SORPTION OF METAL IONS FROM AQUEOUS SOLUTION BY POLYMER RESINS:DEVELOPMENT OF A GENERALIZED KINETIC MODEL

BY

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DECLARATION

I solemnly declare that this thesis is solely the record of my research work, and to the best of my knowledge has not been presented in any previous application for a higher degree. All literature consulted have duly been acknowledged in the references.

Akpan, U.G.
(July, 1995)

CERTIFICATION

This thesis entitled "**SORPTION OF METAL IONS FROM AQUEOUS SOLUTION BY POLYMER RESINS: DEVELOPMENT OF A GENERALIZED KINETIC MODEL**", by AKPAN, U. George meets the regulations governing the award of the degree of Master of Science (Chemical Engineering) of Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

With appreciations and thanks to GOD, this work is dedicated to:

- My heavenly Father
- My Brothers, Mr. Etim G. Akpan, Mr. Emmanuel G. Akpan, Mr. Boniface G. Akpan, Mr. Matthew G. Akpan;
- My Sisters, Mrs. Emah I. Iniedu, Miss. Comfort G. Akpan

and

- All Believers of the same precious Faith of all ages.

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QUOTATION

"Be patient therefore, brethren, unto the coming of the LORD. Behold, the husbandman waited for the precious fruit of the earth, and hath long patience for it, until he receive the early and latter rain."
(James 5:7)

"And so, after he had patiently endured, he obtained the promise."
(Hebrews 6:15)

THEREFORE

"After ye have done all, there is need of patience; that ye may obtain the fruit of thine labour and see the expected end of the LORD."

(Akpan, U. G.)
June 20, 1995.

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ABSTRACT

A generalised kinetic model for sorption of metal ions by some sets of polymer resins from aqueous solutions has been developed. For this to be effectively done, one resin type (amberlite IRA 400 CI^-, AD 54 OH^-, and amberlite IR 45 OH^-) was respectively chosen from each set having similar properties for the kinetic study.

All attempts to conduct the sorption of tungsten by amberlite IR 45 OH^- became impossible. The rate of sorption of molybdenum by amberlite IRA 400 CI^- was faster than the sorption of tungsten by amberlite 400 CI^- and sorption of tungsten by AD 54 OH^- resins. The activation energy of sorption was respectively found to be 11.60KJ, 21.90KJ and 32.50KJ.

AD 54 OH^- resin possess better mechanical property, and hence, more selective, (though it exhibited low exchange rate) in tungsten solution as it was found to be stable in same solution even at 70°C operation temperature. But amberlite 400 CI^- dissolved in both tungsten and molybdenum solutions at temperature slightly higher than 40°C.

A two active sites first order reversible kinetic model was proposed to test the sorption processes thus:

$$C = (C_0-C_e)*(eexp(-C_0/(C_0-C_e))K_1t + (l-6)exp(-C_0/(C_0-C_e))K_2t) + C_e$$

This model was found to fit the sorption of tungsten by both amberlite IRA 400 CI^- and IONAC AD 54 OH^-, and the sorption of molybdenum by amberlite IRA 400 CI^- to over 90 % confidence limits.

TABLE OF CONTENTS

		Page
Title Page		i
Declaration		ii
Certification		iii
Dedication		iv
Quotations		v
Acknowledgement		vi
Abstract		ix
Table of Contents		x
List of Illustrations		xiv
List of Tables		xviii
List of Symbols		xx
Chapter One		
1.0	INTRODUCTION	1
Chapter Two		
2.0	LITERATURE SURVEY	4
2.1	ION EXCHANGE	5
2.1.1	Ion Exchange Resins	6
2.1.2	Types of Ion Exchange Resins	7
2.1.3	Swelling of Ion Exchange Resins	9
2.1.4	Exchange Rate	11
2.2	CATALYSIS WITH ION EXCHANGE RESINS	12
2.2.1	Mechanism of Ion Exchange	14

2.2.2	Selection of Catalysts and Operating Conditions	1
2.3	ION EXCHANGE EQUILIBRIUM	1
2.4	QUANTITATIVE DETERMINATION OF TUNGSTEN AND MOLYBDENUM	1
2.4.1	Thiocyanate Method for Colorimetric Determination of Molybdenum	1
2.4.2	Thiocyanate Method for Colorimetric Determination of Tungsten	2
2.5	KINETICS STUDY	2
2.5.1	Resolving Kinetics Data	2
2.5.2	Temperature Dependence of Rate Constant	2
2.6	RESIN PRETREATMENT	2

Chapter Three

3.0	MATERIALS, INSTRUMENTATION AND EQUIPMENT	2
3.1	Equipment and Instrumentation	2
3.2	Materials - Reagents	2

Chapter Four

4.0	EXPERIMENTAL PROCEDURE	2
4.1	EXPERIMENTAL DETAILS FOR ANALYSIS OF TUNGSTEN	2
4.1.1	Standard Tungsten Solution	2

4.1.2	Stannous Chloride Solution (0.5%)	28
4.1.3	Titanous Chloride Solution	28
4.2	PROCEDURE FOR TUNGSTEN ANALYSIS	29
4.3	EXPERIMENTAL DETAILS FOR ANALYSIS OF MOLYBDENUM	29
4.3.1	Standard Molybdenum solution	29
4.3.2	Ammonium Ferrous Sulphate Solution (1%)	30
4.3.3	Stannous Chloride Solution (10%)	30
4.4	PROCEDURE FOR ANALYSIS OF MOLYBDENUM	30
4.5	SORPTION PROCESS	31
4.6	OPERATING CONDITIONS	32
4.6.1	Variation of Initial Concentration of Catalyst at Constant Temperature and Weight of Resin	32
4.6.2	Variation of Operating Temperature at Fixed Weight of Resin and Initial Concentration of Catalysts	33
4.6.3	Variation of Weight of Resins at Constant Temperature and Fixed Concentration of Catalyst	33

Chapter Five

Chapter Five

5.0	RESULTS AND DISCUSSION	34
5.1	KINETICS OF SORPTION	35
5.1.1	Effect of Concentration of Catalyst on Sorption Rate	36
5.1.2	Effect of Weight of Resin on Sorption Rate	37
5.1.3	Effect of Temperature on Sorption Rate	43
5.2	SORPTION RATE MODEL	60
5.3	COMPARISON BETWEEN THE RATE OF SORPTION OF TUNGSTEN AND MOLYBDENUM BY AMBERLITE IRA 400 Cl^- AND AD 54 OH^- ION EXCHANGE RESINS	75

Chapter Six

6.0	CONCLUSION AND RECOMMENDATION	78
6.1	CONCLUSION	78
6.2	RECOMMENDATION	82

References 84

Appendices 87

LIST OF ILLUSTRATIONS

Figure		Page
5-1a	A Plot Of The Ratio Of Concentration At Time, t To Initial Concentration Versus Time For The Sorption Of Tungsten by Amberlite IRA 400Cl⁻	38
5-1b	A Plot Of The Ratio Of Concentration At Time, t To Initial Concentration Versus Time For The Sorption Of Tungsten by IONAC AD 54 OH⁻	39
5-1c	Concentration-Time Curves for Sorption of Molybdenum by Amberlite IRA 400Cl⁻ at Various Initial Concentrations	40
5-2	Plot of log $[r_{sorp}]_0$ versus log$[W]_0$ for Sorption of Tungsten by Amberlite IRA 400 Cl⁻ and IONAC AD 54 OH⁻ Resins	41
5-3	A plot of log $[r_{sorp}]_0$ versus log$[Mo]_0$ for Sorption of Molybdenum by Amberlite 400 Cl⁻ Resin	42
5-4a	Concentration-Time Curves in a series where the amount of Amberlite IRA 400 Cl⁻ was Varied for Sorption of Tungsten	44
5-4b	Concentration-Time Curves in a series where the amount of IONAC 54 OH⁻ was Varied for Sorption of Tungsten	45

Figure		Page
5-4c	Concentration-Time Curves in a series where the amount of Amberlite IRA 400 Cl^- was Varied for Sorption of Molybdenum	46
5-5a	Concentration-Time Curves for Sorption of Tungsten by Amberlite IRA 400 Cl^- Resin at Various Temperatures	47
5-5b	Concentration-Time Curves for Sorption of Tungsten by IONAC AD 54 OH^- Ion exchange Resin at Various Temperatures	48
5-5c	Concentration-Time Curves for Sorption of Molybdenum by Amberlite IRA 400 Cl^- Resin at Various Temperatures	49
5-6	Plot of log $[r_{sorp}]_0$ against log [Wt] for Sorption of Tungsten by both Amberlite IRA 400 Cl^- and IONAC AD 54 OH^- Resins	50
5-7	Plot of log $[r_{sorp}]_0$ against log [Wt] for Sorption of Tungsten by both Amberlite IRA 400 Cl^- Resin	51
5-8a	A Plot of r_{sorp} against [W] for Sorption of Tungsten by Amberlite IRA 400 Cl^- Resins	53
5-8b	A Plot of r_{sorp} against [W] for Sorption of Tungsten by IONAC AD 54 OH^- Resin	54
5-8c	A Plot of r_{sorp} against [Mo] for Sorption of Molybdenum by Amberlite IRA 400 Cl^- Resins	55

Figure		Page
5-9a	A Plot of ln K_{sorp} against 1/T for Sorption of Tungsten by Amberlite IRA 400 Cl^- Resins	57
5-9b	A Plot of ln K_{sorp} against 1/T for Sorption of Tungsten by IONAC AD 54 OH^- Resins	58
5-9c	A Plot of ln K_{sorp} against 1/T for Sorption of Molybdenum by Amberlite IRA 400 Cl^- Resins	59
5-10a	A Plot Showing Comparison Between Experiments And Models For The Sorption Of Tungsten By Amberlite IRA 400 Cl^- Resin	61
5-10b	A Plot Showing Comparison Between Experiments And Models For The Sorption Of Tungsten By IONAC AD 54 OH^- Resin	62
5-10c	A Plot Showing Comparison Between Experiments And Models For The Sorption Of Molybdenum By Amberlite IRA 400 Cl^- Resin	63
5-11a	Plot of r_{sorp} against [W] for sorption	
11	of Tungsten by Amberlite IRA 400 Cl^- Resins	65
5-11b	Plot of r_{sorp} against [W] for sorption of Tungsten by IONAC AD 54 OH^- Resins	66
5-11c	Plot of r_{sorp} against [Mo] for sorption of Tungsten by Amberlite IRA 400 Cl^- Resins	67
5-12a	Experiments Compared With 2-Active Sites Reversible Model For The Sorption Of Tungsten By Amberlite IRA 400 Cl^- Resin	72

Figure		Page
5-12b	Experiments Compared With 2-Active Sites Reversible Model For The Sorption Of Tungsten By IONAC AD 54 OH^- Resin	73
5-12c	Experiments Compared With 2-Active Sites Reversible Model For The Sorption Of Molybdenum By Amberlite IRA 400 Cl^- Resin	74

LIST OF TABLES

Table		page
5-1	SORPTION RATE CONSTANT AT DIFFERENT TEMPERATURES	52
	(a) For sorption of tungsten by amberlite IRA 400 Cl^- ion-exchange resins.	52
	(b) For sorption of tungsten by AD 54 OH^- ion-exchange resin.	52
	(c) For sorption of molybdenum by amberlite IRA 400 Cl^- ion-exchange resin.	52
5-2	ACTIVATION ENERGY FOR SORPTION PROCESSES.	56
5-3	SUMMARY OF THE VALUES OF K_1, K_2 and θ.	68
A-1	COMPARISON BETWEEN ONE AND TWO ACTIVE SITE(S) IRREVERSIBLE FIRST ORDER MODELS WITH EXPERIMENTAL DATA.	87
	(a) For sorption of tungsten by amberlite IRA 400 Cl^- ion exchange resin.	87
	(b) For sorption of tungsten by AD 54 OH^- ion-exchange resin.	87
	(c) For sorption of molybdenum by amberlite IRA 400 Cl^- ion-exchange resin.	88
A-2	COMPARISON OF TWO ACTIVE SITES REVERSIBLE MODEL WITH THE EXPERIMENTAL DATA.	88
	(a) Sorption of tungsten by amberlite IRA 400 Cl^- Ion-exchange Resin.	88

Table		page
	(b) Sorption of tungsten by AD 54 OH^- Ion-exchange Resin.	89
	(c) Sorption of molybdenum by amberlite IRA 400 Cl^-exchange Resin.	89
A-3	COMPARISON OF TWO ACTIVE SITES REVERSIBLE MODEL WITH THE EXPERIMENTAL DATA FOR EACH SERIES OF EXPERIMENT.	90
	(a) Sorption of tungsten by amberlite IRA 400 Cl^- Ion exchange Resin.	90
	(b) Sorption of tungsten by AD 54 OH^- Ion exchange Resin.	91
	(c) Sorption of molybdenum by amberlite IRA 400 Cl^- exchange Resin.	93
A-4	PROPERTIES OF ION EXCHANGE RESINS	96

LIST OF SYMBOLS

Symbol	Meaning
a_A, a_B	activities of A and B in liquid-phase (g mol/ml).
a_{TA}, a_{TB}	activities of A and B in solid-phase (g mol/ml).
n, z	valences of ion A & B
[A] & [B]	concentrations of A & B measured in solution (g ion/ml)
(A) & (B)	concentrations of A & B measured in solid (g ion/ml)
C	composition or concentration (mol/l)
C_e, $[]_e$	equilibrium concentration of sorbent (mol/l)
C_0	initial concentration of sorbent (mol/l)
dC_A	change in concentration (mol/l)
dt	change in time (min)
E_a	activation energy (KJ)
E_{sorp}	activation energy of sorption (KJ)
f_A, f_B	ions' activity coefficients in solid phase (dimensionless)

K_1	sorption rate constant corresponding to the first active sites (min^{-1})
K_2	sorption rate constant corresponding to the second active sites (min^{-1})
$K_{0,R}(T)$	temperature depended rate constant (min^{-1})
K_{sorp}	sorption rate constant (min^{-1})
K_x	apparent equilibrium constant (min^{-1})
$[M], [M]_0$	molybdenum concentration in (mol/l) at any time t, & t=0
P	pressure (N/m^2)
r	rate (mol/l.min)
r_{sorp}, r_{sorpo}	sorption rate in (mol/l.min) at any time t, & t=0
R	gas constant ($J/^0K.mol$)
$[Sorb],[Sorb]_0$	sorbent concentrations in (mol/l) at any time t, & t=o
t	time (min)
T	temperature (^0C or ^0K)
$[W], [W]_0$	tungsten concentration in(mol/l) at anytime, t & t=0
θ	fraction of sorbent uptake by the first active sites

	(dimensionless)
1-θ	fraction of sorbent uptake by the second active sites (dimensionless)
γ_A & γ_B	ions' activities coefficients in solid phase

CHAPTER ONE

1.0 INTRODUCTION

In the past few years, rapid advances have been made in the area of transition metals homogeneous catalysis. It has been established that many selective liquid-phase oxidations of organic compounds can be accomplished through the intermediacy of compounds of the less common metallic elements exemplified by W, Mo, V, Os, Ti, Zr, U, Ru, Rh, Ta, and Se [Allan and Neogi, 1969, 1970]. These catalysts are generally more selective and function under milder conditions than their heterogenous counterparts. However, when such materials are used as soluble catalysts in oxidation reactions, the ultimate products are usually not free from contamination. Attempts made to free the products from impurities led to the development of an insoluble macromolecule support (polymeric resin) containing the catalyst element which has gained a combination of advantages. Among several of these advantages are, high selectivity, easy separation, easy recovery and reusability of the catalyst, and obtaining catalyst-free product. The support can also improve dissipation of reaction heat, retard the sintering of metal crystallites with resultant loss of active surface and increase poison resistance, thus promoting a longer working life for the catalyst.

The numerous advantages of the macromolecular catalyst over the homogeneous counterpart have necessitated the

investigation of the means by which the catalyst element is attached to the resin. The catalyst is anchored to the resin by ion-exchange process.

Ion exchange is a reversible process of interchanging of ions between solid and liquid phases in which there is no permanent change in the structure of the solid. If adsorption processes are strictly considered as confined to changes occurring at an interface or surface of solids and absorption as those processes involving solids engulfing substances throughout their entire structure, then ion exchange phenomena may fall into both categories. Therefore, sorption - a word that avoid the prefixes ad and ab is better employed, and in this work "sorption" will be used. In addition, sorption is a process that is capable of taking up and storing one or more solute species originally contained in the fluid.

A thorough review of literature has revealed that among the metallic elements aforementioned for the liquid-phase oxidation of organic compounds, tungsten (W) and molybdenum (Mo) are especially more selective and act more effectively than others [Allan and Neogi, 1969]. Therefore, in this work, sorption of tungsten and molybdenum by polymer supports (ion exchange resins) was considered. The metals can be highly dispersed throughout the pore system of support. Consequently, a large active metal surface is produced relative to the weight of metal used. The supported catalysts can then be used to catalyse reaction.

Recently in this field, Iyuke (1994) prepared an immobilized molybdenum catalyst by anchoring molybdenum ions on the active sites of a polymer resin (Amberlite IRA 400 Cl^-). He proposed a kinetic model for the sorption of molybdenum.

This project is therefore aimed at generalising such a kinetic model for sorption of tungsten and molybdenum catalysts on a wider range of polymer resins.

CHAPTER TWO

2.0 LITERATURE SURVEY

Transition metals have found applications in the area of homogeneous catalysis [Collmam, 1968]. For example, new soluble transition metal complexes have been found which catalyze the reduction of unsaturated organic [O'connor and Wilkinson, 1968] and inorganic molecules[Bercaw et al,1968], the hydroformylation of olefins [Capka et al, 1971], the polymerization of olefins [Natta et al, 1964] and oxidation and epoxidation of unsaturated hydrocarbons [Allan and Neogi, 1970]. However, when such materials are used as soluble catalysts in the redox reaction, the final products are not free from contamination [Allan and Neogi, 1969]. It was for this reason that Allan and Neogi (1969) developed an insoluble macromolecule (polymeric resin) containing the catalyst element for oxidation of maleic acid. First, they [Allan and Neogi, 1969] anchored the catalyst element to the resin, thereafter, the macromolecular catalyst was employed in the oxidation process. This type of catalyst has gained a combination of advantages of both homogeneous and heterogeneous catalysts. Like in homogeneous catalysis, it enhances activity and selectivity. On the other hand, like in heterogeneous catalysis, it is easy to separate the costly catalyst and reuse it in further reactions.

The anchoring of the catalyst to the polymer resin is by

ion exchange.

2.1 ION EXCHANGE

Ion exchange may be defined as the reversible interchange of ions between a solid and a liquid phase in which there is no permanent change in the structure of the solid. The solid is the ion exchange material. Ion exchange has important applications in water conditioning, such as softening and deionization. It provides a method of separation useful in many chemical processes and analyses.

Ion exchange has been found to occur in a wide variety of substances such as silicates, phosphates, fluorides, humus, cellulose, wool, proteins, alumina, resins, lignin, living cells, glass, barium sulphate, and silver chloride.

Though ion exchange had been in existence dating back to the middle of the nineteenth century, researchers were, not until about four decades ago indifferent to the process. This was so because suitable ion exchangers that could be utilized readily for the many problems that could be approached by means of ion exchange techniques were by then not available. The discovery, or preparation of polymeric ion exchange resins stimulated much interest in ion exchange, with numerous applications. Use of resins in ulcer therapy, in edema therapy, as artificial kidneys, as bacterial adsorbents, and as catalysts as well as the conventional uses testify to the widespread applications for these resins.

Ion exchange has been defined as a reversible interchange of ions between a solid and a liquid phase. The ease with which the surface ions may be replaced by another ions depends largely on the following:

(1) the nature of the forces binding the ions to the crystal,
(2) the concentration of the exchanging ion
(3) the charge of the exchanging ion
(4) sizes of the two ions
(5) the accessibility of lattice ions, and
(6) solubility effects.

Kunin (1958) reported that the various cation and anion exchange resins may be considered as insoluble high molecular weight polymeric electrolytes. Therefore, though lacking in crystallinity, the mechanism of ion exchange in ion-exchange resins is quite similar to the exchange of crystal lattice ion.

2.1.1 Ion Exchange Resins

Ion exchange resins are insoluble high molecular weight polymeric electrolytes, with ions of one charge anchored to an insoluble but permeable matrix, the ions of opposite charge being small and mobile, and therefore exchangeable with other ions. They may be cationic, anionic, or amphoteric. Before considering the types of resins, it is necessary to consider some basic requirements that a resin must possess so as to be described as a good type.

To be generally useful, the ion exchange resin must meet

the following basic requirements:

(1) It is required that the ion exchanger have a high total capacity, that is, a high degree of ionic substitution or low equivalent weight.

(2) The resin should be so structured chemically as to exhibit good equilibrium characteristics when handling the expected solute. It should be designed for operation in the proper pH range and with a degree of selectivity sufficient for the purpose and yet be capable of regeneration.

(3) Extremely low solubility is required. When the ions on the resins are more soluble in the solute, hydrolysis will result and may predominate the exchange of the ions, hence the aim of the ion-exchange is defeated.

(4) A good chemical stability is required.

(5) Good physical stability: The resin should be physically stable. Dependent on degree of cross linkage and exchange capacity, the ion-exchange resins absorbs water and assumes physical structures ranging from soft and mushy to hard and brittle.

(6) Finally, it is expected that the ion exchanger be available at affordable cost.

2.1.2 Types of Ion-exchange Resins

There are basically two types of ion exchange resins, namely; cationic and anionic resins. The third is a combination of these two and it is known as amphoteric ion

exchanger.

(a) Cation exchange resin

Cation exchange resins are high polymeric and tightly cross-linked structures containing fixed polar anionic groups whose negative charges are balanced by cations. They may be considered to be highly insoluble electrolytes consisting of an large non-diffusible anion and a simple diffusible cation.

(b) Anion exchange resin

The exchange of anions in ion exchange resins has been limited primarily to the amine-type resins. However sulphonium anion exchange resins have been prepared [Kunin, 1958].

The disappearance of anions has been explained either by the acid adsorption mechanism

$$RNH_2 + HX \rightleftharpoons RNH_3X \qquad (2.1)$$

or by the exchange mechanism,

$$RNH_3^+ + OH^- + X^- \rightleftharpoons RNH_3X + OH^-$$

$$OH^- + H^+ \rightleftharpoons H_2O \qquad (2.2)$$

Jenny (1946), Wiklander (1946), Kunin and Myers (1946) suggest that the polyamine-type anion exchange resins are polymeric electrolytes, the cations of which are highly cross-linked non-diffusible ions whose charges are balanced by a diffusible anion. Amine-type exchangers are weakly basic, but analogy between "free base" of these insoluble amines and soluble amines can be drawn. Since soluble amines behave in aqueous solutions according to the equilibrium

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^- \qquad (2.3)$$

we may reason, quite logically, that the polymeric amines behave quite similarly,

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^- \qquad (2.4)$$

When acid is added to such a system, the hydroxyl ions may be replaced by the anion of the acid, the hydroxyl ion combining with the hydronium ion of the acid. As the hydroxyl ions are neutralized, the equilibrium of the foregoing reaction is shifted to the right.

The magnitude of the ionic strength effect increases as the basicity of the resin decreases. It must be recognized that if the ionization constant is so small, the hydrolysis of its corresponding salt with the exchanger will be so great as to permit very little exchange.

The importance of hydrolysis of the exchange salt is quite apparent on comparing the adsorption of silicic and boric acid on a weak-and strong-base anion exchanger. Whereas the hydrolysis of the salts of these acids and weakly basic anion exchanger is so great as to cut the adsorption of the silicate and borate ions to a minimum, a strongly basic exchanger exhibits a marked degree of exchange [Kunin and Myers, 1947].

2.1.3 Swelling of Ion-exchange Resins

For a resin to exhibit appreciable ion exchange capacity, it must need swell in the solvent, although some are sufficiently porous to permit ready access of solvents and ions without undergoing a great deal of swelling. The extent to

which a resin swells depend on the chemical nature of the polymer, the degree of cross-linking, the ionizable groups in the resin and the nature of ions thereby released by them, the concentration of the surrounding solution, and the temperature.

When immersed in a solvent, any cross-linked polymer resin swells to some extent. The degree of cross-linking of the resin matrix has an obvious effect on the physical and mechanical properties of a resin. If the degree of cross-linking is low (ie the devinylbenzene content of a polystyrene - based resin is very low), it swells considerably in water and can be smeared or possibly even dissolved). In the case of a higher divinylbenzene content, the ion-exchange resin is more solid and has a better mechanical resistance. Furthermore, a strongly cross-linked structure means higher selectivity, lower pore size, lower swelling capacity, low rate of ion exchange and lower capacity referred to the dry resin.

The swelling is encouraged by the entropy of mixing. The heat of mixing may either encourage or discourage swelling of the resin, depending on whether this heat is negative or positive.

It must be noted that cases exist in which a resin must swell in order to accommodate very large ions. Again, an important consideration in designing equipment is the extent of resin swelling.

Generally, resins swell more in polar solvents than in non-polar solvents, and porous resins swell more than more

highly cross-linked analogues.

2.1.4 Exchange Rate

The speed with which ion-exchange takes place determines the portion of the equilibrium capacity which may be utilized in a practical dynamic situation. Inorganic exchangers are slow in kinetics as compared to the resinous types.

Overall exchange rates may be influenced by a change in solvent nature and content, the particle size, temperature, and the functional group (kind and concentration). Exchange rates are most rapid in water systems and becoming increasingly slow with less polar solvents. This holds true because of the closely related facts that the solutes are more highly ionized in the more polar solvents and that the ion-exchange resins are, simultaneously, more highly swollen. Similarly, exchange rates are more rapid in lower cross-linked resins of the same dry-basis capacity because of the higher moisture content. The ion-exchange process involves diffusion throughout the film of solution in close contact with the resins, and also diffusion within the particle of resin itself. Film diffusion becomes rate-controlling at low concentrations, particles diffuse at high concentrations. Elevated temperatures increase exchange rates, but no quantitative relationship is known to have been derived.

2.2 CATALYSIS WITH ION EXCHANGE RESINS

The catalytic properties of ion exchange materials have been known and have been employed commercially for many years [Kunin, 1958]. Rice (1918) and Puri et al (1927, 1953) on the study of catalytic properties of soil and clay found the acid or hydrogen forms to possess the ability to catalyze the inversion of sucrose and hydrolysis of ethyl acetate. Other early workers found that various naturally occurring zeolites were effective as catalysts for certain oxidative reactions. To a large extent these zeolites with high porosity and thermal stability served merely as carriers for certain metallic catalysts. Jaeger (1929,1930) prepared a zeolite catalyst containing vanadium which was effective for the oxidation of sulphur dioxide to sulphur trioxide.

Jaeger's zeolite catalysts containing non-exchangeable nickel, copper or manganese were effective for several reduction reactions including ammonia synthesis, reduction of nitrobenzene to aniline, and puridine to piperidine, and the hydrogenation of naphthalene, acetylene and linseed oil.

In the field of catalysis, ion exchange materials have found application in petroleum-refining industry in its cracking and refining processes.

Many other works have been done in the field of catalysis using solid ion exchangers. Allan and Neogi (1969,1970) used ion exchange resins for the catalytic epoxidation of maleic acid. Recently, work has been carried out in this field by

Iyuke (1994). Molybdenum was anchored to Amberlite IRA-400 chloride form ion exchange resin, and was ultimately used to catalyze the epoxidation reaction of maleic acid. It was shown that the percentage activity of the immobilized catalyst(molybdenum anchored to resin) was generally higher compared to its homogeneous counterpart. Furthermore, a mathematical model was proposed for the sorption process. It is important to note that there are advantages to the use of solid ion exchangers (both inorganic substances and resins) over homogeneous catalysis [Helfferich 1954, 1954, 1952]. Several of the more important advantages are as follows:

(1) By a simple filtration step, catalyst-free products can be obtained, and the catalyst can be recovered frequently.

(2) Continuous reactions can be obtained by passage of the reactants through beds of ion exchange resin catalyst.

(3) High selectivity effects are possible

(4) Side reactions can be kept at minimum and hence the purity of the product is superior.

(5) Special corrosion - resistance equipment is not necessary as with some soluble catalysts.

The advantages of the catalyst-free products is evidently seen, for costly and difficult neutralization, precipitation, distillation, and extraction steps are avoided. In addition, although most homogeneous catalysts are not expensive, the

direct catalyst recovery is significant from economic standpoint. However, resin stability plays an important role in the economics of these processes, since processes resulting in resin destruction or irreversible fouling have been observed. Aldol condensation, for example, frequently causes fouling of the anion exchange catalyst with resinous materials which can be removed only with great difficulty [Kunin, 1958].

As aforementioned in section 2.1, the ease with which the surface ions may be replaced depends on a number of factors, among which is the accessibility of lattice ion. The resinous ion exchangers are superior to the inorganic ion exchangers because of the higher mobility of the reactants and products in the pores of the resinous catalyst.

2.2.1 Mechanism of Ion-exchange

It had been stated in Chapter 1 that ion exchange is a phenomenon which integrates both the adsorption and absorption processes. It is of a great interest therefore to note that the pores of an ion exchanger which is in contact with a solution contains solvent, solutes, and the counter ions which are mobile and solvated. The counter ions in the pores of the resin display catalytic activity which is in principle not different from that by homogeneous catalysis by a dissolved electrolyte. It can therefore be said that the mechanisms of catalysis by dissolved electrolyte and that of the heterogeneous catalysis by a resin are essentially the same.

These observations have been confirmed by experimental data which show that the actual chemical reaction is the same in both cases. Therefore, catalysis of liquid phase reactions by ion-exchange resins is thus not a true case of heterogeneous catalysis, but may be described more adequately as homogeneous catalysis in the pore liquid [Helfferich, 1954]. However, since the reaction must need take place in the pore of the resins, there are some significant differences between homogeneous catalysis and that by resins. Since the reaction occurs in the pore liquid only, the reactants must diffuse into the reaction zone and the product must diffuse out, hence resistances to diffusion may build up in form of film resistance, and adversely affect the reaction. Secondly, the matrix and the fixed ionic groups may affect the reaction.

2.2.2 Selection of Catalysts and Operating Conditions

With a given amount of catalyst, the highest possible reaction rate is desirable in any application. This can be achieved by a proper choice of the catalyst and the operating conditions.

The first consideration in seeking a catalyst for a desired reaction is to recognize the type of reaction under investigation. Reactions such as isomerization, polymerization, hydration, etc, have been recognized as being acid- or base-catalyzed and the search should be made therefore for this type of catalyst. The implication of this is that a

suitable resin type and solvent should be selected in such a way that the resin is chemically stable and swells substantially in the solvent, and that equilibrium sorption of the reactants is high. The requirements have earlier been enumerated in Section 2.1.1.

Increase in temperature enhances both the rates of chemical reaction and diffusion and thus gives a higher overall rate. It must be noted that the operating temperature is usually limited by the thermal stabilities of the resin or the compounds involved.

2.3 ION EXCHANGE EQUILIBRIUM

Ion exchange processes may be represented by chemical equation. In general, when A ions of n valence and B ions of Z valence are exchanged on a cation exchanger in contact with an electrolytic solution, the equation is as follows:

$$zR\text{-}A + nB^{z'} \rightleftharpoons nR\text{-}B + zA^{+n} \qquad (2.5)$$

In the equation R is the equivalent amount of the ion exchanger anion. Applying the mass action law to the equilibrium set up we have:

$$K = \frac{a_{rB}^{n} \cdot a_{A}^{z}}{a_{rA}^{z} \cdot a_{B}^{n}} \qquad (2.6)$$

where a_A and a_B are the activities of A and B ions measured in

the liquid phase, and a_{fA} and a_{fB} are the mean activities measured in the solid phase. K is the thermodynamic equilibrium constant, which depends solely on the temperature and not on the change of activities. The activities of ions in the solid phase are however not easy to define.

In equation (2.6) the products of analytical concentrations and activity coefficients can be inserted instead of activities:

$$K=\frac{(B)^n.\gamma_B^n}{(A)^z.\gamma_A^z}X\frac{[A]^z.f_A^z}{[B]^n.f_B^n} \qquad (2.7)$$

(A) and (B) are the concentrations measured in the solid phase and [A] and [B] are those in the solution in units of g ion/ml or in mg equiv/ml. γ_A and γ_B are the activity coefficients of the ions in the solid phase, f_A and f_B those of the ions in the solution. Rearranging equation (2.7), we have

$$K.\frac{\gamma_A^z f_B^n}{\gamma_B^n f_A^z}=\frac{[A]^z(B)^n}{[B]^n(A)^z} \qquad (2.8)$$

If a so-called apparent equilibrium constant is inserted instead of the left-hand side, the following simple expression is obtained:

$$K_x=\frac{[A]^z.(B)^n}{[B]^n.(A)^z} \qquad (2.9)$$

This expression contains quantities which can be measured by analytical methods. The amounts of ions absorbed by the resin can be determined directly after burning the resin to ashes or indirectly from the known concentration of the solution. According to these measurements the apparent equilibrium constant is not a real constant and depends on the properties of the ion exchanger, on the composition of the electrolyte, on the concentration of the solution, etc. If a series of experiments is made with an ion exchanger and solution containing A and B ions in various concentration ratios, and the values of $(A)^z/(B)^n$ plotted against the values of $[A]^z/[B]^n$, a straight line should be obtained if K_x is constant. Inczedy (1966) showed that the slope of such curves is different, depending on the nature of the ions, that is K_x values are different for different ions.

2.4 QUANTITATIVE DETERMINATION OF TUNGSTEN AND MOLYBDENUM

There are many methods for quantitative determination of molybdenum and tungsten, but most of these methods are less or not reliable example - gravimetric and titrimetric methods. Colorimetric methods are more reliable than both the gravimetric and titrimetric methods, and consequently more advantageous over both. Hence, in analysing molybdenum and tungsten in this work, colorimetric method will be employed.

COLORIMETRIC METHODS

The colorimetric methods have the advantages of simplicity, rapidity, and sensitivity over gravimetric and titrimetric methods. When accuracy is required colorimetric method is usually restricted to determinations involving low percentages, say below about 2%, but where extreme accuracy is not required, determinations for larger levels, up to about 10% and occasionally, even higher can be made [Elwell and Wood, 1971].

The two colorimetric methods of outstanding importance for the determination of molybdenum and tungsten are based on the use of thiocyanate and dithiol.

Dithiol is less selective than thiocyanate, but it is more sensitive and can often be used to advantage when small amounts of both molybdenum and tungsten are to be determined. Therefore, the thiocyanate method is preferred in this work.

2.4.1 Thiocyanate Method for Colorimetric Determination of Molybdenum

Molybdenum forms an orange-red complex with thiocyanate ions in mineral acid solution in the presence of a reducing agent [Sandell, 1959]. Stannous chloride is the most widely used reducing agent in the thiocyante method, but other reagents such as potassium iodide [Hope, 1957] and copper(II) chloride [Crouthamel and Johnson, 1954] have been used. The method involving the use of copper(II) chloride, however, has certain disadvantages. For example, iron interferes seriously,

and the volume of sample is restricted to only a few millilitres.

Molybdenum(VI) in acid solution when treated with stannous chloride (best in the presence of a little ferrous ion for maximum development of colour) is converted largely into molybdenum (v).

When molybdenum is determined directly in aqueous solution, the colour intensity depends on several other factors, including acidity, thiocyanate concentration, and time for development of colour. But to increase the sensitivity of the method and improve the stability of the colour, the complex can be extracted into an organic solvent; extractants commonly used include isoamyl alcohol, isopropyl ether and butyl acetate. Alternatively, the colour can be intensified and stabilized by using a water-miscible solvent, such as acetone [Grimaldi and Wells, 1943] or butyl digol (butyl carbitol) [Kapron and Hehman, 1945]. Perchloric acid is also used as a stabilizer [Pigott, 1953].

2.4.2 Thiocyanate Method for Colorimetric Determination of Tungsten.

In hydrochloric acid or a sulphuric/hydrochloric acid solution, tungsten (vi) forms a yellow complex with thiocyanate in the presence of a reducing agent such as stannous or titanous chloride; the complex contains tungsten (v), and has maximum absorption at about 400nm [Sandell, 1959, Clark, 1927]. The complex can be developed and measured in aqueous solution,

or it can be extracted into an immiscible solvent; isopropyl ether, diethyl ether, a mixture of isoamyl alcohol and chloroform (1+1), and a mixture of n-butyl alcohol and chloroform (2+3) have been used [Elwell and Wood, 1971].

In an aqueous system, the colour is best developed in a solution which is at least 8M with respect to hydrochloric acid, the total acidity 10M, and the concentration of thiocyanate 0.2M.

Some metals like vanadium interfere in aqueous solution and the interference effect can be removed by the use of a compensation solution for moderate amounts of vanadium, but large amounts should be separated. Copper, which if present in moderate amounts can be precipitated as cuprous thiocyanate, chromium, nickel, and cobalt are other interferences in aqueous solution. Molybdenum also gives a colour with thiocyanate, but the colour fades on standing; after 20 minutes the colour due to molybdenum is about one-hundredth of that due to an equal weight of tungsten. Interference from molybdenum is greater if solvent extraction is made.

It is advantageous to determine tungsten in an aqueous solution if a large amount of titanium or niobium is present, because of interference by these metals in the organic medium.

2.5 KINETIC STUDY

The increasing application of resinous materials in sorption processes has prompted the study of kinetics of such

processes. The kinetic study provides information about rate of reaction and factors influencing the rate; which are the needed parameters in the design of a reactor and specifying of operating conditions of the reactor.

Generally, the rate of any chemical reaction is dependent on composition (C) of reactants, reaction temperature (T), and pressure (P). Hence, the rate can be expressed as a function of these parameters thus:

$$r = F(C,T,P) \qquad (2.10)$$

Nevertheless, these parameters - pressure, temperature, and composition are interdependent in that the pressure is determined given the temperature and composition of the phase. Thus equation (2.10), without loss of generality could be written as

$$r = F(C,T) \qquad (2.11)$$

Though this is assumed to be much more valid at equilibrium, it is also assumed to be valid for non-equilibrium system which are not changing too rapidly.

The course of a reaction is normally measured by the change in concentration of a reactant or product. Particularly in gaseous reactions, volume changes may also occur. Then, concentration changes arise from a change in volume as well as from reaction.

Considering a reaction whose volume or density is constant, equation describing the rate is given as:

$$r_A = \frac{dC_A}{dt} \qquad (2.11)$$

2.5.1 Resolving Kinetics Data

The most common experimental procedure for establishing rate equations is to measure the composition of the reaction mixture at various times during the course of the reaction. With these information of composition and time at hand, two methods are basically available for analyzing kinetics data; viz: the integral and differential methods.

The integral method is used for fitting simple reactions (reversible or irreversible) corresponding to elementary reactions. The most suitable analysing method for unknown or complex reaction mechanism is the differential method.

2.5.2 Temperature Dependence of Rate Constant

The rate constant, K of any reaction scheme is a temperature dependent-term. Obviously, deduction of rate law alone without due considerations to temperature, pressure, etc. is not enough for a complete characterization of a chemical reaction.

For many reactions, and particularly elementary reactions, the dependency of K on temperature follows the Arrhenius equation.

$$K_{(T)} = K_0 \exp(-E_a/RT) \qquad (2.12)$$

To evaluate K_0 and E_a, take natural Logarithms of both sides of equation (2.12), hence

$$lnK_{(T)} = lnK_o - \frac{E_a}{RT} \qquad (2.13)$$

A plot of $InK_{(T)}$ against 1/T gives a straight line and hence K_0 and E_a could be evaluated. The intercept on $InK_{(T)}$-axis = InK_0 while the slope of the plot = - E_a/R.

2.6 RESIN PRETREATMENT

The importance of pretreatment of ion exchange resins before examination or characterization or use can not be overruled. It is by pretreatment that the resin sample is put in its proper ionic state. This is especially necessary if the resin sample has been previously used for some other applications.

In order to obtain a complete evaluation, the resin sample is placed in 2-inch diameter column similar to that employed in any ion exchange columnar operation and backwashed at 100 per cent bed expansion until a clear backwash effluent is obtained. The resin bed is then permitted to settle.

In the case of sulphonic acid and quaternary ammonium anion exchange resins, the bed is treated with five-to-ten-bed volumes of a 10% NaCl solution and then rinsed with deionized water. Weak-base resins are regenerated with three-to-five-bed volumes of 1M NaOH and carboxylics with three-to-five-bed

volumes of 1M HCl and then rinsed with deionized water. These treatments convert resins to the forms that are most convenient for subsequent examination. The sample is then drained on a Buchner funnel with very mild suction applied until the free or excess water is removed. The resin is then transferred into a jar and kept for further examination.

CHAPTER THREE

3.0 MATERIALS, INSTRUMENTATION AND EQUIPMENT

3.1 EQUIPMENT AND INSTRUMENTATION

1. A jacketed experimental micro batch reactor (50ml)
2. Oven, the Heracus Model
3. Cecil Instruments Spectrophotometer
4. Gallenhamp magnetic Stirrer regulator hot plate/bar
5. Oil-/Water-bath thermostat
6. Weighing balance, the Sauter model
7. Stop watch
8. Condensers
9. Thermometer
10. Separation Funnels (250ml)
11. Measuring cylinders, burettes, pipettes, wash glass, beakers, conical and volumetric flasks.

3.2 MATERIALS - REAGENTS

1. Tungstic Oxide BDH Chemicals Ltd.
2. Sodium hydroxide solution (10%) BDH Chemicals Ltd.
3. Titanous Chloride
4. Stannous chloride, ($SnCl_2.2H_2O$) Brocades-Stheeman & Pharmacia Chemicals Ltd.
5. Ammonium thiocyanate (NH_4SCN) (25%) BDH Chemical Ltd.
6. Potassium thiocyanate (KSCN) (10%), BDH Chemical.
7. Ammonium Ferrous Sulphate Solution (1%) BDH Chemical.

8. Ammonium molybdate, BDH Chemical Ltd.

9. Hydrochloric acid (concentrated), BDH Chemical Ltd.

10. Isopropyl ether, BDH Chemicals Ltd.

11. Amberlite IRA 400 (chloride form) ion exchange resin BDH Chemical Ltd.

12. IONAC AD 54 (OH^- form) ion exchange resin.

CHAPTER FOUR

EXPERIMENTAL PROCEDURE

4.1 EXPERIMENTAL DETAILS FOR ANALYSIS OF TUNGSTEN

4.1.1 Standard Tungsten Solution

This solution was prepared by dissolving 2.522g of tungstic oxide (heated at 750 ^{0}C) in 25ml of sodium hydroxide (10%), and then cooled. The resultant solution was transferred into a 1-litre calibrated volumetric flask and diluted to the mark.

1 ml of the solution = 2mg of tungsten

4.1.2 Stannous Chloride Solution (0.5%)

Freshly prepared solution was obtained by transferring 2.5g stannous chloride into a breaker (600ml), and 250ml of concentrated hydrochloric acid added and warmed until a clear solution was obtained. The solution was then cooled, diluted to 500ml and stored in a 500ml volumetric flask.

4.1.3 Titanous Chloride Solution

1g of titanium metal was dissolved in 25ml of concentrated hydrochloric acid. The solution was assisted by warming it gently, and then cooled, and diluted to 100ml. This solution was also freshly prepared.

4.2 *PROCEDURE FOR TUNGSTEN ANALYSIS*

0.5ml of the standard tungsten solution (1ml = 2mg tungsten) was placed in a 25ml volumetric flask. 20ml of the stannous chloride solution was added, then 1.5ml of ammonium thiocyanate solution (25%) and 0.5ml of the titanous chloride solution were subsequently added. This solution was diluted to the mark and was shaken for about 20 seconds, and allowed to stand for 5 minutes. A blank was also prepared by placing 20ml of stannous chloride in a 25ml volumetric flask and diluting to the mark with distilled water. The absorbance was measured at the wave length of 400nm.

The standard tungsten solution was diluted to several dilution ratios: 25ml W (of standard tungsten solution)/5ml H_2O, 20ml W/10ml H_2O, 15ml W/15ml H_2O, 12ml W/18ml H_2O, 10ml W/20ml H_2O, 6ml W/18ml H_2O and 3ml W/27ml H_2O. The procedure as described above was repeated for each, hence the calibration curve plotted.

4.3 EXPERIMENTAL DETAILS FOR ANALYSIS OF MOLYBDENUM

4.3.1 Standard Molybdenum Solution

This solution was prepared by dissolving 0.184g of analytical reagent ammonium molybdate in 1 litre of distilled water in a volumetric flask.

1ml of this solution = 1×10^{-4}g of molybdenum.

4.3.2 Ammonium Ferrous Sulphate Solution (1%)

1g of ammonium ferrous sulphate was dissolved in 100ml of a very dilute sulphuric acid.

4.3.3 Stannous Chloride Solution (10%)

10g of stannous chloride was dissolved in 100ml of hydrochloric acid (10%).

4.4 PROCEDURE FOR ANALYSIS OF MOLYBDENUM

The standard molybdenum solution was diluted to various ratios (1:1, 2:3, 3:7, 1:4 & 1:9), and 0.5ml of each dilution was transferred to individual separating funnels. To each of the funnels was added 2.0ml of concentrated hydrochloric acid, 1.0ml of the ammonium ferrous sulphate solution, and 3.0ml of potassium thiocyanate (10%). When this was gently shaken for about 10 seconds, 3.0ml of the stannous chloride solution was introduced, and to bring to a total volume of 25ml in each separating funnel, water was added and mixed. Finally, 5.0ml of iso-propyl ether was introduced into each of the funnels and was individually shaken for 30 seconds, and each funnel was allowed to stand until the extraction was completed. When the two phases were clearly separated, the aqueous lower layer was carefully run off. The stopper was then removed and the organic extract was carefully transferred into a curvet for absorbance measurement against an iso-propyl ether blank at 465nm. The method for the determination of molybdenum used here

was a modification of that described by Vogel (1961).

4.5 SORPTION PROCESS

A desired volume of each of the standard tungsten solution and standard molybdenum solution was diluted with water.

30ml of the diluted tungsten or molybdenum solution was introduced into the experimental batch reactor and was allowed to stand until the temperature was equilibrated. Then 0.4g of the ion exchange resin was added for the sorption of tungsten by IONAC AD 54 OH^- and for the sorption of molybdenum by amberlite IRA 400 Cl^-, while 0.2g was added for the sorption of tungsten by amberlite IRA 400 Cl^- resin.

A prototype experiment was conducted over a period of one hour at constant temperature using a thermostated water bath at 40 ^0C. The mixture at this temperature was constantly stirred using a magnetic stirrer hot plate under reflux. The result of this experiment showed that the sorption process practically tends to equilibrium in 30 minutes process time. Hence, all other subsequent experiments were carried out for 30 minutes. During the 30 minutes of the experiment, 0.5ml aliquot was taken at 0, 5, 10, 20 and 30 minutes and set for instrumental analyses as described in Sections 4.2. for tungsten, and 4.4. for molybdenum. The absorbance was read from the instrument, hence the concentration corresponding to such an absorbance determined from the calibration curve.

With this, the rate of sorption of either tungsten or

molybdenum into the resins was evaluated.

The 0.5ml aliquot was chosen so that the overall effect of taking 5 such samples will be 2.5ml which is negligible in comparison to the total reaction mixture volume of 30ml.

4.6 OPERATING CONDITIONS

In order to determine the rate of sorption of the metal ions (tungsten/molybdenum) by the resin, it was obviously necessary to fix all other parameters while only one parameter was varied at a time. This helped in the determination of the rate of sorption with respect to the varied parameter. Therefore, this section has naturally been divided into the following:

(1) the initial metal ions concentration is varied while temperature and weight of the resin are fixed.

(2) the weight of resin is varied while initial ions' concentration and temperature are fixed

(3) the temperature is varied while initial concentration of metal ions and weight of resin are fixed.

4.6.1 Variation of Initial Concentration of Metal Ions at Constant Temperature and Weight of Resin

Solutions of different concentrations ranging from 1.08 to 3.26×10^{-4} mol/l for tungsten, and 0.782 to 7.82×10^{-6} mol/l for molybdenum were taken for the sorption process at constant temperature of 40 ^{0}C. Fixed weight of resin, 0.4g or 0.2g as the case may be were added; and the process as detailed in

CHAPTER FIVE

5.0 RESULTS AND DISCUSSIONS

The numerous advantages of macromolecular catalysts (which include high selectivity, easy separation, easy recovery and reusability of the catalyst, and obtaining catalyst-free product) over the homogeneous counterpart have necessitated a thorough study of the kinetics of sorption (a process by which the catalyst is anchored to the resin). The kinetic study is especially important because it enhances the synthesis of the macromolecular catalyst itself. With kinetic information, when a particular amount (concentration) of the sorbent is taken with a known weight of resin, the time for the sorption to attain equilibrium or go into completion can be estimated. In a more generalized term, kinetic study provides information about rate and factors affecting rate of a process, which are in turn used for setting experimental conditions and reactor design.

The high selectivity and effectiveness of tungsten and molybdenum over other metallic elements for liquid-phase oxidations of organic compounds had been a guide to the choice of tungsten (in the form of tungstic oxide), and molybdenum (in the form of ammunium molybdate) as sorbents in this work. The following resins were selected as ion-exchange materials:

Group1 (1) Amberlite IRA 400 Cl^-

(2) Amberlite IRA 410 Cl^-

(3) Amberlite IRA 938 Cl^-

(4) Duolite A 116 Cl^-

Group2 (5) IONAC AD 54 OH^-

(6) Duolite A 113 Cl^-

(7) Amberlyst' A-26 Cl^-

Group3 (8) Amberlite IR 45 OH^-

(9) Amberlyst' A-21 (free base)

(10) Duolite' A 378 (free base)

for the purpose of comparison. Nevertheless, the inavailability of these ion-exchange resins necessitated the study of one in each of the series having similar properties (see Appendix 4). As such, amberlite IRA 400 Cl^- was selected to represent the first series, IONAC AD 54 OH^- to represent the second series, and amberlite IR 45 OH^- to represent its series.

The course of the experiment revealed that sorption of tungsten by amberlite IR 45 OH^- is at least difficult, while the other two resins functioned well in the sorption process.

5.1 KINETICS OF SORPTION

Kinetic study of sorption was carried out based on the underlisted experimental conditions:

(1) Sorption temperature for all the processes = $40+0.5^0C$

(2) Sorption of tungsten by amberlite IRA 400Cl^-

-resin weight = 0.2g

-tungsten concentration = 2.66×10^{-4}mol/l

(3) Sorption of tungsten by AD 54 OH^-

-resin weight = 0.4g

-tungsten concentration = 2.73 x 10^{-4}mol/l

(4) Sorption of molybdenum by amberlite 400 Cl^-

-resin weight = 0.4g

-molybdenum concentration = 7.82 x 10^{-6}mol/l.

The results of kinetic study revealed that sorption process was very fast in all the above mentioned system. Observations showed that equilibrium was practically established in each of the system within the first 10 minutes of the process (see **Figure** 5-1, 5-4, 5-5).

As previously mentioned, the overall exchange rate is dependent on concentration of solution (sorbent), amount of resin, and temperature at which the sorption process is taking place. To this effect, investigations on the sorption process have been carried out to study individual effect of temperature, amount of resins and initial concentrations of sorbent. In order to evaluate the effect of individual parameters, one parameter was varied while others were allowed to remain fixed. **Figures** 5-1, 5-4 & 5-5 show various conditions with various resins used.

5.1.1 Effect of Concentration on Sorption Rate

The effect of concentration on sorption rates was studied at constant temperature and fixed weight of resin for each metal ion (sorbent) and resin types. Series of concentration -

time runs were carried out as shown in **Figures 5-1a, 5-1b & 5-1c**. Observation of the curves shows the rate to be proportional to concentration.

Application of a standard analytical method (differential) for kinetics data on curves (**Figures 5-1a, 5-1b & 5-1c**), initial rates were obtained and plotted against corresponding initial concentrations on a log-log graph paper (**Figures 5-2 & 5-3**). The slope of the plot of log of initial rate against log of initial concentration, (which is the order of reaction with respect to concentration) was evaluated for the respective system to be:

(a) 1.02 for the sorption of molybdenum by amberlite IRA 400 Cl^- ion-exchange resin.

(b) 0.982 for the sorption of tungsten by amberlite IRA 400 Cl^- ion-exchange resin.

(c) 1.012 for the sorption of tungsten by IONAC AD 54 OH^- ion-exchange resin.

Consequently, it could be said that the sorption process was first order with respect to concentration of the sorbents used in this work.

5.1.2 Effect of Weight of Resin on Sorption Rate

The effect of weight of resin on sorption rate was also investigated. At constant temperature and fixed concentration of sorbent, the weight of the resin was varied. Consequently,

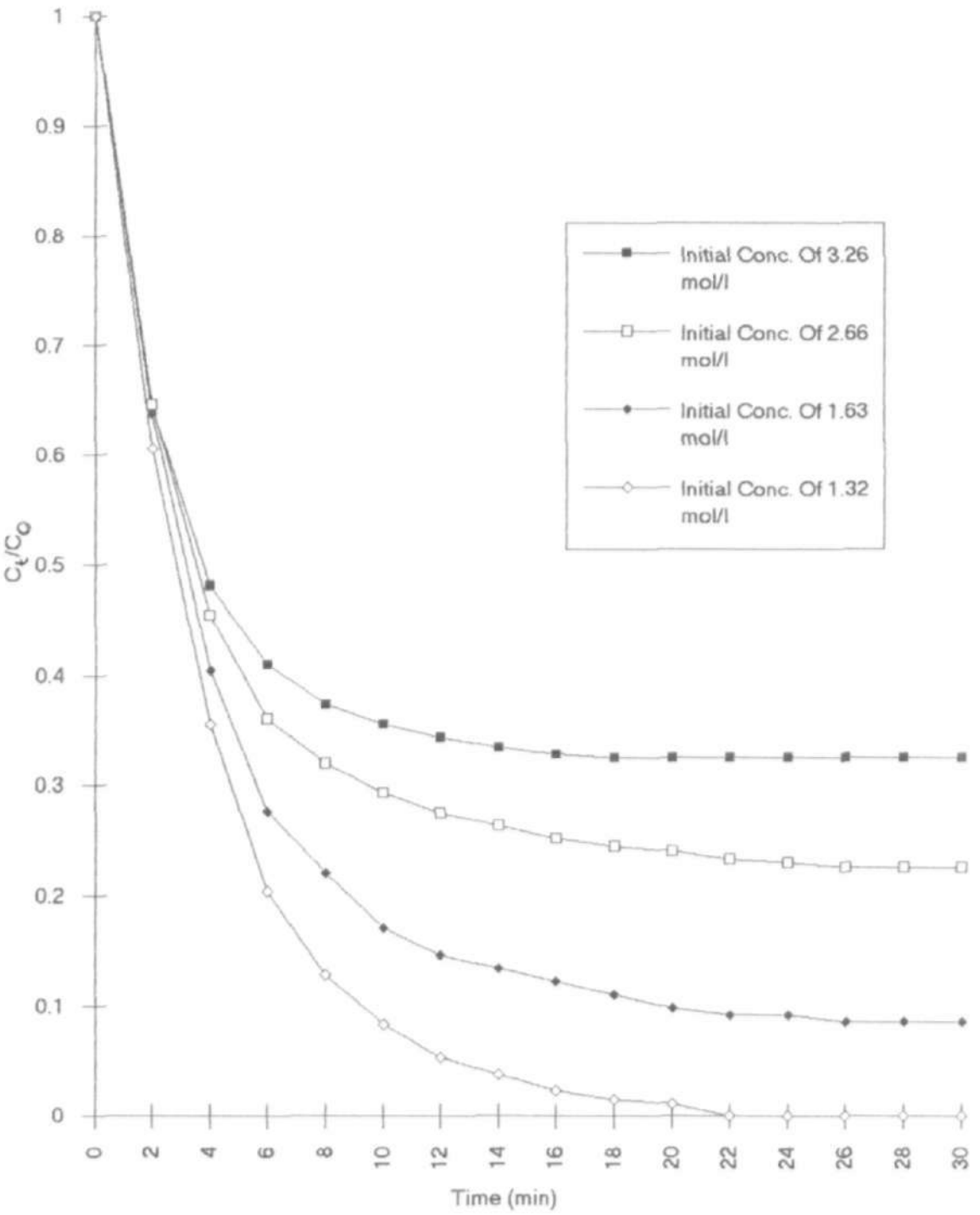


Fig 5-1a: A Plot Of The Ratio Of Concentration At Time, t To Initial Concentration Versus Time For The Sorption Of Tungsten By Amberlite IRA 400 Cl^-

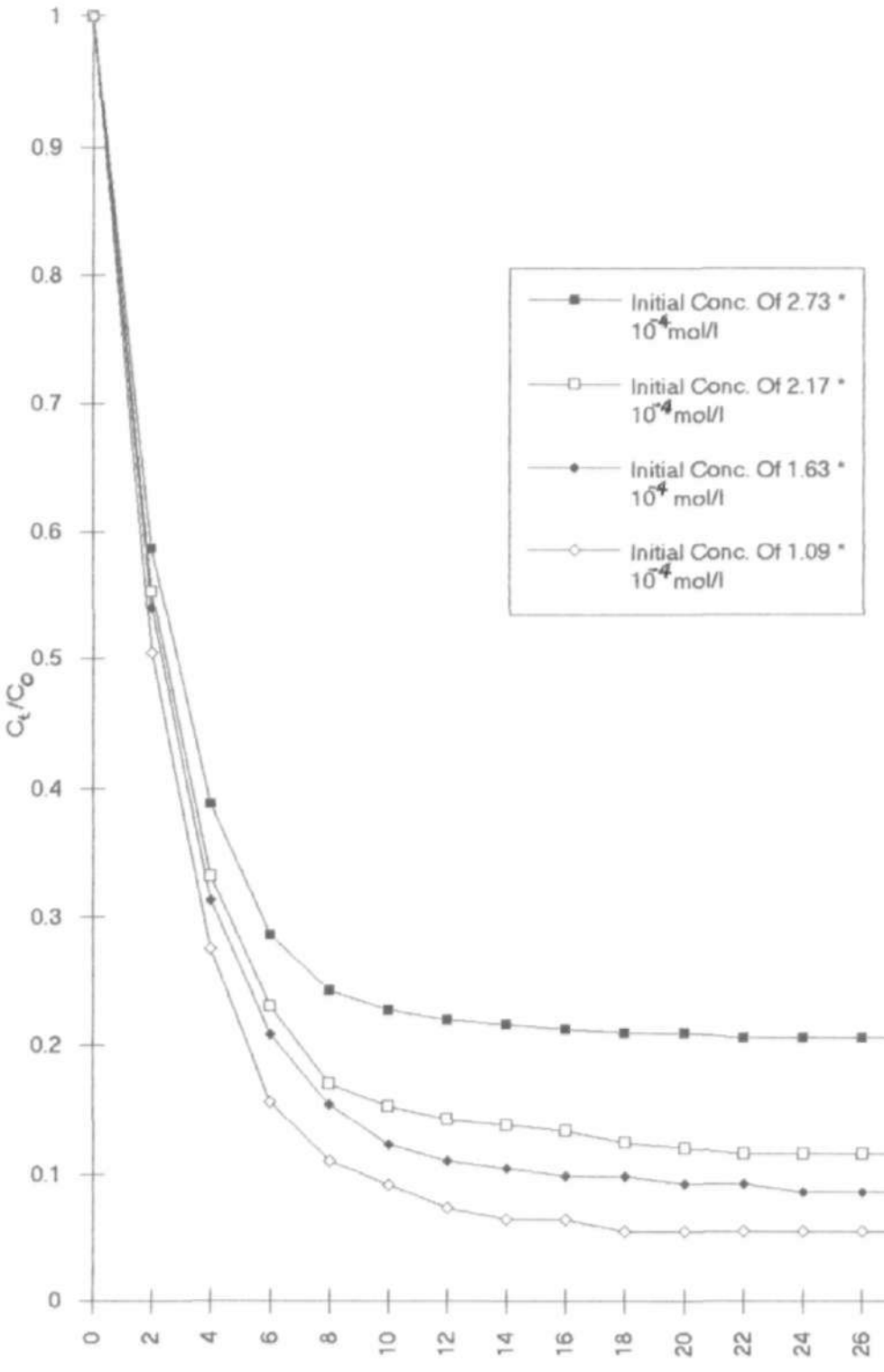


Fig 5-1b: A Plot Of The Ratio Of Concentration At Time, t To Initial Concentration Versus Time For The Sorption Of Tungsten By IONAC AD 54 OH^-

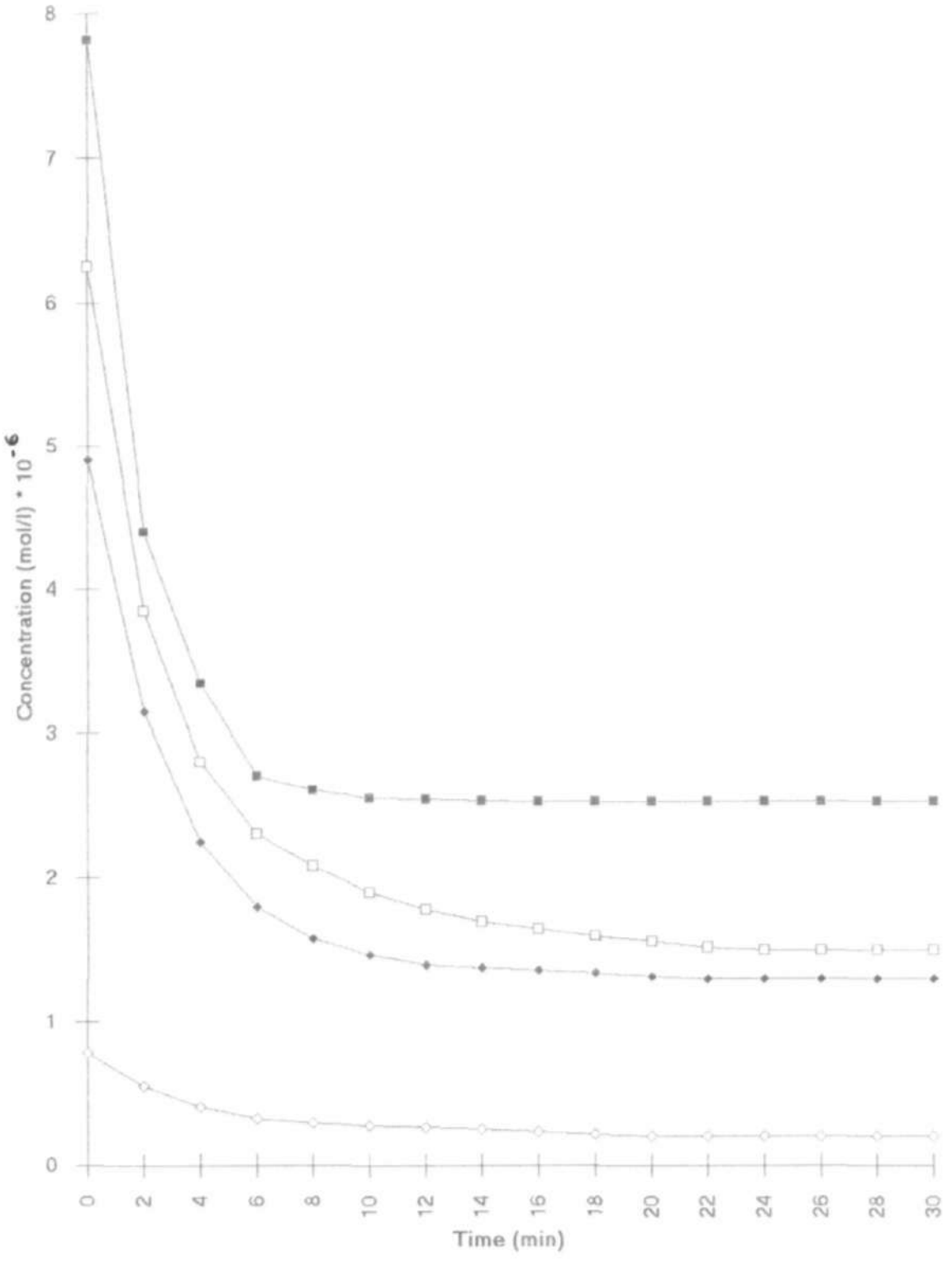


Fig 5-1c: Concentration - Time Curves For Sorption Of Molybdenum By Amberlite IRA 400 Cl^- Resin At Various Initial Concentrations

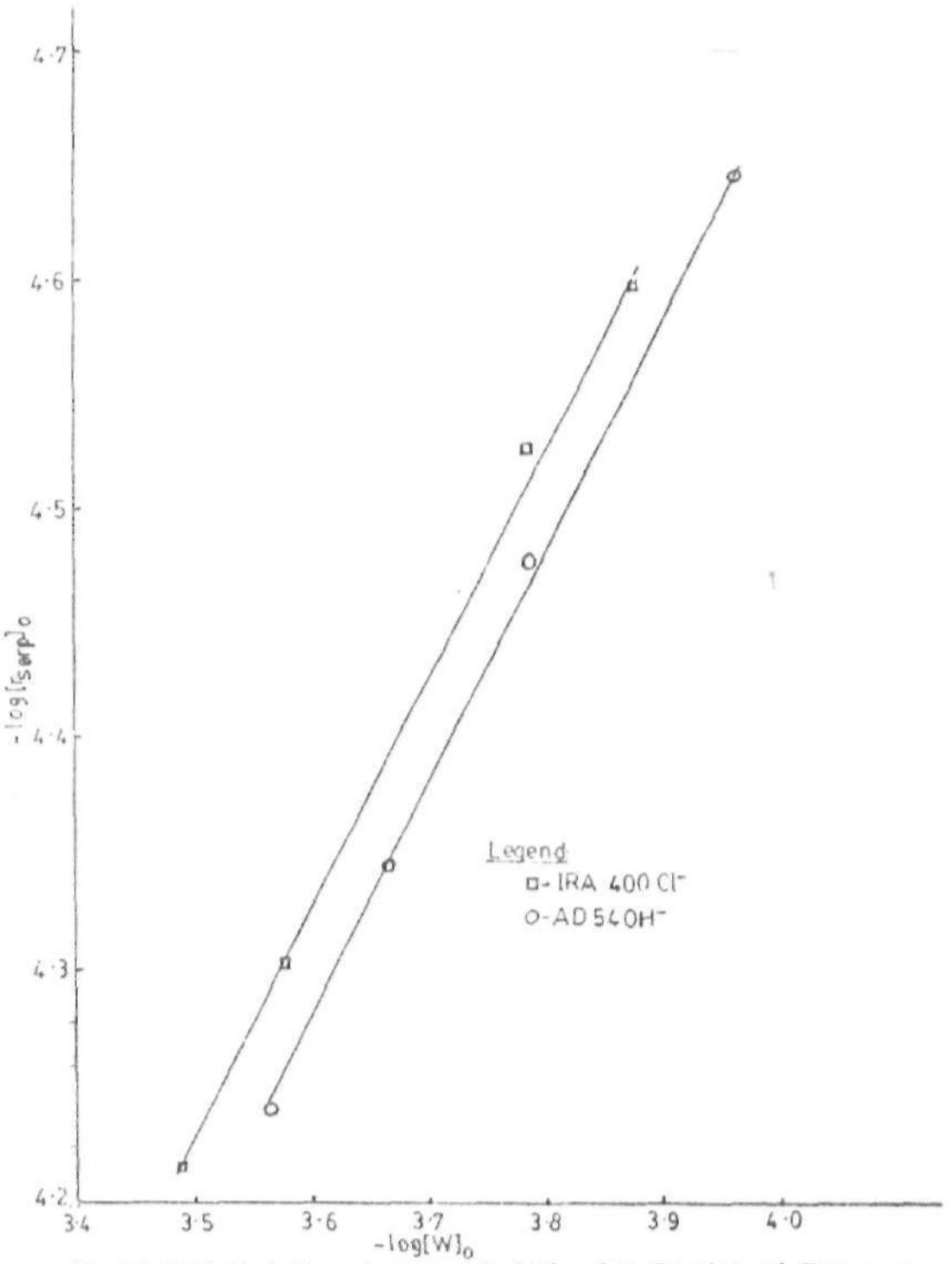


Fig 5-2: Plot of $\log[r_{Sorp}]_o$ versus $\log[W]_o$ for Sorption of Tungsten by Amberlite IRA 400 Cl^- and IONAC AD 54 OH^- Resins

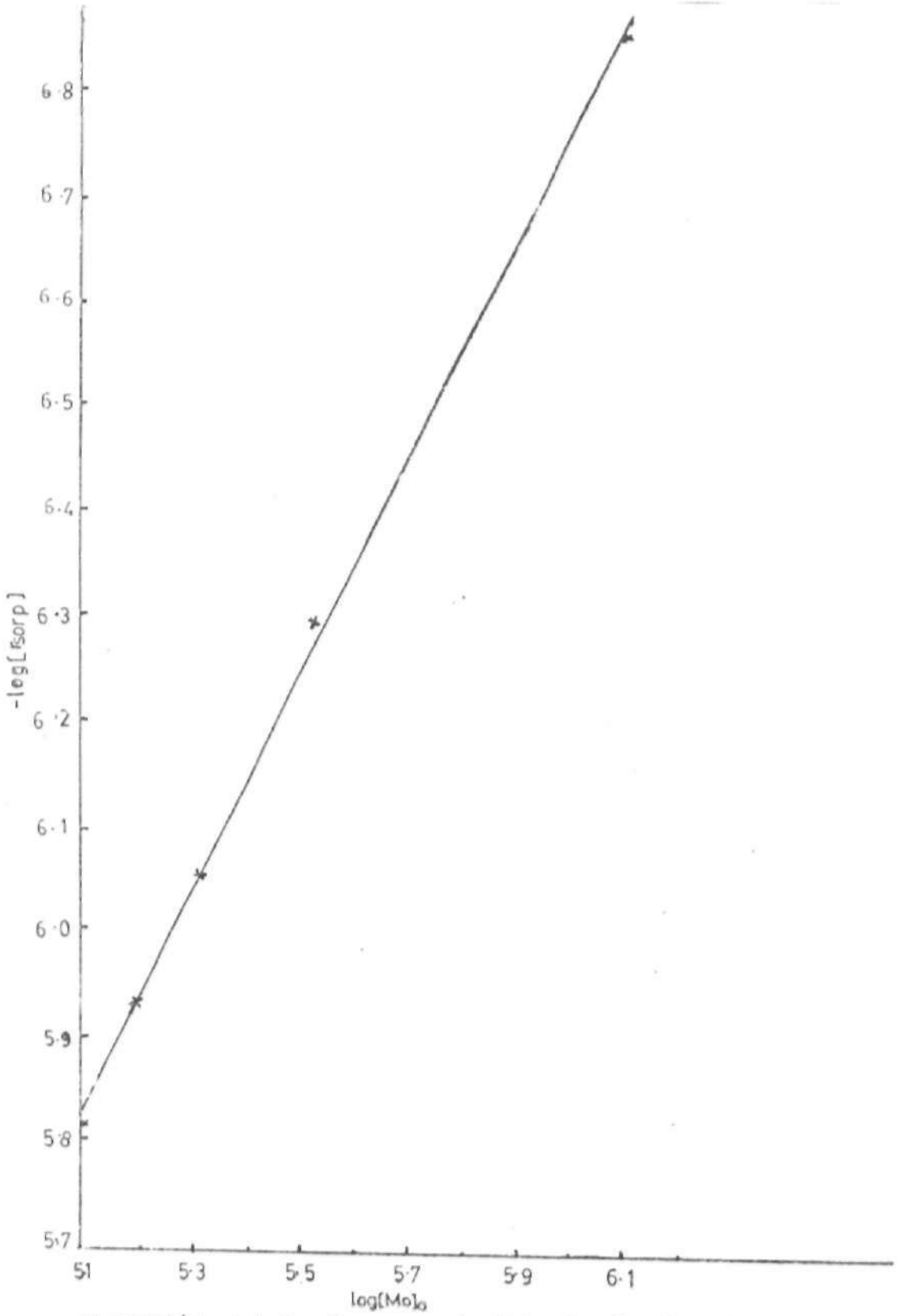


Fig 5-3: Plot of $\log[r_{sorp}]_0$ versus $\log[Mo]_0$ for Sorption of Molybdenum by Amberlite IRA 400 Cl^- Resin

series of concentration-time curves were plotted as shown in Figures 5-4a, 5-4b & 5-4c for each set of conditions of sorbent and resin types. The rate was found to increase with increase in the amount of resin.

The data (curves) on Figures 5-4a, 5-4b & 5-4c were treated by differential method and the initial rates corresponding to their weights were evaluated. The rates obtained here were plotted against the weight of resin on a log-log graph paper (Figures 5-5 & 5-6). The slope (order of the process) of the plot were as below for each system.

(a) 1.07 for sorption of molybdenum by amberlite IRA 400 Cl^-

(b) 1.20 for the sorption of tungsten by amberlite IRA 400Cl^-

(c) 1.30 for the sorption of tungsten by IONAC AD 54 OH^-.

5.1.3 Effect Of Temperature On Sorption Rate

Temperature effect on sorption was also studied. The weight of resin and concentration of sorbent were fixed, while the temperature was allowed to vary. Concentration-time curves were plotted as shown in Figures 5-7a, 5-7b & 5-7c From these figures, it could be seen that the amount of sorbent taken up increases with temperature. Obviously therefore, the rate of sorption increases with temperature.

To investigate the effect of temperature on rate constant, K (which in turn affects the rate), differential method

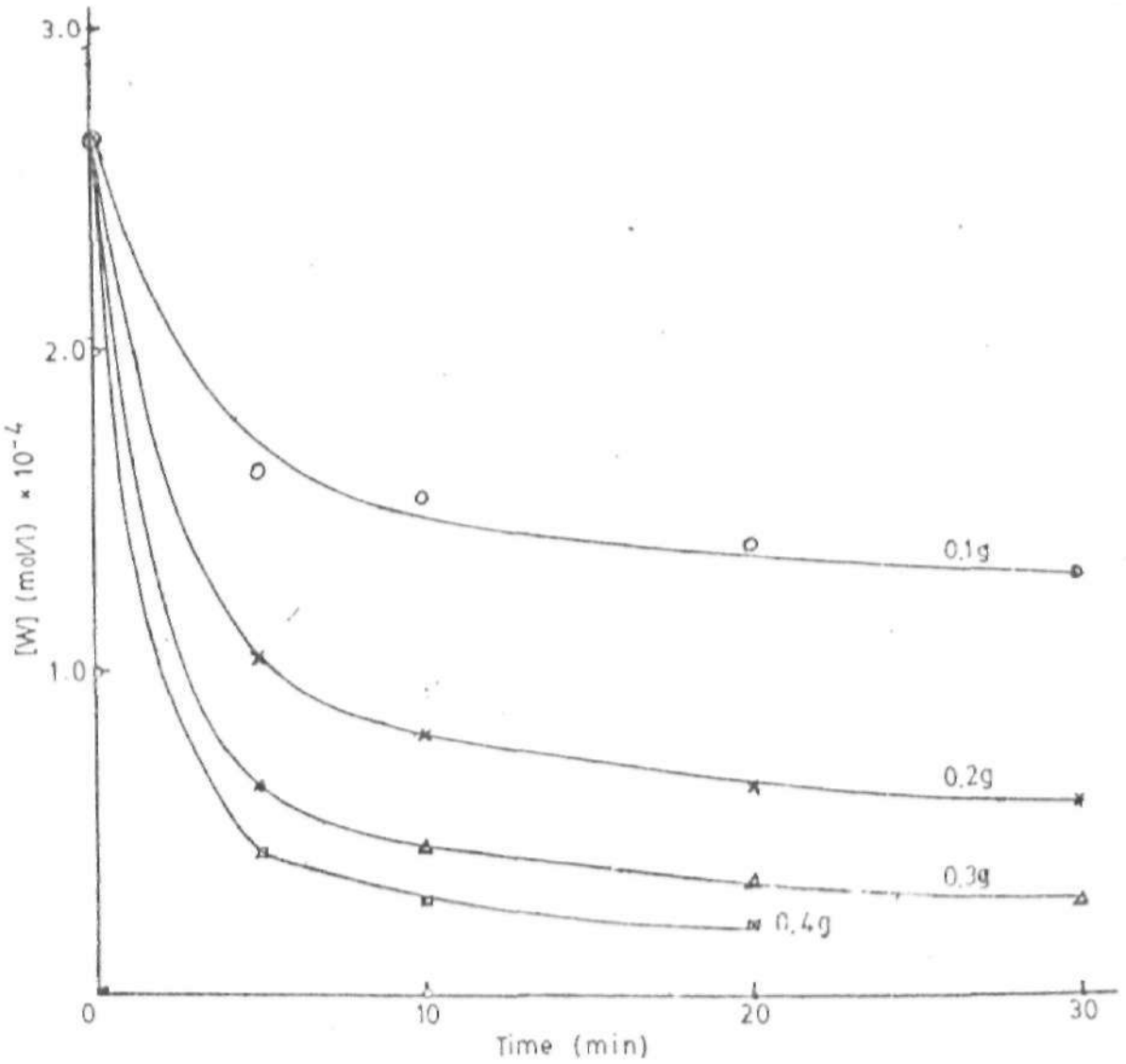


Fig 5-4a: Concentration-Time Curves in a series where the Amount of Amberlite IRA 400 Cl^- was Varied for Sorption of Tungsten

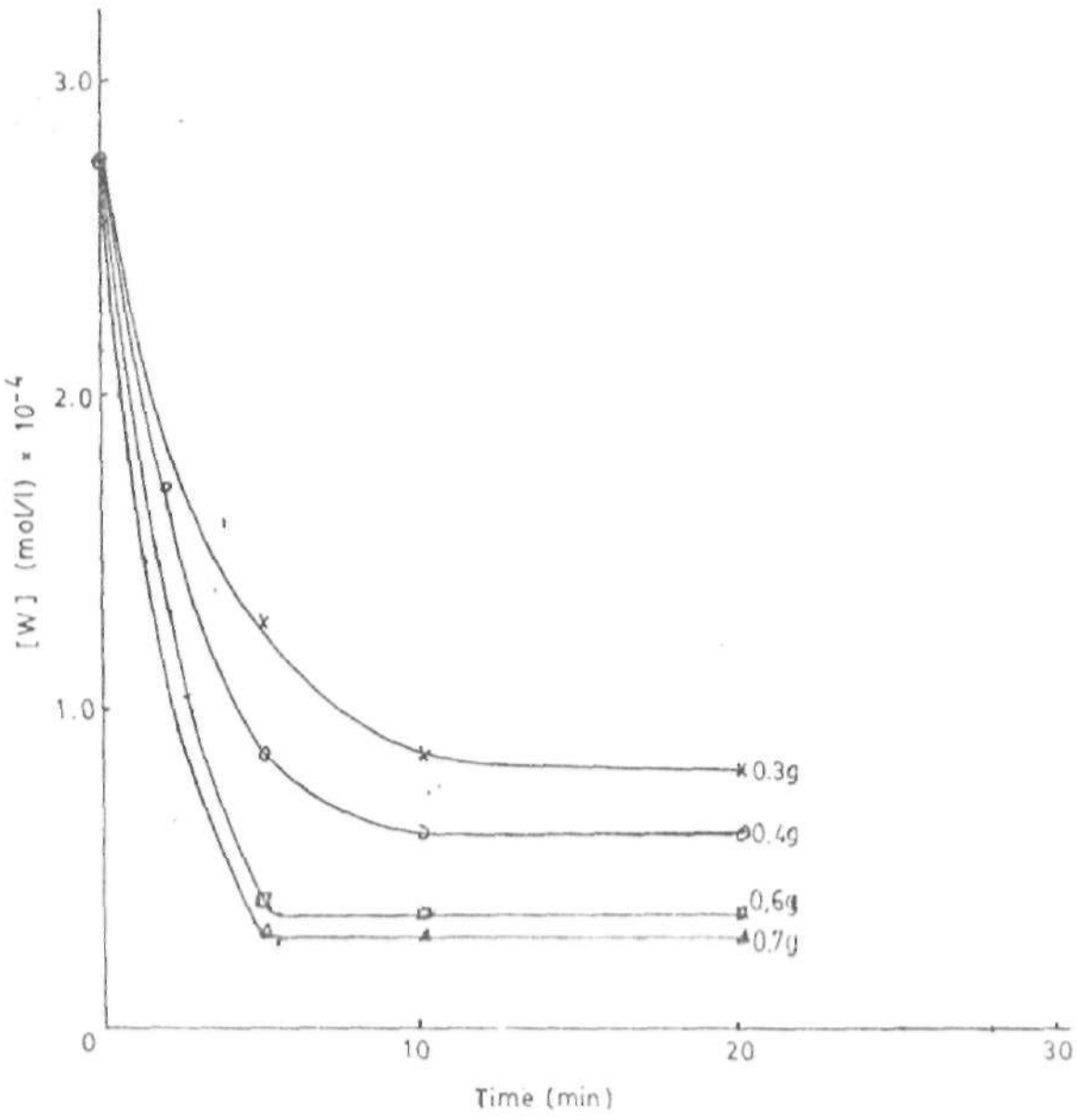


Fig 5-4b: Concentration - Time Curves in a series where the Amount of IONAC AD54 OH^- Resin was Varied for the Sorption of Tungsten

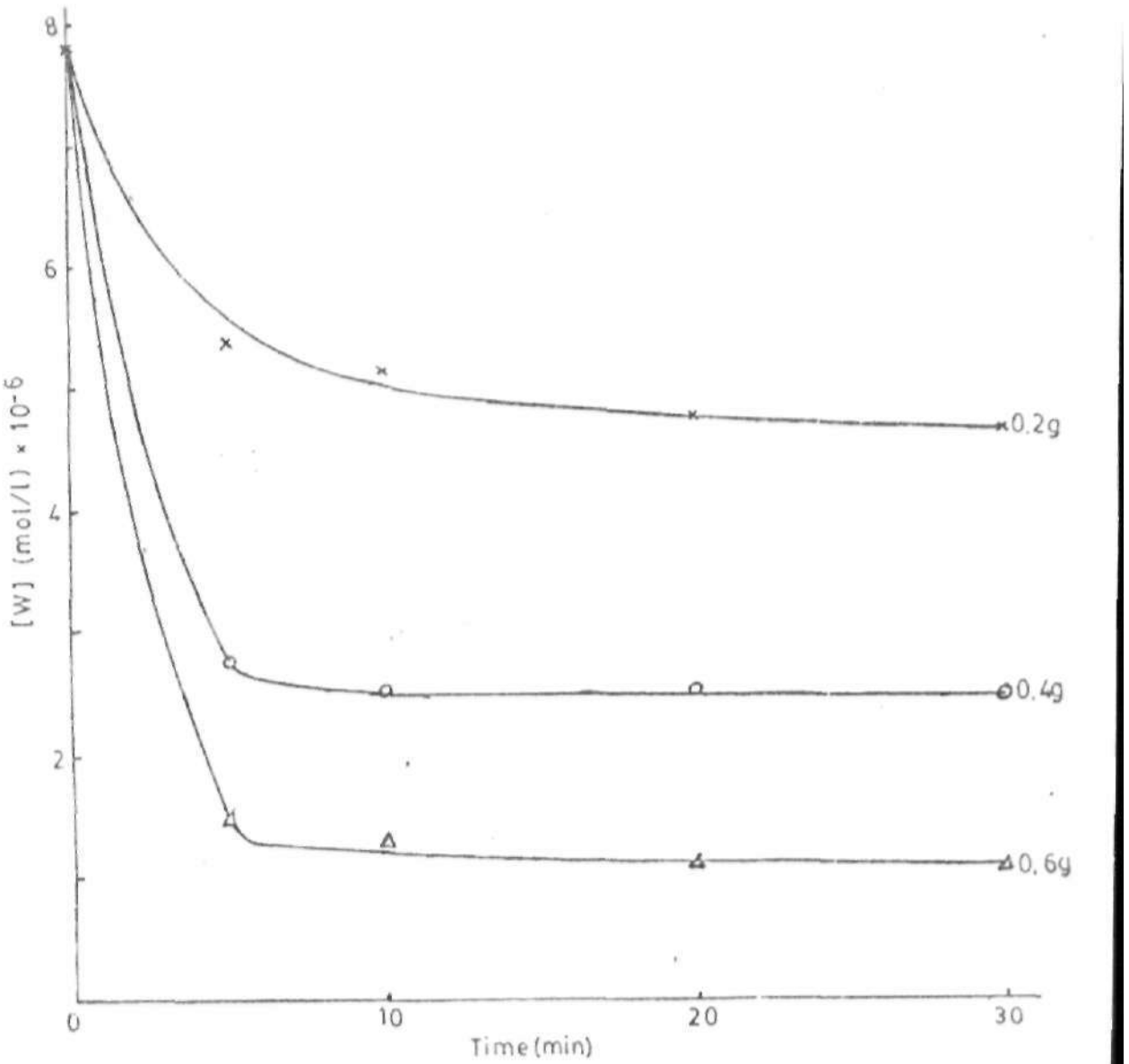


Fig 5-4c: Concentration-Time Curves in a series where the Amount of Amberlite IRA 400Cl⁻ was Varied for Sorption of Molybdenum

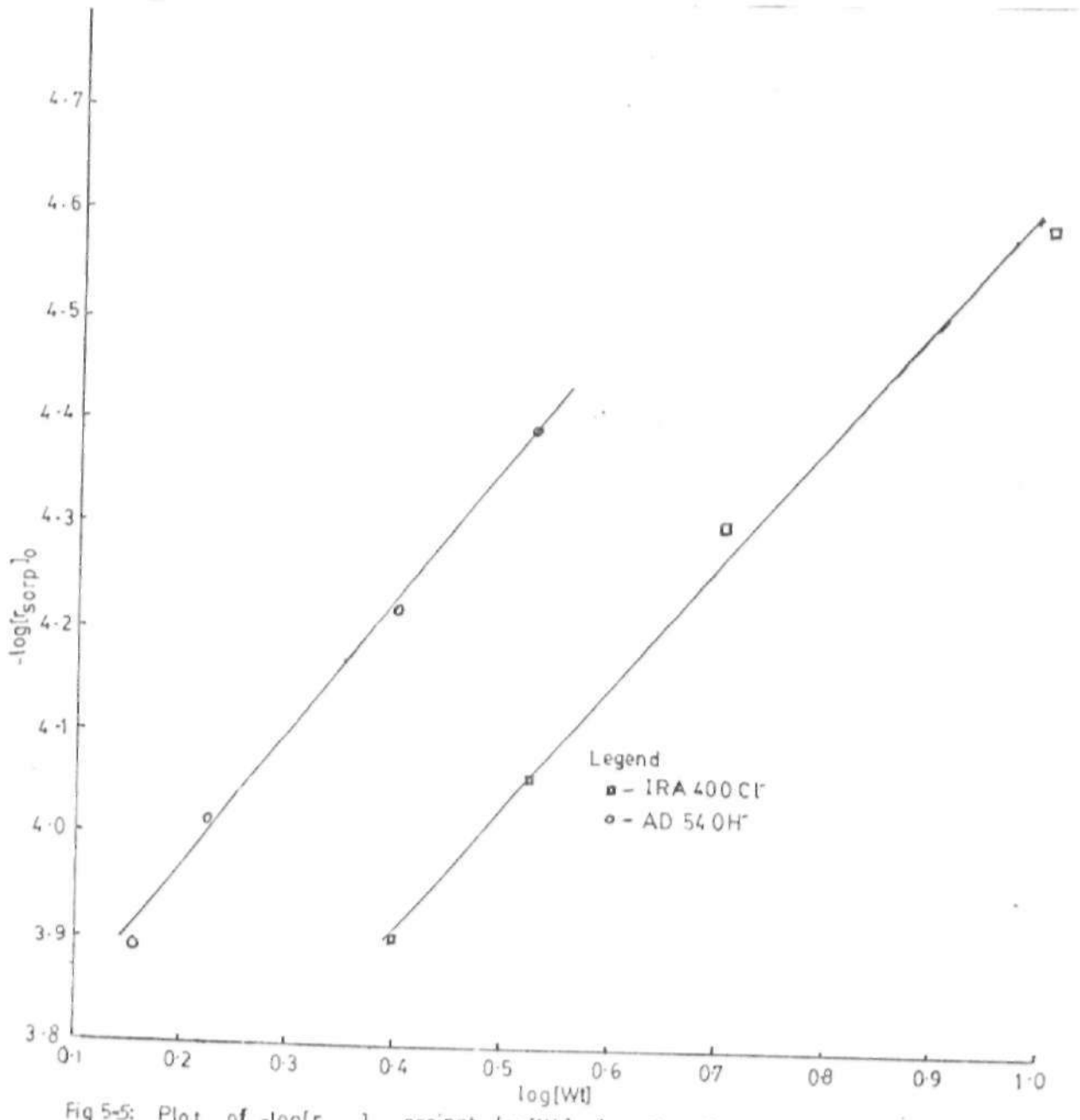


Fig 5-5: Plot of $-\log[r_{sorp}]_o$ against -log[Wt] for Sorption of Tungsten by Amberlite IRA 400 Cl^- and IONAC AD54 OH^- Resins

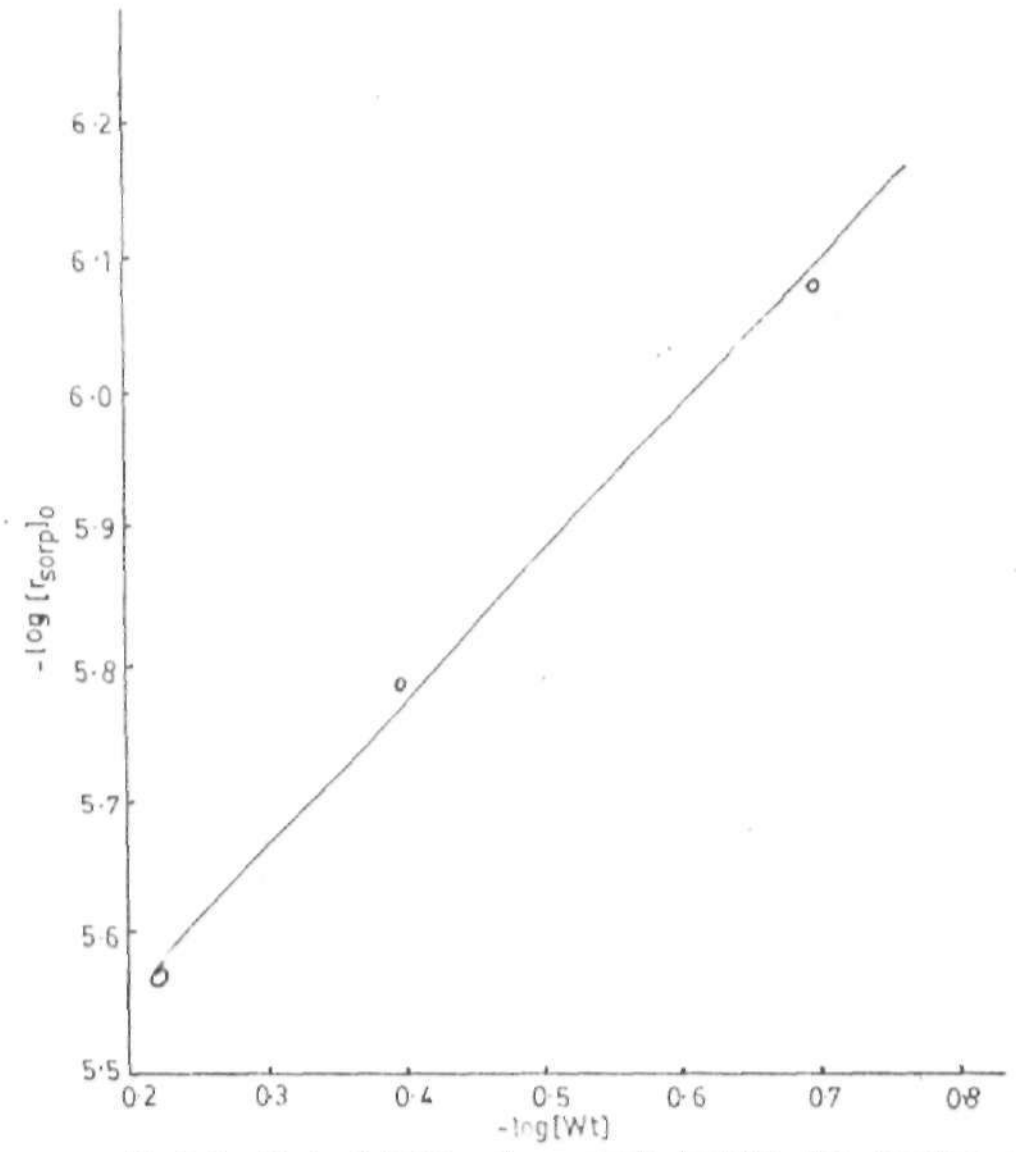


Fig 5-6 Plot of $-\log[r_{sorp}]_o$ against -log[Wt] for Sorption of Molybdenum by Amberlite IRA 400 Cl^- Resin

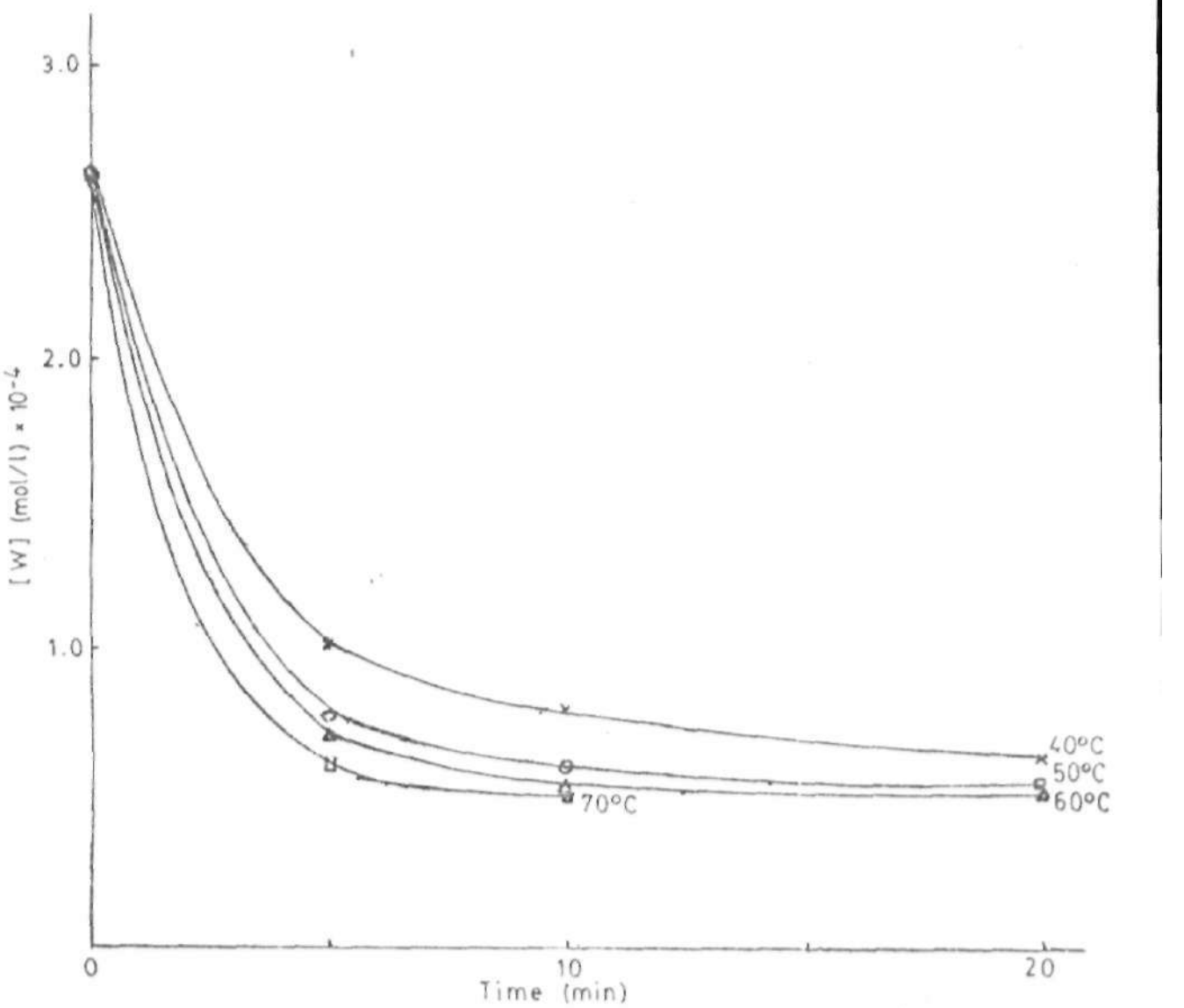


Fig5-7a: Concentration-Time Curves for Sorption of Tungsten by Amberlite IRA 400 Cl Resin at Various Temperature

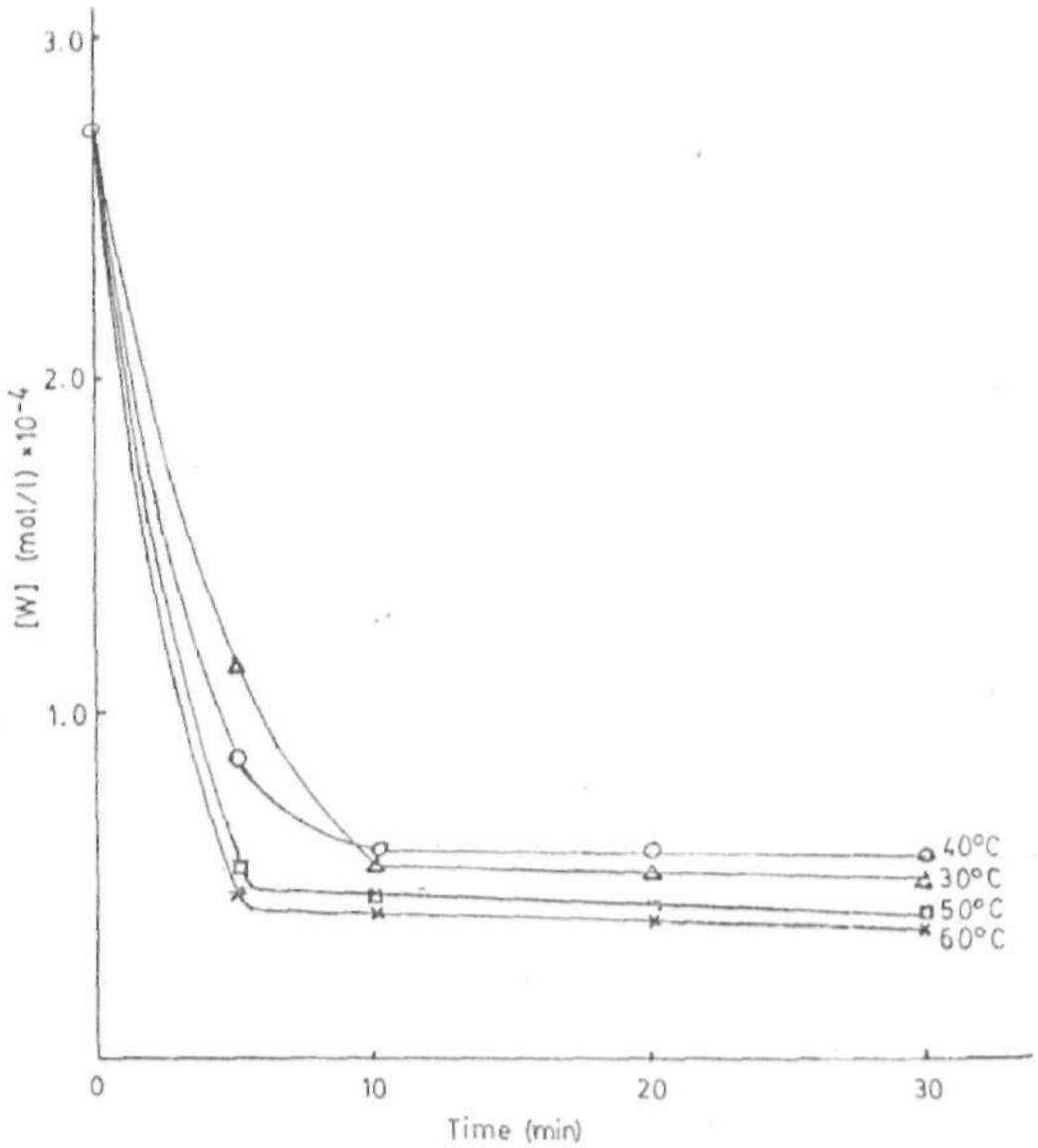


Fig 5-7b: Concentration-Time Curves for Sorption of Tungsten by IONAC AD 54 OH^- Resin at Various Temperature

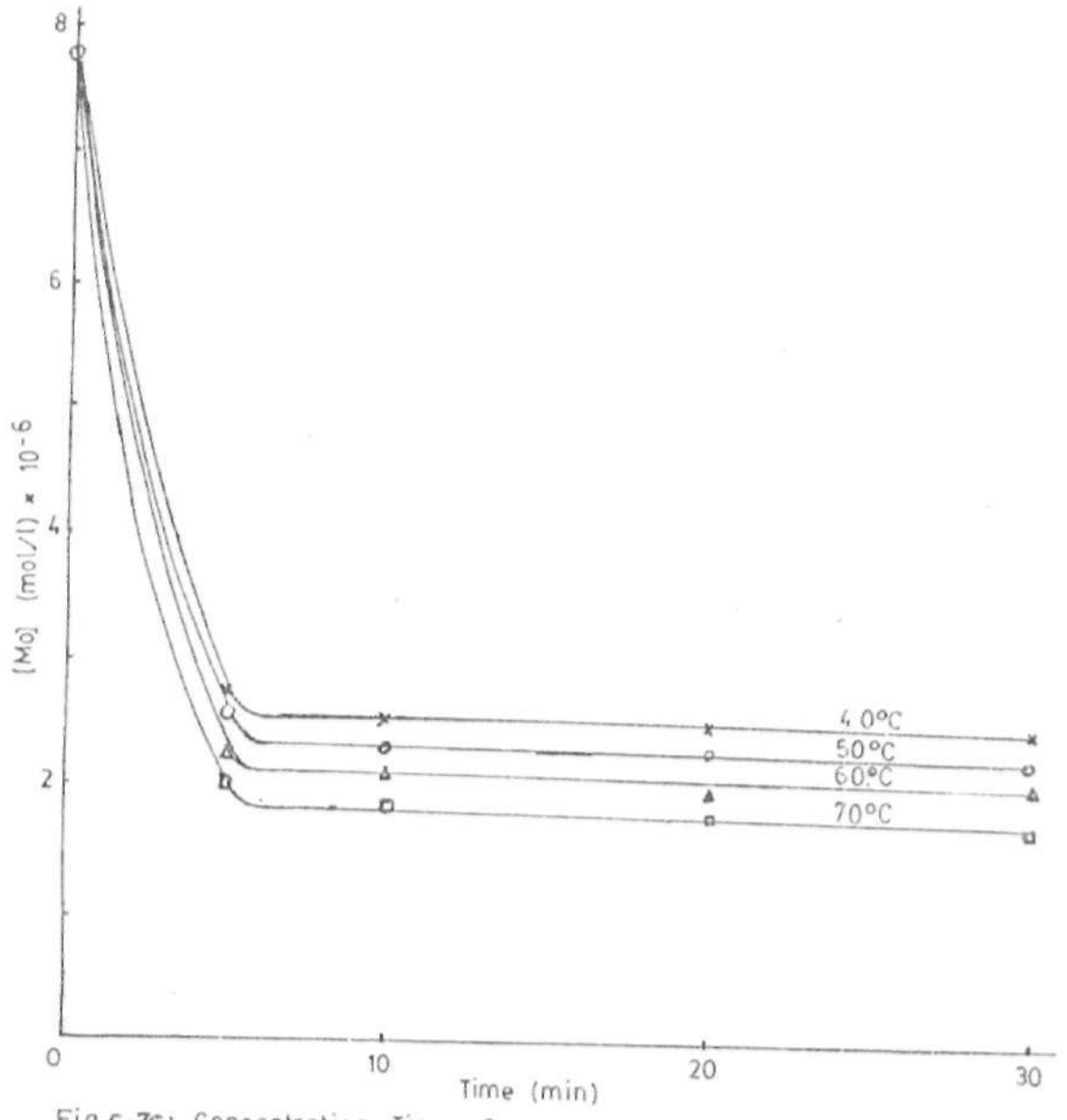


Fig 5-7c: Concentration-Time Curves for Sorption of Molybdenum by Amberlite IRA 400 Cl^- Resin at Various Temperature

[Levenpiel, 1972, Smith, 1970] was adopted to evaluate the rate of sorption at various concentrations on curves of **Figures 5-5a, 5-5b & 5-5c**. Sorption rate, r_{sorp} was plotted against sorbent concentration **(Figures 5-8a,b & c)**, and the slopes (K_{sorp}) were evaluated and tabulated in Table **5-1a, b and c**. Two values of K_{sorp} were obtained for each sorption temperature.

Table 5-1 SORPTION RATE CONSTANT AT DIFFERENT TEMPERATURE
(a) For sorption of tungsten by amberlite 400 Cl^- ion-exchange resin.

Temp ^0C	Temp T^0K	K_{sorp1} (min^{-1})	K_{sorp2} (min^{-1})	In K_{sorp1}	In K_{sorp2}	$1/T\ ^0K^{-1}$ 10^{-3}
40	313	0.1381	0.4055	-1.980	-0.9026	3.195
50	323	0.2843	0.4722	-1.258	-0.7503	3.096
60	333	0.3598	0.5435	-1.022	-0.6098	3.003
70	343	0.4597	0.6154	-0.777	-0.4855	2.916

(b) For sorption of tungsten by AD 54 OH^- ion- exchange resin.

Temp T^0K	K_{sorp1} (min^{-1})	K_{sorp2} (min^{-1})	ln K_{sorp1}	In K_{sorp2}	$1/T\ ^0K^{-1}$ 10^{-3}
303	0.1389	0.3896	-1.974	-0.943	3.300
313	0.2210	0.5036	-1.510	-0.686	3.195
323	0.2841	0.5357	-1.258	-0.624	3.096
333	0.4375	0.6035	-0.827	-0.505	3.003

(c) For sorption of molybdenum by amberlite 400 Cl^- ion-exchange resin.

Temp T^0K	K_{sorp1} (min^{-1})	K_{sorp2} (min^{-1})	ln K_{sorp1}	ln K_{sorp2}	$1/T\ ^0K^{-1}$ 10^{-3}
313	0.2212	1.005	-1.509	0.005	3.195
323	0.2565	1.073	-1.361	0.070	3.096
333	0.2947	1.128	-1.222	0.121	3.003
343	0.3333	1.181	-1.099	0.617	2.916

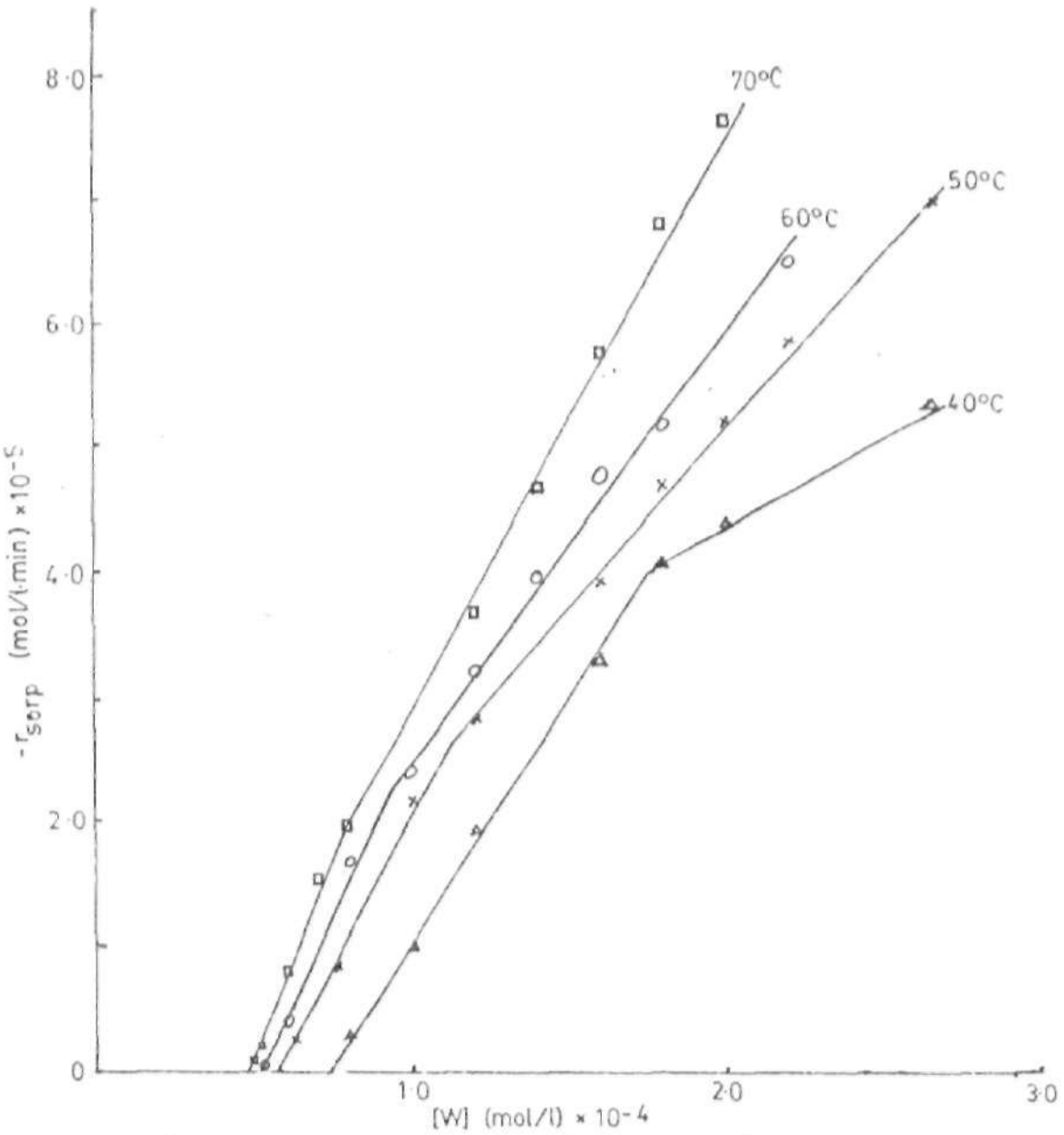


Fig 5-8a: Plot of r_{sorp} against [W] for Sorption of Tungsten by Amberlite IRA 400 Cl^- Resin

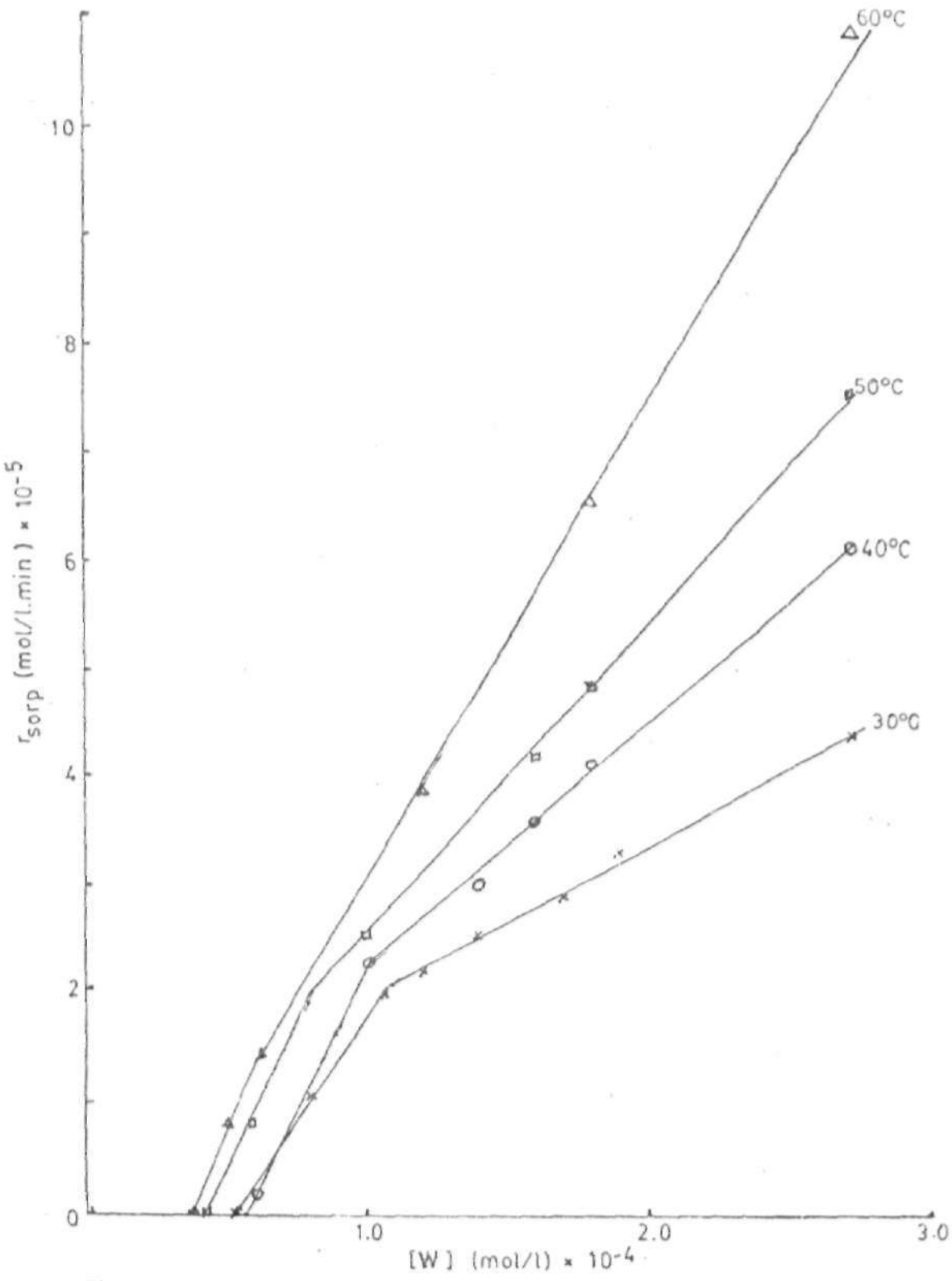
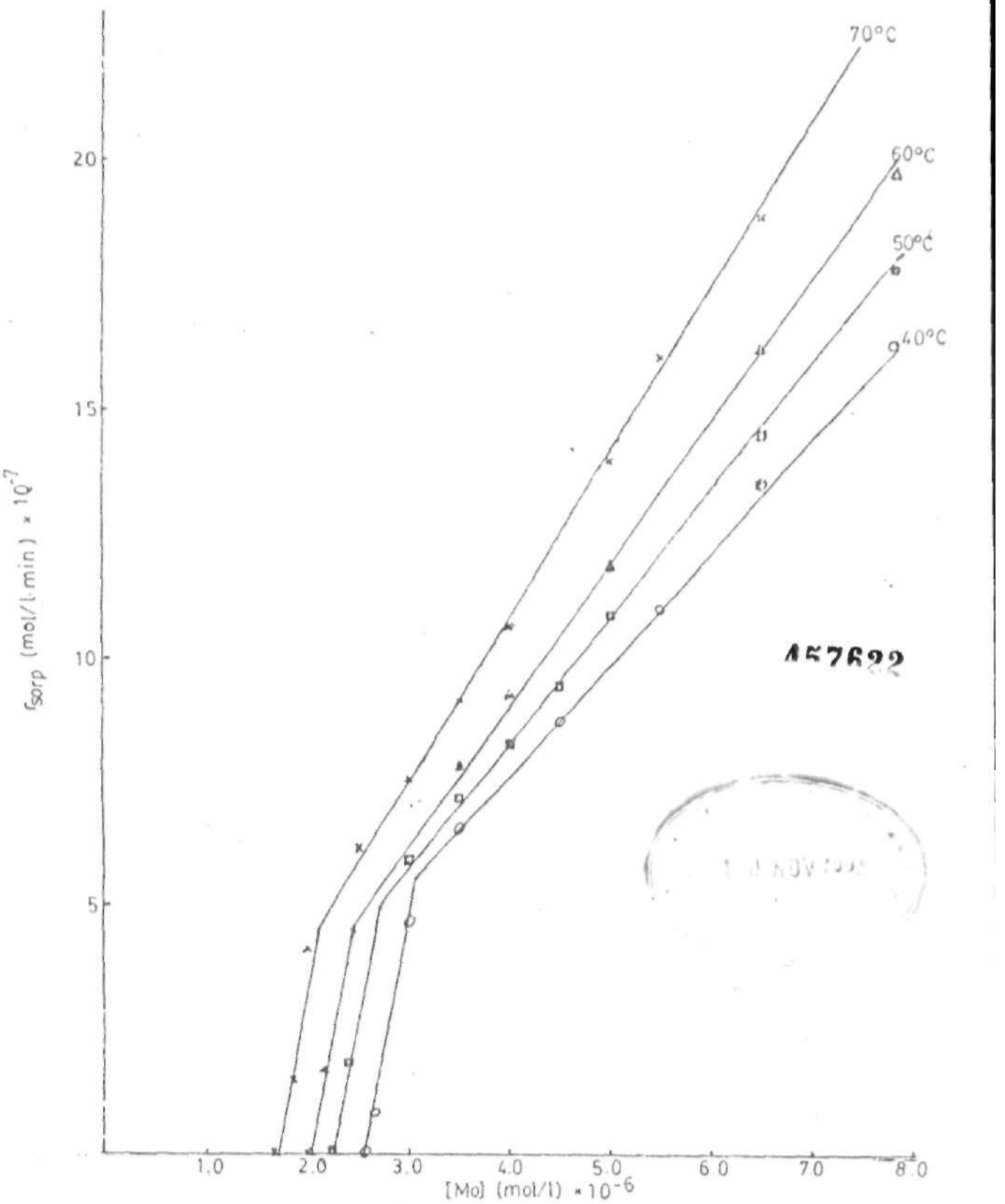


Fig 5-8b: A Plot of r_{sorp} against [W] for Sorption of Tungsten by IONAC AD 54 OH^- Resin



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Fig 5-8c: A Plot of r_{sorp} against [Mo] for Sorption of Molybdenum by Ambertite IRA 400 Cl^- Resin

With the evaluated values of K_{sorp} and temperature, Arrhenius equation:

$$K_{sorp}=K_{sorp_o}\exp(-E_{sorp}/RT) \qquad (5.1)$$

was applied to evaluate the activation energy of the process. Hence, taking natural logarithm of both sides of equation (5.1), we have

$$\ln K_{sorp}=\ln K_{sorp_o}-\frac{E_{sorp}}{RT} \qquad (5.2)$$

Hence, plotting ln K_{sorp} against 1/T, the slope = $-E_{sorp}/R$ (**Figures 5-9a,b & c**). Therefore, the activation energy (E_{sorp}) for sorption were evaluated and the summary is given in Table 5.2.

TABLE 5-2 ACTIVATION ENERGY FOR SORPTION PROCESSES

Activation Energy	Sorption of Tungsten by Amberlite 400 Cl^-	Sorption of Tungsten by AD 54 OH^-	Sorption of Molybdenum by Amberlite 400Cl^-
E_1 (KJ)	21.90	32.50	11.600
E_2 (KJ)	12.37	10.20	4.732

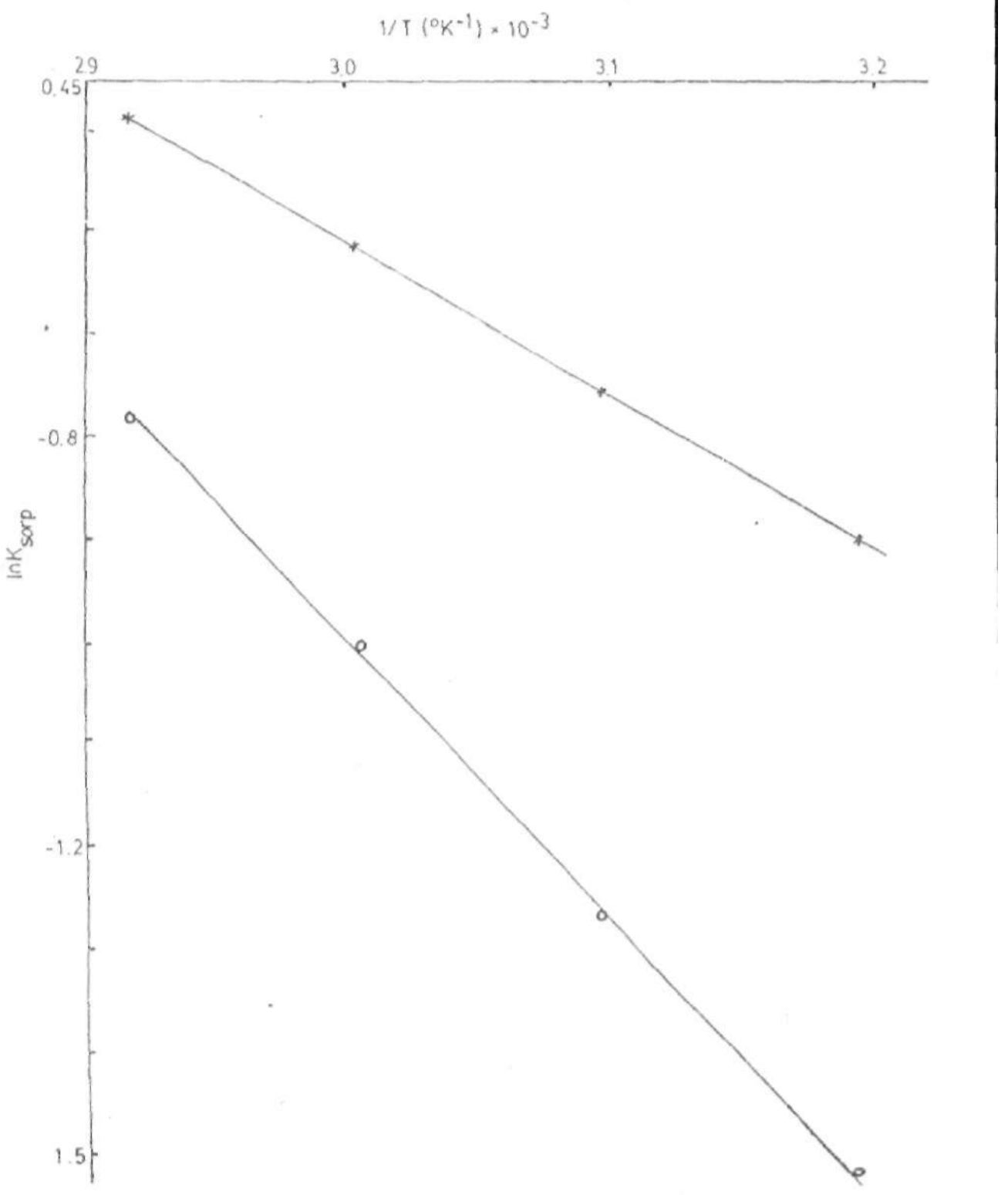


Fig 5-9a: A Plot of $\ln K_{sorp}$ against 1/T for Sorption of Tungsten by Amberlite IRA 400 Cl⁻ Resin

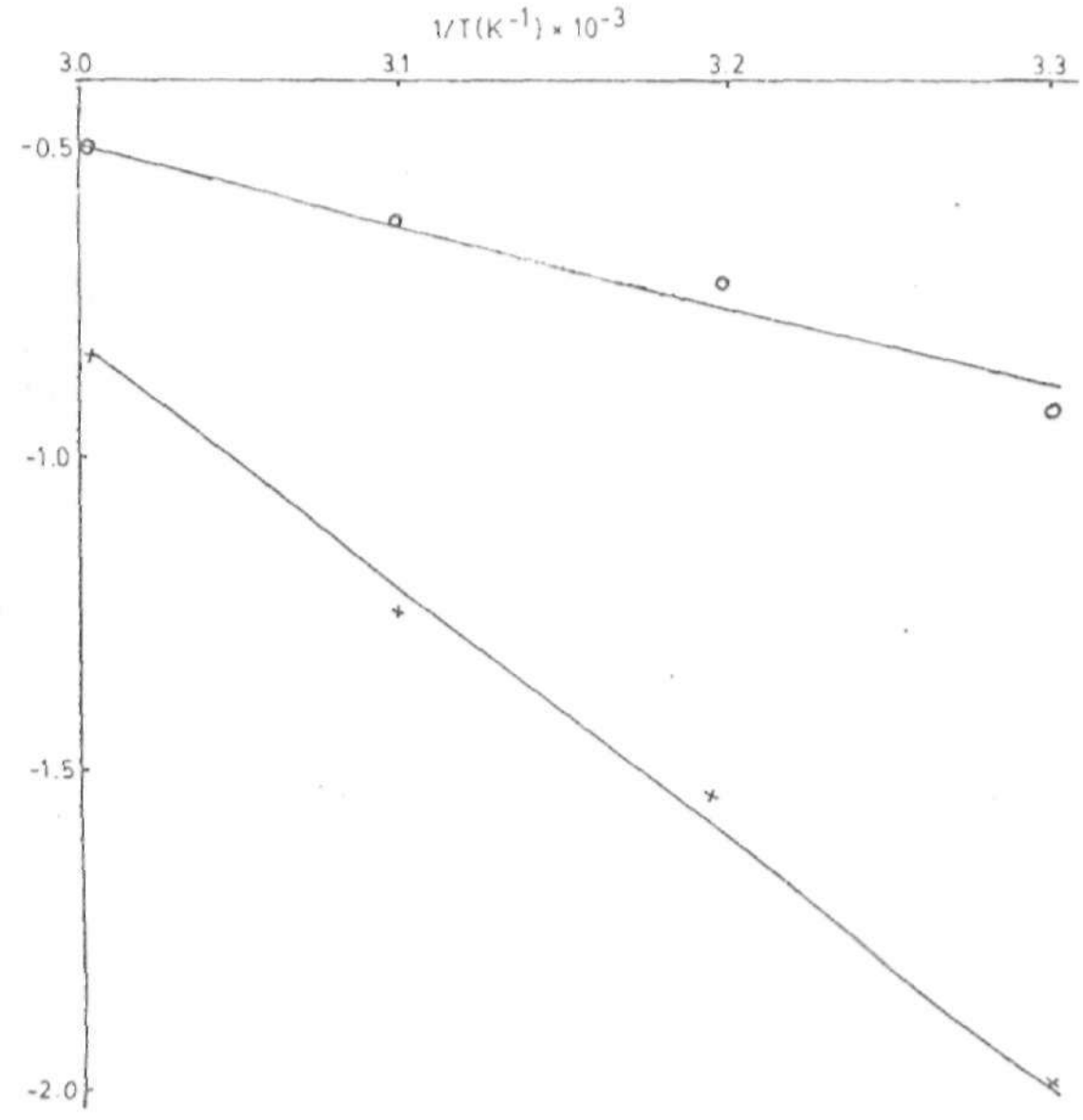


Fig 5-9b: A Plot of $\ln K_{sorp}$ against 1/T for Sorption of Tungsten by IQNAC AD 54 OH^- Resin

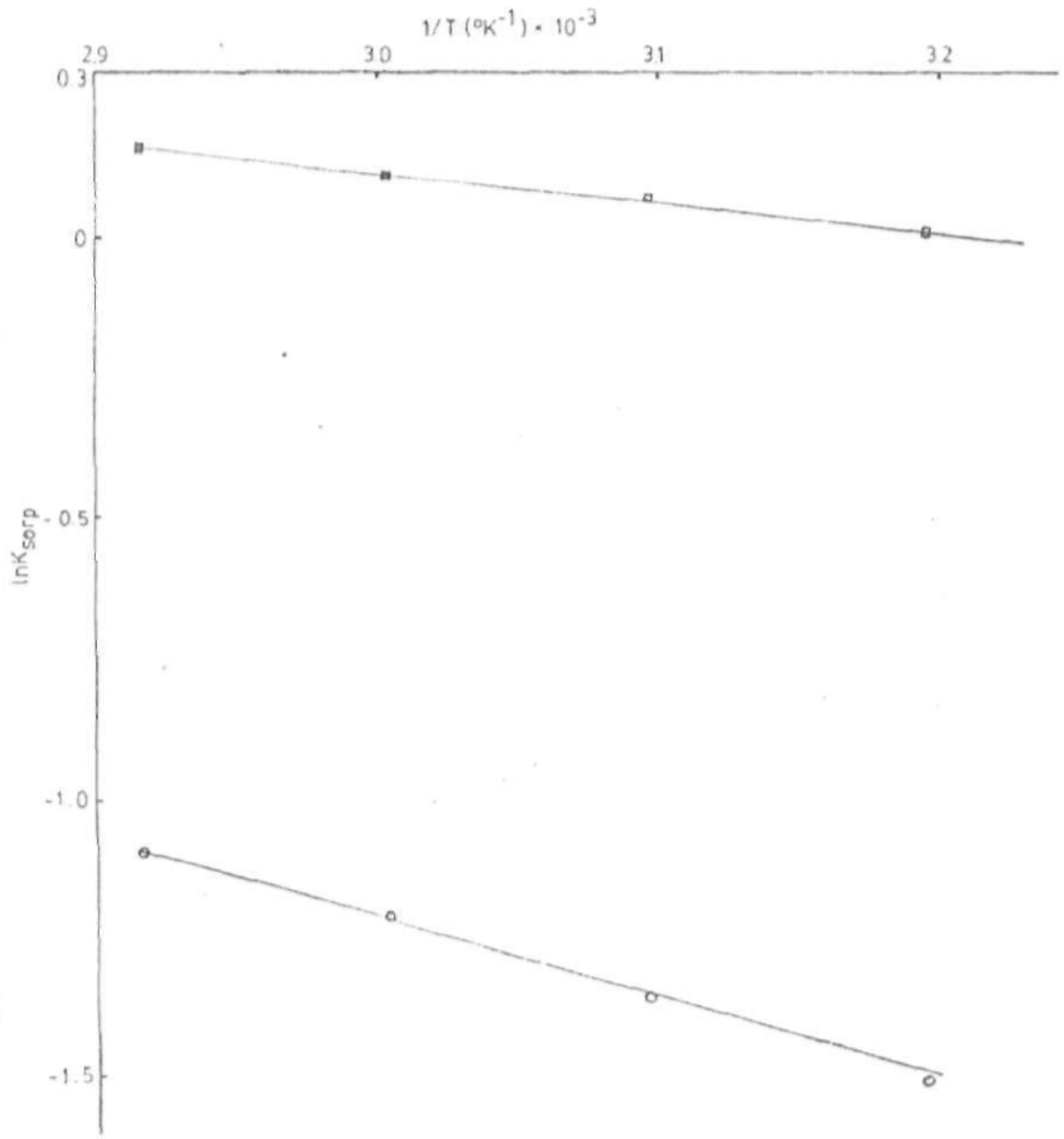


Fig5-9c: A Plot of $\ln K_{sorp}$ against 1/T for Sorption of Molybdenum by Amberlite IRA 400 Cl^- Resin

5.2 SORPTION RATE MODEL

The results obtained in Section 5.1.1 suggest a simple first order reaction rate in terms of the sorbent concentration. Consequently, a simple first order rate equation model was proposed as follows:

$$[Sorb] = [sorb]_0 * \exp(-K_{sorp}t) \qquad (5.3)$$

where [Sorb] and $[Sorb]_0$ are respectively sorbent concentrations at any time, t and t=0.

K_{sorp} = sorption rate constant.

Equation (5.3) on taking natural logarithms of both sides yields:

$$\ln [Sorb] = \ln[Sorb]_0 - K_{sorp}t \qquad (5.4)$$

hence

$$-\ln\frac{[sorb]_o}{[sorb]} = K_{sorp}t \qquad (5.5)$$

K_{sorp} is the slope of the plot of $-\ln ([sorb]_0/[sorb])$ against t. The values of K_{sorp} for the first 10 minutes of the sorption were evaluated and used in equation(5.3).

When the model rate equation (5.3) was tested, a remarkable disagreement was observed between the experimentally obtained data and that obtained by the model equation (5.3). This is illustrated in Figures 5-10a,b & c for respective sorption of tungsten by amberlite IRA 400 Cl^-, sorption of tungsten by IONAC AD 54 OH^- and sorption of molybdenum by

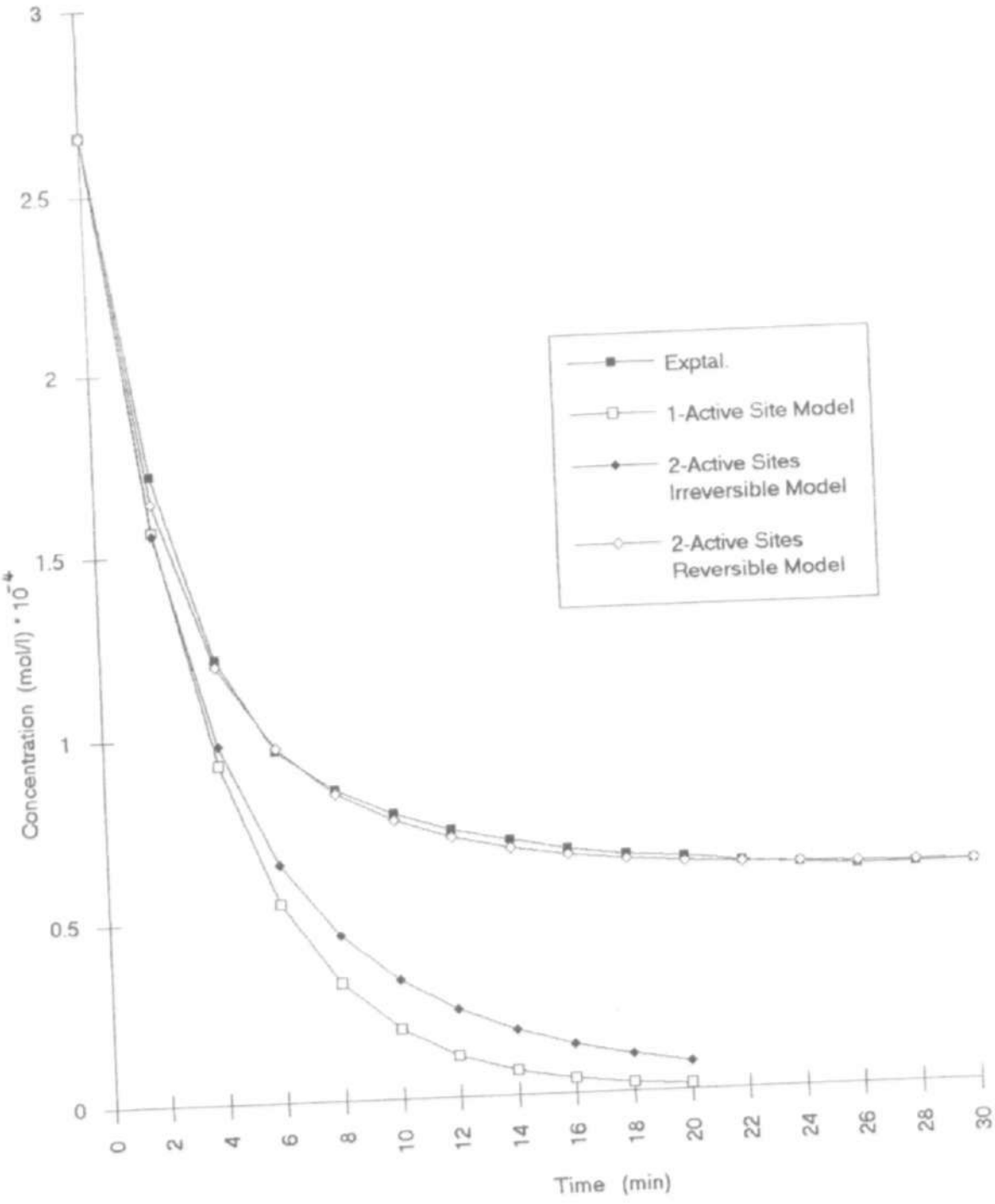


Fig.5-10a A Plot Showing Comparison Between Experiment And Models For Sorption Of Tungsten By Amberlite IRA 400 Cl^- Ion Exchange Resin

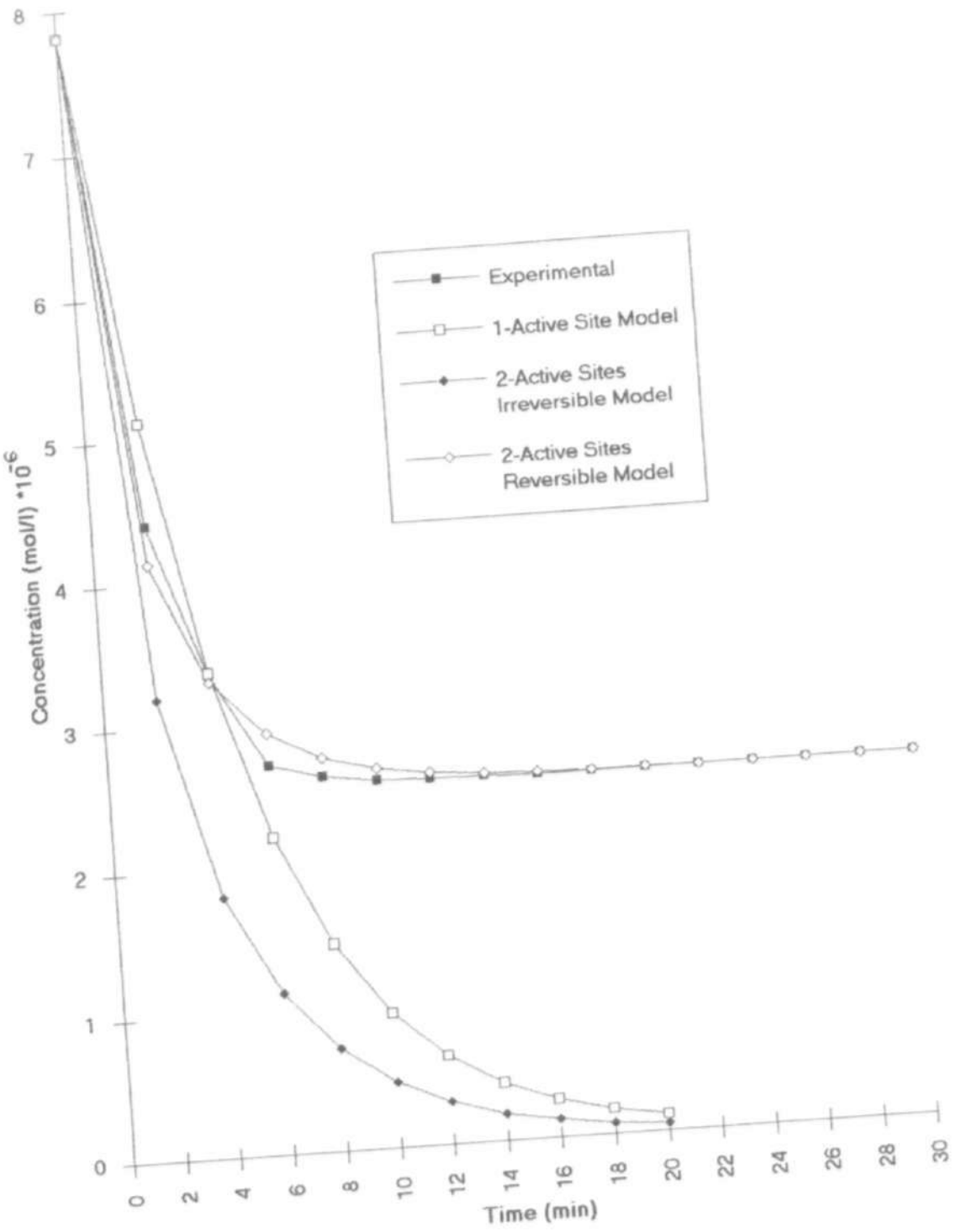


Fig.5-10c A Plot Showing Comparison Between Experiment And Models For Sorption Of Molybdenum By Amberlite IRA 400 Cl^- Ion Exchange Resin

amberlite IRA 400 Cl^- ion-exchange resins. To further ascertain the degree of disagreement between the experiment and the one active site model, it was necessary to calculate the the percentage variation of the concentrations evaluated by the model equation 5.3 and those obtained from the experiments. This is shown on Table A-1a,b & c. From the Tables A-1a,b & c, it could be observed that, at the process time of 20 minutes, the variation of the one active site model from the experiment is over 90 % in each of the aforementioned processes (see the Table A-1 in the Appendix).

The discrimination between the one-site model and the experimentally obtained data may probably be attributable to the resinous beads formation. The formation of the resinous beads leads to non-uniformity of the surface of the resins. Consequently, there is high possibility that the resins have more than one active site which indeed was the case in this work. In the course of evaluating the activation energy for the sorption process (Section 5.1.3), two distinct gradients (rate constants) were obtained from the plot of rates against concentrations. As a result, analysis as presented in Figure 5-11 was carried out, and two values of K_{SORP} were obtained for each sorption process. This postulates the possibility of having two active sites in the resins where the sorption of sorbent(s) takes place in parallel. Hence, a model for two parallel first order reactions having a common product was thus proposed to test the assumption of existence of two active

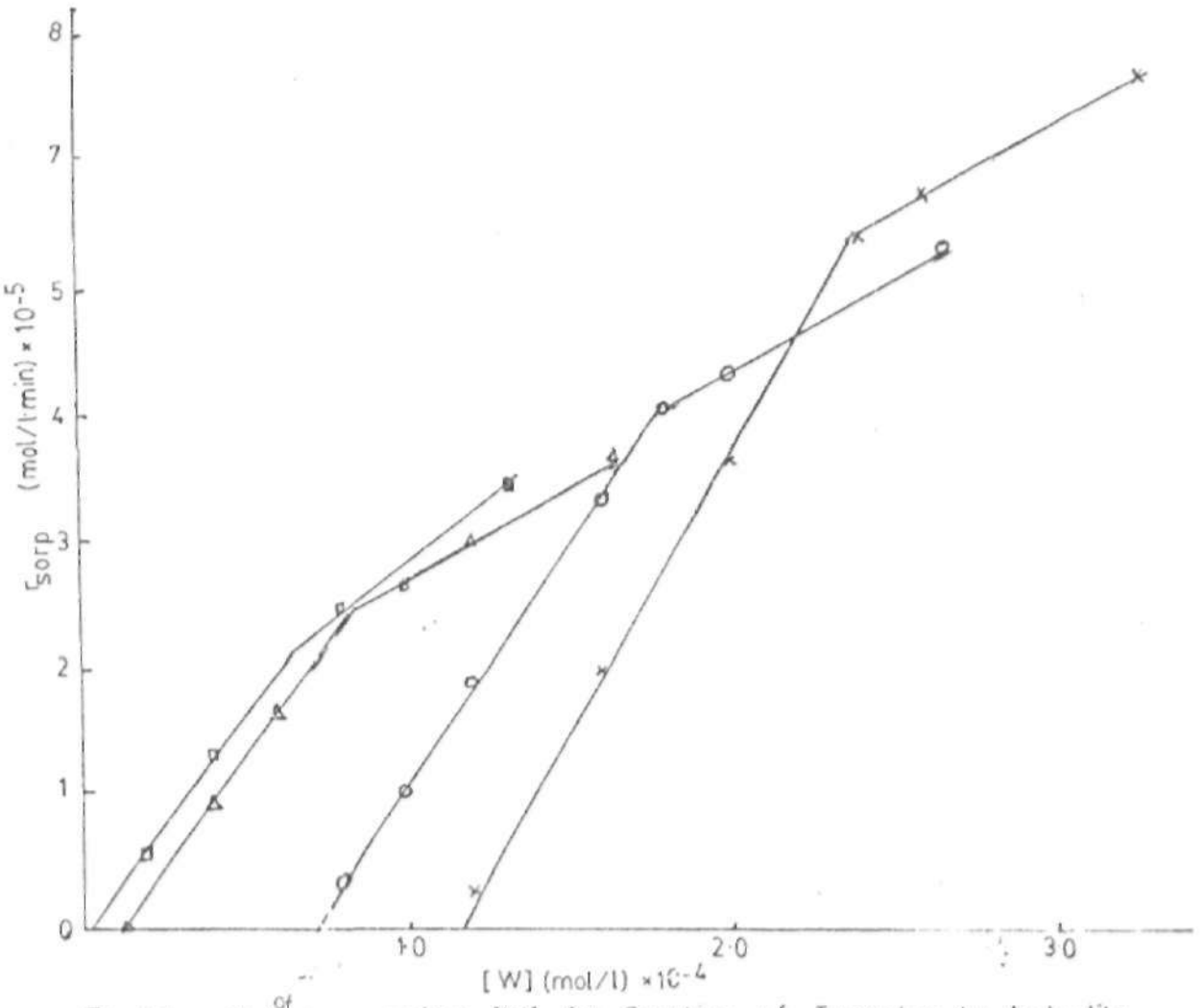


Fig 5-11a: Plot of S_{sorp} against [W] for Sorption of Tungsten by Amberlite IRA 400Cl⁻ Resin

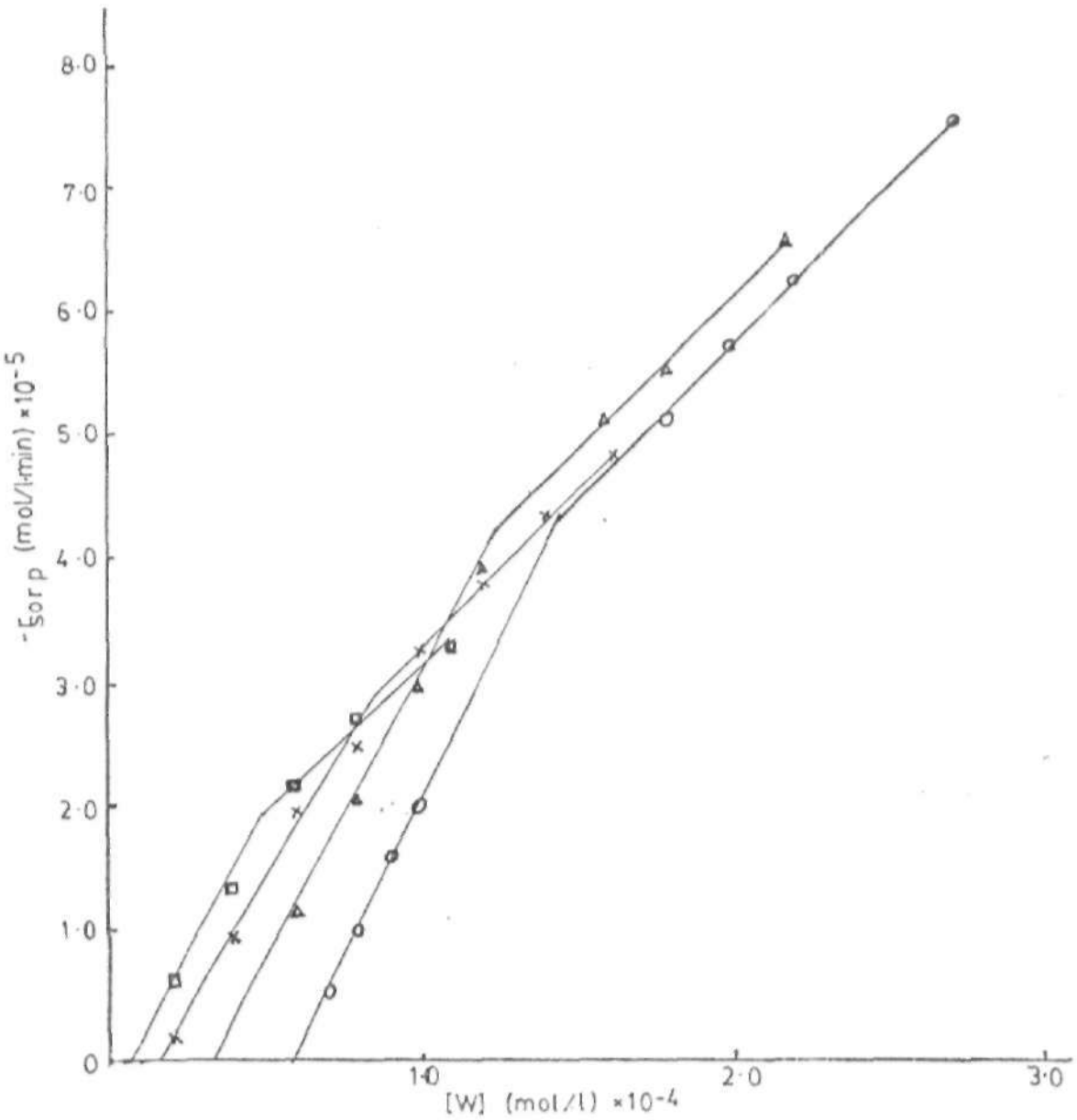


Fig 5-11b: Plot of r_{sorp} against [W] for Sorption of Tungsten by IONAC AD 54 OH^- Resin

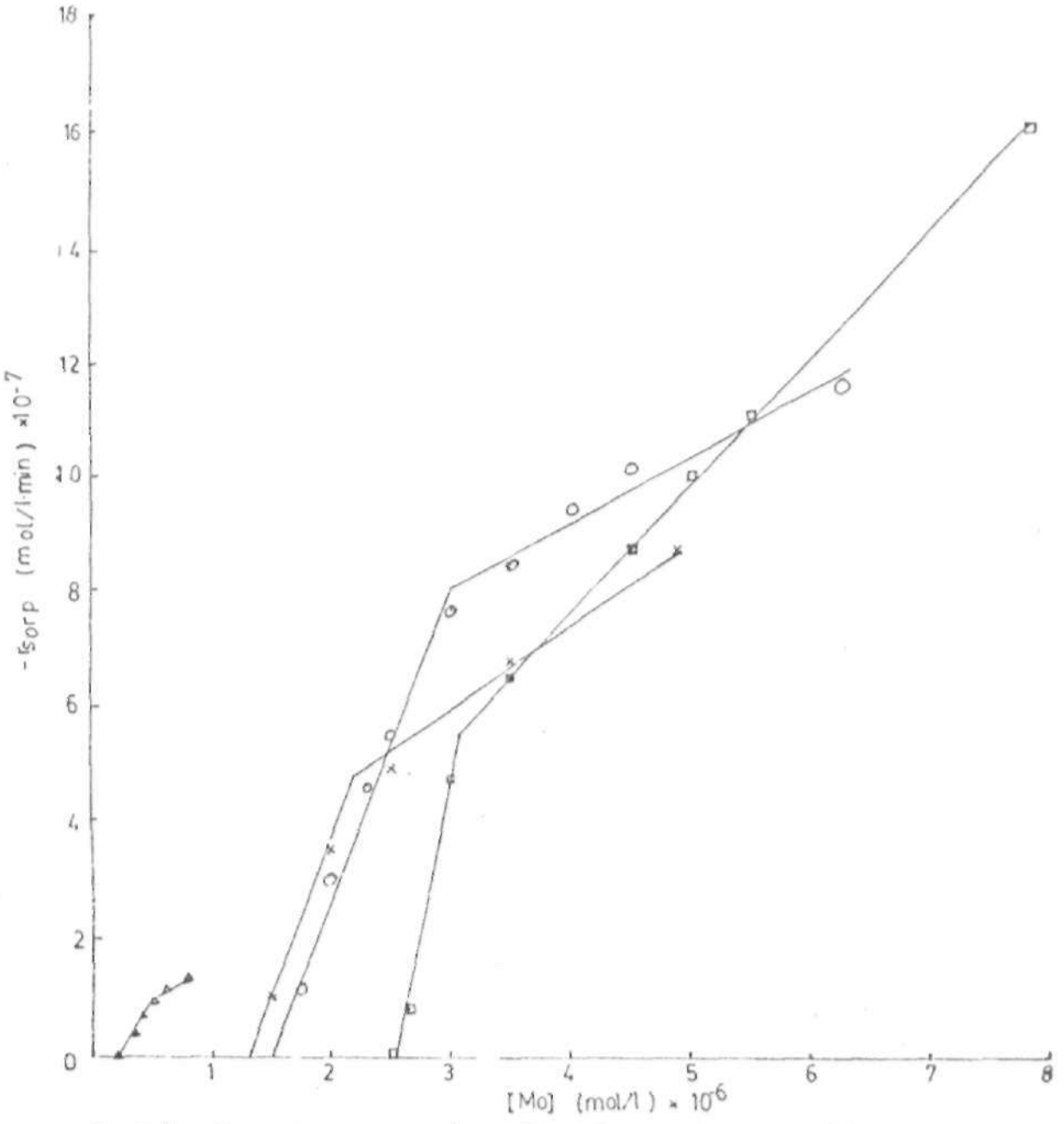


Fig 5-IIc: Plot of r_{sorp} against [Mo] for Sorption of Molybdenum by Amberlite IRA 400 Cl^- Resin

sites:

$$[Sorb] = [Sorb]_o * (\theta \exp(-K_1 t) + (1-\theta)\exp(-K_2 t)) \qquad (5.6)$$

Where θ = fraction of metal ions sorbed by the first active site, with sorption rate constant K_1

$1 - \theta$ = fraction of metal ions sorbed by the second active site with sorption rate constant K_2.

With the evaluated values of K_1, K_2 and θ from the plot of r_{sorp} against concentration (Figures 5-11,b & c), a simple computer program was written in BASIC (see Appendix) to evaluate the analytical concentration at any time, t. The summary of the values of K_1, K_2 and θ obtained is presented in table 5-3.

TABLE 5-3 SUMMARY OF THE VALUES OF K_1, K_2 and θ

Parameter	Sorption of tungsten by amberlite 400 Cl^- resin	Sorption of tungsten by AD 54 OH^-	Sorption of molybdenum by amberlite 400 Cl^- resin
K_1 (min^{-1})	0.1381	0.2566	0.5150
K_2 (min^{-1})	0.4055	0.5150	1.0050
θ	0.4500	0.5600	0.5400
$[Sorb]_o$ (mol/l)	2.66×10^{-4}	2.73×10^{-4}	7.82×10^{-6}

The two sites model (equation 5.6), when tested was not in consonance with the experimentally obtained data, rather a remarkable disagreement was also observed (see Table A-1). The sorption process in all the systems starts to approach

equilibrium within the first ten minutes of the process.

The recent work [Iyuke, 1994] done in this field showed some good degrees of agreement between the two active sites irreversible first order model with the experimentally obtained data to about 60 minutes of the sorption of molybdenum by amberlite IRA 400 Cl^- ion exchange resin. This is completely in contrast to what is obtained in this present work. The review of literature, the work done by Iyuke [Iyuke, 1994], and the present work are evidences that sorption is an equilibrium process.The present work further reveals that sorption is as well a fast process that approaches equilibrium in about 10 minutes of the process. The model thus proposed by Iyuke does not comply with either of these, and hence must be re-examined.

With the established fact that sorption is a reversible process, coupled with the assumptions of the presence of two active sites in the resins, a two active sites first order equilibrium model was proposed as follows:

$$C = (C_0-C_e)*(X+Y) + C_e \qquad (5.7)$$

where $X = \theta*\exp(-C_0/(C_0-C_e))*K_1t$

$Y = (1-\theta)*\exp(-C_0/(C_0-C_e))*K_2t$

C_0 = initial concentration

C_e = equilibrium concentration

With the values of K_1, K_2 and θ evaluated (Table 5-3), again, a simple computer program was written in BASIC to evaluate the analytical concentration of the sorbent at any time, t. When each set of these parameters (K_1, K_2, and θ) was

tested, a high degree of agreement was observed between the experimentally determined concentrations and those evaluated by the model equation (5.7) over the process time of 30 minutes (see **Figure 5-10**). Again, to ascertain the degree of agreement between the two active sites first order reversible model with the experiments, the percentage variations of the concentrations evaluated by model equation (5.7) from those obtained from the experiments were calculated and presented on Table A-2 in the Appendix. Observations of Table A-2 revealed that the two active sites first order reversible model has a maximum deviation of 8.87 % from the experiments, and hence an agreement of over 90% was obtained between this model and the experiments. This validates the assumptions of the existence of two active sites in the resins, and the reversibility of the process.

Equation (5.7) can be written in detail for each of the sorption processes as follows:

(1) For sorption of tungsten by amberlite IRA 400 Cl^- ion-exchange resin

$$[W] = ([W]_o - [W]_e) * (0.45 * \exp(\frac{-[W]_o}{[W]_o - [W]_e}) K_1 t + 0.55 \exp(\frac{-[W]}{[W]_o - [W]_e}) * K_2 t) + [W]_e \qquad (5.8)$$

(2) For sorption of tungsten by IONAC AD 54 OH^- ion exchange resin

$$[W] = ([W]_o - [W]_e) * (0.56\exp(\frac{-[W]_o}{[W]_o - [W]_e}) * K_1 t$$

$$+0.44\exp(-\frac{[W]_o}{[W]_o - [W]_e}) * K_2 t) + [W]_e \qquad (5.9)$$

(3) For sorption of molybdenum by amberlite IRA 400 Cl^- ion exchange resins

$$[Mo] = ([Mo]_o - [Mo]_e) * (0.54\exp(\frac{-[Mo]_o}{[Mo]_o - [Mo]_e}) * K_1 t$$

$$+0.46\exp(-\frac{[Mo]_o}{[Mo]_o - [Mo]_e}) * K_2 t) + [Mo]_e \qquad (5.10)$$

The model equation (5.7) was then tested on the entire experimental points of Figures 5-1a, 5-1b and 5-1c. Good agreement was also observed between the experimentally obtained concentrations and those obtained by the model equation (5.7). These are presented on Figures 5-12a, b & c. The percentage variations of model equation (5.7) from the experiments is present on Table A-3 in the Appendix.

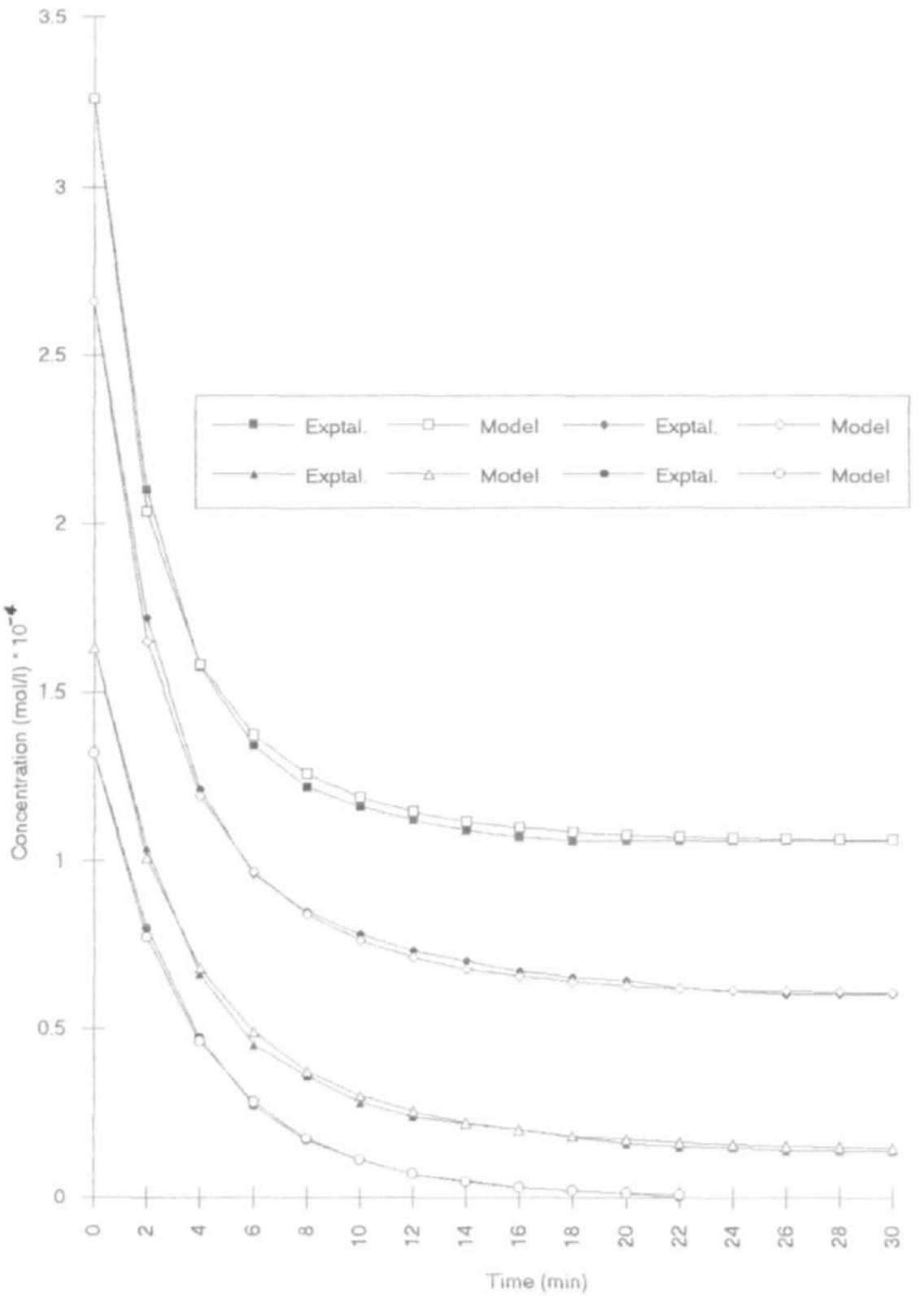


Fig.12a: Experiments Compared With The 2-Active Sites Reversible Model For Sorption Of Tungsten By Amberlite IRA 400 Cl^- Ion Exchange Resin

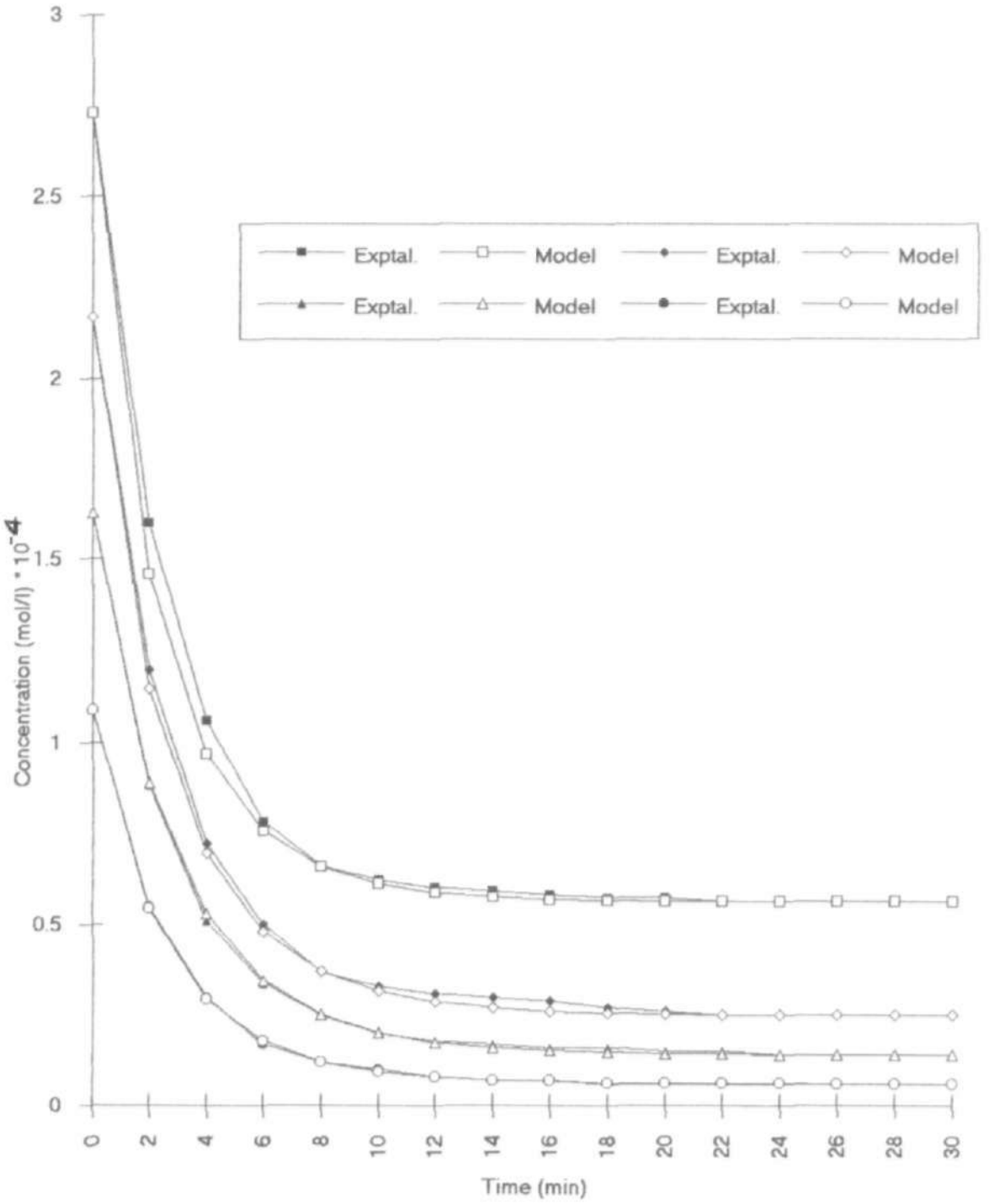


Fig.12b: Experiments Compared With The 2-Active Sites Reversible Model For Sorption Of Tungsten By IONAC AD 54 OH^- Ion Exchange Resin

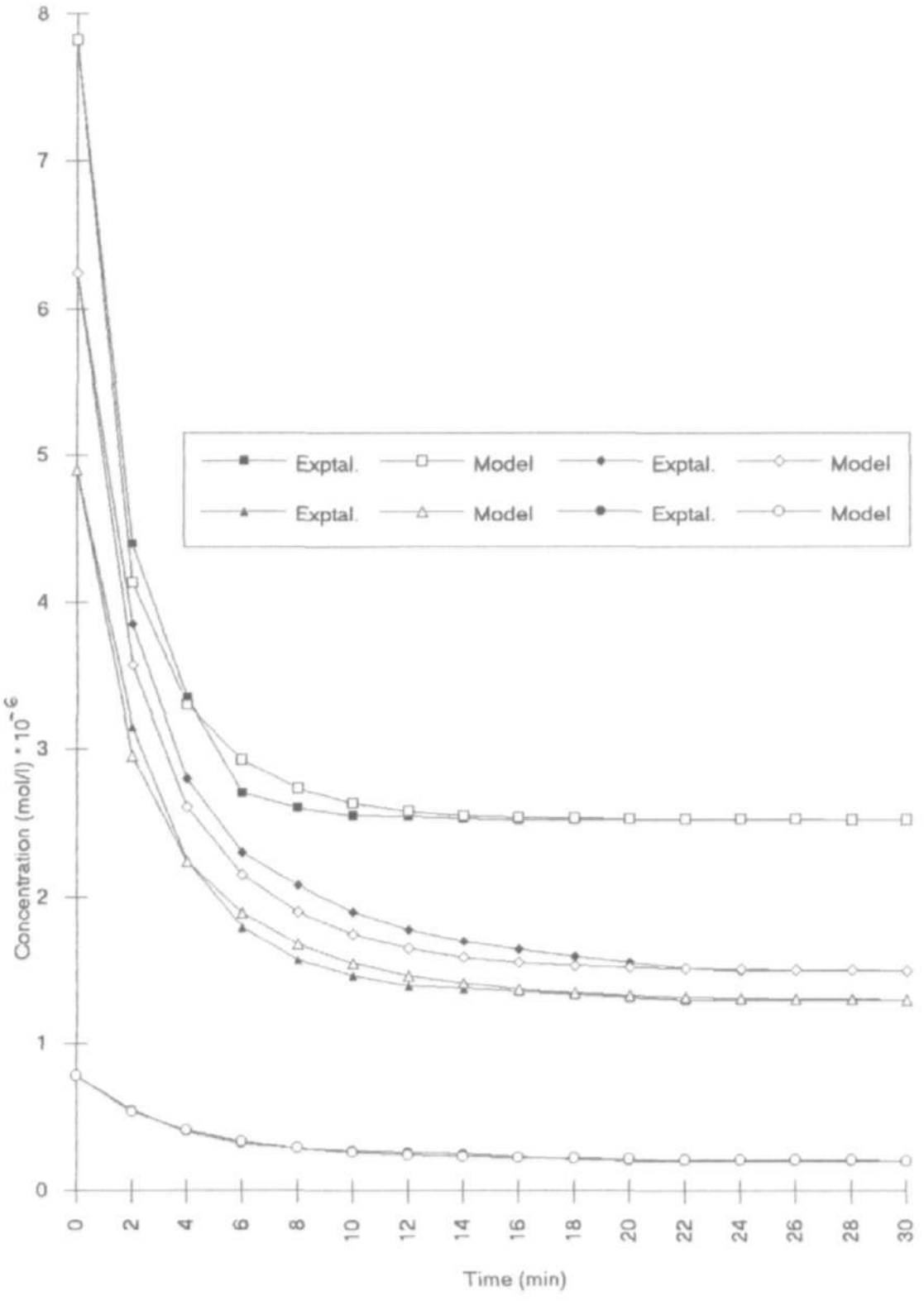


Fig.12c: Experiments Compared With The 2-Active Sites Reversible Model For Sorption Of Molybdenum By Amberlite IRA 400 Cl^- Ion Exchange Resin

In a more generalised term, model equation (5.7) has been found to adequately describe the other three model equations 5.8, 5.9 & 5.10 for the respective sorption of tungsten by amberlite IRA 400 Cl^- ion-exchange resin, sorption of tungsten by IONAC AD 54 OH^- ion-exchange resin and sorption of molybdenum by amberlite IRA 400 Cl^- ion-exchange resin

5.3 COMPARISON BETWEEN THE RATE OF SORPTION OF TUNGSTEN AND MOLYBDENUM BY AMBERLITE 400 Cl^- AND AD54 OH^- ION-EXCHANGE RESINS

The degree of cross-linking of the resin matrix has an obvious effect on the physical and mechanical properties of the resin. A resin with low degree of cross-linkage swells considerably in water and may be smeared or possibly dissolved. But a highly cross-linked structure enhances better mechanical properties, higher selectivity, lower pore size, lower swelling capacity and low rate of ion-exchange.

The rate of sorption of tungsten by amberlite IRA 400 Cl^- ion-exchange resin was found to be higher than that by IONAC AD 54 OH^- ion-exchange resin. Though the degree of cross-linkage is not specified for IONAC AD 54 OH^- ion-exchange resin, a better mechanical property was observed during the sorption of tungsten by this resin. It was also noticed that it swells to a lesser degree than its amberlite IRA 400 Cl^- counterpart which swell considerably in both the tungsten and molybdenum solutions and starts to dissolve at temperatures higher than 40^0C in the same solutions.

The activation energy of sorption revealed that more energy (32.50KJ) is needed to set the sorption of tungsten by IONAC AD 54 OH^- in progress than the energy (21.90KJ) required for the sorption of tungsten by amberlite IRA 400 Cl^- ion-exchange resin and 11.60KJ required for the sorption of molybdenum by amberlite 400 Cl^- ion-exchange resin. Activation energy for sorption greatly influences the sorption rate constant, K_{sorp} which is a measure of fastness or slowness of sorption rates. The bigger the E_{sorp}, the smaller the K_{sorp} and hence the lower the rate. Smaller values of E_{sorp} imply higher values of K_{sorp} and hence higher the rate. Therefore, from the values obtained for the activation energies (Table 5-2), it is clear that sorption of molybdenum by amberlite 400Cl^- ion-exchange resin is faster than the sorption of tungsten by the same resin, which is in turn faster than the sorption of tungsten by IONAC AD 54 OH^- ion-exchange resin.

One of the advantages of macromolecular catalyst is to obtain products that are free from the catalyst. As aforementioned in this section, amberlite 400 Cl^- resin starts to dissolve at temperatures greater than 40 ^0C; and consequently the sorbent in the core of the resin will be released into the ambient solution. In effect, the use of this type of macromolecular catalyst (tungsten or molybdenum anchored to amberlite 400 Cl^- resin) to catalyse reaction at temperatures up to 50-70 ^0C will not achieve the desired advantage, rather some impurities such as the dissolved resin particles would be

introduced, and the products obtained would not be catalyst-free. At such temperatures therefore, catalysis will no longer take place in the core of the resin, but in direct contact with the substrate.

On the other hand, a good mechanical property was observed with AD 54 OH^- ion-exchange resin even at 70 ^0C. Since the macromolecular catalyst is not dissolved in the sorbent even at 70 ^0C, it is possible to obtain catalyst-free product when it is employed as catalyst in any catalytic reaction.

CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

6.1 CONCLUSION

The sorption of tungsten by both amberlite IRA 400 Cl^- and IONAC AD 54 OH^- ion-exchange resins and the sorption of molybdenum by amberlite IRA 400 Cl^- ion-exchange resin have been carried out. The operating temperature (40 ^0C) was same for all the three processes. The other operating conditions were as follows:

(1) 0.2g weight of amberlite IRA 400 Cl^- ion exchange resin for sorption of tungsten (initial concentration was $2.66x10^{-4}$ mol/l).

(2) 0.4g weight of resin for the sorption of tungsten (where initial concentration was $2.73x10^{-4}$ mol/l) by AD 54 OH^- ion-exchange resin.

(3) 0.4g weight of amberlite 400 Cl^- ion-exchange resin for sorption of molybdenum (initial concentration was $7.82x10^{-6}$ mol/l).

In all the three systems, the sorption process was found to be first-order with respect to sorbent (tungsten or molybdenum) concentration. With respect to the amount of resin, first-order was obtained for sorption of molybdenum by amberlite IRA 400 Cl^- ion-exchange resin while fractional orders were observed for sorption of tungsten by both amberlite IRA 400 Cl^- and AD 54 OH^- ion-exchange resins. Order with respect to

amount of resin for sorption of tungsten by amberlite IRA 400 Cl^- = 1.2. Order with respect to amount of resin for sorption of tungsten by AD 54 OH^- =1.3.

The sorption of tungsten by both amberlite IRA 400 Cl^- and AD 54 OH^- ion-exchange resins, and the sorption of molybdenum by amberlite IRA 400 Cl^- ion-exchange resin are fast processes which pratically attain equilibrium within the first ten minutes of the process in each case.

Analyses of the kinetic data at each stated conditions proved the existence of two active sites in the resins which is in consonance with the conceived idea that the preparation of the resin leads to non-uniformity of the surface of the resins. The irreversible two active sites model proposed was not in agreement with the experimentally obtained data at time,t>10 minutes. Nevertheless, the reversible two active sites model proposed was in harmony with the experimental data to over 90% confidence limits and spread over the whole process time (30 minutes). This is a proof that sorption is a reversible process. Therefore it could be concluded that sorption of tungsten by both amberlite IRA 400 Cl^- and AD 54 OH^- ion-exchange resins and the sorption of molybdenum by amberlite IRA 400 Cl^- are fast and equilibrium processes. A more generalized two active sites first order reversible model equation that fit these processes is given below:

$$C = (C_0 - C_e) * (X + Y) + C_e \qquad (6.1)$$

where $X = 8 * \exp(-(C_0/(C_0-C_e)) * K_2 t)$

$Y = (1-9) * \exp(-(C_0/(C_r C_e)) * K_2 t)$

C_0 = initial concentration of sorbent and

C_e = equilibrium concentration of sorbent

For each set of conditions, the equation (6.1) is presented as follows:

(1) For sorption of tungsten by amberlite IRA 400 CI" ion exchange resin

*m - (im $_0$- Mm) *(0.45 *SXP (-p-r_____r£r-) ^ t*

+0.S5exp(*w l ^ w j * ^ * ^ '* (6 ' 2)

2) For sorption of tungsten by AD IONAC 54 OH" ion exchange resin

[m=am$_0$-[m$_e$)*(o.56exp(*$_m$™*M >**i

+0 .44exp{ ~ $_m$ *[M$_o$l* > *JC>t> * lW] $_\#$ (6.3)

(3) For sorption of molybdenum by amberlite IRA 400 Cl^- ion exchange resins

$$[Mo] = ([Mo]_o - [Mo]_e) * (0.54\exp(\frac{-[Mo]_o}{[Mo]_o - [Mo]_e}) * K_1 t$$

$$+0.46\exp(-\frac{[Mo]_o}{[Mo]_o - [Mo]_e}) * K_2 t) + [Mo]_e \qquad (6.4)$$

A comparison of the three sorption model equations 6.2, 6.3 and 6.4 shows that all three model equations can be described by a single model equation 6.1, except that the parameters K_1, K_2, θ and sorbent initial concentration, C_0 will be fixed into the equation as obtained from individual sorption process.

The amberlite IRA 400 Cl^- ion-exchange resins start to dissolve in both tungsten and molybdenum solutions at temperatures slightly higher than 40 ^{0}C, while the IONAC AD 54 OH^- ion-exchange resin was mechanically stable in tungsten solution even at 70 ^{0}C operating temperature. Though amberlite IRA 400 Cl^- dissolved in the considered solutions, lesser energy (11.60KJ) was required to set the sorption of molybdenum by it in progress than the energy (21.90KJ) required for the sorption of tungsten by the same resin and the energy (32.50KJ) required for the sorption of tungsten by IONAC AD 54 OH^- ion-exchange resin. This is an indication that the rate of sorption of molybdenum by amberlite IRA 400 Cl^- ion-exchange resin is higher

than the sorption of tungsten by the same resin which is in turn higher than the sorption of tungsten by IONAC AD 54 OH^- ion-exchange resin.

6.2 RECOMMENDATIONS

The difficulties encountered in the course of this work, and the results obtained in the work have necessitated the following recommendations:

(1) Amberlite IRA 400 Cl^- ion-exchange resin should not be employed as a tungsten- or molybdenum- macro-molecular catalyst in any catalytic reaction taking place at temperatures higher than 40 ^0C since the product would not be free from impurities introduced by the dissolved resins at such temperatures. Also, at such temperatures catalyst - free products can not be obtained.

(2) AD 54 OH^- ion-exchange resin (though it has low rate of exchange) should better be employed in catalyzing reactions at temperatures higher than 40 ^0C since it has higher selectivity and better mechanical properties than amberlite 400 Cl^- ion-exchange resin.

(3) More research should be carried out to further investigate the effect other sorbents/or resins types will exert on the sorption of such sorbents.

(4) The Department and any other interested institution(s) should assist any researcher that go into researching on this topic as there were difficulties encountered in obtaining the resins and the needed chemicals for the sorption processes.

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APPENDIX 1

TABLE A-1 COMPARISON BETWEEN ONE AND TWO ACTIVE SITE(S) IRREVERSIBLE FIRST ORDER MODELS WITH EXPERIMENTAL DATA

(a) For sorption of tungsten by amberlite 400 Cl^- ion-exchange resin.

Time (min)	Concentration (mol/l) $x10^{-4}$				
	Experimental	Model		% Variation from Experimental	
		One site	Two sites	One site	Two sites
0	2.66	2.660	2.660	0.00	0.00
2	1.72	1.568	1.558	8.84	9.42
4	1.21	0.925	0.978	23.55	19.17
6	0.96	0.545	0.651	43.23	32.19
8	0.85	0.321	0.454	62.24	46.59
10	0.78	0.189	0.326	75.77	58.21
12	0.73	0.112	0.240	84.66	67.12
14	0.70	0.066	0.178	90.57	74.57
16	0.67	0.039	0.134	94.18	80.00
18	0.65	0.023	0.101	96.46	84.46
20	0.64	0.014	0.076	97.81	88.13

(b) For sorption of tungsten by AD 54 OH^- ion-exchange resin.

Time (min)	Concentration (mol/l) $x10^{-4}$				
	Experimental	Model		% Variation from Experimental	
		One site	Two sites	One site	Two sites
0	2.73	2.730	2.730	0.00	0.00
2	1.60	1.717	1.344	-7.31	16.00
4	1.06	1.079	0.701	-1.79	33.90
6	0.78	0.679	0.383	12.95	50.90
8	0.66	0.427	0.216	35.30	67.30
10	0.62	0.268	0.124	56.77	80.00
12	0.60	0.169	0.073	71.83	87.80
14	0.59	0.106	0.043	82.03	92.70
16	0.58	0.067	0.026	88.45	95.50
18	0.57	0.042	0.015	92.63	97.40
20	0.57	0.026	0.009	95.44	98.40

(c) For sorption of molybdenum by amberlite 400 Cl^- ion-exchange resin.

Time (min)	Concentrations (mol/l) $x10^{-6}$				
	Experimental	Model		% Variation from Experimental	
		One Site	Two Sites	One Site	Two Sites
0	7.82	7.820	7.820	0.00	0.00
2	4.40	5.125	3.200	-16.48	27.27
4	3.35	3.359	1.808	-0.27	46.03
6	2.70	2.201	1.129	18.48	58.19
8	2.60	1.442	0.721	44.54	72.27
10	2.55	0.945	0.463	62.94	81.84
12	2.54	0.620	0.297	75.59	88.31
14	2.53	0.406	0.191	83.95	92.45
16	2.52	0.266	0.123	89.44	95.12
18	2.52	0.174	0.079	93.10	96.87
20	2.52	0.114	0.051	94.72	97.98

APPENDIX 2

TABLE A-2 COMPARISON OF TWO ACTIVE SITES REVERSIBLE MODEL WITH THE EXPERIMENTAL DATA

(a) Sorption of tungsten by amberlite IRA 400 Cl^- Ion-exchange Resin

Time (min)	Concentration (mol/l) $x10^{-4}$		
	Experimental	Model	% Agreement with Experimental Data
0	2.66	2.660	0.00
2	1.72	1.647	-4.24
4	1.21	1.194	-1.32
6	0.96	0.967	0.73
8	0.85	0.840	-1.18
10	0.78	0.762	-2.31
12	0.73	0.711	-2.60
14	0.70	0.677	-3.29
16	0.67	0.654	-2.39
18	0.65	0.638	-1.85
20	0.64	0.626	-2.19
22	0.62	0.618	-0.32
24	0.60	0.613	0.49
26	0.60	0.609	1.50
28	0.60	0.606	1.00
30	0.60	0.604	0.67

(b) Sorption of tungsten by IONAC AD 54 OH^- Ion-exchange Resin

Time (min)	Concentration (mol/l) $x10^{-4}$		
	Experimental	Model	% Agreement with Experimental Data
0	2.73	2.730	0.00
2	1.60	1.459	8.81
4	1.06	0.966	8.87
6	0.78	0.755	3.21
8	0.66	0.657	0.46
10	0.62	0.610	1.61
12	0.60	0.586	2.33
14	0.59	0.573	2.88
16	0.58	0.567	2.24
18	0.57	0.564	1.05
20	0.57	0.562	1.40
22	0.56	0.561	-0.18
24	0.56	0.561	-0.18
26	0.56	0.560	0.00
28	0.56	0.560	0.00
30	0.56	0.560	0.00

(c) Sorption of molybdenum by amberlite IRA 400 Cl^- exchange Resin

Time (min)	Concentration (mol/l) $x10^{-6}$		
	Experimental	Model	% Agreement with Experimental Data
0	7.82	7.820	0.00
2	4.40	4.136	6.00
4	3.35	3.302	1.43
6	2.70	2.924	-4.43
8	2.60	2.730	-5.00
10	2.55	2.630	-3.14
12	2.54	2.580	-1.46
14	2.53	2.550	-0.79
16	2.52	2.536	-0.64
18	2.52	2.528	-0.32
20	2.52	2.524	-0.16
22	2.52	2.522	-0.08
24	2.52	2.521	-0.40
26	2.52	2.521	0.00
28	2.52	2.520	0.00
30	2.52	2.520	0.00

TABLE A-3 COMPARISON OF TWO ACTIVE SITES REVERSIBLE MODEL WITH THE EXPERIMENTAL DATA FOR EACH SERIES OF EXPERIMENT

(a) Sorption of tungsten by amberlite IRA 400 Cl^- Ion-exchange Resin

Time (min)	Concentration (mol/l) x 10^{-4}		
	Experimental	Model	% Agreement with Experimental Data
0	3.26	3.260	0.00
2	2.10	2.035	3.10
4	1.57	1.580	-0.64
6	1.34	1.371	-2.31
8	1.22	1.258	-3.12
10	1.16	1.189	-2.50
12	1.12	1.145	-2.23
14	1.09	1.116	-2.39
16	1.07	1.097	-2.52
18	1.06	1.085	-2.36
20	1.06	1.076	-1.51
22	1.06	1.071	-1.04
24	1.06	1.067	-0.66
26	1.06	1.065	-0.47
28	1.06	1.063	-0.28
30	1.06	1.062	-0.19

Time (min)	Concentration (mol/l) x 10^{-4}		
	Experimental	Model	% Agreement with Experimental Data
0	1.63	1.630	0.00
2	1.04	1.011	2.79
4	0.66	0.678	-2.73
6	0.45	0.488	-8.44
8	0.36	0.374	-3.89
10	0.28	0.302	-7.86
12	0.24	0.255	-6.25
14	0.22	0.222	-0.91
16	0.20	0.200	0.00
18	0.18	0.183	-1.67
20	0.16	0.172	-7.50
22	0.15	0.163	-8.67
24	0.15	0.157	-4.67
26	0.15	0.153	-9.29
28	0.14	0.149	-6.43
30	0.14	0.147	-5.00

Time (min)	Concentration (mol/l) x 10^{-4}		
	Experimental	Model	% Agreement with Experimental Data
0	1.320	1.320	0.00
2	0.800	0.771	3.63
4	0.470	0.461	1.92
6	0.270	0.281	-4.07
8	0.170	0.175	-2.94
10	0.110	0.110	0.00
12	0.070	0.071	-1.43
14	0.050	0.046	8.00
16	0.030	0.030	0.00
18	0.020	0.020	0.00
20	0.015	0.013	7.14
22	0.000	0.009	

(b) Sorption of tungsten by IONAC AD 54 OH^- Ion-exchange Resin

Time (min)	Concentration (mol/l) x10^{-4}		
	Experimental	Model	% Agreement with Experimental Data
0	2.17	2.17	0.00
2	1.20	1.15	4.33
4	0.72	0.695	3.47
6	0.50	0.481	3.80
8	0.37	0.373	0.81
10	0.33	0.318	3.64
12	0.31	0.288	7.10
14	0.30	0.271	9.67
16	0.29	0.262	9.66
18	0.27	0.257	4.82
20	0.26	0.254	2.31
22	0.25	0.252	-0.80
24	0.25	0.251	-0.40
26	0.25	0.251	-0.40
28	0.25	0.250	0.00
30	0.25	0.250	0.00

Time (min)	Concentration (mol/l) $x10^{-4}$		
	Experimental	Model	% Agreement with Experimental Data
0	1.63	1.630	0.00
2	0.88	0.889	-1.02
4	0.51	0.529	-3.73
6	0.34	0.348	-2.35
8	0.25	0.254	-1.60
10	0.20	0.203	-1.50
12	0.18	0.176	2.22
14	0.17	0.160	5.88
16	0.16	0.152	5.00
18	0.16	0.147	8.13
20	0.15	0.144	4.00
22	0.15	0.142	5.33
24	0.14	0.141	0.71
26	0.14	0.141	-0.71
28	0.14	0.141	-0.71
30	0.14	0.140	0.00

Time (min)	Concentration (mol/l) $x10^{-4}$		
	Experimental	Model	% Agreement with Experimental Data
0	1.09	1.090	0.00
2	0.55	0.544	1.09
4	0.30	0.296	1.33
6	0.17	0.179	-5.29
8	0.12	0.122	-1.67
10	0.10	0.093	7.00
12	0.08	0.078	2.50
14	0.07	0.070	0.00
16	0.07	0.070	0.00
18	0.06	0.063	-5.00
20	0.06	0.062	-3.33
22	0.06	0.061	-1.67
24	0.06	0.061	-1.67
26	0.06	0.060	0.00
28	0.06	0.060	0.00
30	0.06	0.060	0.00

(c) Sorption of molybdenum by amberlite IRA 400 Cl^- exchange Resin

Time (min)	Concentration (mol/l) $x10^{-6}$		
	Experimental	Model	% Agreement with Experimental Data
0	6.25	6.250	0.00
2	3.85	3.574	7.17
4	2.80	2.610	6.79
6	2.30	2.151	6.48
8	2.08	1.899	8.70
10	1.90	1.748	8.00
12	1.78	1.655	7.02
14	1.70	1.597	6.06
16	1.65	1.561	5.39
18	1.60	1.538	3.88
20	1.56	1.524	2.31
22	1.52	1.515	0.33
24	1.50	1.509	-0.60
26	1.50	1.506	-0.40
28	1.50	1.504	-0.27
0	1.50	1.502	-0.13

Time (min)	Concentration (mol/l) $x10^{-6}$		
	Experimental	Model	% Agreement with Experimental Data
0	4.90	4.900	0.00
2	3.15	2.955	6.19
4	2.25	2.242	0.36
6	1.80	1.892	-5.11
8	1.58	1.687	-6.77
10	1.47	1.556	-5.85
12	1.40	1.470	-5.00
14	1.38	1.414	-2.46
16	1.36	1.376	-1.18
18	1.34	1.350	-0.75
20	1.32	1.334	-0.76
22	1.30	1.322	-1.06
24	1.30	1.315	-1.15
26	1.30	1.310	-0.77
28	1.30	1.307	-0.54
30	1.30	1.304	-0.31

Time (min)	Concentration (mol/l) $x10^{-6}$		
	Experimental	Model	% Agreement with Experimental Data
0	0.78	0.780	0.00
2	0.55	0.537	2.36
4	0.40	0.408	-2.00
6	0.32	0.334	-4.38
8	0.29	0.289	0.35
10	0.27	0.261	3.33
12	0.26	0.242	6.92
14	0.25	0.230	8.00
16	0.23	0.221	3.91
18	0.21	0.215	-2.38
20	0.20	0.210	-5.00
22	0.20	0.207	-3.50
24	0.20	0.205	-2.50
26	0.20	0.204	-2.00
28	0.20	0.203	-1.50
30	0.20	0.202	-1.00

APPENDIX 4

Table A-4 PROPERTIES OF ION EXCHANGE RESINS

	Resin	Grade	Form	Mesh	Moisture content %	Wet density g/ml	Exchange capacity	Cross linkage %	Max. Opt Temp °C	PH range
	Group 1									
1.	Amberlite IRA 400	Standard	Cl^-	14-52	42-48	0.70	Wet:1.4 meq/ml Dry:3.8 meq/g	8	77	1-12
2.	Amberlite IRA 410	Standard	Cl^-	14-52	40-45	0.70	Wet:1.4 meq/ml Dry:3.7 meq/g	8	77	1-12
3.	Amberlite IRA 938	Standard	Cl^-	18-52	72-78	0.64	Dry:3.8 meq/g	-	77	1-14
4.	Duolite A 116	Standard	Cl^-	14-52	43-50	0.76	Wet:1.4 meq/ml	Not Given	75	-
	Group 2									
1.	Amberlite IR 45	Standard	OH^-	14-52	40-45	0.67	Wet:1.9 meq/ml Dry:5.0 meq/g	Not Given	100	1-9
2.	Amberlyst' A-21		Free base		45-53	0.61-0.68	Wet:1.5-1.7 meq/ml Dry:5.0 meq/g	-	100	
3.	Duolite' A 378	Standard	Free base	14-52	55-61	0.70	Wet:1.6 meq/ml	-	100	
	Group 3									
1.	IONAC AD 54		OH^-	14-52	42-56	0.64-0.72	Wet:1.3 meq/ml Dry:4.1 meq/g	Unspecified	-	-
2.	Duolite' A 113	Standard	Cl^-	14-52	48-55	0.73	Wet:1.3 meq/ml	Not Given	100	1-14
3.	Amberlyst' A-26		Cl^-		61-65	0.62-0.69	Wet:0.95-1.1meq/ml Dry:4.1-4.4 meq/g	-	77	-

Source: Laboratory Chemicals & Biochemicals, BDH Chemicals Limited, (1984/1985).

APPENDIX 5

A BASIC PROGRAM TO EVALUATE THE ANALYTICAL CONCENTRATIONS FOR THE IRREVERSIBLE FIRST ORDER MODEL

```
OPEN "b:AKp.bas" FOR OUTPUT AS #1
CLS : Co = ""
     K1 = ""
     K2 = ""
     FOR d = .42 TO .45 STEP .01
PRINT #1, "W Q ="; d, "K1 ="; K1, "K2
="; K2,
FOR t = 0 TO 31 STEP 2
     a = d * EXP(-K1 * t)
     b = (1 - d) * EXP(-K2 * t)
     C = Co * (a + b)
     PRINT #1, t, 10000 * C
     NEXT t: NEXT d: BEEP: BEEP: END
```

APPENDIX 6

A BASIC PROGRAM TO EVALUATE THE ANALYTICAL CONCENTRATIONS FOR THE REVERSIBLE FIRST ORDER MODEL

```
OPEN "AK.bas" FOR OUTPUT AS #1
CLS : Co = ""
     Ce = ""
     K1 = ""
     K2 = ""
     FOR d = .43 TO .47 STEP .01
PRINT #1, "W Q ="; d, "K1 ="; K1, "K2
="; K2, "Ce ="; Ce
FOR t = 0 TO 31 STEP 2
     a = (Co / (Co - Ce)) * K1
     b = (Co / (Co - Ce)) * K2
     X = d * EXP(-a * t)
     Y = (1 - d) * EXP(-b * t)
     C = (Co - Ce) * (X + Y) + Ce
     PRINT #1, t, 10000 * C
     NEXT t: NEXT d: BEEP: BEEP: END
```