

Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be “used for any purpose other than private study, scholarship, or research.” If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of “fair use” that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation

Printing note: If you do not wish to print this page, then select “Pages from: first page # to: last page #” on the print dialog screen

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

ABSTRACT

MIXED METAL REMOVAL AND RECOVERY BY HOLLOW FIBER MEMBRANE- BASED EXTRACTIVE ADSORBER

by
Ramprakash Chilukuri

The feasibility and efficiency of simultaneous removal of multiple cations as well as anionic heavy metals from wastewater into a mixed extractant kept stagnant on the shell side of a 2-fiber-set hollow fiber membrane extractor operated as a fixed bed adsorber was explored. The novel extracting solvent was a mixture of an acidic or chelating extracting agent for one or more cations and a basic extracting agent, e.g., trioctylamine (TOA) for extracting anions; both were dissolved in the same diluent kerosene for simultaneous and synergistic extraction of cations and anions. In the stripping part of the fixed bed operation, alkaline stripping solution was passed through one set of fibers to strip anions while acidic stripping solution was passed through the second fiber set to recover and concentrate cations. For removal and individual recovery of Cu(II), Cr(VI) and Zn(II), one module of this research will replace five modules needed for individual removal and recovery of these heavy metals.

Batch experiments conducted for Cu(II) and Cr(VI) system using a mixed extractant containing LIX 84 and TOA in kerosene showed that Cu(II) and Cr(VI) can be efficiently removed simultaneously. Fixed bed studies showed that Cu(II) and Cr(VI) concentrations can be reduced to less than 1 ppm from a feed containing about 200 ppm Cu(II) and 100 ppm Cr(VI). Batch and fixed bed experiments conducted for Cu(II), Zn(II) and Cr(VI) system using a mixed extractant containing LIX 84, di-2-ethylhexyl phosphoric acid (D2EHPA) and TOA in kerosene showed that, Cu(II), Zn(II) and Cr(VI) can be efficiently removed simultaneously.

**MIXED METAL REMOVAL AND RECOVERY BY HOLLOW FIBER
MEMBRANE-BASED EXTRACTIVE ADSORBER**

by
Ramprakash Chilukuri

A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Master of Science in Chemical Engineering

Department of Chemical Engineering,
Chemistry, and Environmental Science

October 1997

Blank Page

APPROVAL PAGE

**MIXED METAL REMOVAL AND RECOVERY BY HOLLOW FIBER
MEMBRANE-BASED EXTRACTIVE ADSORBER**

Ramprakash Chilukuri

Dr. Kamallesh K. Sirkar, Thesis Advisor Date
Professor of Chemical Engineering
New Jersey Institute of Technology

Dr. Robert Luo, Committee Member Date
Assistant Professor of Chemical Engineering
New Jersey Institute of Technology

Dr. Norman Loney, Committee Member Date
Associate Professor of Chemical Engineering
New Jersey Institute of Technology

BIOGRAPHICAL SKETCH

Author: Ramprakash Chilukuri

Degree: Master of Science

Date: October 1997

Undergraduate and Graduate Education:

- Master of Science in Chemical Engineering,
New Jersey Institute of Technology, Newark, NJ, 1997
- Bachelor of Technology in Chemical Engineering (B.Tech),
Indian Institute of Technology (IIT),
Kharagpur, India, 1995

Major: Chemical Engineering

To my parents

ACKNOWLEDGEMENT

I would like to express my sincere thanks to my advisor, Professor Kamalesh K. Sirkar, for his valuable advice and constant support and guidance throughout this research. I would also like to thank Dr. Norman Loney and Dr. Robert Luo for participating in my thesis committee.

I would like to thank all members of the Membrane Separation and Biotechnology group for their constant support and timely suggestions. In particular, I would like to thank Dr. Majumdar, Dr. Shanbag and Mr. Sarma for helping me in making the module. I would also like to thank Dr. Yang for helping me in the initial stages of research. I would like to thank Mr. Clint Brockway for his constant help throughout this research. I would like to specially thank Ashish and Das for their help and friendship.

Finally, I would like to express my sincere gratitude to my family members and brother-in-law for their incessant encouragement and moral support.

TABLE OF CONTENTS

Chapter	Page
1 INTRODUCTION	1
1.1 The Problem Genesis	1
1.2 Membrane Based Solvent Extraction.....	2
1.3 Metal Extraction Chemistry	4
1.4 Hollow Fiber Membrane Extractor Configurations	7
1.5 Present Research	9
2 EXPERIMENTAL.....	11
2.1 Chemicals Used	11
2.2 Extractive Adsorber and its Fabrication.....	11
2.3 Analytical.....	13
2.4 Batch Extraction/ Back Extraction Experiments	13
2.4.1 Copper -Chromium System	13
2.4.2 Copper, Zinc and Chromium System.....	14
2.2 Extractive Membrane Adsorber Operation	14
2.6 Calculated Quantities	16
3 RESULTS AND DISCUSSION	19
3.1 Copper and Chromium System.....	19
3.1.1 Batch Extraction Results.....	19
3.1.2 Introduction to Fixed Bed Extraction Results.....	26
3.1.3 Effect of Mixed Extractant Composition on the Breakthrough Behavior of Cu(II)	26

TABLE OF CONTENTS
(Continued)

Chapter	Page
3.1.4 Effect of Mixed Extractant Composition on the Breakthrough Behavior of Cr(VI)	32
3.1.5 Effect of Feed Flow Rate on the Breakthrough Behavior of Cu(II)	35
3.1.6 Effect of Feed Flow Rate on the Breakthrough Behavior of Cr(VI)	35
3.1.7 Effect of Feed Concentration on the Breakthrough Behavior of Cu(II) and Cr(VI).....	38
3.1.8 Variation of pH with Time.....	38
3.1.8 Fixed Bed Stripping Results	46
3.2 Copper, Zinc and Chromium System	47
3.2.1 Batch Extraction Results	47
3.2.2 Fixed Bed Extraction Results	52
3.2.3 Effect of Feed Flow Rate on Extraction of Cu(II), Zn(II) and Cr(VI)	53
3.2.4 Effect of Mixed Extractant Composition on Extraction of Cu(II), Zn(II) and Cr(VI)	53
4 MODELING	64
4.1 Simplified Model for Batch Extraction of Cu(II) with LIX 84 and TOA in Kerosene	64
5 CONCLUSIONS	71
APPENDIX A.....	73
A.1 Bed Volume Calculations	73
A.2 Computer Program for solving the equation set in chapter 4	74a
REFERENCES	75

LIST OF TABLES

Table	Page
2.1 Technical Information on LIX 84.....	18
3.1 Batch Experimental Results for Copper and Chromium System with 0.156 M LIX 84 + 0.156 M TOA in Kerosene	20
3.2 Batch Experimental Results for Copper and Chromium System with 0.234 M LIX 84 + 0.234 M TOA in Kerosene	20
3.3 Batch Experimental Results for Copper and Chromium System with 0.312 M LIX 84 + 0.312 M TOA in Kerosene	21
3.4 Extractor Performance for Cu(II) = 225 ppm, Cr(VI) = 108 ppm, pH = 4.1, LIX 84 = 15%, TOA = 10%, Flow Rate = 1.4 mL/min	41
3.5 Extractor Performance for Cu(II) = 225 ppm, Cr(VI) = 108 ppm, pH = 4.1, LIX 84 = 15%, TOA = 10%, Flow Rate = 1.9 mL/min	41
3.6 Extractor Performance for Cu(II) = 225 ppm, Cr(VI) = 108 ppm, pH = 4.1, LIX 84 = 15%, TOA = 5%, Flow Rate = 1.0 mL/min	42
3.7 Extractor Performance for Cu(II) = 235 ppm, Cr(VI) = 107 ppm, pH = 4.1, LIX 84 = 15%, TOA = 5%, Flow Rate = 2.0 mL/min	42
3.8 Extractor Performance for Cu(II) = 215 ppm, Cr(VI) = 98 ppm, pH = 4.1, LIX 84 = 10%, TOA = 5%, Flow Rate = 2.0 mL/min	43
3.9 Extractor Performance for Cu(II) = 215 ppm, Cr(VI) = 98 ppm, pH = 4.1, LIX 84 = 10%, TOA = 5%, Flow Rate = 1.0 mL/min	43
3.10 Extractor Performance for Cu(II) = 215 ppm, Cr(VI) = 98 ppm, pH = 4.1, LIX 84 = 20%, TOA = 10%, Flow Rate = 2.0 mL/min	44
3.11 Extractor Performance for Cu(II) = 215 ppm, Cr(VI) = 98 ppm, pH = 4.1, LIX 84 = 20%, TOA = 10%, Flow Rate = 1.0 mL/min	44
3.12 Extractor Performance for Cu(II) = 215 ppm, Cr(VI) = 98 ppm, pH = 4.1, LIX 84 = 20%, TOA = 10%, Flow Rate = 3.0 mL/min	45
3.13 Extractor Performance for Cu(II) = 195 ppm, Cr(VI) = 258 ppm, pH = 4.1, LIX 84 = 25%, TOA = 16.67%, Flow Rate = 2.0 mL/min.....	45

LIST OF TABLES
(Continued)

Table	Page
3.14 Extractor Performance for Cu(II) = 350 ppm, Cr(VI) = 258 ppm, pH = 4.1, LIX 84 = 20%, TOA = 5%, Flow Rate = 2.0 mL/min	46
3.15 Stripping Performance at 2 M H ₂ SO ₄ , Flow rate = 0.6 mL/min, 0.1 M NaOH Flow rate = 0.4 mL/min	46
3.16 Batch Experimental Results for Copper, Zinc and Chromium System with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, LIX 84 = 5%, TOA = 15%, D2EHPA = 5%.....	48
3.17 Batch Experimental Results for Copper, Zinc and Chromium System with Cu(II) = 110 ppm, , Zn(II) = 153 ppm, Cr(VI) = 147 ppm LIX 84 = 10%, TOA = 15%, D2EHPA = 10%.....	48
3.18 Batch Experimental Results for Copper, Zinc and Chromium System with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, LIX 84 = 5%, TOA = 20%, D2EHPA = 5%.....	49
3.19 Batch Experimental Results for Copper, Zinc and Chromium System with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, LIX 84 = 10%, TOA = 10%, D2EHPA = 10%.....	49
3.20 Batch Experimental Results for Copper, Zinc and Chromium System with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, LIX 84 = 0%, TOA = 10%, D2EHPA = 20%.....	50
3.21 Batch Experimental Results for Copper, Zinc and Chromium System with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, LIX 84 = 0%, TOA = 5%, D2EHPA = 10%.....	50
3.22 Batch Experimental Results for Copper, Zinc and Chromium System at Different Mixed Extractant Compositions at a Feed pH of 4.0.....	51
3.23 Extractor Performance for Cu(II) = 105.2 ppm, Zn(II) = 115 ppm, Cr(VI) = 65 ppm, Flow Rate = 0.775 mL/min, pH ~ 4.1, LIX 84 = 15%, D2EHPA = 15%, TOA = 7%.....	54

LIST OF TABLES
(Continued)

Table	Page
3.24 Extractor Performance for Cu(II) = 160 ppm, Zn(II) = 93 ppm, Cr(VI) = 69.6 ppm, Flow Rate = 0.60 mL/min, pH ~ 4.1, LIX 84 = 15%, D2EHPA = 15%, TOA = 8%.....	55
3.25 Extractor Performance for Cu(II) = 160 ppm, Zn(II) = 93 ppm, Cr(VI) = 69.6 ppm, Flow Rate = 0.40 mL/min, pH ~ 4.1, LIX 84 = 15%, D2EHPA = 15%, TOA = 7%.....	55
3.26 Extractor Performance for Cu(II) = 156 ppm, Zn(II) = 97.5 ppm, Cr(VI) = 79 ppm, Flow Rate = 0.40 mL/min, pH ~ 4.1, LIX 84 = 15%, D2EHPA = 15%, TOA = 8%.....	56
3.27 Extractor Performance for Cu(II) = 156 ppm, Zn(II) = 97.5 ppm, Cr(VI) = 79 ppm, Flow Rate = 0.80 mL/min, pH ~ 4.1, LIX 84 = 15%, D2EHPA = 15%, TOA = 8%.....	56
3.28 Extractor Performance for Cu(II) = 140 ppm, Zn(II) = 100 ppm, Cr(VI) = 69 ppm, Flow Rate = 1.0 mL/min, pH ~ 4.1, LIX 84 = 10%, D2EHPA = 10%, TOA = 7%.....	57
3.29 Extractor Performance for Cu(II) = 140 ppm, Zn(II) = 100 ppm, Cr(VI) = 69 ppm, Flow Rate = 0.65 mL/min, pH ~ 4.1, LIX 84 = 10%, D2EHPA = 10%, TOA = 7%.....	57
4.1 Comparison Between Experimental Results and Simulated Results for Batch Extraction of Cu(II) with a Mixed Extractant Containing 0.156 M LIX 84 + 0.156 M TOA in Kerosene.....	67
4.2 Comparison Between Experimental Results and Simulated Results for Batch Extraction of Cu(II) with a Mixed Extractant Containing 0.234 M LIX 84 + 0.234 M TOA in Kerosene.....	68

LIST OF FIGURES

Figure	Page
1.1 Nondispersive Solvent Extraction Concept Employing Either a Microporous Hydrophobic Membrane or a Microporous Hydrophilic Membrane.....	3
2.1 Setup of The Extractive Adsorber for Simultaneous Removal of Heavy Metals from Wastewater	15
2.2 Setup of Simultaneous and Individual Stripping of Heavy Metals from the Extractive Adsorber	17
3.1 Effect of Feed Concentration on the Distribution Coefficient of Cr(VI) at Different Mixed Extractant Concentrations in a Batch Extraction System	22
3.2 Effect of Feed Concentration on the Distribution Coefficient of Cu(II) at Different Mixed Extractant Concentrations in a Batch Extraction System	23
3.3 Effect of Feed Concentration on the Equilibrium pH at Different Mixed Extractant Concentrations	25
3.4 Effect of Feed Concentration on the Distribution Coefficients of Cu(II) and Cr(VI)	27
3.5 Effect of Feed Concentration on the Distribution Coefficients of Cu(II) and Cr(VI)	28
3.6 Effect of Feed Concentration on the Distribution Coefficients of Cu(II) and Cr(VI)	29
3.7 Effect of Mixed Extractant Composition on the Breakthrough Behavior of Cu(II) at a Feed Flow Rate of 2 mL/min	30
3.8 Effect of Mixed Extractant Composition on the Breakthrough Behavior of Cu(II) at a Feed Flow Rate of 1 mL/min	31
3.9 Effect of Mixed Extractant Composition on the Breakthrough Behavior of Cr(VI) at a Feed Flow Rate of 2 mL/min	33
3.10 Effect of Mixed Extractant Composition on the Breakthrough Behavior of Cr(VI) at a Feed Flow Rate of 1 mL/min	34

LIST OF FIGURES
(Continued)

Table	Page
3.11 Effect of Feed Flow Rate on the Breakthrough Behavior of Cu(II) at a Mixed Extractant Composition of LIX 84 = 20 %, TOA = 10 % in Kerosene	36
3.12 Effect of Feed Flow Rate on the Breakthrough Behavior of Cr(VI) at a Mixed Extractant Composition of LIX 84 = 20 %, TOA = 10 % in Kerosene	37
3.13 Variation of pH with Time for Different Feed Flow Rates at a Mixed Extractant Composition of LIX 84 = 20 %, TOA = 10 % in Kerosene	39
3.14 Variation of pH with Time for Different Mixed Extractant Compositions at a Feed Flow Rate of 2 mL/min	40
3.15 Effect of Feed Flow Rate on the Breakthrough Behavior of Zn(II).....	58
3.16 Effect of Feed Flow Rate on the Breakthrough Behavior of Cu(II)	59
3.17 Effect of Feed Flow Rate on the Breakthrough Behavior of Cr(VI).....	60
3.18 Effect of Mixed Extractant Composition on the Breakthrough Behavior of Zn(II).....	61
3.19 Effect of Mixed Extractant Composition on the Breakthrough Behavior of Cu(II)	62
3.20 Effect of Mixed Extractant Composition on the Breakthrough Behavior of Cr(VI)	63
4.1 Comparison Between Experimental Results and Simulated Results for Batch Extraction of Cu(II) with a Mixed Extractant Containing 0.156 M LIX 84 + 0.156 M TOA in Kerosene.....	69
4.2 Comparison Between Experimental Results and Simulated Results for Batch Extraction of Cu(II) with a Mixed Extractant Containing 0.156 M LIX 84 + 0.156 M TOA in Kerosene.....	70

CHAPTER 1

INTRODUCTION

1.1 Problem Genesis

Electroplating, electronics, photographic, smelting, nuclear industries, etc. produce large volumes of dilute but hazardous waste streams containing a variety of heavy metals. In addition, surface and ground waters in many places are similarly contaminated. Current treatment of heavy metal-contaminated industrial waste waters rely often on precipitation creating a solid waste stream needing disposal. It would be most useful to recover these metals individually in a concentrated form for reuse at the location or elsewhere and simultaneously obtain treated water for reuse. Although many chemical, physical and biological treatment technologies are available, they all have advantages and shortcomings.

Solvent extraction may be used to remove efficiently toxic heavy metals, e.g., Zn, Cu, Cr, Cd, Hg, etc. from effluents to environmentally acceptable levels and recycle these metals to the original processes (Ritcey and Ashbrook, 1984; Lo et al., 1983). Pilot plant studies have been made (Lo et al., 1983), but no economic information is available. It is also widely employed in the separation of organic acids and purification of bioproducts, e.g., antibiotics, amino acids, peptides etc. Conventionally-practiced solvent extraction relies on dispersion which causes loss of extractants as well as the solute. Dispersion-free contacting of immiscible phase pairs using microporous membranes is being explored increasingly for equilibrium separation of liquid solutions or gaseous mixtures. Microporous membrane-based nondispersive solvent extraction techniques have been developed recently (Kiani et

al., 1984; Prasad and Sirkar, 1988; Yun et al., 1993; Seibert and Sengupta, 1994). The basic principle of nondispersive extraction is the immobilization of the aqueous-organic interface in the pores of hydrophobic membranes employing preferential wetting tendencies and appropriately applied static pressure differences (Kiani et al., 1984).

1.2 Membrane-Based Solvent Extraction

Dispersion free membrane-based solvent extraction has been implemented with both microporous hydrophobic membranes and microporous hydrophilic membranes. In the case of microporous hydrophobic membranes, an organic phase on one side will spontaneously wet the membrane and come out to the other side through the membrane pores. This can be prevented if an immiscible aqueous phase is maintained on the other side at a pressure higher than that of the organic phase (Kiani et al., 1984). The aqueous-organic interface is immobilized at each pore mouth on the aqueous side of the membrane (Figure 1.1). Solutes or solute transfer through the phase interfaces from one phase to another and then to the bulk of the latter phase. The aqueous phase will not appear on the other side unless the excess aqueous phase pressure exceeds a critical value, Δp_{cr} , called the breakthrough pressure.

Similarly, in the case of hydrophilic microporous membranes, pores are preferentially filled with the aqueous phase and the aqueous-organic interface is immobilized at each pore mouth on the organic side of the membrane. The organic phase will not appear on the other side unless the excess pressure of the organic phase exceeds the critical pressure, Δp_{cr} . Hollow fiber membranes in the shell-and-tube module form have been commonly employed for membrane-based solvent extraction (Prasad and Sirkar, 1992).

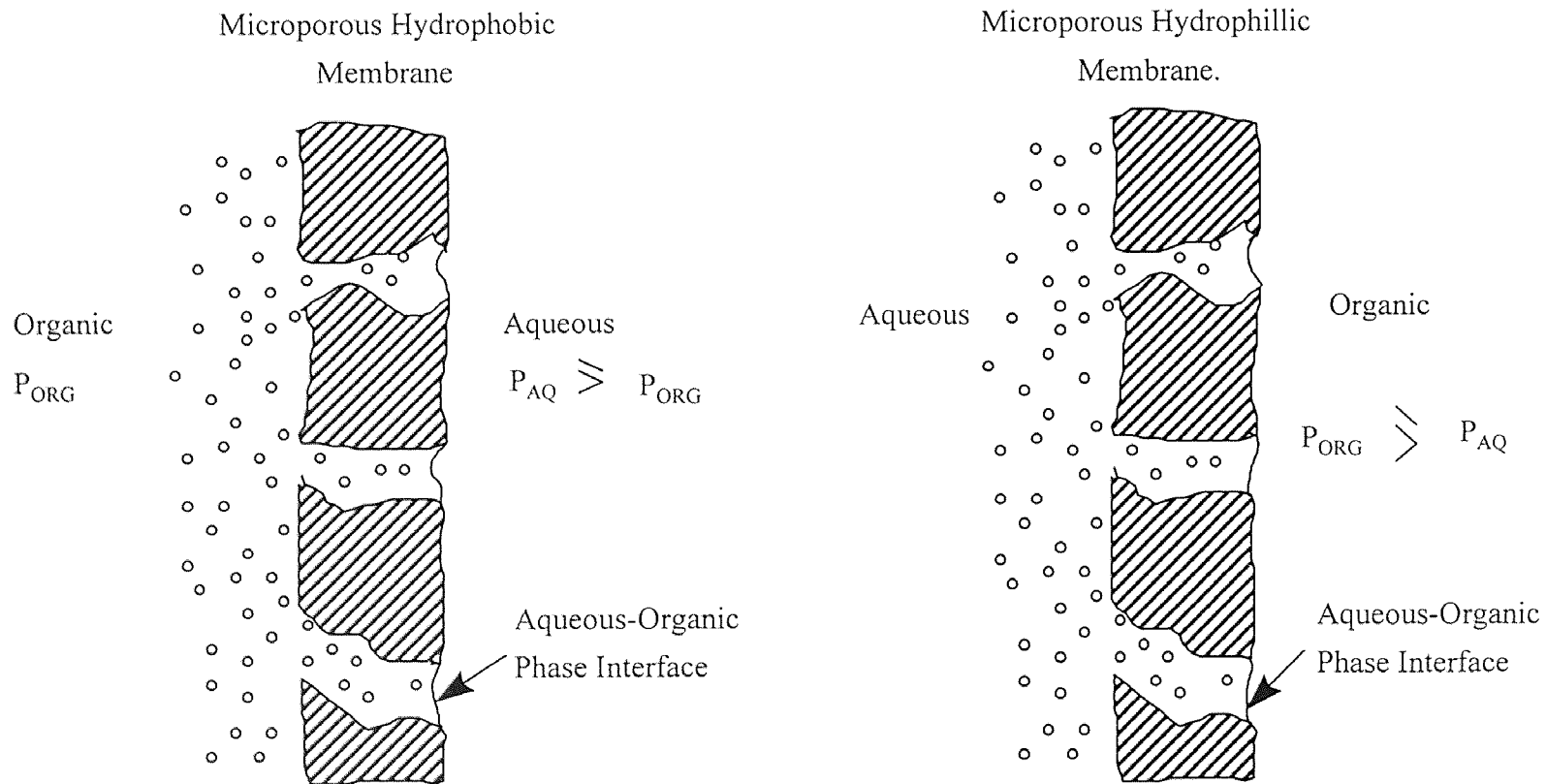


Figure 1.1 Nondispersive solvent extraction concept employing either a microporous hydrophobic or a microporous hydrophilic membrane

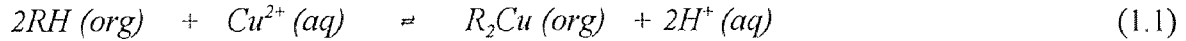
Such a technique with microporous hollow fibers (MHF) can provide high mass transfer rates per unit volume since hollow fibers can pack an enormous surface area (Kiani et al., 1984). The technique also overcomes other shortcomings such as flooding limitations on independent variation of phase flow rates, requirement of density difference, and the inability to handle particulates. These advantages suggest exploration of membrane-based extraction to solve important problems. This technique has already been applied to a large variety of systems. These include metal extraction, organic acid extraction, alcohol extraction, protein extraction, priority pollutant extraction, pharmaceutical products extraction, aromatics extraction etc.

1.3 Metal Extraction Chemistry

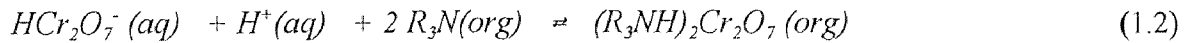
Heavy metal-contaminated wastewaters often contain a mixture of different cations and anions. For example, Cu, Zn, Ni etc. are present as cations whereas Cr(VI), Hg, Cd etc. are commonly found as anions. To prevent pollution while achieving resource recovery/recycling, heavy metals are to be recovered individually from such waste streams and concentrated. Selective solvent extraction/concentration of individual heavy metals using metal-specific extractants is an attractive option.

Solvent extraction of one metal over another having the same ionic form in an aqueous waste stream by a given organic extractant is highly pH dependent (Ritcey and Ashbrook, 1984). Even the extraction of an individual metal depends strongly on the aqueous solution pH. If a heavy metal is present as a cation, it can be extracted by an organic acidic or chelating extractant present in an organic diluent (Ritcey and Ashbrook, 1984). For

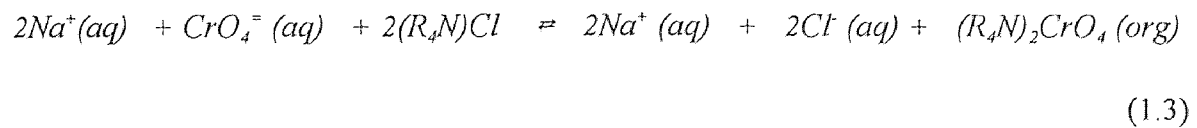
example, copper can be successfully and selectively extracted using a chelating extractant like LIX 64, a liquid ion exchanger (represented as RH), in an organic diluent (Lee et al., 1978; Pearson, 1983):



The heavy metal may be present as an anion. For example, in a highly acidic solution Cr(VI) will be primarily present as $HCr_2O_7^-$ (Hochhauser and Cussler, 1975). It can be extracted via ion-pair formation with a proton using a long chain alkyl amine (say, a tertiary amine represented as R_3N):



Alternatively, if the feed aqueous solution is basic, Cr(VI) will be present primarily as CrO_4^{2-} . Then one can extract Cr(VI) from an aqueous solution of, say, Na_2CrO_4 by anion-exchange with quaternary ammonium compounds (R_4NCl) like Aliquat 336 in a diluent:

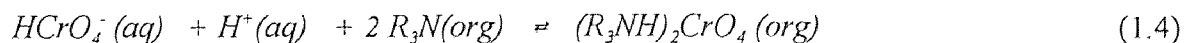


Such extractions of metal into an organic extractant present in a diluent have been carried out successfully and nondispersively using hollow fiber membrane extractors (Yun et al., 1993). Simultaneous back-extraction of a metal into a very acidic stripping solution (for Cu^{2+}) or a very alkaline stripping solution (for Cr(VI)) has been successfully achieved in a hollow fiber contained liquid membrane (HFCLM) device in a stable fashion

(Guha et al., 1994). In one of the studies mentioned above (Yun et al., 1993), the first phase involved determination of the distribution coefficient/equilibrium constant of each metal between the aqueous solution and the organic diluent having a suitable extracting agent. This was followed by the extraction of each heavy metal using a microporous hydrophobic hollow fiber module in separate experiments with the aqueous solution flowing on the tube side and the extracting solvent phase flowing countercurrently on the shell side.

In the extraction of copper, as the proton is released to the waste solution, the effective distribution coefficient m_i of copper between the organic extractant and the wastewater is reduced; this can significantly and depending on the pH range drastically reduce copper extraction efficiency (Yun et al., 1993). The same is true with Zn^{2+} and Ni^{2+} etc.

If, however, a heavy metal present as an anion in the wastewater is simultaneously extracted into a basic amine-containing organic extractant via an ion-pair formation mechanism, the proton released by reaction (1) will be consumed; the pH range in the wastewater may be controlled (Yang et al., 1996a). An example of such a synergy is provided if Cr(VI), in the form of $HCrO_4^-$, say, is simultaneously extracted via the reaction:



which consumes the protons released by reaction (1). It is important to recognize here that individual recovery of each of the metals, Cu(II) and Cr(VI), in this fashion requires that we have two separate organic streams, one containing an acidic/chelating extractant and the other containing a basic amine extractant, contact the aqueous waste stream locally.

1.4 Hollow Fiber Membrane Extractor Configurations

Such an extractor configuration was conveniently realized via microporous hollow fiber membrane-based solvent extraction (Yun et al., 1993) and two-separate-fiber-set-based membrane extractor by Yang et al. (1996a). Through the bore of one set of microporous hydrophobic hollow fibers flowed an acidic extractant e.g. LIX 84 in a diluent; through the bore of the other set of microporous hydrophobic hollow fibers flowed a basic organic extractant such as n-trioctylamine (TOA) in a diluent. The aqueous waste stream is allowed to flow on the shell side of the membrane extractor. Metals present as cations (Cu^{2+} , Zn^{2+} , Ni^{2+} etc.) were extracted nondispersively into the acidic extractant stream flowing through the bore of the fiber set 1; metals present as anions (HCrO_4^-) were extracted into the basic extractant stream in fiber set 2, simultaneously and locally. Thus synergy due to pH control was achieved in such a configuration.

Using such a device and hollow fiber membrane-based solvent extraction, Yang et al. (1996a) were able to achieve another new dimension in metal extraction. They considered individual recovery of two cations, Cu^{2+} and Zn^{2+} , often present simultaneously in leach streams in hydrometallurgical processes. It is well known that LIX 84 and D2EHPA can extract individually and selectively Cu^{2+} and Zn^{2+} respectively under particular conditions (Lo et al., 1983). In reality, a lot of Cu^{2+} and Zn^{2+} will be coextracted by D2EHPA and LIX 84 respectively, leading to a poorer separation of Zn^{2+} and Cu^{2+} .

Yang et al. (1996a) used the hollow fiber membrane device mentioned above to selectively extract Cu^{2+} and Zn^{2+} , which is achieved due to synergy. Through the bore of one set of hollow fibers flowed LIX 84 in a diluent and D2EHPA in a diluent flowed through

the bore of the other set of fibers as the aqueous feed containing Cu^{2+} and Zn^{2+} flowed on the shell side. As Cu^{2+} was extracted by the extractant LIX 84 in fiber set 1, less Cu^{2+} was available for extraction by D2EHPA in fiber set 2. Similarly, as Zn^{2+} was extracted by D2EHPA, less Zn^{2+} was available in the shell side aqueous stream for extraction by LIX 84 in the fiber set 1. Thus LIX 84 stream contained much less coextracted Zn^{2+} as the D2EHPA stream coextracted much less Cu^{2+} . A much higher selectivity was achieved in the individual extraction of both Cu^{2+} and Zn^{2+} .

Yang et al. (1996b) went further and proposed a mixed solvent extraction system containing an acidic as well as a basic organic extractant in an organic diluent. Yang et al. (1996b) showed via batch stirred solvent extraction studies that both cationic as well as anionic heavy metallic species could be simultaneously and efficiently extracted into the mixed extractant. Thus, it was no longer necessary to have separate organic extractant phases to extract cationic and anionic forms of heavy metal ions in a solution as was done by Yang et al. (1996a). They also studied the back extraction (stripping) of each heavy metal into a separate and appropriate aqueous stripping solution consecutively. They next constructed a tubular device containing three different sets of intermingled microporous hydrophobic hollow fibers to simultaneously extract cationic and anionic heavy metallic species from waste water flowing through the bore of one set of hollow fibers into the shell-side organic solvent containing mixed extractant in a diluent. Two separate aqueous stripping solutions (one highly acidic for the cationic species and another basic for the anionic species) were passed through the bores of two additional and separate fiber sets.

1.5 Present Research

The objectives of the present research are as follows.

- 1) Study the feasibility, efficiency and equilibrium behavior in simultaneous extraction of a mixture of cationic heavy metals (Cu^{2+} , Zn^{2+} , Ni^{2+} etc.) and anionic heavy metals (Cr^{6+} present as HCrO_4^- etc.) into a solvent mixture of acidic extractants (e.g. anti-2-hydroxy-5-nonylacetophenone oxime (LIX 84), di-2-ethylhexyl phosphoric acid (D2EHPA) and basic extractants (e.g. TOA) in a diluent.
- 2) Study the fixed-bed behavior of a hollow fiber membrane-based extractor acting as an extractive adsorber for a mixed metal feed solution and a stagnant mixed extractant on the shell side.
- 3) Study the regeneration of the shell-side mixed extractant by sequential stripping of cations and simultaneous stripping of anions employing a two-fiber-set membrane extractor.

To achieve these objectives, research was conducted in several phases. The first phase involved the study of batch extraction equilibrium behavior of mixed heavy metals between water and a mixed organic extractant followed by a study of the batch stripping behavior of mixed heavy metals from the mixed extractant into a sequence of stripping solutions (highly acidic for cations and highly basic for anions). In the second phase, a microporous hollow fiber membrane-based device was developed and the extraction process was studied where the device functioned as a fixed bed adsorber. This involved fixed bed extraction study of the breakthrough behavior of mixed heavy metals in aqueous waste solutions. Finally, this study involved the sequential stripping of metal cations and simultaneous stripping of anions from the shell-side solvent in the hollow fiber device.

One such module will replace five modules needed for individual removal and recovery of Cu^{2+} , Zn^{2+} , and Cr^{6+} (Yang et al., 1996a). The fixed bed adsorber fabricated consisted of two sets of microporous hydrophobic polypropylene hollow fibers. The aqueous stream containing a mixture of heavy metals flowed through the bores of both set of hollow fibers and the shell side contained the stagnant mixed extractant in a diluent. The tube-side pressure was always maintained higher than the shell-side pressure (Kiani et al., 1984; Prasad and Sirkar, 1988) to keep the reaction interface at the inside wall of the lumen, since the membrane was hydrophobic.

Batch extraction experiments were done with aqueous feeds containing Cu^{2+} and Cr^{6+} and a mixed extractant consisting of LIX 84 and TOA in kerosene. This was followed by fixed bed extraction study of the breakthrough behavior of Cu^{2+} and Cr^{6+} . Batch extraction experiments were also conducted with aqueous feeds containing Cu^{2+} , Zn^{2+} , and Cr^{6+} and a mixed extractant consisting of LIX 84, D2EHPA and TOA in kerosene. This was followed by fixed bed extraction study of the breakthrough behavior of Cu^{2+} , Zn^{2+} , and Cr^{6+} . Preliminary modeling of Cu^{2+} extraction in a batch system of mixed extractants containing LIX 84 and TOA in kerosene has been carried out.

CHAPTER 2

EXPERIMENTAL

2.1 Chemicals Used

LIX 84 (anti-2-hydroxy-5-nonylacetophenone oxime) (Henkel, Tucson, AZ) , tri-n-octylamine (TOA) (Fluka, Ronkonkoma, NY) and di-2-ethylhexyl phosphoric acid (D2EHPA) (Sigma, St Louis, MO) diluted in kerosene (Fisher Scientific, Springfield, NJ) were used as extractants for Cu^{+2} , Cr^{+6} and Zn^{+2} respectively. Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) (Fisher Scientific, Springfield, NJ) were used for preparing the feed solution. The pH of the feed solution was adjusted using 0.1M H_2SO_4 or 0.1M NaOH.

2.2 Extractive Adsorber and its Fabrication

The extractive adsorber consisted of two sets (1000 fibers each) of microporous hydrophobic hollow fiber membranes (HFM) of polypropylene (Celgard X-10, 100 μm I.D, 150 μm O.D ; Hoechst Celanese SPD, Charlotte, NC). The first step in the fabrication procedure involved counting of the first set of 1000 fibers and laying them over a polyethylene sheet on a table. Six fibers were carefully taken at a time from the spool and cut to the desired length. The fibers were kept in place using a scotch tape at both ends. The left over sticky portion of the scotch tape was covered with pieces of scotch tape. After laying out the first set of 1000 fibers, a scotch tape was placed on the earlier scotch tape all along its length. The second step involved laying the second set of 1000 fibers

symmetrically over the first set of 1000 fibers. The ends of these fibers were stuck to the scotch tape which was placed on the first scotch tape. The left over sticky parts of the scotch tape were covered with pieces of scotch tape. Then the scotch tapes at the end were removed from the fiber mat which was kept wet with water. Both sets of fibers were mixed properly and were rolled into a bundle with two separate ends on each side. The two ends of each set of fiber bundles were tied with cotton threads and the scotch tape was removed.

The two-fiber-set bundle was soaked in water and pulled into a transparent Teflon FEP tube (1.27 cm I.D, and 1.43 cm O.D; Cole Parmer, Chicago, IL) which was used as the shell for the extractive adsorber. The shell was connected to cross joints at both ends through which the two sets of hollow fibers were pulled. The module was next dried with air for about 24 hrs. The module was then ready for potting of the tube sheet. The first layer (outer layer) of potting was made of a mixture of A-2 resin and Activator A (Armstrong Products, Easton, MA). The module was then left for curing for about 24 hours. The second layer (inner layer) of potting was made by mixing C-4 resin and D activator (Beacon Chemicals, Mt. Vernon, NY) in a 4 to 1 weight proportion. The module potting was allowed to cure for about a week. After a week the module was pressure tested at about 10 psi for any leaks by passing water in the shell side. The pumps used were Masterflex Model 250 (Cole Parmer, Chicago, IL).

2.3 Analytical

Thermo-Jarrel Model 12 Atomic Absorption Spectrophotometer (AAS) was used for measuring concentrations of Cu^{+2} , Cr^{+6} and Zn^{+2} in the aqueous solutions using individual hollow cathode lamps and conventional flame condition with fuel (acetylene) to air ratio of 3:9. For measurement of Cu^{+2} , high concentrations were diluted to a linear calibration range of 1-40 mg/L; measurements were made at 216.5 nm with a slit width of 0.15 nm. The concentration measurement of chromium was similar to that of copper except that the linear calibration range was 1-20 mg/L, and the wavelength and the slit width used were 425.4 nm and 0.5 nm respectively. For measurement of Zn^{+2} , high concentrations were diluted to a linear calibration range of 0-0.4 mg/L; measurements were made at a wavelength of 213.9 with a slit width of 1.0 nm. The pH of the aqueous phase was measured using a Corning pH meter (Model 250, relative accuracy = 0.001 pH error, Fisher Scientific, Springfield, NJ).

2.4 Batch Extraction/Back- Extraction Experiments

2.4.1 Copper-chromium System

Extraction was carried out by stirring 20 mL of aqueous feed solution containing copper sulfate and potassium dichromate with 20 mL of solvent containing LIX84 and TOA in kerosene for about 30 min. After separating the aqueous and organic phases, the loaded organic containing Cu^{+2} and Cr^{+6} was stirred with 20 mL of 0.1M NaOH solution for about 30 min. After separation of the aqueous and organic phases, the organic phase containing mostly Cu^{+2} was stirred with 20 mL of 2M H_2SO_4 for another 30 min. These

experiments were carried out in a 150 mL beaker. The aqueous and organic phases were separated using a separating funnel. The pH of the raffinate phase was measured after every extraction.

2.4.2 Copper, Zinc and Chromium System

Feed solution was made by dissolving copper sulfate, zinc sulfate and potassium dichromate in deionized water. The organic extractant contained LIX 84, DE2HPA and TOA in the diluent kerosene. The optimum feed pH for extraction was determined by a series of batch extraction experiments with feed solutions of pH's ranging from 2.5-4.5. The operation of the extractive adsorber involved exactly similar conditions and is provided below.

2.5 Extractive Membrane Adsorber Operation

During the extraction phase, the feed solution was pumped through the bores of both sets of hollow fiber membranes (Figure 2.1). The shell side was filled up with the stagnant organic phase consisting of LIX 84 and TOA in the diluent kerosene. Extraction was carried out until breakthrough was observed (typically after 4-6 hours), i.e. the treated solution started showing significant heavy metal concentration. Samples were collected after every 20-30 min for about 10-20 min and the flow rates were measured. pH of the samples collected was measured. Feed solution was prepared by dissolving cupric sulfate and potassium dichromate in deionized water. After the breakthrough, the tube side and the shell side were flushed with deionized water and heptane respectively for about 20-30

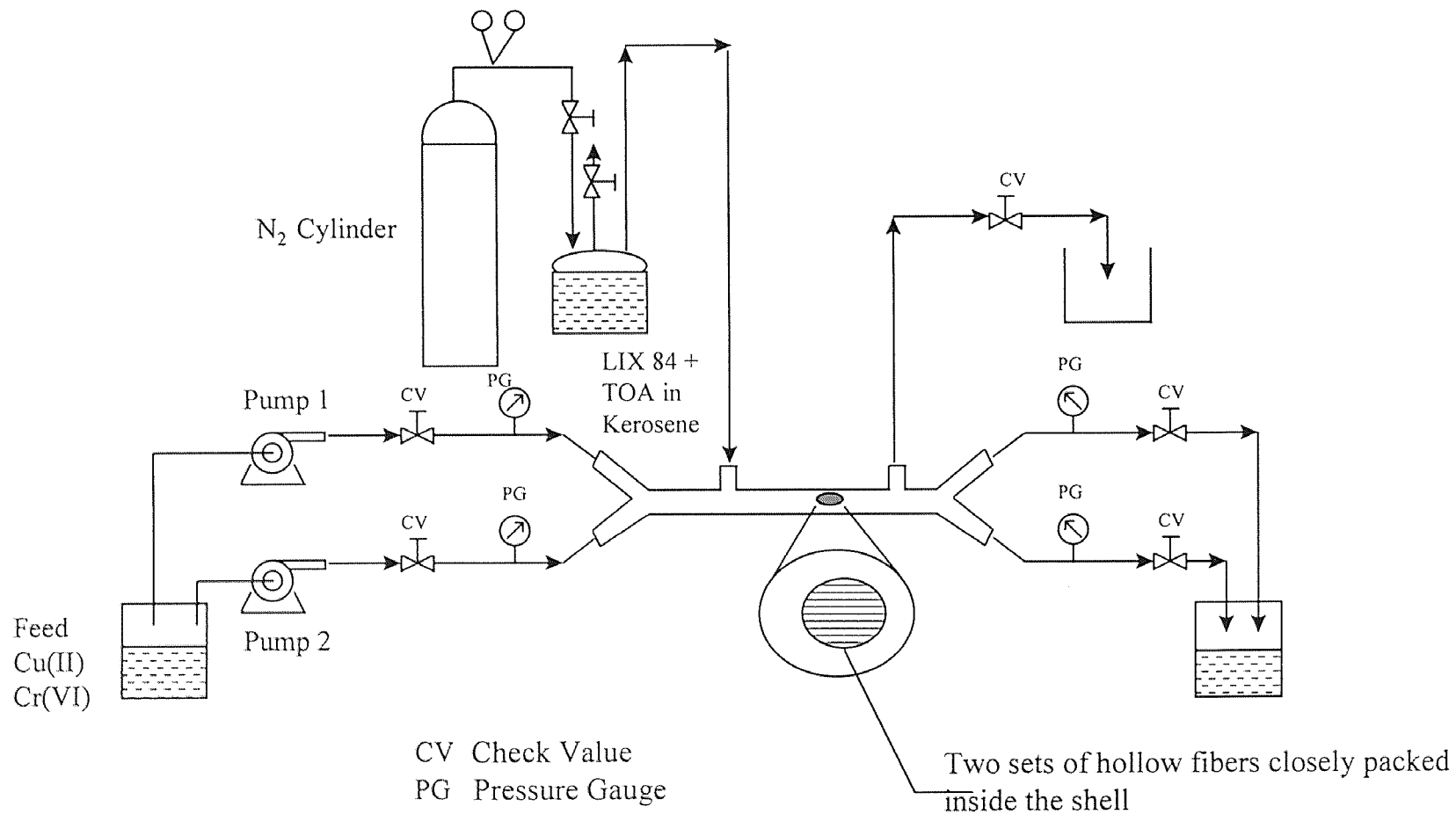


Figure 2.1. Setup of the extractive adsorber for simultaneous removal of heavy metals from wastewater

minutes. The loaded organic containing very high concentrations of Cu^{+2} and Cr^{+6} (in the form of complexes) was collected in a beaker.

During stripping, 2M H_2SO_4 solution was pumped through the bore of one set of hollow fibers and 0.1M NaOH solution was pumped through the bore of another set of hollow fibers (Figure 2.2). The shell side was filled with the loaded organic, which was collected after the extraction phase. The static pressure on the shell side was always maintained 3 psi lower than the tube side pressure (6 psig for the aqueous phase and 3 psig for the organic phase), since the hydrophobic membranes were wetted by the organic extractant.

2.6 Calculated Quantities

The distribution coefficient (m_i) for a particular metal between the aqueous phase and the mixed extractant is defined by:

$$m_i = \frac{\text{concentration of the metal in the organic phase}}{\text{concentration of the metal in the aqueous phase}} \quad (2.1)$$

The following calculations show the volume of LIX 84 and kerosene required to make 0.156 M LIX 84 in kerosene.

Molarity of LIX 84 solution = 1.56 mol/L

Therefore for making one liter solution containing 0.156M LIX 84, $(1000/1.56) * 0.156$
= 100 mL of LIX 84 solution and 900 mL of kerosene should be used. The properties of

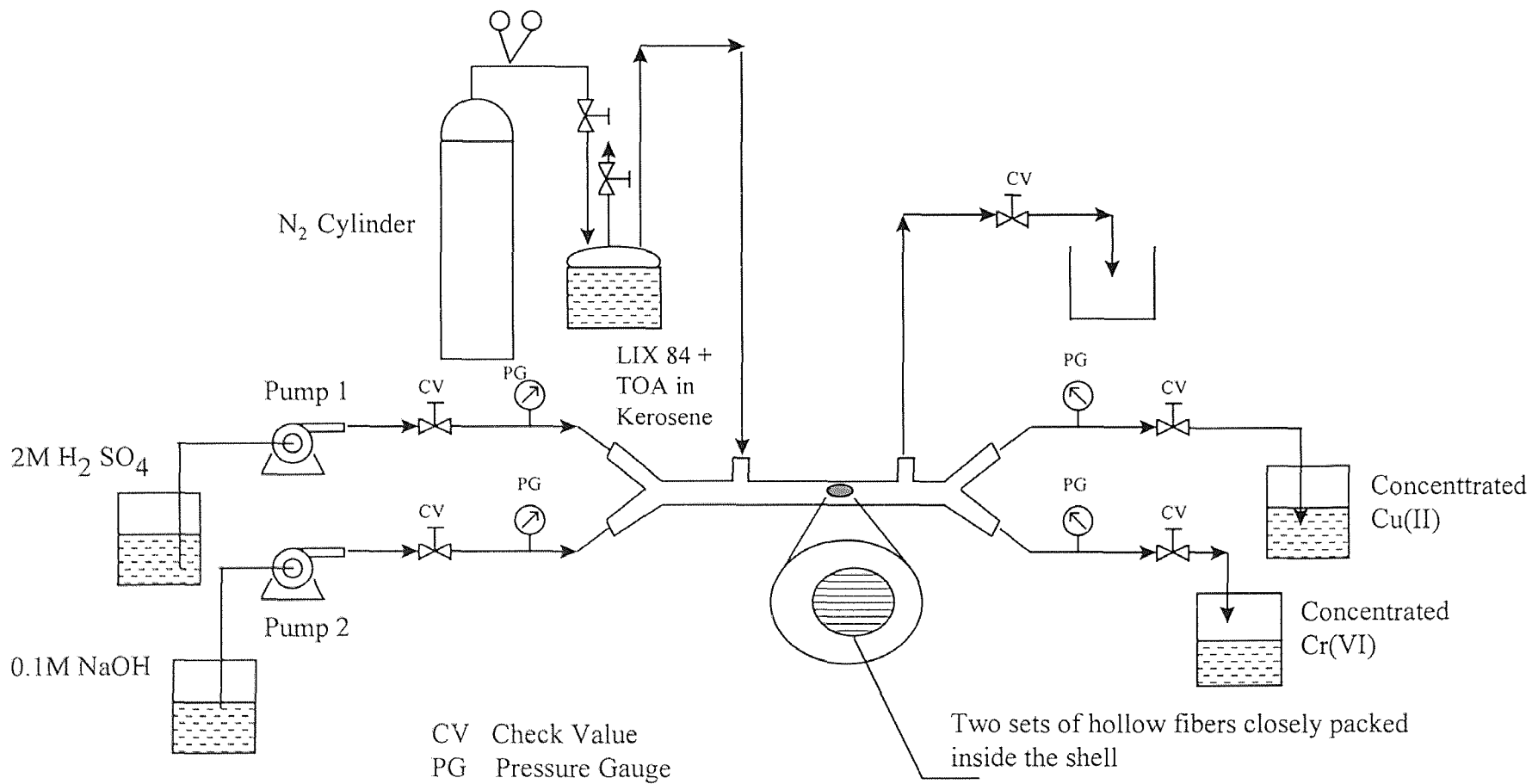


Figure 2.2. Setup of simultaneous and individual stripping of heavy metals from the extractive adsorber

LIX 84 solution are listed in Table 2.1. A 100 mL mixed extractant containing 10% LIX 84 and 10% TOA has 10 mL of LIX 84 solution and 10 mL TOA solution in 80 mL of kerosene.

Table 2.1. Technical information on LIX 84*

General Chemical and Physical properties

Net wt% of oxime	48 wt% in kerosene
Specific Gravity	0.90
Copper Complex Solubility	Completely soluble
Maximum Copper Loading 10 v/v %	4.75~4.80 g/L Cu

Performance Parameters

Extraction Isotherm Point	≥ 3.75 g/L Cu
Extraction Kinetics	90% at 60 seconds
Extraction Copper/Iron Selectivity	≥ 2000
Extraction Phase Disengagement	≤ 90 seconds
Strip Point	about 0.30 g/L Cu
Net Copper Transfer	3.45 ~ 3.5 g/l Cu

* Obtained from Henkel Corporation (Tucson, AZ)

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Copper and Chromium System

3.1.1 Batch Extraction Results

Batch experiments were conducted with different concentrations of copper and chromium in the aqueous phase at three different mixed extractant concentrations, containing LIX 84 and TOA in equimolar proportions. In all experiments, the ratio of copper concentration to chromium concentration remained constant at 1.36 : 1. Distribution coefficients (m_i) for copper and chromium were calculated after analyzing the aqueous raffinate phase using the atomic absorption spectrophotometer.

Tables 3.1 to 3.3 show the batch extraction results for copper and chromium system at three different mixed extractant concentrations. Figure 3.1 illustrates the variation of the distribution coefficient of chromium with concentration of chromium at three different mixed extractant concentrations. At low concentrations of chromium, the distribution coefficient of chromium does not vary significantly as the mixed extractant concentration is increased. At a particular mixed extractant concentration of, say, 0.234 M LIX 84 + 0.234 M TOA in kerosene, distribution coefficient of chromium increases with the concentration of chromium. At a lower mixed extractant concentration of, say, 0.156 M LIX 84 + 0.156 M TOA in kerosene, distribution coefficient goes through a maximum and then decreases with increasing concentration of chromium. At high concentrations of chromium, the distribution coefficient of chromium increases very rapidly as the mixed extractant concentration is increased.

Table 3.1 Batch experimental results for copper and chromium system with 0.156 M LIX 84 + 0.156 M TOA in kerosene

Feed concentration		Raffinate phase			Distribution coefficient	
Cr(VI) ppm	Cu(II) ppm	pH	Cu(II) ppm	Cr(VI) ppm	Cr(VI)	Cu(II)
74	101	4.85	1.2	22.0	2.36	83.2
222	303	4.82	1.1	58.4	2.80	274
370	505	4.77	1.4	73.7	4.01	360
592	808	4.53	1.3	68.1	7.69	621
740	1010	4.45	1.3	64.5	10.50	776
1480	2020	3.57	2.4	23.8	61.20	841
2220	3030	2.97	240	10.9	203	11.6
3700	5050	2.76	1275	15.5	238	2.9

Table 3.2 Batch experimental results for copper and chromium system with 0.234 M LIX 84 + 0.234 M TOA in kerosene

Feed concentration		Raffinate phase			Distribution coefficient	
Cr(VI) ppm	Cu(II) ppm	pH	Cu(II) ppm	Cr(VI) ppm	Cr(VI)	Cu(II)
74	101	5.48	0.4	27.7	1.6	252
222	303	5.18	0.6	63.2	2.5	504
370	505	5.07	0.5	74.8	3.9	1010
592	808	4.85	0.5	84.4	6.0	1620
740	1010	4.92	0.6	92.0	7.0	1680
1480	2020	4.44	0.8	51.3	27.8	2520
2220	3030	3.82	1.2	29.9	73.1	206
3700	5050	2.95	340	26.3	140	2.94

Table 3.3 Batch experimental results for copper and chromium system with 0.312 M LIX 84 + 0.312 M TOA in kerosene

Feed concentration		Raffinate phase			Distribution coefficient	
Cr(VI) ppm	Cu(II) ppm	pH	Cu(II) ppm	Cr(VI) ppm	Cr(VI)	Cu(II)
74	101	5.71	0.1	17.9	3.1	1010
222	303	5.46	0.1	41.1	4.4	3030
370	505	5.44	0.1	60.9	5.0	5050
592	808	5.33	0.1	78.4	6.5	8080
740	1010	5.31	0.1	88.0	7.4	10100
1480	2020	4.92	0.2	67.0	21.0	10100
2220	3030	4.54	0.3	34.9	62.6	10100
3700	5050	3.62	31.8	11.0	335	158

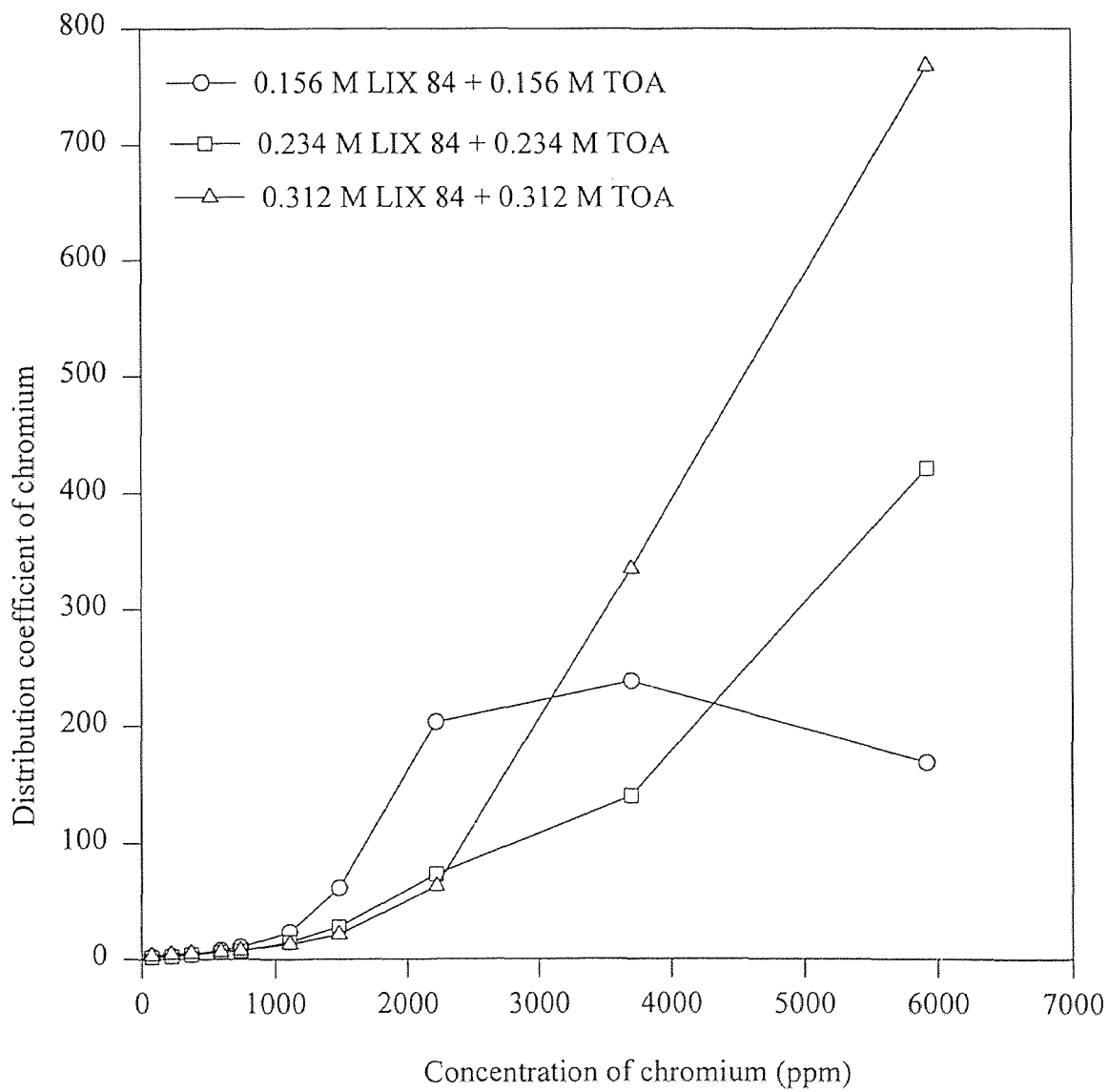


Figure 3.1. Effect of feed concentration on the distribution coefficient of Cr(VI) at different mixed extractant concentrations in a batch extraction system

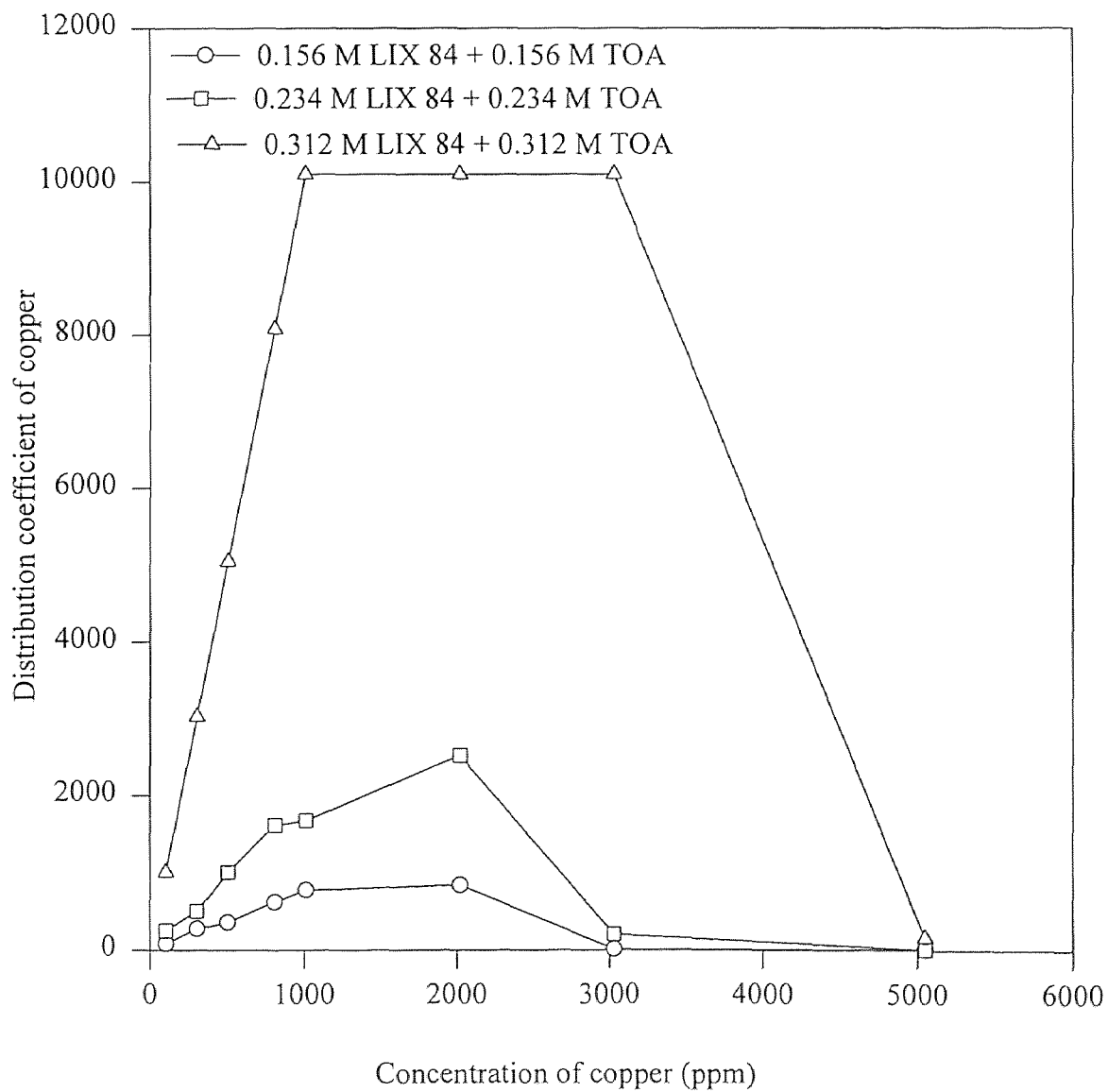


Figure 3.2. Effect of feed concentration on the distribution coefficient of Cu(II) at different mixed extractant concentrations in a batch extraction system

Figure 3.2 illustrates the variation of the distribution coefficient of copper with the concentration of copper at three different mixed extractant concentrations. The distribution coefficient of copper goes through a maximum and then decreases drastically as the concentration of copper increases. For example, at a copper concentration of 2020 ppm and a mixed extractant concentration of 0.312 M LIX 84 + 0.312 M TOA in kerosene, distribution coefficient of copper was 10100. At the same mixed extractant concentration, distribution coefficient of copper drops to 158 when the copper concentration was 5050 ppm. Distribution coefficient of copper increases drastically on increasing the mixed extractant concentration upto a certain concentration of copper.

Figure 3.3 illustrates the variation of the aqueous equilibrium pH with the metal concentration at three different mixed extractant concentrations. The starting aqueous phase was maintained at 4.0. At a particular mixed extractant concentration, the equilibrium pH decreases with increasing metal concentration. This can be explained as follows: when the concentration of copper in the feed is increased, more copper is being extracted into the mixed extractant causing a large number of protons to be released into the aqueous phase and all the protons released are not used up in extraction of chromium. At a particular metal concentration, as the mixed extractant concentration is increased, the aqueous equilibrium pH also increases. This is due to the fact that, as the mixed extractant concentration increases the metal extraction capacity and the distribution coefficient increases. Also, when the concentration of TOA is increased, more sulfate ions can be extracted thus leading to a higher pH.

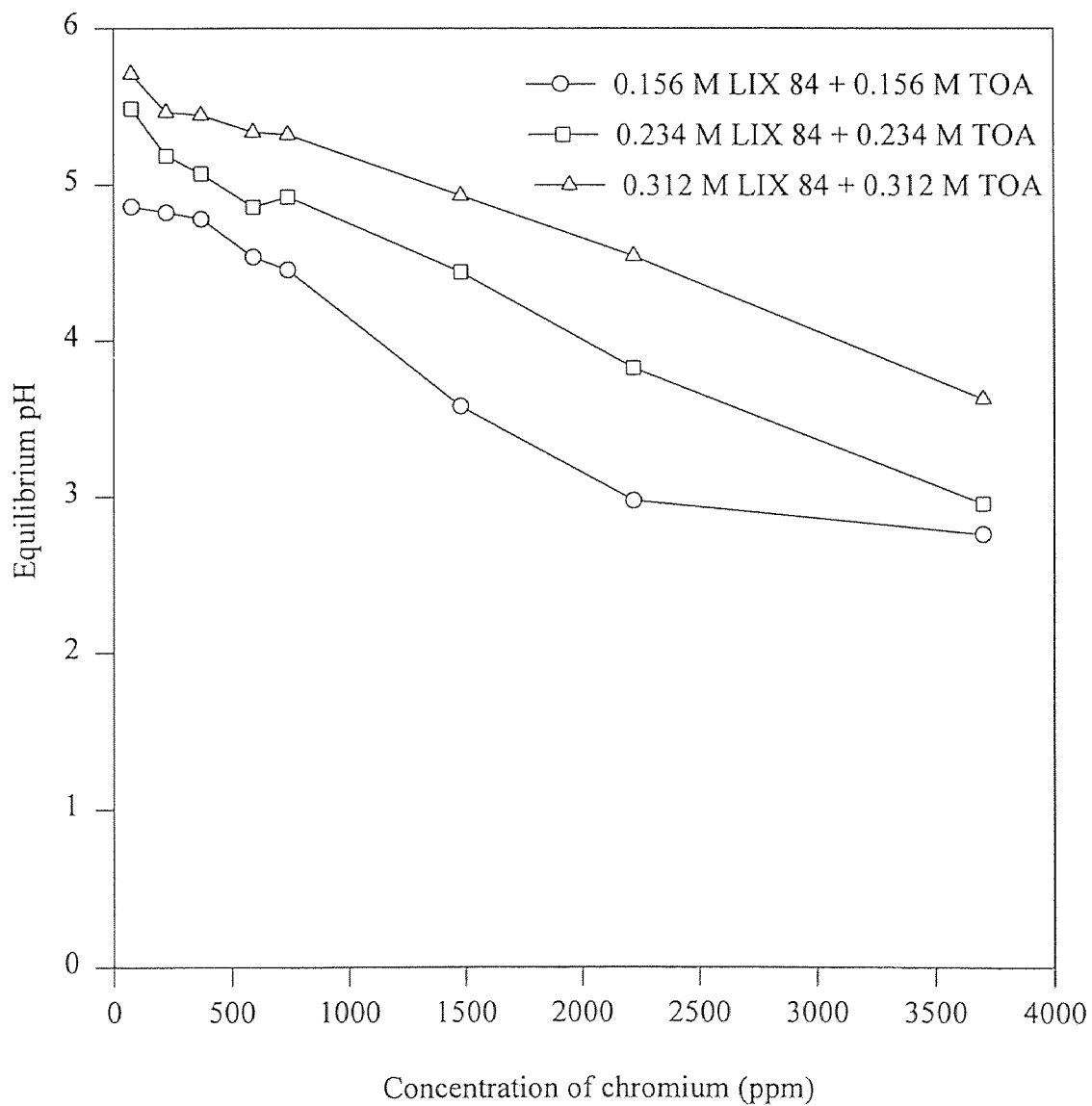


Figure 3.3. Effect of feed concentration on the equilibrium pH at different mixed extractant concentrations

Figures 3.4, 3.5 and 3.6 illustrate the variation of the distribution coefficient of Cu(II) and Cr(VI) as the metal ion concentration is varied at mixed extractant concentrations respectively of 0.156 M LIX 84 + 0.156 M TOA in kerosene, 0.234 M LIX 84 + 0.234 M TOA in kerosene, 0.312 M LIX 84 + 0.312 M TOA in kerosene.

3.1.2 Introduction to Fixed Bed Extraction Results

Fixed bed extraction experiments were conducted at different feed concentrations, different mixed extractant compositions and different flow rates. The starting pH was maintained at around 4.1. The results indicate that the metal concentrations (both Cu(II) and Cr(VI)) could be reduced to about 0.1 ppm from a feed concentration of about 225 ppm Cu(II) and 100 ppm Cr(VI) using appropriate mixed extractant composition and feed flow rates. Feed flow rates of 1 mL/min and 2 mL/min were most commonly used. Figures 3.7 to 3.14 show the experimental results for fixed bed extraction for different feed concentrations, mixed extractant compositions and feed flow rates. The corresponding numerical values are provided in Tables 3.4 through 3.14.

3.1.3 Effect of Mixed Extractant Composition on the Breakthrough Behavior of Cu(II)

The effect of mixed extractant composition on the breakthrough behavior of Cu(II) was studied by keeping the feed concentrations of Cu(II) and Cr(VI) constant. The behavior was studied at two different feed flow rates of 1 mL/min and 2 mL/min. Figures 3.7 and 3.8 show the variation in breakthrough behavior for Cu(II) at different mixed extractant compositions, at feed flow rates of 2 mL/min and 1 mL/min respectively . At a high mixed organic

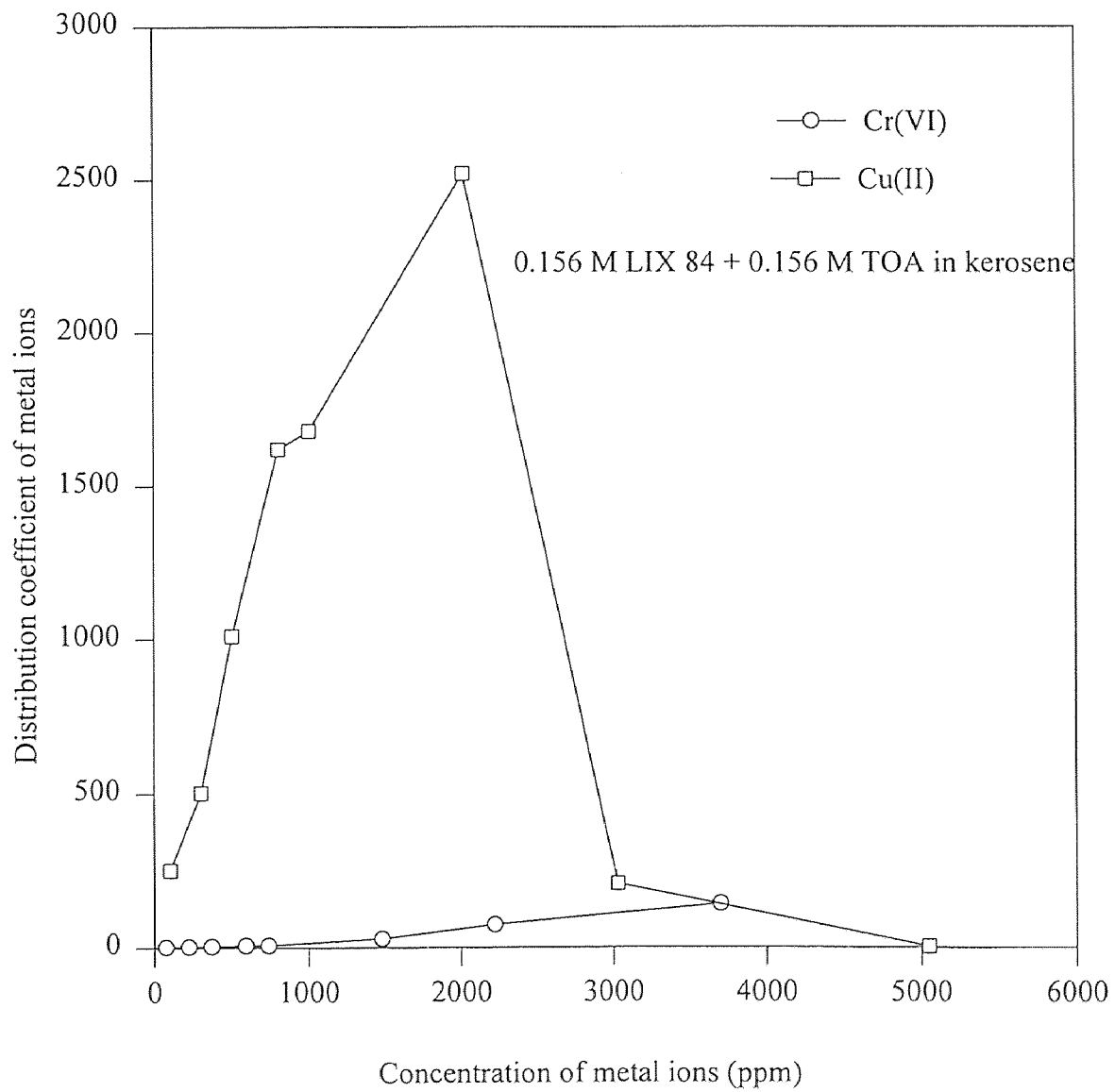


Figure 3.4. Effect of feed concentration on the distribution coefficients of Cu(II) and Cr(VI)

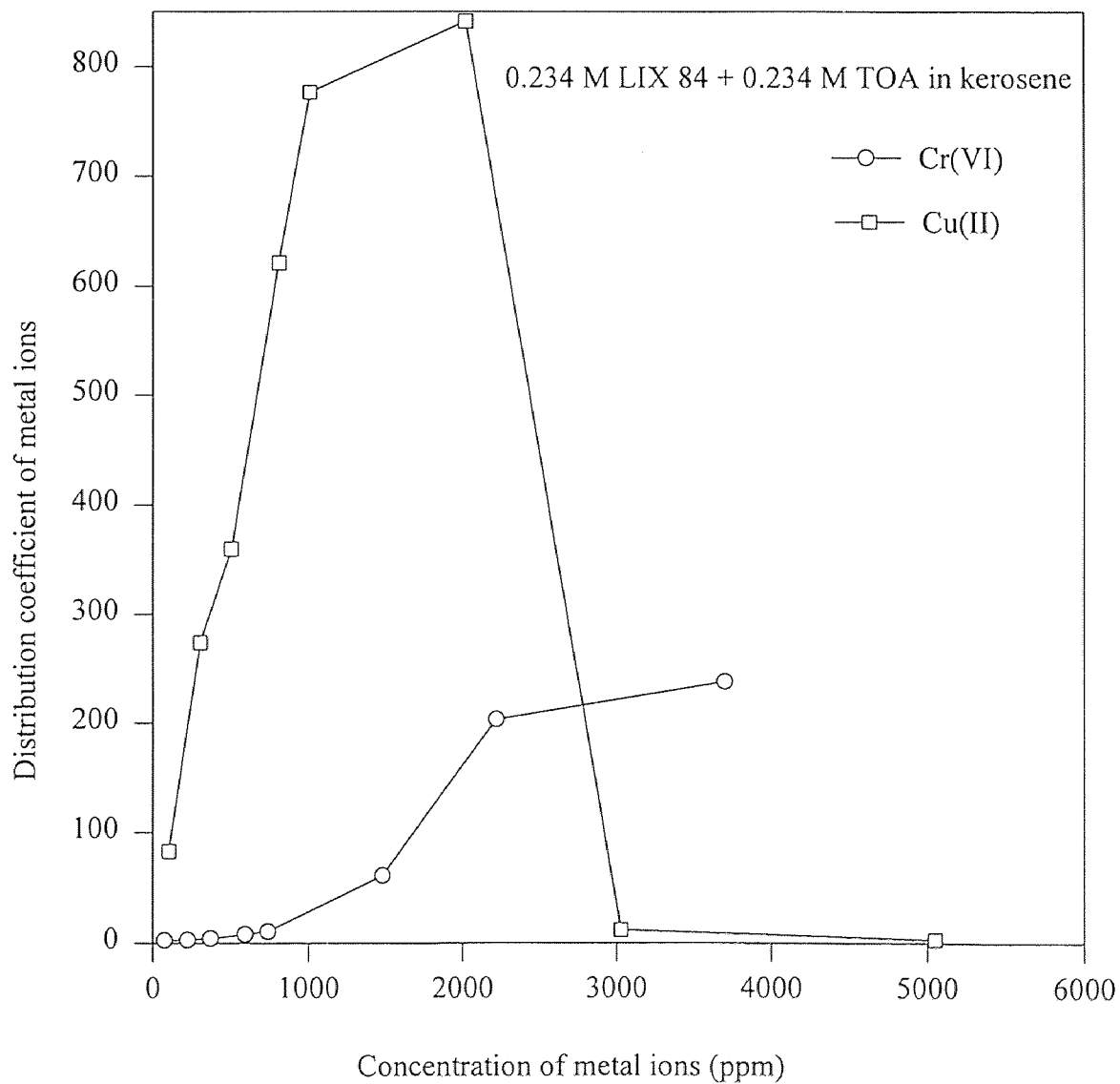


Figure 3.5. Effect of feed concentration on the distribution coefficients of Cu(II) and Cr(VI)

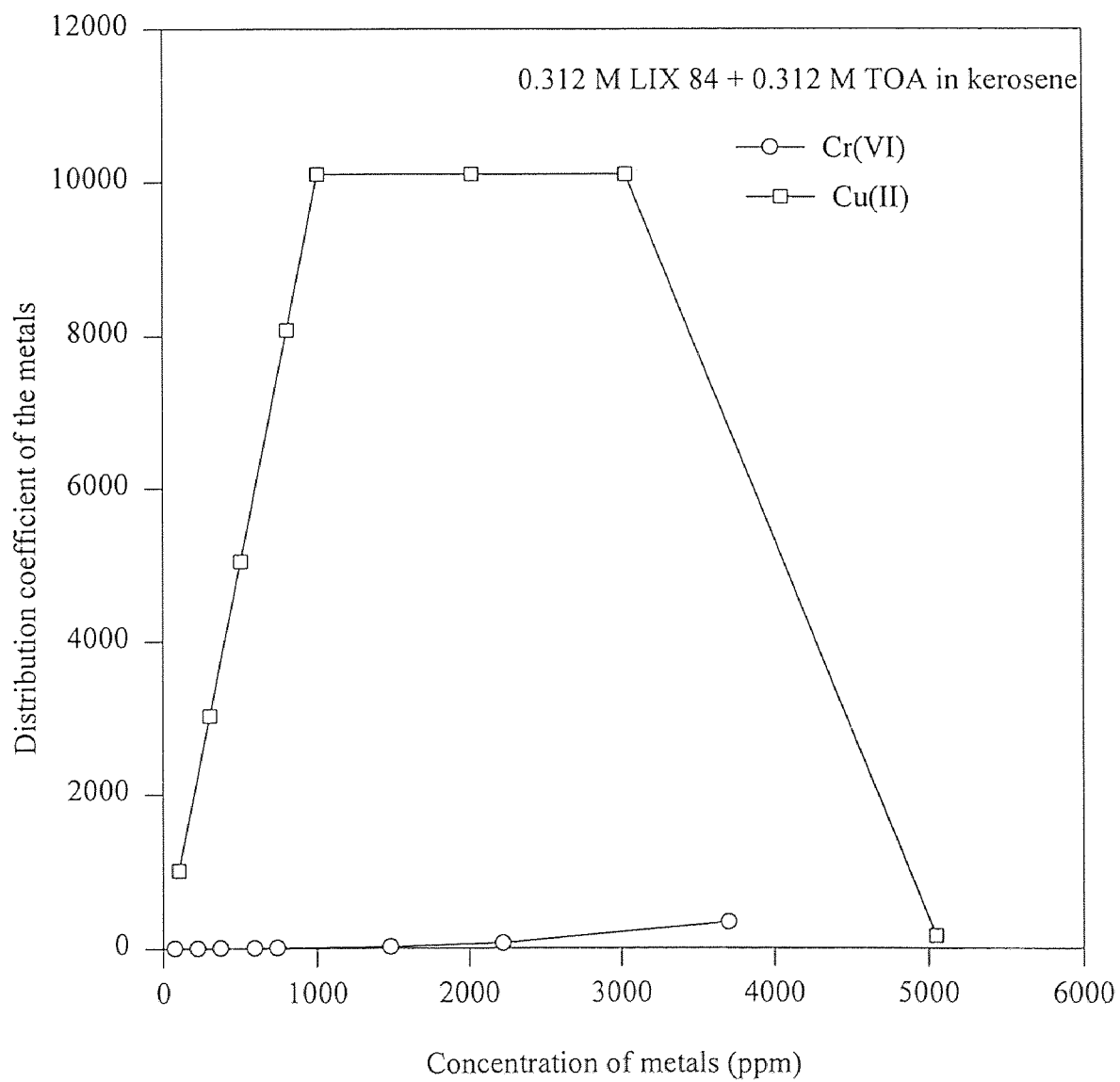
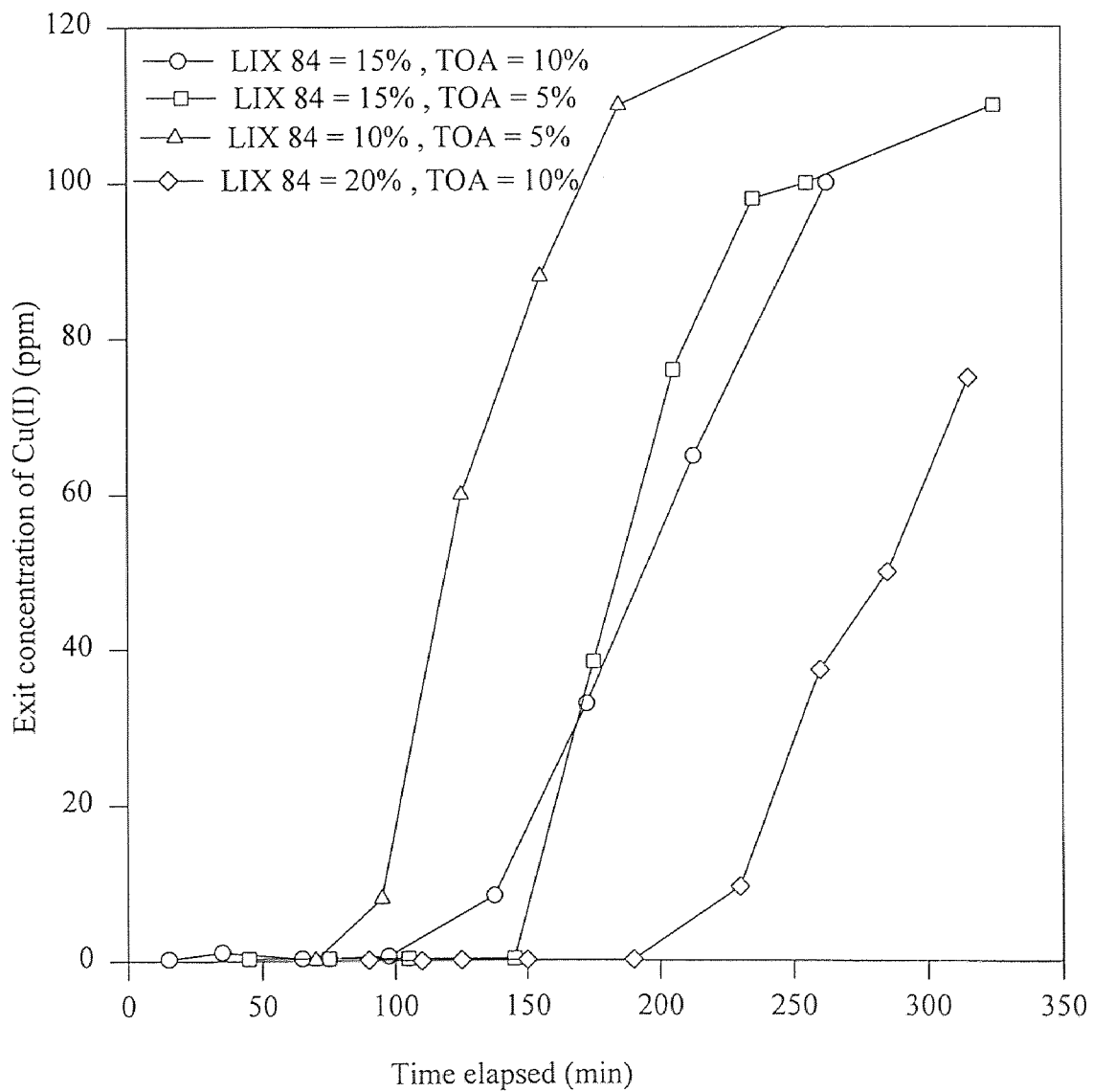
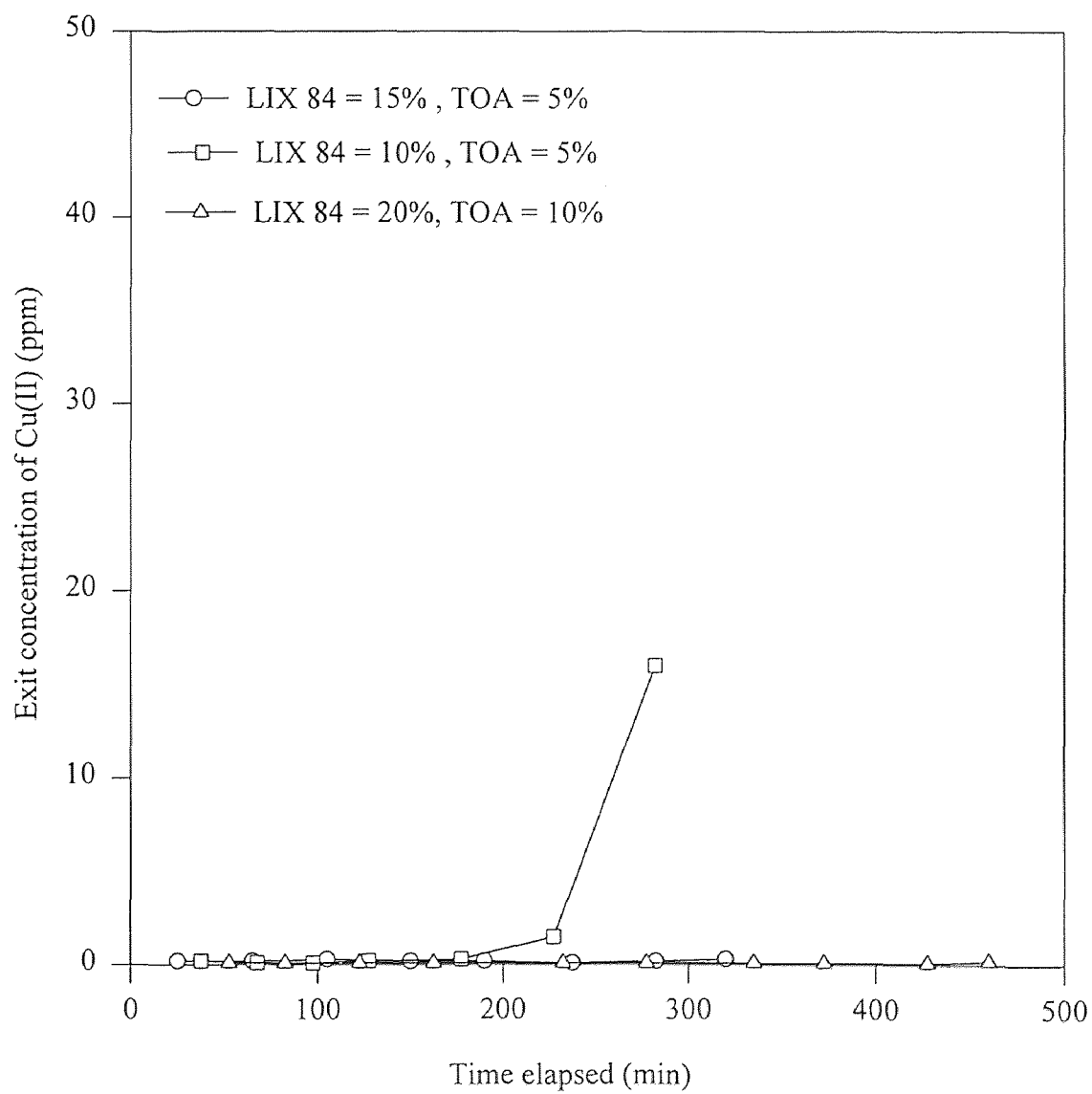


Figure 3.6. Effect of feed concentration on the distribution coefficients of Cu(II) and Cr(VI)



Feed composition: Cu(II) = 215-225-235 ppm, Cr(II) = 98-107-108 ppm

Figure 3.7. Effect of mixed extractant composition on the breakthrough behavior of Cu(II) at a feed flow rate of 2 mL/min.



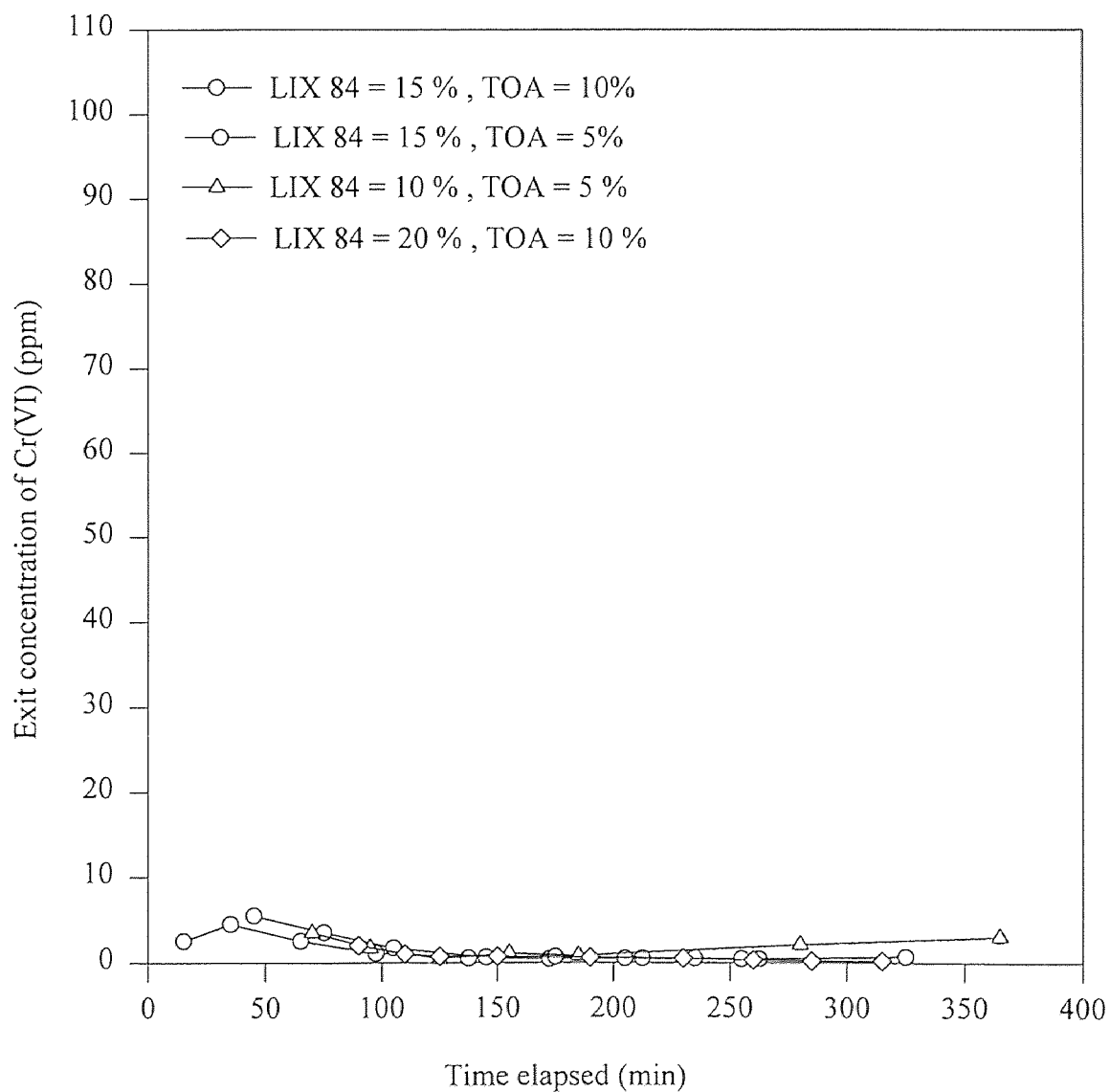
Feed composition: Cu(II) = 215-225-235 ppm, Cr(VI) = 98-107-108 ppm

Figure 3.8. Effect of mixed extractant composition on the breakthrough behavior of Cu(II) at a feed flow rate of 1 mL/min

concentration of 20% LIX 84 + 10% TOA in kerosene and a flow rate of 2 mL/min, breakthrough for Cu(II) occurs after 180 min, whereas, at a lower mixed extractant concentration of 10% LIX 84 + 5% TOA in kerosene and the same flow rate of 2 mL/min, breakthrough for Cu(II) occurs much earlier after about 90 min. This is due to the increased metal extraction capacity of 20% LIX 84 + 10% TOA in kerosene over 10% LIX 84 + 5% TOA in kerosene. When the feed flow rate is decreased to 1 mL/min for the same feed concentration, breakthrough for Cu(II) does not occur even after 400 min for mixed extractant compositions of 15% LIX 84 + 5% TOA and 20% LIX 84 + 10% TOA in kerosene; however, for a mixed extractant composition of 10% LIX 84 + 5% TOA in kerosene, breakthrough for Cu(II) occurs after about 220min. It can be seen that any one of the above mixed extractant compositions can be used to reduce the copper concentration to about 0.1 ppm from a feed containing about 225 ppm Cu(II) using appropriate flow rates. There was not much change in the Cu(II) concentration before the breakthrough when the mixed extractant composition was changed at both flow rates of 1 mL/min and 2 mL/min.

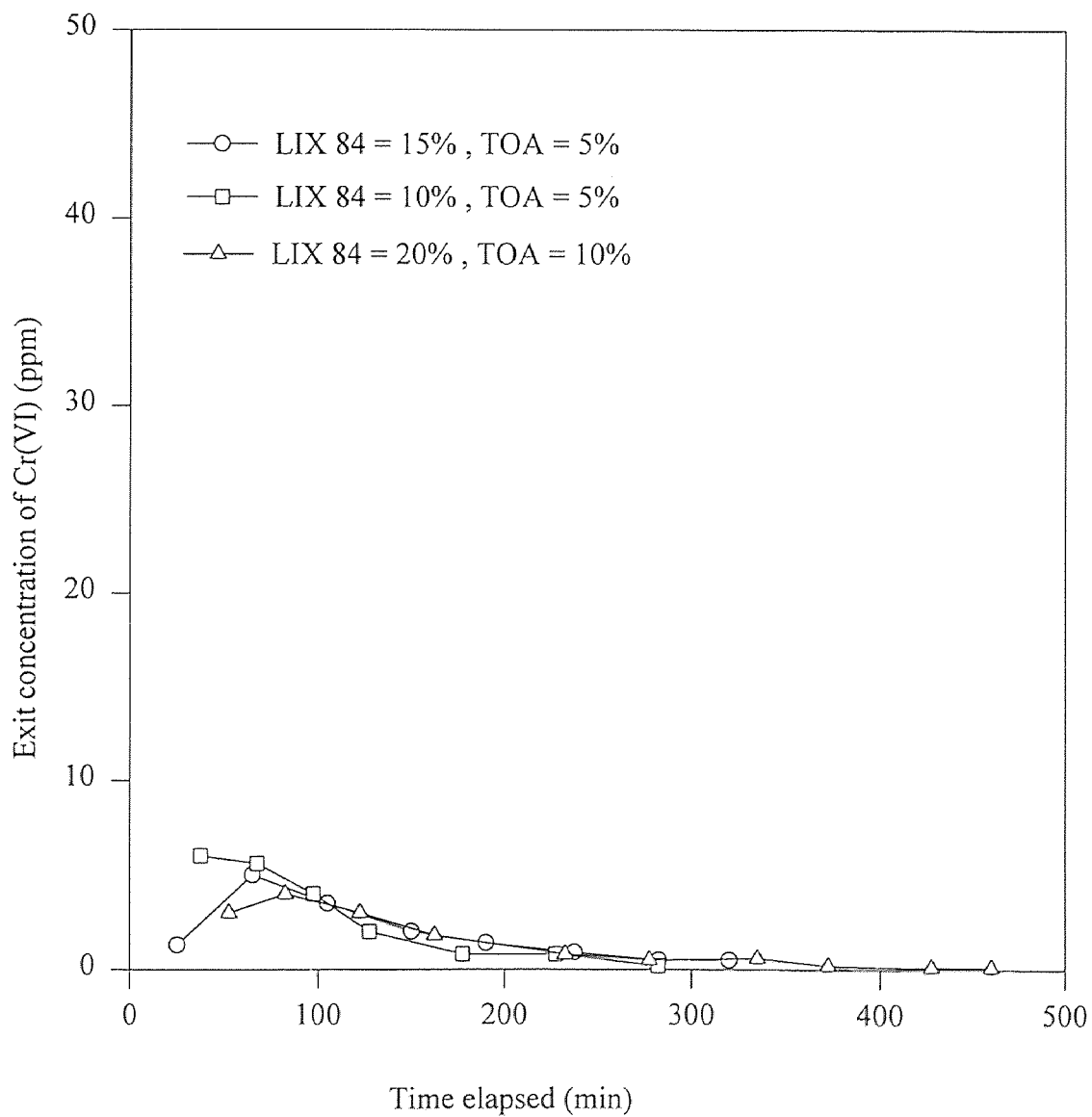
3.1.4 Effect of Mixed Extractant Composition on the Breakthrough Behavior of Cr(VI)

The effect of mixed extractant composition on the breakthrough behavior of Cr(VI) was studied by keeping the feed concentration of Cu(II) and Cr(VI) constant. The behavior was studied at two different feed flow rates of 1 mL/min and 2 mL/min. Figures 3.9 and 3.10 illustrate the breakthrough behavior of Cr(VI) at different mixed extractant compositions for two different flow rates. No breakthrough was observed for Cr(VI) even after 400 min for all mixed extractant compositions at both feed flow rates of 1 mL/min and 2 mL/min. It can



Feed composition: Cu(II) = 215-225-235 ppm, Cr(II) = 98-107-108 ppm

Figure 3.9. Effect of mixed extractant composition on the breakthrough behavior of Cr(VI) at feed flow rate of 2 mL/min



Feed composition: Cu(II) = 215-225-235 ppm, Cr(VI) = 98-107-108 ppm

Figure 3.10. Effect of mixed extractant composition on the breakthrough behavior of Cr(VI) at a feed flow rate of 1 mL/min

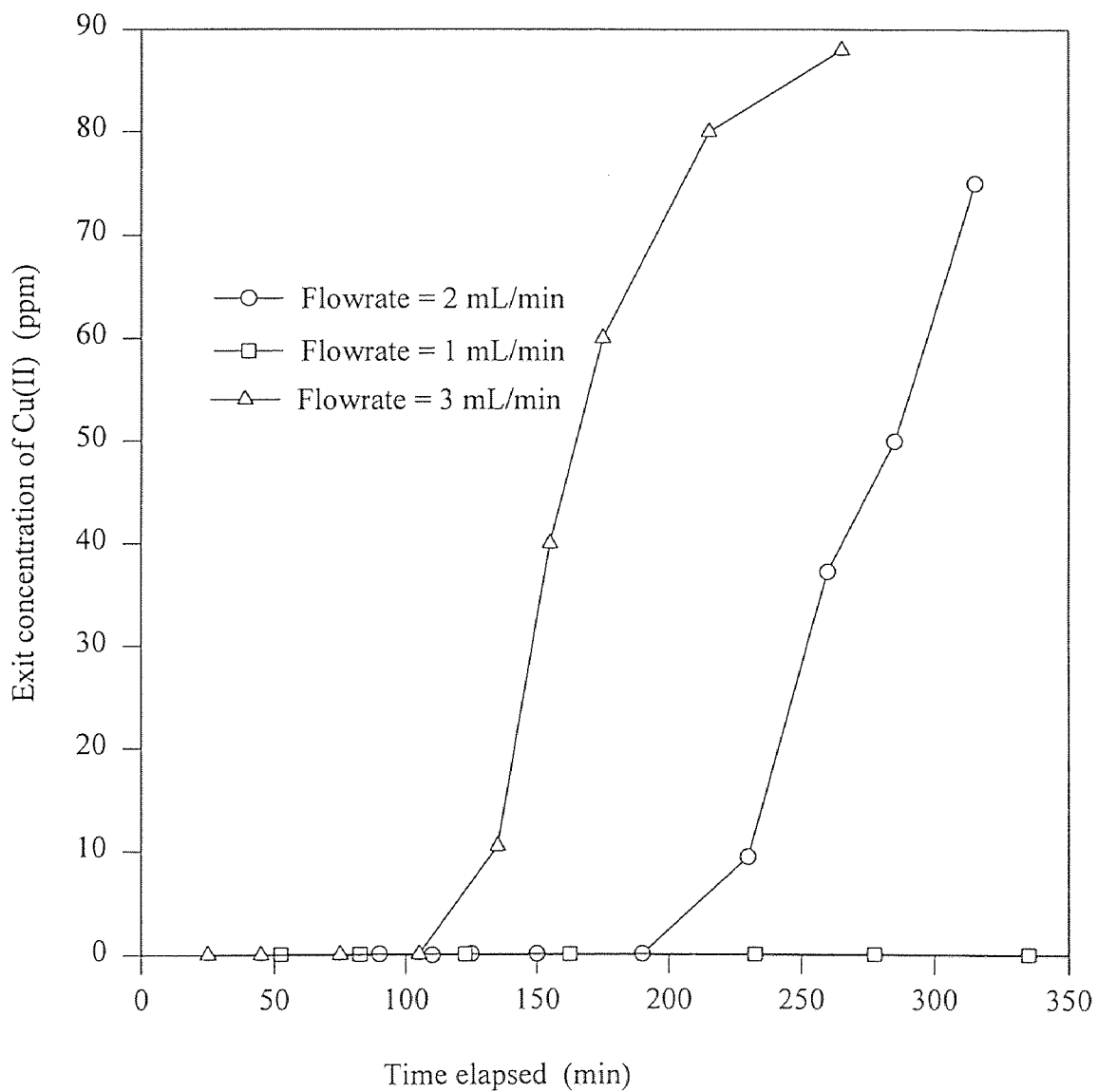
be seen that any one of the above mixed extractant compositions can be used to reduce the chromium concentration to less than 1ppm from a feed containing about 100 ppm Cr(VI) using appropriate flow rates. There was not much change in the exit Cr(VI) concentration after extraction when the mixed extractant composition was changed at both feed flow rates of 1 mL/min and 2 mL/min.

3.1.5 Effect of Feed Flow Rate on the Breakthrough Behavior of Cu(II)

The effect of feed flow rate on the breakthrough behavior of Cu(II) was studied by keeping the feed concentrations of Cu(II) and Cr(VI) constant and by keeping the mixed extractant composition constant. Figure 3.11 shows the breakthrough behavior of Cu(II) for a mixed extractant composition of 20% LIX 84 + 10 % TOA in kerosene at three different feed flow rates of 1 mL/min, 2 mL/min and 3 mL/min. As the feed flow rate was increased, the time after which the breakthrough occurred decreased; in fact, no breakthrough was observed for Cu(II) at a feed flow rate of 1 mL/min even after 330 min. There was not much change in the exit Cu(II) concentration before the breakthrough when the feed flow rate was changed.

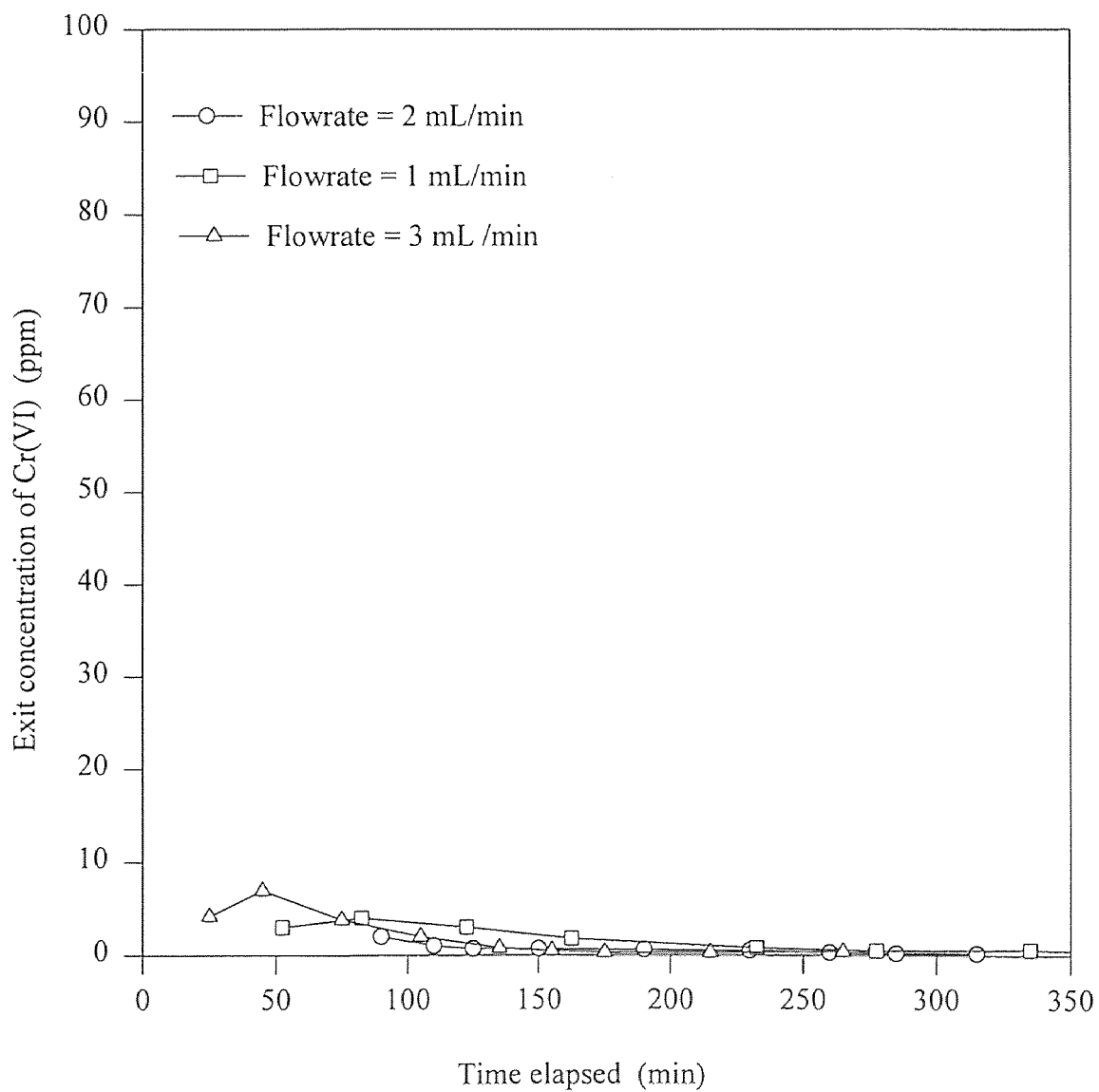
3.1.6 Effect of Feed Flow Rate on the Breakthrough Behavior of Cr(VI)

The effect of feed flow rate on the breakthrough behavior of Cr(VI) was studied by keeping the feed concentration of Cu(II) and Cr(VI) constant and by keeping the mixed extractant composition constant. Figure 3.12 shows the breakthrough behavior of Cr(VI) for a mixed extractant composition of 20% LIX 84 + 10 % TOA in kerosene at three different feed flow



Feed composition: Cu(II) = 215 ppm, Cr(VI) = 98 ppm

Figure 3.11. Effect of feed flow rate on the breakthrough behavior of Cu(II) at a mixed extractant composition of LIX 84 = 20% , TOA = 10% in kerosene



Feed composition: Cu(II) = 215 ppm, Cr(VI) = 98 ppm

Figure 3.12. Effect of feed flow rate on the breakthrough behavior of Cr(VI) at a mixed extractant composition of LIX 84 = 20% , TOA =10% in kerosene

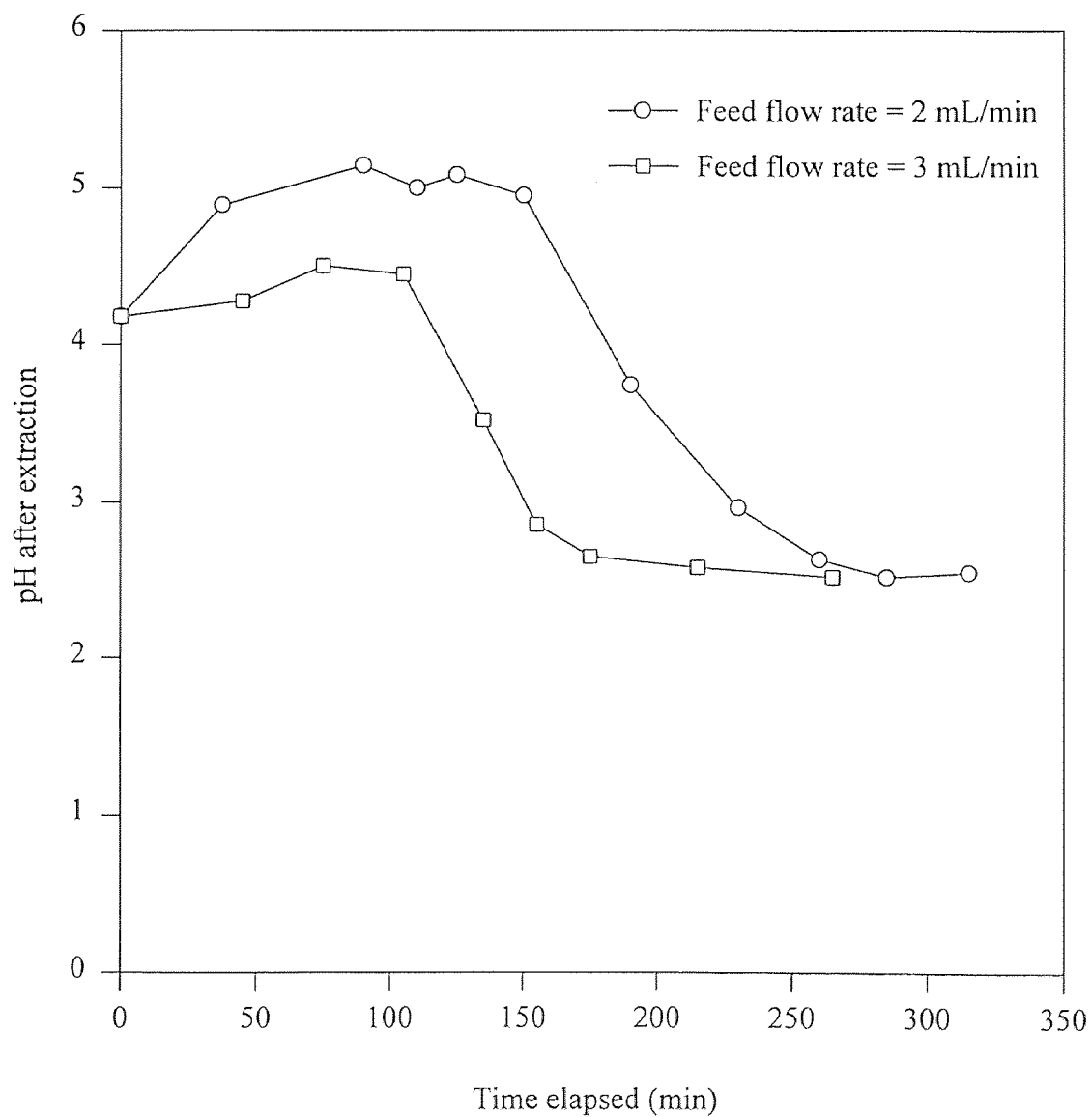
rates of 1 mL/min, 2 mL/min and 3 mL/min. No breakthrough was observed for Cr(VI) even after 400 min at all three flow rates. There was not much change in the exit Cr(VI) concentration after the extraction when the feed flow rate was changed.

3.1.7 Effect of Feed Concentration on the Breakthrough Behavior of Cu(II) and Cr(VI)

Table 3.14 shows the extraction performance for a higher feed concentration of Cu(II) = 350 ppm and Cr(VI) = 258 ppm at a feed flow rate of 2 mL/min. Breakthrough for Cu(II) was observed very early after about 120 min even though a high mixed extractant concentration of 20% LIX 84 + 5% TOA in kerosene was used. Breakthrough of Cu(II) can be delayed either by using a higher mixed extractant concentration or by using a lower feed flow rate. No breakthrough was observed for Cr(VI) even after 300 min, but the concentration after the extraction showed a slight increase.

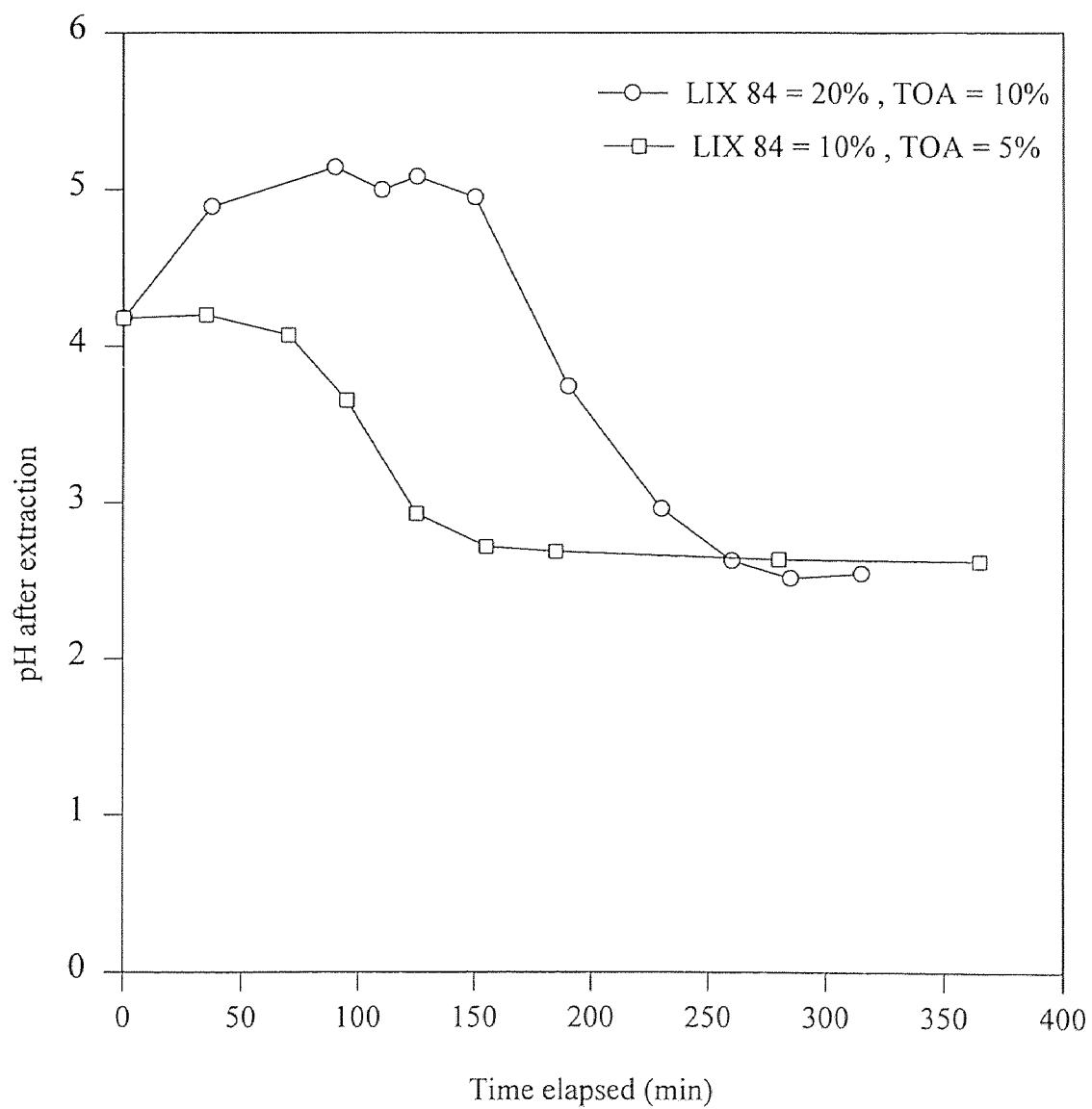
3.1.8 Variation of pH with Time

Figure 3.13 illustrates variation of pH with time for different feed flow rates at a mixed extractant composition of LIX 84 = 20% and TOA = 10% in kerosene. Figure 3.14 illustrates the variation of pH with time for different mixed extractant compositions at a feed flow rate of 2 mL/min. Higher pH was seen during the initial phase of the experiment when a higher mixed extractant concentration is used. This is due to a higher concentration of free TOA, which leads to better extraction of H_2SO_4 thereby, yielding a higher pH.



Feed composition: Cu(II) = 215 ppm, Cr(VI) = 98 ppm

Figure 3.13. Variation of pH with time for different feed flow rates at a mixed extractant composition of LIX 84 = 20% , TOA = 10% in kerosene



Feed composition: Cu(II) = 215 ppm, Cr(VI) = 98 ppm

Figure 3.14. Variation of pH with time for different mixed extractant compositions at a feed flow rate of 2 mL/min

Table 3.4. Extractor performance for Cu(II) = 225 ppm, Cr(VI) = 108 ppm, pH~4.1, LIX 84 = 15% , TOA = 10% , flow rate = 1.4 mL/min.

Time elapsed (min)	[Cu(II)] ppm	[Cr(VI)] ppm
27.5	0.0	0.9
57.5	0.1	1.5
87.5	0.0	1.8
122.5	0.2	1.4
157.5	0.1	0.8
197.5	0.4	0.6
300	22	0.7
360	50	0.6

Table 3.5. Extractor performance for Cu(II) = 225 ppm, Cr(VI) = 108 ppm, pH ~ 4.1, LIX 84 = 15% , TOA = 10% , flow rate = 1.9 mL/min.

Time elapsed (min)	[Cu(II)] ppm	[Cr(VI)] ppm
15	0.2	2.5
35	1.1	4.5
65	0.3	2.5
97.5	0.6	1.1
137.5	8.4	0.5
172.5	33	0.4
212.5	65	0.5
262.5	100	0.4

Table 3.6. Extractor performance for Cu(II) = 225 ppm, Cr(VI) = 108 ppm, pH ~ 4.1, LIX 84 = 15% , TOA = 5% , flow rate = 1.0 mL/min.

Time elapsed (min)	[Cu(II)] ppm	[Cr(VI)] ppm
25	0.2	1.3
65	0.2	5.0
105	0.3	3.5
150	0.2	2.0
190	0.2	1.4
237	0.1	0.9
282	0.2	0.5
320	0.3	0.5

Table 3.7. Extractor performance for Cu(II) = 235 ppm, Cr(VI) = 107 ppm, pH ~ 4.1, LIX 84 = 15% , TOA = 5% , flow rate = 2.0 mL/min.

Time elapsed (min)	[Cu(II)] ppm	[Cr(VI)] ppm
45	0.3	5.5
75	0.3	3.5
105	0.3	1.7
145	0.3	0.6
175	38.4	0.7
205	76.0	0.5
235	98.0	0.5
255	100	0.4
325	110	0.7

Table 3.8. Extractor performance for Cu(II) = 215 ppm, Cr(VI) = 98 ppm, pH ~ 4.1, LIX 84 = 10% , TOA = 5% , flow rate = 2.0 mL/min.

Time elapsed (min)	[Cu(II)] ppm	[Cr(VI)] ppm
70	0.1	3.5
95	8.0	1.7
125	60.0	0.4
155	88.0	1.1
185	110	0.8
280	125	2.1
365	135	3.0

Table 3.9. Extractor performance for Cu(II) = 215 ppm, Cr(VI) = 98 ppm, pH ~ 4.1, LIX 84 = 10% , TOA = 5% , flow rate = 1.0 mL/min.

Time elapsed (min)	[Cu(II)] ppm	[Cr(VI)] ppm
37.5	0.2	6.0
67.5	0.1	5.6
97.5	0.1	4.0
127.5	0.2	2.0
177.5	0.3	0.8
227.5	1.5	0.8
282.5	16	0.2

Table 3.10. Extractor performance for Cu(II) = 215 ppm, Cr(VI) = 98 ppm, pH ~ 4.1, LIX 84 = 20% , TOA = 10% , flow rate = 2.0 mL/min.

Time elapsed (min)	[Cu(II)] ppm	[Cr(VI)] ppm
90	0.1	2.0
110	0.0	1.0
125	0.1	0.7
150	0.1	0.7
190	0.1	0.6
230	9.5	0.5
260	37.3	0.3
285	50.0	0.2
315	75.0	0.2

Table 3.11. Extractor performance for Cu(II) = 215 ppm, Cr(VI) = 98 ppm, pH ~ 4.1, LIX 84 = 20% , TOA = 10% , flow rate = 1.0 mL/min.

Time elapsed (min)	[Cu(II)] ppm	[Cr(VI)] ppm
52.5	0.1	3.0
82.5	0.1	4.0
122.5	0.1	3.0
162.5	0.1	1.8
232.5	0.1	0.8
277.5	0.1	0.5
335.0	0.1	0.6
372.5	0.1	0.2
427.5	0.1	0.1
460.0	0.2	0.1

Table 3.12. Extractor performance for Cu(II) = 215 ppm, Cr(VI) = 98 ppm, pH ~ 4.1, LIX 84 = 20% , TOA = 10% , flow rate = 3.0 mL/min.

Time elapsed (min)	[Cu(II)] ppm	[Cr(VI)] ppm
25	0.02	4.2
45	0.04	7.0
75	0.06	3.8
105	0.08	2.0
135	10.5	0.8
155	40.0	0.5
175	60.0	0.3
215	80.0	0.3
265	88.0	0.4

Table 3.13. Extractor performance for Cu(II) = 195 ppm, Cr(VI) = 258 ppm, pH ~ 4.1, LIX 84 = 25% , TOA = 16.67% , flow rate = 2.0 mL/min.

Time elapsed (min)	[Cu(II)] ppm	[Cr(VI)] ppm
15	0.01	10.0
50	0.19	14.5
90	0.06	9.5
115	0.05	6.5
175	0.07	4.0
245	0.12	1.5
285	0.15	1.2
317.5	0.16	0.8
340	0.25	0.6

Table 3.14. Extraction performance for Cu(II) = 350 ppm, Cr(VI) = 258 ppm, pH ~ 4.1, LIX 84 = 20% , TOA = 5% , flow rate = 2.0 mL/min.

Time elapsed (min)	[Cu(II)] ppm	[Cr(VI)] ppm
20	0.12	10.0
85	0.14	5.1
120	2.48	2.1
155	36.4	1.8
235	96.0	1.4
295	120	1.0

3.1.9 Fixed Bed Stripping Results

During stripping, lower flow rates of about 0.3-0.6 mL/min were used for both 2 M H₂SO₄ and 0.1 M NaOH. Both copper and chromium were concentrated about 5-6 times their feed concentrations (120 ppm Cu(II) and 56 ppm Cr(VI)) in a once through mode. Higher concentrations could be obtained if recirculation mode is used. Table 3.15 shows the experimental results.

Table 3.15. Stripping performance at 2 M H₂SO₄ flow rate = 0.6 mL/min, 0.1 M NaOH flow rate = 0.4 mL/min

Time elapsed (min)	[Cu(II)] ppm	Cr(VI) ppm
55	625	237.5
85	325	225
120	275	200

3.2 Copper, Zinc and Chromium System

3.2.1 Batch Extraction Results

Batch extraction experiments were conducted with a mixed extractant containing different concentrations of LIX 84, TOA and D2EHPA in kerosene. The feed concentration was kept constant at $\text{Cu(II)} = 110 \text{ ppm}$, $\text{Zn(II)} = 153 \text{ ppm}$, $\text{Cr(VI)} = 147 \text{ ppm}$ for all experiments. Initial phase involved batch experiments to determine the optimum starting aqueous phase pH. Tables 3.16 to 3.22 show the experimental results for different compositions of the mixed extractant at different starting aqueous feed pH. Results show that a feed pH of around 4.0 could be used for efficient extraction of three metals.

At high concentrations of TOA, extraction of Cr(VI) is excellent but extraction of Zn(II) and Cu(II) is very poor (Table 3.16). This may be due to the fact that, most of the LIX 84 and D2EHPA form a complex with TOA and thus lesser amounts of free LIX 84 and D2EHPA are available for extraction of Cu(II) and Zn(II). Since a high concentration of TOA is used, a significant amount of free TOA is left after complexation thereby leading to a good extraction of Cr(VI). When a mixed extractant composition of 10% LIX 84, 10% D2EHPA and 5% TOA in kerosene was used at a initial feed pH of 4.0, a reasonable extraction of all three metals could be achieved (Table 3.17).

A much lower raffinate pH of 2.43 was obtained when the mixed extractant composition was 10% LIX 84, 10% D2EHPA and 5% TOA in kerosene (Table 3.17) compared to a raffinate pH of 4.083, which was obtained when the mixed extractant composition was 5% LIX 84, 5% D2EHPA and 20% TOA in kerosene, for the same feed concentration and same initial feed pH of 4.0 (Table 3.18). This is due to a greater extent of extraction of Cu(II) and

Table 3.16. Batch experimental results for copper, zinc and chromium system with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, LIX 84 = 5%, TOA = 15%, D2EHPA = 5%

Initial pH	Raffinate pH	[Zn(II)] ppm	[Cu(II)] ppm	[Cr(VI)] ppm
2.5	3.101	125	36.50	0.49
3.0	3.478	101.5	7.09	0.15
3.5	3.613	91	3.42	0.26
4.0	3.716	72.5	1.88	0.22
4.4	3.72	90	2.2	0.31

Table 3.17. Batch experimental results for copper, zinc and chromium system with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, LIX 84 = 10%, TOA = 5 %, D2EHPA=10%

Initial pH	Raffinate pH	[Zn(II)] ppm	[Cu(II)] ppm	[Cr(VI)] ppm
2.5	2.281	42.5	20	18.97
3.0	2.373	21.5	13.3	20.10
3.5	2.418	16	10.5	17.90
4.0	2.431	15	8.5	20.00
4.4	2.424	16	9.55	>20.0

Table 3.18. Batch experimental results for copper, zinc and chromium system with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, LIX 84 = 5%, TOA = 20%, D2EHPA = 5%

Initial pH	Raffinate pH	[Zn(II)] ppm	[Cu(II)] ppm	[Cr(VI)] ppm
2.5	3.200	126.50	>40	0.52
3.0	3.789	105.50	11.81	0.11
3.5	3.952	107.50	6.23	0.21
4.0	4.083	75.0	3.80	0.01
4.4	4.153	95.0	4.8	0.42

Table 3.19. Batch experimental results for copper, zinc and chromium system with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, LIX 84 = 10%, TOA = 10%, D2EHPA=10%

Initial pH	Raffinate pH	[Zn(II)] ppm	[Cu(II)] ppm	[Cr(VI)] ppm
2.5	2.554	57.50	>40	0.95
3.0	2.684	36	31.50	0.68
3.5	2.714	31.50	25.88	0.40
4.0	2.758	25.5	26.47	0.69
4.4	2.769	29.50	24.86	0.45

Table 3.20. Batch experimental results for copper, zinc and chromium system with Cu(II) = 110ppm, Zn(II) = 153 ppm, Cr(VI)=147 ppm, pH = 4.0, LIX 84 = 0 % TOA = 10%, D2EHPA = 20%

Initial pH	Raffinate pH	[Zn(II)] ppm	[Cu(II)] ppm	[Cr(VI)] ppm
2.5	2.289	14.0	86.40	1.0
3.0	2.421	6.0	76.0	0.29
3.5	2.466	5.5	76.4	1.0
4.0	2.478	6.5	74.80	0.49
4.4	2.502	4.0	72.0	1.16

Table 3.21. Batch experimental results for copper, zinc and chromium system with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, pH = 4.0, LIX 84 = 0 % TOA = 5 %, D2EHPA = 10%

Initial pH	Raffinate pH	[Zn(II)] ppm	[Cu(II)] ppm	[Cr(VI)] ppm
2.5	2.341	23.5	84.2	0.80
3.0	2.531	4.5	75.0	1.25
3.5	2.584	5.5	76.20	1.39
4.0	2.604	6.0	75.60	1.67
4.4	2.656	5.0	74.40	1.50

Table 3.22. Batch experimental results for copper, zinc and chromium system at different mixed extractant compositions at a feed pH of 4.0

Organic composition			Feed composition			Raffinate composition		
LIX 84 %	TOA %	D2EHPA %	Cu(II) ppm	Cr(VI) ppm	Zn(II) ppm	Cu(II) ppm	Cr(VI) ppm	Zn(II) ppm
10	5	15	110	153	147	34	10	8.4
15	5	15	110	153	147	5.4	3.5	10.5
15	5	10	110	153	147	5.2	8.0	17.5
15	10	10	110	153	147	32.0	1.12	85.5

of extraction of Cu(II) and Zn(II) by LIX 84 and D2EHPA at mixed extractant composition of 10% LIX 84, 10% D2EHPA and 5% TOA in kerosene, which leads to the release of higher number of protons (H^+).

Batch experiments were also done with a mixed extractant containing D2EHPA and TOA in kerosene for the three metal system at different feed pH. Results indicate that there was good extraction of Zn(II) and Cr(VI) but, there was poor extraction of Cu(II) (Tables 3.20 and 3.21). This indicates that a mixed extractant containing D2EHPA and TOA in kerosene could be used for efficient removal of Zn(II) and Cr(II) simultaneously.

Table 3.22 summarizes batch experimental results for three metal system at different mixed extractant compositions for a feed pH of 4.0 and same feed concentration. Results show that a mixed extractant containing 15% LIX 84, 15% D2EHPA, 5% TOA in kerosene provides the best metal loading capacity. It can be seen that, if one of the extractants concentration in the mixed extractant is altered, extraction performance of all the three metals is altered. This is due to a change in the concentration of LIX 84-TOA complex and D2EHPA-TOA complex when one of the extractants concentration is altered and thereby concentrations of free LIX 84, D2EHPA and TOA get altered.

3.2.2 Fixed Bed Extraction Results

Fixed bed extraction experiments were done with copper, zinc and chromium system at different mixed extractant compositions, different feed concentrations and different feed flow rates. Starting feed pH was maintained around 4.1. The results indicate that the metal concentrations (Cu(II), Zn(II) and Cr(VI)) could be reduced to less than 2 ppm from a feed

concentration of Cu(II) = 150 ppm, Zn(II) = 100 ppm and Cr(VI) = 70 ppm using appropriate feed flow rates. Feed flow rates of less than 1 mL/min yielded best results. Tables 3.23 to 3.29 show experimental results for different feed concentrations, mixed extractant compositions and flow rates. At all feed flow rates and mixed extractant compositions used in the experimental studies, there was a steady increase in the concentration of all the three metals with time. Therefore, classical breakthrough behavior was not observed.

3.2.3 Effect of Feed Flow Rate on Extraction of Cu(II), Cr(VI) and Zn(II)

Figures 3.15, 3.16 and 3.17 show the effect of feed flow rate on extraction of Zn(II), Cu(II) and Cr(VI) at a mixed extractant composition of 15% LIX 84, 15% D2EHPA and 8% TOA in kerosene. Extraction of all the three metals was best at a low flow rate of 0.4 mL/min. There was a sharp increase in concentration of the metals over time at a flow rate of 0.8 mL/min compared to a gradual increase in concentration over time for a flow rate of 0.4 mL/min. There was not much change in the concentration of the metals during the initial stage of the experiment, but, as time increases, higher concentrations of metals were obtained at higher flow rates.

3.2.4 Effect of Mixed Extractant Composition on Extraction of Cu(II), Cr(VI) and Zn(II)

Figures 3.18, 3.19 and 3.20 show the effect of mixed extractant composition on extraction of Cu(II), Cr(VI) and Zn(II). At a mixed extractant composition of 15% LIX 84, 15% D2EHPA and 7% TOA, lower concentrations of LIX 84-TOA complex and D2EHPA-TOA

complex are formed compared to when, a mixed extractant composition of 15% LIX 84, 15% D2EHPA and 8% TOA is used, leading to a higher concentration of free LIX 84 and free D2EHPA and a lower concentration of free TOA . Therefore, extraction of Cu(II) and Zn(II) was better when mixed extraction composition was 15% LIX 84, 15% D2EHPA and 7% TOA in kerosene. Extraction of Cr(VI) was better when mixed extractant composition was 15% LIX 84, 15% D2EHPA and 8% TOA. At a mixed extractant composition of 10% LIX 84, 10% D2EHPA and 7% TOA, best extraction results for Cr(VI) were obtained while worst extraction results for Cu(II) and Zn(II) were obtained.

Table 3.23. Extractor performance for Cu(II) = 105.2 ppm, Zn(II) = 115 ppm, Cr(VI) = 65 ppm, flow rate = 0.775 ml/min, pH ~ 4.1, LIX 84 = 15%, D2EHPA = 15%, TOA = 7%

Time Elapsed (min)	[Zn(II)] (ppm)	[Cu(II)] (ppm)	Cr(VI) (ppm)	pH
35	3.1	1.61	1.52	2.65
80	7.5	3.63	3.42	2.39
120	10	3.47	7.55	2.19
175	13	4.43	11.02	2.17
245	23	9.6	14.61	2.15

Table 3.24. Extractor performance for Cu(II) = 160 ppm, Zn(II) = 93 ppm, Cr(VI) = 69.6 ppm, flow rate = 0.60 ml/min, pH ~ 4.1, LIX 84 = 15%, D2EHPA = 15%, TOA = 8%

Time Elapsed (min)	[Zn(II)] (ppm)	[Cu(II)] (ppm)	Cr(VI) (ppm)
50	4.2	2.19	0.25
90	12.0	3.85	0.55
140	18.5	9.45	1.25
190	20.0	16.72	2.54
310	25.0	41.45	9.04

Table 3.25. Extractor performance for Cu(II) = 160 ppm, Zn(II) = 93 ppm, Cr(VI) = 69.6 ppm, flow rate = 0.40 ml/min, pH ~ 4.1, LIX 84 = 15%, D2EHPA = 15%, TOA = 7%

Time Elapsed (min)	[Zn(II)] (ppm)	[Cu(II)] (ppm)	Cr(VI) (ppm)
55	1.2	3.55	2.01
175	5.0	10.5	4.35
235	6.5	13.65	6.40
315	7.5	18.26	6.52

Table 3.26. Extractor performance for Cu(II) = 156 ppm, Zn(II) = 97.5 ppm, Cr(VI) = 79 ppm, flow rate = 0.40 ml/min, pH ~ 4.1, LIX 84 = 15%, D2EHPA = 15%, TOA = 8%

Time Elapsed (min)	[Zn(II)] (ppm)	[Cu(II)] (ppm)	Cr(VI) (ppm)
55	0.10	2.42	2.10
115	6.0	12.25	3.75
175	9.0	14.42	2.56
205	11.0	15.45	1.62
295	14.0	20.35	1.00
385	17.0	28.10	1.29

Table 3.27. Extractor performance for Cu(II) = 156 ppm, Zn(II) = 97.5 ppm, Cr(VI) = 79 ppm, flowrate = 0.80 ml/min, pH ~ 4.1, LIX 84 = 15%, D2EHPA = 15%, TOA = 8%

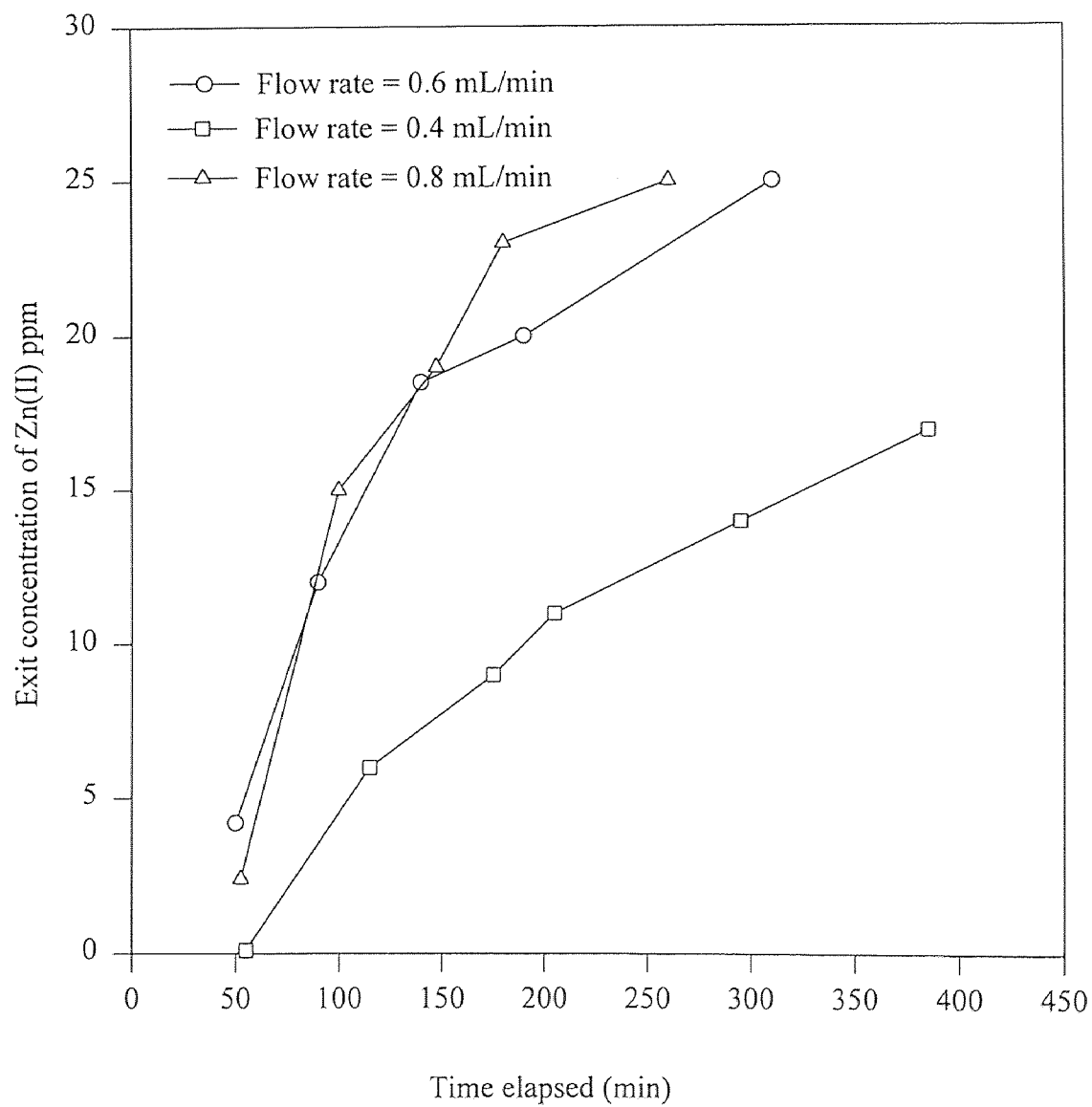
Time Elapsed (min)	[Zn(II)] (ppm)	[Cu(II)] (ppm)	Cr(VI) (ppm)
52.5	2.40	5.25	4.25
100	15.0	20.55	7.2
147.5	19.0	33.05	3.63
180	23.0	>40	4.85
260	25.0	>40	8.72

Table 3.28. Extractor performance for Cu(II) = 140 ppm, Zn(II) = 100 ppm, Cr(VI) = 69 ppm, flow rate = 1.0 ml/min, pH ~ 4.1, LIX 84 = 10%, D2EHPA = 10%, TOA = 7%

Time Elapsed (min)	[Zn(II)] (ppm)	[Cu(II)] (ppm)	Cr(VI) (ppm)
50	6.6	7.45	0.85
90	31.0	33.50	0.38
130	40.0	50	0.48
180	55.0	60	0.82
240	60.0	64	1.20

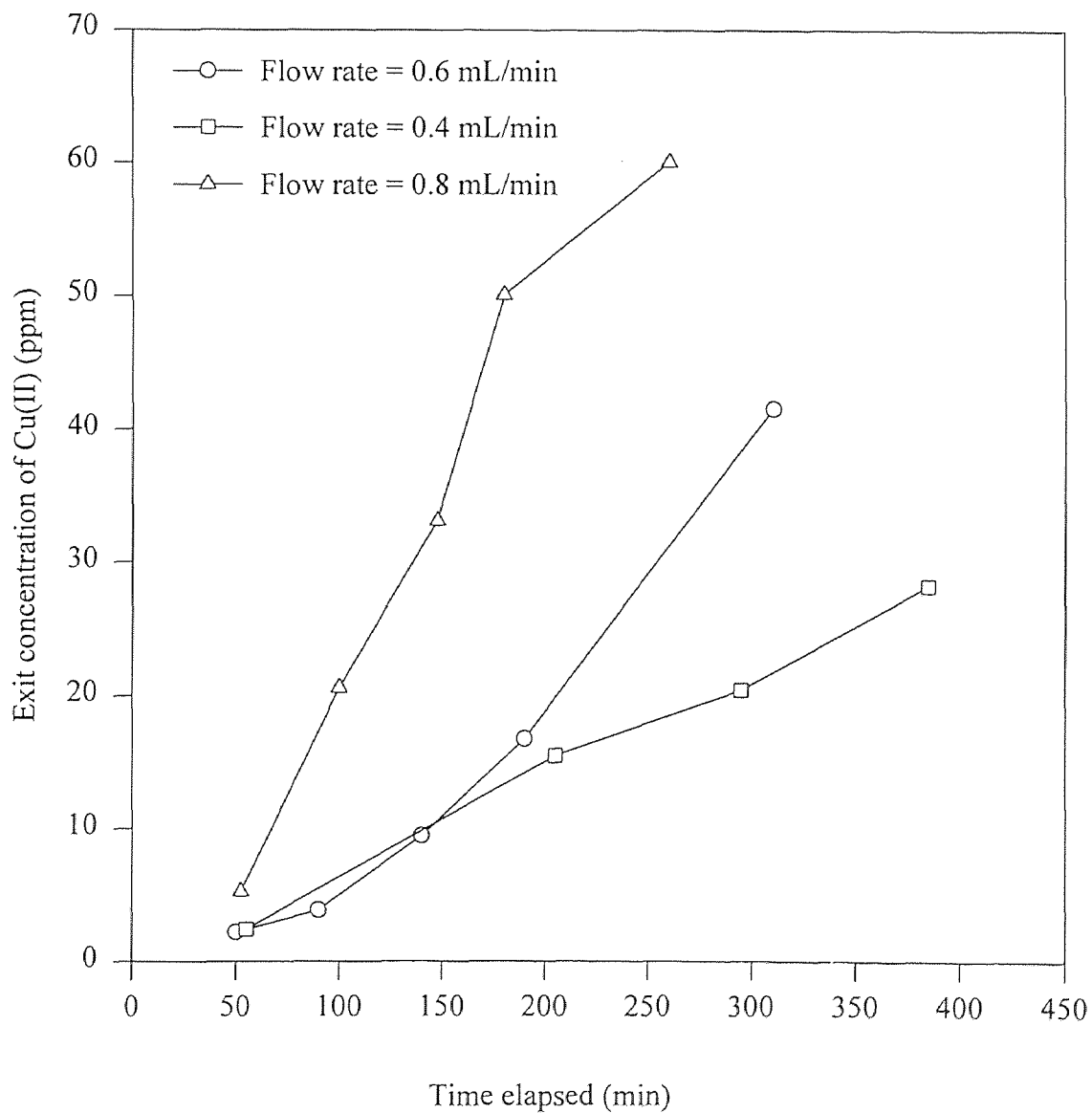
Table 3.29. Extractor performance for Cu(II) = 140 ppm, Zn(II) = 100 ppm, Cr(VI) = 69 ppm, flow rate = 0.65 ml/min, pH ~ 4.1, LIX 84 = 10%, D2EHPA = 10%, TOA = 7%

Time Elapsed (min)	[Zn(II)] (ppm)	[Cu(II)] (ppm)	Cr(VI) (ppm)
50	5.1	6.20	1.25
90	25.0	28.13	0.80
170	45.0	48.4	0.41
240	57.0	58.0	0.45
310	61.0	64.0	0.85
370	64.0	68.60	2.69



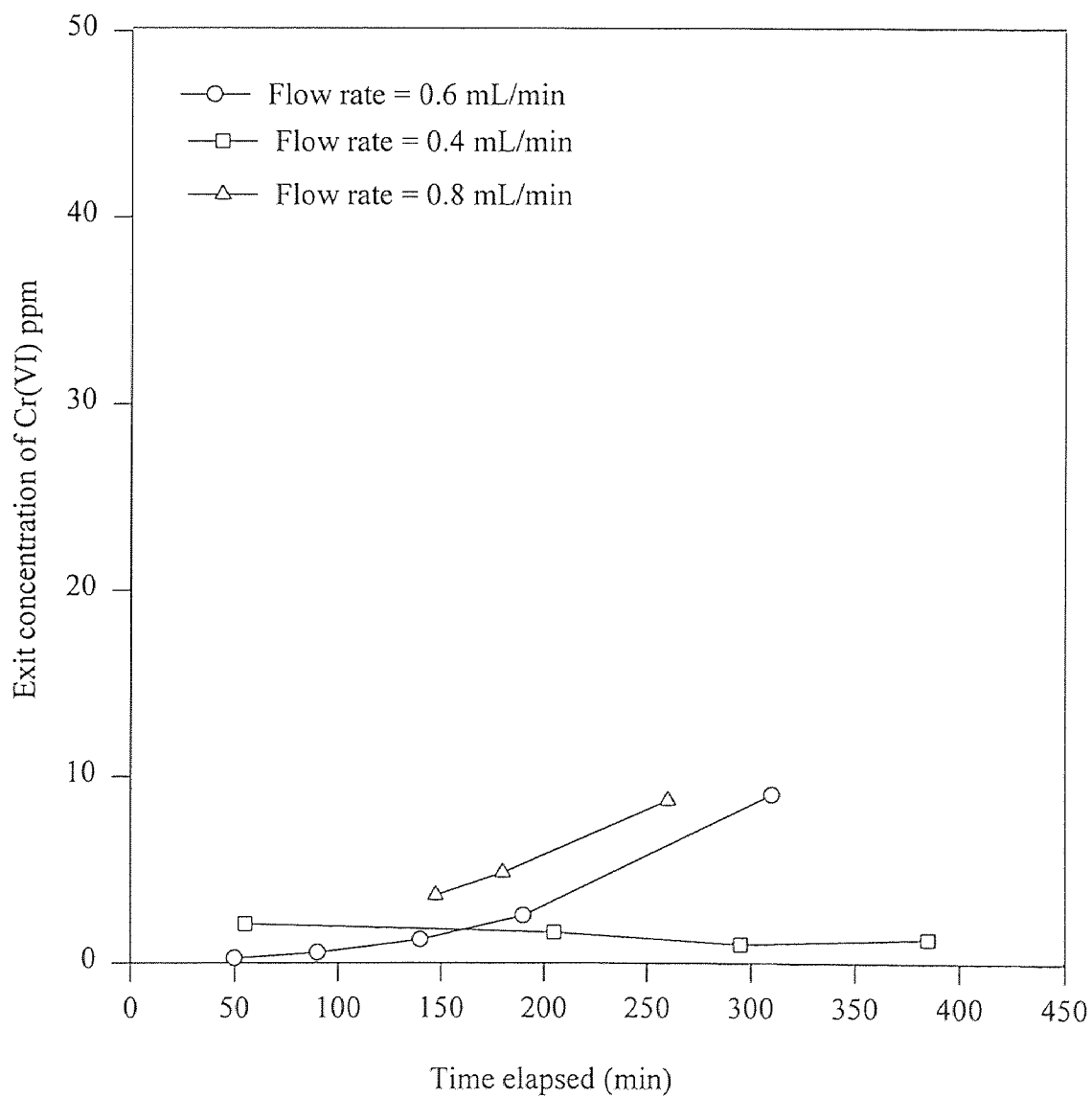
LIX 84 = 15%, D2EHPA = 15%, TOA = 8%
Cu(II) = 160-156 ppm, Zn(II) = 93-97.5-97.5 ppm, Cr(VI) = 69.6-79-79 ppm

Figure 3.15. Effect of feed flow rate on the breakthrough behavior of Zn(II)



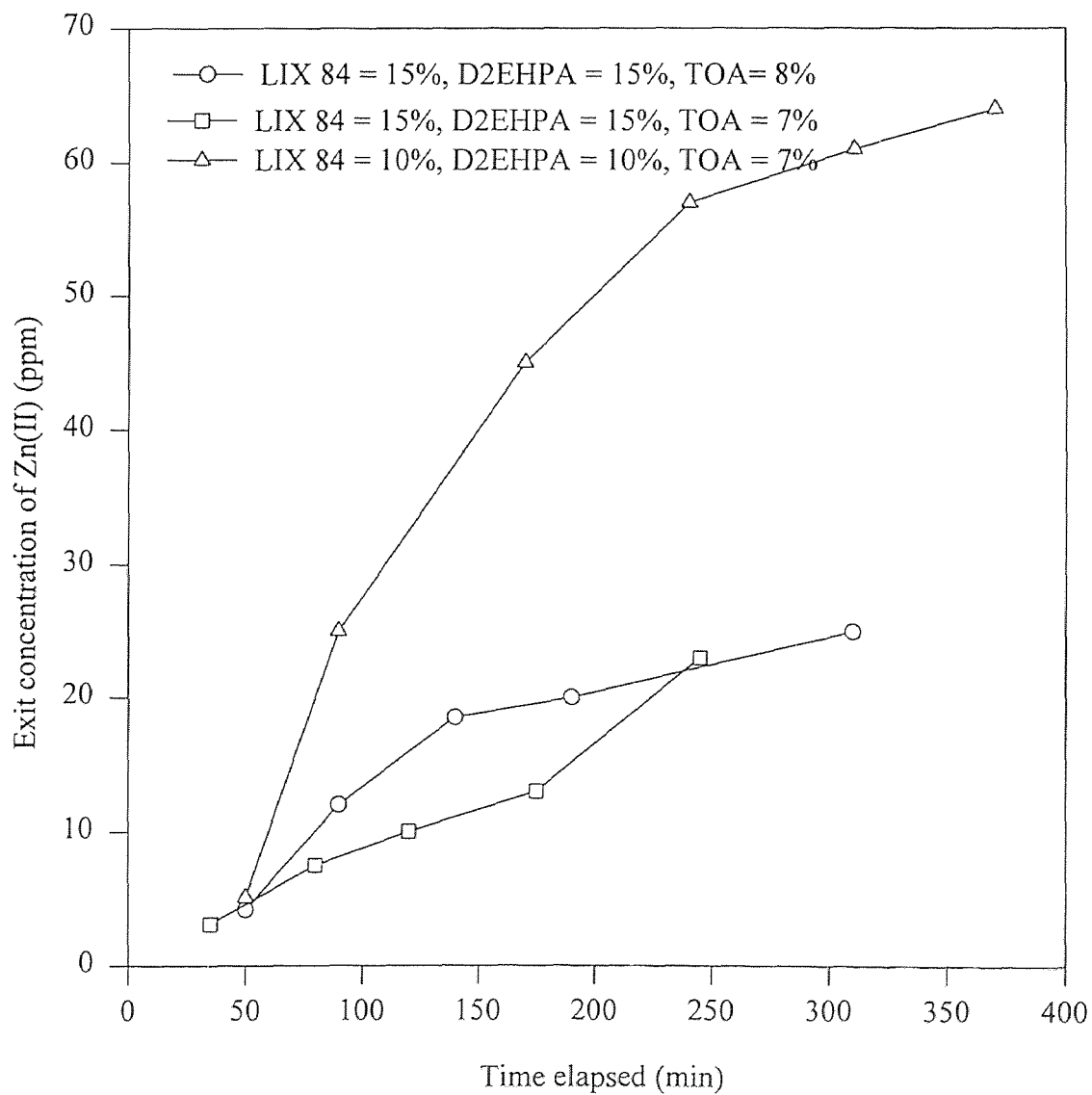
Cu(II) = 160-156 ppm, Zn(II) = 93-97.5-97.5 ppm, Cr(VI) = 69.6-79-79 ppm
LIX 84 = 15%, D2EHPA = 15%, TOA = 8%

Figure 3.16. Effect of feed flow rate on the breakthrough behavior of Cu(II)



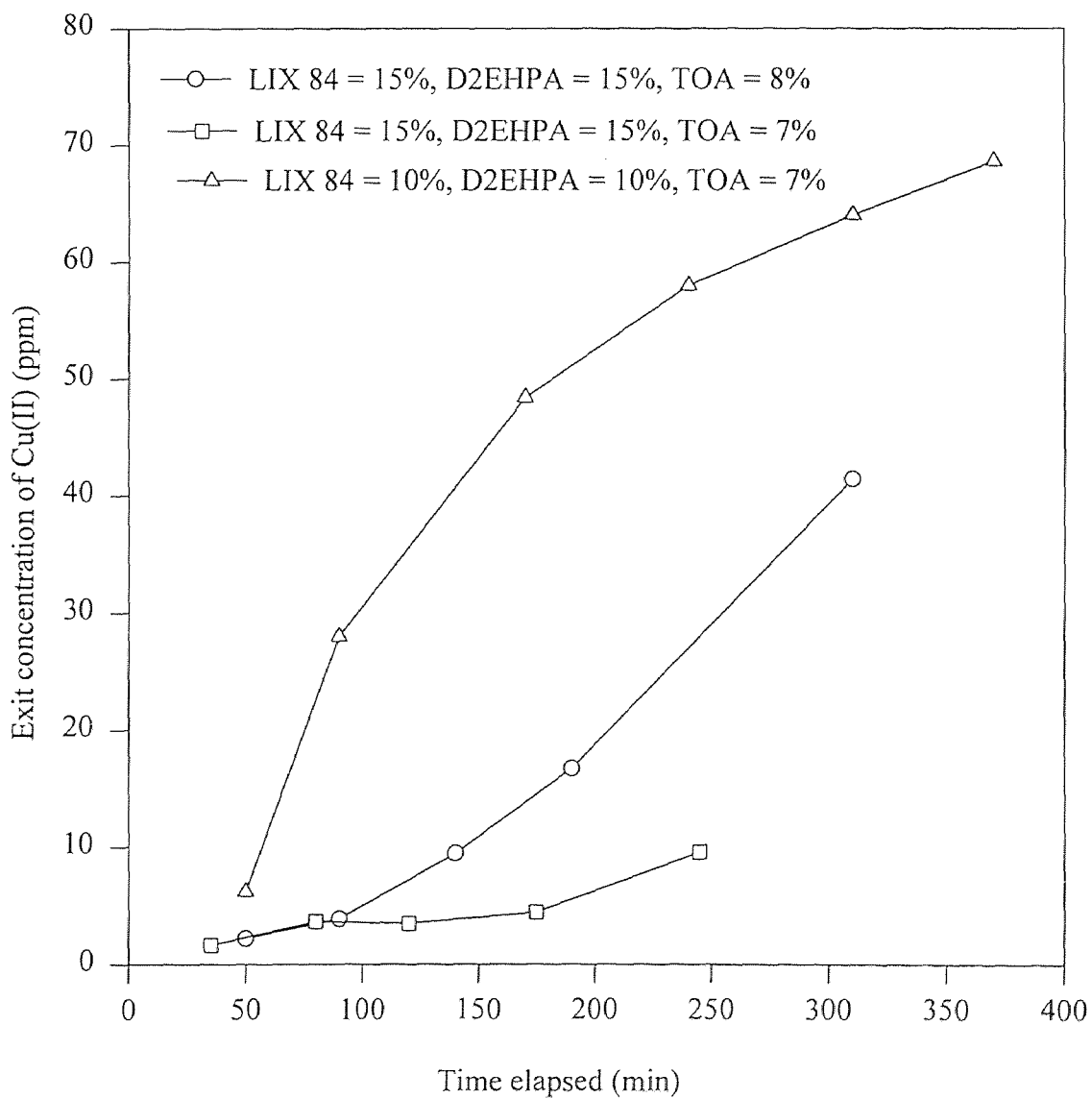
Cu(II) = 160-156 ppm, Zn(II) = 93-97.5-97.5 ppm, Cr(VI) = 69.6-79-79 ppm
LIX 84 = 15%, D2EHPA = 15%, TOA = 8%

Figure 3.17. Effect of feed flow rate on the breakthrough behavior of Cr(VI)



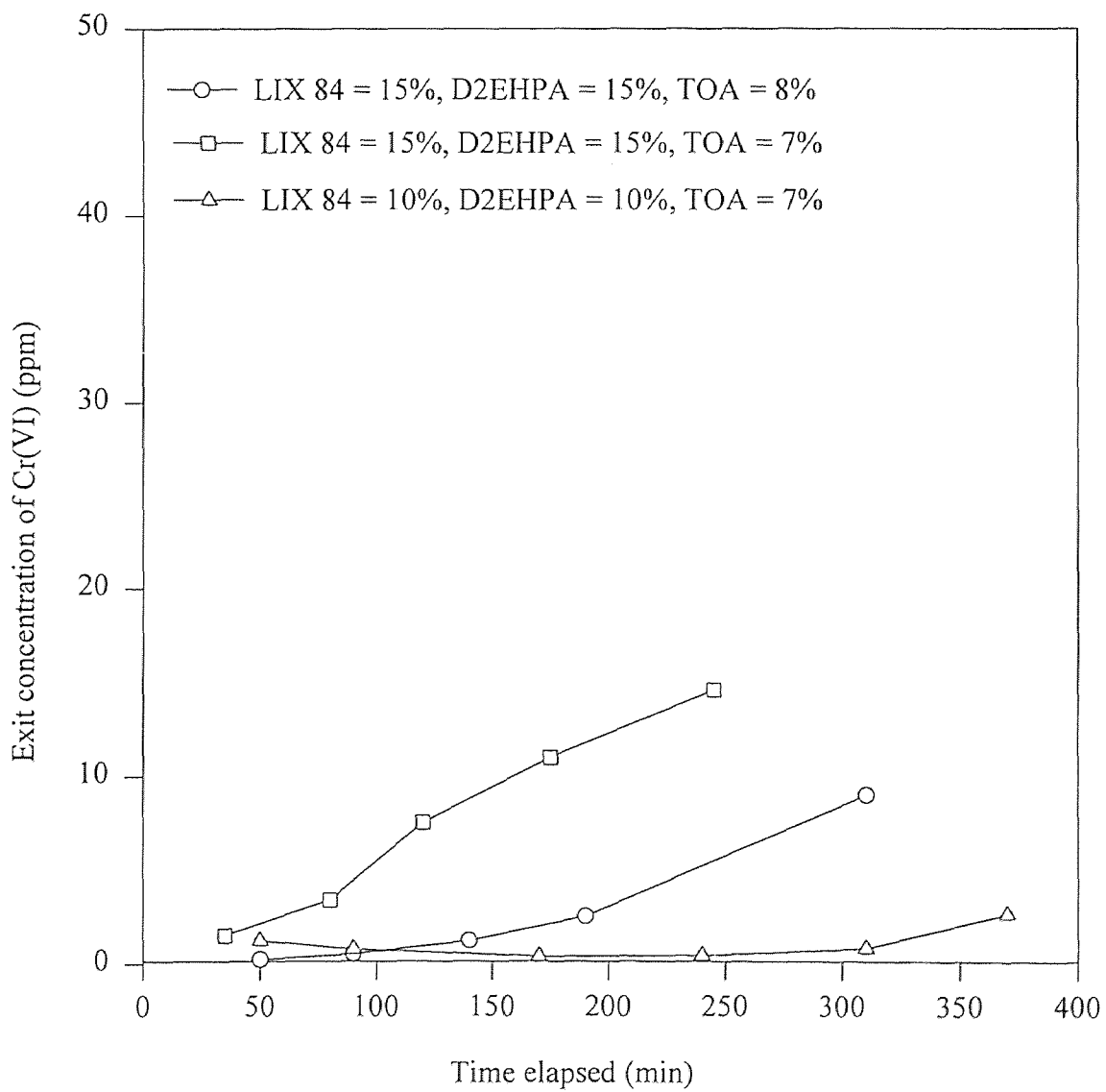
Cu(II) = 160 - 105.2 - 140 ppm, Zn(II) = 93 - 115 - 100 ppm, Cr(VI) = 69.6 - 65 - 69 ppm
 Flow rate = 0.6 - 0.775 - 0.65 mL/min

Figure 3.18. Effect of mixed extractant composition on the breakthrough behavior of Zn(II)



Cu(II) = 160 - 105.2 - 140 ppm, Zn(II) = 93 - 115 - 100 ppm, Cr(VI) = 69.6 - 65 - 69 ppm
 Flow rate = 0.6 - 0.775 - 0.65 mL/min

Figure 3.19. Effect of mixed extractant composition on the breakthrough behavior of Cu(II)



Cu(II) = 160 - 105.2 - 140 ppm, Zn(II) = 93 - 115 - 100 ppm, Cr(VI) = 69.6 - 65 - 69 ppm
 Flow rate = 0.6 - 0.775 - 0.65 mL/min

Figure 3.20. Effect of mixed extractant composition on the breakthrough behavior of Cr(VI)

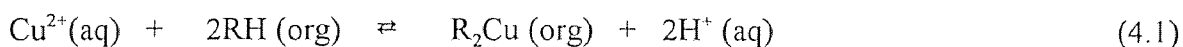
CHAPTER 4

MODELING

4.1 Simplified Model for Batch Extraction of Cu^{2+} with LIX 84 and TOA in Kerosene

Batch extraction of Cu^{2+} with LIX 84 and TOA in kerosene was modeled assuming that the following chemical reactions take place in the system:

1) Extraction of Cu^{2+} by LIX 84:



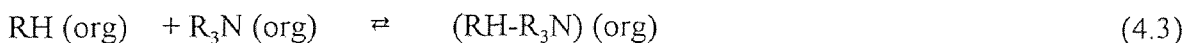
where RH stands for LIX 84.

2) Extraction of H_2SO_4 by TOA:



where R_3N stands for TOA.

3) Formation of LIX 84-TOA complex:



Mass balance on Cu^{2+} , SO_4^{-2} , H^+ , R_3N and RH respectively yield the following equations:

$$[\text{Cu}^{2+}] = [\text{Cu}^{2+}]_0 - [\text{R}_2\text{Cu}] \quad (4.4)$$

$$[\text{SO}_4^{-2}] = [\text{SO}_4^{-2}]_0 - [(\text{R}_3\text{N})\text{H}_2\text{SO}_4] \quad (4.5)$$

$$[\text{H}^+] = [\text{H}^+]_0 + 2\{[\text{Cu}^{2+}]_0 - [\text{Cu}^{2+}]\} - 2\{[\text{SO}_4^{-2}]_0 - [\text{SO}_4^{-2}]\} \quad (4.6)$$

$$[\text{R}_3\text{N}] = [\text{R}_3\text{N}]_0 - [(\text{R}_3\text{N})\text{H}_2\text{SO}_4] - [\text{RH}-\text{R}_3\text{N}] \quad (4.7)$$

$$[\text{RH}] = [\text{RH}]_0 - 2[\text{R}_2\text{Cu}] - [\text{RH}-\text{R}_3\text{N}] \quad (4.8)$$

where subscript o indicates starting concentrations.

Using equations (4.4) and (4.5), equations (4.7) and (4.8) can be modified to:

$$[R_3N] = [R_3N]_o - ([SO_4^{-2}]_o - [SO_4^{-2}]) - [RH-R_3N] \quad (4.9)$$

$$[RH] = [RH]_o - 2 ([Cu^{2+}]_o - [Cu^{2+}]) - [RH-R_3N] \quad (4.10)$$

Equilibrium constants for reactions (4.1) , (4.2) and (4.3) can be written in terms of their molar concentrations as :

$$K_{Cu}^{eq} = \frac{[R_2Cu][H^+]^2}{[RH]^2[Cu^{2+}]} \quad (4.11)$$

$$K_{SO_4}^{eq} = \frac{[(R_3N)H_2SO_4]}{[H^+]^2[SO_4^{-2}][R_3N]} \quad (4.12)$$

$$K = \frac{[RH-R_3N]}{[R_3N][RH]} \quad (4.13)$$

Using equations (4.4) and (4.5), equations (4.11) and (4.12) can be modified to:

$$K_{Cu}^{eq} = \frac{([Cu^{2+}]_o - [Cu^{2+}])[H^+]^2}{[RH]^2[Cu^{2+}]} \quad (4.14)$$

$$K_{SO_4}^{eq} = \frac{([SO_4^{-2}]_o - [SO_4^{-2}])}{[H^+]^2[SO_4^{-2}][R_3N]} \quad (4.15)$$

Equilibrium constant for extraction of copper by LIX 84 has been determined by a number of researchers (Teramoto and Tanimoto, 1983; Yun et al., 1993). Here, the value of K_{Cu} chosen was 1.7 (Yun et al., 1993). In the extraction of sulfuric acid by TOA, salts of many kinds form at varying ratios of initial concentrations of the two reactants (Allen, 1956; Wilson, 1967). In the present model, it is being assumed that reaction (4.2) is predominant and the equilibrium constant was chosen to be $5 \times 10^8 \text{ (mol/L)}^{-3}$ (Wang et al., 1993).

Equations (4.6), (4.9), (4.10), (4.14) and (4.15) were solved simultaneously using the programs in MATHEMATICA (Version 2.1) assuming different values (100, 150 and 200) for K (equilibrium constant for equation (4.13)). A value of $K=150$ gave the best results, i.e., the calculated equilibrium concentrations of various species were close to experimental results when K was chosen as 150. Tables 4.1 and 4.2 compare the batch experimental results for extraction of copper using two different mixed extractant concentrations with simulated results. Simulated raffinate Cu(II) concentration and pH were closer to the experimental raffinate Cu(II) concentration and pH when mixed extractant containing 0.156 M LIX 84 + 0.156 M TOA in kerosene was used compared to when mixed extractant containing 0.234 M LIX 84 + 0.234 M TOA was used. Figures 4.1 and 4.2 show the comparison between the experimental results and simulated results for batch extraction of copper with a mixed extractant containing 0.156 M LIX 84 + 0.156 M TOA.

Table 4.1 Comparison between experimental results and simulated results for batch extraction of Cu(II) with a mixed extractant containing 0.156 M LIX 84 + 0.156 M TOA in kerosene

Experimental Results			Simulated Results					
Feed [Cu(II)] (ppm)	Raffinate [Cu(II)] (ppm)	pH	Raffinate [Cu(II)] (ppm)	pH	[LIX 84] (M)	[TOA] (M)	[LIX 84 - TOA] (M)	[SO ₄ ⁻²] (M) X 10 ⁴
92	0.04	3.54	0.01	3.40	0.0281	0.0296	0.1250	5.4
192	0.09	3.44	0.04	3.27	0.0270	0.0302	0.1229	6.2
380	0.12	3.41	0.18	3.14	0.0251	0.0314	0.1188	7.0
880	0.14	3.33	1.0	3.02	0.0206	0.0348	0.107	8.4

Table 4.2 Comparison between experimental results and simulated results for batch extraction of Cu(II) with a mixed extractant containing 0.234 M LIX 84 + 0.234 M TOA in kerosene

Experimental Results			Simulated Results					
Feed [Cu(II)] (ppm)	Raffinate [Cu(II)] (ppm)	pH	Raffinate [Cu(II)] (ppm)	pH	[LIX 84] (M)	[TOA] (M)	[LIX 84 - TOA] (M)	[SO ₄ ²⁻] (M) X 10 ⁴
92	0.02	4.458	0.005	3.443	0.0353	0.0369	0.1958	5.3
192	0.09	4.334	0.024	3.30	0.0343	0.0375	0.1936	5.99
380	0.26	4.020	0.09	3.18	0.0325	0.0388	0.1894	6.8
880	0.30	3.870	0.51	3.06	0.0281	0.0402	0.1783	8.0

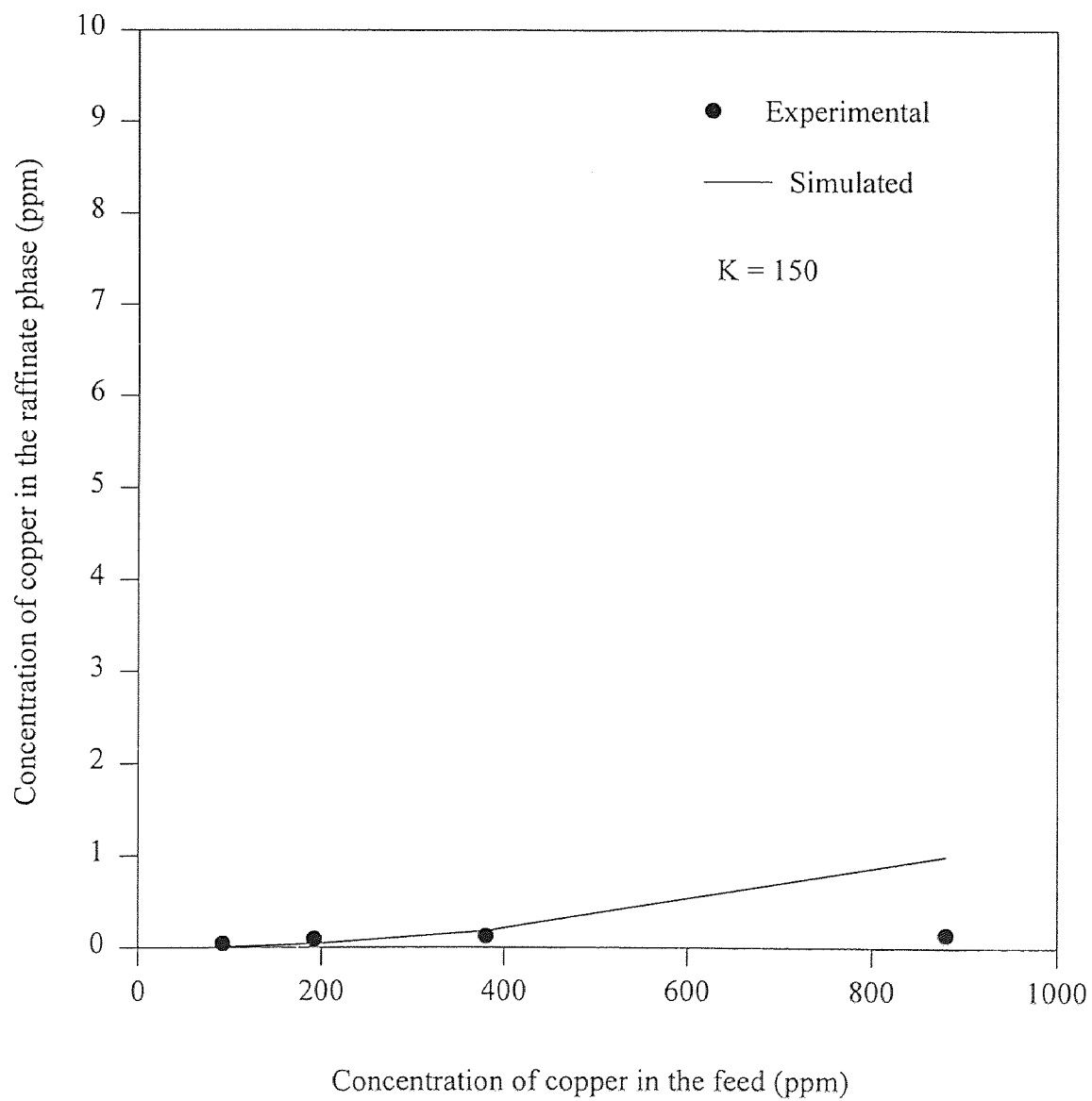


Figure 4.1. Comparison between experimental results and simulated results for batch extraction of Cu(II) with a mixed extractant containing 0.156 M LIX 84 + 0.156 M TOA in kerosene

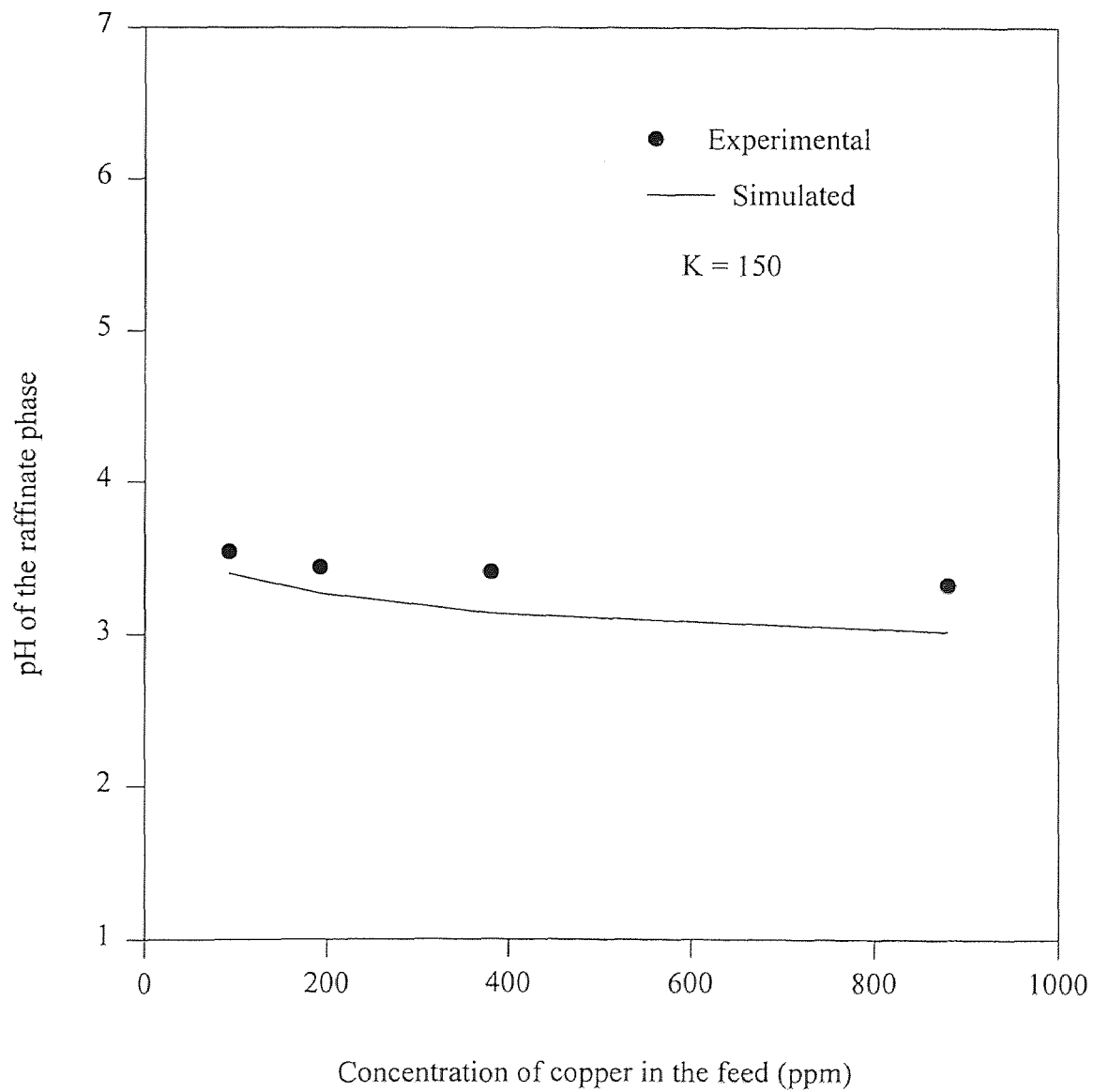


Figure 4.2. Comparison between experimental results and simulated results for batch extraction of Cu(II) with a mixed extractant containing 0.156 M LIX 84 + 0.156 M TOA in kerosene

CHAPTER 5

CONCLUSIONS

The following conclusions were drawn from the study of mixed metal removal and recovery by a mixed extractant containing an acidic extractant (for cations) and a basic extractant (for anions) in a diluent.

1. Batch experimental results for copper and chromium system showed that a mixed extractant containing LIX 84 and TOA in kerosene could be used efficiently for simultaneous removal of copper and chromium. Distribution coefficients of copper and chromium were dependent on the feed concentration of the metal ions and the mixed extractant composition. Raffinate phase pH was also dependent on the feed concentration of the metal ions and the mixed extractant composition.
2. Fixed bed extraction studies for copper and chromium system indicate that copper and chromium concentration could be reduced to less than 1 ppm from a feed concentration of 200 ppm copper and 100 ppm chromium using appropriate mixed extractant composition and feed flow rates. Both feed flow rate and mixed extractant composition were found to affect the time after which breakthrough of copper occurred. Delayed breakthrough for copper could be obtained using higher mixed extractant concentration and lower feed flow rates. No breakthrough was observed for chromium at all the mixed extractant compositions and concentrations and feed flow rates. When higher feed concentrations are used, breakthrough of copper can be delayed using either higher mixed extractant concentration or lower feed flow rate.

3. Batch experimental results for copper, zinc and chromium system showed that a mixed extractant containing LIX 84, D2EHPA and TOA in kerosene could be used efficiently for simultaneous removal of copper, zinc and chromium. Extraction of copper, zinc and chromium was highly dependent on the relative concentrations of LIX 84, D2EHPA and TOA in the mixed extractant. A starting feed pH of 4.0 could be used for efficient extraction performance. A mixed extractant containing D2EHPA and TOA in kerosene could be used efficiently for simultaneous removal of zinc and chromium.

4. Fixed bed extraction studies for copper, zinc and chromium system indicate that copper, zinc and chromium concentration could be reduced to less than 2 ppm from a feed concentration of 150 ppm copper, 100 ppm zinc and 70 ppm chromium using appropriate mixed extractant composition and feed flow rates. Good extraction performance was obtained at low feed flow rates. Any change in the relative concentration of LIX 84, D2EHPA and TOA in the mixed extractant altered the extraction of all three metals.

5. Preliminary modeling of Cu(II) extraction in a batch system of mixed extractants containing LIX 84 and TOA in kerosene has been carried out. Reasonable estimates could be obtained for raffinate Cu(II) concentration and pH when this model is employed. Simulated raffinate Cu(II) concentration and pH were closer to experimental raffinate Cu(II) concentration and pH when mixed extractant containing 0.156 M LIX 84 + 0.156 M TOA in kerosene was used compared to when mixed extractant containing 0.234 M + 0.234 TOA in kerosene was used.

6. These preliminary studies indicate that this process can easily clean up 12-17 bed volumes (depending on the bed volume definition) of wastewater to the level of less than 1 ppm of mixed metals (Calculations are shown in appendix A).

APPENDIX A

A.1 Calculations for Number of Bed Volumes Treated

I.D of the shell = 1.27 cm

Length of the shell = 30 cm

$$\begin{aligned} \text{Total shell volume} &= \frac{\pi*(1.27)^2*30}{4} \text{ c.c} \\ &= 37.38 \text{ c.c} \end{aligned}$$

O.D of the fiber = 150 μm

No. of fibers = 2000

Length of the fiber = 30 cm

$$\begin{aligned} \text{Volume occupied by the fibers} &= \frac{\pi*(150*10^{-4})^2*30*2000}{4} \text{ c.c} \\ &= 10.59 \text{ c.c} \end{aligned}$$

Therefore volume occupied by the mixed extractant = 37.38 - 10.59 c.c

$$= 26.78 \text{ c.c}$$

When the mixed extractant composition was 20% LIX 84, 10% TOA in kerosene and the feed flow rate was 1.0 mL/min (Table 3.11), breakthrough does not occur for both the metals (Cu(II) and Cr(VI)) even after 460 minutes.

Therefore volume of aqueous feed treated before the breakthrough = 460 c.c

Number of bed volumes treated = $460/26.78$

~ 17

When the calculation is based on total shell volume, number of bed volumes treated

= $460/37.38$

~ 12

A.2 Computer Program for Solving the Equation Set in Chapter 4

```

equ = {1.7- ((([Cu]-m)*(h^2)/((a^2)*m)))-=0,
       5*10^8 - ((([SO4]-s)/(h^2*s*b)))-=0,
       150- (c/(a*b))-=0,
       a- [LIX84]+2(.0014-m)+c ==0,
       b- [TOA] +.0018-s+c==0,
       [H+] - h+2(.0014-m)-2(.0018-s)==0};
NSolve[equ{a,b,c,m,s,h}]
FindRoot[equ,{a,.025},{b,.04},{c,.12},{m,3.14*10^-7},{s,10^-4},{h,10^-3.5}]

```

Where

[Cu], m = Initial and equilibrium copper ion concentration (mol/L)
 [SO4], s = Initial and equilibrium sulfate ion concentration (mol/L)
 [H+], h = Initial and equilibrium hydrogen ion concentration (mol/L)
 a, b = Equilibrium concentration of LIX 84 and TOA (mol/L)

REFERENCES

- Allen, K. A. "The Equilibrium Between Tri-*n*-Octylamine and Sulfuric Acid". *J. Phys. Chem.* **1956**, 60, 239-245
- Guha, A. K.; Yun, C. H.; Basu, R.; Sirkar, K. K. "Heavy Metals Removal and Recovery by Contained Liquid Membrane Permeator". *AIChE J.* **1994**, 40 (7), 1223-1237.
- Hochhauser, A. M.; Cussler, E. L. "Concentrating Chromium with Liquid Surfactant Membranes". *AIChE Symp. ser.* **1975**, 71(152), 136.
- Kiani, A.; Bhave, R. R.; Sirkar, K. K. "Solvent Extraction with Immobilized Interfaces in a Microporous Hydrophobic Membrane". *J. Membr. Sci.* **1984**, 20 (2), 125.
- Lee, K.; Evans, D. F.; Cussler, E. L. "Selective Copper Recovery with Two Types of Liquid Membranes". *AIChE J.* **1978**, 24, 860.
- Lo, T. -C.; Baird, M. H. I.; Hansen, C. *Handbook of Solvent Extraction*, Wiley-Interscience **1983**, New York, NY.
- Pearson, D. "Supported Liquid Membranes for Metal Extraction from Dilute Solutions". *Ion Exchange Membranes*; Chapter 4. Ed. Flett, D. S.; Ellis Horwood Limited, U.K, **1983**.
- Prasad, R.; Sirkar, K. K. "Dispersion-free Solvent Extraction with Microporous Hollow-fiber Modules". *AIChE J.* **1988**, 34(2), 177.
- Prasad, R.; Sirkar, K. K. "Membrane-based solvent Extraction" *Membrane Handbook*; Chapter 42. Ed. Winston, W. S.; Sirkar K. K.; Van Nostrand Reinhold, New York, NY, **1992**.
- Ritcey, G. M.; Ashbrook, A. W. *Solvent Extraction*, Part I; Elsevier: Amsterdam, **1984**.
- Sengupta, A. K.; Basu, R.; Sirkar, K. K. "Separation of Solutes from Aqueous Solutions by Contained Liquid Membranes". *AIChE J.* **1988**, 34, 1698-1708.
- Seibert, A. F.; Sengupta, A. "Liquid- Liquid Extraction Studies on Semi-pilot Scale Using Recently Commercialized Large Membrane Contactors and Systems". *AIChE Annual Meeting*, San Francisco, **1994**; Paper No. 153e.
- Teramoto, M.; Tanimoto, H. "Mechanism of Copper Permeation Through Hollow Fiber Liquid Membranes". *Sep. Sci. and Tech.* **1983**, 18, 871.

- Yang, Z. F.; Guha, A. K.; Sirkar, K. K. "Novel Membrane-Based Synergistic Metal Extraction and Recovery Processes". *I & E Chem. Res.* **1996a**, 35, 1383-1394.
- Yang, Z. F.; Guha, A. K.; Sirkar, K. K. "Simultaneous and Synergistic Extraction of Cationic and Anionic Heavy Metallic Species by a Mixed Extraction System and a Novel Contained Liquid Membrane Device" *I & E Chem. Res.* **1996b**, 35, 4214-4220.
- Yun, C. H.; Prasad, R.; Sirkar, K. K. "Hollow Fiber Solvent Extraction of Removal of Toxic Heavy Metals from Aqueous Waste Streams". *I & E Chem. Res.* **1993**, 32(6), 1186-1195.
- Wang, M. -L; Hu, K. -H. "Model of Chemical Reaction Equilibrium of Sulfuric Acid Salts of Trioctylamine" . *Chem. Eng. Comm*, **1993**, 126, 43-57.
- Wilson, A. S. "The Extraction of Sulfuric Acid into Benzene by Tri-*n*-Octylamine" In *Solvent Extraction Chemistry*; Dyresen, D., Liljenzin, J. O., Rydberg, J., Eds; North-Holland: Amstredam, **1967**, pp 369-374.