To the Graduate Council:

I am submitting herewith a thesis written by Yeak-Chong Wong entitled "An Experimental Investigation of Heavy Metal Adsorption by a Commercial Chelating Ion Exchange Resin." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

George C. Frazier

George C. Frazier, Major Professor

We have read this thesis
and recommend its acceptance:

Robert M. Counce

Joseph J. Corona

Accepted for the Council

Associate Vice Chancellor and
Dean of the Graduate School

An Experimental Investigation of Heavy Metal Adsorption by a Commercial Chelating Ion Exchange Resin

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Yeak-Chong Wong

May 1997

DEDICATION

This thesis is dedicated to my parents

Mr. Choh Man Wong

and

Mrs. Pak Thye Wong

who have given me invaluable educational opportunities

ACKNOWLEDGEMENTS

The author wishes to acknowledge, with sincere gratitude, the guidance and suggestion given by his major professor, Dr. George C. Frazier. The author also wishes to thank the members of his research committee, Dr. Joseph J. Perona and Dr. Robert M. Counce. The author extends special thanks to Miss Sharon Hale in Environmental Engineering for her help and advice on the analysis work. For special help, the author would also like to recognize and thank Miss Cynthia French for her sharing of her precious experimental experience. The author's sincere appreciation goes to Sybron Chemicals Inc. for providing the Ionac®SR-5 resin used in this study. Finally, The author's deepest appreciation goes to Miss Ning Ku and to his family for their support and encouragement during the course of this work.

ABSTRACT

A series of binary equilibrium experiments were conducted in order to provide sufficient data for the determination of the equilibrium constants and binary interaction parameters for the systems Cd^{++}/Cu^{++}, Na^{+}/Cd^{++} and Na^{+}/Cu^{++} on a commercial, chelating ion exchange resin, SR-5, marketed by Sybron Chemicals Inc. The Pitzer equation was used to determine the liquid phase activity coefficients, while the procedure proposed by Smith and Woodburn along with the Wilson model was used to determine the equilibrium constants K_{AB} and the binary interaction parameters Λ_{AB} and Λ_{BA}. The binary parameters were then used to predict the behavior of the three component system Na^{+}, Cd^{++} and Cu^{++} on the same resin, using the mass action equilibrium model and to evaluate the average separation factors for these systems. These separation factors were then used to estimate the breakthrough time for each of the three cations from a fixed bed of resin by the simple, multicomponent, equilibrium, non-dispersion model of Helfferich.

TABLE OF CONTENTS

CHAPTER	PAGE
1. **INTRODUCTION**	**1**
1.1 Objective	4
1.2 Methodology	5
2. **BACKGROUND**	**6**
2.1. History	6
2.2. Water Purification [Metals Removal]	7
2.3. Properties of Ion Exchange Resins	8
2.3.1. Basic Structure and Chemical Composition	8
2.3.2. Properties	9
2.4 Theory of Multicomponent Ion Exchange	9
2.4.1. Equilibrium Model	10
2.4.2. Batch Kinetics	15
2.4.3. Fixed Bed Model	17
3. **EQUILIBRIUM STUDIES**	**20**
3.1. Materials and Equipment	20
3.2. Batch Equilibrium Experiments, Binary Systems	22
3.3. Binary Equilibrium Results and Interpretation	25
3.4. Batch Equilibrium Experiments, Multicomponent Systems	31
3.5. Multicomponent Equilibrium Results and Interpretation	34

4. **BATCH KINETICS STUDY** 57

4.1. Multicomponent Kinetics Experiment 57

4.2. Multicomponent Kinetics Experimental Results 58

5. **FIXED BED SIMULATION** 60

5.1. Determination of Separation Factor 60

5.2. Simulation of Fixed Bed Effluent Concentration History 61

6. **SUMMARY and CONCLUSIONS** 71

7. **FUTURE WORK** 74

BIBLIOGRAPHY 75

APPENDICES 78

APPENDIX A : EXPERIMENTAL INFORMATION 79

APPENDIX B : COMPUTER CODES MATLAB M-FILES 87

VITA 100

LIST OF FIGURES

2.1	Binary System A-B equilibrium	13
2.2	Computation Scheme of Binary Equilibrium	14
3.1	Algorithm of modeling binary equilibrium experimental data for Cd^{++}/Cu^{++} and Na^{+}/Cd^{++} systems	26
3.2	Isotherm of Cd^{++}/Cu^{++} binary system	28
3.3	Isotherm of Na^{+}/Cd^{++} binary system	29
3.4	Isotherm of Na^{+}/Cu^{++} binary system	30
3.5	Multicomponent equilibrium experiments, Cu^{++} isotherm	35
3.6	Multicomponent equilibrium experiments, Cd^{++} isotherm	36
3.7	Multicomponent equilibrium experiments, Na^{+} isotherm	37
3.8	Algorithm of predicting the multicomponent equilibrium from binary interaction parameters	39
3.9	Three components Na^{+}, Cu^{++} and Cd^{++} Equilibrium on SR-5, 1st experiment, Cu^{++} isotherm	40
3.10	Three components Na^{+}, Cu^{++} and Cd^{++} Equilibrium on SR-5, 1st experiment, Cd^{++} isotherm	41
3.11	Three components Na^{+}, Cu^{++} and Cd^{++} Equilibrium on SR-5, 1st experiment, Na^{+} isotherm	42
3.12	Three components Na^{+}, Cu^{++} and Cd^{++} Equilibrium on SR-5, 2nd experiment, Cu^{++} isotherm	43
3.13	Three components Na^{+}, Cu^{++} and Cd^{++} Equilibrium on SR-5, 2nd experiment, Cd^{++} isotherm	44

3.14 Three components Na^+, Cu^{++} and Cd^{++} Equilibrium on SR-5, 2nd experiment, Na^+ isotherm 45

3.15 Three components Na^+, Cu^{++} and Cd^{++} Equilibrium on SR-5, 3rd experiment, Cu^{++} isotherm 46

3.16 Three components Na^+, Cu^{++} and Cd^{++} Equilibrium on SR-5, 3rd experiment, Cd^{++} isotherm 47

3.17 Three components Na^+, Cu^{++} and Cd^{++} Equilibrium on SR-5, 3rd experiment, Na^+ isotherm 48

3.18 Multicomponent equilibrium behavior predicted by model : constant Cu^{++} concentration, Cd^{++} isotherm 50

3.19 Multicomponent equilibrium behavior predicted by model : constant Cu^{++} concentration, Na^+ isotherm 51

3.20 Multicomponent equilibrium behavior predicted by model : constant Na^+ concentration, Cu^{++} isotherm 52

3.21 Multicomponent equilibrium behavior predicted by model : constant Na^+ concentration, Cu^{++} isotherm 53

3.22 Multicomponent equilibrium behavior predicted by model : constant Cd^{++} concentration, Cu^{++} isotherm 55

3.23 Multicomponent equilibrium behavior predicted by model : constant Cd^{++} concentration, Na^+ isotherm 56

4.1 Batch Kinetics Experiment of Cu^{++}, Cd^{++} and Na^+ loading on SR-5 resin 59

5.1 Binary isotherms of Cu^{++}/Cd^{++} and Cu^{++}/Na^+ used for determination of α_{CuCd} and α_{CuNa}. 62

5.2 Calculated h_i profiles of h-analysis 66

5.3 Effluent concentration history of a three component system estimated according to the Equilibrium, non Dispersion model. 68

5.4 Loading composition on the fixed bed ion exchange column corresponding to the condition of the example 70

LIST OF TABLES

3.1.	Properties of Ionac® SR-5 Ion Exchange Resin	21
3.2.	Preparation of ionic solutions with different Na^{+}/Cu^{++} ratio	24
3.3	Equilibrium constants and Wilson's parameters for the SR-5 Resin	31
3.4	Preparation of 1st multicomponent experiment	32
3.5	Preparation of 2nd and 3rd multicomponent experiments	33

LIST OF SYMBOLS AND ABBREVIATIONS

Batch Equilibrium Model:

B_{ij}, C_{ij}	Pitzer correlation variables
I	ionic strength
b	a constant in Pitzer equation = 1.2
z	valence of ion
C_i	normality of species i in liquid phase
F	quotient objective function
K_{AB}	equilibrium constant
x_i	equivalent ionic fraction of component i in the liquid phase
y_i	equivalent ionic fraction of component i in the solid phase
Λij	Wilson binary interaction parameters
γ^s_i	solid phase activity coefficient of species i
γ_i	liquid phase activity coefficient of species i
λ	equilibrium quotient

Batch Kinetics:

c	pore phase concentration
c_b	bulk phase concentration
c_o	initial pore phase concentration
ε_p	porosity of adsorbent pellets
$f(c)$	defines the isotherm $q = f(c)$
c_s	concentration at surface
B	defined as ka_p/D_p
τ	defined as $D_p t/a_p^2$
k	film mass transfer coefficient
D_p	pore diffusion coefficient

Fixed Bed Kinetics:

α_{ij}	separation factor for species i and j; stationary phase preference order is i over j species, preference order is i>j>k.
h_i	ith root of H function, dimensionless
P_k	constant defined in Eq.(13)
R	ratio defined in Eq.(11)
T	throughput rate
x_i	equivalent ionic fraction of component i in the liquid phase
y_i	equivalent ionic fraction of component i in the solid phase

CHAPTER 1
INTRODUCTION

Ion exchange is one of the most important liquid purification techniques which has been developed and used for a very long time. About 330 BC, Aristotle stated that sea water loses part of its salt content when percolating through certain sands. This observation may be one of the earliest records about ion exchange[Miller, 1955]. Since then ion exchange has been developed into a useful water purification technique along with the development of synthetic organic ion exchange resins. Other than water purification, ion exchange was widely used in many applications which can be categorized into five main groups[Kunin, 1958] :

(1) Transformation of ionic constituents: softening of water, removal of sodium in milk.

(2) Fractionation of ionic substances: separation of hydrochloric and hydrocyanic acids, ion exchange chromatography.

(3) Concentration of ionic substances: recovery of magnesium from sea water, analysis of copper in milk and recovery of uranium from ore leach liquors.

(4) Removal of ionic substances: deionization or demineralization by mixed bed of anion and cation exchange resins.

(5) Miscellaneous applications: adsorption of acidic and basic gases such as SO_2 and NH_3, used as catalysts and permselective membrane.

A large amount of research has been conducted, in order to improve the properties of synthetic ion exchange resins and to find new applications for these ion exchangers. The research work and the theory of ion exchange can be grouped into three main aspects: equilibria, batch kinetics and fixed bed model.

Equilibrium is a property of ion exchange which relates the ion distribution behavior between ion exchangers and solutions. The exchange capacity of a resin which is the maximum amount of ions that can be exchanged at a specific temperature is an important equilibrium property. Most of the theoretical work about equilibria is based on the basic physical factors of ion exchange including capacity, degree of crosslinking and swelling. By controlling the structure, capacity and degree of crosslinking of a synthetic ion exchanger, investigators are able to consider these physical properties separately. Several equilibria theories which are in good agreement with experiment results have been developed. However, in this research, our objective is to describe ion exchange equilibria of a specific kind of ion exchanger by various quantities which include, ion exchange isotherm, separation factor, selectivity coefficient and equilibrium constant. The ion exchange isotherm shows the equilibrium ion concentration on the solid with respect to experimental conditions which are solution concentration and temperature. The separation factor is the quotient of the concentration ratios of the two counter ions in the ion exchanger and in the solution. The definition of selectivity coefficient is similar to the separation factor but contains ionic valences as exponents. The equilibrium constant is used in theoretical studies because it is the basic parameter in thermodynamics. A suitable

model will be used to calculate these quantities from experimental data. Then, batch kinetics experiment can be conducted in order to check the equilibrium model used and the validity of the calculated equilibrium quantities.

Ion exchange is a time dependent process in which ions transport and diffuse through several media including solution, film around solid, solid pore and solid surface. The theory of ion exchange kinetics is studied in order to understand this complicated process. The mechanism of the process and the rate determining step are first assumed in order to present a rate law. Rate of ion exchange can be predicted if the assumptions are reasonable. The basic concept of kinetic theory is Fick's second law which describes the time dependence of concentration as interrelated with the flux by material balance. Batch kinetics experiments conducted in a thoroughly agitated solution are used to examine the actual exchange mechanism. The concentration data which are collected in different time increments until the system reaches equilibrium can be fitted to a suitable rate law and the rate of ion exchange and diffusion coefficients in ion exchangers can be calculated. Eventually, the batch kinetics results can be extended to fixed bed kinetics which is the ultimate goal of our research as well as a useful unit operation technique in chemical industries.

Practical use of ion exchange is normally carried out in fixed bed column. A solution is passed through a bed of ion exchange beads to perform ion exchange process until specific ion breakthrough occurs from the column. The kinetics of the column process is complex and involves mass transfer and equilibria. Many theories which satisfy different levels of complexity of the process were developed. These

theories are based on various drastic simplifications or semiempirical approaches. Suitable theories are useful to determine ion exchange column performance, the breakthrough curve, and the column history. A high performance column requires a self-sharpening concentration boundary. A nonsharpening boundary will leave a larger portion of unused bed.

The column performance is controlled by several factors which including particle size of the ion exchange resin, volumetric flow rate, operating temperature, selectivity of the ion exchanger for the counter ion from the feed, and aspect ratio of the column. For binary systems, column kinetics is analogous to adsorption processes in fixed beds. Dealing with a multi-component system further raises the complexity of the system but the theory of interference for multicomponent chromatography[Helfferich, 1970] seems to be a promising approach.

1.1 Objective

The objective of this work is to use an ion exchange resin in separation of multicomponent metal ions contamination in water. Batch and fixed bed experiments are to be conducted to find a suitable equilibrium model, batch kinetics model and fixed bed model to describe the system. Parameters of these models can be calculated from data collected from specially designed experiments. With suitable models and parameters, laboratory operation can be scaled-up to larger commercial size and the best operating condition can be found which allowed saving time in pilot plant experiment.

1.2 Methodology

Two approach methods will be used in this research. Batch experiments conducted in a batch cell with good agitation is to be used to determine equilibrium behavior and batch kinetics behavior. Suitable model incorporate with computer programming in MATLAB will be used to interpret the experimental data and used to simulate the equilibrium and kinetics behavior of multicomponent ion exchange systems in batch and fixed bed operation.

CHAPTER 2

BACKGROUND

2.1 History

Ion exchange has an interesting history. The earliest ancient reference is found in the Holy Bible [Exodus 15:23-25] that reads, " They could not drink of the waters of Marah, for they were bitter .... And he cried unto Jehovah; and Jehovah showed him a tree, and he cast it into the waters, and the waters were made sweet." [Helfferich 1962]. In this incident the water was undoubtedly purified by an ion exchange process which took place among the tree and bitter water. As we began to realize the importance and usefulness of the ion exchange process, the development of ion exchange techniques were never stopped and there are some important mile stones in this progress. In 1850, Thompson and Way rediscovered cation exchange in soils. In 1903, Harm and Rumpler, two German chemists, prepared the first synthetic industrial ion exchanger. In 1935, two English chemists, Adams and Holmes, showed that crushed phonograph records exhibit ion-exchange properties and led the inventors to the synthesis of organic ion exchange resins which had much better properties than any previous products. These new synthetic resins were developed and improved by the former I. G. Farbenindustrie in Germany. Nearly all current industrial and laboratory applications of ion exchange are based on such resins [Helfferich 1962].

Today, ion exchange has become an important unit operation and is a valuable supplement to other processes such as filtration, distillation and adsorption. Ion exchange has become a basic need in our life for purification and demineralization of drinking water. In industry, it is used in numerous plants, accomplishing tasks that range from the recovery of metals from industrial wastes to the separation of rare earths, and from catalysis of organic reactions to decontamination of water in cooling systems of nuclear reactors. In the laboratory, ion exchangers are used as an aid in analytical and preparative chemistry, biophysics and biotechnology [Helfferich 1962].

2.2 Water Purification [Metals Removal]

Ion exchange is the most outstanding and simplest operation to remove ion contamination in water especially for low concentration contamination. The most widely used processes include water softening, deionization and metals removal. The common technologies for metals control used in industry are essentially based on precipitation. However precipitation process will generate metals containing sludge that causes a disposal problem. Ion exchange is a typical example of "conservative technology", offers advantages in terms of :

(1) Recovery of metals and water for reuse;

(2) High concentration of metals in the elution streams;

(3) Relatively low cost.

2.3 Properties of Ion Exchange Resins

2.3.1 Basic Structure and Chemical Composition

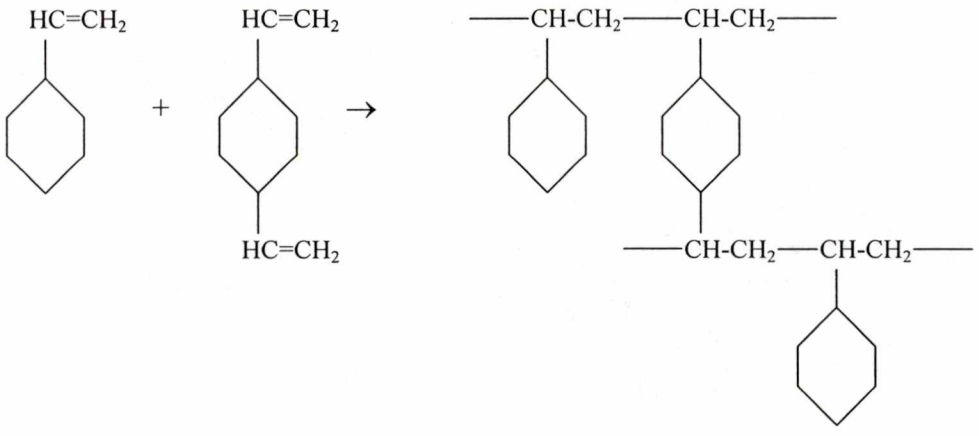
Organic ion exchange resins are the most important class of ion exchangers. They are constructed of irregular three dimensional matrix of hydrocarbon chains. The matrix carries ionic functional groups such as

$-SO_3^-$ $-COO^-$ $-PO_3^{2-}$ $-AsO_3^{2-}$

in cation exchangers, and

$-NH_3^+$ $-NH_2^+-$ $-N^+-$ $-S^+-$

in anion exchangers. For amphoteric ion exchangers, both types of ionic functional groups can be found in the matrix. In other words, these resins are crosslinked polyelectrolytes. The most common matrix is prepared by copolymerization of styrene with varying amounts of divinylbenzene which acts as crosslinking agent, as shown by the following reaction[Helfferich 1962].



2.3.2 Properties

The ion exchange behavior of the resins is mainly determined by the fixed ionic functional groups. The number of the groups determines the ion exchange capacity. The chemical nature of the groups greatly affects ion exchange equilibria. The nature of the fixed ionic groups also affects the selectivity of the resins. Counter ions that tend to form ion pairs or complexes with the fixed functional groups are preferred by the resins [Helfferich 1962].

By understanding of these general rules, ion exchange resins with specific properties can be tailor made by controlling the nature and number of the fixed ionic functional groups, the composition and the degree of crosslinking of the matrix.

2.4 Theory of Multicomponent Ion Exchange

Nearly all practical and important ion exchange processes deal with more than two exchangeable ions[Lucas, 1992]. However, most research works are based on investigations of binary systems. Ion exchange involving multiple ions exchange is a very complex process which not only involves mass transfer and equilibria but also involves the interaction between various ions. The prediction of the equilibrium of multicomponent ion exchange by using a suitable model is the starting point for the design of exchangers. Then the mass transfer behavior can be added in to the system so that batch kinetics can be described. The final goal is modeling the continuous ion exchange operation that takes place in a fixed bed column. The suitable fixed bed model will allow us to characterize column performance and breakthrough behavior.

2.4.1 Equilibrium Model

In 1978, a general scheme for predicting multicomponent ion exchange equilibria for the ternary system SO_4^{2-}, NO_3^-, Cl^- from the data for binary systems was presented by Smith and Woodburn [Smith and Woodburn 1978]. The multicomponent model proposed by Smith and Woodburn was modified by Shallcross et al. [Shallcross et al., 1988] to investigate ion exchange equilibrium of the ternary system Mg^{2+} , Ca^{2+} , Na^+ with Cl^-. The Smith model was again modified and used by Lucas et al. to determine ion exchange equilibrium of Ca^{2+} , Mg^{2+} , K^+ , Na^+ and H^+ ions on Amberlite IR-120 from binary ion exchange equilibrium data [Lucas et al., 1992 and 1993]. In 1993, Perona modified the Smith model in order to model Sr^{2+} , Cs^+ , Ca^{2+} , Mg^{2+} , Na^+ ion exchange equilibria on Chabazite [Perona, 1993]. In our research, we follow the Smith model modified by Shallcross but we extend it to predict a three component system.

For a binary exchange reaction,

$$bA^{+a} + a\mathbf{B}^{+b} \Leftrightarrow b\mathbf{A}^{+a} + aB^{+b}.$$

the equilibrium constant, K_{AB}, is given by:

$$K_{AB} = \left(\frac{\mathbf{a}_A}{a_A}\right)^b \left(\frac{a_B}{\mathbf{a}_B}\right)^a = \frac{(\gamma^s_A y_A)^b (\gamma_B C_B)^a}{(\gamma_A C_A)^b (\gamma^s_B y_B)^a}. \qquad (2.1)$$

The activity coefficient of component i in the solid phase can be calculated from the Wilson Model [Wilson, 1964],

$$\ln \gamma_i^s = 1 - \ln(\sum_j y_j \Lambda_{ij}) - \sum_k (\frac{y_k \Lambda_{ki}}{\sum_j y_j \Lambda_{kj}}). \qquad (2.2)$$

The activity coefficient of electrolyte CA in liquid phase can be calculated from the Pitzer Equations which have the relation [Pitzer,1974],

$$\begin{aligned}
\ln \gamma_{CA} &= |z^+ z^-| f^\gamma + \frac{2\nu_+}{\nu} \sum_a m_a \left[B_{Ca} + (\sum mz) C_{Ca} + \frac{\nu_-}{\nu_+} \theta_{Aa} \right] \\
&+ \frac{2\nu_-}{\nu} \sum_c m_c \left[B_{cA} + (\sum mz) C_{cA} + \frac{\nu_+}{\nu_-} \theta_{Cc} \right] \\
&+ \sum_c \sum_a m_c m_a \left[|z_+ z_-| B'_{ca} + \frac{1}{\nu} (2\nu_+ z_+ C_{ca} + \nu_+ \psi_{Cca} + \nu_- \psi_{caA} \right] \\
&+ \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} \left[\frac{\nu_-}{\nu} \psi_{cc'A} + |z_+ z_-| \theta'_{cc'} \right] \\
&+ \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} \left[\frac{\nu_+}{\nu} \psi_{Caa'} + |z_+ z_-| \theta'_{aa'} \right] \qquad (2.3)
\end{aligned}$$

with:

$$f^\gamma = -A_\phi \left[\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b} \ln(1 + b\sqrt{I}) \right]$$

$$B_{ij} = \beta_0 + \frac{2\beta_1}{\alpha^2 I} \left\{ 1 - (1 + \alpha\sqrt{I}) \exp(-\alpha\sqrt{I}) \right\}$$

$$B'_{ij} = \frac{2\beta_1}{\alpha^2 I^2} \left\{ -1 + (1 + \alpha\sqrt{I} + \tfrac{1}{2}\alpha^2 I) \exp(-\alpha\sqrt{I}) \right\}$$

$$C_{ij} = \frac{C_{ij}^\phi}{2\sqrt{z_+ z_-}}$$

$$C_{ij}^\phi = \frac{3}{\sqrt{\nu_+ \nu_-}} \left[\nu_+ \Lambda_{Iij} + \nu_- \Lambda_{iJj} \right]$$

$$\theta_{ij} = \lambda_{ij} - \frac{z_j}{2z_i} \lambda_{ii} - \frac{z_i}{2z_j} \lambda_{jj}$$

$$\theta'_{ij} = \frac{\partial \theta_{ij}}{\partial I}$$

$$\psi_{ijk} = 6\Lambda_{ijk} - \frac{3z_j}{z_i}\Lambda_{iij} - \frac{3z_i}{z_j}\Lambda_{jjk}$$

Activity coefficients in the liquid phase can be calculated using the Pitzer method. However, the method required to estimate the solid phase activity coefficients and the equilibrium constant is more complicated. The procedure proposed by Smith and Woodburn is presented here. The 'equilibrium quotient' which is a form of corrected selectivity coefficient, λ, is defined as:

$$\lambda_{AB} = \frac{(\gamma_B C_B)^a y_A^b}{(\gamma_A C_A)^b y_B^a} \tag{2.4}$$

This equilibrium quotient can be expressed in terms of the equilibrium constant:

$$\lambda_{AB} = K_{AB} \frac{\gamma_B^{S^a}}{\gamma_A^{S^b}} \tag{2.5}$$

Combining the Wilson equation with this expression of equilibrium quotient yields:

$$\begin{aligned} \ln \lambda_{AB} = \ln K_{AB} - b\left[1 - \ln(y_A + y_B\Lambda_{AB}) - \left(\frac{y_A}{y_A + y_B\Lambda_{AB}} + \frac{y_B\Lambda_{BA}}{y_A\Lambda_{BA} + y_B}\right)\right] \\ +a\left[1 - \ln(y_A\Lambda_{BA} + y_B) - \left(\frac{y_A\Lambda_{AB}}{y_A + y_B\Lambda_{AB}} - \frac{y_B}{y_A\Lambda_{BA} + y_B}\right)\right] \end{aligned} \tag{2.6}$$

Experimental equilibrium data for a binary system can be used to determine values for the equilibrium constant K_{AB} and the two interaction parameters Λ_{AB} and Λ_{BA}. Typical experimental data for a A-B binary system is shown in Figure 2.1. The experiments are to be designed to provide a wide range in values for y_A and x_A.

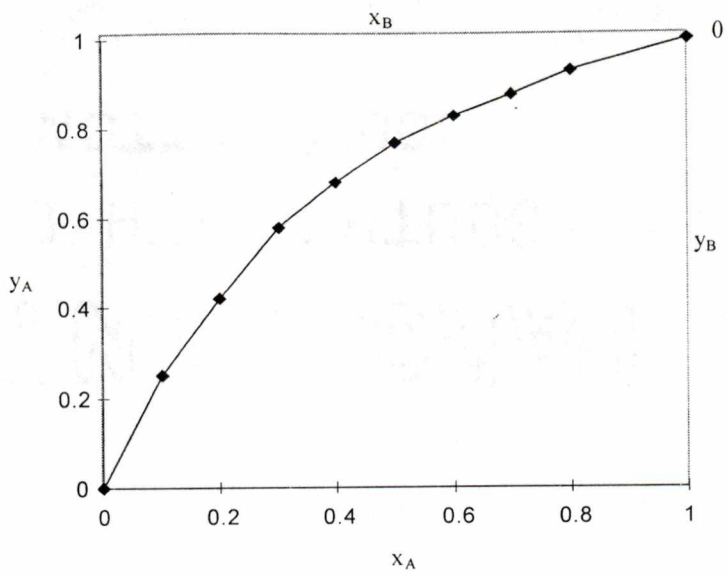


Figure 2.1 : Binary System A-B equilibrium

Each data point on the graph represents compositions of the liquid and solid phases that are in equilibrium with one another. A value of equilibrium quotient, λ^{exp}, may be calculated from Eq. 2.4 for each of these data points. Values for the quotient, λ^{fit}, may also be calculated for each point using Eq. 2.6 and trial values for K_{AB}, Λ_{AB} and Λ_{BA}. The function F which is the sum of the squares of the deviations between experimental and predicted values is used as a criterion for best fit of N data points:

$$F_{12} = \sum_{i=1}^{N} \left(\frac{\lambda_i^{exp} - \lambda_i^{fit}}{\lambda_i^{exp}} \right)^2 \qquad (2.7)$$

The values of K_{AB}, Λ_{AB} and Λ_{BA} are true when the value of function F_{AB} is minimum. Generally, each system has only a unique set of values for K_{AB}, Λ_{AB} and Λ_{BA} for which F_{AB} will be minimum. The computation scheme for determine the minimum value of F_{AB} is shown in Figure 2.2.

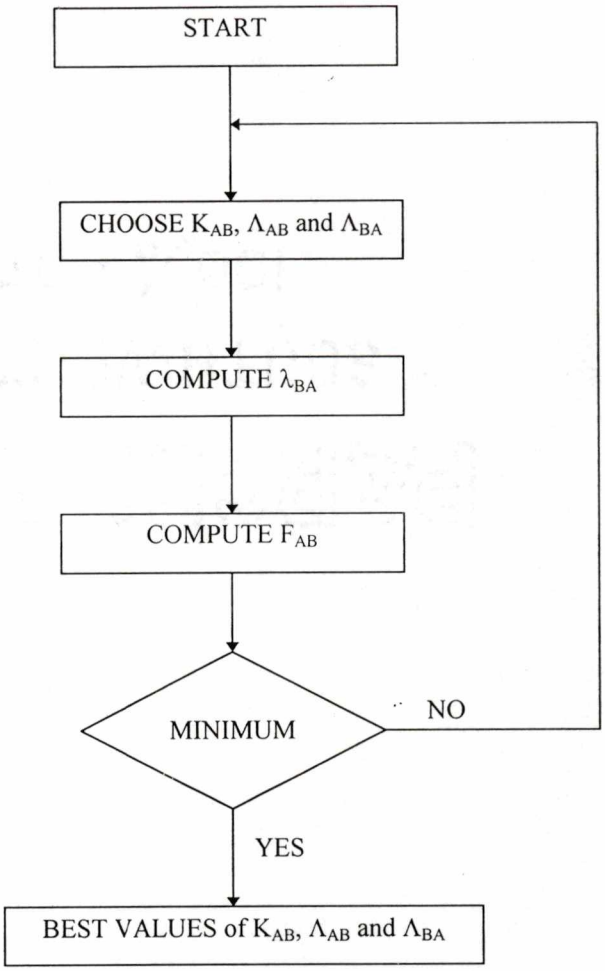


Figure 2.2 : Computation Scheme of Binary Equilibrium

The determination of equilibrium constant and Wilson binary interaction parameters which include a equilibrium experiment for a binary system and a computer computation for the best fit values of K_{AB}, Λ_{AB} and Λ_{BA}, is repeated for each binary system of interest until all values of K and Λ are known. Then the interaction parameters can be substituted into Eq. 2.1 to calculate the solid phase activity coefficient. The liquid phase activity coefficient can be calculated from Pitzer equation Eq. 2.3 and note that when the solutions are very dilute, only the first term in Pitzer equation is significant.

2.4.2 Batch Kinetics

The rate of ion exchange is determined by diffusion process. Rate laws can be derived by applying the well-known diffusion equations to ion-exchange systems. However, the problem has been solved only for certain limiting cases due to the complicated process which involves diffusion-induced electric forces, selectivity, interaction and swelling [Helfferich F.,1962]. The difficulties are chiefly mathematical which make the rate equations difficult to be solved for a given multi-component ion-exchange system. A kinetics model developed by Yao C. and Tien C. make a good approximation of uptake rate of spherical adsorbent and can be easily extended to model the batch kinetics of a multi-components ion-exchange system [Yao C. and Tien C., 1993]. The concentration layer concept which is the foundation of this model provides valid uptake rates at small as well as large times. For pore

diffusion control, the average pore phase concentration can be determined by the following equations.

$$[\varepsilon_p + f'(c)]\frac{dc}{d\tau} = 6(\frac{c_s - c_o}{c - c_o} + \frac{1}{2})(c_s - c) \tag{2.8}$$

$$B(c_b - c_s) = 2(\frac{c_s - c_o}{c - c_o} + \frac{1}{2})(c_s - c) \tag{2.9}$$

where,

c : pore phase concentration

c_b : bulk phase concentration

c_o : initial pore phase concentration

ε_p : porosity of adsorbent pellets

$f(c)$: defines the isotherm $q = f(c)$

c_s : concentration at surface

B : defined as ka_p/D_p

τ : defined as $D_p t/a_p^2$

k : film mass transfer coefficient

D_p : pore diffusion coefficient

a_p : radius of adsorbent pellets

t : time

The uptake rate expressed by Eq. 2.8 will be referred to as the parabolic concentration layer approximation and is valid for small τ.

2.4.3 Fixed Bed Model

Theory for multicomponent ion exchange in fixed beds with interference as developed by previous investigators, especially Helfferich, provides a very useful tool for the estimation of breakthrough curves and compositions of exhausted ion-exchange beds [Clifford, 1982]. The use of the "h transformation" proposed by Helfferich [Helfferich, 1970] to orthogonalize the composition path grids greatly simplifies the calculation of composition velocities and zone composition for the constant separation factor case. Helfferich's theory is based on his concept of "coherence", a condition which he has shown to be attained from arbitrary initial conditions which is characterized by the fact that, at any point in the column, the velocities of all components are equal which can be achieved by constant feed and uniform initial bed compositions. The calculation method of this model is described in Perry's Chemical Engineering Handbook Section 16. In this transformation the n mobile and stationary phase composition variables, x_i and y_i, are replaced with n-1 composition variables, h_i. The new composition variables are the roots in h of the nonlinear transformation equation

$$H(h, X, \alpha) = \sum_i \left[\prod_{j \neq i} \left(h - \alpha_{1j} \right) x_i \right] = 0 \tag{2.10}$$

Each concentration path can be identified fully by a parameter from each of two sets, one defined by the presaturated sorbent h_P and one by the feed h_F. Each set contains n-1 values, for a system with total number n of components. For the presaturated sorbent, h_P values are obtained as the roots of the equation

$$\sum_{i=1}^{n} \frac{y_{in}}{\left(1/h_p\right) - \alpha_{i1}} = 0 \tag{2.11}$$

where y_{in} is the concentration of component i in the presaturated sorbent. For the feed, h_F values are roots of the equation

$$\sum_{i=1}^{n} \frac{x_{i1}}{h_F - \alpha_{1i}} = 0 \tag{2.12}$$

where x_{i1} is the concentration of component i in the feed.

The roots of Eqs. 2.11 and 2.12 are indexed in accordance with the condition

$$\alpha_{1i} \leq h_i \leq \alpha_{1,i+1} \qquad (i = 1, \ldots, n\text{-}1)$$

which corresponds to the convention that the selectivity of the sorbent for the various components decreases in the order i = 1, . . . , n-1. No specific connection exists between h_i and the concentration of component i.

If some of the n components of the system are absent from the presaturated sorbent or the feed, Eq. 2.11 or 2.12 will give fewer than n-1 roots. If k is an absent component, then either $h_{k\text{-}1}$ or h_k equals α_{1k}. In this manner, n-1 h_i values can be indexed without ambiguity. Once the roots have been established for any plateau zone k, the corresponding x_{jk} and y_{jk} may be calculated as

$$x_{jk} = \frac{\prod_{i} \left(h_{ik} - \alpha_{1j}\right)}{\prod_{i \neq j} \left(\alpha_{1i} - \alpha_{1j}\right)} \tag{2.13}$$

$$y_{jk} = \frac{\prod_{i}\left[\left(1/h_{ik}\right) - \alpha_{j1}\right]}{\prod_{i \neq j}\left(\alpha_{i1} - \alpha_{j1}\right)} \tag{2.14}$$

where the h_{ik} are the values applicable to plateau zone k.

An equivalent R value for transition k, k+1 is obtained from the relation

$$R_{k,k+1} = h_{kP}/h_{kF} \tag{2.15}$$

Thus the transition is abrupt if $R < 1$ and gradual if $R > 1$. The stoichiometric center of transition k, $k+1$ is given by

$$\overline{T}_{k,k+1} = \left(h_{kP} h_{kF} P_k\right)^{-1} \tag{2.16}$$

where

$$P_k = \prod_{\substack{i=1 \\ (i \neq k)}}^{n-1} h_{ik} \prod_{i=1}^{n} \alpha_{i1} \tag{2.17}$$

For an abrupt transition, the T value thus found represents the actual position of the abrupt change. For a gradual transition, the local-equilibrium concentration profiles are given by Eqs.14 and 15 using the R value determined by Eq. 2.18.

$$X = \frac{R - \sqrt{R\overline{T}/T}}{R-1} \tag{2.18}$$

$$Y = \frac{\sqrt{RT/\overline{T}} - 1}{R-1} \tag{2.19}$$

where local-equilibrium values X and Y values are identical for all components, calculated in relation to the two adjacent plateau compositions.

CHAPTER 3

EQUILIBRIUM STUDIES

3.1. Materials and Equipment

The ion-exchange material to be studied is a macroporous chelating resin based on iminodiacetic acid functionality for the selective recovery of heavy metal ions from waste treatment streams and process liquids. The resin is manufactured by Sybron Chemicals Inc. and carries a commercial name of Ionac®SR-5. General purchasing specifications, physical and chemical properties of Ionac®SR-5 resin provided by Sybron Chemicals Inc. are shown in Table 3.1. Cations to be investigated include copper (Cu^{++}), cadmium (Cd^{++}) and sodium (Na^{+}) and chloride solution is prepared to perform batch equilibrium and batch kinetics experiments . Copper chloride solution was prepared from Fisher Scientific Co. cupric chloride ($CuCl_2 \cdot 2H_2O$). Cadmium chloride solution was prepared from Mallinckrodt Specialty Chemicals Co. anhydrous cadmium chloride ($CdCl_2$, Analytical Reagent). Sodium chloride solution was prepared from Sigma Chemical Co. sodium chloride (NaCl, >99.5%). All solutions prepared from these salts were dissolved in double distilled de-ionized water to ensure the precision and accuracy of experiment and to eliminate interference of other ions.

Table 3.1. Properties of Ionac®SR-5 Ion Exchange Resin

Polymer Structure	Styrene - Divinylbenzene Copolymer
Functional Groups	Iminodiacetic Acid
Physical Form	Moist Spherical Beads
Ionic Form (as shipped)	Sodium
Selective Copper Capacity (Na form)	1.7meq/ml
Reversible Swelling (H to Na)	20% (approx.)
Particle Size Distribution (wet)	0.3-1.2mm
Effective Size (mm)	0.47-0.53mm
pH Range (Stability)	1-14
Solubility	Insoluble in all common solvents
Order of selectivity	$Cu^{2+}>Pb^{2+}>Ni^{2+}>Co^{2+}>Cd^{2+}>Fe^{3+}>Mn^{2+}>Ca^{2+}>Na^{+}$

Batch equilibrium experiments were carried out using 125ml capped NALGENE® PMP bottles and the bottles filled with 100ml ionic solution and a predetermined specific weight of resin were attached to a Heidolph Wheaton tumbling machine to enhance mixing and mass transfer to achieve equilibrium in three days.

The concentrations of heavy metal ions in solution were analyzed by the atomic absorption method. An Instrumentation Laboratory Inc. Video 12 AA/AE Spectrophotometer with air-acetylene flame was used in this research. Standard solution used in AA analyzing of Na^+, Cu^{++} and Cd^{++} cations were 1000ppm standard solution manufactured by LabChem Inc. and Mallinckridt Chemical Inc.. The pH value of solution was measured by a ATI Orion model 250A pH meter with 9107 BN pH triode™. All glassware and containers used in the research were washed and rinsed by double distilled de-ionized water.

3.2. Batch Equilibrium Experiments, Binary Systems

Binary batch equilibrium between sodium (Na^+) and copper (Cu^{++}), between sodium (Na^+) and cadmium (Cd^{++}) and between cadmium (Cd^{++}) and copper (Cu^{++}) are to be investigated and modeled.

Before conducting binary equilibrium experiments of Na^+ versus Cu^{++} and Na^+ versus Cd^{++}. The Ionac®SR-5 resin from manufacturer was conditioned and loaded with 0.2N NaCl solution. Fresh 0.2N NaCl was added to the Ionac®SR-5 resin and agitated to fully loaded the resin with Na^+ ions. This procedure was repeated until

the pH value of the 0.2N NaCl solution in contact with the resin was stable. After the resins were fully loaded with Na^+ ions, the resins was washed by using double distilled de-ionized water. For the binary equilibrium experiment of Cd^{++} versus Cu^{++}, the conditioning and loading procedure was the same as above but 0.2N $CdCl_2$ solution was used to load Cd^{++} on the resin instead of Na^+.

After the conditioning and loading procedure, the washed resin was transformed into a column with 1.5cm inner diameter and 26cm in length. Vacuum drying which was driven by flowing of water through an aspirator was performed in the column for 20 minutes to dry out the surface water of the resins. The washed and dried resins were weighted in a balance to measure the weight of the resins in wet basis which considered that only the surface water of the resins being dried out while the pores of the resins still filled with water.

Solutions of NaCl, $CuCl_2$ and $CdCl_2$ were prepared from their chloride salts in a concentration of 0.04N respectively. In the binary equilibrium experiment of Na^+ versus Cu^{++}, different volumes of 0.04N NaCl and $CuCl_2$ solutions were mixed together to prepare ionic solutions with different Na^+/Cu^{++} ratio. When these solutions in contact and equilibrium with the resins loaded with Na^+ ions, an isotherm of this Na^+/Cu^{++} binary system can be constructed. The total volume of solution was 100ml and the weight of resins used to contact was 1.00g. A typical table of preparation of ionic solution is shown in Table 3.2.

Table 3.2. Preparation of ionic solutions with different Na^+/Cu^{++} ratio

Sample number	Volume of 0.04N NaCl solution (ml)	Volume of 0.04N $CdCl_2$ solution (ml)	Total volume (ml)
1	50	50	100
2	55	45	100
3	60	40	100
4	65	35	100
5	70	30	100
6	75	25	100
7	80	20	100
8	85	15	100
9	90	10	100
10	92	8	100
11	95	5	100
12	97	3	100

The solution and resin was mixed in a 125ml capped NALGENE® PMP bottles and tumbled for three days to achieved equilibrium. The equilibrium solution concentration was then diluted to a suitable concentration and analyzed by AA machine. The original 0.04N ionic solution was also measured at this time to check the exact concentration. The loadings of specific ions on the resins were calculated by comparing the equilibrium concentration and initial concentration with mass balance relation. The pH values were measured for each sample and the exchange consistency was check by comparing the amount of Na^+ ions coming out from the resin and Cu^{++} ions loaded on the resins. If the ion exchange between Na^+ and Cu^{++} ions was valid then the isotherm can be constructed.

This procedure can be repeated for the both the Na^{+}/Cd^{++} and Cd^{++}/Cu^{++} binary systems. The experimental data can be modeled and the equilibrium constant and both Wilson's parameters can be found for each binary systems.

3.3. Binary Equilibrium Results and Interpretation

Binary isotherm for Na^{+}/Cu^{++}, Na^{+}/Cd^{++} and Cd^{++}/Cu^{++} systems were found using Eq. 2.1 and the Wilson Model Eq. 2.2 and a Matlab computer code was used to fit the data with three parameters. The flow diagram of algorithm for fitting Cd^{++}/Cu^{++} and Na^{+}/Cd^{++} experimental data with equilibrium constant and Wilson's parameters is shown in Figure 3.1.

First, the liquid phase activity coefficients were calculated for each experimental data point from the Pitzer equation, Eq. 2.3, neglecting all terms on the right hand side except for the first term, which contains the ionic strength function f^{γ}. Then, the experimental equilibrium quotients λ_{BA}^{exp} were computed for each data point by Eq 2.4. A set of parameters (K_{AB}, Λ_{AB} and Λ_{BA}) was guessed to start the optimization routine. Then, the optimization routine will search for the best values of K_{AB}, Λ_{AB} and Λ_{BA} by comparing the value of λ_{Ba}^{fit} calculated from Eq. 2.6. If the minimum of the sum of error function $F_{12} = \sum_{i=1}^{N}\left(\frac{\lambda_i^{exp} - \lambda_i^{fit}}{\lambda_i^{exp}}\right)^2$ was achieved, the values of K_{AB}, Λ_{AB} and Λ_{BA} were optimized.

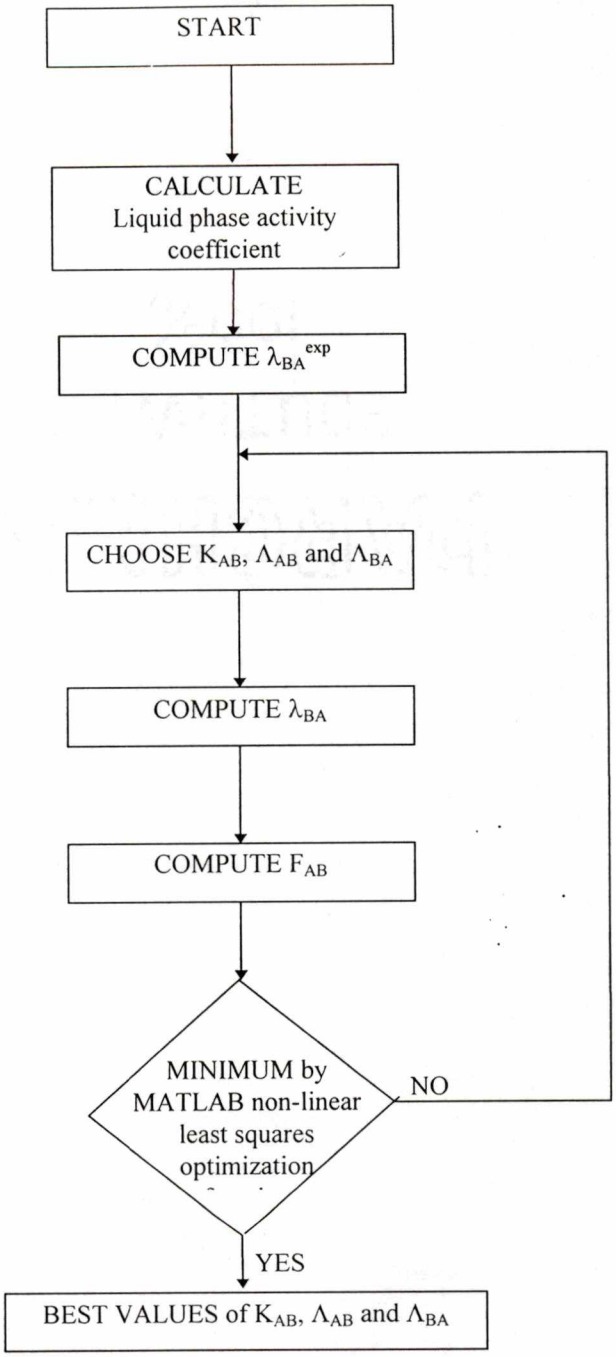


Figure 3.1 Algorithm of modeling binary equilibrium experimental data for Cd^{++}/Cu^{++} and Na^{+}/Cd^{++} systems

The MATLAB™ optimization toolbox non-linear least squares optimization function was use in the algorithm to determine the optimal values of the parameters [Grace Andrew, 1990],[Math Works Inc., 1992]. The function implements the Levenberg-Marquart method and the Gauss-Newton method to find the solution.

For Cd^{++}/Cu^{++} system A and B stands for Cd^{++} and Cu^{++} respectively, and for Na^{+}/Cd^{++} system A and B is stand for Na^{+} and Cd^{++} respectively. The results was shown in Figure 3.2 for Cd^{++}/Cu^{++} system and in Figure 3.3 for Na^{+}/Cd^{++} system. After K_{CdCu}, Λ_{CdCu}, Λ_{CuCd}, K_{NaCd}, Λ_{NaCd} and Λ_{CdNa} was found, the K_{NaCu} was calculated by applying the triangular relation $K_{NaCu} = K_{NaCu} \times K_{CdCu}$. The modeling algorithm of Na^{+}/Cu^{++} system was different from the previous algorithm. Only the two Wilson's parameters Λ_{NaCu}, Λ_{CuNa} were calculated from the least square optimization algorithm while the basic structure of the algorithm stayed the same. The binary isotherm of Na^{+}/Cu^{++} system was shown in Figure 3.4. The values of the three parameters are shown in Table 3.3.

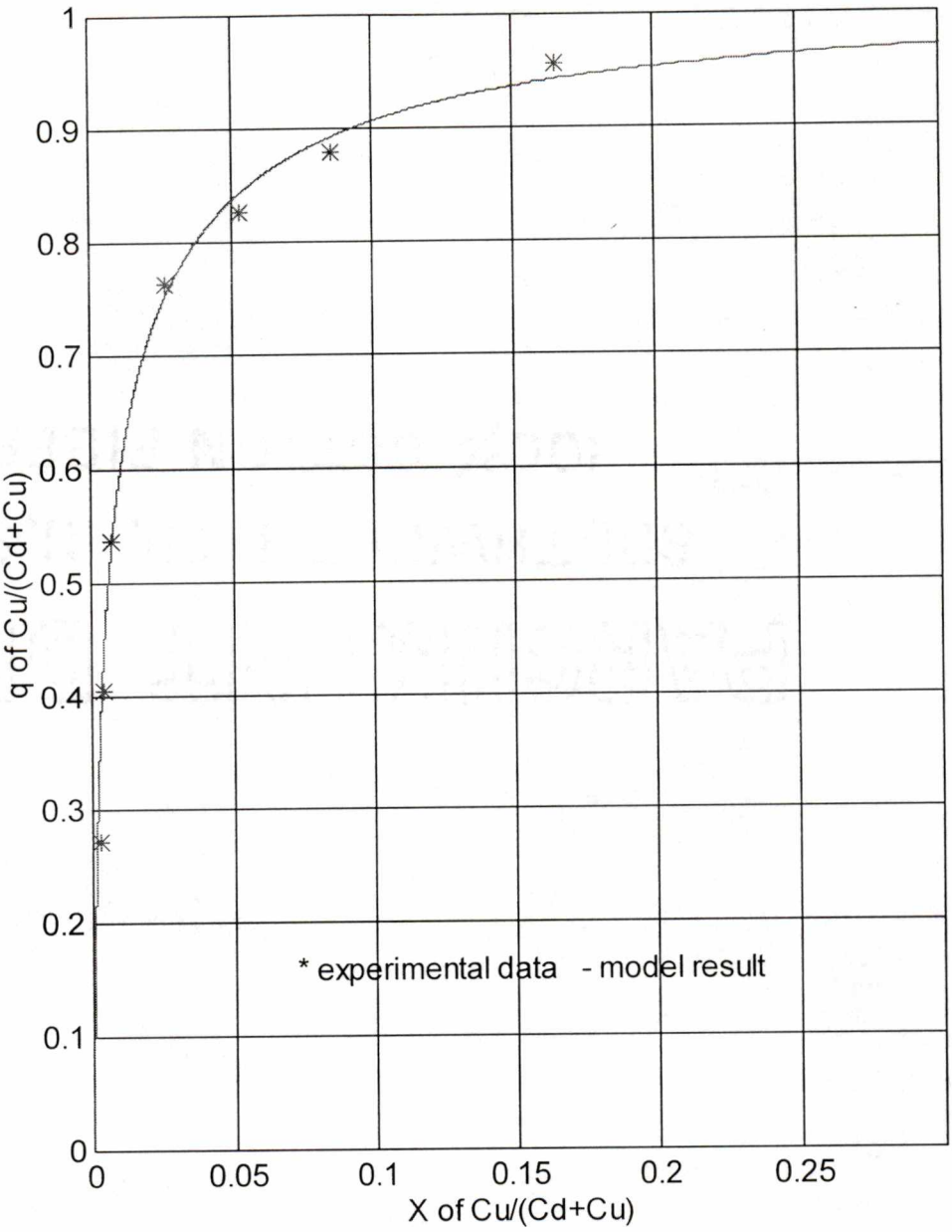


Figure 3.2 Isotherm of Cd^{++}/Cu^{++} binary system

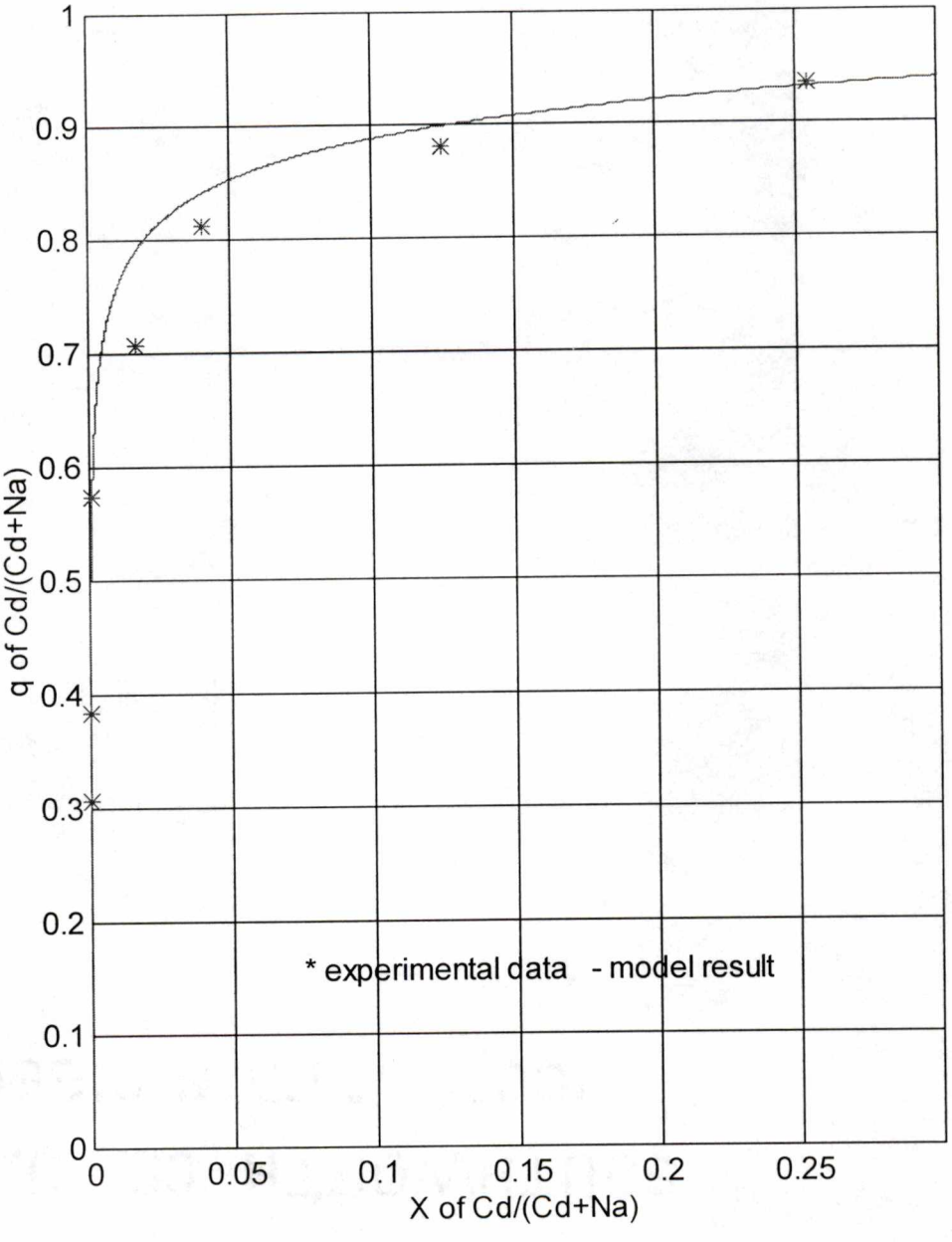


Figure 3.3 Isotherm of Na^{+}/Cd^{++} binary system

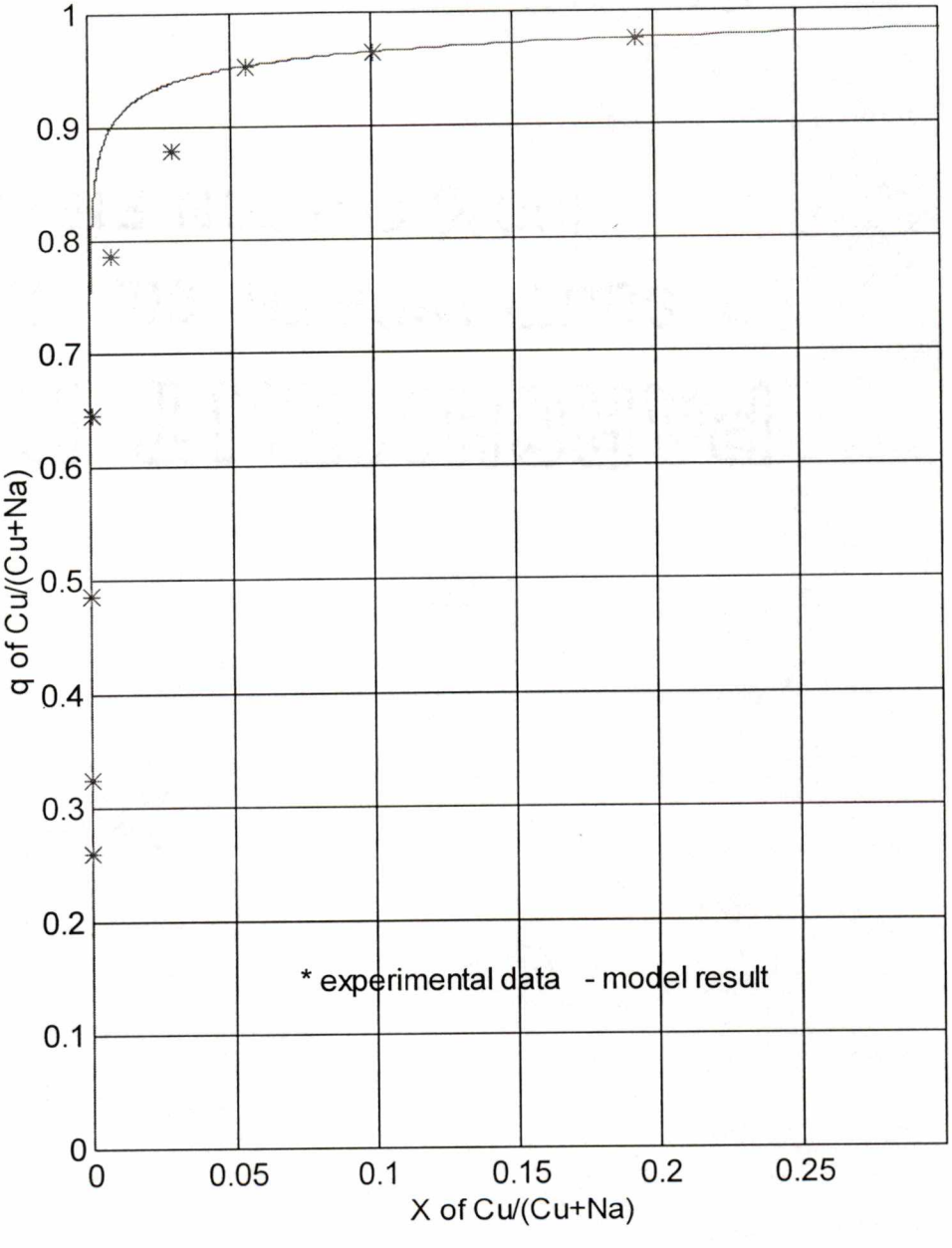


Figure 3.4 Isotherm of Na^{+}/Cu^{++} binary system

Table 3.3 Equilibrium constants and Wilson's parameters for the SR-5 Resin

Binary System A/B	Equilibrium Constant K_{AB}	Parameter Λ_{AB}	Parameter Λ_{BA}
Cd^{++}/Cu^{++}	0.00714118	1.00458	1.61908
Na^{+}/Cd^{++}	0.016605	2.44194	2.56662
Na^{+}/Cu^{++}	0.000118579	3.33537	3.06561

3.4. Batch Equilibrium Experiments, Multicomponent Systems

Equilibrium properties between multicomponent systems of Na^{+}, Cu^{++} and Cd^{++} was studied. Experiments were conducted to find the multicomponent equilibrium behavior and the experimental data can be used to check the accuracy of the predicted values from the multicomponent equilibrium model. The resins used in this part of experiments were conditioned and loaded with Na^{+} by using the same procedure as described in the binary equilibrium experiments. Then the resins were washed, dried and contacted with an ionic solution with three kinds of cations : Na^{+}, Cu^{++} and Cd^{++}. Equilibrium was reached after the mixture of ionic solution and resins stayed in the tumbling machine for three days. Then, the equilibrium solutions were diluted and analyzed by AA machine to determine the concentration of each of the cations. By applying the mass balance rule before and after the ion exchange, the isotherm of this multicomponent equilibrium can be determined and plotted.

Three experiments of multicomponent system were conducted to ensure a coverage of a wide concentration range and to check the reproducibility of the experimental data. The first experiment was conducted according to the initial volume ratio shown in Table 3.4.

Table 3.4 Preparation of 1st multicomponent experiment

Sample number	Volume of 0.04N NaCl (ml)	Volume of 0.04N $CuCl_2$ (ml)	Volume of 0.04N $CdCl_2$ (ml)	Total Volume (ml)
1	70	3	27	100
2	70	5	25	100
3	70	7	23	100
4	70	10	20	100
5	70	12	18	100
6	70	14	16	100
7	70	15	15	100
8	70	18	12	100
9	70	20	10	100
10	70	23	7	100
11	70	25	5	100
12	70	27	3	100

In the 2nd and 3rd experiments the volume ratio is shown in Table 3.5.

Table 3.5 Preparation of 2nd and 3rd multicomponent experiments

Sample number	Volume of 0.04N NaCl (ml)	Volume of 0.04N $CuCl_2$ (ml)	Volume of 0.04N $CdCl_2$ (ml)	Total Volume (ml)
1	74	2	24	100
2	74	4	22	100
3	74	6	20	100
4	74	8	18	100
5	74	10	16	100
6	74	12	14	100
7	74	14	12	100
8	74	16	10	100
9	74	18	8	100
10	74	20	6	100
11	74	22	4	100
12	74	24	2	100

The washing procedure of the resins after loaded with Na^+ of the three experiments were operate in three different ways in order to check the influence of washing procedure for the resins loaded with Na^+ ions to the final experimental results. In the 1st experiment, after the resins were loaded with Na^+ ions, they were washed with 500ml double distilled deionized water in one batch. For the 2nd experiment, the resins were dried out with vacuum method immediately after loading with 0.2N NaCl solution without washing by water. In the 3rd experiment the resins loaded with Na^+ ions were washed with 500ml 0.04N NaCl solution and dried. For all three experiments, in each sample, 1.00g of resins were used to mix with 100ml solution.

3.5. Multicomponent Equilibrium Results and Interpretation

The results of the three experiments are plotted in Figures 3.5, 3.6 and 3.7 for Cu^{++}, Cd^{++} and Na^{+}, respectively. Figure 3.5 shows that the loading on Cu^{++} was higher in the 1st experiment than 2nd and 3rd experiments. The difference is clearly due the difference in ratio of Cu^{++} among the experiments where the 1st experiment had the higher $Cu^{++}/(Na^{+}+Cu^{++}+Cd^{++})$ ratio. The curves of the 2nd and 3rd experiments are similar and close to each other shows that the washing procedure had a limited influence on the final experimental results. Figure 3.6 shows a similar results, that 2nd and 3rd experiments are close and the higher Cd^{++} liquid phase concentration is due to the fact that there was less Na^{+} ions in the system, that is, 70ml of Na^{+} solution were added in the first experiment whereas 74ml were added in the second and third experiments. Figure 3.7 confirms the fact that the concentration of Na^{+} in liquid phase in the 1st experiment were lower than in the 2nd and 3rd experiments.

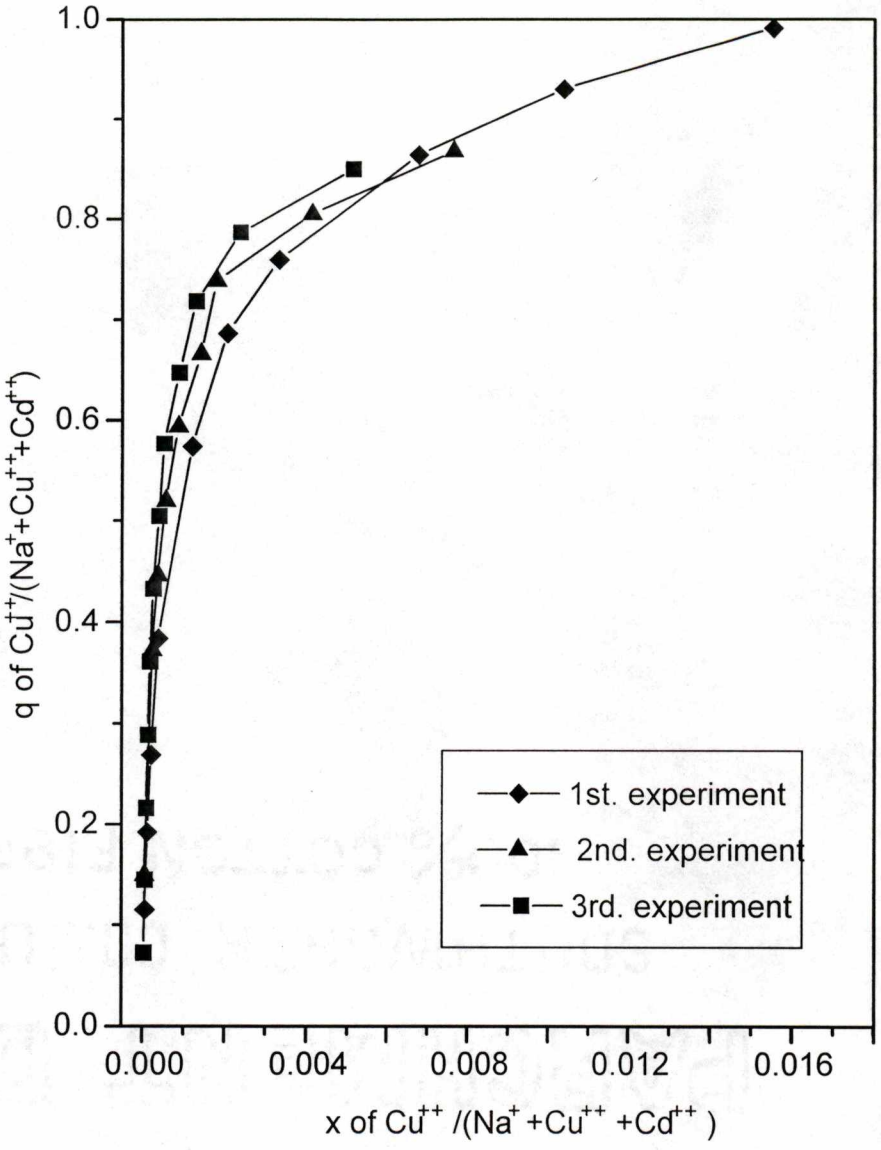


Figure 3.5 Multicomponent equilibrium experiments, Cu^{++} isotherm

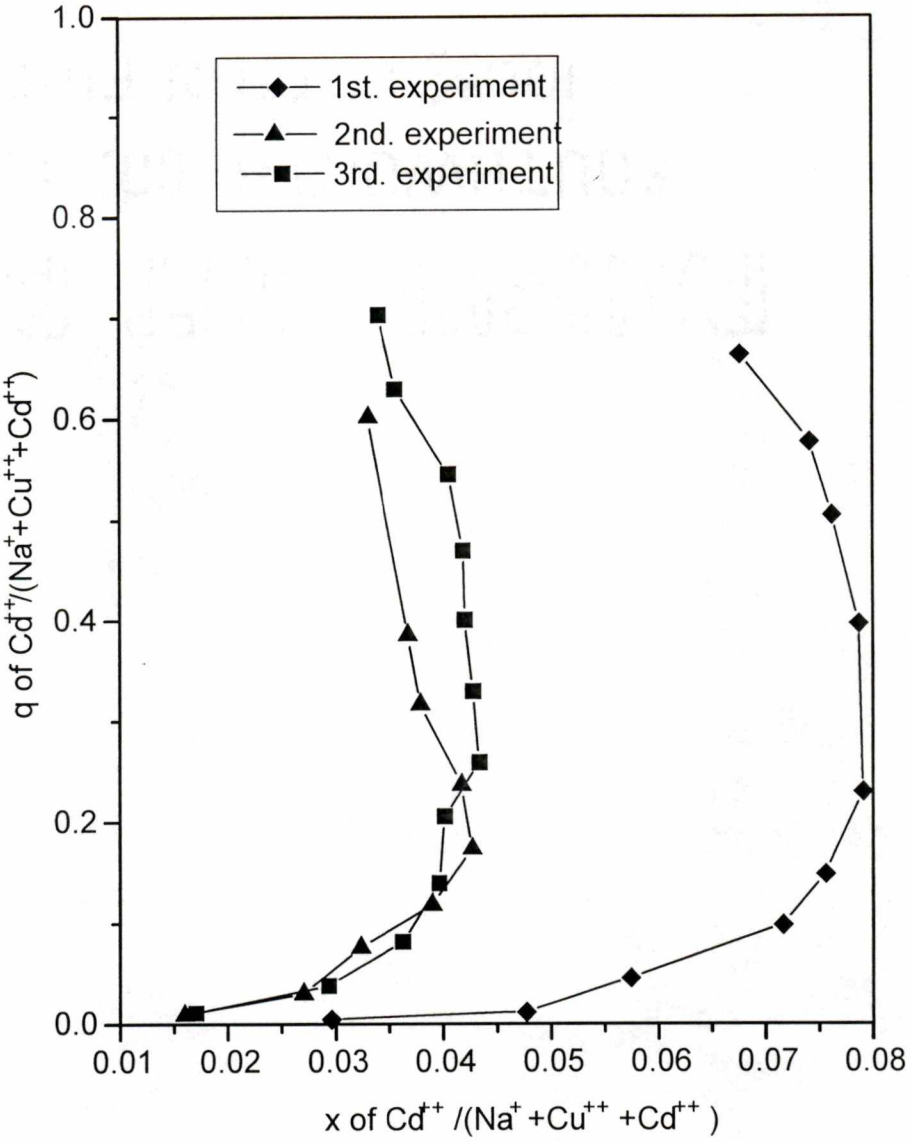


Figure 3.6 Multicomponent equilibrium experiments, Cd^{++} isotherm

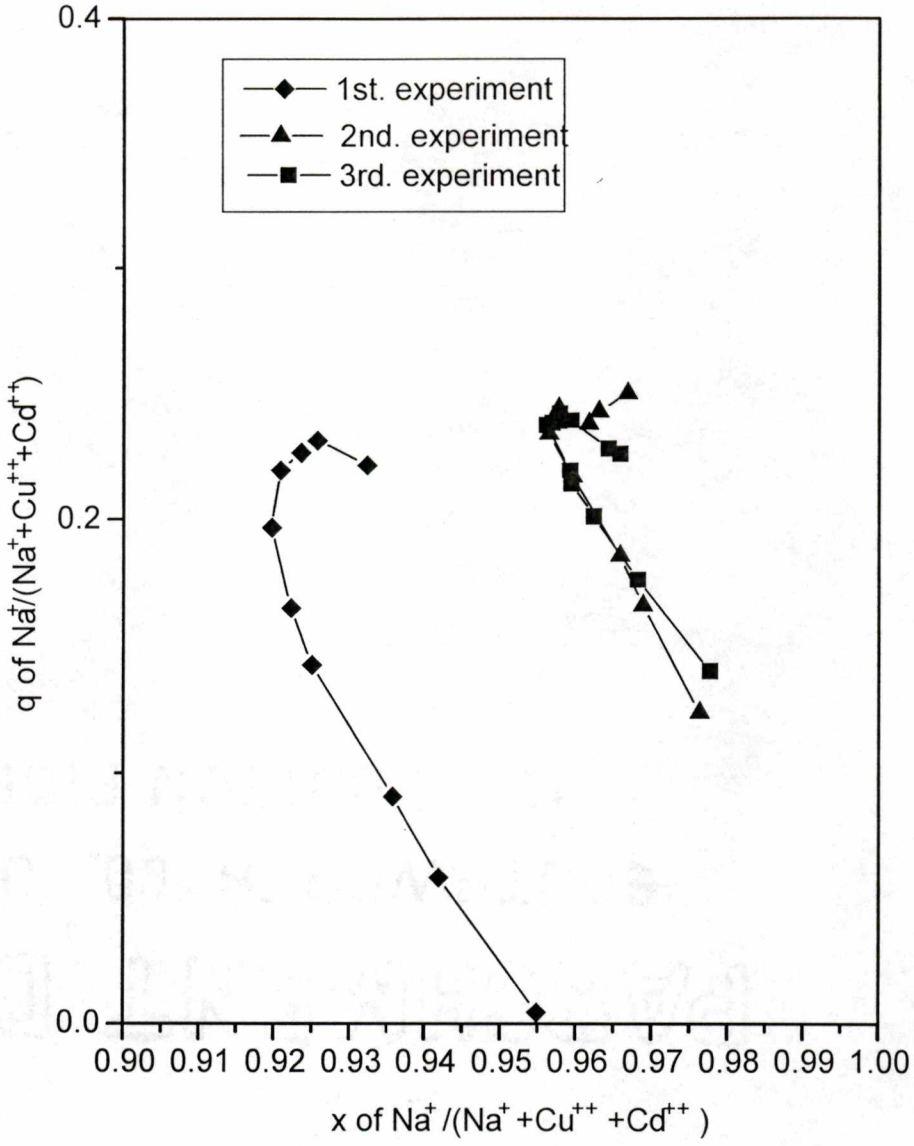


Figure 3.7 Multicomponent equilibrium experiments, Na^+ isotherm

The equilibrium constants and Wilson's parameters found from the binary equilibrium experiments and modeling which is shown in Table 3.3 can be used to predict the loading of each type ions on the resins q for the multicomponent system in equilibrium by the given liquid phase equivalent fraction of each species. Liquid phase equivalent fraction of each experimental data point was input to a MATLAB™ computer code to calculate the predicted values of the relevant loading on the solid phase or resins. Then the predicted values were compared with the experimental loading values on the resins that are calculated by applying mass balance rule. The structure of the computer code written in MATLAB™ format to solve for the loading on solid phase is shown in Figure 3.8. The predicted values of loading on resins and experimental data of loading is plotted together against equivalent fractions in liquid phase of each component for all three experiments in Figure 3.9 to Figure 3.17.

The predicted values match the experimental data quite well and compare to the different ratio of Na^+ ratio in the 1st experiment to the 2nd and 3rd experiments the predicted values still hold in a similar approximation. In the Cu^{++} isotherm, the prediction values from the model deviated to larger degree when the equivalent fraction of Cu^{++} in the liquid phase increase. This phenomena is postulated to be caused by the presence of H^+ ions in the resins.

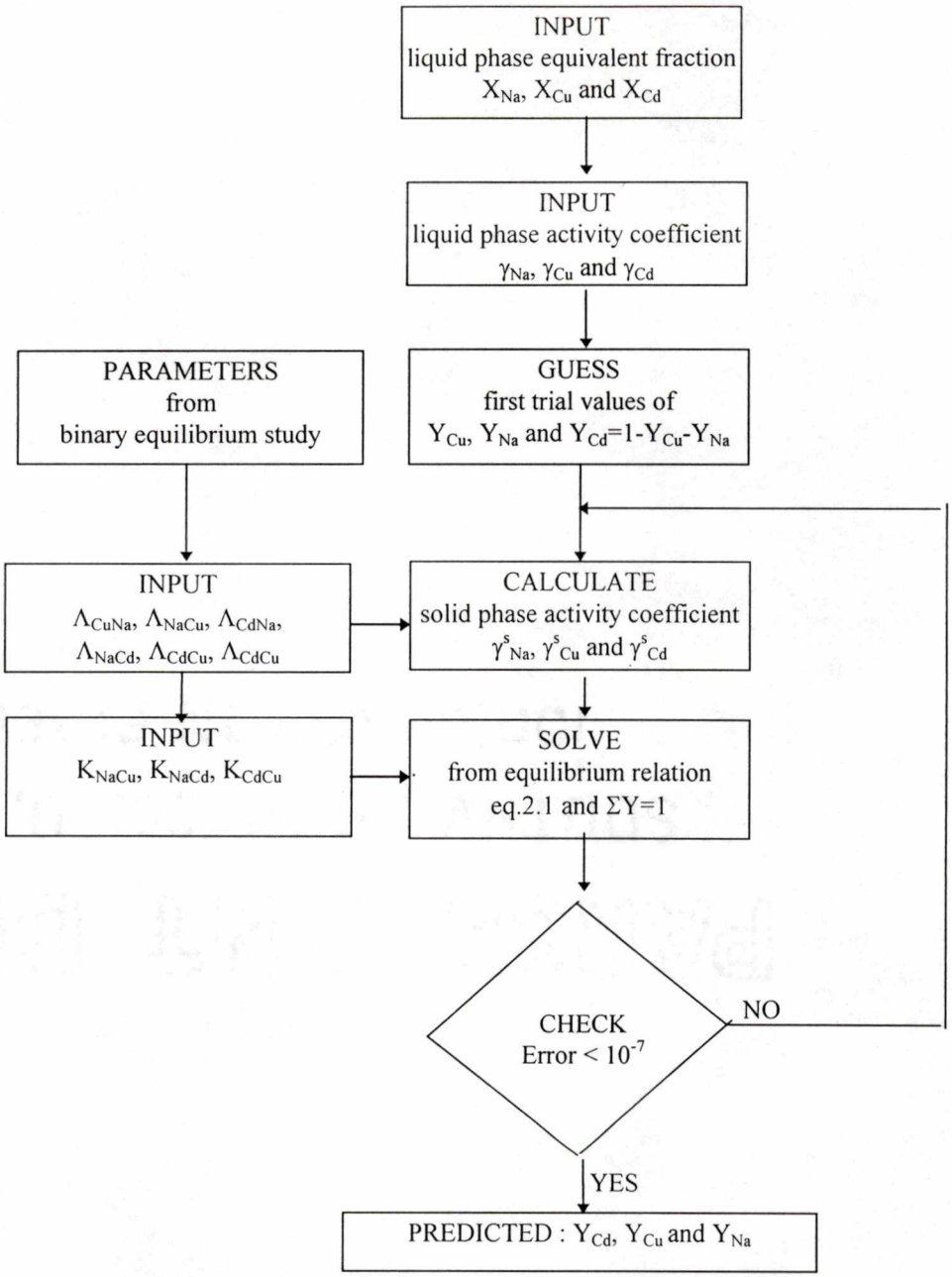


Figure 3.8. Algorithm of predicting the multicomponent equilibrium from binary interaction parameters

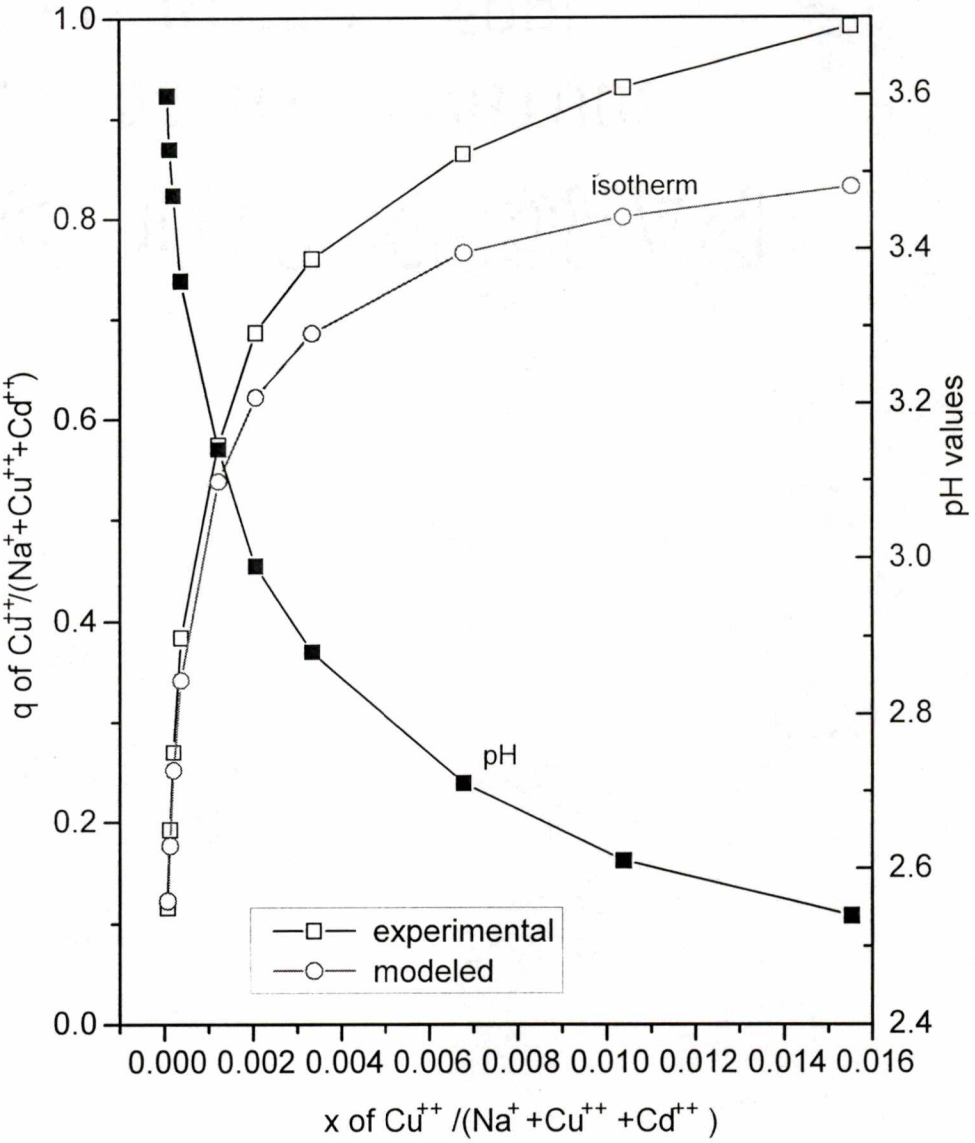


Figure 3.9 Three components Na^{+}, Cu^{++} and Cd^{++} Equilibrium on SR-5, 1st experiment, Cu^{++} isotherm

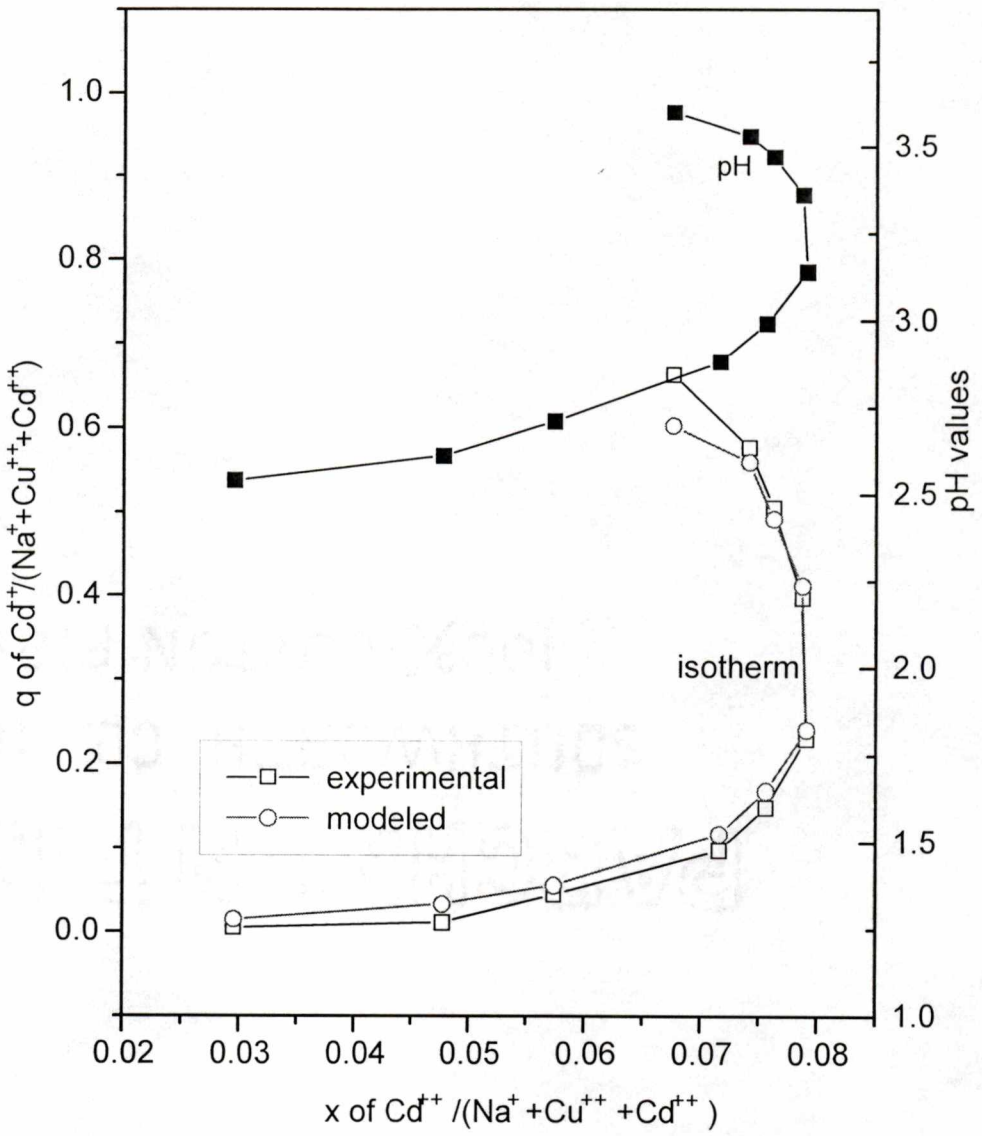


Figure 3.10 Three components Na^{+}, Cu^{++} and Cd^{++} Equilibrium on SR-5, 1st experiment, Cd^{++} isotherm

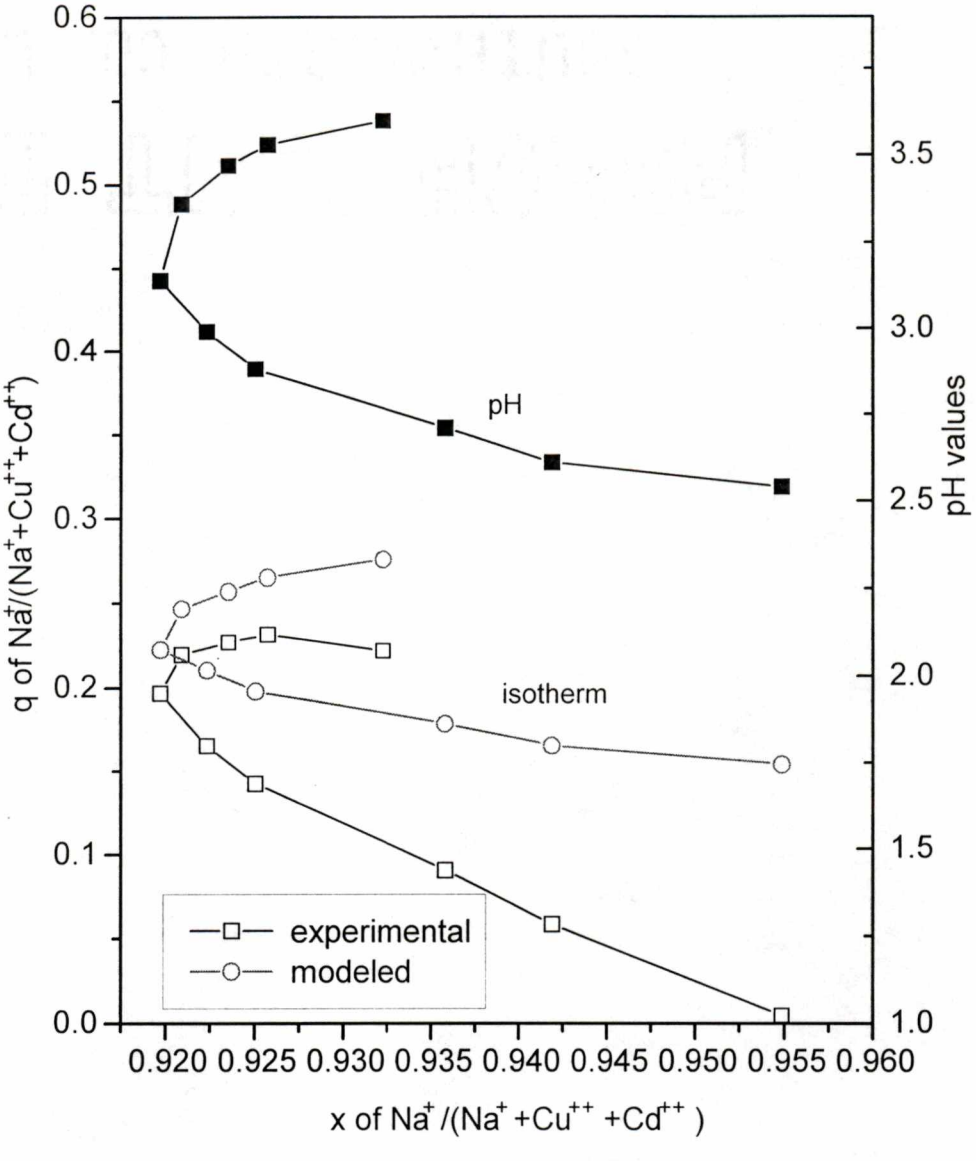


Figure 3.11 Three components Na^{+}, Cu^{++} and Cd^{++} Equilibrium on SR-5, 1st experiment, Na^{+} isotherm

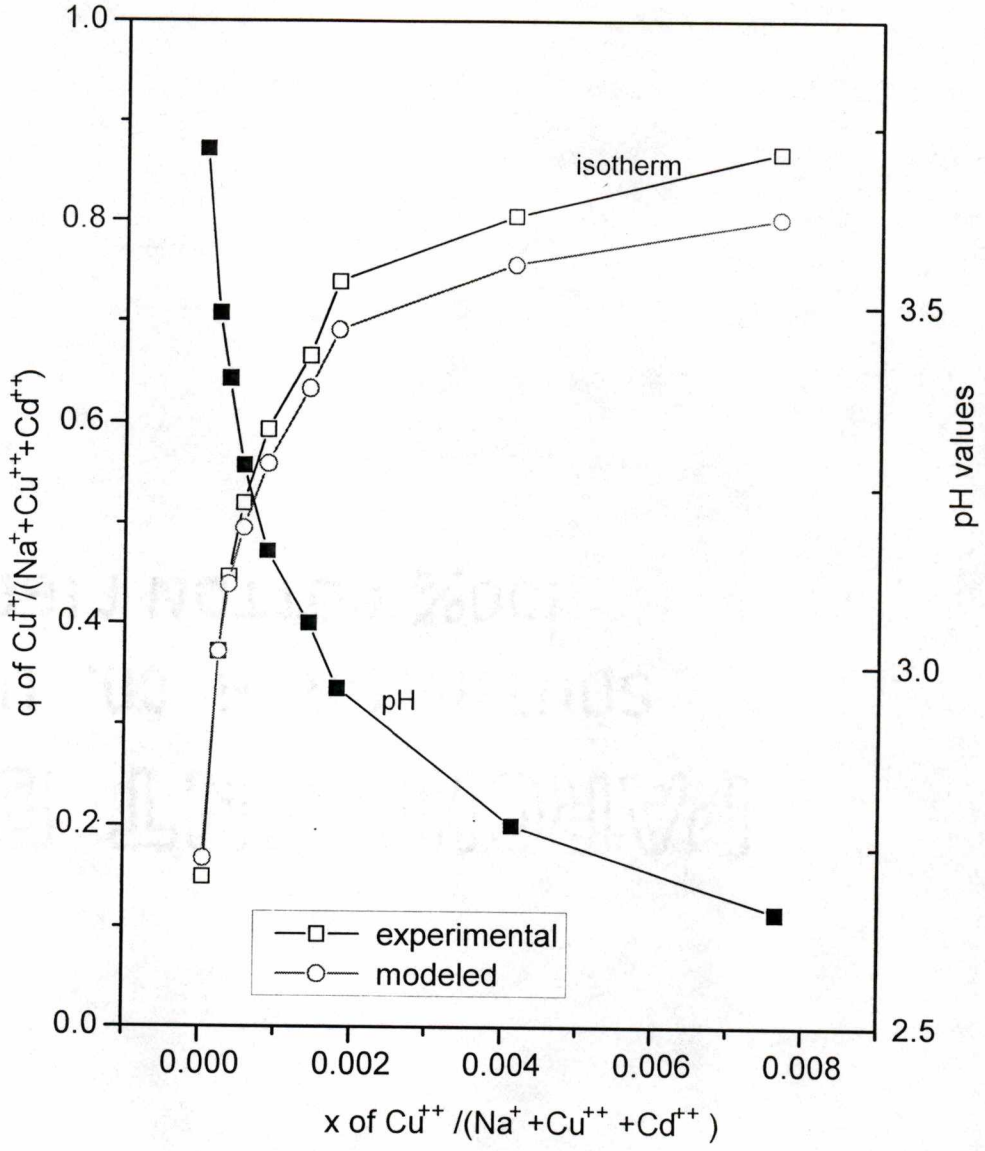


Figure 3.12 Three components Na^{+}, Cu^{++} and Cd^{++} Equilibrium on SR-5, 2nd experiment, Cu^{++} isotherm

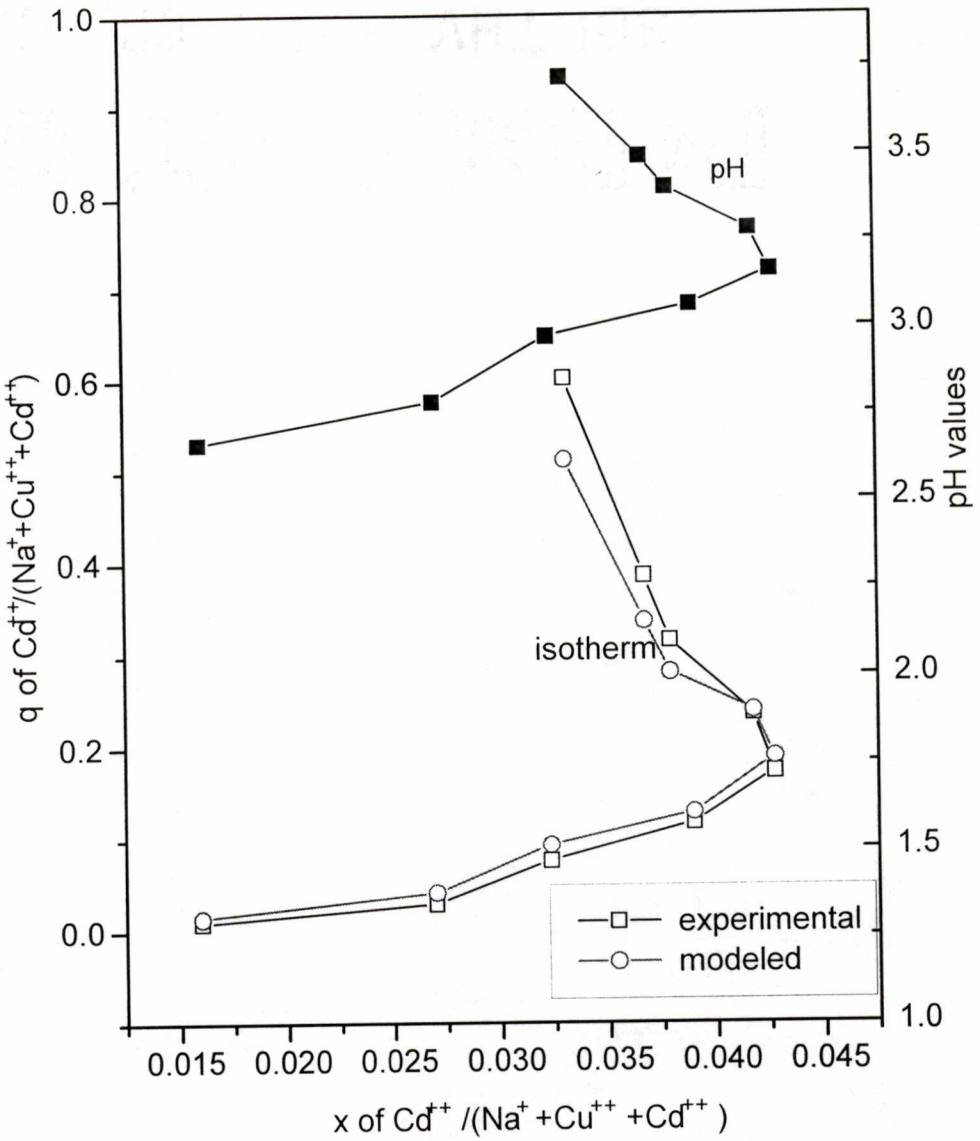


Figure 3.13 Three components Na^{+}, Cu^{++} and Cd^{++} Equilibrium on SR-5, 2nd experiment, Cd^{++} isotherm

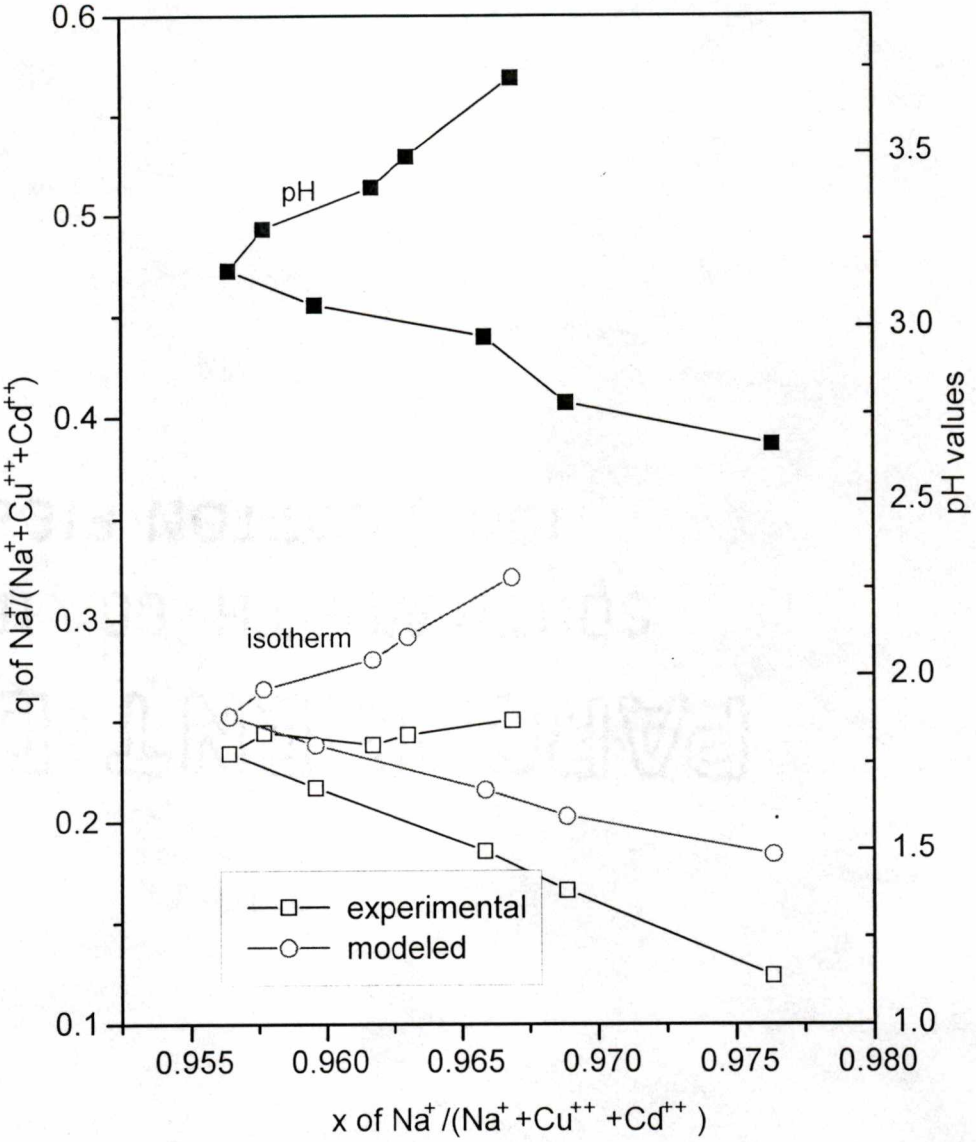


Figure 3.14 Three components Na^+, Cu^{++} and Cd^{++} Equilibrium on SR-5, 2nd experiment, Na^+ isotherm

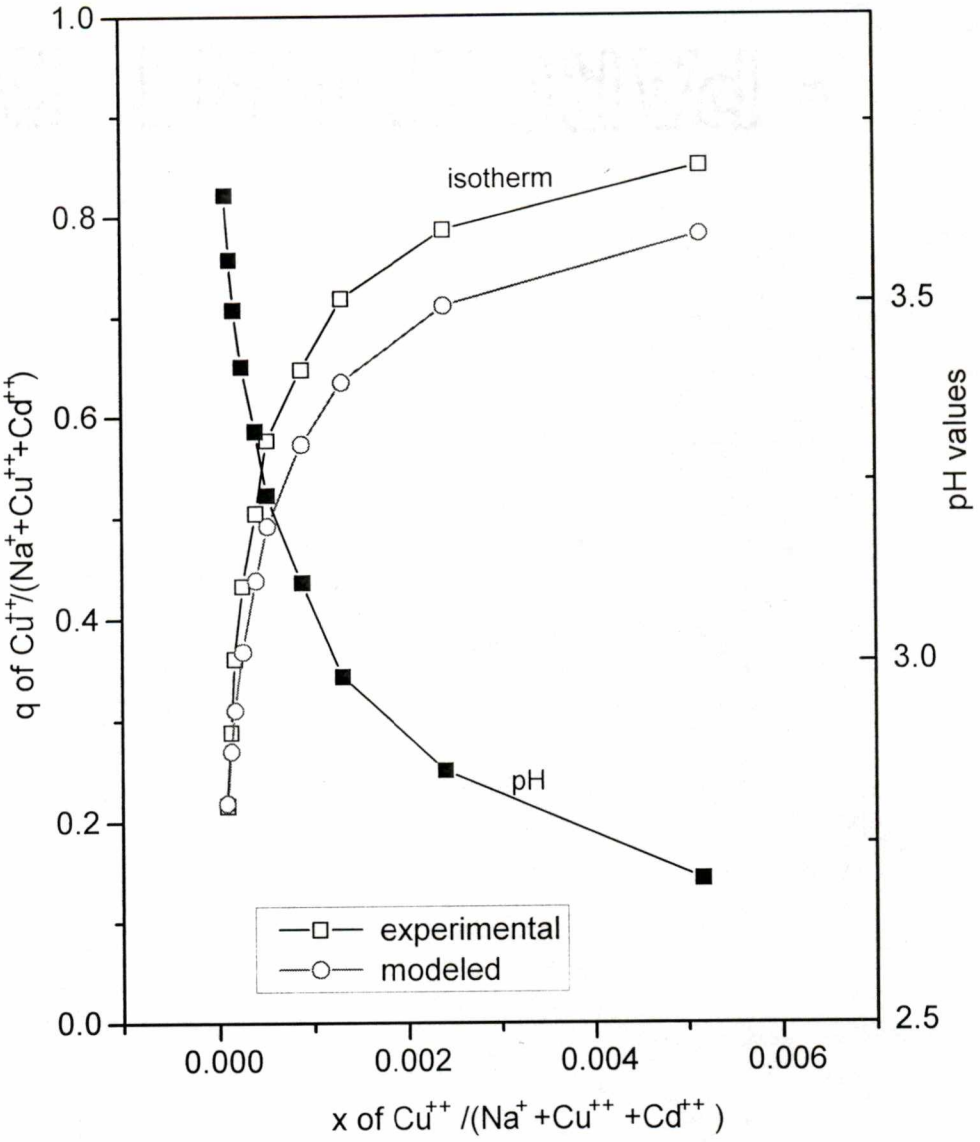


Figure 3.15 Three components Na^{+}, Cu^{++} and Cd^{++} Equilibrium on SR-5, 3rd experiment, Cu^{++} isotherm

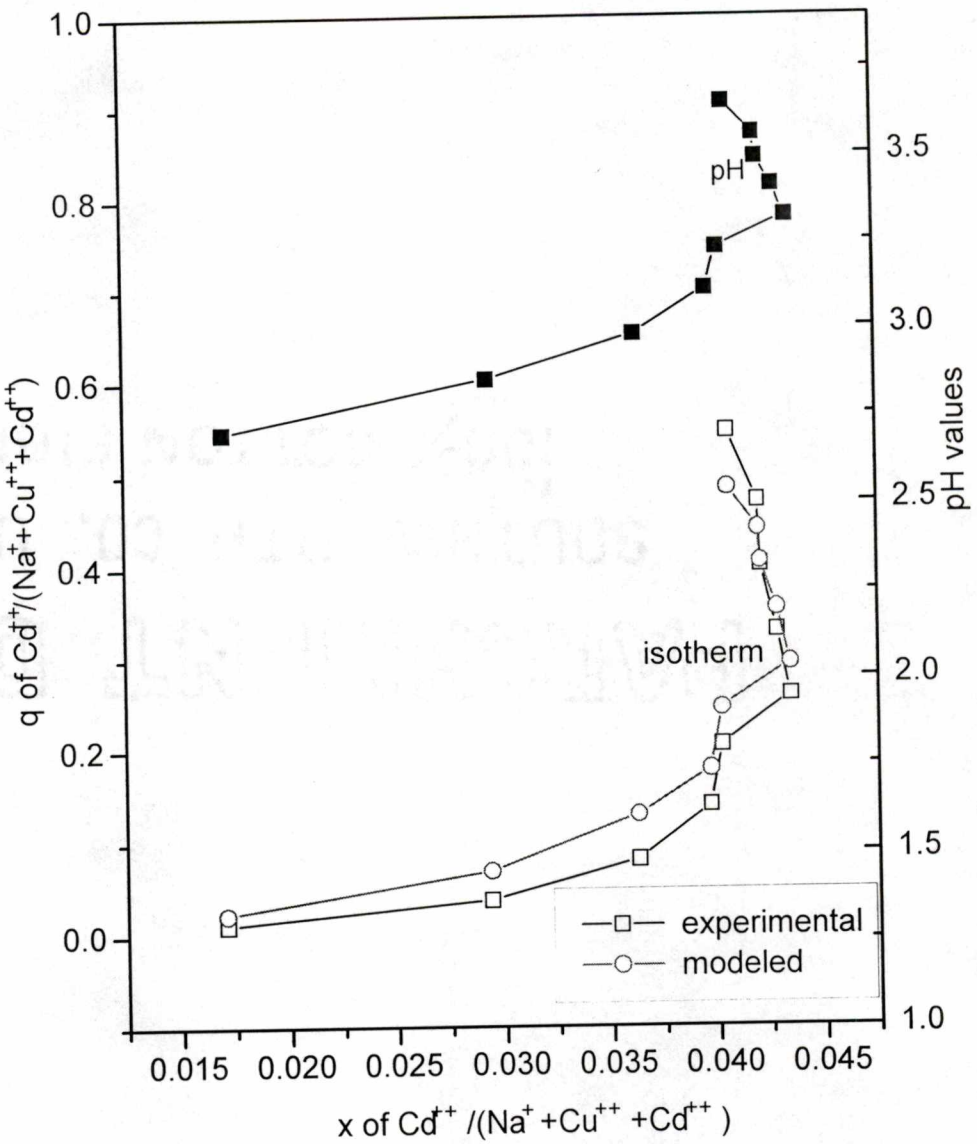


Figure 3.16 Three components Na^{+}, Cu^{++} and Cd^{++} Equilibrium on SR-5, 3rd experiment, Cd^{++} isotherm

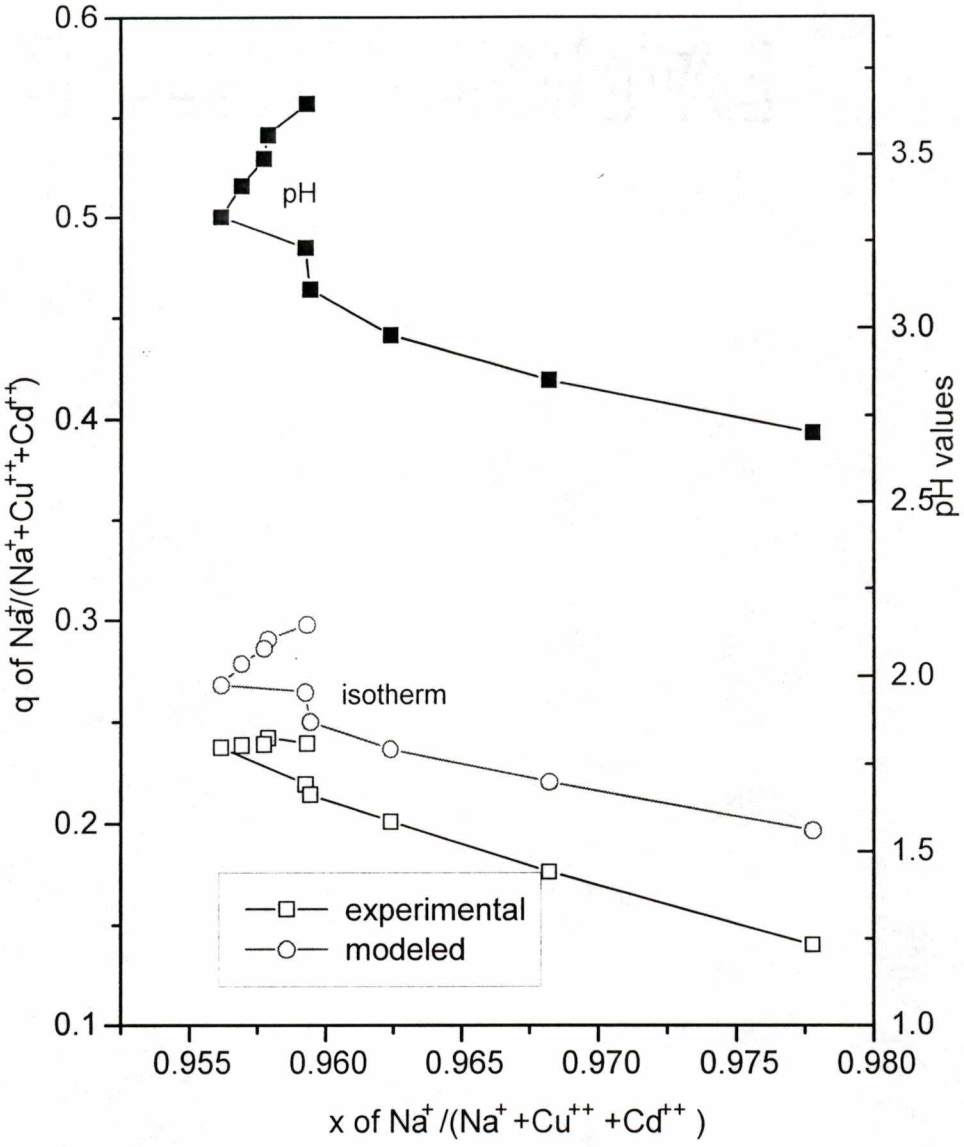


Figure 3.17 Three components Na^{+}, Cu^{++} and Cd^{++} Equilibrium on SR-5, 3rd experiment, Na^{+} isotherm

In our model, the resin is assumed to be fully loaded with only Na^+ ions. However, due to the difficulty to load the entire ion exchange resins with Na^+ ions in an aqueous solution, the H^+ ions does influence the equilibrium behavior while high concentration of Cu^{++} displaced the trace of H^+ ions out of the resins and decrease the pH values of the solutions, as shown in Figure 3.9.

In the experiment the equilibrium solution with perfect ratio was impossible to be prepared, thus it is useful to perform some analysis using the multicomponent equilibrium model in order to understand the multicomponent ion exchange behavior on the SR-5 resins. Figures 3.18 to 3.23 were constructed by input different values of equivalent fractions of each components and calculated the predicted values of loading on the resins.

The total number of equivalent of cations in the liquid phase was set as a constant to 0.04N in the model. In Figures 3.18 and 3.19, the liquid phase equivalent fraction of Cu^{++} is constant on each line. As the equivalent fraction of Cu^{++} decreases from 0.01 to 0.0001, both the loading fraction of Cd^{++} and Na^+ increase. In this situation that the Cu^{++} equivalent fraction is constant, Cd^{++} and Na^+ are actually competing against each other for the loading position on the resin. The slightly concave down of Cd^{++} isotherm and concave up of Na+ isotherm, shows that Cd^{++} is slightly prefer over Na^+ as ion exchange take place on the SR-5 resins.

In figure 3.20 and 3.21, the liquid phase equilibrium fraction of Na^+ is constant on each line. Figure 3.20 shows that when the equivalent fraction of Na^+ decrease in a large degree from 0.95 to 0.85, the loading of Cu^{++} also decrease. This

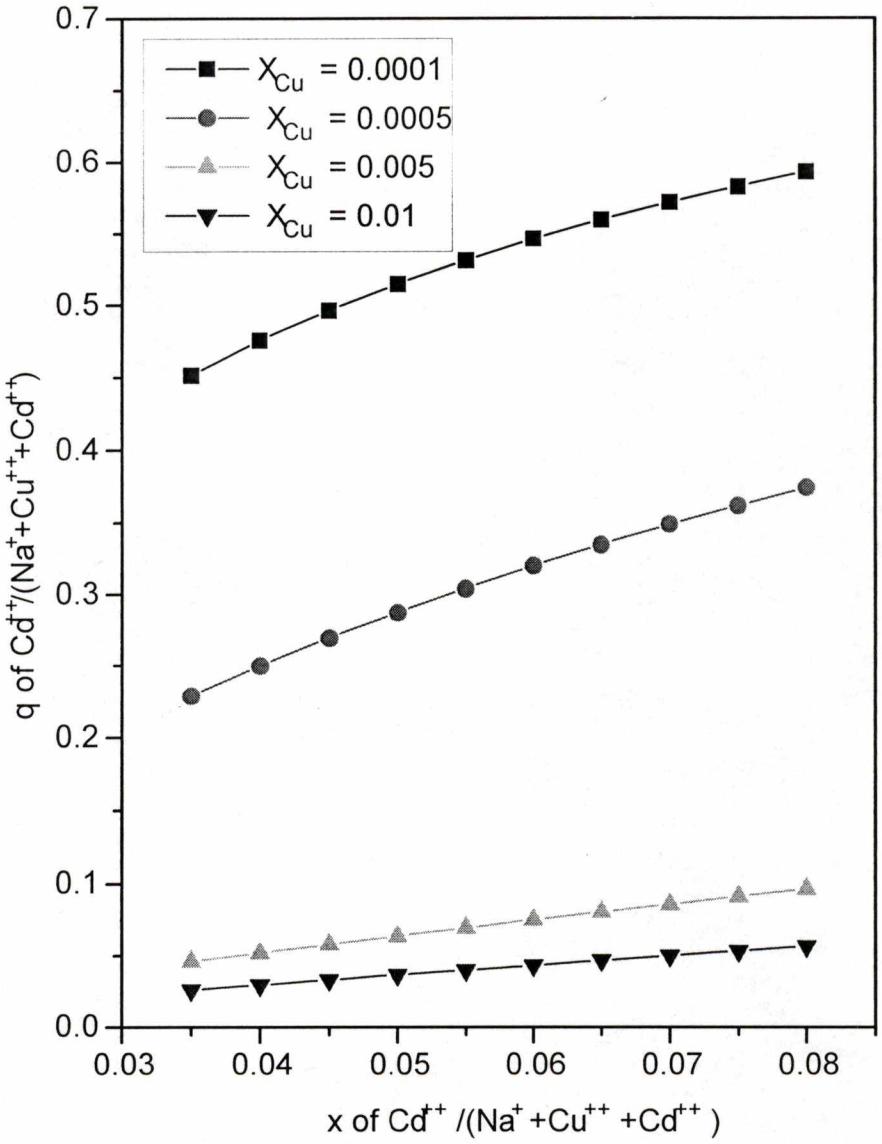


Figure 3.18 Multicomponent equilibrium behavior predicted by model : constant Cu^{++} concentration, Cd^{++} isotherm

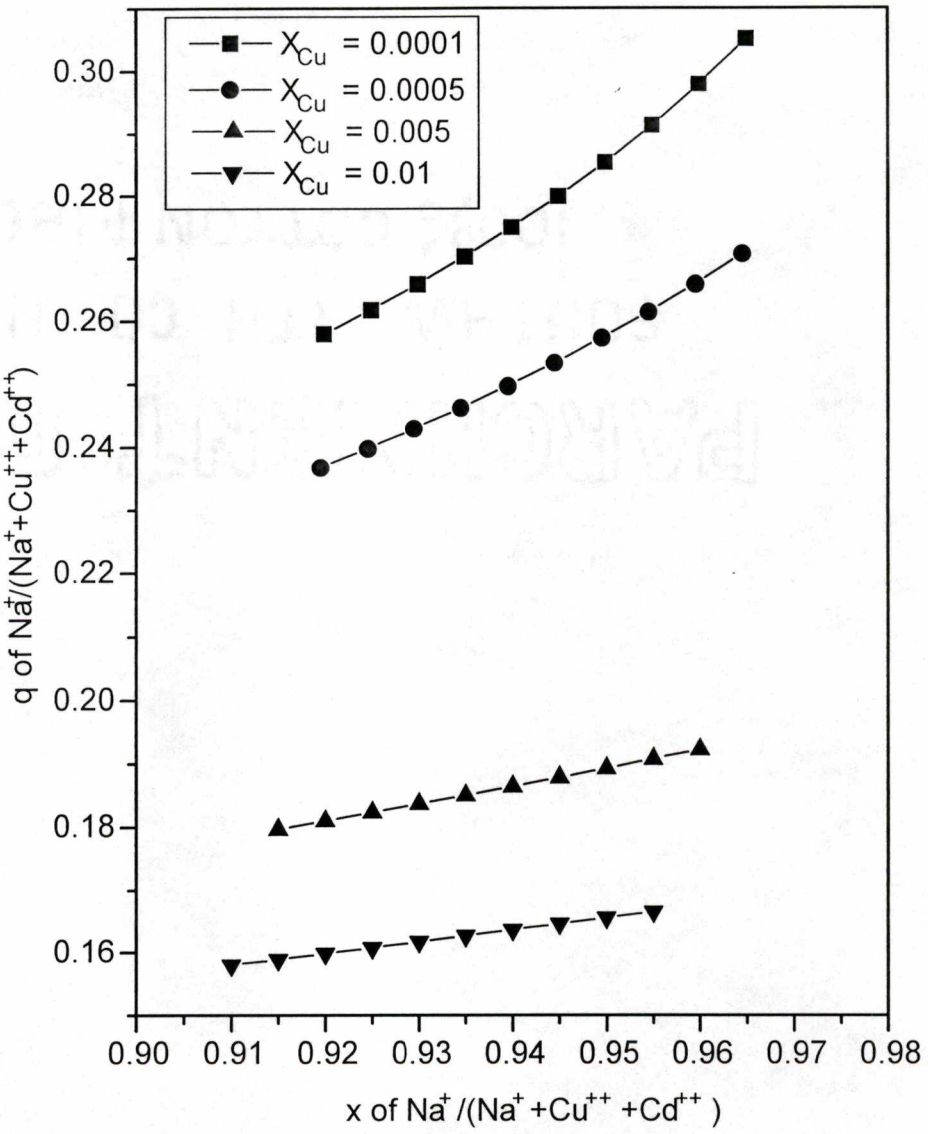


Figure 3.19 Multicomponent equilibrium behavior predicted by model : constant Cu^{++} concentration, Na^{+} isotherm

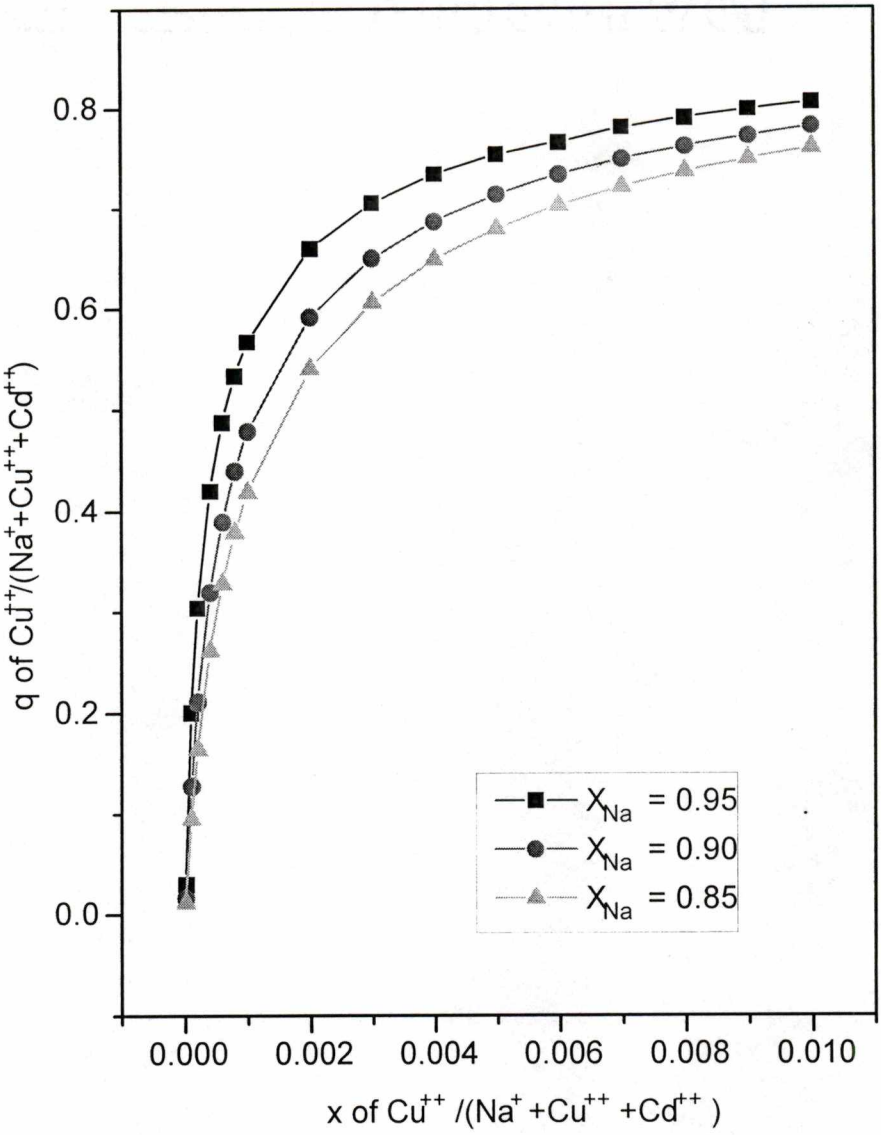


Figure 3.20 Multicomponent equilibrium behavior predicted by model : constant Na^{+} concentration, Cu^{++} isotherm

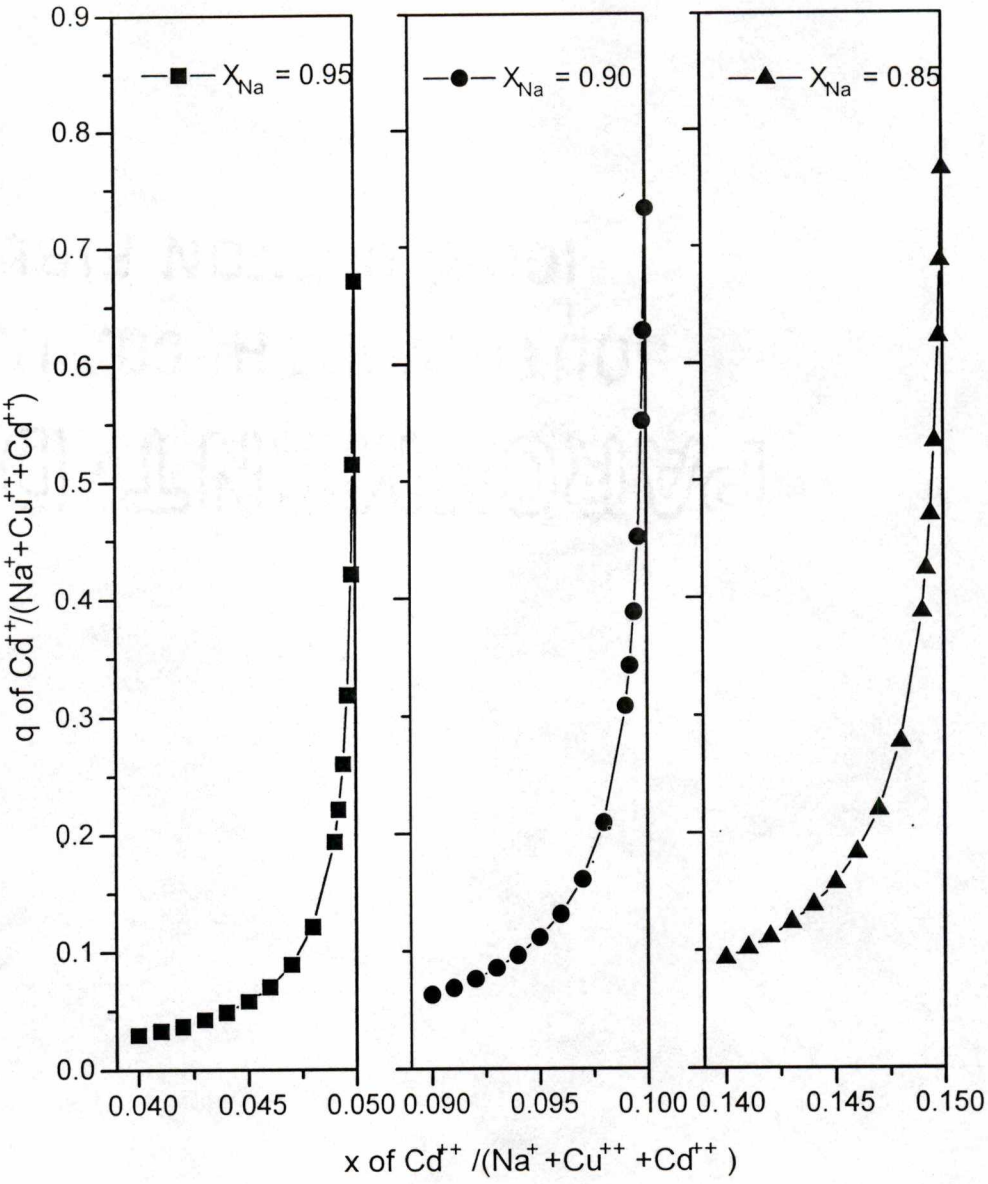


Figure 3.21 Multicomponent equilibrium behavior predicted by model : constant Na^{+} concentration, Cu^{++} isotherm

phenomena can be explained by studying Figure 3.21 together. When equivalent fraction of Na^+ in liquid phase decrease, the equivalent fraction of Cd^{++} in liquid phase is set to increase more than Cu^{++}. As a result, loading fraction of Cd^{++} on the resins increase while loading fraction of Cu^{++} decrease, in contrary to their order of preferences.

In figure 3.22 and 3.33, the liquid phase equilibrium equivalent fraction of Cd^{++} is set constant for each line. While the equivalent fraction of Cd^{++} in the liquid phase decreases, both of the loading of Cu^{++} and Na^+ increase. The increase of the loading of Cu^{++} is due to the fact that this ion is highly preferred over Na^+ and Cd^{++} on SR-5 resins. The increase of the loading fraction of Na^+ is due to the increase of equivalent fraction of Na^+ in the liquid phase.

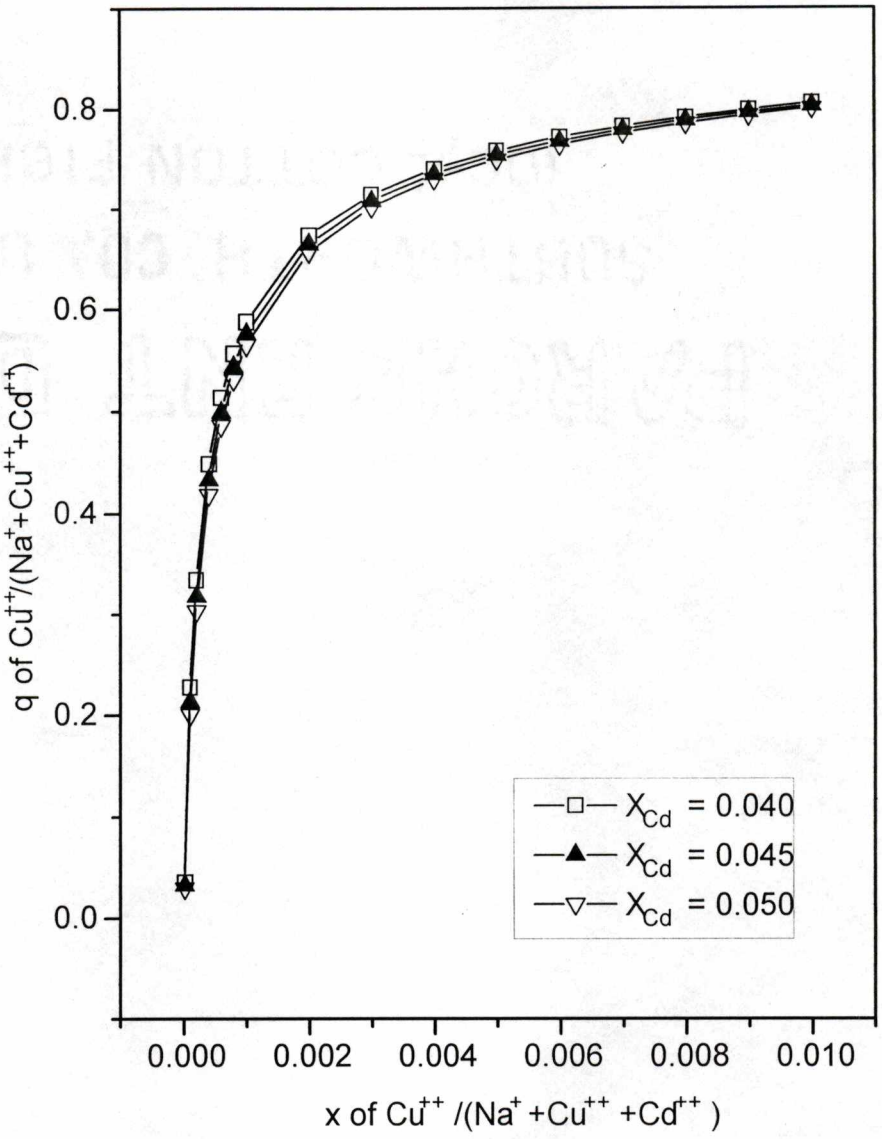


Figure 3.22 Multicomponent equilibrium behavior predicted by model : constant Cd^{++} concentration, Cu^{++} isotherm

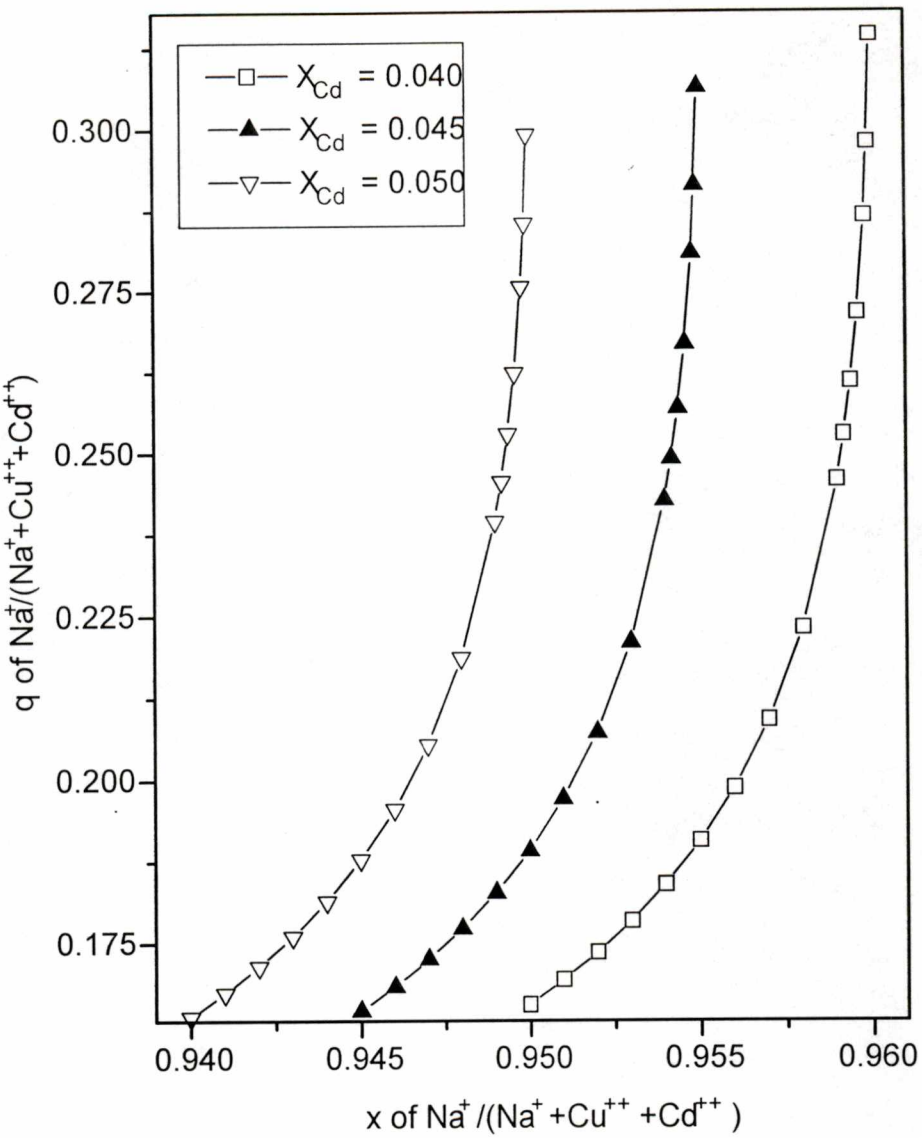


Figure 3.23 Multicomponent equilibrium behavior predicted by model : constant Cd^{++} concentration, Na^+ isotherm

CHAPTER 4

BATCH KINETICS STUDY

4.1. Multicomponent Kinetics Experiment

The resins used in this part of experiment were conditioned and loaded with Na^+ by using the same procedure as described in the binary equilibrium experiments, then the resins were washed with 500ml 0.04N NaCl solution and dried by the same vacuum method as in the binary equilibrium experiments. A mixture consisting of 740 ml 0.04N NaCl solution, 120ml 0.04N $CuCl_2$ solution and 140ml 0.04N $CdCl_2$ solution were prepared to form the initial ionic solution with a total volume of 1000ml. The batch kinetics experiment is setup with a 2000ml Pyrex® beaker, where 10.00 grams of fresh loaded SR-5 resin is mixed with the prepared ionic solution. Mechanical agitation is performed by a T-line laboratory stirrer to achieve pore diffusion limitation conditions. Samples of solution are collected at different times to determine the change in concentration of the exchanging ion with increase in contacting time. The samples were then diluted to a suitable concentration and analyzed by the AA machine described in Section 3.1.

The initial concentration of the solution determined by using the AA machine was 0.00541N of Cu^{++}, 0.00610N of Cd^{++} and 0.030N of Na^+.

4.2. Multicomponent Kinetics Experimental Results

The results of the experiment are shown in Figure 4.1 with 29 data points collected from time zero to 120 minutes of contacting time. Figure 4.1 shows that most of the ion exchange is taking place in the first 60 minutes of contacting and until 100 minutes the system is almost in equilibrium between liquid phase and solid phase. While the loading of Na^{+} in the solid phase decreases, both the loading of Cu^{++} and Cd^{++} increase due to the fact that Cu^{++} and Cd^{++} are more preferred over Na^{+} cation to the SR-5 ion exchange resin. The rates of loading of Cu^{++} and Cd^{++} are similar and this phenomena can be explained by the fact that the two cations have a close atomic radius and the same valence.

An attempt at modeling of the experiment data was not successful because there are some parameters which were not determined. Inparticular, the particle size, the porosity and the diffusion coefficients of the ions in the SR-5 ion exchange pellets are not available. Additional experimental works needs to be done in order to determine these parameters and generate results from the model.

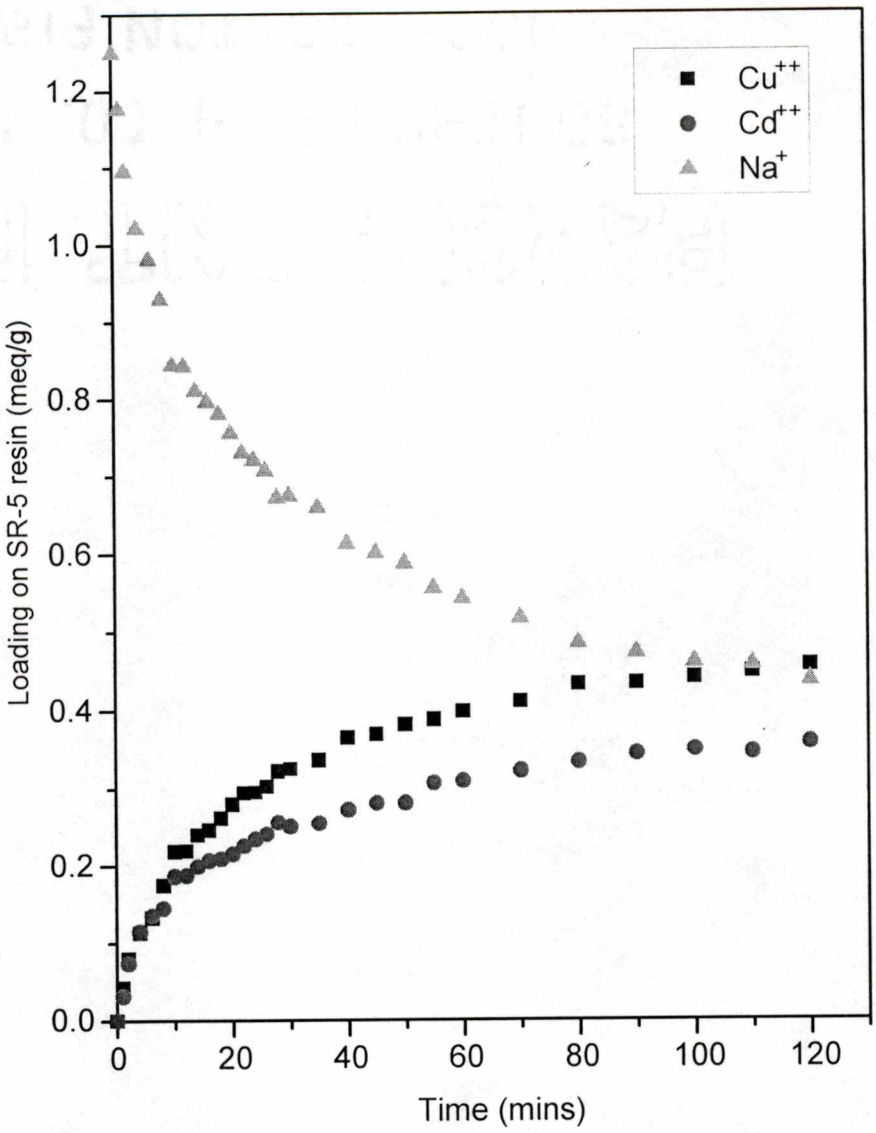


Figure 4.1 Batch Kinetics Experiment of Cu^{++}, Cd^{++} and Na^{+} loading on SR-5 resin

CHAPTER 5

FIXED BED SIMULATION

The equilibrium data obtained in Chapter 3 along with a simple, equilibrium, non dispersion model of an ion exchange column are used to simulate the behavior of a three component heavy metal system. The results of this analysis are predicted in this chapter. Experimental data may be compared with these simple model predictions when such data are available.

5.1. Determination of Separation Factors

Isotherms from the binary equilibrium experiments can be used to determine the separation factors needed for the simulation of fixed bed ion exchange column according to a simple model. A relation between the average separation factor (α_{ij}) and the areas above and below the isotherm was developed by Clifford [Clifford, 1976]. Eq. 5.1 is used to determine the average separation factor from the entire isotherm data collected from the binary batch equilibrium experiments. It can be solved by trial and error after the areas are measured.

$$Ratio = \frac{\text{area below isotherm}}{\text{area above isotherm}} = \frac{\left(\alpha^2 - \alpha - \alpha\ln\alpha\right)\Big/(\alpha-1)^2}{1-\left[\left(\alpha^2 - \alpha - \alpha\ln\alpha\right)\Big/(\alpha-1)^2\right]} \qquad (5.1)$$

Figure 5.1 shows the binary isotherms of Cu^{++}/Cd^{++} and Cu^{++}/Na^{+}. The area above and below the isotherm can be calculate by the summation of the products of X(q) and constant interval Δq over the entire range from 0 to 1.00 which is $\Sigma(X(q)*\Delta q)$. The average separation factors α_{CuCd} and α_{CuNa} can be calculated from Eq. 5.1 by trial and error using the MATLAB™ **fzero** function. The ratio of areas for the Cu^{++}/Cd^{++} system is 0.0381/0.9619 and the value of α_{CuCd} found is 95.7468. For the Cu^{++}/Na^{+} system, the ratio is equal to 0.1530/0.9847 and α_{CuNa} is equal to 312.2610.

5.2 Simulation of Fixed Bed Effluent Concentration History

The calculation procedure of determine the effluent-concentration history by the *h*-function analysis is outlined in Section 2.4.3. First, suitable assumptions and values must be set in order to get a correct approximation. The assumptions are :

(a) Three components systems, cations: Cu^{++}, Cd^{++}, Na^{+}

(b) $\Sigma x_i = 1.0$, $\Sigma y_i = 1.0$

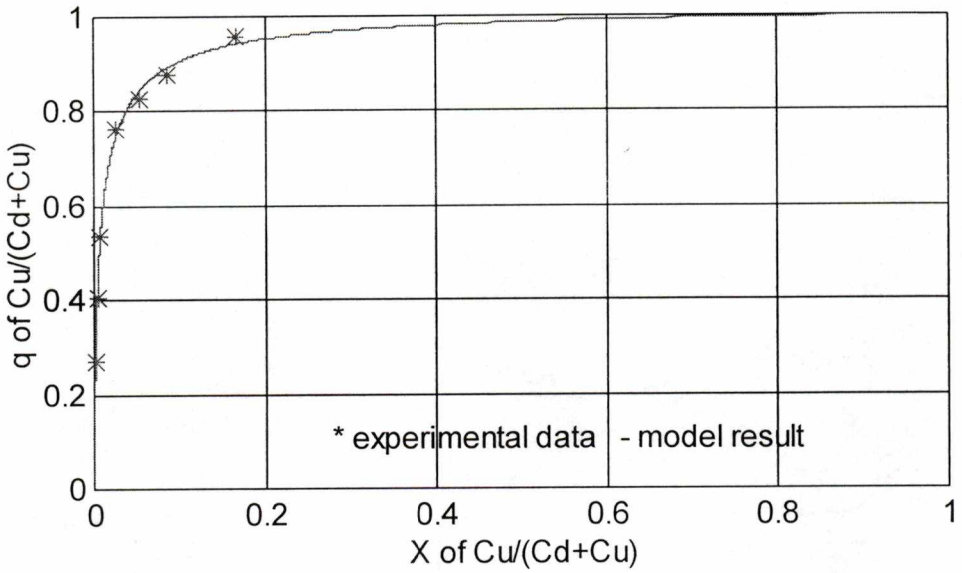
(c) Constant influent concentration and uniform presaturation composition.

(d) Constant separation factors, α_{CuCu}, α_{CuCd} and α_{CuNa}.

(e) Three plateau zones and two transitions.

(f) Instantaneous equilibrium, which implies negligible mass transfer resistance between the liquid and solid phases and through the resin beads.

(g) Negligible axial dispersion.



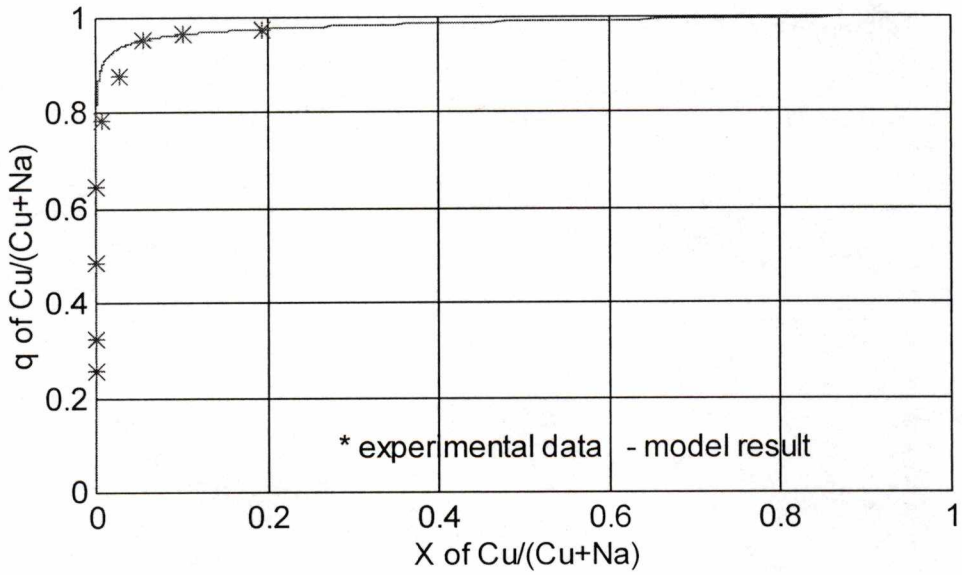


Figure 5.1 Binary isotherms of Cu^{++}/Cd^{++} and Cu^{++}/Na^{+} used for determination of α_{CuCd} and α_{CuNa}.

The following initial conditions and parameters are given to start the simulation of the breakthrough of Cu++ and Cd++ in a fixed bed ion exchange column,

(a) Influent concentrations, $x_{Cu,1} = 0.25$, $x_{Cd,1} = 0.30$, $x_{Na,1} = 0.45$

(b) Presaturation concentration, $y_{Cu,3} = 0.00$, $y_{Cd,3} = 0.00$, $y_{Na,3} = 1.00$

(c) Constant separation factors, $\alpha_{CuCu} = 1.00$, $\alpha_{CuCd} = 95.7468$ and $\alpha_{CuNa} = 312.2610$

(d) The index of components are set as Cu=1, Cd=2 and Na=3 which corresponds to the convention that the selectivity of the sorbent for the various components decrease in the order i = 1, 2 .....n.

The second step is to calculate the values of $h_{i,f}$ and $h_{i,p}$ for each of the components. By using Eq. 2.12, $\sum_{i=1}^{n} \frac{x_{i1}}{h_F - \alpha_{1i}} = 0$, the equation needed to be solved becomes,

$$\frac{x_{Cu,1}}{h_F - \alpha_{CuCu}} + \frac{x_{Cd,1}}{h_F - \alpha_{CuCd}} + \frac{x_{Na,1}}{h_F - \alpha_{CuNa}} = 0 \qquad (5.2)$$

Solving the above equation, two roots are found, $h_F = 37.7170$ and 201.7993. The next step is to index the roots, applying the criteria that $\alpha_{1i} \le h_i \le \alpha_{1,i+1}$, thus

$\alpha_{CuCu} = 1.00 \le 37.7170 \le \alpha_{CuCd} = 95.7468$, therefore $h_{1,F} = 37.7170$

$\alpha_{CuCd} = 95.7468 \le 201.7993 \le \alpha_{CuNa} = 312.2610$, therefore $h_{2,F} = 201.7993$

As the presaturation composition only comprises one component in this example, Eq. 2.11 is not required to be solved. The value of h_p is given by α_{CuCu} and α_{CuCd}. Therefore,

$h_{1,P} = 1.00$ and $h_{2,P} = 95.7468$.

The next step is to check whether or not the two transition zones are abrupt or gradual by using Eq. 2.15,

$$R_{k,k+1} = {h_{kP}}/{h_{kF}} \tag{2.15}$$

$R_{1,2} = h_{1,P}/h_{1,F} = 1.00/37.7170 < 1$, therefore the 1,2 transition is abrupt and $R_{2,3} = h_{2,P}/h_{2,F} = 1.00/(95.7468 \times 201) < 1$, therefore the 2,3 transition is also abrupt. And, the stoichiometric center of transition k,k+1 is given by Eqs.2.16 and 2.17,

$$\overline{T}_{k,k+1} = \left(h_{kP} h_{kF} P_k\right)^{-1} \tag{2.16}$$

where

$$P_k = \prod_{\substack{i=1 \\ (i \neq k)}}^{n-1} h_{ik} \prod_{i=1}^{n} \alpha_{il} \tag{2.17}$$

The throughput ratio T, or non dimensional time, is defined as,

$$T = \frac{V - \varepsilon v_b}{V_{stoic}} = \frac{t - \left(\varepsilon v_b / F\right)}{t_{stoic}} \tag{5.3}$$

v_b is the bulk volume of the bed and ε is the interstitial void fraction, and εv_b the bed void volume. F is the volumetric flow rate; V is the fluid volume that has entered the bed since start; therefore $V-\varepsilon v_b$ is the volume that has reached the end of the bed,

corresponding to time t-(εv_b/F). V_{stoic} is the fluid volume holding enough cations to saturate packed volume of ion exchange resin v completely If all the cations were transferred to it and t_{stoic} is the corresponding time. In other words, throughput ratio T is a non dimensional time which value depends on the packed operation parameters including concentration of influent, interstitial void fraction and flow rate.

Inserting the values into the equations, $P_1 = h_{11}\times h_{21}\times\alpha_{31}\times\ \alpha_{21}\times\alpha_{11} = 0.2546$ and $P_2 = h_{12}\times h_{22}\times\alpha_{31}\times\ \alpha_{21}\times\alpha_{11} = 6.7496 \times 10^{-3}$. Therefore, $\overline{T}_{1,2} = \left(h_{1P}h_{1F}P_1\right)^{-1} = 0.1041$ and $\overline{T}_{2,3} = \left(h_{2P}h_{2F}P_2\right)^{-1} = 7.6679\times10^{-3}$.

The plot of h values in the three zones is illustrated in Figure 5.2.

In plateau zone 1, the set of h_i is h_{1F} and h_{2F} and in plateau zone 2, the set of h_i is h_{1P} and h_{2F}. In plateau zone 3, the set of hi is h_{1P} and h_{2P}. The composition of each plateau zone is now calculated by the relation given in Eq.2.13 :

$$x_{jk} = \frac{\prod_{i}\left(h_{ik} - \alpha_{1j}\right)}{\prod_{i\neq j}\left(\alpha_{1i} - \alpha_{1j}\right)} \tag{2.13}$$

In zone 1,

$$x_{11} = \frac{(h_{11} - \alpha_{11})(h_{21} - \alpha_{11})}{(\alpha_{12} - \alpha_{11})(\alpha_{13} - \alpha_{11})} \tag{5.3}$$

$$x_{21} = \frac{(h_{11} - \alpha_{12})(h_{21} - \alpha_{12})}{(\alpha_{11} - \alpha_{12})(\alpha_{13} - \alpha_{12})} \tag{5.4}$$

Inserting the corresponding values into the equations gives $x_{11} = 0.25$, $x_{21} = 0.30$ and $x_{31} = 0.45$, which agrees with the influent concentrations we set.

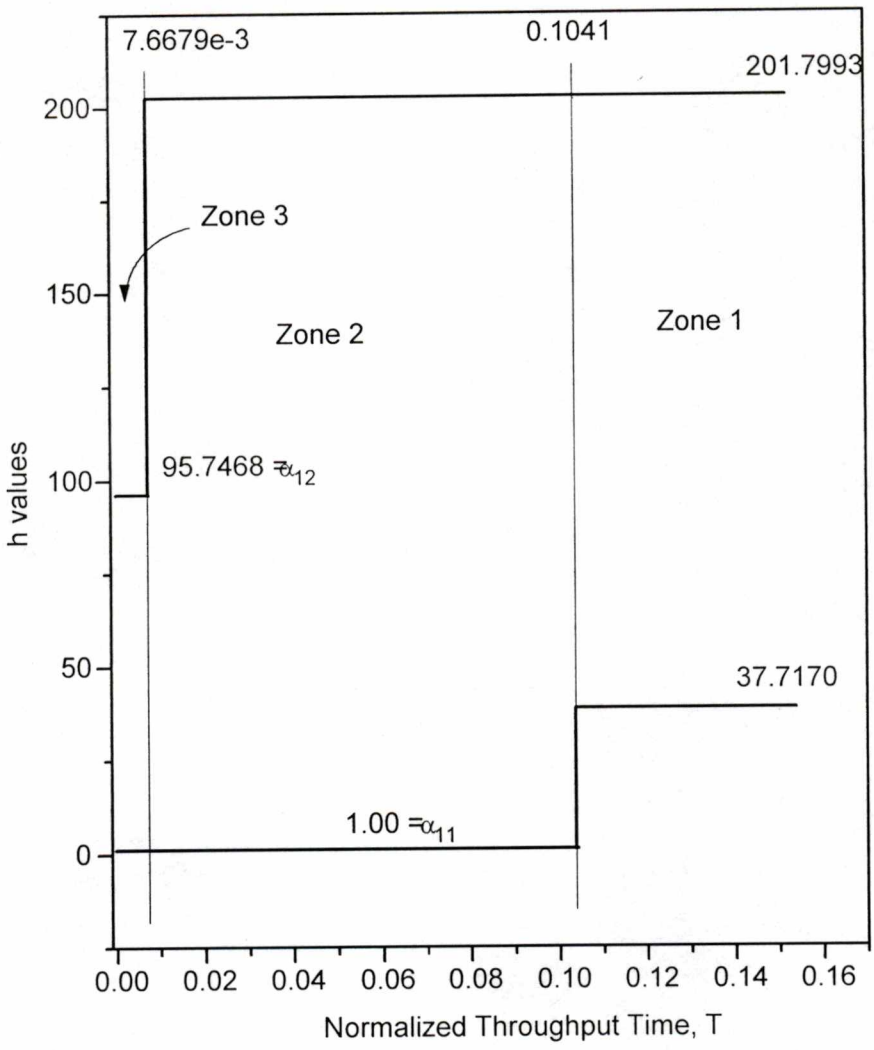


Figure 5.2 Calculated h_i profiles of h-analysis

In zone 2,

$$x_{12} = \frac{(h_{12} - \alpha_{11})(h_{22} - \alpha_{11})}{(\alpha_{12} - \alpha_{11})(\alpha_{13} - \alpha_{11})} \tag{5.5}$$

$$x_{22} = \frac{(h_{12} - \alpha_{12})(h_{22} - \alpha_{12})}{(\alpha_{11} - \alpha_{12})(\alpha_{13} - \alpha_{12})} \tag{5.6}$$

And, the values of $x_{12} = 0.00$, $x_{22} = 0.4898$ and $x_{32} = 1.00 - x_{12} - x_{22} = 0.5102$.

In zone 3, by applying the same equation Eq. 2.13 the values of x_{13}, x_{23} and x_{33} were calculated as $x_{13} = 0.00$, $x_{23} = 0.00$ and $x_{33} = 1.00$. The final results of the simulation of fixed bed effluent concentration history corresponding to the condition set initially is shown in Figure 5.3.

The composition on the solid phase of each plateau zone can be calculated from Eq. 2.14 :

$$y_{jk} = \frac{\prod_i \left[\left(1/h_{ik} \right) - \alpha_{j1} \right]}{\prod_{i \neq j} \left(\alpha_{i1} - \alpha_{j1} \right)} \tag{2.14}$$

In zone 1,

$$y_{11} = \frac{(1/h_{11} - \alpha_{11})(1/h_{21} - \alpha_{11})}{(\alpha_{21} - \alpha_{11})(\alpha_{31} - \alpha_{11})} \tag{5.3}$$

$$y_{21} = \frac{(1/h_{11} - \alpha_{21})(1/h_{21} - \alpha_{21})}{(\alpha_{11} - \alpha_{21})(\alpha_{31} - \alpha_{21})} \tag{5.4}$$

Inserting the corresponding values into the equations gives $y_{11} = 0.9823$, $y_{21} = 0.012308$ and $y_{31} = 1.00 - y_{11} - y_{21} = 5.662 \times 10^{-3}$.

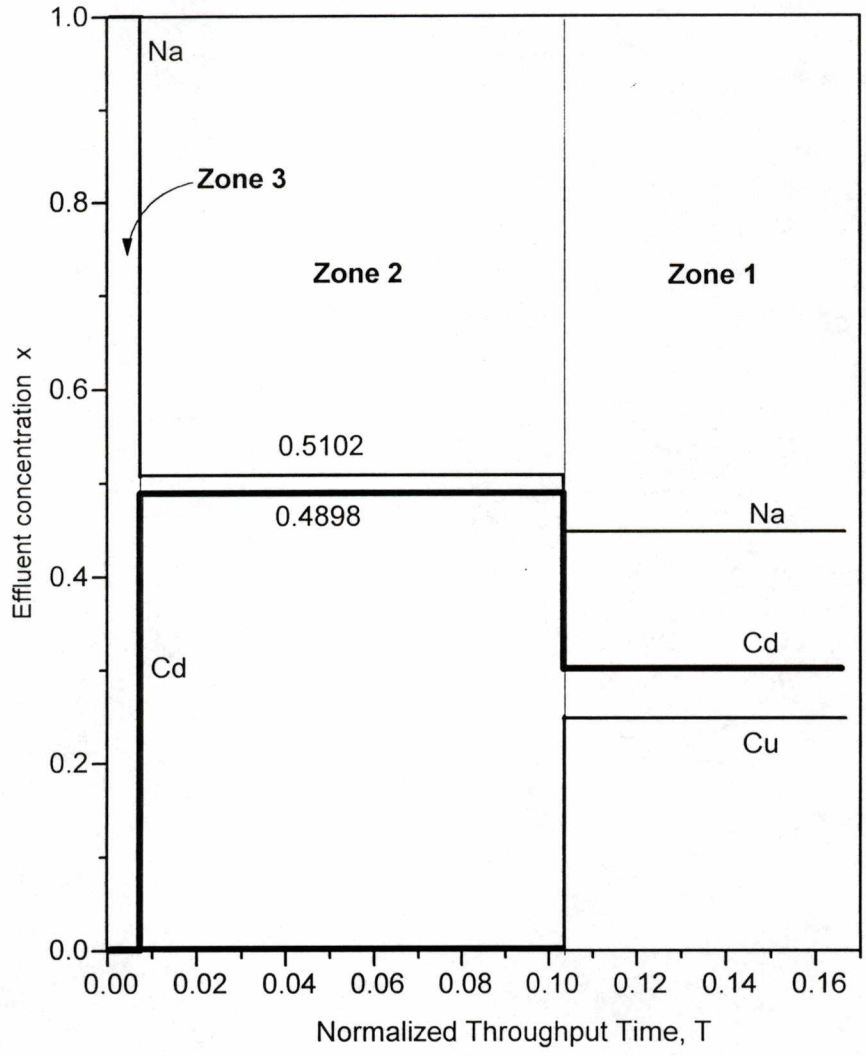


Figure 5.3 Effluent concentration history of a three component system estimated according to the Equilibrium, non Dispersion model.

In zone 2,

$$y_{12} = \frac{(1/h_{12} - \alpha_{11})(1/h_{22} - \alpha_{11})}{(\alpha_{21} - \alpha_{11})(\alpha_{31} - \alpha_{11})} \tag{5.5}$$

$$y_{22} = \frac{(1/h_{12} - \alpha_{21})(1/h_{22} - \alpha_{21})}{(\alpha_{11} - \alpha_{21})(\alpha_{31} - \alpha_{21})} \tag{5.6}$$

And, the values of $y_{12} = 0.00$, $y_{22} = 0.75794$ and $x_{32} = 1.00 - x_{12} - x_{22} = 0.24206$.

In zone 3, by applying the same equation Eq. 2.14 the values of y_{13}, y_{23} and y_{33} were calculated as $y_{13} = 0.00$, $y_{23} = 0.00$ and $y_{33} = 1.00$. The final results of the simulation of loading composition on the fixed bed ion exchange column corresponding to the condition set initially is shown in Figure 5.4.

The instantaneous equilibrium is an acceptable assumption while the fixed bed are deep and the flow rate is slow enough. The constant separation factor assumption does gives a close result with the mass action multicomponent system calculation on the loading of the resin phase described in Section 3.5. Where constant separation factor assumption gives $y_{11} = 0.9823$, $y_{21} = 0.012308$ and $y_{31} = 5.662 \times 10^{-3}$, the mass action assumption calculation gives $y_{11} = 0.946786$, $y_{21} = 0.0179827$ and $y_{31} = 0.0352311$. Using the assumption of constant separation factors, uniform presaturation composition, and constant feed concentration, the Helfferich model gives a useful engineering approximation to describe the breakthrough of a fixed bed ion exchange column. However, experiments must be done in order to confirm its validity on a packed bed filled with SR-5 ion exchange resin.

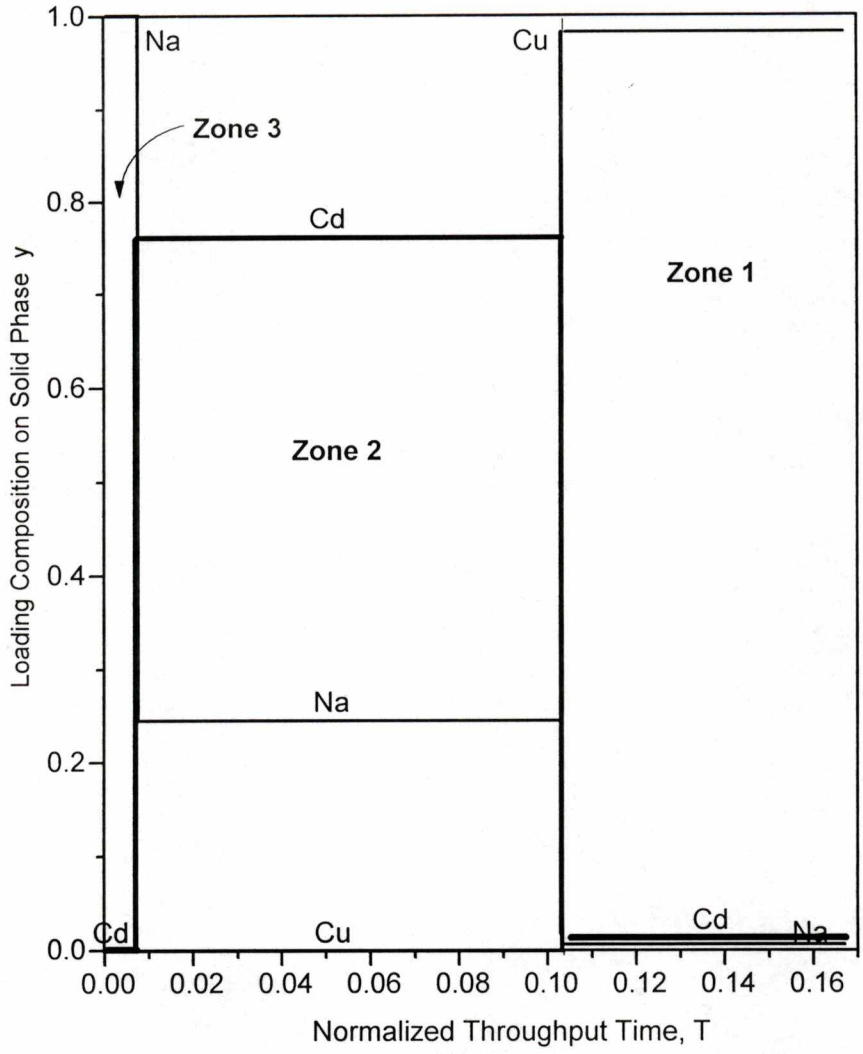


Figure 5.4 Loading composition on the fixed bed ion exchange column corresponding to the condition of the example

CHAPTER 6

SUMMARY and CONCLUSIONS

A series of binary equilibrium experiments were conducted in order to provide sufficient data for the determination of the equilibrium constants and binary interaction parameters for the systems Cd^{++}/Cu^{++}, Na^{+}/Cd^{++} and Na^{+}/Cu^{++} on a commercial, chelating ion exchange resin, SR-5, marketed by Sybron Chemicals Inc. The Pitzer equation was used to determine the liquid phase activity coefficients, while the procedure proposed by Smith and Woodburn along with the Wilson model were used to determine the equilibrium constants K_{AB} and the binary interaction parameters Λ_{AB} and Λ_{BA}. The binary parameters were then used to predict the behavior of the three component system Na^{+}, Cd^{++} and Cu^{++} on the same resin, using the mass action equilibrium model and to evaluate the average separation factors for these systems. These separation factors were then used to estimate the breakthrough time for each of the three cations from a fixed bed of resin by the simple, multicomponent, equilibrium, non-dispersion model of Helfferich.

Based on the data obtained, the following conclusions are made :

1. The binary experimental results were modeled and a set of best fit equilibrium constants K_{AB} and interaction parameters Λ_{AB} and Λ_{BA} were found for each of the three binary systems. The modeled results and the experimental results match very well with these parameters. The values of these binary equilibrium parameters found for the ion exchange of Cu^{++}, Cd^{++} and Na^{+} on SR-5 ion exchange resin are:

Binary System A/B	Equilibrium Constant K_{AB}	Parameter Λ_{AB}	Parameter Λ_{BA}
Cd^{++}/Cu^{++}	0.00714118	1.00458	1.61908
Na^{+}/Cd^{++}	0.016605	2.44194	2.56662
Na^{+}/Cu^{++}	0.000118579	3.33537	3.06561

2. Applying the mass action multicomponent system equilibrium theory and using the binary equilibrium parameters found from the binary equilibrium experiments, the equilibrium behavior of three components, Cu^{++}, Cd^{++} and Na^{+}, on SR-5 ion exchange resin can be predicted. The three component equilibrium experimental results confirm the validity of the values predicted by the mass action theory. However, there is a systematic deviation between the predicted values and the experimental results. As the concentration of Cu^{++} increases, the deviation increases, while the pH value of the solution decreases from 3.75 to 2.5. The

deviation thus increases with the increasing of H^+ ion presence in the liquid phase. Therefore, the observed deviation may be due to the competition of H^+ ions for the resin sites at high H^+ concentration. If this should be the case, the system should be modeled as a four component rather than as a three component system. Additional experimental work is required in order to confirm this supposition.

3. Using the assumption of constant separation factors, uniform presaturation of the resin, and constant feed concentration, the Helfferich model is able to generate a useful engineering approximation describing the breakthrough of Cd^{++} and Cu^{++} in a fixed bed ion exchange column presaturated with Na^+ ions. However, additional experiments must be done in order to confirm the accuracy and validity of this model on a packed bed filled with SR-5 ion exchange resin.

In addition, a series of batch kinetics experiments were also performed for the Na^+, Cd^{++} and Cu^{++} system in the SR-5 resin. Equilibrium was attained in approximately 120 minutes. The results appear complex and could not be adequately modeled at this time.

CHAPTER 7

FUTURE WORK

1. Improvement of experimental method should lead to a better results. The possible ways of improvement include :
    i. Improve the cation concentration analysis method by using a more precise atomic adsorption machine.
    ii. Consider the H^+ ion in the experiment as well as in the models.
    iii. Use of a non-aqueous medium, for example CH_3OH, while loading a single type of cation on SR-5 ion exchange resin might be a possible way to eliminate the influence of H^+ ions.

2. Integration of the mass action equilibrium theory with the Helfferich fixed bed model of ion exchange should improve the accuracy of the breakthrough prediction. However, this will lead to an increase of mathematical difficulties of the model when the constant separation factor assumption is released. Future work can be set in this direction, in order to develop an integrated theory of ion exchange which includes equilibrium, kinetics and fixed bed theory.

BIBLIOGRAPHY

BIBLIOGRAPHY

Clifford, D. A. Ph.D Thesis, University of Michigan, Ann Abor, MI, 1976.

Clifford, Dennis, Multicomponent Ion-Exchange Calculation for Selected Ion Separations, Ind. Eng. Chem. Fundam., 21, 141-153 (1982).

Grace Andrew, Optimization Toolbox User's guide, Math Works Inc., MA, 1990.

Helfferich, Friedrich, Ion Exchange, McGraw-Hill Book Company, Inc., New York, 1962.

Helfferich and Klein, Multicomponent Chromatography, Maurice Dekker, New York, 1970.

Kunin, Robert, Ion Exchange Resins, John Wiley & Sons, Inc., New York, 1958.

Lucas, A., Zarca, J. and Canizares, P., Ion-Exchange Equilibrium of Ca^{+}, Mg^{2+}, K^{+}, and H^{+} Ions on Amberlite IR-120: Experimental Determination and Theoretical Prediction of the Ternary and Quaternary Equilibrium Data, Separation Science and Technology, 27(6), 823-841 (1992).

Lucas, A., Zarca, J. and Canizares, P., Binary Ion Exchange Equilibrium for Ca^{+}, Mg^{2+}, K^{+}, Na^{+} and H^{+} Ions on Amberlite IR-120, Chem. Eng. Technol. 16, 35-39 (1993).

Math Works Inc., The Student Edition of Matlab, Prentice Hall, Englewood Cliffs NJ, 1992.

Miller, Durando, Power, 99, 73-7(1955).

Perona, J. J., Model for Sr-Cs-Ca-Mg-Na Ion-Exchange Equilibria on Chabazite, AIChE Journal, 39(10), 1716-1720 (1993).

Perry, R.H. and Cecil H. Chilton, Chemical Engineer's Handbook, Sixth Edition, McGraw-Hill Book Company, New York, 1980.

Pitzer, K.S., Theory: Ion Interaction Approach in Activity Coefficients in Electrolyte Solutions, Vol 1., CRC Press, Florida, 1979.

Shallcross, D. C., Herrmann, C. C. and McCoy, B. J., An Improved Model for the Prediction of Multicomponent Ion Exchange Equilibria, Chem. Engr. Sci., 43(2), 279-288 (1988).

Smith, R. P. and Woodburn, E. T., Prediction of Multicomponent Ion Exchange Equilibria for the Ternary System SO^{2-}_4 -NO^{-}_3 -Cl from Data of Binary Systems, AIChE Journal, 24(4), 577-587 (1978).

Sybron Chemicals Inc., SR-5 Ionac Data Sheet - Selected Metal Recovery.

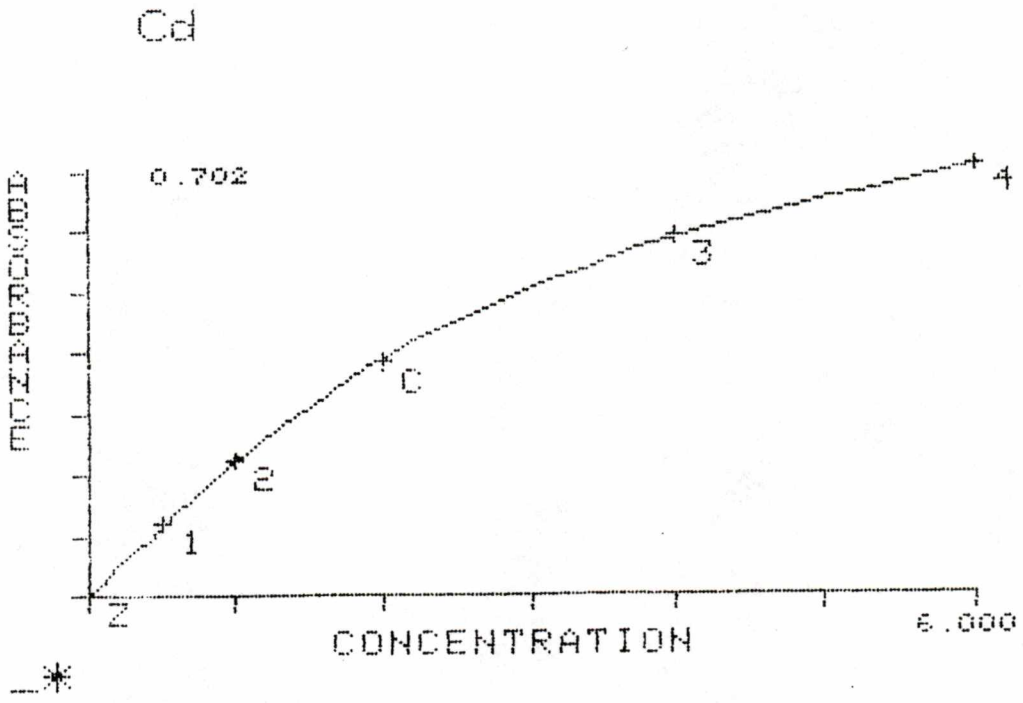
Yao, C and Tien, C., Approximations of Uptake Rate of Spherical Adsorbent Pellets and Their Application to Batch Adsorption Calculations, Chem. Engr. Sci., 48(1), 187-198 (1993).

APPENDICES

APPENDIX A

EXPERIMENTAL INFORMATION

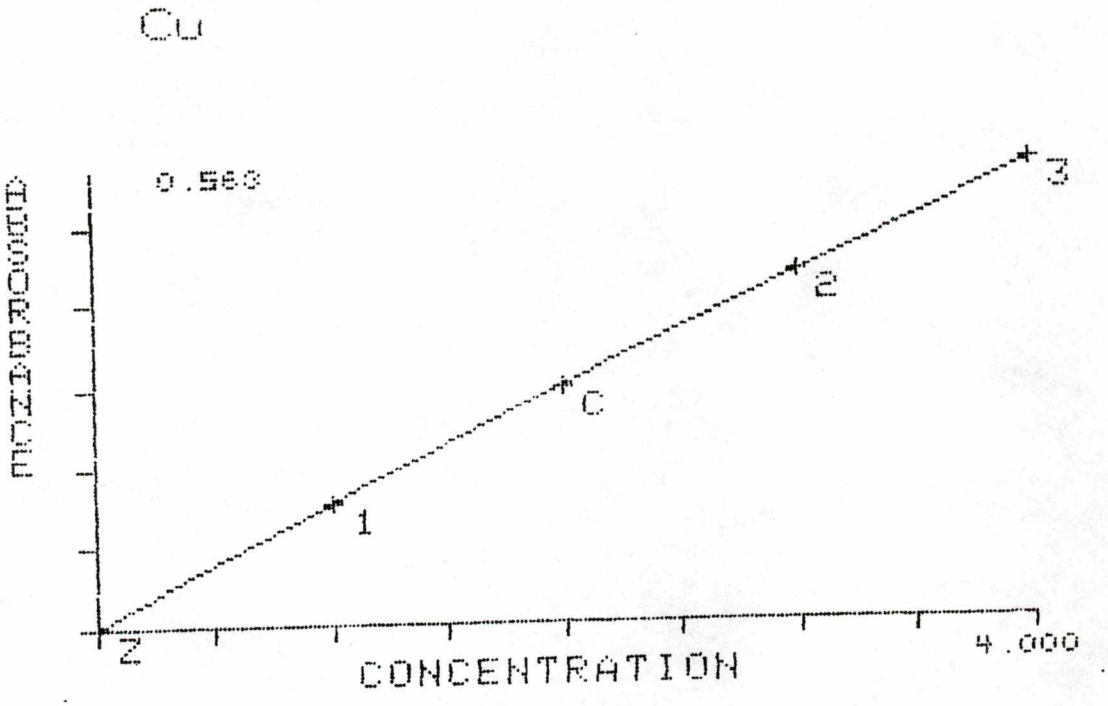
A1. ATOMIC ADSORPTION CALIBRATION CURVE of Cd



CALIBRATION TABLE

STD	Concentration (ppm)	Apparent Conc. (ppm)
Z	0.000	0.000
C	2.000	1.986
1	0.500	0.509
2	1.000	1.011
3	4.000	4.020
4	6.000	5.999

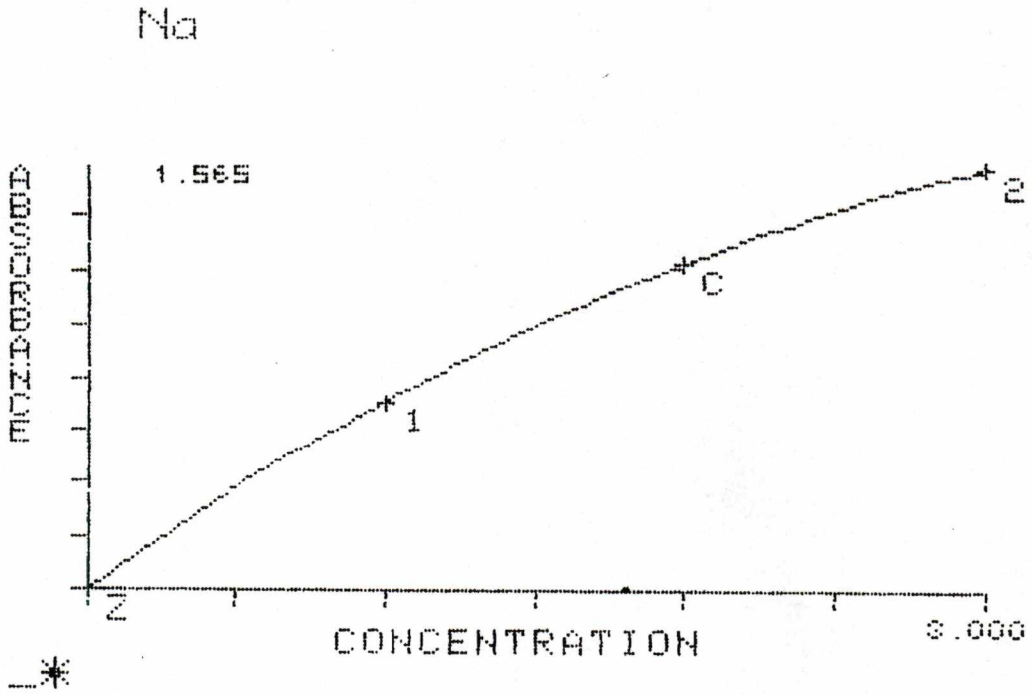
A2. ATOMIC ADSORPTION CALIBRATION CURVE of Cu



CALIBRATION TABLE

STD	Concentration (ppm)	Apparent Conc. (ppm)
Z	0.000	0.000
C	2.000	1.988
1	1.000	1.007
2	3.000	3.009
3	4.000	3.999

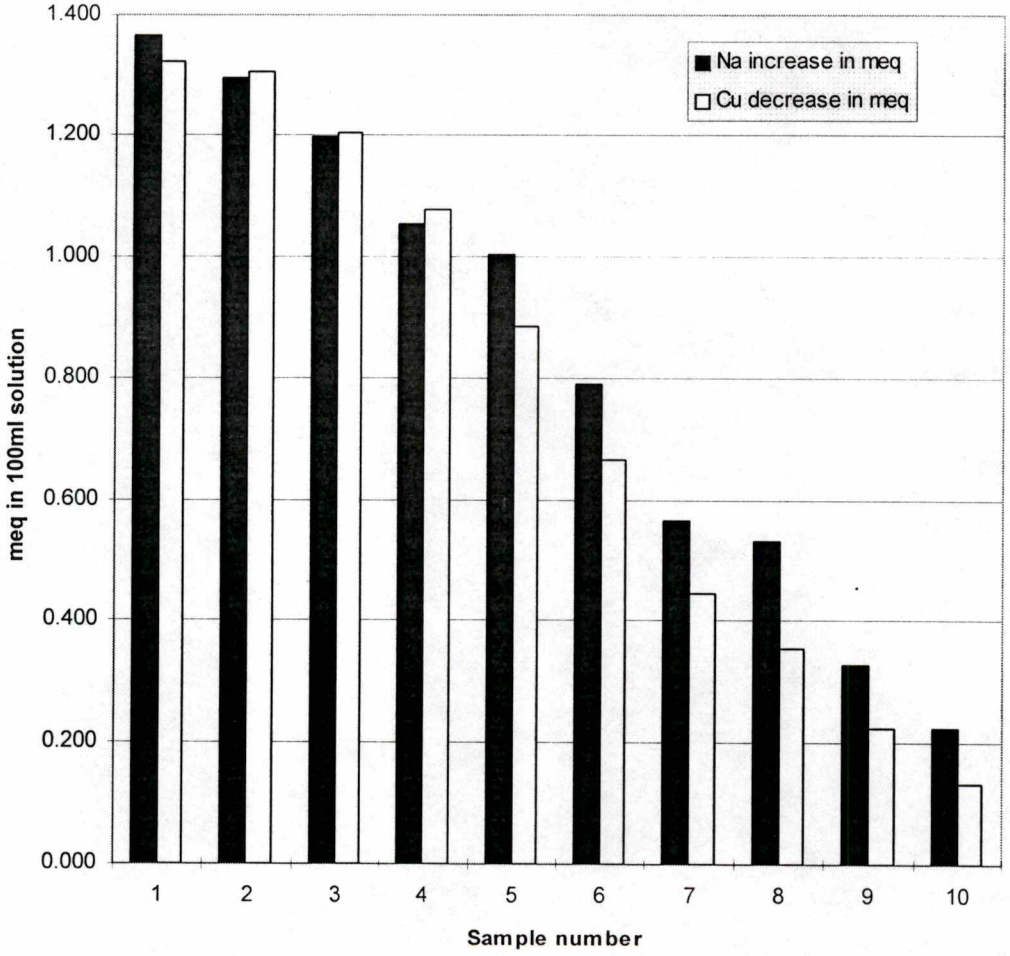
A3. ATOMIC ADSORPTION CALIBRATION CURVE of Na



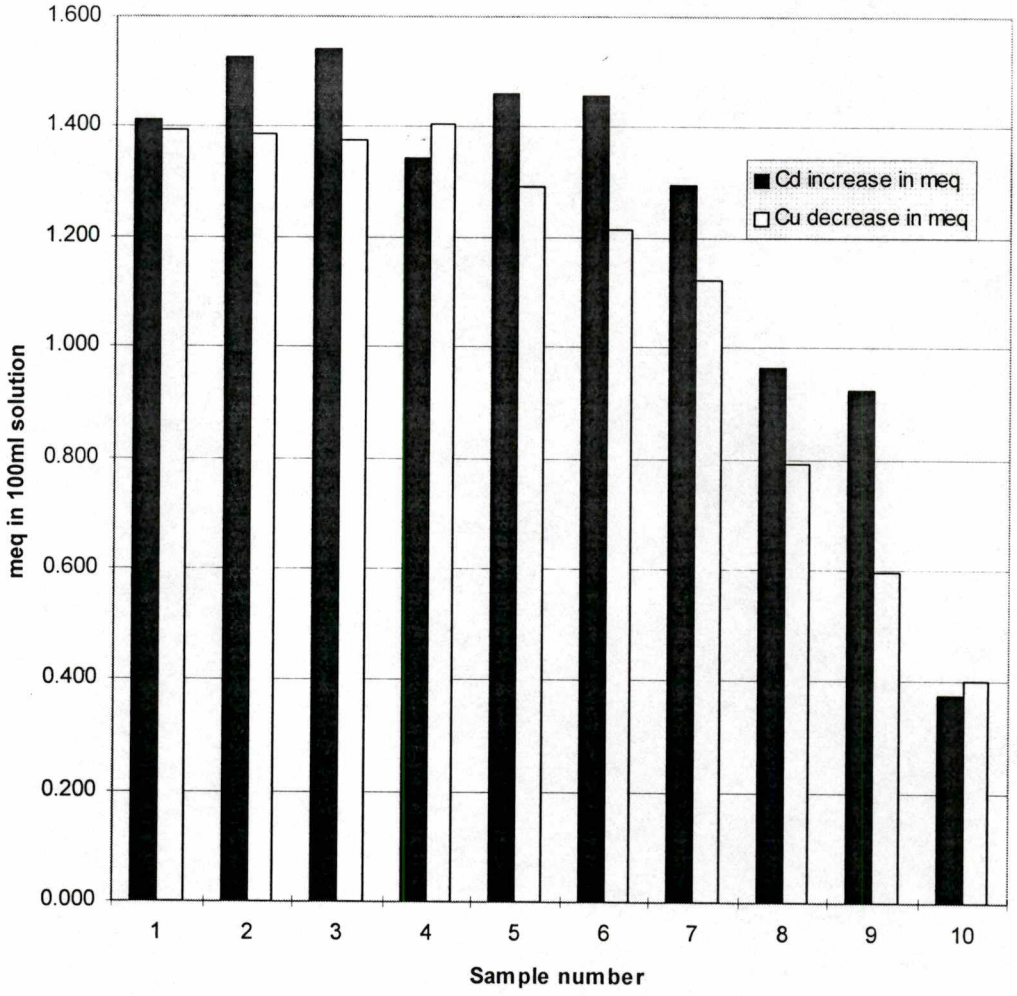
CALIBRATION TABLE

STD	Concentration (ppm)	Apparent Conc. (ppm)
Z	0.000	0.000
C	2.000	1.990
1	1.000	1.008
2	3.000	3.008

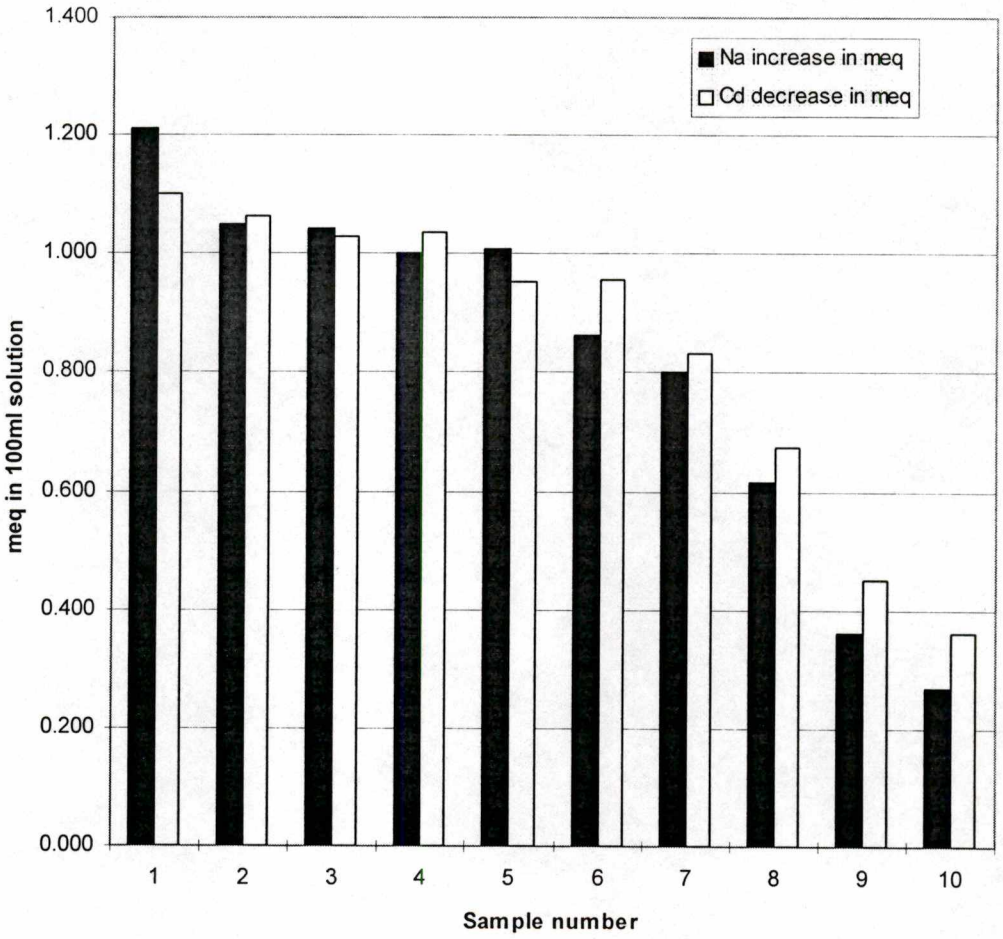
A4. Confirmation of ion exchange in liquid phase : Binary equilibrium Na^{+}/Cu^{++} on SR-5 resin.



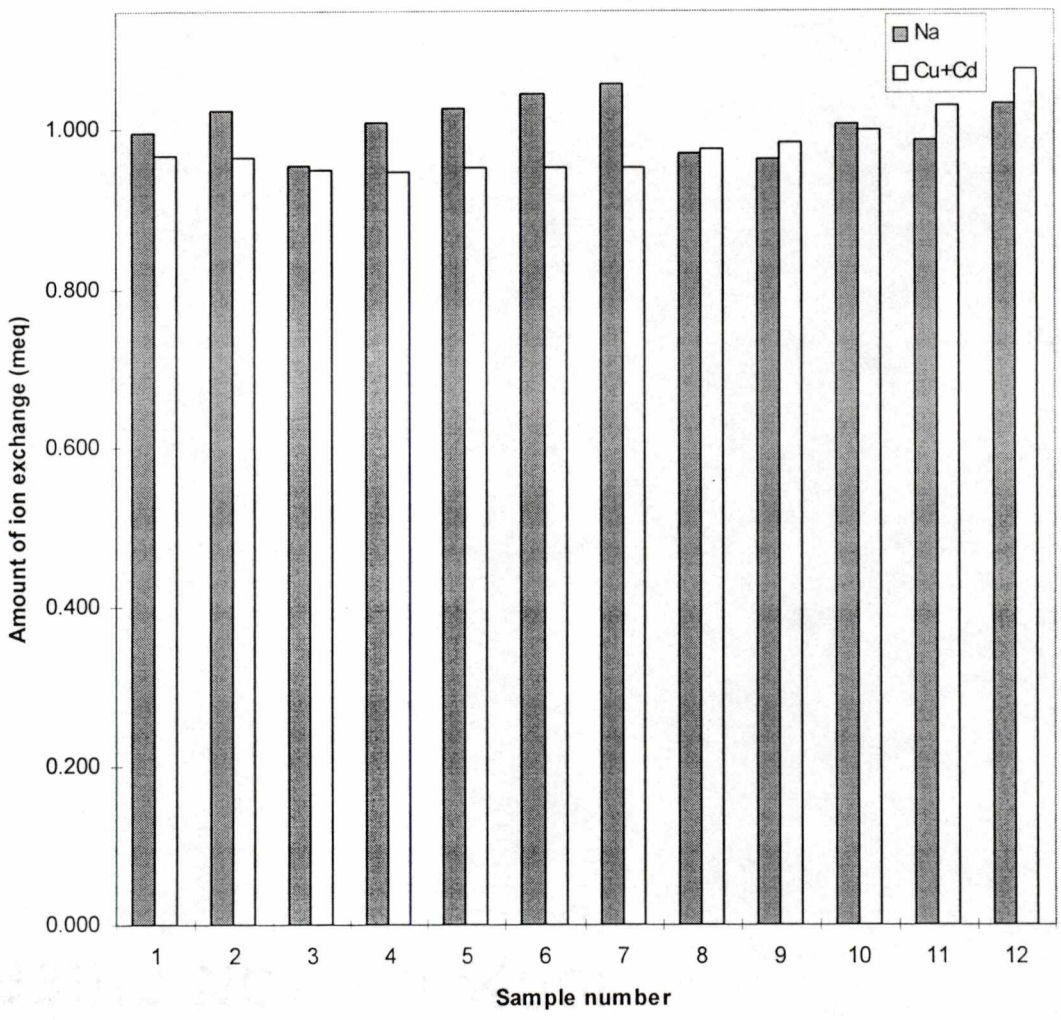
A5. Confirmation of ion exchange in liquid phase : Binary equilibrium Cd^{++}/Cu^{++} on SR-5 resin.



A6. Confirmation of ion exchange in liquid phase : Binary equilibrium Na^{+}/Cd^{++} on SR-5 resin.



A7. Confirmation of ion exchange in liquid phase : 3rd experiment of multicomponent system Cu^{++}, Cd^{++} and Na^{+} equilibrium on SR-5 resin.



APPENDIX B

COMPUTER CODES

MATLAB M-FILES

B1. Matlab M-file for Solving Binary Equilibrium Parameters, Cd^{++}/Cu^{++}

filename : CdCu.m

```
clear
hold off
clg
X=[];    Y1=[];   Y2=[];
global X Y1 Y2 lambdaexp lfit Err

%        x          y
DATA= [          .0025169          .2717064
                 .0041250          .4056327
                 .0071060          .5369900
                 .0261613          .7628810
                 .0525036          .8267998
                 .0850602          .8780873
                 .1656543          .9564701];



%%%%%%%%%%%%1=Cd 2=Cu        %%%%%%%%%%%%

X=DATA(:,1);
Y=DATA(:,2);
%rmm=20;
Co=.041;
Y2=Y; Y1=1-Y; C2=X*Co; C1=(1-X)*Co;
% ACTCOEL1=.89;                              :
% ACTCOEL2=.70;
lambdaexp = [];
lambdafit = [];

for i=1:1:length(X)

I(i)= 0.5*(C1(i)*2+C2(i)*2+Co)
f(i)= -0.3910*(I(i)^.5/(1+1.2*I(i)^.5)+2/1.2*log(1+1.2*I(i)^.5))
ACTCOEL1(i)= exp(4*f(i))
ACTCOEL2(i)= exp(4*f(i))
lambdaexp(i)=(ACTCOEL2(i)*C2(i)*Y1(i))/(ACTCOEL1(i)*C1(i)*Y2(i));
end
pause
AVEactcoel1=sum(ACTCOEL1)/length(X)
AVEactcoel2=sum(ACTCOEL2)/length(X)
pause
STARTV=[.009 1.0 1.71];


OPTIONS(1)=1e-999;
OPTIONS(2)=1e-999;
```

```
%OPTIONS(5)=1;
KAA=leastsq('ksmall',STARTV,OPTIONS);

%%%
```

```
ylabel('q of Cu/(Cd+Cu)');
%txt=sprintf('K = %g; A1= %g; A2 = %g', KAA );
%txt2=sprintf('Error = %g',Err);
%gtext(txt);
%gtext(txt2);
txt2=sprintf('* experimental data   - model result');
gtext(txt2);
grid;
```

B2. Matlab M-file for Solving Binary Equilibrium Parameters, Na^{+}/Cd^{++}

filename : NaCd.m

```
clear
hold off
clg
X=[];    Y1=[];   Y2=[];
global X Y1 Y2 lambdaexp lfit Err

%        x          y
DATA= [          4.27e-5  .307057
                 8.08e-5  .383721
                 .000756 .573239
                 .01634   .707341
                 .040382 .811981
                 .124921 .880541
                 .254342 .935651];



%%%%%%%%%%%%1=Na 2=Cd        %%%%%%%%%%%%

X=DATA(:,1);
Y=DATA(:,2);
%rmm=20;
Co=.043;
Y2=Y; Y1=1-Y; C2=X*Co; C1=(1-X)*Co;
% ACTCOEL1=.89;
% ACTCOEL2=.70;
lambdaexp = [];
lambdafit = [];

for i=1:1:length(X)

I(i)= 0.5*(C1(i)*1+C2(i)*4/2+Co)
f(i)= -0.3910*(I(i)^.5/(1+1.2*I(i)^.5)+2/1.2*log(1+1.2*I(i)^.5))
ACTCOEL1(i)= exp(4*f(i))
ACTCOEL2(i)= exp(4*f(i))
lambdaexp(i)=ACTCOEL2(i)*C2(i)*Y1(i)^2/(ACTCOEL1(i)*C1(i))^2/Y2(i);
end
pause
AVEactcoel1=sum(ACTCOEL1)/length(X)
AVEactcoel2=sum(ACTCOEL2)/length(X)
pause
STARTV=[.0166050 2.44194 2.56662];

OPTIONS(14)=9;
```

```
OPTIONS(1)=1e-999;
OPTIONS(2)=1e-999;
%OPTIONS(5)=1;
KAA=leastsq('ksmall',STARTV,OPTIONS)

%%%
```

```
xlabel('X of Cd/(Cd+Na)');
ylabel('q of Cd/(Cd+Na)');
txt=sprintf('K = %g; A1= %g; A2 = %g', KAA );
txt2=sprintf('Error = %g',Err);
%gtext(txt);
%gtext(txt2);
grid;
txt2=sprintf('* experimental data   - model result');
gtext(txt2);
```

B3. Matlab M-file for Solving Binary Equilibrium Parameters, Na^{+}/Cu^{++}

filename : KnaCu.m

```
clear
knacuclg
hold off
X=[];    Y1=[];   Y2=[];
global X Y1 Y2 lambdaexp lfit Err KAA1

%       x          y
DATA= [        .194274          0.976173712
               .100464          0.965710315
               .055626          0.953314879
               .028826          0.878303078
               .007516          0.785779919
               .000865          0.645252718
               8.0727e-5        0.485842747
               6.2257e-5        0.323866833
               5.4777e-5        0.259074629];


%%%%%%%%%%%%1=Na 2=Cu        %%%%%%%%%%%%

X=DATA(:,1);
Y=DATA(:,2);
%rmm=20;
Co=.045;
Y2=Y; Y1=1-Y; C2=X*Co; C1=(1-X)*Co;
% ACTCOEL1=.89;
% ACTCOEL2=.70;
lambdaexp = [];
lambdafit = [];

for i=1:1:length(X)

I(i)= 0.5*(C1(i)*1+C2(i)*4/2+Co)
f(i)= -0.3910*(I(i)^.5/(1+1.2*I(i)^.5)+2/1.2*log(1+1.2*I(i)^.5))
ACTCOEL1(i)= exp(1*f(i))
ACTCOEL2(i)= exp(4*f(i))
lambdaexp(i)=ACTCOEL2(i)*C2(i)*Y1(i)^2/(ACTCOEL1(i)*C1(i))^2/Y2(i);
end
pause
AVEactcoel1=sum(ACTCOEL1)/length(X)
AVEactcoel2=sum(ACTCOEL2)/length(X)
pause
STARTV=[3.34 3.02];


OPTIONS(1)=1e-999;
```

```
OPTIONS(2)=1e-999;
OPTIONS(5)=1;
KAA=leastsq('klarge',STARTV,OPTIONS)

%%%
```

```
X2(i)=(-bb(i)-(bb(i)^2-4*aa(i)*cc(i))^(1/2))/2/aa(i);
end
%KAA
%axis ('square');
%subplot(212)
axis ([0 .30 0 1])
plot (X2,Y2,'-r');
%title('NaR vs. Cu');
xlabel('X of Cu/(Cu+Na)');
ylabel('q of Cu/(Cu+Na)');
txt=sprintf('K = %g; A1= %g; A2 = %g', KAA );
txt2=sprintf('Error = %g',Err);
%gtext(txt);
%gtext(txt2);
grid;
txt2=sprintf('* experimental data   - model result');
gtext(txt2);
```

B4. Matlab M-file for Solving Binary Equilibrium Parameters : Subroutine

filename : Ksmall.m

```
function ErroR = small(KAA)

global X Y1 Y2 lambdaexp lfit Err

for i=1:1:length(X)
lambdafit(i)=exp(log(KAA(1))-(1-log(Y1(i)+Y2(i)*KAA(2))...
        -(Y1(i)/(Y1(i)+Y2(i)*KAA(2))+Y2(i)*KAA(3)/(Y1(i)*KAA(3)+Y2(i))))...
        +2*(1-log(Y1(i)*KAA(3)+Y2(i))-Y1(i)*KAA(2)/(Y1(i)+Y2(i)*KAA(2)))...
        -Y2(i)/(Y1(i)*KAA(3)+Y2(i))));
sErroR(i) = ((lambdaexp(i)-lambdafit(i))/lambdaexp(i))^2;
end

ErroR=sum(sErroR)
%ErroR = sum(((lambdaexp-lambdafit)).^2)
KAA
%pause
lfit =lambdafit;
Err=ErroR;
```

filename : Klarge.m

```
function ErroR = small(KAA)

global X Y1 Y2 lambdaexp lfit Err
KAA1=1.1857929e-4;
for i=1:1:length(X)
lambdafit(i)=exp(log(KAA1)-(1-log(Y1(i)+Y2(i)*KAA(1))...
        -(Y1(i)/(Y1(i)+Y2(i)*KAA(1))+Y2(i)*KAA(2)/(Y1(i)*KAA(2)+Y2(i))))...
        +2*(1-log(Y1(i)*KAA(2)+Y2(i))-Y1(i)*KAA(1)/(Y1(i)+Y2(i)*KAA(1)))...
        -Y2(i)/(Y1(i)*KAA(2)+Y2(i))));
sErroR(i) = ((lambdaexp(i)-lambdafit(i))/lambdaexp(i))^2;
end

ErroR=sum(sErroR)
%ErroR = sum(((lambdaexp-lambdafit)).^2)
KAA
%pause
lfit =lambdafit;
Err=ErroR;
```

B5. Matlab M-file for Solving Three Components Equilibrium

filename : Multieq.m

```
clear
%input Xna, Xcu, Xcd.

Xcu=.25
Xcd=.3

Xna=1-Xcu-Xcd
Co=.0424
Cna=Xna*Co;
Ccu=Xcu*Co;
Ccd=Xcd*Co;
I= 0.5*(Cna+Ccu*2+Ccd*2+Co)
f= -0.3910*(I^.5/(1+1.2*I^.5)+2/1.2*log(1+1.2*I^.5))
ACTCOELna= exp(1*f);
ACTCOELcu= exp(4*f);
ACTCOELcd= exp(4*f);

%pause

Acuna=3.06561;  Anacu=3.33537;  Kcuna=1/.000118579;
Anacd=2.44194;  Acdna=2.56662;  Kcdna=1/.016605;
Acucd=1.61908;  Acdcu=1.00458;  Kcdcu=0.00714118;


Yna=.12;          %first guest value
Ycu=.51;
Error=1;
Ycd=1-Yna-Ycu;
while Error>1e-7

Gsna=exp(1-log(Yna+Ycu*Anacu+Ycd*Anacd)...
        -Yna/(Yna+Ycu*Anacu+Ycd*Anacd)...
        -Ycu*Acuna/(Yna*Acuna+Ycu+Ycd*Acucd)...
        -Ycd*Acdna/(Yna*Acdna+Ycu*Acdcu+Ycd));

Gscu=exp(1-log(Yna*Acuna+Ycu+Ycd*Acucd)...
        -Yna*Anacu/(Yna+Ycu*Anacu+Ycd*Anacd)...
        -Ycu/(Yna*Acuna+Ycu+Ycd*Acucd)...
        -Ycd*Acdcu/(Yna*Acdna+Ycu*Acdcu+Ycd));

Gscd=exp(1-log(Yna*Acdna+Ycu*Acdcu+Ycd)...
        -Yna*Anacd/(Yna+Ycu*Anacu+Ycd*Anacd)...
        -Ycu*Acucd/(Yna*Acuna+Ycu+Ycd*Acucd)...
        -Ycd/(Yna*Acdna+Ycu*Acdcu+Ycd));
```

```
F1=Kcuna*Gsna^2*ACTCOELcu*Ccu/(ACTCOELna*Cna)^2/Gscu;
F2=Kcdna*Gsna^2*ACTCOELcd*Ccd/(ACTCOELna*Cna)^2/Gscd;

YnaNew=(-1.00+(1+4*(F1+F2))^0.50)/2.00/(F1+F2);
YcuNew=F1*YnaNew^2;
YcdNew=F2*YnaNew^2;
add=YnaNew+YcuNew+YcdNew;

Error=abs(YnaNew-Yna)+abs(YcuNew-Ycu)+abs(YcdNew-Ycd)

Yna=YnaNew;
Ycu=YcuNew;
Ycd=YcdNew;

end

fprintf(' Yna= %g\n',Yna)
fprintf(' Ycu= %g\n',Ycu)
fprintf(' Ycd= %g\n',Ycd)
```

VITA

Yeak-Chong Wong was born in Selangor, Malaysia on November 29,1970. He completed his high school studies at Chong Hwa Independent High School, Selangor, Malaysia in 1988. He attended the Overseas Chinese Pre-University Class, Taiwan in 1989 and entered National Taiwan University, Taipei, Taiwan during October of 1990, where, he received the Bachelor of Science in Chemical Engineering in June, 1994. In January of 1995, he entered the Master's program in Chemical Engineering at the University of Tennessee, Knoxville. He completed his Master's degree in December, 1996.