse Osmosis process. The former one suffer from some shortcomings such as high energy consumption and capital cost, labor intensive stage-wise operation, corrosion and scale formation. The latter is facing low water recoveries and membrane fouling especially a serious problem that is currently undergoing tremendous investigations. Liquid membrane has gained wide interest since it offers great potential and merits compared to solid membranes such as higher permeability, simplicity in separation, high selectivity, low energy consumption and absence if pores to be blocked or fouled as in solid membranes. Usually diffusion coefficient in liquid is three- four orders of value higher than the one in solid phase. The difference of concentrations in the two aqueous solutions separated by the membrane results in a shift of ion exchange of the carrier at both sides of membrane. Therefore, it creates a concentration gradient of salt form of the carrier in the membrane. When the extractant exhibits acidic properties, coupled counter-transport takes place. The cations will be extracted by the carrier and then transferred and concentrated in the strip solutions. When basic or neutral extractants are used, coupled anions and cations coextraction takes place.

With the combination of several Supported Liquid Membrane based processes in one plant, it will be possible to remove both cations and anions from salty and sea water. As the result new seawater treatment process based on SLM without using any external
pressure or electrical voltage will be economical and will be efficient from the energy and environmental point of view. Moreover, the appropriate carriers which are impregnated in different hollow fiber modules will have selectivity of certain ion over others. The various cations and anions in the salty and sea water can then be separated and concentrated in the various strip solutions. The recovery of ions in salty and sea water by SLM will be a significant technological breakthrough over other desalination methods.

8.2.3 Recovery and Separation of Organic Acids

Recovery and concentration of organic acids, as well as separation of acid mixtures, have attracted a great interest of researchers, especially in their recovery from fermentation broths, reaction mixtures and waste solutions [1]. Several processes employing partitioning of components on one or two liquid/liquid (L/L) interfaces have been developed to achieve separation of organic acid mixtures. Supported Liquid Membrane, a membrane-based solvent extraction technology is a relatively new alternative of classical solvent extraction. In SLM system, mass transfer between immiscible liquids occurs from the immobilised L/L interface at the mouth of pores of a microporous wall. The extraction and re-extraction are taken place at two sides of membrane/liquid interface simultaneously in one technological step. The solvent can be regenerated by where the targeted organic acid is re-extracted into the stripping solution. In this way, recovery of the solvent and concentration of the solute can be achieved.
8.2.4 Separation of Amino Acid Enantiomers

It is widely known that chirality of molecules plays a vital role in most chemical and biochemical processes where specific and selective interactions between chemical species take place. Normally only one enantiomer is known to be biological active. Thus, there is an increasing demand for optically pure enantiomers in the pharmaceutical, food and chemical industries. Many researches have been done to separate optically active compounds. However, these techniques require further processing (solvent extraction, crystallization, etc.) to separate enantio-derivative from another enantiomer.

One of the techniques scarcely applied for chiral separation is the use of SLM technology. Developing chiral carriers could be promising for large scale separation of enantiomers by SLM in hollow fiber membrane contactor. To obtain optimal conditions for chiral separation of enantiomerica amino acids by SLM, extraction is usually achieved by incorporating a chiral selector into the hydrophobic membrane material. The chiral selector can serve as a complexing agent and carriers one of the enantiomers through membrane phase into the strip phase. Various types of carrier molecules have been designed and applied for this purpose. The most important group consists of macrocyclic compounds derived from crown ethers [2, 3]. Only minute amounts of expensive chiral selectors required in order to achieve resolutions of enantiomers can serve as a powerful tool for examining specific stereo-interactions between selectors and biological active amino acids.
All the modifiers, diluents are achiral organic solvents which have dramatic influence on the extraction of chiral molecules because of solvate effect, hydrogen bridging, etc. [4]. The appropriate choice of achiral membrane solvent or diluent should be conducted because all of them may fundamentally determine membrane enantioseparation success of failure [5].
References


LIST OF PUBLICATIONS

Journal Paper:


**Conference Paper:**


**Patent filing:**

1. Q. Yang, T.S. Chung, Modification of the commercial carrier in supported liquid membrane system to enhance lactic acid flux and to separate L, D-lactic acid enantiomers.