ADSORPTION AND PERSISTENCE OF METOXURON AND TEBUTHIURON ON SOIL COLLOIDS AND MODEL CLAY-ORGANO COMPLEXES-A PHYSICO CHEMICAL STUDY

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No part of the thesis has been submitted for any other degree or diploma or has been published. Published part has been fully acknowledged. All the assistance and help received during the course of the investigations have been duly acknowledged by him.

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DECLARATION

I, **Mr.P.CHANDRASEKHAR RAO,** hereby declare that the thesis entitled **"ADSORPTION AND PERSISTENCE OF METOXURON AND TEBUTHIURON ON SOIL COLLOIDS AND MODEL CLAY-ORGANO COMPLEXES - A PHYSICOCHEMICAL STUDY"** submitted to Andhra Pradesh Agricultural University for the degree of **Doctor of Philosophy** is the result of original research work done by me. I also declare that the material contained in the thesis has not been submitted for a degree of any University.

P.Chandrasekhar Rao

(P.CHANDRASEKHAR RAO)

LIST OF ABBREVIATIONS

A°	=	Angstrom unit
A.A.	=	Amount Adsorbed
a.i.	=	active ingradient
APAU	=	Andhra Pradesh Agricultural University
ARI	=	Agricultural Research Institute
CEC	=	Cation Exchange Capacity
CIP	=	Crystalline Ionic Potential
CIR	=	Crystalline Ionic Radius
$Cmolkg^{-1}$	=	Centimoles/kg
EC	=	Electrical conductivity
Eq.C	=	Equilibrium concentration
FC	=	Field Capacity
50% FC	=	50 per cent Field Capacity
FA	=	Fulvic Acid
HA	=	Humic Acid
h	=	Hours
HIP	=	Hydrated Ionic Potential
HIR	=	Hydrated Ionic Radius
ICRISAT	=	International Crops Research Institute For Semi Arid Tropics
I_n.C	=	Initial concentration
IR	=	Infrared
I.U.P.A.C	=	International Union of Pure and Applied Chemists
µg	=	microgram
min	=	minutes
-M	=	montmorillonite

List of Abbreviations (Contd..)

nL = milliliter

mm = millimeter

nm = nanometer

NMR = Nuclear Magnetic Resonance

OM = Organic Matter

PMA = Polymaleic Acid

-R = -Resin

rpm = revolutions per minute

Sat = Saturation

Sm^{-1} = Siemens/meter

TV = titre value

UV = Ultravoilet

X = Chi

EPTC = Ethyl N, N-dipropyl thiol carbamate

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ABSTRACT

The studies on the "Adsorption and Persistence of metoxuron and tebuthiuron on soil colloids and model clay-organo Complexes - A Physico-chemical study" were undertaken to understand the nature and mechanism of interaction of these chemicals with soil colloids in dilute suspensions and to evaluate the role played by clay-organo complexes in the adsorption of these chemicals, using model clay-organo complexes. Polymaleic acid was characterised as a model for soil FA and its interaction with homoionic clays to form model clay-organo complexes was studied. Detailed adsorption of metoxuron and tebuthiuron was studied on homoionic resins to assess their suitability as model adsorbents for homoionic clays. Kinetics and mechanism of persis-tence of metoxuron and tebuthiuron was worked out under

carefully controlled conditions of moisture and temperature as a prelude to using these simple experimental parameters to predict pesticide residues under field conditions.

Montmorillonitic clay was chosen for the study because of large specific surface area and charge, and the effect of cation saturating the exchange complex was evaluated. The clay samples (predominently monmorillonitic) were fractionated to < 2 μ fraction. Homoionic montmorillonites/IR-120 resins were prepared by saturating them with 1M nitrate salts of these ions. The ions chosen belonged to a wide range with respect to ionic properties like charge, size, tendency for complexation and ease of hydration and comprised of H^+, trivalent (Fe - and Al-) divalent 3d ions (Ni-, Cu-, Co- and Zn-), alkaline earth ions (Ca-, Ba, and Mg-) and monovalent ions (K-, Na- and NH_4). Adsorption of metoxuron and tebuthiuron was conducted on these homoionic clay suspensions and resins. The extent of adsorption of both metoxuron and tebuthiuron was governed mainly by the charge and polarizing power of the cations and followed the order H- and trivalent > divalent > monovalent. Among the divalent ions, transition metal ions had a much higher capacity for adsorption as compared to alkaline earth ions. The adsorption isotherms of metoxuron and tebuthiuron on homoionic montmorillonites gave S-shaped isotherms indicating a stronger competition by water

molecules to the surface as compared to the herbicides. The data was analysed by Freundlich equation and a new mathematical equation was used for the analysis of S-shaped isotherms. The analysis of effect of different ionic properties of the exchange cations on the adsorption parameters indicated distinct differences in the nature of binding. Crystalline ion potential was found to be the most important factor governing adsorption, mainly for alkali and alkaline earth ions. The possible mechanisms of bonding include dipole-dipole, ion-dipole and ion-induced dipole interactions mediated through water molecules. The unique grouping of transition metal ions point to the formation of coordination complexes. The variation in adsorption parameters for these ions may be deemed as indirect evidence for such interactions in suspensions. In the case of Fe- and Al-, bonding through hydroxy bridges may be an additional factor to reckon with. Apart from enthalpy considerations, changes in entropy during adsorption may be critical. Based on the extent of adsorption it was concluded that the herbicides are adsorbed mostly on edges and do not penetrate the interlayers of crystal lattice. Ion saturated resins were more similar to organic matter because of extensive organic net work present on them. Hence the effect of exchange cations may be overshadowed. The exchange cations are likely to be involved in similar mechanisms of bonding as in the case of homoionic montmorillonites.

Polymaleic acid was characterised as a synthetic model for soil FA. It was analysed for functional groups. Potentiometric and conductometric titrations carried out for the first time reflected the structural features similar to soil FA. The adsorption of PMA on homoionic clays was much higher as compared to metoxuron and tebuthiuron. The magnitude of adsorption of PMA on different homoionic montmorillonites followed the same order as that of metoxuron and tebuthiuron. The adsorption isotherms were mainly parabolic in nature with a tendency to reach surface saturation. Crystalline ion potential was found to be the most important factor mainly for alkali and alkaline earth ions. The possible mechanisms could be grouped as ion-dipole, ligand exchange, H-bonding and Van der Waal's forces of attraction. Transition metal ions adsorbed much more PMA than the alkaline earth ions and this could be attributed to the formation of coordination bonds between PMA and these ions. The role of entropy genetration was also considered to be an important factor in the adsorption of PMA. The extent of adsorption did not rule out interlayer penetration. The adsorption of PMA on homocationic resins also indicated similar results.

The studies on comparative adsorption of metoxuron and tebuthiuron on model clay organo complexes were attempted for the first time. There was a consistent increase in the adsorption of these herbicides on model montmorillonite-PMA complexes as compared to

cationic montmorillonites. The PMA complexes of alkali and alkaline earth montmorillonites brought about a larger increase in the adsorption of both the herbicides as compared to transition metal ions and Fe-PMA complexes.

The studies on the persistence of metoxuron and tebuthiuron in an alfisol and vertisol under well defined conditions of moisture and temperature showed that these herbicides distribute themselves into two compartments, which may be termed labile and bound pools, as suggested earlier by Hamaker and Goring (1976). There were two distinct path ways for disappearance, a faster one and a much slower one. The rate constants were calculated for the different steps. As a first approximation the rate of re-entry of herbicide from bound pool was considered negligible and first order kinetics was used for entry into bound pool and disappearance from labile pool. The rate of entry into bound pool was high for vertisol as compared to alfisol and decreased with decrease in soil moisture. The rate of degradation was high for alfisol as compared to vertisol. These were related to clay and organic matter content.

Adsorption of metoxuron and tebuthiuron was studied on 2 mm soil fraction, < 50 μ fraction and Humic acid of four soils of Hyderabad. The amount adsorbed per gram of adsorbent decreased in the order HA > < 50 μ soil

fractions > 2 mm soil fractions. The adsorption of metoxuron and tebuthiuron as computed from the 50μ fraction and HA was higher than 2 mm soil fraction. This was attributed the larger specific surface area of the colloidal fraction and the formation of clay-organo complexes in soil.

INTRODUCTION

CHAPTER I

INTRODUCTION

With an increase in the intensity of cultivation, the use of chemicals for control of weeds has become immimnent especially in irrigated agriculture. Most of these chemicals are added to the soil, where they interact mainly with the colloidal fractions of soil. Thus, clays, which constitute the major mineral fraction, and humus, the organic matter fraction are the most important participants in these interactions.

Although it has become necessary to use more and more of these chemicals to meet the growing demands of agricultural production, it has now been clearly shown that, indiscriminate use of these chemicals may pose a danger to the environment (Saroja Raman, 1985). Hence, to strike a balance between these two factors, it is imperative that complete details of their interactions with soil components be known. Detailed physico-chemical studies on the interaction of these chemicals can successfully predict their fate in soil, for more efficient and safer use. Soil adsorption-desorption is the most important factor that controls directly or indirectly all other

factors deciding the fate of soil applied chemicals. Adsorption of a soil applied chemical is an indication of its bioavailability and phytotoxicity. Although, adsorption generally helps in protecting the chemicals from microbial activity and environmental factors like temperature and moisture, it may enhance their degradation to non-toxic products in some cases, like, chloro-s-triazines and carbamates.

Although investigations to determine the exact role of soil coilloids, both mineral and organic, and the mechanism of adsorption of organic chemicals have been going on actively for over two decades, a lot more ground still remains to be covered in this area.

It has been shown, that, when organic matter content exceeds six per cent as is generally found in soils of temperate and cold regions, the interactions of soil-applied chemicals are mostly dominated by organic matter. However, when the organic matter content is less than six per cent, both mineral and organic surfaces are involved in adsorption (Walker and Crawford, 1968). Thus, in tropical soils, which often contain less than six per cent of organic matter and where mineral colloids constitute a much larger percentage, the latter may play the lead role in soil pesticide interactions.

Several earlier workers (Mustafa and Gamar, 1972; Stevenson, 1976; Theng, 1974 and 1979) have shown that mineral surfaces play a very important role in the interaction of soil-applied chemicals. The expanding lattice minerals like montmorillonite and vermiculite are active in adsorption since they have large and active surface as compared to illite and kaolinite (Khan, 1978; Yuen and Hilton, 1962). In addition to surface area and charge, it has been shown that the nature of cation in the exchange complex of clays, especially in montmorillonites, is important in deciding the extent and mechanism of binding of organic chemicals.

Specific types of bonding between the exchange cations and adsorbed organic chemicals have been verified especially through IR techniques in systems containing very little water, indicating that metal ions can bind with the adsorbate through the highly perturbed water molecules in the co-ordination sphere of exchange cations or even directly through co-ordination bonds (Green, 1974; Mortland, 1970).

However, much less information is available about the nature of such interactions in suspensions which are more realistic in field conditions. Under these conditions, the interactions are clouded by the dominating and mediatory role of water molecules

present in the hydration sphere of the cations and outside it. Although scattered accounts on the effect of these cations are available in literature, no systematic investigation seems to have been carried out to test the importance of different ionic properties like charge, radius, ion potential etc. in the binding of these chemicals. In this context, the adsorption on ion saturated resins may serve as important models for studying the interactions between clays and pesticides.

In recent times, it has been realised that the inorganic and organic colloids of soil exist mostly as an intimate complex phase which may be of more relevance in the adsorption of organic chemicals than either of them alone. Very little information concerning the nature, behaviour and importance of clay-organo complexes in the adsorption of soil applied chemicals is available in literature. The possible formation of clay-organo complexes through the interaction of homoionic montmorillonites and soil HA and FA have been reported by Theng and Scharpenseel (1975) and Challa and Raman (1985). The role of clay-organo complexes as adsorbents for soil applied chemicals, is relevant in tropical soils which are mineral dominated and in which organic matter is intimately associated with the clay fraction as clay-

metal-OM complexes. Hance (1969) suggested that, in tropical soils, clay and organic matter may associate in such a manner, that, little of clay mineral surface is accessible to pesticide molecule. The dominant factors determining the nature of clay-organic interactions are the properties of organic compound, water content of the system, nature of the exchangeable cations on the clay surface and the properties of clay mineral (Mortland, 1970). Thus, a study on the formation and binding of model clay-organo complexes and their role in adsorption of soil applied chemicals needs lot more attention than hitherto provided. It is quite clear that polyvalent cations of the soils determine the nature and extent of binding of HA and FA with the clay system (Theng and Scharpens eel, 1975).

Since soil organic constituents like FA and HA are highly complex and difficult to characterise on account of their complex structures and the conformational changes they undergo, the use of model organic polymers of well characterised properties may serve as an important starting point to understand the more complex interactions of their naturally occuring counterparts. Anderson and Russell (1976) proposed that polymaleic acid (PMA) can serve as a model for soil fulvic acid (FA). They observed similarities between PMA and FA in the elemental analysis, IR

spectra and a number of acid hydrolysis products. Linehan (1977) stated that PMA, while structurally similar to FA, has an added advantage of its structural homogeneity, because it is a product of a well defined polymerisation process.

Experience from liberal use of the organic chemicals in more advanced countries has shown that a lot of harm can be done in the form of permanent environmental and ecological damage if their use is not carefully controlled. One of the most important properties of pesticides pertaining to the environment is their persistence, which may be defined as their "residence time" in the soil. It is now well realised, that pesticides should persist in the soil long enough to achieve the intended action but not longer than desired, causing damage to subsequent crops or environment. Persistence of soil applied chemicals is related to their structure, soil properties and other environmental factors like moisture and temperature. Conventional methods of quantifying persistence through periodical analysis of soil samples is empirical and cumbersome and not capable of leading to unified concepts and possible forecasts. In this context, the work initiated by Walker, 0974 and 1976;) Walker and Smith, (1979) to deduce small mathematical models, based on experiments with soils, incubated in the laboratory under well defined conditions, to predict

pesticide residues in field conditions is of great significance. The present day availability of sophisticated computers even in developing countries holds out a great promise to test these hypotheses and models, with the aim of using them for predictions under field conditions.

The present investigation was undertaken keeping in mind the above priorities. Attempt has been made to make a beginning in these frontier areas, which are still nebulous and need more attention.

Metoxuron and Tebuthiuron, which are substituted urea herbicides, were chosen as models for the study. Their choice in the current investigation stems from the fact that they remain structurally neutral and unaltered over a wide range of pH conditions prevalent in soils and are free from other complications like hydrolysis, oxidation and isomerisation which may vitiate the results.

The substituted urea herbicides are of recent origin and are now widely used in India and other places as soil applied herbicides for control of broad leaved weeds and grasses.

The present investigation was undertaken to study the physico-chemical aspects of interactions of metoxuron and tebuthiuron with soil colloidal

constituents with the following objectives.

I To study the mechanism of interactions of metoxuron and tebuthiuron with homoionic clay suspensions and to evaluate the role of exchange cations on their adsorption,

II To study the nature and quantum of adsorption of metoxuron and tebuthiuron on homoionic resins as model adsorbents,

III To synthesize and characterize polymaleic acid (PMA), a model organic polymer and study its interaction with homoionic montmorillonite and also with cationic resins,

IV To prepare model clay-organo complexes with clays by the interaction of PMA with homoionic montmorillonites and to study the nature of adsorption of metoxuron and tebuthiuron on these complexes,

V To study the persistence of metoxuron and tebuthiuron in two different soils keeping in view Walker, (1974 and 1976) and Hamaker and Goring (1976) model of using laboratory incubated soils for prediction of residues in soil, and

VI To study the nature and quantum of adsorption of metoxuron and tebuthiuron on individual mineral and organic colloids of four different soils from

Hyderabad and also on the whole soils to assess their individual and associative effects on the adsorption of these pesticides.

REVIEW OF LITERATURE

CHAPTER II

REVIEW OF LITERATURE

Existing statistics predicts that pesticides worth about 90 billion dollars are likely to be used in 1990's in world agriculture as herbicides, insecticidon and fungicidon (Khan, 1980). This shows the enormity of the problem facing mankind, in keeping these chemicals under proper control so that they do not create more problems than they are intended to solve. The interaction of these chemicals with soil colloidal constituents viz., clays and organic matter is an important factor affecting the fate of these chemicals in the soil environment. In spite of two decades of research, there is lack of precise information on clay - pesticide interaction, clay-OM interaction and the role of clay-organic complexes on the adsorption of pesticides and their bioavailability. The complexity of natural organic matter precludes a clear understanding of interaction between them and clays and pesticides. Hence, model polymers like Polymaleic Acid (PMA) are considered useful in getting a more fundamental knowledge about these interactions. Reliable methods of predicting residues in field from more precise and simpler studies on the laboratory incubated soil, will go a long way in evaluating and combating many of the environmental

problems which have now surfaced, due to extensive and sometimes indiscriminate use of these chemicals.

This review pertains mostly to the factors mentioned above which have formed the basis for defining the objectives of this investigation. The review is organised under the following heads :

1. General structure and properties of substituted urea herbicides with emphasis on metoxuron and tebuthiuron.

2. Physico-chemical studies on the adsorption of herbicides with soil and its constitutents.

3. Factors affecting adsorption-desorption of herbicides

4. Mechanisms of adsorption of herbicides on clays, organic matter and soils

5. Characterisation of humic substances

6. Polymaleic Acid as a model for soil fulvic acid

7. Clay-organo complexes

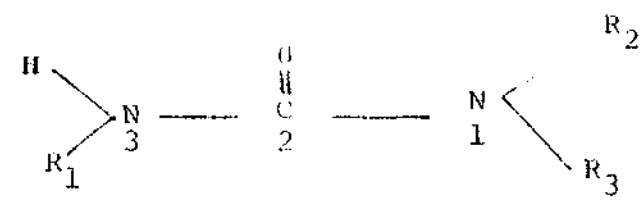
8. Adsorption of pesticides on clay-organo complexes.

9. Persistence of pesticides in soil

2.1 GENERAL STRUCTURE AND PROPERTIES OF SUBSTITUTED UREA HERBICIDES :

The substituted urea herbicides may be considered as derivatives of urea, the first synthetic organic chemical. Most of these herbicides are relatively nonselective and are directly applied to the soil. However, some are active through the foliage.

The general structure of asymmetrically substituted ureas is as follows :



where R_1 represents a non-halogenated or halogenated aromatic hydrocarbon or heterocyclic moiety and R_2 and R_3 represent alkyl/H groups.

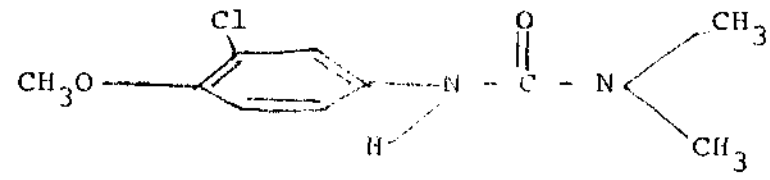
In general, substituted urea herbicides exhibit intermediate melting ranges, low water solubilities and low vapour pressures. These properties, besides determining their use in the field, may also affect their behaviour in various biological environments. These herbicides are stable towards oxidation and hydrolysis under conditions normally prevalent in agriculture. The water and lipoid solubilities of these herbicides are greatly changed by the successive substitutions of hydrogen on the nitrogen groups by a variety of substituents (Worthing, 1979).

Inhibition of Hill reaction of photosynthesis is generally acknowledged as the primary site of action of urea herbicides. This involves the site of oxygen evolution in photosynthesis-II. This prevents the formation of ATP and NADPH which are required for CO_2 assimilation (Rao, 1983).

Two urea herbicides viz., Metoxuron and Tebuthiuron were selected for study, in the present investigation. Their structure and detailed properties are presented below.

2.1.1 Structure and properties of Metoxuron :

Structural formula :



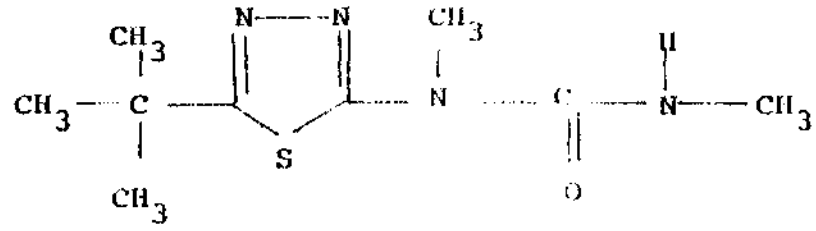
I.U.P.A.C. Name : 3-(3-Chloro-4-methoxy phenyl)-1, 1-dimethyl urea

Molecular formula	:	$C_{10}H_{13}ClN_2O_2$
Molecular weight	:	228.7
Trade name	:	Dosanex w.p.
Appearance	:	Colourless crystalline powder
Melting point	:	126-127°C
Vapour pressure	:	4.2×10^{-8} mm Hg at 20°C
Solubility	:	678 mg/L water at 24°C. Soluble in acetone, hot ethanol and cyclo hexanone.

Mode of action	:	Inhibits Hill reaction
Uses	:	Selective herbicide pre and post emergence in cereals and carrots against black-grass, silky bent grass, wild oats, rye grass and most annual broad leaved weeds. Dosage @ 1.2 to 3.2 kg.a.i./ha.

2.1.2 Structure and properties of Tebuthiuron

Structural formula :



I.U.P.A.C. Name	:	1-(5tertbutyl-1, ,3,4-thiadiazol-2-yl)-1,3-dimethyl urea
Molecular formula	:	$C_9H_{16}N_4OS$
Molecular weight	:	228.32
Trade name	:	Perflan (Europe) Spike (U.S.A., Canada)
Physical appearance	:	Colourless crystals
Melting point	:	161.5 to 161°C
Vapour pressure	:	2.7×10^{-6} mm Hg at 20°C
Solubility	:	2.3 g/L water at 25°C
		6.1 g/L benzene : 170 g/L methanol
		6.1 g/L hexane (all at 25°C)

Mode of action : Soil herbicide with low selectivity; inhibits photosynthesis.

Uses : Total control of herbaceous and woody plants in non-cropped areas; control of woody plants in grassland and pastures.

Some other members of substituted urea herbicides are:

Methabenzthiazuron [1-(benzothiazol-2-yl)-1,3,-dimethyl urea)]

Isoproturon [3-(4-isopropyl phenyl)-1,1 dimethyl urea)]

Metobromuron [3-(4-bromophenyl)-1-methoxy-1-methyl urea]

Linuron [3-(3-4-dichlorophenyl)-1-methoxy-1-methyl urea]

Monolinuron [3-(4-chlorophenyl)-1-methoxy-1-methyl urea]

Monuron [3-(4-chlorophenyl)-1,1-dimethyl urea]

2.2 PHYSICO-CHEMICAL STUDIES ON THE ADSORPTION OF HERBICIDES WITH SOIL AND ITS CONSTITUENTS

Several factors are known to influence the fate of soil applied chemicals. All soil applied organic chemicals must eventually be altered to become a part of the soil complex. Detailed physico-chemical studies on the interaction of herbicides with physical, chemical and edaphic factors of soil, can successfully reveal the actual behaviour and fate of soil applied chemicals.

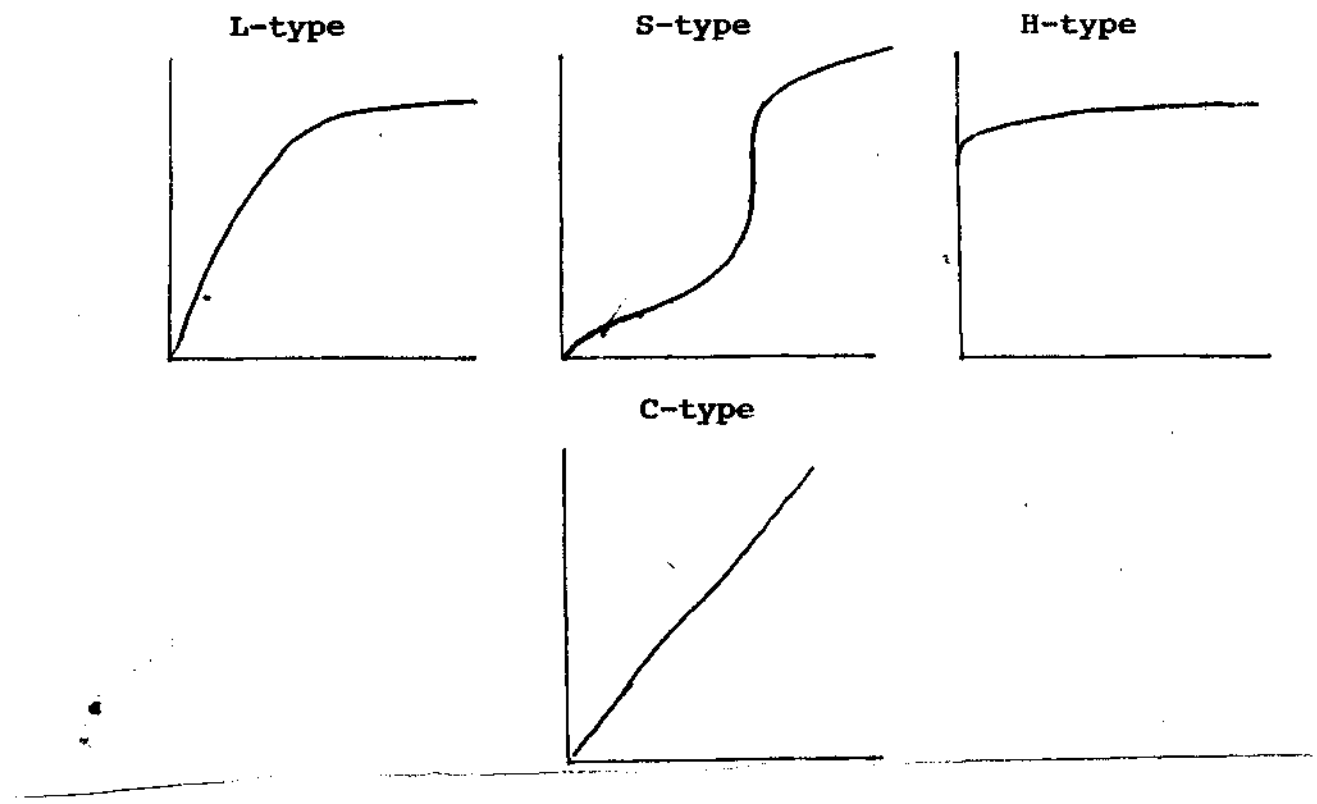
Among the several factors which are known to influence the fate of soil applied chemical, the predominant ones are 1) Adsorption-desorption equilibrium of the chemical in soil, 2) Persistence and degradation, 3) Transport properties and 4) Plant uptake. Adsorption directly or indirectly controls the magnitude of the effect of all the other factors, and is of prime importance. Adsorption is a surface phenomenon, which reduces the concentration of soil applied chemicals in soil solution, thus rendering only a part of the applied chemical available to the target species.

2.2.1 Adsorption isotherms :

Among the various approaches to the study of adsorption phenomenon, adsorption isotherms have been extensively used. An adsorption isotherm represents the relation between amount of herbicide adsorbed per unit weight of adsorbent and the equilibrium concentration of herbicide in solution at a constant temperature. Thus the adsorption isotherms are very useful in quantifying the extent of adsorbed pesticide available to the target. Besides this, several other important thermodynamic parameters like the standard free energy of adsorption, as also enthalpy and entropy of adsorption can be derived from the adsorption data. The slope of the isotherm at any point gives some indication

of the ease with which the species is adsorbed and can give a clue to the nature of binding sites.

Giles et al. (1960) developed an empirical classification of adsorption isotherms into four main classes according to their initial slope (Fig.1). The L-type curve, the "Langmuir" or Freundlich isotherms are the most common type of adsorption isotherms seen for adsorption of solute on a solid from solution. They represent a relatively high affinity between the adsorbent solid surface and the solute, in the initial stages of adsorption. As more sites in the adsorbent are filled, it becomes increasingly difficult for solute molecules to find vacant space on the adsorbent and finally a virtual saturation of the surface occurs.



The S-type isotherms are common when the adsorbent has a high affinity for the solvent. These isotherms usually appear when the solute molecule is mono-functional, has moderate inter-molecular attraction and needs a strong competition for adsorbent sites from molecules of solvent or other adsorbed species. Recognition of such isotherms are of fairly recent origin in soil systems and have been reported by Gaillardon (1975) for adsorption of terbutryne on Ca-montmorrillonite, by Obulapathy (1977) for adsorption of humic acid on cation saturated montmorillonites, Saroja Raman and Ranga Rao (1984) and Shea and Weber (1983) for the adsorption of fluoridone on mineral clays.

The C-type curves indicate constant partitioning of the solute between solution and adsorbent right upto the maximum possible adsorption where, an abrupt change to a horizontal plateau may occur. This type of adsorption is not usually observed in soil-pesticide interactions except when highly non-polar compounds and soils with high organic matter are involved (Chiou et al., 1979).

The H-type curves are rare and occur when there is a very high affinity between the solute and the solid surface. This is a special case of L-shaped

curve in which the solute has such a high affinity, that, in dilute solutions it is completely adsorbed, or at least there is no measurable amount remaining in the solution. The initial part of isotherm is therefore almost vertical. Such isotherms were obtained for the adsorption of paraquat and diquat on Na-or Ca-montmorillonites and on fen peat (Calderbank and Tomlinson, 1969; Khan, 1974).

2.2.1.1 Mathematical models for adsorption :

The adsorption of organic chemicals on soils is generally L-shaped and hence Freundlich and Langmuir adsorption equations have been normally used to describe the adsorption of pesticides by soil, organic matter and clay minerals in a majority of published reports. The Freundlich equation is purely empirical and can be expressed as

$$\frac{x}{m} = K_F C^{\alpha}$$

where $\frac{x}{m}$ = amount adsorbed per unit mass of adsorbent

C = equilibrium concentration, and α is a constant which is less than 1. The equilibrium constant 'K_F' is related to strength of binding and depends on temperature. α and K_F are determined from a logarithmatic transformation of the equation, which is linear

$$\log x/m = \log K_F + \alpha \log C$$

The Freundlich isotherm implies that the heat of adsorption decreases logarithmically as the fraction of surface covered increases. This is attributed to surface heterogeneity. The empirical nature of Freundlich equation is shown by the fact that no limiting value of the surface concentration of the adsorbate is approached as the equilibrium solution concentration of the adsorbate is increased. This is hardly a reasonable conclusion since any adsorbent should have a limited amount of surface and, hence, maximum for the amount of adsorption that can occur. However, although the Freundlich equation has no established theoretical basis, it works well for intermediate concentration in most cases and is frequently used in comparing the adsorption behaviour of a series of adsorbates, on soil. Since the concentration of pesticides hardly reaches a concentration of a few ppm in soils, the theoretical constraints for Freundlich equation, do not pose any problem in interpreting the practical situation.

Many scientists have successfully applied Freundlich equation to the studies concerning adsorption of substituted urea herbicides on soil organic and mineral fractions.

Thus Bailey et al. (1968) reported that the adsorption of 3-phenyl urea, fenuron, monuron, diuron on H- and

Na-montmorillonite confirmed to Freundlich equation. Grower and Hance (1970) used Freundlich isotherm to compare the adsorption of linuron and atrazine on soils in three different soil to water ratios. Carvelli et al. (1975) expressed the adsorption of five substituted urea herbicides in terms of Freundlich K-values and showed the following order of adsorption:

Fenuron < monuron < diuron < linuron < neburon

Usoroh (1976) while studying the adsorption of linuron on soils, obtained Freundlich K-values ranging from 34 (for soils with low clay & OM) to 109 (for soils of high clay & OM). Shive and Wang (1977) expressed the adsorption of monuron and diuron on Taiwan sugarcane soils in terms of Freundlich equation. Peck et al. (1980) expressed the adsorption of diuron on fresh water sediments in California in terms of Freundlich K-values and correlated the adsorption with other soil constituents. Kamalya et al. (1982) observed the adsorption of terbutryne on different homoionic clays to follow Freundlich and Langmuir adsorption isotherms.

2.2.1.2 Langmuir adsorption equation :

In contrast to Freundlich equation, the Langmuir equation has a sound conceptual basis. It was developed for the adsorption of gases on solids

using the following assumptions :

1. The energy of adsorption is constant and independent of surface coverage.

2. Adsorption is on localized sites and there is no interaction between adsorbate molecules.

3. The maximum adsorption possible is that of a complete monolayer.

The Langmuir equation may be written in the form of

$$A = \frac{K_L\ VC}{1 + K_L C}$$

Where A is the amount of substance adsorbed per unit mass of adsorbent, V is the adsorption at full monolayer surface coverage per unit mass of adsorbent, K_L is the equilibrium constant or constant related to binding energy, and C is the equilibrium concentration. K_L can also be written as $K_L = \frac{\theta}{1-\theta} \times \frac{1}{C}$ where θ is the fraction of the surface covered. Thus at $\theta = 0.5$ which is also the state of unit activity for the surface, $K_L = \frac{1}{C_{0.5}}$ where $C_{0.5}$ is the equilibrium concentration at 0.5.

In general the Langmuir equation is not successful in predicting adsorption from solutions

as it is for gases. For soil, the failure of Langmuir equation is often due to untenability of the rigorous assumptions especially the homogeneity of adsorbing sites. Nevertheless, it has been sometimes used in quantifying the adsorption in soils, although the exact significance of the constants V and K_L may not be strictly valid.

2.2.1.3 Mathematical models for S-shaped isotherms :

There has been no report on the mathematical characterisation of S-shaped isotherms. S shaped isotherms are infact a combination of the Freundlich type $A = KC^{\alpha}$ where α is > 1 in initial stages and < 1 in later parts. Quantitatively an S-shaped isotherm represents an initial slow increase in adsorption followed by a steep rise and ending with a slower increase and finally a levelling off in adsorption.

An attempt was made by Saroja Raman (1981) to mathematically characterise a complete S-shaped isotherm from an analogy of the growth curves of crystal growth or heterogenous precipitation of a sparingly soluble substance from a saturated solution. The similarity lies purely in the shape of growth curves in all these cases, so that similar mathematical equation can be applied. Thus equation-1 was used to describe an S-shaped isotherm.

$$\frac{df}{dc} = kf^{2/3}(1-f) \quad \ldots\ldots\ldots \quad 1$$

where $\frac{df}{dc}$-is the rate of increase of adsorption sites with concentration and f is the fraction of herbicide adsorbed at equilibrium concentration 'C', 'f' is calculated as the ratio of the actual amount adsorbed to that adsorbed at maximum surface coverage. According to this, the factor $f^{2/3}$ may be considered as a function of the surface already covered with the organic compound and (1-f) is the fraction of solute present in solution and effective in adsorption. Equation 1 satisfies qualitatively the events in S-shaped isotherms. At very low concentrations in solution $f \longrightarrow 0$ and so the rate of change of adsorption sites $\frac{df}{dc}$ also tends to become zero. Similarly at high concentration in solution $f \longrightarrow 1$ and so $(1-f) \longrightarrow 0$ and the slope tends to become zero. In the intermediate concentrations both f and (1-f) reinforce adsorption and there is a sharp increase in adsorption. The contribution of $f^{2/3}$ term represents the cooperativity of the fraction of solute already adsorbed. The constant 'k' is the specific adsorption rate and decides the ease with which adsorption occurs from solution. To obtain the value of k, the integrated form of equation-1 was used (Saroja Raman, 1981).

$$\chi = \frac{(f^{2/3}+f^{1/3}+1)}{(1-f)} + \sqrt{3}\tan^{-1}\frac{2f^{1/3}+1}{\sqrt{3}} = kC + \sqrt{3}\tan^{-1}\frac{1}{\sqrt{3}} \quad -2$$

Saroja Raman and Ranga Rao (1984) applied this equation to the adsorption of methabenzthiazuron on six soils of Hyderabad and obtained K values ranging from 0.0700 to 0.975 $\mu g^{-1}mL$.

2.3 FACTORS AFFECTING ADSORPTION-DESORPTION OF HERBICIDES IN SOILS

Since high specific surface area is associated with small particle size, the colloidal fraction of soil is the dominant factor in the adsorption-desorption equilibrium of herbicides in soil. Thus, clay minerals and organic matter fraction are the most important in the adsorption of soil applied organic chemicals.

2.3.1 Type of clay minerals :

Clays are the most important soil mineral constituents in adsorption because of their abundance and their surface properties. The 1 : 1 minerals, primarily those of kaolin group, because of their low CEC and low surface area, have very small adsorption capacities. The 2 : 1 expansible minerals like smectites and vermiculites which are held together by Van der Waal's forces between the adjacent planes of oxygen and are relatively weakly bonded and can expand, have

high CEC and surface area (Khan, 1980). As a result, the extent of adsorption is sufficiently high to be readily measured, in many cases even the spectra of adsorbed molecule may be observed (Russell et al., 1968).

The greater uptake by montmorillonite as compared with illite and kaolinite is partly due to its larger hydratable surface (Theng, 1974). Its capacity to take up herbicide is greatly enhanced when organic species can penetrate the interlayer space of the mineral. However, only a limited interlayer penetration could be expected with non-ionics like metoxuron and tebuthiuron, unless the silicate layers have already been separated, as is the case of Na-montmorillonite in water or salt solutions. Farmer and Ahlrichs (1969) reported that phenylurea herbicide adsorption by montmorillonite may be attributed to an interaction of the carbonyl of the herbicide with exchangeable cations on the external surfaces and with edge aluminum groups because phenylureas were not adsorbed in the interlayer space and, therefore, did not have access to the exchangeable cations in the interlayer space as adsorption sites.

Petkova (1978) showed that clay minerals bentonite and kaolinite adsorbed prometryne and reduced

its phytotoxicity but for other herbicides like fluometuron and metobromuron, these clay minerals have little effect in reducing phytotoxicity. Chang (1978) correlated the adsorption of simazine and linuron with clay content of soil. He showed that the soil mobility of herbicides decreased with increase in the clay and organic matter content.

Terce and Calvet (1978) found that the adsorption of monuron, isoproturon, methabenzthiazuron, atrazine and terbutryne was higher in smectite followed by illite and kaolinite. Meyer et al. (1979) observed that sorption of chlortoluron, methabenzthiazuron and terbutryne decreased with increase in clay content. Patterson and Buchanan (1980) showed that highest adsorption of fluometuron occurred in a loam, the clay fraction of which contained 30 per cent montmorillonite. The non-expanding 2 : 1 minerals like illite and chlorite (2 : 2) are intermediate in adsorption capacities between 1 : 1 and 2 : 1 expending types. Weber et al. (1974) reported that the adsorption of fluometuron was greatly modified by montmorillonite.

Yuen and Hilton (1962), while studying the adsorption of monuron and diuron on Hawaiin sugarcane soils, showed that adsorption of monuron was highest in those soils in which montmorillonite was the major clay constituent.

Mustafa and Gamar (1972) concluded that CEC and specific surface area of the clays are the most important factors determining the adsorption of diuron and possibly other substituted urea herbicides in the arid zone soils.

2.3.2 Charge density :

Charge density plays an important role in adsorption, but in most cases, the total charge and surface area are more important than the surface density of charge in adsorption of herbicides. Though, no specific reference is available on the influence of the surface density on the adsorption of substituted ureas, sufficient evidences are there which reveal the influence of charge density on adsorption of cationic herbicides, like bipyridilium herbicides (Weed and Weber, 1968).

2.3.3 Orientation of adsorbate :

It was found that saturated and unsaturated ring compounds form two main types of complexes depending on whether the ring lies parelles to 001 axis of montmorillonite or paripendicular to it (Green — Kelly, 1955). Greenland et al (1962) found that adsorbed 1-n-alkyl pyridinium cations normally lie along the surface of montmorillonite, adsorption of larger amounts of these ions giving rise to two to three layer complexes.

Weed and Weber (1968) reported d_{001} spacings of 12.8 to 12.9Å for montmorillonite saturated with paraquat and diquat indicating one layer complex with the rings of organic cations parellel to the clay.

2.3.4 Nature of Adsorbate :

Bailey et al. (1968) showed that the properties of adsorbate that affect adsorption are chemical character, shape and configuration, acidity or basicity of molecule, water solubility, charge distribution, polarity and molecular size. The nature of functional groups determine, whether a compound is acidic or basic and indicates its ability to hydrogen bonding or coordinate covalent bonding. The nature and position of substituting groups may affect the ability of molecule to undergo intermolecular hydrogen bonding. Raman and Mortland (1969) concluded that proton transfer, from protonated species adsorbed on the clay surface, to an uncharged molecule dependends upon the relative basicities and concentrations of the reactants and products. Molecular size and shape have a profound effect on adsorption, especially where access to binding sites is restricted by the dimensions of the pore openings, and where one molecule of a charged adsorbate species covers more than an equivalent number of charged sites on the adsorbent surface (Greenland and Hayes, 1978).

2.3.5 Soil reaction :

Bailey and White (1964) postulated that the effect of pH on the adsorption of a particular herbicide may be related to its degree of dissociation or association with protons. This would affect the amount adsorbed and the strength with which it is held, since the energy and the changes of adsorption may be vastly different for the dissociated and associated forms.

Bailey et al. (1968) showed that many urea herbicides (fenuron, monuron, diuron) and s-triazine herbicides were adsorbed more by the highly acidic H-montmorillonite (pH 3.3) than near neutral Na-montmorillonite (pH 6.8). The reaction of urea with acid montmorillonite gave evidence of protonation of amino group and subsequent reaction with silicate surface. Increasing the H^+ ion concentration in solution was found to favour an increase in the adsorption of certain substituted ureas on cellulose by Coggins and Crafts (1959). Gaillardon et al. (1980) found that the adsorption of certain phenylurea herbicides (diuron, linuron, metoxuron, isoproturon) by humic acid increased as the pH decreased. They attributed this to the establishment of H-bonds between herbicide molecule and the undissociated carboxyl group of humic acid.

Bottger et al. (1977) found that the adsorption of MBT and chlortoluron was unaffected by pH. Weber (1980) found that adsorption of buthidiazole, VEL-3510, tebuthiuron and fluridone increased with decreasing pH suggesting that the adsorption mechanism was molecular under neutral pH condition and ionic under acid conditions.

Saroja Raman and Ranga Rao (1984) found that decreasing the solution pH from 7 to 5 resulted only in minimal increase in the adsorption of methabenzthiazuron. Saroja Raman and Reddy (1987) reported that the changes in pH of soil solution did not modify the adsorption behaviour of isoproturon significantly because of its non-ionic nature and low pKa.

2.3.6 Temperature :

Adsorption is generally an exothermic process, and hence the higher the temperature, the lower the adsorption (Harris and Warren, 1964). Temperature may also influence the adsorption through its effect on solubility and vapour pressure. Under some situations, an increase in temperature may increase the adsorption (Freed et al., 1962). The variation in temperature affects surface - solute interactions as well as water-solute interactions. It is the balance between these two effects which determines the observed behaviour

and this may result in adsorption increasing, decreasing or remaining unaffected, with an increase in temperature (Calvet, 1980). Studies of Peck et al. (1980) indicated that adsorption of diuron by fresh water sediments decreased as the temperature increased from 5°C to 40°C. Burns et al. (1973) did not observe much change in the adsorption of paraquat on humic acid over a temperature range of 30 - 70°C.

Kausalya et al. (1982) found a decrease in the values of equilibrium constants with temperature for the adsorption of terbutryne on a series of homoionic montmorillonites. Gupta et al. (1985) reported that adsorption and Freundlich K decreased slowly with an increase in temperature for terbutryne on soils.

2.3.7 Soil Organic Matter :

It is well established from several studies that soil organic matter plays a major role in the adsorption of herbicides. When it is more than six per cent, it is the only factor that governs adsorption (Stevenson, 1976). Even for soils with low organic matter it is often the most important factor governing the adsorption.

There are a number of reports in literature about the positive effect of organic matter on the adsorption of urea herbicides. The adsorption of

urea and a number of its derivatives by different soils was investigated by Hance (1965). He found that organic matter content is the only soil property that could be related to adsorption capacity. Linuron adsorption by ten New Jersey soils was generally higher in the A than the B horizon indicating that organic matter may play major role in adsorption (Mac Namara and Toth, 1970).

Bottger et al. (1977) showed that the adsorption of methabenzthiazuron and chlortoluron increased with increasing organic matter content of soil. The rate of adsorption these two herbicides were unaffected by pH. Chang and Stritske (1977) observed that the adsorption was more in soil having high organic matter content and desorption was more difficult in soils having high organic matter content than in the soils with low organic matter content.

Meyer et al. (1979) in their examination of the behaviour of methabenzthiazuron, terbutryne and chlortoluron showed that sorption increased with increasing organic matter content but decreased with increasing clay content. Gajanan (1978) found that adsorption of simazine, monuron and 2,4-D were influenced by the organic matter content, pH and nature and amount of clay content in the soil. Chang (1971) in trials with clay loam, loam and sandy loam soils found that

adsorption of simazine and linuron correlated positively with soil organic matter and clay contents. Peck et al. (1980), in their experiments with the adsorption of diuron on fresh water sediments, found that Freundlich constant K was positively correlated to the amount of organic carbon present. Patterson and Buchanan (1980) found that adsorption of ^{14}C-fluometuron was greatest in soils with high organic matter content and montmorillonite. Petkova (1981) correlated adsorption of metobromuron and fluometuron with soil texture, the quantity of loamy fraction, organic matter content and the specific surface area. Chang (1981) found good correlation between the adsorption of diuron, isuron, monoisuron with soil organic matter content.

Saroja Raman and Ranga Rao (1984) observed a positive and significant correlation for the adsorption of tribunil with the soil organic matter content in six soils from Hyderabad. Kosak and Weber (1983) found that soil organic matter content is the most important factor influencing the adsorption of metabromuron, monolinuron, linuron and chlorbromuron.

Briggs (1981) related the adsorption of several non-ionic organic chemicals including urea herbicides from 17 Australian soils to the organic matter content of soils. Reddy (1984) reported a significant correlation between Freundlich K values

and the organic matter content for adsorption of isoproturon on different soils of Hyderabad. Similar results were reported by Saroja Raman and Laximinarayana (1986) for the adsorption of atrazine and isoproturon on 16 black and 11 red soils from Andhra Pradesh.

Savage (1973) found that there was no significant linear correlation between adsorption of chlorbromuron and soil texture, organic matter content, pH or water holding capacity. Carvelli et al. (1975) did not find direct or exponential relationship between the Freundlich K values and soil organic matter content.

2.4 MECHANISMS OF ADSORPTION ON CLAYS :

It has been customary to describe adsorption as physical adsorption and chemisorption, depending on the strength of the forces that bind the molecules to the surface. Physical adsorption usually involve weak forces like dipole-dipole interactions, Van der Waals forces, dispersion forces etc., which are short range forces and result in interaction or binding energy of < 80 kJ $mole^{-1}$. Physical adsorption is generally not oriented specifically and are usually spread over the polar and non-polar regions of the molecule. Although individually they may be weak, their spread over a number of atomic centres and bonds, brings about strong attachement of the adsorbed molecules

to the adsorbent.

Chemisorption on the other hand involves much stronger forces like ionic bonds, direct ion-dipole bonds, ligand exchange, hydrogen bonds which involve binding energy of > 80 kJ $mole^{-1}$. Chemisorption takes place at specific adsorption sites and generally involve an activation energy.

The mechanisms of adsorption of pesticides on clays have been already reviewed by Mortland (1970), Green (1974) and Sposito (1984). Since clay minerals constitute considerable active sites within which the negative charges are balanced by cations, the adsorption of organic chemicals to clays are invariably mediated through the exchange cations and can be termed as most by chemisorption. In addition to adsorption on the edges or the external surfaces, expansible minerals like montmorillonites and vermiculites can also give rise to interlayer adsorption of organic chemicals, when conditions are favourable. Thus, the nature of cations and the hydration status of the system become highly important in determining the extent and nature of adsorption of organic chemicals on clay minerals.

The exchange cations on clays can be broadly divided into two classes 1) the main group cations,

with filled ionic orbitals like alkali, alkaline earth ions and Al^{3+} which have filled inner orbitals and 2) transition metal ions like Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} which have vacant d orbitals with low energy d orbital electrons. The former generally act through their polarizing power. Russell et al. (1968) found protonation of 3-amino triazole to increase in the order of $Ca^{2+} < Mg^{2+} < Al^{3+}$ and attributed this to increased polarizing power of cations. The latter can form strong ligand exchange bonds or coordination bonds which can be considered as direct ion interaction with ligand dipole.

Binding of polar pesticides to clays is mainly electrostatic in nature which are generally stronger than Van der Waal's forces. These can be broadly divided into 1) Ionic bonds 2) Cation-dipole and coordination or ligand exchange bonds and 3) dipole-dipole bonds.

2.4.1.1 Ionic Bonds :

These are important for cationic pesticides like paraquat and diquat and also for basic pesticides like triazines which can be protonated at low pH. Cation exchange occurs in these cases with exchange cation on the clay surface such as

$$P^{2} + M^{2+}\text{—clay} \rightleftharpoons P^{2+}\text{—clay} + M^{2+}$$

where P^{2+} is the cationic pesticide and M^{2+}, the exchange cation.

In the case of basic pesticides, cation exchange occurs between protonated pesticide and exchange cations. Considerable protonation of pesticide can occur in solution if the pH is lower than pKa of the pesticide. Alternately, protonation can also occur at the clay surface, where the pH is generally two to three units lower than the bulk. Protonation of pesticide on clay surface can take place in three ways :

i) exchangeable hydrogen ions protonate the base, ii) water of hydration of a strongly electro positive exchange cation like Al^{3+}, may dissociate to produce a hydrogen ion which can protonate the base.

$$\text{Clay} - M - (H_2O) + B \rightleftharpoons \text{Clay-M-OH} + BH^+$$

The equilibrium depends on the electronegativity of the cation and pKa of the base. For example, urea is protonated on Al^{3+} and Fe^{3+} montmorillonite but not on Ca^{2+} or Na^+ montmorillonite (Mortland, 1968). iii) A proton may be transferred to the pesticide from another protonated base of lower basicity.

$$\text{Clay } B_1H^+ + B_2 \rightleftharpoons \text{Clay-}B_2H^+ + B_1$$

Protonation of 3-amino triazole by NH_4-montmorillonite was shown by Russell et al. (1968).

2.4.1.2 Cation-dipole and coordination bonds :

Cation-dipole interaction refers to direct interaction between the cation and pesticide without the mediation of water of hydration. This is possible mainly in dehydrated clay adsorbate systems upon exposure to water vapour or water, the highly polar and better nucleophile water displaces the organic molecule.

The coordinate bond can be seen as an extension of direct ion-dipole interactions involving stronger orbital overlapping and electron distribution between the metal and the ligand. This type of bond is more probable for the transition metal ions like Cu^{2+}, Ni^{2+}, Zn^{2+} etc. The basic difference between ion-dipole and coordination bond was demonstrated by Mortland (1970) in the case of clay-amino triazine complexes. While clays saturated with Al^{3+} released 73% in six washings with 0.01M $MgCl_2$ only 30% was desorbed from Cu^{2+}-clay. Ion-dipole or coordination types of interactions have been noted for a wide group of polar molecules viz., NH_3 (Mortland, 1970), urea and amides (Mortland, 1966; Tahaun and Mortland, 1966) EPTC (Mortland and Meggitt, 1966).

2.4.1.3 Dipole-dipole interactions :

Dipole - dipole interactions are the most important in the normal environment in which pesticides

act. Most of the pesticides are polar in nature and may compete for adsorption with water molecules. In the presence of water, the exchange cations are in a hydrated state and direct ion-dipole interaction is not possible, unless the ligand is very powerful. Interaction between cation and pesticide is mediated mainly through polarised water molecules around the cation.

2.4.1.4 Hydrogen bonding :

It is a special type of dipole-dipole interaction in which H atoms serve as a bridge between two electronegative atoms. Earlier studies have shown that these are mainly associated with N-H and O-H groups and N and O atoms so that most herbicide molecules can form hydrogen bonds. Two kinds of hydrogen bonds have been shown to occur in the adsorption of organic molecules with clays

a) between the adsorbed water molecules and adsorbed organic molecules, and

b) between surface groups and organic molecule.

Infrared results have shown that H-bond is associated more often with the water bridge between the exchange cation and a polar pesticide.

$$> C = O + H_2O\text{-M Clay} \rightleftharpoons > C \cdots O \begin{matrix} H \\ H \end{matrix} > \text{— O-M Clay}$$

As seen above, the hydration status of cations are important in deciding the nature and extent of binding of pesticides. It also assists in interlayer penetration of pesticides due to expansion of the interlayer.

2.4.1.5 Interlayer penetration and hydration status of clay minerals :

Hydration status of clay minerals is important in deciding the nature and extent of binding of pesticides. It also assists in interlayer penetration of pesticides due to expansion of the interlayer. Thus, Bowman et al. (1970) found that 40 per cent moisture was necessary for the entry of malathion into interlayer space. It was shown by Schnitzer and Kodama (1966) in the laboratory that a fulvic acid would penetrate the interlamellar regions of montmorillonite. However a different example of importance of water at clay mineral surface has been provided by Yaron (1978) who demonstrated that there was a decrease in the amount of parathion adsorbed by attapulgite with an increase in hydration status of mineral. The high adsorption in a dry system was attributed to the effective competition of polar parathion molecules for adsorption sites on clays. But in partially hydrated systems, water molecules compete with parathion for the adsorption sites on clays resulting in a decrease in adsorption capacity of attapulgite for parathion

2.4.2 Mechanism of Adsorption of Urea Herbicides:

The previous section reviewed in general, the types of possible mechanisms of interaction between pesticides and clay minerals. The types of mechanism that have been specifically postulated by different workers, for the adsorption of urea herbicides on clay minerals have been reviewed in this section.

In the case of urea herbicides, apart from physical adsorption, ligand exchange and H-bonding have been reported by many workers to be the major modes of interaction with clays. In addition to this, protonation of amino group of these herbicides have also been confirmed in the case of mainly H^+- and Al^{3+}-clays.

Mortland (1966) reported evidence for the protonation of urea amino groups by the acidic montmorillonite systems. This was proved by IR spectra of the adsorbed urea, which was identical to its HCl salt. Hance (1969, 1971) and Khan (1974) suggested that substituted urea herbicides were coordinated to exchangeable cations on bentonite and montmorillonite. They obtained the following sequence for the adsorption of linuron

$Fe^{3+} > Ce^{4+} > Cu^{2+} > Ni^{2+} > Ca^{2+}$ (Hance, 1971)

$Al^{3+} \geq Cu^{2+} \geq Ni^{2+} > H^{+} > Mg^{2+}$ (Khan, 1974)

However, Farmer and Ahlrichs (1969) obtained evidence for interlayer adsorption of deuterated urea on montmorillonite through coordination of carbonyl group with the exchange cations.

Hance (1971) also suggested that the results of adsorption of linuron with soils were consistent with complex formation with exchangeable cations as possible mechanisms of adsorption.

Purkayastha and Mishra (1985) reported that the amount of methabenzthiazuron adsorbed by homoionic clay decreased in the order $Al^{3+} > Zn^{2+} > Mg^{2+} > Ca^{2+}$. Thus the mode of adsorption was mainly due to polarizing power of the ions.

The IR spectroscopic studies of Shive and Wang (1977) showed that monuron and diuron were adsorbed on humic substances by chemisorption. The study of IR spectra of adsorption of linuron by Czuchajowska (1978) indicated that besides ligand exchange, H-bonding of linuron to soil constituents occurs. Senesi and Testini (1980) obtained IR spectroscopic data on the adsorption of some substituted urea herbicides indicating that the adsorption occurs involving such mechanisms as H-bonding, Van der Waal's forces in substituted urea-humic acid complexes. Gaillardon et al. (1980)

attributed the increase in the adsorption of diuron, linuron, metoxuron, isotoproturon by humid acid as the pH diminished to the establishment of H-bonds between herbicide molecules and the functional groups not dissociated with humid acid.

Maier-Bode and Bartel (1981) indicated that essential mechanisms of sorption to clay minerals are ion-exchange, protonation, formation of coordination complexes and H-bonding. In the absorption of linuron to clay minerals, the formation of complexes with exchangeable cations seems to play a major role.

2.4.3 Mechanisms for the adsorption of herbicides on organic matter ;

The complex nature of soil orglanic matter and the varied nature of organic herbicides suggest that several adsorption mechanisms could be operative, frequently in combination. The process is more complex than adsorption on clay minerals since the organic surface is less rigid and its properties vary with the exchange population (Weed and Weber, 1974). Mechanisms proposed by the various workers as being responsible for the retention of herbicides by organic matter include, a) cation exchange applicable for cationic herbicides and those which can accept a proton (Bailey and White, 1970); b) hydrogen bonding applicable where there is an abundance of carboxyl, hydroxyl

and amino groups present on the organic matter. Carboxyl oxygens on herbicide may be bonded to amino hydrogens or hydroxyl groups on organic matter. Bailey and White (1970) and Mortland (1970) have shown that more complex attachment involving hydrogen bonding may consist of a water bridge between an exchangeable metal cation and the herbicide molecule as in clay organic systems. These water molecules held by the cation by ion-dipole bonding can bond to the carbonyl oxygen of the herbicide molecules by hydrogen bonding which are not strong bonds and thus the adsorbed molecules can be readily desorbed, c) Non-polar Van der Waal's forces though very weak operate in all adsorbent-adsorbate relationships (Adamson, 1960). In this, each atom of the molecule and of an adsorbent contributes to the total bond energy. Contribution of these forces increase with its parachor and also with its capacity to adapt to the surface of the adsorbent. d) Ligand exchange - incompletely chelated transition metals have been suggested as sites for such adsorption (Hayes, 1970; Green, 1974) e) reactions involving stable organic free redicals i.e., molecules containing unpaired or odd electrons have been shown to occur in relatively high concentrations in soil humic matter (Steelink and Tollin,1967). f) Hydro-phobic bonding - Non-polar pesticides or compounds whose molecules often have non-

polar regions of significant size in proportion to polar regions are likely to adsorb onto hydrophobic regions of soil organic matter. Water molecules present in the system will not compete with non-polar molecules for adsorption on hydrophobic surfaces. The potential importance of hydrophobic fractions of organic matter for retention of pesticides was cited by Hance (1969). This type of bonding may also be largely responsible for strong adsorption of DDT and other organochlorine insecticides (Stevenson, 1966). The association of non-polar pesticide with lipid fraction of humus might be described by hydrophobic bonding (Pierce et al., 1971). Non polar portions of the humic polymers and hydrophobic molecules trapped within the polymer could also provide hydrophobic bonding sites for pesticides (Pierce et al., 1971). The hydrophobic portions of peats can significantly adsorb phenyl ureas (Hance, 1969; Morita, 1976). The adsorption of pesticides involving this mechanism would be independent of pH (Walker and Crawford, 1968). Carringer et al. (1975) suggested that adsorption of fluometuron is by hydrophobic bonding.

Chiou et al. (1979) proposed that soil uptake of the organic compounds was a simple partitioning of these chemicals between hydrophobic organic matter phase and water. The adsorption of neutral chemicals

from water by soils from Europe and North America was best correlated with the soil organic matter content (Hamaker and Thompson, 1972). Briggs (1981) found that the uptake of several pesticides including phenyl ureas from aqeous solutions by seventeen soils of Australia was highly correlated to the organic matter content of the soils. The soil organic matter/water distribution (K_{om}) for each chemical was similar in all the soils and could be predicted from the Octanol/water distribution (K_{ow}) of the chemical. An objection to the concept of simple partitioning of non-ionic organic compounds between soil-organic phase and water was raised by Mingelgrin and Gerstl (1983) on the basis that soil adsorption of these chemicals are not often linear but may appear linear at low surface coverage. To overcome this Saroja Raman (1987) indicated the possibility of estimating the sorption capacity of different particle size fractions from a knowledge of their organic carbon content and Freundlich constant in a single or limited number of fractions. Dzombak and Luthy (1984) have discussed the possibility of predicting the adsorption of a number of polycyclic aromatic hydrocarbons in soils, based on soil organic carbon content and characteristics of organic compound.

2.4.4 Mechanisms of Adsorption of Herbicides in Soils

The mechanisms observed for the adsorption of herbicides in soils are complex because of the

adsorption on clay and organic matter. The main modes of binding and various forces influencing adsorption depend on the nature of adsorbate, type of clay, nature of exchange cations etc. Besides, the adsorption on clay organo complexes also needs to be considered. Almost all types of mechanisms proposed for clay and organic matter can be simultaneously operating in soils. Excellent reviews have been written by Sposito (1984), Calvet (1980), Khan (1980), Greenland and Hayes (1978).

2.5 CHARACTERISATION OF HUMIC SUBSTANCES IN SOIL :

Soil organic matter is a complex system consisting of myraid of products, which range from undecomposed plant and animal residues, through empirical products of decomposition to fairly stable amorphous black to brown material bearing no trace of anatomical structure of the material from which it derived. To simplify this complex system, organic matter is divided into two groups : a) non-humic substances and b) humic substances.

Non-humic substances include the compounds that exhibit still recognizable chemical characteristics. To this class of compounds belong carbohydrates, proteins, peptides, amino acids, fats, waxes, pigments and other low molecular weight organic substances.

The bulk of organic matter in most soils consist of humid substances. These are amorphous, brown or black, hydrophilic, acidic, polydisperse substances of molecular weights ranging from several hundreds to tends of thousands. Based on their solubility in alkali and acid, humic substances are divided into three main fractions : i) Humid acid (HA) which is soluble in dilute alkaline solution but is precipitated by the acid. ii) Fulvic acid (FA) that which is soluble in both acid and base and iii) the humin fraction that can not be extracted in dilute base and acid. Column chromatographic techniques have been used to separate humic acids into more homogenous fractions (Khan, 1970; Schnitzer and Skinner, 1968). Purification of humic acids and fulvic acids by adsorption on activated Charcoal (Sinha, 1971) gave fractions of sufficient purity for analytical works.

2.5.1 Characterisation :

Humic substances are characterised on the basis of their elemental composition, functional group, molecular weight, spectral properties, X-ray analysis, thermal analysis and degradation methods.

Elemental composition provides useful inventory of the distribution of major elements in humic substances. Fulvic acids contain less carbon and nitrogen but

more oxygen than humic acids. A variety of functional groups, including-COOH, phenolic OH, enolic OH, quinone, alcoholic OH, have been reported in humic substances. Most methods for determining reactive groups in humic substances have been based on acidic properties of the group involved. Khan and Sowden (1971) reported aspartic acid and glycine to be present in the largest amounts with smaller amounts of alanine and glutamic acid. Threonine, Serine, Valine and Leucine were present in the amounts equivalent to half of those of glycine or aspartic acid. Banarjee and Mukharjee (1973) reported fulvic acids to contain sugars and amino acids in varying quantities.

Excellant reviews on the characterisation of humic and fulvic acids are reviewed by several workers (Gieseking, 1975; Schnitzer and Khan, 1978; Stevenson, 1982).

2.5.1.2 Spectral Properties :

Adsorption spectra of HA and FA were featureless with neither maxima nor minima. Higher absorbance at shorter wavelength was attributed to the increased mobilities of electrons over 'aromatic' nucleii and over unsaturated structures conjugated with those nucleii. The ratio of absorbances at 465 and 665 nm, referred to as E4/E6 ratio, has been widely used for

characterisation purposes. The E4/E6 ratio humic acids are usually < 5.0; those for fulvic acids from 6.0 to 8.5 (Schnitzer and Khan, 1978). According to Chen et al. (1977) the best procedure for determining the E4/E6 ratio is to dissolve 2 to 4 mg of HA or FA in 10 ml of 0.05 N $NaHCO_3$ which gives optimum pH range for absorbance measurements.

The IR spectra provide information on the nature, reactivity and structural arrangement of oxygen containing functional groups. Fulvic acids extracted from peat and fractionated by anion and cation exchange resins showed the presence of amino groups. The IR spectral study confirmed the presence of carboxyl, phenolic and amino groups (MacCarthy and O'Cinniede, 1974).

Electron spin resonance spectra of humic substances have revealed the occurrance of stable free radicals. The origin of free radicals is unknown, but quinone groups of various types are suspect. The technique of NMR spectroscopy can be used as a research tool in the study of soil organic matter (Stevenson, 1982).

The electron microscopic studies provide direct method for observing the confirmational changes in sizes and shapes of humic substances (Schnitzer

and Khan, 1972). Difficulties arise in examining HA by these means, because the particles are transperant to electron rays and can not be easily distinguished from the supporting film. Flaig et al. (1975) have made extensive studies on the morphological features of humic acids by electron microscopy.

2.6 POLYMALEIC ACID AS A MODEL FOR SOIL FULVIC ACID

Despite a long history of interest and research, the soil humic substances still defy a precise chemical description, because of their inherent complexity and heterogeneity, in contrast to clays which are crystalline and can be had inpure forms. Anderson and Russell (1976) proposed that polymaleic acid (PMA) could serve as a model for fulvic acid, after observing remarkable similarities between the two materials in elemental analysis, IR spectra and a number of hydrolysis products. Polymaleic acid was prepared by the polymerisation of maleic anhydride in the presence of pyridine and washed free of excess of pyridine with chloroform and acetone. The similarities to soil fulvic acid which were found to be especially striking were : a) the occurrence of vicinal carboxyl groups readily converting to anhydrides (b) unsaturation which accounts for IR absorption bands near 1620 cm^{-1}. On the basis of their analytical data, they concluded

that FA consisted of mainly PMA type structures. Linehan (1977) stated that PMA while structurally similar to soil FA, had the added advantage of structural homogeneity, and suggested that it could be possible to obtain structural modifications during the polymerisation of PMA for better understanding of the relationship between nature and growth promoting properties.

Spiteller and Schnitzer (1983) reported that there were lot of similarities between PMA and Soil FA in a number of characteristics, but minor differences could be observed in fluorescence, ^{13}C NMR spectra and in oxidation products. Compared to FA, PMA appeared to be better organised and more homogeneous at the molecular level, richer in olefin structures and less aromatic structures.

2.7 CLAY-ORGANO COMPLEXES IN SOIL :

Soil is a complex system comprising of the surface reactive organic and inorganic colloids. The intricate manner in which soils are formed through interaction of a number of factors and forces, ensure that colloidal clay and organic fractions do not exist in pure form, independant of each other, but, form stable clay-organo complexes. They exert a profound influence on the soil environment by controlling the physical, chemical and biological properties of the

soil. Soil physical properties like aeration, porosity, water holding capacity which depend on size and extent of aggregates, weathering process and soil formation are largely affected by clay-organo complexes (Mortland, 1970). Similarly stabilisation and immobilization of soil enzymes are known to take place on soil clay-organo complexes (Ladd, 1978, 1985).

2.7.1 Bonding Mechanisms of Clay-organo Complexes:

Mechanisms governing the reactions between clays and known organic compounds and humic substance have been reviewed by Mortland (1970), Greenland (1971) and Theng (1979). The main mechanisms that relate to reactions between clays and humic substances are: a) ion-dipole, anion exchange reactions, b) ligand exchange reactions and c) hydrogen bonding. These have been discussed in a nutshell by Theng (1979) (Table 1).

The role of Fe^{3+} and Al^{3+} at the clay surfaces has been considered to be very important in binding of HA to clays. These ions form polyhydroxy complexes which can be protonated below pH 8.0 and can associate with organic anions through columbic forces. At higher pH they can facilitate anion exchange with HA and FA. Alexandrova (1981) studied the humic complexes in soils and reported that the organic part of organo

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Table 1 : Possible modes of bonding between humic substances and clay mineral surfaces (Theng, 1979)

	Group on polymer	Groups and sites on mineral	Remarks
A.Primary interactions: Ion-dipole including			
(a) Cation bridging	Anionic (carboxylate) and unchanged polar groups such as amino, carboxyl, hydroxyl	Exchangeable cations at external, basal surfaces. At low pH (<4.5) also those on inter-layer surfaces	Weekly hydrated and non-hydrated monovalent cations. Polyvalent cations in dehydrated systems. Desorbable by sodium salts
(b) Water bridging	Anionic (carboxylate) and uncharged polar groups, such as amino, carbonyl, hydroxyl	Exchangeable cations at external, basal surfaces. At low pH (<4.5) also those on interlayer surfaces	Polyvalent cations in hydrated systems. Desorbate by sodium salts, water, and ultrasonic treatment.
Anion exchange	Anionic groups	Crystal edge surfaces. Polyhydroxy compounds of iron and aluminium at external, basal surfaces	Acidic pH conditions and when exchange sites are occupied by iron and aluminium ions. Desorbable by other anion in solution, such as chloride, nitrate
Ligand exchange	Anionic groups	Crystal edge surfaces. Polyhydroxy compounds of iron and aluminium at external, basal surfaces	When exchange sites are occupied by iron and aluminium ions. In soils, on hydrous oxides of iron and aluminium. Desorable by other specifically but more strongly adsorbed anions, such as hydroxyl
B.Secondary interactions			
Hydrogen bonding	Amino, carboxyl, hydroxyl	Oxygens of external basal surfaces (siloxane sheet)	Weak
Van der Waals	Uncharged portions of polymer chain	Mainly at external, basal surfaces.	Not very important in hydrated systems. They become significant at high ionic strength and when the systems is allowed to dehydrate. Short-range weak but additive.
C.Indirect interactions			
Entropy effects			Arising from the gain in entropy by the system due to displacement of many water molecules from the clay surface by a single polymer chain

mineral complexes consist of fulvic acid forming complex heteropolar salts with Fe-and Al- as well as phenols, and low molecular weight acids which form hetero-polar and complex heteropolar salts. Emerson and Oades (1983) discussed organic-clay complexes in relation to soil aggregation and soil structure and reported that polysaccharide fraction is responsible for binding to clay fraction and fulvic acid also interacts with clays through cation bridge. The binding of smaller aggregates plus silt and clay particles into larger aggregates depend on the possible interactions between Fe- and Al-and organic materials. According to Edwards and Bremner (1967), the soil organic matter and clay particles are linked via polyvalent metal ions to form microaggregates.

Similarly the polyhydroxy nature of Fe & Al at the clay surface makes them potential candidates for H-bonding. They can also act as centres for covalent bonds to fulvic acid (Greenland, 1971; Edwards and Bremner, 1967).

Green (1974) considered H-bonding to be the main force between humic polymers and clay surface. The possibility of availability of large number of such sites on HA and FA produces relatively stable aggregates. The H-bonding may be through centres containing-NH_2, -COOH, -C=O groups on HA. Mortland

(1970) opined that H-bonding between the bridging cations and HA or FA takes place through the formation of water bridges with the help of molecules present in primary hydration shell.

Apart from the above mechanisms of interactions between HA and clays, the role of exchange cations is also important. Exchange cations determine the surface acidity of clay and may act as electron acceptors by interacting with electron donating functional groups of humic substances. The energy of ion-dipole or coordination type bonds formed will depend on the nature of exchangeable cation and also on the level of hydration of the system. The contribution of the clay surface to total adsorption energy is maximal when ions of low solvation energy occupy cation exchange sites, and is minimal when they are occupied by cations with higher solvation energies (Mortland, 1970). He stressed the formation of 'water bridges' linking polar organic molecules to exchangeable metal ions through water molecule in the primary hydration shell.

Transition metal ions like Cu^{+2}, Ni^{+2}, Zn^{+2}, Co^{+2} etc., which have vacant d orbitals can directly enter into cooordination bonds with HA and Fa or they may form bridges through solvated water molecules. B-diketone groups in fulvic acid reacted with Cu^{2+}-

in or on the clay to form acetylacetonate type chelates (Schnitzer and Kodama, 1972).

Theng (1976) and Theng and Scharpens eel (1975) from their studies on formation and stability of clay-humus complexes found out that the extent to which fulvate sample was adsorbed rose with an increase in cation valency. This again indicates that cation acts as a bridge between functional groups on fulvate and negatively charged clay surface. Obulpathy (1977) observed the adsorption of HA and FA on homoionic clays followed the order : Cu-> Zn-> Mg-> Ca- in the case of HA and Cu-> Zn-> Mg-> Ca- in the case of fulvic acids. He reported that the amount adsorbed in the case of fulvic acids per gram of clay was more than the corresponding humic acids.

Effect of saturating montmorillonite with different cations on the interlayer adsorption of humic acid was studied by Kodama and Schnitzer (1968), the d_{001} spacings decreased in the order

Pb^{2+}- > Cu^{2+}> Na^{+}> Zn^{2+}> Co^{2+}> Mn^{2+}> Mg^{2+}> Ca^{2+}>Fe^{3+}>Ni^{2+}

They suggested that variations in d_{001} spacing were not a function of capacity of different ions to form stable complexes with FA nor were they related to ion potentials of metals.

Humic acid and fulvic acid can also enter into interlayer spacing of expanding clays through the help of exchange cations present on the clays. This is especially true at low pH where FA and HA exist in undissociated form (Theng, 1979). Thus Schnitzer and Kodama (1972) observed that at pH 2.5, the FA entered the interlamellar spacing of Cu-montrmorillonite and increased its d_{001} spacing from 10.0 to 15.1 Å. Interlayer adsorption of humic acid by homoionic montmorillonite was also observed by Theng and Scharpens eel (1975) and Theng (1976). Obalpathy (1977) has also found an increase in interlamellar spacing when humic acid was adsorbed on homoionic montmorillonites from his studies on X-ray diffraction patterns.

2.8 ADSORPTION OF PESTICIDES ON CLAY-ORGANO COMPLEXES :

Walker and Crawford (1968) quoted that upto organic matter content of about 6 per cent both the mineral and organic surfaces are involved in adsorption. At higher organic matter contents, adsorption occurs mostly on the organic surfaces. Stevenson (1976) indicated that the amount of organic matter required to coat the clay depends on soil type and the kind and amount of clay that is present.

In soil, clay and organic matter are present as intimate associations. This intimate association of clay with organic matter may cause some modification of their adsorption capacities, or they may compliment one another in the role of pesticide adsorption. Hance (1969) suggested that in soil, clay and organic matter associate in such a manner that little of clay mineral surface will be accessible to pesticide molecule. Thus, the contribution of the clay fraction in soils would be much less than studies which the isolated minerals would indicate. On the otherhand, Mortland (1968) is of the opinion that organic compound in soil organic matter, upon interaction with clay, may facilitate and stabilise adsorption of pesticides beyond that observed is purely inorganic clay systems. Burns (1972) pointed out that humus-clay micro enciron-ment is a site of high biological and non-biological activity and more basic information concerning soil pesticide interaction can be obtained here. The adsorp-tive capacities of sedimentary organo-mineral complexes for lindane and parathion were found to be much greater than those corresponding mineral fraction.

Khan (1974) investigated the adsorption of 2,4-D by FA-clay complex and observed that FA-clay complex adsorbed about 6.5 and 5.1 μ moles of 2,4-D per g of complex at 5°C and 25°C respectively. This

FA complex was similar to the naturally occuring organo-clay complexes found in the soil (Kodama and Schnitzer, 1971).

Khan (1973) found that diquat and paraquat were present in the form of organo-clay complexes. He reported that FA, which is the most prominent humic compound in soil solution on interaction with clay minerals will facilitate adsorption of pesticides on clays in soils. Saltzman et al. (1972) suggested that mineral OM interaction determines the adsorption capacity of each soil.

2.9 PERSISTENCE OF PESTICIDES IN SOIL :

The term 'Persistence' has been employed for the pesticides that retain their biological activity for a much longer period than originally intended. It may be interpreted as the residence time of pesticide in soil environment. The residence time may be considered as the period in which the pesticide remains in soil regardless of the method by which it is quantified. It may be expressed in terms of units of time. The persistence of soil applied chemical is dependant, on a host of conditions, such as soil type, organic matter content, clay content, pH, nature of soil colloids structure of pesticide molecule, and environmental factors like moisture and temperature.

The concept of half life is widely used for prediction of persistence of pesticides in soil. The term half life has the characteristics of being a constant inversely proportional to the rate constant and independant of concentration. It is usually calculated on the presumption that the disappearance of the pesticide occurs through the first order Kinetics (Hamaker, 1972). The practical indices such as 50 per cent disappearance time DT_{50}, have been found to give an idea of persistence (Hamaker, 1972) of a given chemical.

Herbicides show a wide spectrum of persistence ranging from a few weeks for carbamates to a year and a half for certain s-triazines and urea herbicides (Khan, 1980).

There are marked differences in the degree of persistence of various substituted ureas. In this class, increased ring chlorination and increased N-alkylation appear to increase the persistence (Kearney, 1976). Khan et al. (1976) investigated the persistence of diuron and its degradation product, 3-4-dichloroaniline, in an orchard soil, which received diuron annually @ 4 lbs/ac for seven years. Accumulation of residues was not observed at significant levels, although carry over of herbicide occurred between years. The degradation rate of diuron generally followed first order

Kinetics and residual levels in the soil were highly phytotoxic to oat plants during the three years after last application.

Besides, the nature of pesticide, environmental factors like soil type, nature and extent of clay and organic matter, temperature and moisture affect the persistence of a given pesticide. The soil environment, into which herbicides are introduced, determines to a large extent, the rate of disappearance and many differences in persistence, among soils can be attributed to variations of temperature and moisture levels. The effects of soil temperature, moisture and herbicide concentration on the rate of degradation of Dinitramine were measured by Poku and Zimdahl (1980) in sandy clay loam and sandy loam soil and reported that the rate of degradation increased with increase in temperature and attributed it to non-enzymatic chemical degradation. Majka and Lavy (1977) observed that diuron degraded slightly faster at higher temperature. Hollist and Foy (1971) suggested that increasing soil moisture content blocked the adsorptive sites for trifluralin, thereby increasing the amount available for degradation. The participation of soil organic matter fractions in atrazine degradation has been shown by many workers (Khan, 1978; Schnitzer and Khan, 1972). Khan (1978) suggested that the fulvic acid enhances the hydrolysis of atrazine in aqeous solution.

Persistence of a given pesticide in soil is generally quantified by extracting the chemical remaining on the soil with a suitable solvent at different time intervals and assaying it by suitable method. This enables one to get a rate curve for the disappearance of pesticide.

Pesticide decomposition from soil could be both biotic or abiotic. Although the former is found to be of a general mode of decomposition, chloros-triazines are largely decomposed by abiotic mode (Armstrong et al., 1967). Even where the decomposition is microbiological, moisture, temperature, nature of soil, clays, organic matter etc., play an important role. Non-biological decomposition appears to be moisture and temperature dependant (Harris, 1967). Persistence was found to be less in warm, moist climates than cold and dry climates (Burnside et al., 1969).

Kulshrestha (1983) had shown that soil moisture and soil temperature play an important role in isoproturon dissipation in fine loamy soil. Briggs (1983) suggested a model for degradation in soil, temperature and moisture effects on degradation, effects of soil properties on the persistence of insecticidal esters.

Vacher and Farbe (1983) evaluated the influence of temperature and soil moisture on atrazine degradation

in a clay loam soil in the laboratory and the constants derived from laboratory results were used in conjunction with meteorological data recorded during field experiments to construct a model simulating atrazine persistence in the field. They obtained good correlations between persistence from the field as that predicted by the model. Conventional methods of quantifying persistence through periodical analysis of soil samples is empirical, cumbersome and not capable of leading to unified concepts and possible forecasts. To overcome this, predictive modelling for pesticide persistence was attempted by Walker and coworkers. A computer model for simulation of herbicide persistence was described by Walker (1974) and revised by Walker and Barnes (1981), based on studies in soils incubated in the laboratory under well defined conditions of moisture and temperature.

Walker (1974, 1976, 1978), used energy of activation and moisture levels for predicting the persistence of pesticides. Activation energy is determined from the effect of temperature using Arrhenius equation and moisture effects are characterised using an empirical equation of the form $H = AM^{-B}$, in which H is the half life at moisture content M and A and B are constants. The fit of this equation to the data was evaluated by linear regression analysis of

logarithm of half-life against the logarithm of soil moisture content. This equation was also applied by Saroja Raman et al. (1987) for evaluating the effect of soil moisture on the degradation of atrazine. Their results showed higher values for these constants than those reported by Walker and Zimdahl (1981).

Disappearance of herbicide in soils can be explained by rate curves. Mostly first order kinetics has been employed to describe the disappearance of pesticides in soil (Gingerich and Zimdahl, 1976; Goring and Hamaker, 1972; Hyjzack and Zimdahl, 1974; Khan, 1980). Although simple first order kinetics have largely been used for quantifying the rate of disappearance of a pesticide from soil, more complicated patterns have been reported more recently. As early as 1966, Hamaker proposed a hyperbolic model resembling enzyme kinetics. A well characterized deviation from simple first order was observed by Zimdahl et al. (1970) for atrazine and simazine. These confirmed the existence of more than one phase kinetics for the disappearance of these pesticides.

In order to describe the situation in soils where a simple first order disappearance is not valid, Hamaker and Goring (1976) proposed a model by which

a part of pesticide and its residues are actually bound irreversibly to the soil and are incapable of being extracted by simple solvents. According to their model, a soil applied chemical distributes into two different compartments which may be termed labile and bound. The labile pool consists of the fraction of chemical dissolved in soil solution and that adsorbed reversibly by soil. The pesticide in labile pool is easily degradable and extractable in suitable organic solvents under mild conditions. The bound pool consists of the pesticide adsorbed strongly on more restricted sites on soil and unlike labile pool can not be desorbed by solvents under mild conditions. The scheme of events that take place during the interaction of chemical with soil can be pictured as

$$\text{Org.chemical} + \text{Soil} \longrightarrow \underset{\substack{k_1 \downarrow \uparrow k_{-1} \\ \text{Bound Pool}}}{\text{Labile pool}} \xrightarrow{k} \text{Degradation}$$

where k is the rate constant for degradation of chemical k_1 for entry into bound pool and k_{-1} for reentry into labile pool. As a valid approximation the slowrate for reentry into labile pool (k_{-1}) was not considered important. These rate constants were obtained from a semi-leg plot of herbicide extracted vs time. The disappearance plot consists of two steps, one consisting of an initial faster rate followed by a slow rate

of disappearance. The rate constant for slower rate (k_1) was determined from the slope of the later portion. The slow disappearance portion was then extrapolated to zero time and a difference plot was constructed to meassure the rate constant for faster step (k_1).

Actual examples of bound pesticides were reported as early as 1971 by Bartha and later by Hsu and Bartha (1976) and Vishwanathan et al. (1978) for dichloroaniline. Katan et al. (1976) and Liechtenstein et al. (1977) investigated the binding of ^{14}C-parathion and methyl parathion respectively to soil. Liechtenstein et al. (1977) and later Khan and Hamilton (1980) demonstrated the presence of intact methyl parathion and prometryne in the bound pools.

Thus, in soils and in plants, bound pesticide residues may constitute a potential problem because the nature and/or identity of bound pesticides are difficult to establish and very little is known about the significance of bound residues in terms of their bioavailability, toxicity and accumulative nature. Whether bound pesticide residues are of any environmental significance will remain a matter of conjecture until more data is available. However, judging from the limited information available, it appears that bound residues may not pose much problem as long as

such residues do not accumulate in significant amounts (Capriel et al., 1985; Khan, 1982; Khan and Hamilton, 1980).

MATERIALS AND METHODS

CHAPTER III

MATERIALS AND METHODS

3.1 SOILS :

The soil samples used in this investigation were collected from well characterised soil series of ICRISAT and APAU campus at Patancheru and Rajendranagar locations respectively. The details of samples are given in Table-2. Approximately 8 kg of soils were collected from each of the five to ten spots, quartered, air-dried under shade, pounded in wooden mortar with pestle and passed through 2 mm sieve. This 2 mm processed soil was properly labelled and stored in cloth bags until further use.

The < 50 μ fraction consisting of silt plus clay was separated from these soils by wet sieving method (Jackson, 1956). Suitable quantity of soil was suspended in distilled water for 24 h and then stirred on a mechanical stirrer for 30 min. The suspension was sieved through < 50 μ sieve and the residue was again sieved with a fresh amount of distilled water till the filtrate was free of silt plus clay. The filtered suspension was transfered to reagent bottles and allowed to stand overnight for the settling

Table 2 : Physico-chemical properties of soils under study

S. No.	Location and Depth of Sampling		pH	EC Sm^{-1}	OM (%)	CEC Cmol kg^{-1}	Mechanical composition %			Texture
							Sand	Silt	Clay	
1.	ICRISAT	0 - 10 cm Alfisol	6.6	0.064	0.72	13.6	70.5	8.5	20.0	Sandy loam
2.	ICRISAT	10-20 cm Alfisol	6.4	0.032	0.48	15.9	77.8	8.0	12.5	Sandy loam
3.	ICRISAT	0 - 20cm Vertisol	7.6	0.096	0.55	58.0	23.0	15.0	61.0	Clayey
4.	ICRISAT	20 -40 cm Vertisol	8.5	0.096	0.19	56.9	33.5	13.0	52.0	Clay loam
5.	Water Management	0 -15 cm Alfisol	8.3	0.064	0.67	21.6	59.8	18.5	21.5	Sandy clay loam
6.	ARI Rice Farm	0 - 15 cm Vertisol	6.4	0.144	1.02	46.9	25.3	7.5	62.5	Clayey

of silt plus clay. The clear supernate was siphoned off and the residue containing silt plus clay was air dried under shade, pounded and stored in reagent bottles until further use.

3.1.1 Physico-chemical properties of soils :

The physico-chemical properties of soils are given in Table-2. These were determined as detailed below :

3.1.1.1 Soil reaction :

Soil pH was determined in 1:2.5 soil : water suspension after 30 minutes equilibration using "Digisun" digital pH meter with combined electrode assembly.

3.1.1.2 Total soluble salts :

The total soluble salts were determined by measuring the electrical conductivity of 1 : 2 soil : water extract after 30 minutes of equilibration on "Digisun" conductivity bridge and expressed as Sm^{-1}.

3.1.1.3 Organic carbon :

Organic carbon content of the soils was determined by Walkley and Black method as described by Jackson (1967) and expressed in percentage of organic matter.

3.1.1.4 Cation exchange capacity :

The cation exchange capacity of soil samples was determined by the method of Bowers et al. (1952) as described by Richards (1954). A known amount of soil sample was taken in 50 ml centrifuge tube and three washings were given with 1N sodium acetate (pH 8.2) solution. The excess sodium was removed by washing with alcohol and sodium on the exchange complex was replaced by three washings with 1N ammonium acetate (pH 7.0). The sodium content in ammonium acetate extract was determined on an ELICO flame photometer and the CEC of soils was expressed as C mol kg^{-1}.

3.1.1.5 Mechanical analysis of soils :

Mechanical composition of the soils was determined by the International pipette method (Piper, 1950). The relative proportions of sand, silt and clay of soils were determined to decide their textural class.

3.1.1.6 Moisture retention characteristics of soils:

Moisture retention characteristics were determined in the disturbed samples for two soils, an alfisol (Soil-5) and a vertisol (Soil-6) at 0, 0.1 and 0.3 bars (Richards, 1954) using pressure plate apperatus. Alfisol (Soil-5) sample was found to retain

26, 16 and 8 per cent moisture at saturation, field capacity and 50 per cent field capacity respectively, while vertisol (Soil-6) contained 40, 30 and 15 per cent moisture at saturation, field capacity and 50 per cent field capacity respectively.

3.1.2 Extraction, Isolation and Purification of Humic Acid :

Tyurin's method as described by Kononova (1966) was followed. The extraction and purification involved the following procedure: Suitable quantity of soil (Soil-1) was moistened with a small quantity of 0.5N HCl and then covered with 0.01N HCl. The contents were stirred intermittantly and undecomposed rootlets were removed. After 4 h, the clear supernatant was siphoned off. This treatment was repeated till supernatant was free of calcium. Soil was then washed with 0.1N H_2SO_4.

3.1.2.1 Extraction and purification of humic acid:

Decalcified samples were covered with 0.1 N NaOH and kept for 5 hours with occassional stirring. About 10 g of finely powdered Na_2SO_4 was added, stirred vigorously till the added salt was dissolved and kept aside overnight for settling. The dark coloured supernatant of humic material was siphoned out. The clay

material that came along with this humic material was removed by centrifugation.

Humic acid and Fulvic acids were separated using the differences in the solubility of these fractions in inorganic acid. The alkaline extract was transferred into a beaker and appropriate amount of concentrated H_2SO_4 was added to humic material to give a pH of 2-3. The solution was stirred at 80°C for 30 min. On cooling, the coagulated humic acid settled at bottom and fulvic acid remained in solution. The fulvic acid fraction was siphoned out without disturbing the humic acid fraction.

The humic acid fraction was redissolved in 0.1N NaOH, centrifuged 3 to 4 times to make it free from clay and then reprecipitated with 1N HCl. This material was shaken with HF + HCl (5 mL 48% HF + 5 mL conc. HCl in one litre of distilled water) and the residue was made free of fluoride with the use of 0.1N HCl. This material was transferred to dialysis bags and dialysed exhaustively against water until the water outside the dialysis bags was free of chlorides and then dried. This purified humic acid was used in adsorption studies.

3.2 CLAY SAMPLE :

The clay sample, predominantly montmorillonitic obtained from Sri Rangapur clay deposit in West Godavari district of Andhra Pradesh was used in the study. The clay was ground to a fine powder using porcelain pestle and mortar. The sample was then transferred to a sedementation cylinder after thorough dispersion in 0.05N Na_2CO_3 (pH 9.5). The cylinder was filled with Na_2CO_3 solution and was shaken end over end for a minute and set aside after noting down the time. The sample was taken at 30 cm depth at suitable time as determined by Stoke's Law for 2 μ fraction. After the sample was decanted at desired depth with an upward bent siphon the cylinder was refilled with Na_2CO_3 (pH 9.5). The process of settling for predetermined time and decanting at 30 cm depth was repeated till the yields became very small. The sample was collected in a large container and sodium chloride was added at the rate of 20 g per one litre volume. After flocculation of the clay, the supernatant was easily siphoned off. The clay was collected and stored as suspension after removing the excess salts with distilled water (Jackson, 1956).

3.2.1 Preparation of homoionic montmorillonites:

Suitable amounts of the suspension of the 2 μ fraction were taken separately in 500 mL conical

flasks. To these, IN solutions of $AlCl_3$, $FeCl_3$, $CoCl_2$, $NiCl_2$, $CuSO_4$, $ZnCl_2$, $CaCl_2$, $MgCl_2$, $BaCl_2$, KCl, NH_4Cl and NaCl were added. These were shaken thoroughly and set aside for 24 h The ion saturated clays were washed free of excess ions with distilled water and were redispersed in distilled water and used in adsorption studies.

3.3 PREPARATION OF ION SATURATED RESINS :

Suitable amounts of Amberlite IR-120 resin was taken in separate 250 mL beakers and were saturated with the desired cation by equilibrating with one molar solution of either chloride or nitrate for 12 h and washing them free of excess ions with distilled water. These were air dried and used in adsorption studies. The cations choosen for the study were same as those used for the montmorillonite.

3.4 SPECTROPHOTOMETRIC DETERMINATION OF METOXURON AND TEBUTHIURON :

Technical grade metoxuron (>99%) obtained from M/s. Sandoz (India) Ltd., and technical grade tebuthiuron (>99.5%) obtained from M/s.Eli Lily & Co. USA, were used without further purification.

Spectra of solution of metoxuron and tebuthiuron were scanned in the UV range to determine the

wave length of maximum absorption. Standard curves were constructed for absorbance vs concentration for 0 to 10 μgmL^{-1} solutions of metoxuron and tebuthiuron. The equilibrium concentration in adsorption and persistence studies were determined with respect to these curves. The effect of pH on metoxuron and tebuthiuron was also studied by observing the spectra at pH 1 to 12.

3.5. ADSORPTION STUDIES :

3.5.1 Adsorption on soils :

Adsorption was conducted by equilibrating 2 g soil with initial concentration of metoxuron ranging from 0 to 40 μgmL^{-1} in 2×10^{-2} N $CaCl_2$ solution in plastic containers. These were incubated at 27°C for 24 h with intermittent shaking. Identical soil blanks minus the herbicide were also maintained in every case. The suspensions were centrifuged at 4000 rpm for 15 min. The amount adsorbed was determined by analysing the equilibrium concentration of metoxuron and calculating the difference between this and the initial concentration after correcting for soil blanks. The soils (1, 2, 3 and 4) were used in adsorption studies.

Adsorption was carried out by equilibrating 2 g soil with initial concentration ranging from 0

to 40 μgmL^{-1} of tebuthiuron in 2×10^{-2} N $CaCl_2$ solutions. The procedure explained earlier was followed for measuring the equilibrium concentration and amount adsorbed was calculated as detailed earlier. The soils (1, 2, 3 and 4) were used in adsorption studies.

3.5.2 Adsorption on < 50 μ Fractions :

Adsorption was carried out on 0.5 g portions with the initial concentrations ranging from 0 to 15 μgmL^{-1} for metoxuron and 0 to 50 μgmL^{-1} tebuthiuron. The amount adsorbed was calculated as explained earlier.

3.5.3 Adsorption on humic acid :

Adsorption was carried out by equilibrating 10 mg of humic acid with solutions of metoxuron with initial concentration ranging from 0 to 15 μgmL^{-1} and with tebuthiuron (0-50 μgmL^{-1}) for 24 h at 27°C. The amount adsorbed was determined by determining the equilibrium concentration spectrophotometrically. Compensation for identical blanks was done as explained earlier.

3.5.4 Adsorption on Homoionic Montmorillonites:

Adsorption on homoionic montmorillonites was carried out in quadruplicate by equilibrating 5 mL of suspension (containing approximately~50 mg

clay) with metoxuron and tebuthiuron solutions such that the final volume was 10 mL and the initial concentration of metoxuron and tebuthiuron ranged from 0 to 100 μgmL^{-1} and 0 to 200 μgmL^{-1} respectively. These were incubated at 27°C for 24 h with intermittent shaking and centrifuged at 12,000 rpm for 15 min. The amount adsorbed was obtained from the difference between the initial and the equilibrium concentration after correcting for blanks.

3.5.5 Adsorption on Ion saturated Resins :

Adsorption studies on ion saturated resins was conducted in quadruplicate by equilibrating 100 mg of the corresponding cationic resin with varying levels ranging from 0 to 500 μgmL^{-1} of metoxuron and tebuthiuron respectively in 10 mL total volume. These were incubated at 27°C for 24 h and centrifuged at 5,000 rpm for 15 min. The amount adsorbed was determined as explained earlier.

The ions used to saturate the clays and resins belonged to three each of the highly polarising ions, (Al-, Fe-) alkaline earth ions (Ca-, Ba-, and Mg-) divalent 3d transition group ions (Cu-, Ni-, Co- and Zn-) and the monovalent ions (Na-, K-, NH_4) and H- .

3.6 QUANTITATIVE TREATMENT OF ADSORPTION DATA

The adsorption data was treated mostly by means of Freundlich equation (Eqn I).

$$A = KC^{\alpha} \qquad \text{-I}$$

where A = amount of substance adsorbed per unit mass of adsorbent, C = equilibrium concentration, K and α are the empirical constants dependent on the nature of adsorbent and adsorbate. The constants K and α were obtained by expressing the above equation in logarithmic form,

$$\log A = \log K + \alpha \log C \qquad \text{-II}$$

The relationship between log A and log C is linear with intercept being log K and slope α .

3.6.1 Mathematical treaztment of S-shaped Isotherms:

A new mathematical equation developed by Saroja Raman (1981) was used to analyse the S-shaped isotherms. According to this,

$$\frac{df}{dc} = kf^{2/3}(1-f) \qquad \text{-III}$$

where

$\frac{df}{dc}$ = rate of change of adsorption sites, f = fraction

adsorbed and (1-f) fraction remaining in solution at equilibrium concentration C. This equation was derived from the similarity of the S-shaped isotherms to growth curves in heterogenous precipitation.

Adsorption data was fitted to equation-III by using its integrated form (Eq.IV).

$$\chi = \frac{(f^{2/3}+f^{1/3}+1)^{1/2}}{(1-f)} + \sqrt{3}\tan^{-1}\frac{(2f^{1/3}+1)}{\sqrt{3}} = kC + \sqrt{3}\tan^{-1}\frac{1}{\sqrt{3}} \qquad \text{-IV}$$

For applying the equation (-IV), χ was calculated for f = 0.1 to 0.8 and for each value of f, C, the equilibrium concentration was read from the adsorption isotherms. The values of k were calculated from the slope of the plot of χ vs. C.

3.7 POLYMALEIC ACID :

Polymaleic acid (PMA) was suggested as a model for soil fulvic acid (FA) by several workers (Anderson and Russell, 1976; Linehan, 1977; Spiteller and Schnitzer, 1983). Polymaleic acid has an added advantage of structural homogeneity, while being structurally similar to fulvic acid. It is the product of a well defined polymerization process.

3.7.1 Preparation of PMA :

24.5 g of maleic anlydride (99%) was dissolved in 50 mL acetone. To this, 50 mL of pyridine was

added drop wise (through a separating funnel) with stirring over a magnetic stirrer, the reaction vessel was cooled in a water bath to maintain a temperature of 25°C throughout. The reaction was allowed to proceed for 24 h. The polymer was coagulated by the addition of an excess of chloroform. Following filtration under vacuum, the PMA was redissolved in acetone. The PMA insoluble in acetone was separated by vacuum filtration, washed repeatedly with chloroform and dried at room temperature (Spiteller and Schnitzer, 1983). This fraction was labelled, stored in a plastic container and used for further studies.

3.7.2 Properties of polymaleic acid :

3.7.2.1 Total acidity :

Total acidity in PMA was determined by $Ba(OH)_2$ method. Wright and Schnitzer (1959) applied this method for humic substances. In the modified procedure of Schnitzer and Gupta (1965), the sample was allowed to react with an excess of $Ba(OH)_2$. The unreacted $Ba(OH)_2$ could be determined by back titration with standard acid.

$$Ba(OH)_2 + 2\ HA \longrightarrow BaA_2 + 2\ HOH$$

50 mg and 100 mg of PMA alongwith blanks in duplicate were taken in separate stoppered flasks

and 20 mL of 0.2N $Ba(OH)_2$ was added. The flasks were shaken for 24 h at room temperature. The suspension was filtered and the residue was washed with CO_2 free distilled water. The filtrate and washings were titrated against 0.5N HCl to pH 8.4 potentiometrically. Identical blanks were maintained simultaneously.

$$\text{Total acidity (me/g)} = \frac{(\text{TV for Blank}) - (\text{TV for sample})}{\text{wt. of sample (mg)}} \times 0.5 \times 1000$$

3.7.2.2 Carboxyl groups :

The method is based on the liberation of acetic acid when acids are treated with CaOAc and its titration with standard NaOH

$$2\ RCOOH + (CH_3\ COO)_2\ Ca \longrightarrow (RCOO)_2\ Ca + 2\ CH_3COOH$$

To 50 mg and 100 mg portions of PMA in a stoppered flask, 10 mL of 1N CaOAc and 40 mL of CO_2 free distilled water were added. Blanks were set up simultaneously in duplicate. After shaking at room temperature for 24 h, the suspension was filtered and the residue was washed with CO_2 free distilled water. The filtrate and washings were titrated potentiometrically with standard 0.104N NaOH to pH 9.8.

$$\text{- COOH groups (me/g)} = \frac{(\text{TV for sample}) - (\text{TV for Blank})}{\text{wt. of sample (mg)}} \times 0.104 \times 1000$$

3.7.2.3 Phenolic - OH groups :

The phenolic OH was calculated as the difference between total acidity and - COOH acidity.

Phenolic OH groups (me/g) = (Total acidity) (me/g) - (-COOH groups) (me/g)

3.7.2.4 Dissociation constant (pKa) of PMA :

Dissociation constant of PMA was determined using Henderson - Hesselbalch equation

$$HA \rightleftharpoons A^- + H^+ \qquad \text{- V}$$

$$Ka = \frac{[A^-]\,[H^+]}{[HA]} \qquad \text{- VI}$$

$$\text{Thus } pH = pK + \log \frac{[A^-]}{[HA]} \qquad \text{- VII}$$

From the potentiometric titration data, [HA] and $[A^-]$ were obtained at different pH. Thus pKa was determined as the X-intercept of the plot of $\log \frac{[A^-]}{[HA]}$ vs. pH.

3.7.2.5 Spectral properties :

The spectrum of PMA was recorded in pH range 1 - 7. The pH was adjusted with 0.1 N NaOH and 0.1N HCl. In the UV range, PMA showed a well defined peak at 255 nm (Fig. 23) till pH 4.0. Standard curve was constructed in the concentration ranging

from 0 - 100 $\mu g ml^{-1}$ with reference to which the equilibrium concentrations in adsorption studies were determined. Infra Red spectrum was recorded on KBr pellets on a SP-1200 IR spectrophotometer from 400 to 3500 cm^{-1}

3.7.2.6 Potentiometric titrations :

200 mg of PMA was dissolved in 50 mL distilled water. This was titrated against 1.04 N NaOH potentiometrically on 'Digisun' pH meter using a combined electrode assembly to a pH 12.0.

3.7.2.7 Determination of equivalent weight :

The equivalent weight of PMA was determined by titrating conductimetrically 200 mg PMA with standard 1.04N NaOH. A sharp break was obtained at the end point. Equivalent weight of PMA was determined from the titre value of 200 mg PMA with standard NaOH.

$$\text{Eq.wt.} = \frac{\text{wt. of PMA}}{\text{Eq. of NaOH required for titration}} = \frac{200}{1.872} = 106.8$$

3.7.3 Adsorption of PMA on homoionic montmorillonites and resins :

5 mL of homoionic clay suspension containing approximately 50 mg clay were equilibrated with PMA (0-100 $\mu g mL^{-1}$), the total volume of the final suspension being 10 mL (in quadruplicate). These were incubated

at 27°C for 24 h with intermittent shaking and centrifuged at 12,000 rpm for 15 min. The concentration of PMA in the supernatant was determined at 255 nm and the amount adsorbed was determined from the difference between the initial and equilibrium concentration after correcting for blanks. Adsorption data was analysed according to the equations described earlier.

Adsorption on resins was carried out in the same way by equilibrating 0.1 g of cationic resin (saturated with different cations) with PMA (0 to 500 μgmL^{-1}) at 27°C for 24 h, the total volume being 10mL. The equilibrium concentration was determined in the supernatant at 255 nm after centrifuging at 5000 rpm for 15 min and the amount adsorbed was determined as explained earlier.

3.7.4 Preparation of Model Clay-PMA complexes:

150 mL aliquots of different homoionic montmorillonites (containing approximately 1.5 g of clay) were equilibriated with 300 mL of 100 μgmL^{-1} PMA for 24 h with intermittent shaking in separate conical flasks. The clay-PMA complexes were washed free of excess PMA with distilled water. These clay-PMA complexes suspended in distilled water were used for adsorption studies.

3.7.4.1 Comparison of adsorption of metoxuron and tebuthiuron on homoionic clays and model clay-PMA complexes :

To compare the adsorption of metoxuron and tebuthiuron on different homoionic clays and the corresponding model clay-PMA complexes, adsorption of metoxuron and tebuthiuron was carried out simultaneously on suspensions containing 50 mg of homoionic clay/the corresponding clay-PMA complex. For this two initial concentrations viz. 20 and 50 μgmL^{-1} of metoxuron and tebuthiuron were used and the suspension was shaken for 24 h at 27°C and centrifuged at 12,000 rpm for 15 min. The absorbance of supernatant was determined at 240 nm for metoxuron and 254 nm for tebuthiuron. Identical treatments were carried out with the homoionic clays and clay-PMA blanks, minus the herbicides and corrections for blanks were carried out. The amount adsorbed was calculated from the difference between intial and the equilibrium concentration and expressed in µg/100 mg.

3.8 PERSISTENCE OF METOXURON AND TEBUTHIURON IN SOIL

Two soils, an alfisol (Soil-5) and a vertisol (Soil-6) were used for the study. These soils were air dried and passed through 2 mm sieve. About 2.2 kg soil samples were treated with methanol dissolved metoxuron and tebuthiuron in a fine and uniform spray to give a final concentration of 20 µg/g of dry soil. The soil was thoroughly mixed and methanol was allowed to evaporate.

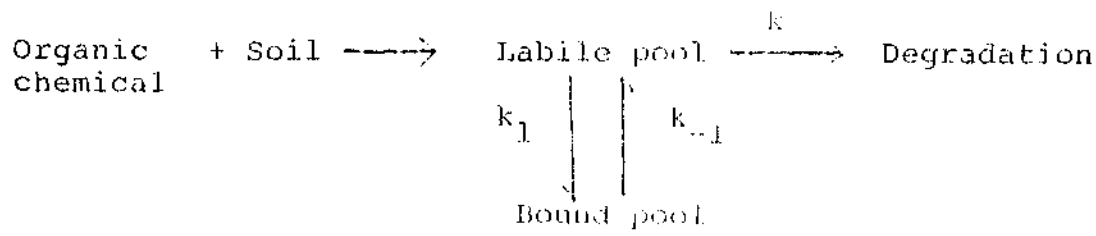
In order to study the effect of moisture, 10 g of duplicate portions of herbicide treated soils were weighed into polythene bags and distilled water was added to give soil moisture levels at saturation, field capacity and 50 per cent field capacity. These bags were sealed air tight. Identical soil blanks without ths herbicide were maintained simultaneously.

The samples after moisture treatment were incubated at 27 $\pm$ 1°C and 10 $\pm$ 1°C in BOD incubators. The soil samples were extracted at 4 day intervals upto 40 days, 8 day intervals till 80 days, 15 day intervals till 125 days and 30 day intervals till 155 days with cold methanol to measure the quantity of herbicide extracted. The procedure followed was as follows :

The individual soil samples at each interval were transferred to screw capped test tubes and shaken with two 20 mL portions of methanol for 30 minutes on mechanical shaker and filtered through Whatman No 1 filter paper. The final volume of the extract was made upto 50 mL and the absorbance mealsured at 240 nm for metoxuron and 254 nm for tebuthiuron. The concentrations of herbicide in methanol were determined with reference to the standard curves.

3.8.1 Kinetics of disappearance of metoxuron and tebuthiuron from soil :

The concentrations of methanol extractable metoxuron and tebuthiuron at different moisture and temperature levels at various time intervals were plotted against time. These were then plotted as logarithm of the amount recovered vs time to determine the rate of disappearance. The disappearance curve consisted of two typical segments, a steeper line followed by a path of much smaller slope indicating two paths of disappearance. The disappearance curve in each case was interpreted in terms of the model suggested initially by Hamaker and Goring (1976). According to this model, a soil applied chemical distributes itself in two compartments, which may be termed as labile and bound. The chemical in the labile pool is easily degradable and extractable in suitable organic solvents. The bound pool consists of the chemical adsorbed on more restricted sites in soil and is not extractable by mild organic solvents. The scheme of events that takes place during the interaction of the chemical with the soil can be pictured as



where k is the rate constant for degradation rate of the chemical, k_1 for entry into the bound pool and k_{-1} for reentry into labile pool. The constants k, k_1 and k_{-1} were calculated as per the method of Hamaker and Goring (1976) as defined below :

$$k_1 = -m - k - \left(1 + \frac{k}{m}\right) k_{-1}$$

$$k_{-1} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Negative values were neglected

Where

$$a = \frac{(R^2-1) \times k^2}{m^2}$$

$$b = \frac{-4k^2}{m} - 2(R^2+1)k$$

$$c = (R^2-1)m^2 - 4mk - 4k^2$$

$$R = \left(\frac{2I}{C_0}\right) - 1$$

k = difference slope of semilog plot

m = slope of the steady state line or smaller slope

I = antilog of intercept of extrapolated line of steady state line or smaller slope.

C_0 = Initial concentration of the chemical.

The above calculations involve a number of interdependent steps and thus lead to large cumulative errors. Since a clear two stage disappearance of the

herbicides was seen in the time over which the experiment was conducted and since the rate of reentry of herbicide from bound pool to labile pool can be considered negligible, as a valid approximation, the steeper slope (k) can be considered as the rate of decomposition and the smaller slope (m) as the rate of entry into bound pool. These were determined from the slope of flatter portion of the curve and from the difference slope of the steep and flatter portion. This is explained in Fig.2 given below :

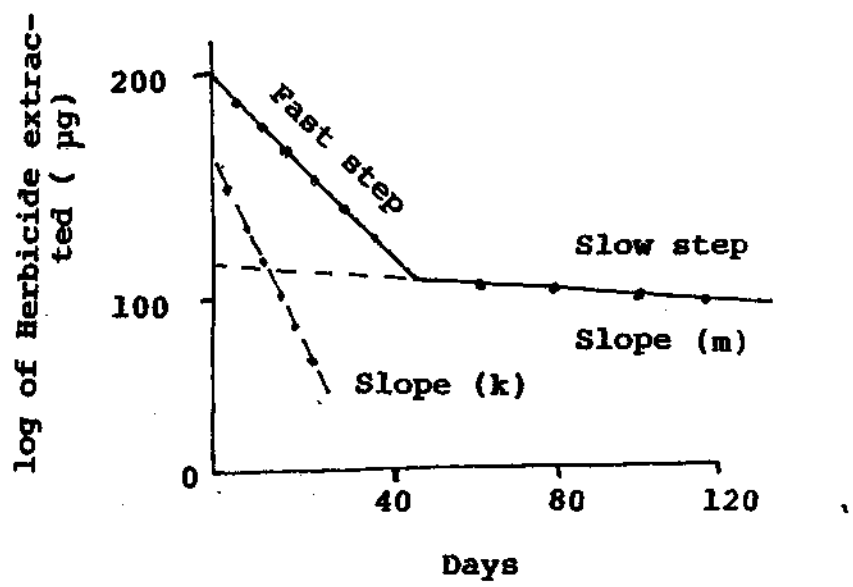


Fig.2 : DISAPPEARANCE CURVE FOR METOXURON AND TEBUTHIURON IN SOIL

RESULTS

CHAPTER IV

RESULTS

The experimental findings of the present study have been presented under the following heads:

1) Adsorption of metoxuron and tebuthiuron on homoionic montmorillonites with adsorption on cation saturated resins as model compounds.

2) Adsorption of metoxuron and tebuthiuron on soils and their constituents.

3) Preparation and characterisation of polymaleic acid as a model for soil fulvic acid, adsorption of PMA on homoionic montmorillonites and comparison of adsorption of metoxuron and tebuthiuron on montmorillonite-PMA complexes.

4) Persistence of metoxuron and tebuthiuron in an alfisol and vertisol, and to evaluate physical and mathematical models to predict residues under field conditions.

4.1 ADSORPTION OF METOXURON AND TEBUTHIURON ON HOMOIONIC MONTMORILLONITES WITH ADSORPTION ON CATION SATURATED RESINS AS MODEL COMPOUNDS:

4.1.1 Spectral characterisation of metoxuron and tebuthiuron :

Metoxuron does not exhibit any absorbance in the visible range. The UV spectra of aqeous solutions of metoxuron gave a sharp absorption peak at 240 nm (Fig.3). Identical spectra were obtained in 10^{-2} NHCl and 10^{-2}N NaOH thus ruling out any changes like protonation, dissociation or decomposition in the metoxuron molecule over the wide range of pH 2-12. Aqueous solutions of tebuthiuron were colourless and gave sharp absorption peak at 254 nm. The spectra was scanned at pH 1-12 (Fig.5). The spectra showed the tebuthiuron undergoes protonation below pH 2.0. The spectra of equilibrium solutions after adsorption on homoionic clays, also ruled out any change in the chemical nature of the herbicides due to adsorption-desorption. Standard curves for metoxuron (Fig.4) and tebuthiuron (Fig.6) passed through the origin and obeyed Beer-Lambert's law in the given range of concentration. The standard curve had a slope of 0.0625 absorbance units per $\mu g mL^{-1}$ for metoxuron and 0.055 absorbance units per $\mu g mL^{-1}$ for tebuthiuron. The equilibrium concentrations of metoxuron and tebuthiuron in the supernatant after adsorption on clays,

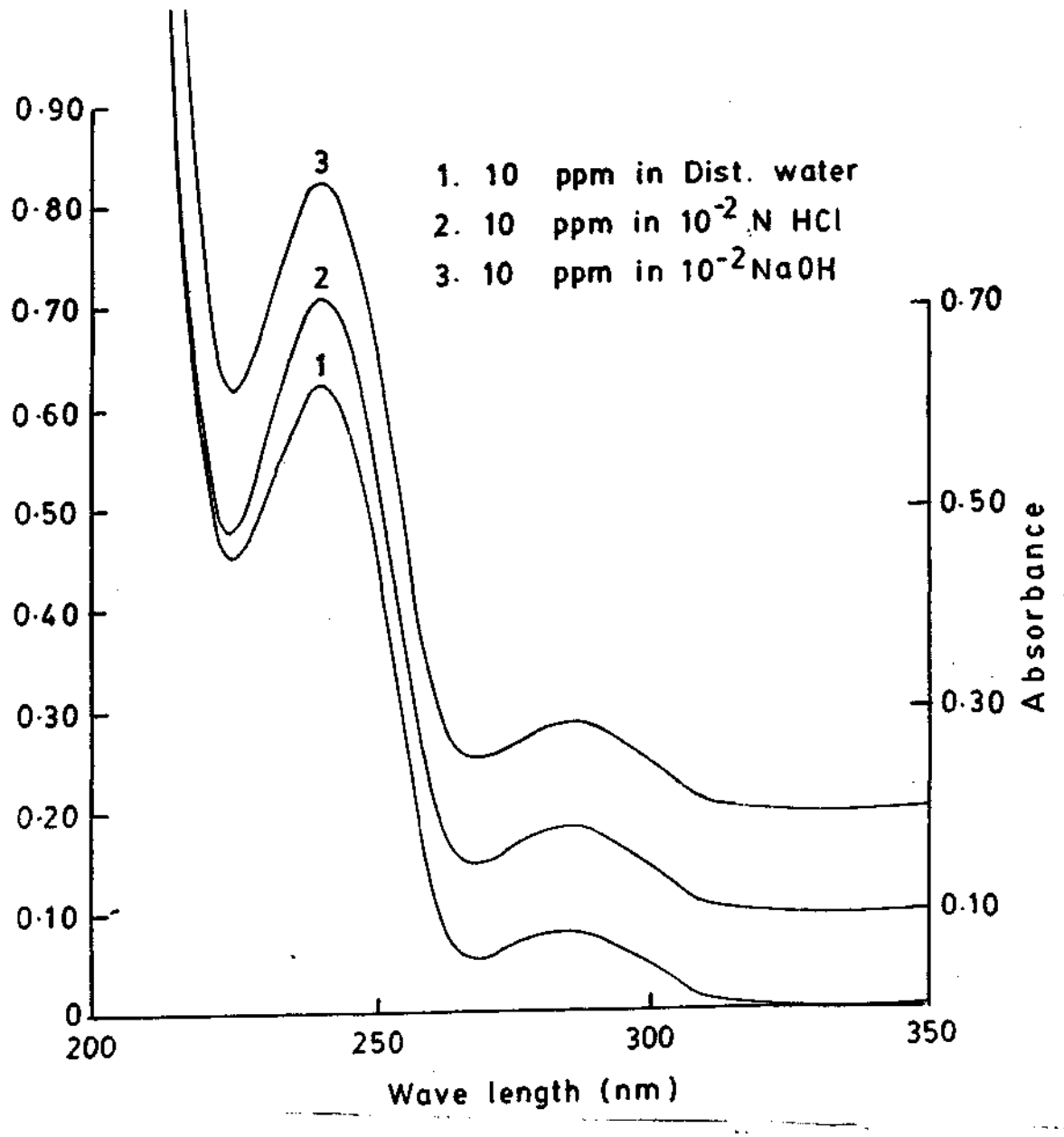


FIG. 3: SPECTRAL SCAN OF METOXURON

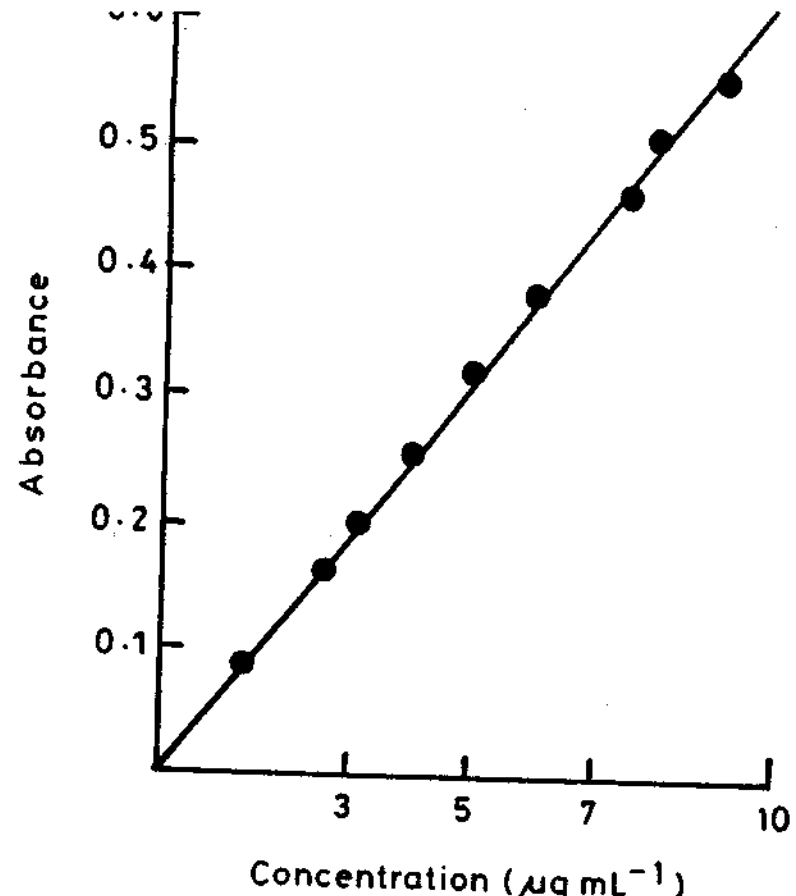
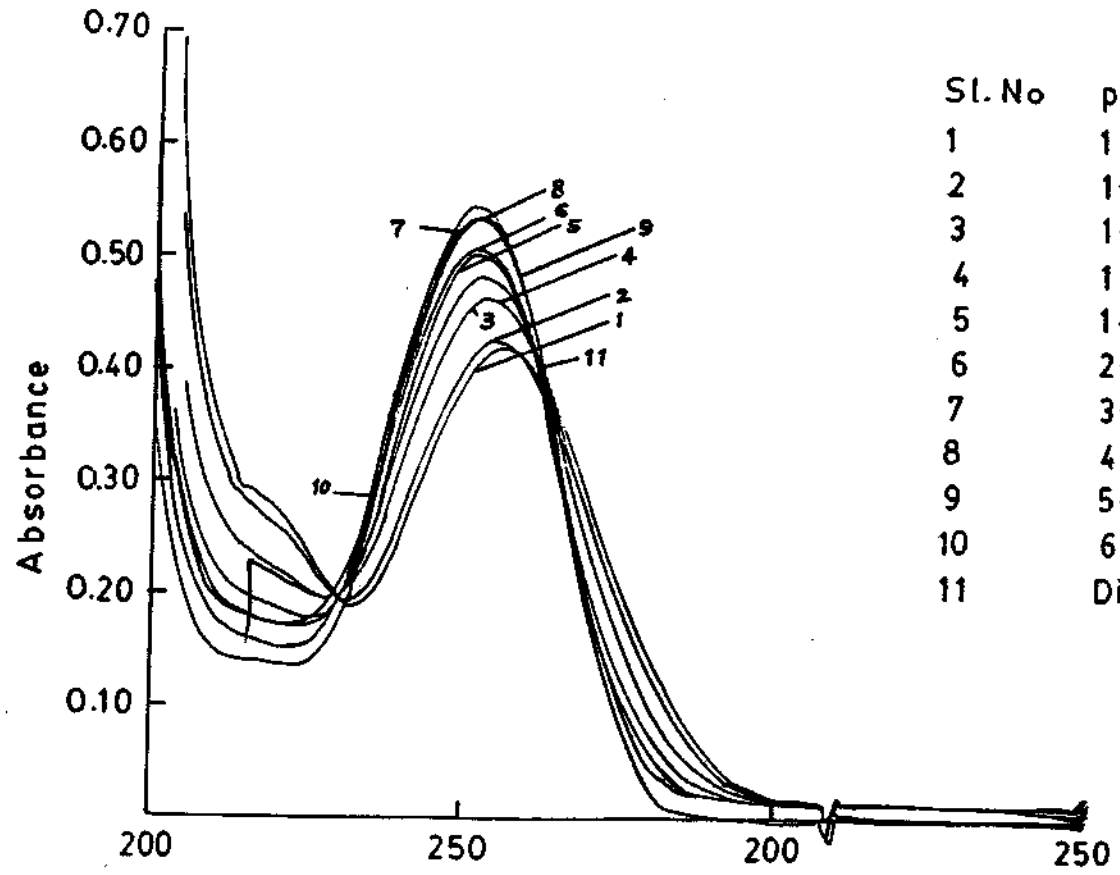


FIG. 4 : STANDARD CURVE FOR METOXURON
(240 nm)



Sl. No	pH
1	1·0
2	1·2
3	1·4
4	1·6
5	1·8
6	2·0
7	3·0
8	4·0
9	5·0
10	6·0
11	Dist. water

FIG. 5 : SPECTRUM OF TEBUTHIURON

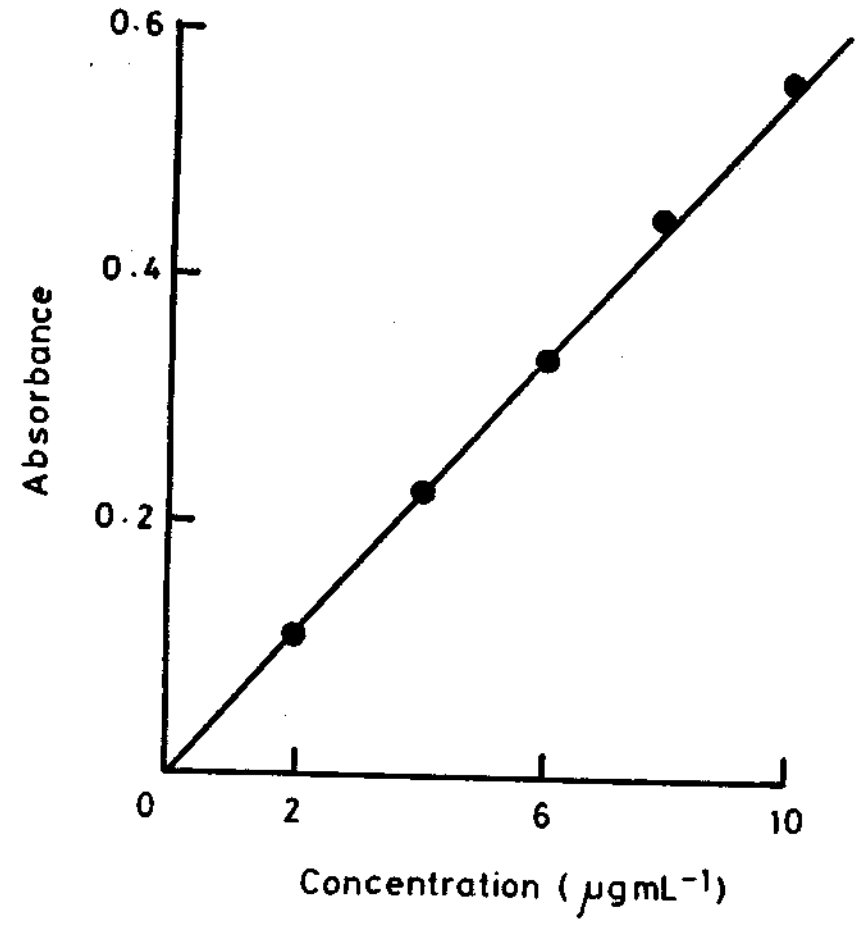


FIG. 6 : STANDARD CURVE FOR TEBUTHIURON (254 nm)

soils, HA or clay-organo complexes were determined with reference to their corresponding standard curves after sub tracting for corresponding blanks.

4.1.2 Adsorption of metoxuron on homoionic montmorillonites:

Adsorption of metoxuron was studied on aqueous suspensions of homoionic H-, Al-, Fe-, Ni-, Cu-, Zn-, Ca-, Ba-, Mg-, K-, Na-, NH_4- montmorillonite, prepared as explained earlier. 5 mL of clay suspension containing ~50 mg clay was equilibrated with 0 to 100 $\mu g mL^{-1}$ initial concentration of metoxuron centrifuged and assayed spectrophotometrically at 240 nm.

Complete adsorption data comprising of initial concentration, equilibrium concentration and the amount adsorbed for the homoionic montmorillonite are given in Table 3.

The different homoionic montmorillonites showed widely different adsorptive capacity. The amount adsorbed increased with increase in initial concentration in all the cases. The range of adsorption for homoionic clays for variation in the initial concentration of metoxuron from 10 to 100 $\mu g mL^{-1}$ was as follows :

The amount adsorbed varied from 9.8 to 406.0 µg/100 mg for H-M, 37.7 to 340.7 µg/100 mg for Fe-M,

35.1 to 290.5 µg/100 mg for Al-M. The adsorption varied from 41.2 to 316.1 µg/100 mg for Ni-M, 16.9 to 270.6 µg/100 mg for Zn-M, 46.5 to 231.8 µg/100 mg for Cu-M. For alkaline earth metals it varied from 39.0 to 245.2 µg/100 mg for Ba-M, 18.5 to 245.2 µg/100 mg for Mg-M, 33.6 to 239.0 µg/100 mg for Ca-M. For the monovalent ions the amount varied from 28.6 to 245.9 µg/100 mg for NH_4-M, 6.9 to 73.5 µg/100 mg for Na-M, 9.2 to 71.2 µg/100 mg for K-M (Table 3).

Adsorption isotherms constructed from the above data are given in Fig.7. These isotherms were generally S-shaped and were fitted to Freundlich model. The constants 'K' and α are given in Table 4. The value for Freundlich 'K' was lowest for K-M (1.24) and highest for Cu-M (11.20). α ranged from 0.67 (for Cu-M) to 1.22 (for Zn-M).

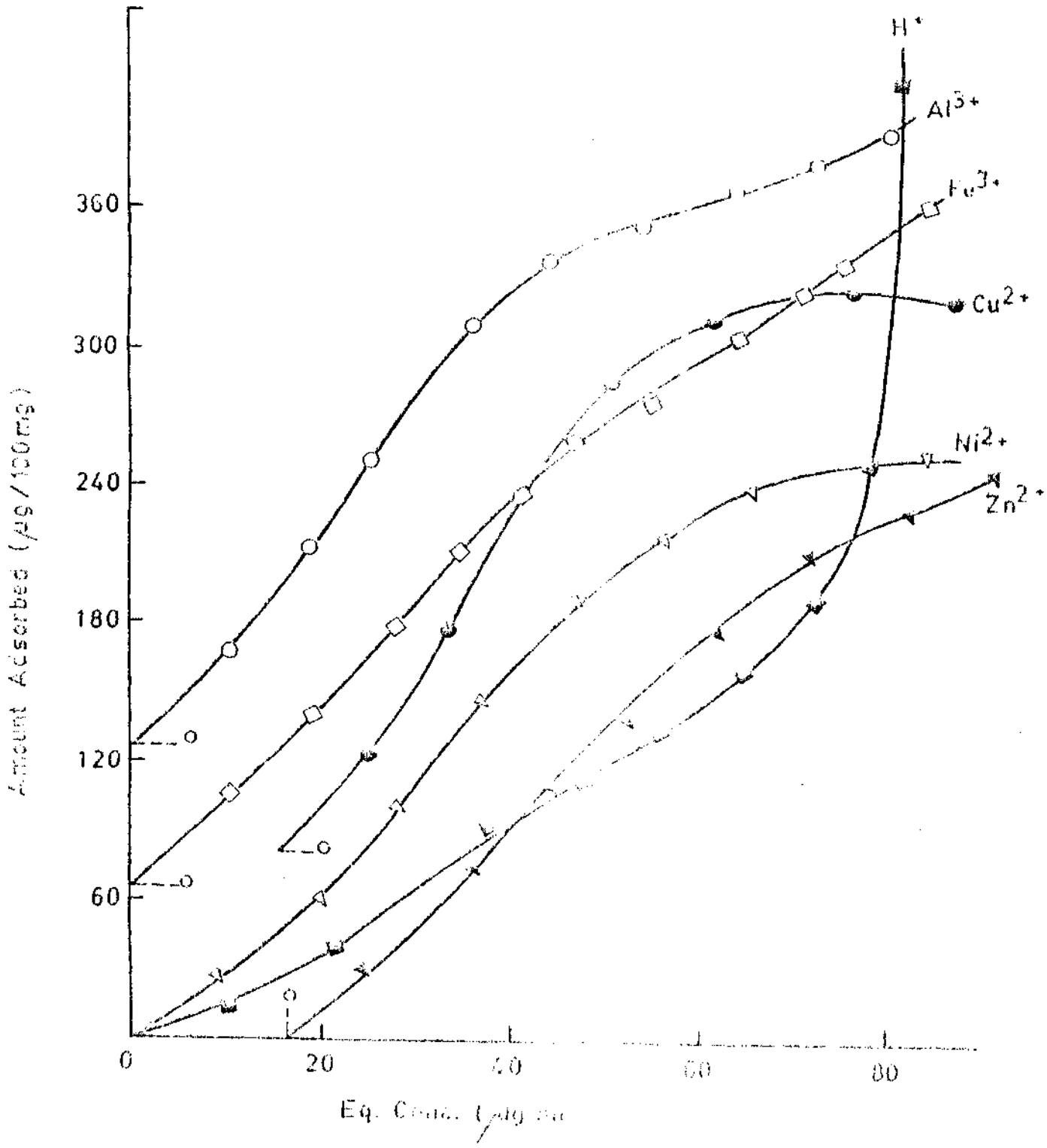
Since the adsorption isotherms were S-shaped, which in general is a result of two driving forces viz., the concentration of metoxuron in soil solution and the cooperativity of metoxuron already adsorbed operating simultaneously, a new mathematical equation as explained under 'Review' (Baroja Raman, 1981) was also tried to quantify the adsorption data. For applying the equation, the value of χ was calculated for "f" 0.1 to 0.8. For each value of f, C, the corresponding

Table 3 : Adsorption of metoxuron on H-, Fe-, Al-, Ni-, Cu-, Zn-, Ca-, Ba-, Mg-, Na-, K-, NH_4 - Montmorillonite

Initial concentration $\mu g\ mL^{-1}$	H-		Fe-		Al-		Ni-		Cu-		Zn-		Ca-		Ba-		Mg-		Na-		K-		NH_4	
	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)
10	8.26	9.81	9.01	37.74	8.77	35.17	8.92	41.24	8.15	46.59	8.76	16.93	8.95	33.67	9.08	39.35	9.13	18.59	9.31	6.92	9.17	9.28	9.42	28.68
20	17.78	29.63	18.74	70.78	17.25	88.94	17.84	71.66	16.00	60.19	17.95	44.75	17.77	73.47	18.44	70.35	18.89	25.21	18.74	19.84	18.13	23.70	18.95	51.37
30	27.59	35.65	28.11	104.12	26.17	112.56	27.68	86.26	26.96	80.25	27.94	71.26	27.79	95.30	27.60	102.66	27.29	54.63	25.77	23.68	26.23	37.27	28.44	92.26
40	35.25	87.32	36.41	132.53	32.36	204.49	34.81	197.37	34.41	134.62	37.09	99.87	36.29	123.27	35.54	190.33	34.32	119.63	35.12	29.09	35.30	49.34	37.45	127.41
50	44.63	97.30	46.65	144.21	43.04	217.46	43.61	218.14	43.62	156.32	46.47	148.75	47.18	155.29	44.86	278.52	44.78	121.88	46.19	31.38	44.34	57.63	46.09	190.12
60	53.85	134.73	54.86	196.88	52.48	231.87	53.43	247.54	52.70	167.89	54.21	233.25	54.14	187.62	54.34	227.49	54.50	139.54	55.87	32.59	54.78	61.22	55.93	190.62
70	62.68	154.32	64.78	224.67	62.17	238.81	62.39	256.35	62.64	179.59	63.29	251.51	63.77	205.22	64.67	227.88	62.78	156.59	65.29	35.33	64.55	70.58	65.40	231.00
80	71.13	244.75	72.87	272.56	70.86	259.91	71.78	297.84	71.32	208.46	73.39	257.05	73.66	209.86	74.48	235.35	72.01	178.89	75.55	63.62	74.13	70.64	74.91	241.75
90	78.94	365.25	82.18	296.93	80.86	263.82	82.27	297.09	80.89	218.33	82.98	261.29	82.93	222.10	83.93	244.30	79.67	222.13	85.74	67.96	84.51	70.86	84.34	245.78
100	84.95	406.66	89.46	340.73	89.96	290.58	91.69	316.18	90.66	231.83	92.74	270.65	92.49	239.08	93.71	248.20	88.43	245.28	94.41	73.59	94.93	71.24	94.68	245.98

Eq.C = Equilibrium concentration; A.A = Amount Adsorbed

FIG. 7 : ADSORPTION ISOTHERMS OF METOXURON ON HOMOIONIC MONTMORILLONITES



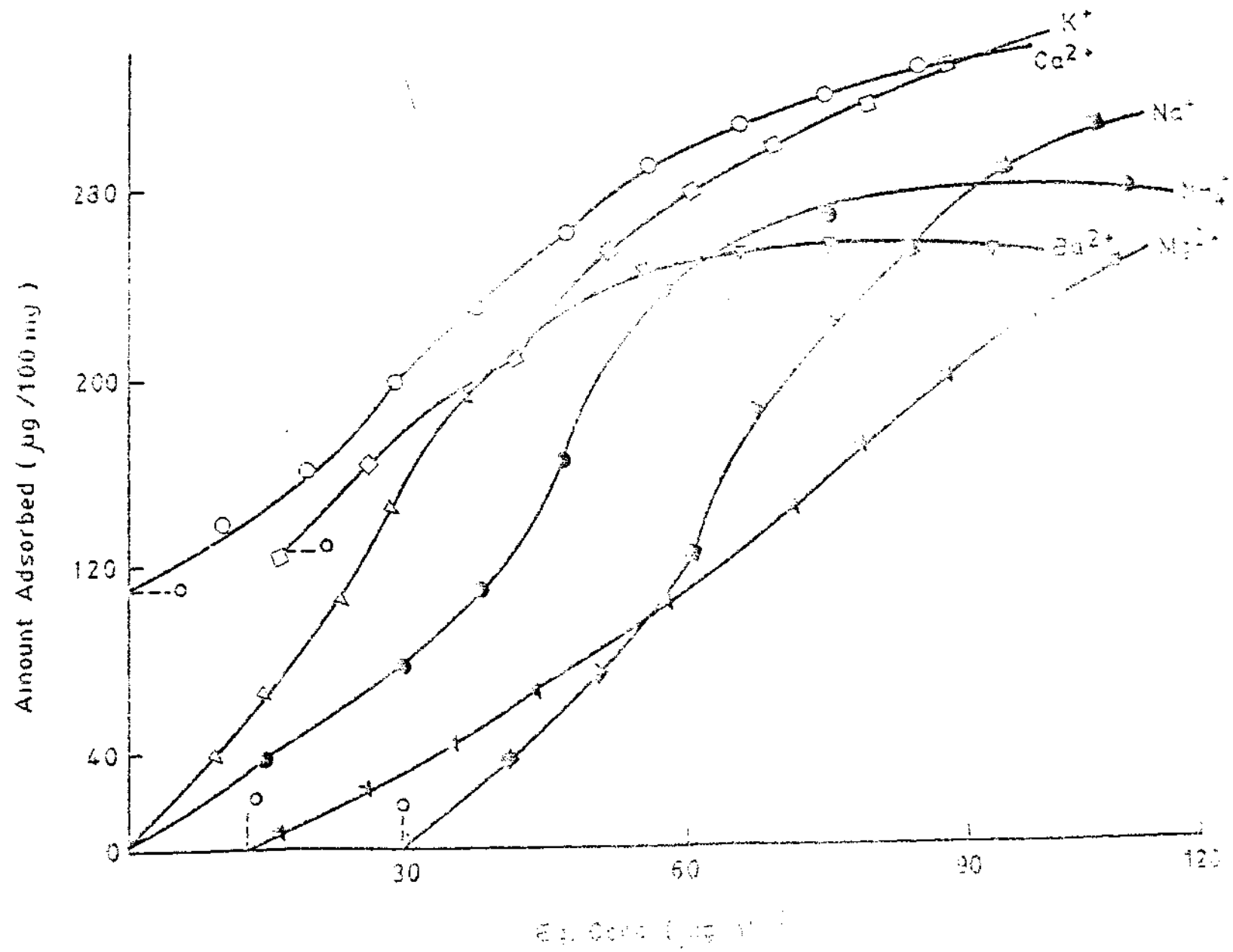

K+
Ca2+
Na+
Ba2+
Mg2+
230
200
120
40
0
30
60
90
Amount Adsorbed (µg /100 mg)

Table 4 : Maximum adsorption, K_L, k, and Freundlich constants of metoxuron on homoionic montmorillonites

Ion saturating the complex	Maximum Adsorption µg/100 mg	K_L μg^{-1}mL	k μg^{-1}mL	Freundlich constants	
				K	α
H-	402*	-	-		
Fe-	340*	0.020	-	4.16	0.97
Al-	290*	0.037	-	4.27	0.86
Cu-	235	0.031	0.068	11.20	0.67
Ni-	316	0.029	0.065	4.62	0.90
Zn-	270	0.034	0.055	1.41	1.22
Ba-	255	0.035	0.063	4.79	0.80
Ca-	240	0.029	0.048	4.79	0.74
Mg-	245	0.024	0.043	2.09	1.15
K-	71	0.039	0.078	1.24	0.97
Na-	73	0.027	0.075	1.29	0.89
NH_4-	245	0.028	0.053	3.55	0.99

* Did not reach surface saturation

equilibrium concentration was read from the adsorption isotherms. The values of Γ and the corresponding C are given in Table 5. In the case of H-M, Al-M and Fe-M, surface saturation was not reached and hence it was not possible to apply the equation. k, the coefficient of increase in adsorption was obtained from the slope of χ vs C (Fig.8). It varied from 0.043 $(\mu g)^{-1}$mL (Mg-M) to 0.078 $(\mu g)^{-1}$mL (K-M).

Although the isotherms were not completely of Langmuir type, since a tendency for surface saturation was present, a comparison of the relative binding strength (K_L) was estimated at 50 per cent surface saturation, which corresponds to unit activity of the surface. Since $K_L = \frac{\theta}{1-\theta} \times \frac{1}{C}$, when $\theta = 0.5$, $K_L = (C_{0.5})^{-1}$ where $C_{0.5}$ corresponds to the equilibrium concentration at 50 per cent surface saturation. The values of maximum adsorption, K_L, k, and Freundlich constants are given in Table 4.

4.1.3 Adsorption of metoxuron on ion saturated resins:

Adsorption of metoxuron was studied on homoionic IR-120 resin saturated with the same cations as in the case of montmorillonite, to evaluate the role of cation exchange resin as a model for the soil clays.

Table 5 : Fraction adsorbed and equilibrium concentration values for metoxuron

Fraction adsorbed f		Equilibrium concentration (μgmL^{-1})								
	X	Ni-	Cu-	Zn-	Ba-	Ca-	Mg-	Na-	K-	NH_4-
0.1	2.335	9.0	4.0	12.5	7.5	7.0	12.5	9.5	7.5	9.0
0.2	2.732	16.5	11.0	22.5	13.5	14.0	25.0	17.0	12.0	17.5
0.3	3.090	22.5	19.5	32.0	18.5	18.5	34.0	25.0	16.0	24.0
0.4	3.410	28.5	26.5	39.0	22.5	28.0	41.0	33.5	20.5	30.0
0.5	3.720	32.0	32.5	44.5	26.5	35.5	48.5	40.5	25.5	35.0
0.6	4.050	37.0	36.0	48.0	30.5	40.0	57.5	47.5	29.5	39.5
0.7	4.440	45.0	46.0	51.5	34.5	44.0	66.0	56.0	34.0	43.0
0.8	4.910	54.0	57.0	54.0	40.0	50.0	74.5	67.0	44.0	50.0

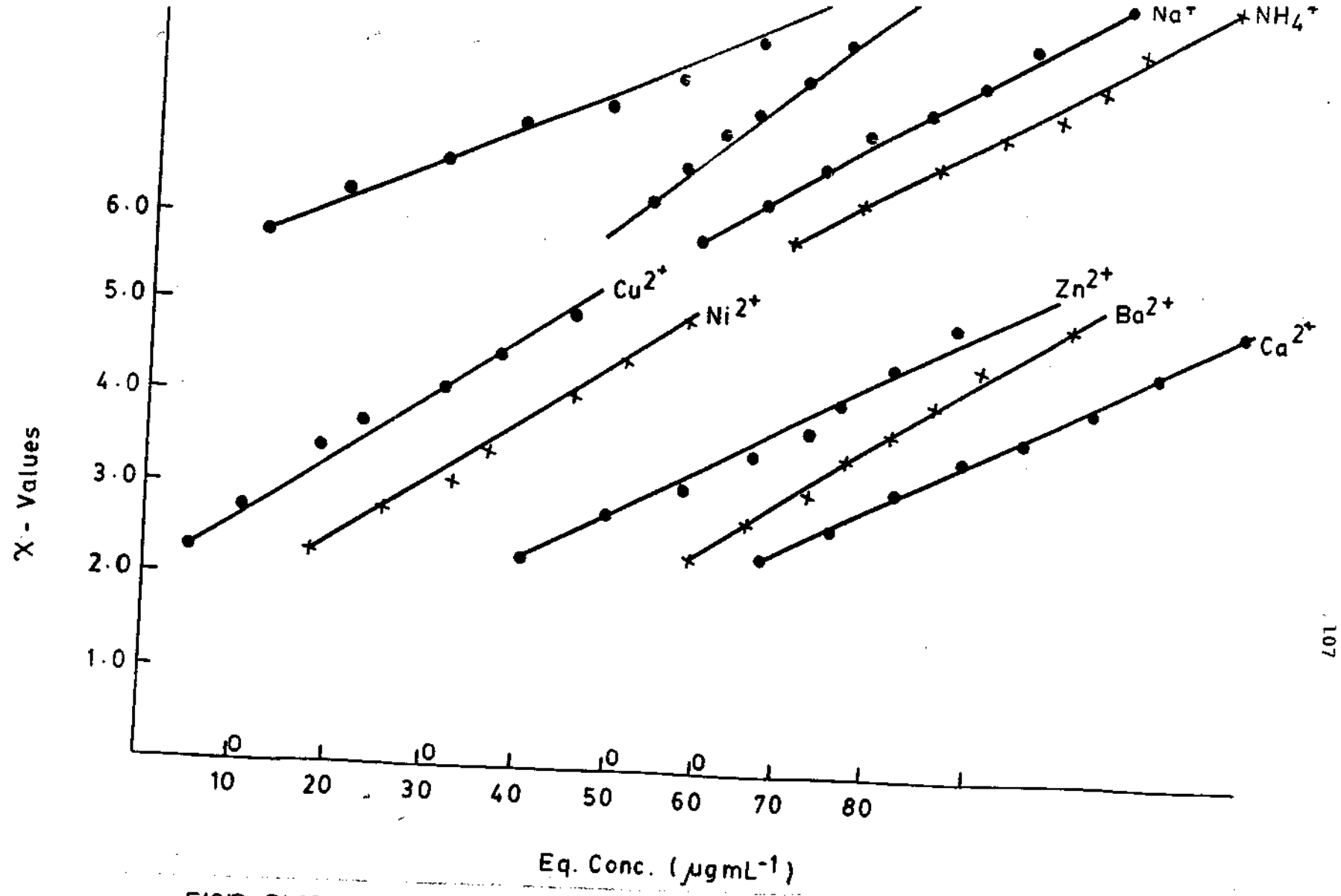


FIG.8. PLOT OF χ vs EQ.CONC FOR ADSORPTION OF METOXURON ON HOMOIONIC MONTMORILLONITES

The amount of metoxuron adsorbed at each initial concentration and the corresponding equilibrium concentration are given in Table 6. As in the case of homoionic montmorillonites, the adsorption was highest for H-R, Fe-R and Al-R. The amount adsorbed varied from 79.9 to 914.6 µg/100 mg for H-R, 80.9 to 890.4 µg/100 mg for Fe-R and 57.3 to 873.8 µg/100 mg for Al-R (Table 6).

The transition metal ions followed H-, Al- Fe- in adsorption. It was 37.3 to 763.4 µg/100 mg for Cu-R, 26.6 to 736.5 µg/100 mg for Co-R, 28.5 to 709.0 µg/100 mg for Zn-R, and 29.7 to 664.7 µg/100 mg for Ni-R as the initial concentration of metoxuron increased from 50 to 500 µg $ml.^{-1}$.

For Ba-R, Ca-R, Mg-R the amount adsorbed varied from 12.8 to 634.3 µg/100 mg, 6.3 to 597.6µg/100 mg 13.3 to 586.7 µg/100 mg respectively.

The amount adsorbed was lowest for resin saturated with monovalent ions and varied from 9.1 to 397.5 µg/100 mg for K-R, 7.3 to 390.1 µg/100 mg for NH_4-R and 10.1 to 310.1 µg/100 mg for Na-R (Table 6). Thus the adsorption on resins followed the same trends as in clays and followed the order trivalent > Divalent> Monovalent.

Table 6 : Adsorption of metoxuron on homoionic resins (IR-120)

Initial concentration $\mu g\ mL^{-1}$	H-		Al-		Fe-		Cu-		Co-		Zn-		Ni-	
	Eq.C (µg/mL)	A.A. (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µ g/mL	A.A (µg/100 mg)	Eq.C (µ g/mL)	A.A (µg/100 mg)	Eq.C (µ g/mL)	A.A (µ g/100 mg)	Eq.C (µg/mL	A.A (µ g/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)
50	42.00	79.90	43.96	57.37	41.90	80.95	46.25	37.30	47.38	26.61	47.14	28.51	46.99	29.70
100	78.69	213.06	79.28	207.14	85.56	144.45	91.90	80.95	85.07	149.90	82.85	171.43	85.53	144.62
150	117.03	329.36	120.95	290.47	119.28	307.14	137.53	124.60	128.73	212.69	130.47	195.23	117.76	320.95
200	152.46	475.32	160.63	393.65	164.92	350.79	172.26	277.30	167.41	325.87	174.12	260.27	158.98	331.75
250	191.60	583.97	195.33	516.67	204.60	453.96	210.95	390.47	207.09	428.88	215.79	342.06	235.25	447.53
300	233.76	662.35	240.00	600.00	246.26	537.30	252.63	473.65	246.79	532.26	253.49	465.07	243.54	564.51
350	277.28	727.14	287.61	623.21	285.93	643.67	294.71	587.14	285.45	646.39	297.14	528.57	293.24	568.51
400	309.65	909.49	319.96	806.35	323.65	840.65	333.96	690.31	327.11	688.89	332.86	671.42	334.09	659.13
450	359.77	987.66	369.61	806.34	360.09	866.07	374.06	788.03	377.73	722.69	362.46	675.39	326.54	664.51
500	406.53	914.61	412.61	873.69	410.95	890.47	423.25	763.46	426.34	736.50	429.07	709.04	435.98	664.75

Contd..

Table 6 (Contd..)

Initial concentration $\mu g\ mL^{-1}$	Ca-		Mg-		Ba-		K-		Na-		NH_4-	
	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	C.C (µg/100 mg)
50	49.36	6.34	48.65	13.31	48.81	12.87	49.24	9.13	48.98	10.15	49.26	7.36
100	90.03	99.68	92.07	77.42	92.24	77.50	94.25	57.51	94.98	50.15	92.36	76.30
150	130.71	192.85	133.32	163.74	133.86	161.31	138.82	111.75	140.54	94.51	138.56	114.01
200	171.38	286.19	174.15	267.74	170.86	291.31	182.24	177.52	178.24	217.52	182.41	175.84
250	213.06	369.52	215.36	346.34	212.68	379.13	225.89	241.05	227.98	220.15	221.98	280.14
300	256.71	482.85	259.38	426.31	258.86	411.31	270.24	297.51	276.24	237.51	266.56	334.35
350	300.34	496.01	302.32	471.73	303.64	494.51	318.98	310.51	324.68	253.17	314.64	353.76
400	344.01	559.84	343.64	543.57	344.64	554.54	364.54	354.54	372.96	270.31	364.36	356.30
450	390.65	593.49	392.25	577.74	390.24	597.51	410.98	390.15	421.54	284.51	411.56	384.37
500	440.28	597.61	441.32	586.74	436.58	634.31	460.24	397.51	468.98	310.15	460.98	390.14

Adsorption isotherms were constructed for all the ions in the initial concentration range of 0 to 500 μgmL^{-1} (Fig.9). These were mainly parabolic in nature with a tendency to reach surface saturation within this concentration range. There was however a tendency for S-shape in the initial stage of adsorption. The adsorption isotherms were analysed according to Freundlich equation. The relative binding energy K_L was also calculated. The Freundlich constants, K_L and maximum adsorption are given in Table 7. Freundlich constant 'K' varied from 1.02 (for Mg-R) to 2.69 (for Al-R) whereas α varied from 0.98 (for Na-R) to 2.17 (for Cu-R). The amount of maximum adsorption varied from 305 µg/100 mg (Na-R) to 945 µg/100 mg (H-R). The value of K_L varied from 0.0046 $\mu g^{-1}mL$ for Zn-R to 0.0065 $\mu g^{-1}mL$ for Na-R.

4.1.4 Adsorption of tebuthiuron on homoionic montmorillonites :

Adsorption of tebuthiuron on homoionic montmorillonites was carried out in the same way as metoxuron, with 0 to 200 μgmL^{-1} of tebuthiuron as initial concentration.

The amount adsorbed followed a similar pattern as metoxuron, and was dependent on the charge of the exchange cation. Thus, the ions fell into the following

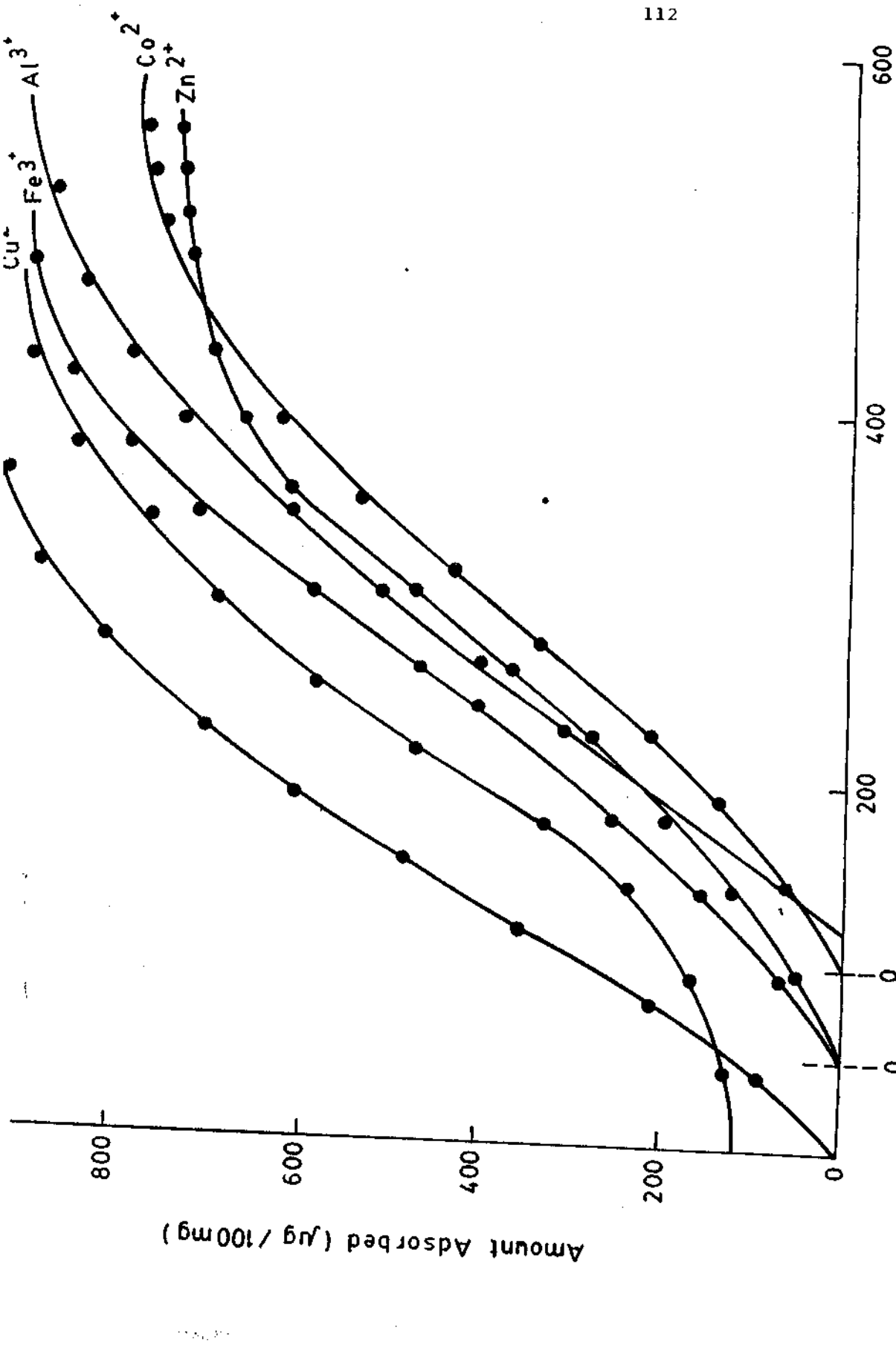


FIG. 9 : ADSORPTION ISOTHERMS OF METOXURON ON HOMOIONIC (I R - 120) RESIN.

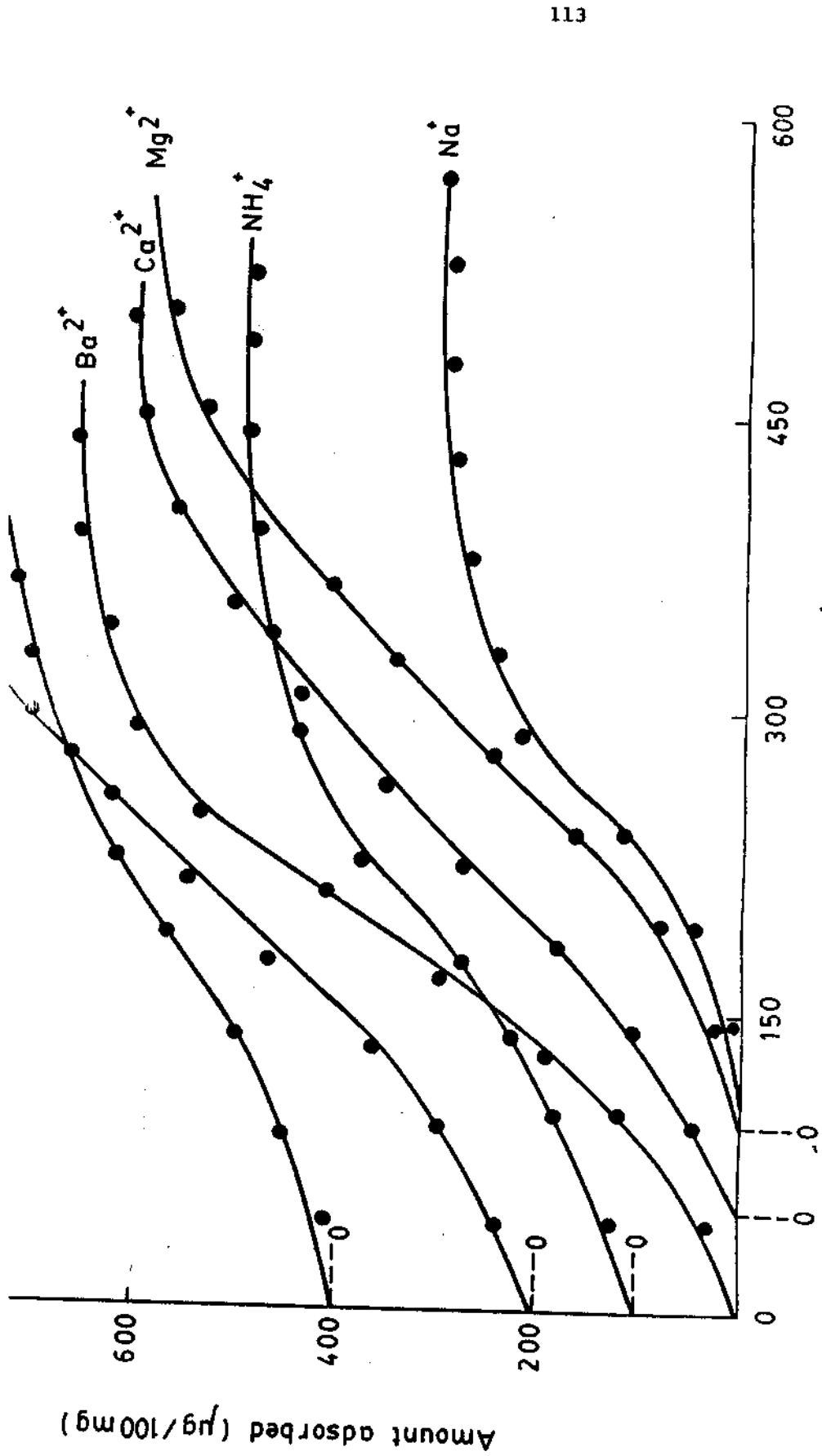


FIG. 9: ADSORPTION OF METOXURON ON HOMOIONIC (IR-120) RESIN.

Table 7 : Freundlich constants, maximum adsorption and K_L values of metoxuron on ion saturated resins and ionic properties

Ion saturating the resin	Freundlich constants K	Freundlich constants a	Maximum Adsorption (µg/ 100 mg)	K_L ($\mu g^{-1}mL$)	Ionic properties CIR (A°)	CIP charge/radius	HIR (A°)	HIP charge/radius
H-	2.04	1.06	945	0.0064				
Al-	2.69	0.97	900	0.0057	0.51	5.88	9.0*	0.330
Fe-	1.11	1.06	900	0.0047	0.64	4.68	9.0*	0.330
Ni-	1.19	1.15	660	0.0057	0.68	2.94	6.0*	0.330
Cu-	1.21	2.17	785	0.0047	0.72	2.78	6.0*	0.330
Ca-	1.17	1.13	765	0.0054	0.72	2.78	6.0*	0.330
Zn-	1.12	1.16	730	0.0046	0.69	2.90	6.0*	0.330
Ca-	1.24	1.13	615	0.0054	1.06	1.88	9.6**	0.208
Mg-	1.08	1.41	600	0.0051	0.76	2.56	10.8**	0.185
Ba-	1.19	1.10	620	0.0053	1.43	1.40	8.8**	0.227
Na-	1.21	0.98	305	0.0065	0.98	1.02	5.6**	0.179
K-	1.10	1.16	380	0.0051	1.33	0.75	3.8**	0.263
NH_4-	1.11	1.17	395	0.0064	1.48	0.67	5.37**	0.186

* Bolt and Bruggenwert (1976)

** Grim (1968)

groups : trivalent > divalent transition metal ions > alkaline earth ions > monovalent.

The amount adsorbed for trivalent ions varied from 61.1 to 341.7 µg/100 mg for Al-M and 42.8 to 306.5 µg/100 mg for Fe-M (Table 8).

Transition metal ions followed trivalent ions in adsorption. The extent of adsorption was 32.0 to 221.1 µg/100 mg for Ni-M, 26.1 to 220.6 µg/100 mg for Cu-M, 31.0 to 180.7 µg/100 mg for Co-M and 24.1 to 177.9 µg/100 mg for Zn-M.

Alkaline earth cations showed similar degree of adsorption. Thus it was 21.6 to 141.6 µg/100 mg for Ca-M, 22.6 to 138.1 µg/100 mg for Ba-M and 28.2 to 138.3 µg/100 mg for Mg-M. For the monovalent ions the extent of adsorption was again very close and was 10.5 to 107.5 µg/100 mg for Na-M, 6.9 to 101.7 µg/100 mg for K-M and 11.2 to 109.1 µg/100 mg for NH_4-M (Table 8).

The adsorption isotherms were constructed for all the samples and are given Fig.10. These were mainly parabolic in nature with a tendency to reach saturation within this range of concentration. There was some S-character in the initial stages of adsorption in most cases. The isotherms were analysed according to Freundlich equation and the constants K and α are

Table 8 : Adsorption of tebuthiuron on Al-, Fe-, Ni-, Cu-, Co-, Zn-, Ca-, Ba-, Mg-, K-, Na-, NH_4 -montmorillonites

Initial concentration $\mu g\ mL^{-1}$	Al-		Fe-		Ni-		Cu-		Co-		Zn-		Ca-		Ba-		Mg-		K-		Na-		NH_4	
	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)
20	16.98	61.12	17.90	42.62	18.09	32.02	17.72	26.12	18.29	31.01	17.72	24.17	18.18	21.64	18.54	22.62	17.63	28.24	19.33	8.97	18.99	10.53	18.89	11
40	33.36	81.89	34.27	73.42	36.27	44.90	35.00	54.34	33.63	63.10	35.09	52.27	35.45	54.10	34.90	50.02	35.81	45.11	38.35	17.26	37.45	25.79	37.23	17.
60	52.45	53.98	52.36	85.38	54.46	63.07	51.36	93.87	50.40	111.28	51.36	71.56	54.54	64.93	53.09	75.09	53.09	72.81	57.07	31.59	56.23	39.52	56.98	30
80	69.72	80.22	72.45	101.73	73.54	78.71	68.63	128.26	66.45	164.29	69.63	125.27	68.18	123.71	70.36	100.37	71.27	84.47	76.54	33.36	75.68	44.43	75.42	55.
100	86.09	81.85	86.63	146.67	90.63	88.01	85.00	163.04	83.85	170.15	88.82	148.93	86.45	132.32	89.45	109.64	89.45	109.64	95.24	33.49	94.89	50.87	94.26	67.
120	103.18	101.48	104.36	152.63	109.9	104.65	102.27	192.68	106.30	180.85	106.90	156.60	106.81	133.71	109.54	119.84	108.54	124.89	113.15	41.37	112.38	75.69	108.42	91.
140	123.36	128.85	123.63	213.28	126.27	130.38	122.72	203.21	126.36	180.85	126.90	158.60	126.36	140.04	128.54	124.50	127.72	127.89	134.64	61.37	130.64	96.42	129.58	107.
160	143.36	139.45	139.72	259.89	142.63	197.37	140.45	220.65	146.36	180.85	148.90	158.62	148.18	141.63	148.54	124.50	146.72	138.39	153.26	71.69	151.27	97.04	149.58	107.
180	161.54	139.45	157.90	288.05	160.81	217.97	160.45	220.65	166.36	180.85	165.09	176.56	168.18	141.63	167.72	127.85	166.72	138.39	171.58	83.94	169.28	117.59	169.58	107.
200	183.36	141.30	176.09	306.50	180.81	221.10	182.45	220.65	186.36	180.85	183.00	177.94	185.18	141.63	186.72	138.15	186.72	138.39	190.69	101.76	189.28	137.59	189.32	109.

Eq.C = Equilibrium concentration; A.A. = Amount Adsorbed

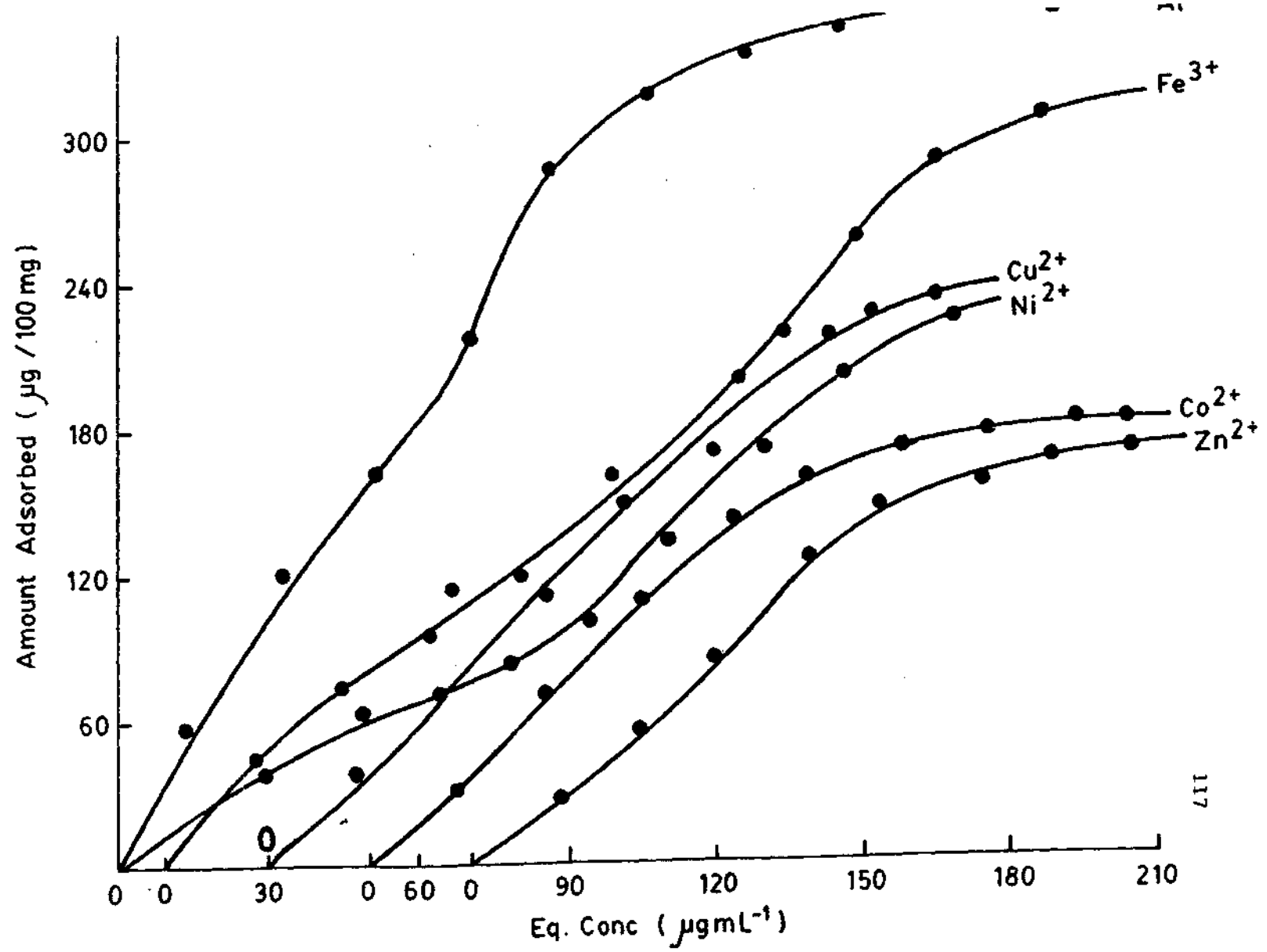


FIG.10: ADSORPTION ISOTHERMS OF TEBUTHIURON ON HOMOIONIC MONTMORILLONITES

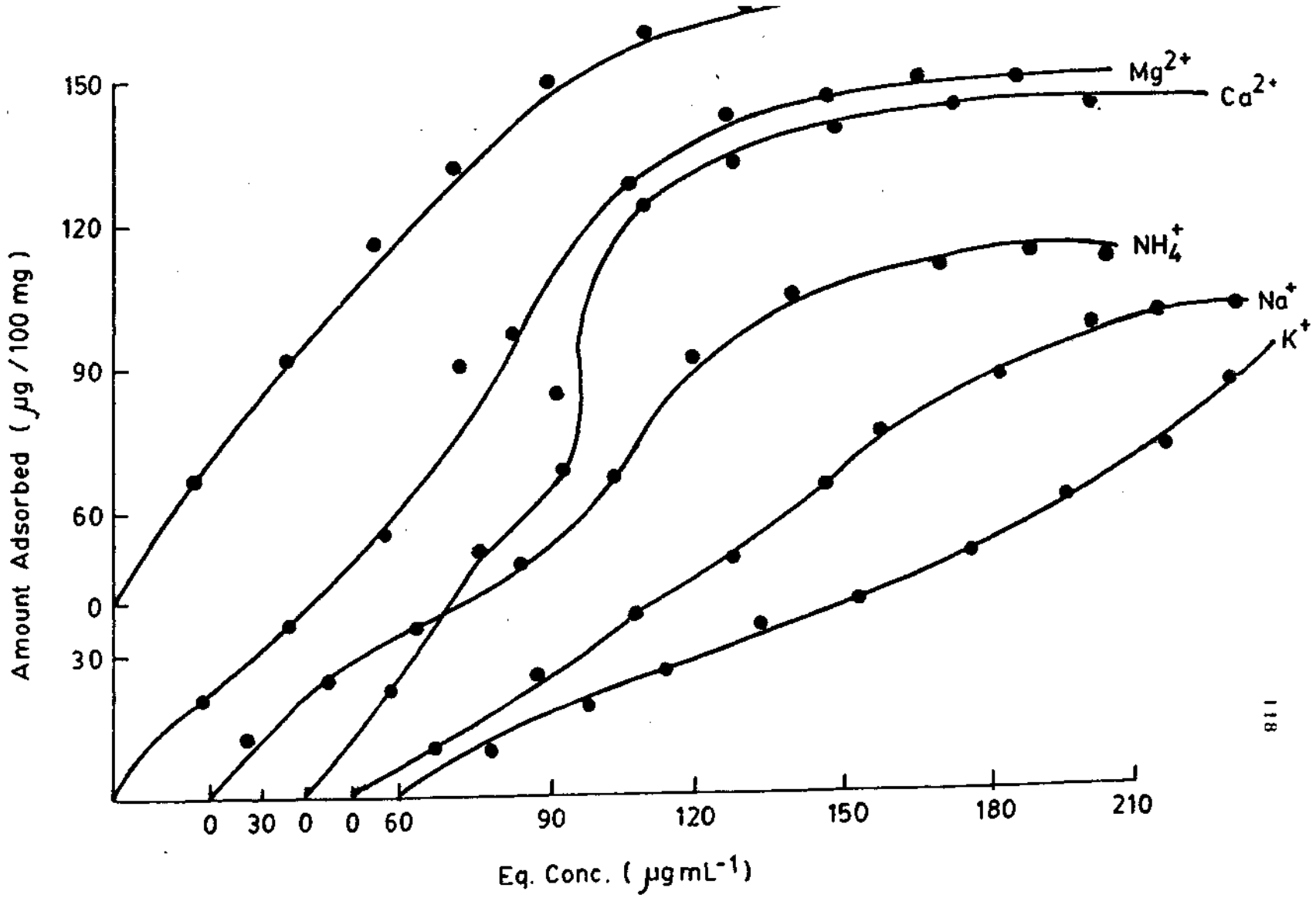


FIG.10: Contd..... ADSORPTION ISOTHERMS OF TEBUTHIURON ON HOMOIONIC MONTMORILLONITES

presented in Table 9. Freundlich K varied from 1.02 (Cu-M) to 14.45 (Al-M) and α from 1.34 (Co-M) to 0.62 (Al-M).

The data was also analysed by the equation $\frac{df}{dc} = kf^{2/3}(1-f)$ as explained earlier, and the values of f and the corresponding 'C' are given in Table 10. The plots of χ vs C for the different metal montmorillonites are given in Fig.11. The value of k determined from the slope of the curve χ vs C varied from 0.018 $\mu g^{-1}mL$ (Na-M and Ni-M) to 0.042 $\mu g^{-1}mL$ (Ca-M).

The relative binding strength (K_L), maximum adsorption (µg/100 mg), 'k' and Freundlich constants are given in Table 9.

4.1.5 Adsorption of tebuthiuron on ion saturated resins :

Adsorption of tebuthiuron on ion saturated resins was carried out in the same way as explained earlier.

Complete quantitative details of adsorption are given in Table 11. As seen, the amount adsorbed increased with increase in initial concentration. The amount adsorbed was highest in H-R, Al-R and Fe - R and varied from 52.8 to 1616.0 µg/100 mg for H-R, 25.4 to 1431.1 µg/100 mg for Al-R, 64.1 to 1285.8 µg/100 mg

Table 9 : Freundlich constants, maximum adsorption, K_L and k values of tebuthiuron on homoionic montmorillonites

Ion saturating the surface	Freundlich constants		Maximum adsorption (µg/100 mg)	K_L (μg^{-1} ml)	k (μg^{-1} ml)
	K	α			
Al-	14.45	0.62	340	0.017	0.035
Fe-	6.16	0.79	306	0.012	0.022
Ni-	1.41	1.01	220	0.009	0.018
Cu-	1.02	1.17	220	0.016	0.030
Co-	1.21	1.34	180	0.022	0.040
Zn-	1.20	1.11	177	0.019	0.039
Ba-	1.67	1.05	138	0.021	0.038
Ca-	1.95	0.87	141	0.021	0.042
Mg-	2.69	0.84	138	0.014	0.023
K-	1.19	1.05	101	0.008	0.022
Na-	1.17	1.08	107	0.012	0.018
NH_4-	1.16	1.06	109	0.012	0.039

Table 10 : Fraction adsorbed and equilibrium concentration values for tebuthiuron

Fraction adsorbed f	X	Equilibrium concentration(μgmL^{-1})											
		Al-	Fe-	Ni-	Cu-	Co-	Zn-	Ca-	Ba-	Mg-	NH_4-	Na-	K-
0.1	2.335	9.5	14.0	19.0	14.0	9.0	12.0	13.0	12.0	14.0	21.0	19.0	29.(
0.2	2.732	18.5	28.0	39.0	25.0	18.0	22.0	22.0	22.0	27.0	42.0	33.0	52.(
0.3	3.090	27.5	52.0	63.0	38.0	28.0	33.0	31.0	31.0	35.0	62.0	45.0	75.(
0.4	3.410	40.0	74.0	85.0	52.0	37.0	43.0	39.0	41.0	46.0	84.0	66.0	90.(
0.5	3.720	55.0	86.0	103.0	61.0	44.0	52.0	46.0	50.0	58.0	106.0	81.0	99.(
0.6	4.050	67.0	99.0	115.0	70.0	54.0	58.0	54.0	60.0	70.0	118.0	97.0	107.(
0.7	4.440	76.0	115.0	126.0	78.0	64.0	67.0	63.0	71.0	80.0	132.0	110.0	110.(
0.8	4.910	86.0	136.0	135.0	90.0	75.0	73.0	72.0	92.0	90.0	155.0	123.0	118.(

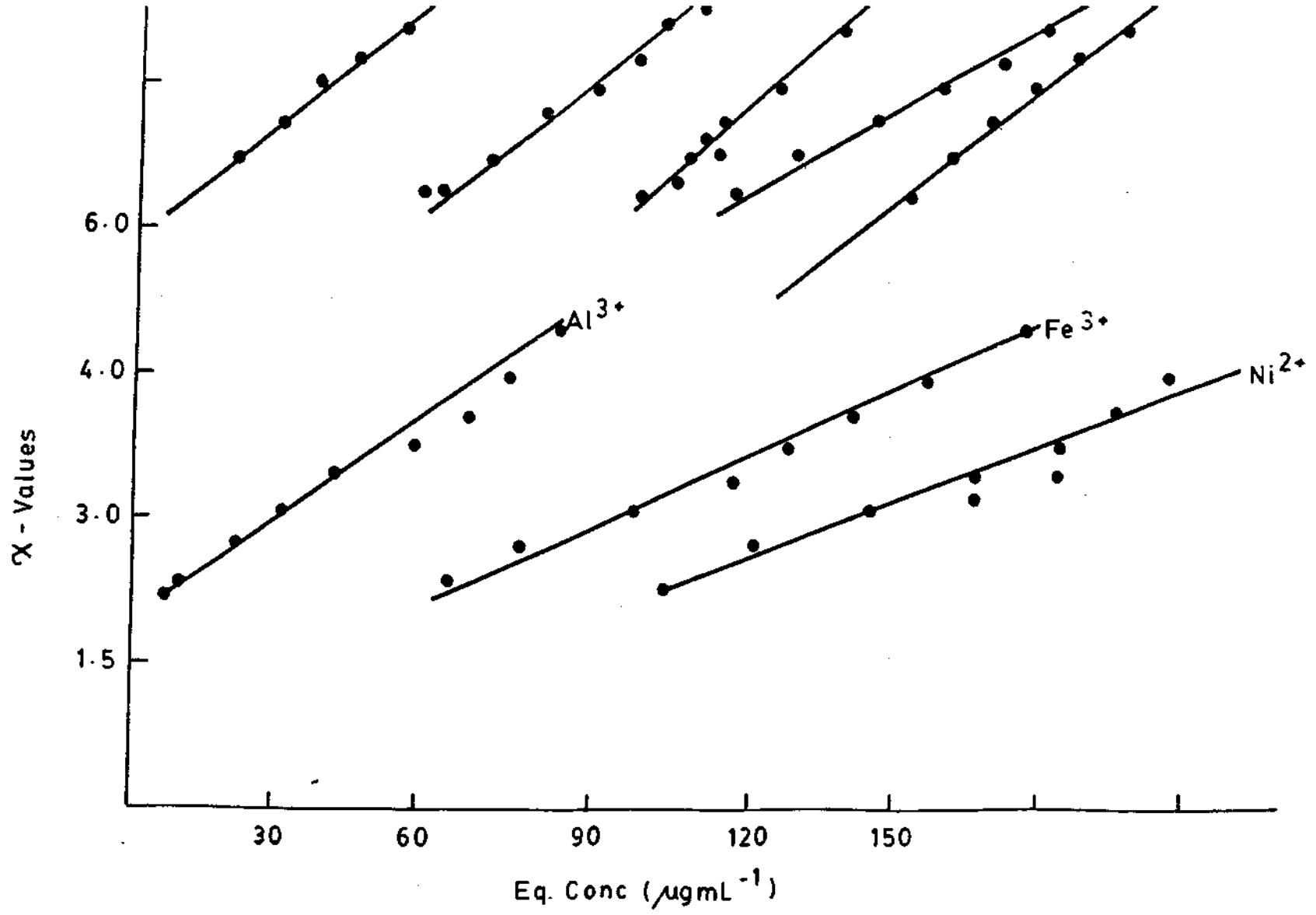


FIG. 11. PLOT OF χ vs. Eq. CONC. VALUES FOR ADSORPTION OF TEBUTHIURON ON HOMOIONIC MONTMORILLONITES

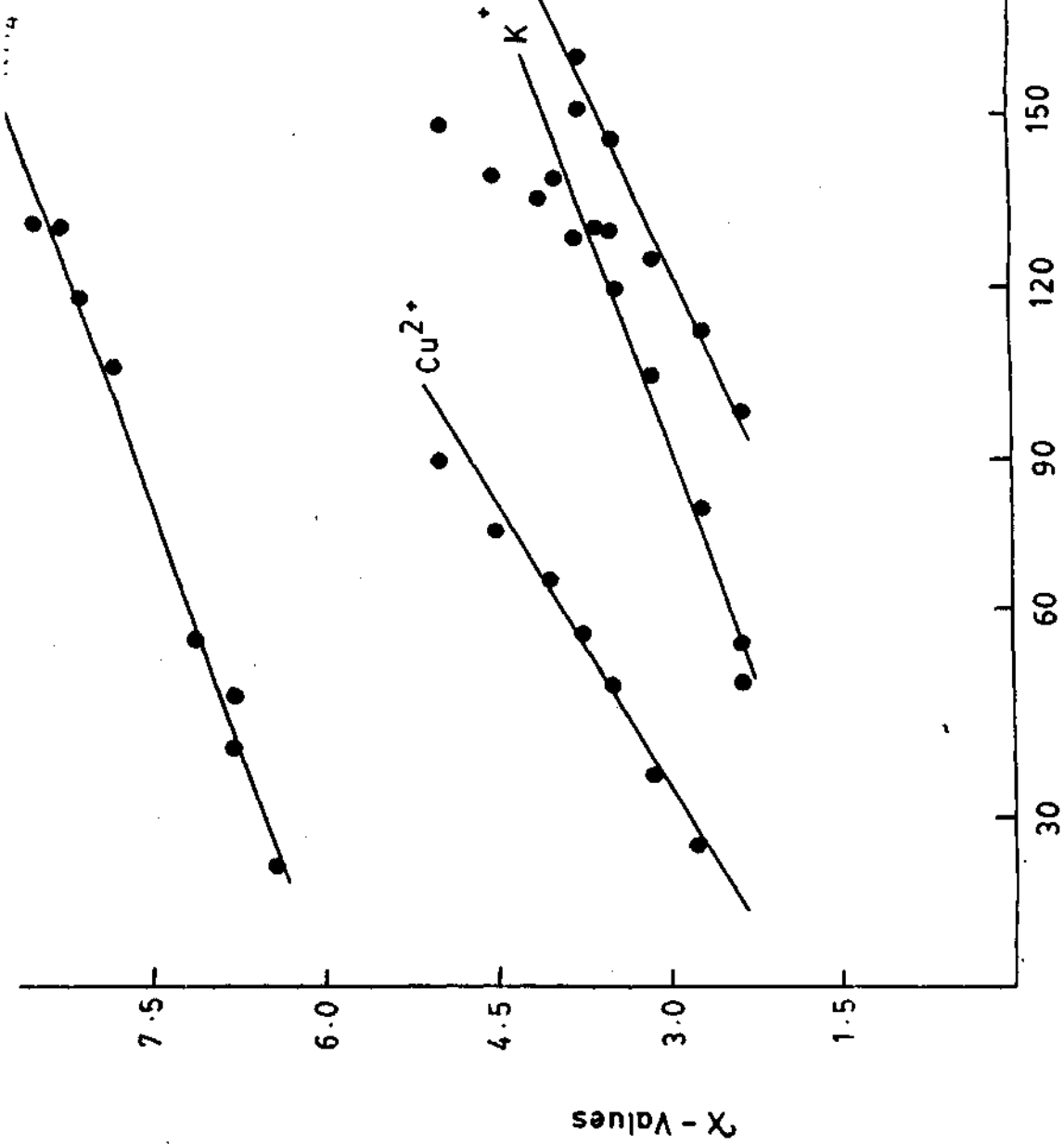


FIG. 11 Contd. PLOT OF χ vs Eq. CONC. VALUES FOR ADSORPTION OF TEBUTHIURON ON HOMOIONIC MONTMORILLONITES.

for Fe-R. For transition metal ions, the extent of adsorption was 20.7 to 1148.1 µg/100 mg for CO-R, 41.5 to 1145.2 µg/100 mg for Cu-R, 21.7 to 604.8 µg/100 mg for Ni-R and 17.9 to 484.9 µg/100 mg for Zn-R. The alkaline earth saturated resins followed next with 18.8 to 612.5 µg/100 mg for Mg-R, 18.6 to 387.6 µg/100 mg for Ba-R and 20.7 to 381.6 µg/100 mg for Ca-R. For monovalent saturated resins the extent of adsorption was 11.3 to 336.7 µg/100 mg for K-R, 50.0 to 273.9 µg/100 mg for Na-R and 11.3 to 308.1 µg/100 mg for NH_4-R (Table 11).

Adsorption isotherms for homoionic resins are presented in Fig.12. The adsorption isotherms were generally parabolic in nature with tendency for S-shape in the initial stages. The data were analysed according to Freundlich equation. The values of k and α, K_L and maximum adsorption are given in Table 12. Freundlich constant 'K' varied from 1.02 (Co-R) to 5.34 (Cu-R); α from 0.53 (Cu-R) to 2.88 (Ni-R). Maximum adsorption (µg/100 mg) varied from 275 µg/100 mg (Na-R) to 1720 µg/100 mg (H-R). The values of K_L varied from 0.0038 $\mu g^{-1}mL$ (Ca-R and Fe-R) to 0.0074 $\mu g^{-1}mL$ (Zn-R).

Table II : Adsorption of Tebuthiuron on IR-120 resin saturated with different cations

Initial concentration ($\mu g\ mL^{-1}$)	H-		Al-		Fe-		Cu-		Co-		Zn-		Ni-	
	Eq.C (μg/mL)	A.A (μg/100 mg)	Eq.C (μg/mL)	A.A (μg/100 mg)	Eq.C (μg/mL)	A.A (μg/100 mg)	Eq.C (μg/mL)	A.A (μg/100 mg)	Eq.C (μg/mL)	A.A (μg/100 mg)	Eq.C (μg/mL)	A.A (μg/100 mg)	Eq.C (μg/mL)	A.A (μg/100 mg)
50	44.75	51.85	47.45	25.47	43.56	64.15	45.84	41.50	47.92	20.75	48.20	17.92	47.80	21.77
100	80.14	199.56	79.76	202.35	76.60	233.96	77.68	223.11	85.66	143.39	85.94	140.56	86.46	135.37
150	110.80	391.96	111.60	383.96	116.98	333.01	114.24	357.54	121.03	289.62	127.51	227.83	122.62	273.77
200	140.28	597.16	146.16	518.39	160.32	396.69	141.36	586.32	158.77	412.26	173.20	267.52	162.42	375.98
250	172.12	779.77	183.53	664.62	196.80	531.15	181.46	685.37	196.50	534.90	209.76	402.35	208.49	415.18
300	193.34	1069.30	210.66	893.39	244.05	599.43	229.81	701.89	228.34	716.50	253.39	466.03	257.30	436.98
350	221.01	1274.15	257.83	921.56	277.07	726.24	274.66	788.37	271.98	781.18	305.24	477.16	295.54	534.52
400	273.53	1254.62	298.63	1013.67	309.92	903.61	314.71	852.83	295.56	1044.23	352.45	477.47	345.75	548.39
450	303.65	1457.09	326.79	1232.17	336.13	1139.62	382.48	873.47	338.01	1119.81	402.33	478.83	388.49	616.06
500	338.39	1619.13	356.88	1431.13	371.41	1285.84	385.47	1145.28	385.18	1148.11	451.50	484.96	439.57	604.82

Contd..

Table 7 (Contd..)

Initial concentration $\frac{\mu g}{mL}$	Ca-		Mg-		Ba-		K-		Na-		NH_4-	
	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)
50	47.92	20.75	48.11	18.86	48.13	18.67	45.86	11.32	44.99	50.00	48.86	11.32
100	92.73	72.64	85.84	141.50	91.91	80.94	96.71	33.00	93.51	64.81	93.51	64.81
150	139.90	100.94	116.98	330.18	140.12	98.77	134.95	150.47	138.86	111.36	137.86	111.36
200	187.07	129.24	162.50	374.99	185.76	142.31	182.12	178.77	181.16	188.30	181.16	160.30
250	235.06	169.33	206.13	438.67	233.25	167.49	231.65	183.49	232.69	173.01	235.57	184.24
300	271.98	280.18	243.86	661.13	269.99	300.00	277.28	247.16	277.32	226.79	277.32	226.79
350	328.86	221.32	291.03	539.60	316.90	300.32	321.48	279.47	325.65	245.89	325.41	245.89
400	386.32	336.79	339.62	600.57	364.03	359.33	369.82	303.77	366.88	311.13	369.66	292.07
450	418.49	366.09	390.79	608.07	412.69	378.00	418.40	325.66	424.79	252.07	421.79	330.39
500	467.83	381.60	438.74	612.54	461.23	387.64	466.32	336.79	472.60	273.96	469.18	308.11

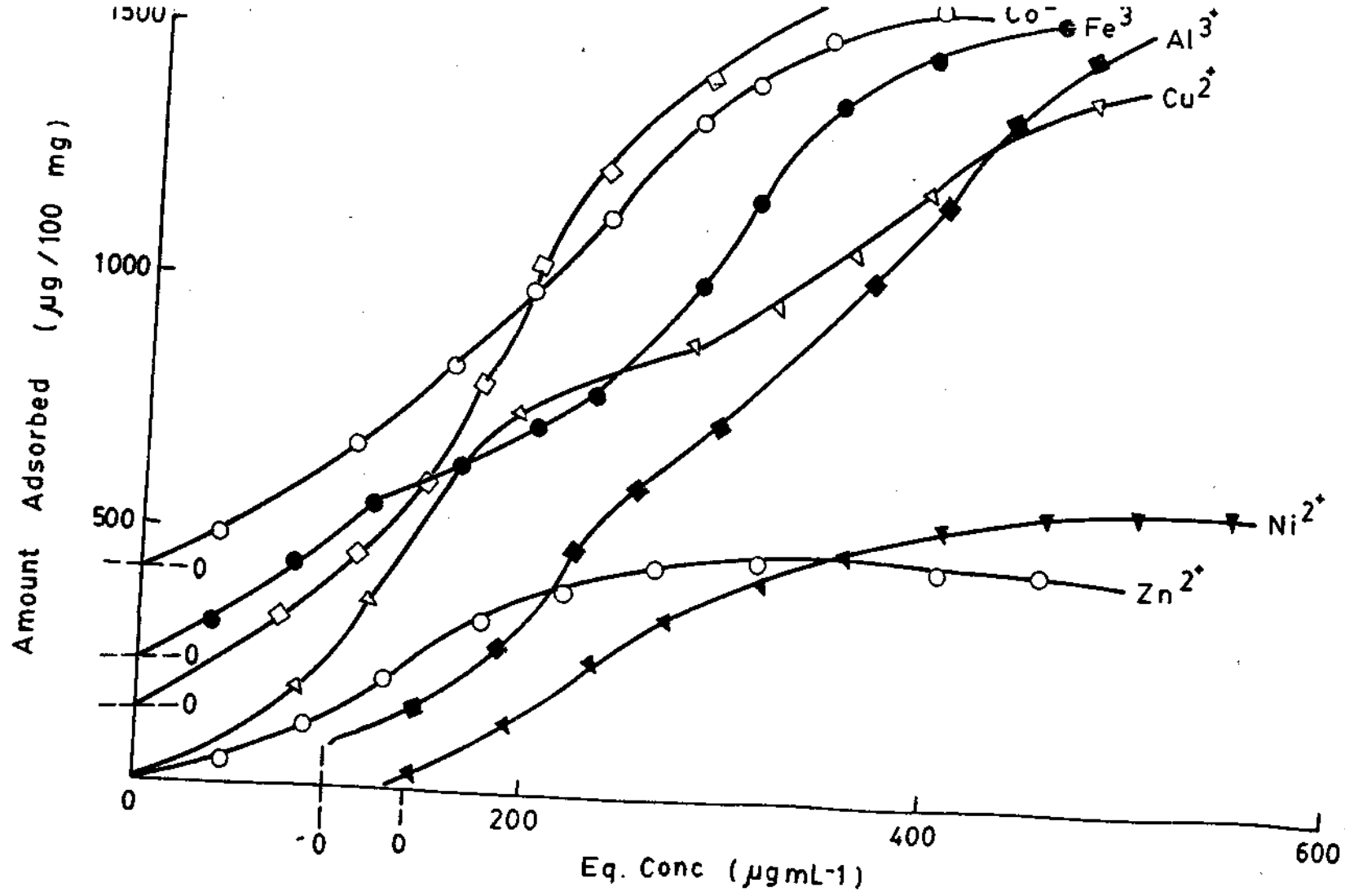


FIG. 12: ADSORPTION ISOTHERMS OF TEBUTHIURON ON HOMOIONIC (IR-120) RESIN

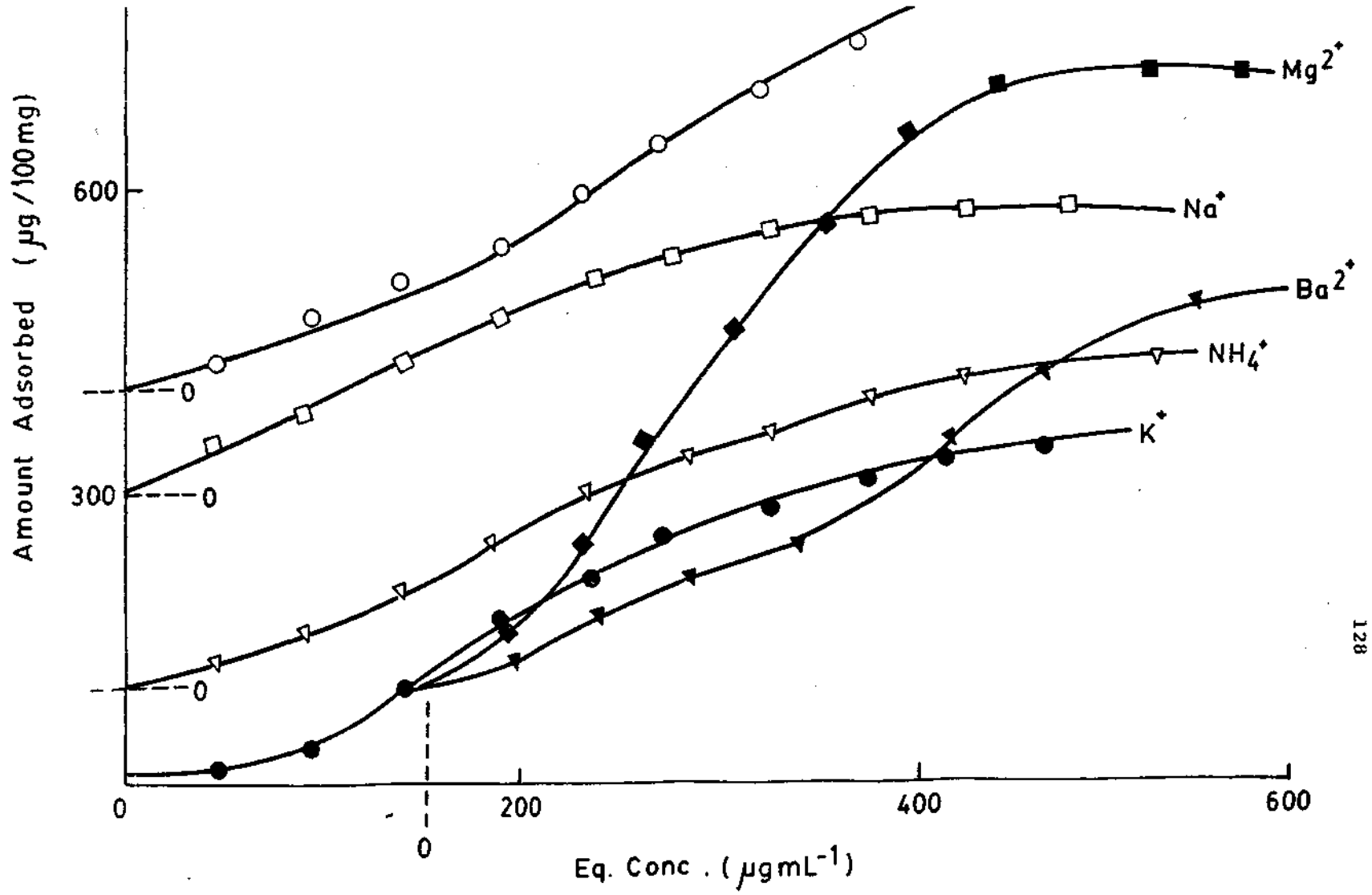


FIG. 12. Contd..... ADSORPTION ISOTHERMS OF TEBUTHIURON ON HOMOIONIC (IR-120) RESIN

Table 12 : Freundlich constants, maximum adsorption, and K_L of tebuthiuron on homoionic resins

Ion saturating the resin	Freundlich constants		Maximum Adsorption	K_L
	K	α	(µg/100 mg)	$\mu g^{-1} mL$
H-	-	-	1720	0.0056
Al-	1.22	1.96	1470	0.0048
Fe-	1.25	1.73	1370	0.0038
Ni-	1.20	2.88	605	0.0071
Cu-	5.24	0.53	1310	0.0053
Co-	1.02	1.90	1190	0.0050
Zn-	1.14	1.22	480	0.0074
Ca-	1.20	1.02	445	0.0038
Mg-	1.20	1.18	605	0.0072
Ba-	1.17	1.06	397	0.0041
Na-	1.18	1.11	275	0.0063
k-	1.73	0.88	342	0.0050
NH_4-	1.13	1.11	315	0.0049

4.2 ADSORPTION OF METOXURON AND TEBUTHIURON ON SOILS AND THEIR CONSTITUENTS :

Physico-chemical properties of soils :

The physico-chemical properties of the soils used for studying adsorption are given in Table 2. The pH of soil samples varied from 6.4 to 8.5. Total soluble salt content as determined by EC varied from 0.032 Sm^{-1} to 0.144 Sm^{-1}. Organic matter content varied from 0.19 to 1.02 per cent, cation exchange capacity varied from 13.6 Cmol kg^{-1} to 98.0 Cmol kg^{-1}. Clay content varied from 12.5 per cent to 62.5 per cent.

4.2.1 Adsorption of metoxuron and tebuthiuron on 2 mm and < 50μ soil fractions :

Adsorption of metoxuron and tebuthiuron was carried out on 2 mm and < 50 μ fractions of soils 1, 2, 3 and 4. Adsorption procedures have already been explained under Materials and Methods. Adsorption isotherms for metoxuron on 2 mm fractions are given in Fig.13. The adsorption isotherms were S-shaped for soils 1 and 2 and were L-shaped for soils 3 and 4. The S-shaped isotherms had an initial plateau followed by a steep rise. Surface saturation was not attained in the concentration range studied. Complete adsorption data are given in Table 13. The amount

Table 13 : Adsorption of metoxuron on 2 mm soil fractions

Initial concentration μgmL^{-1}	Soil-1		Soil-2		Soil-3		Soil-4	
	Eq.C (μgmL^{-1})	A.A ($\mu g/g$)	Eq.C (μgmL^{-1})	A.A ($\mu g/g$)	Eq.C (μgmL^{-1})	A.A ($\mu g/g$)	Eq.C (μgmL^{-1})	A.A ($\mu g/g$)
2	1.63	3.62	1.73	2.92	1.82	1.37	1.62	3.77
4	3.38	6.15	3.65	4.59	3.41	6.19	3.57	4.59
6	5.33	7.18	5.15	8.07	5.44	6.12	5.31	6.88
8	6.92	11.01	7.12	11.30	7.10	8.77	7.38	9.23
10	8.61	13.06	8.54	14.56	9.08	9.14	8.99	10.81
12	9.64	10.78	9.42	14.56	10.08	9.33	9.95	7.16
14	11.75	9.73	10.88	14.88	11.32	11.11	12.74	7.86
16	13.14	12.55	13.11	17.31	12.73	13.18	14.11	7.34
18	15.08	12.81	15.18	17.39	14.47	16.16	14.68	9.66
20	16.79	12.85	16.20	18.30	16.32	16.32	17.76	9.91
30	24.76	20.86	23.58	25.97	26.02	16.44	27.45	11.93
40	32.94	26.99	31.13	35.06	30.64	19.17	34.22	17.27

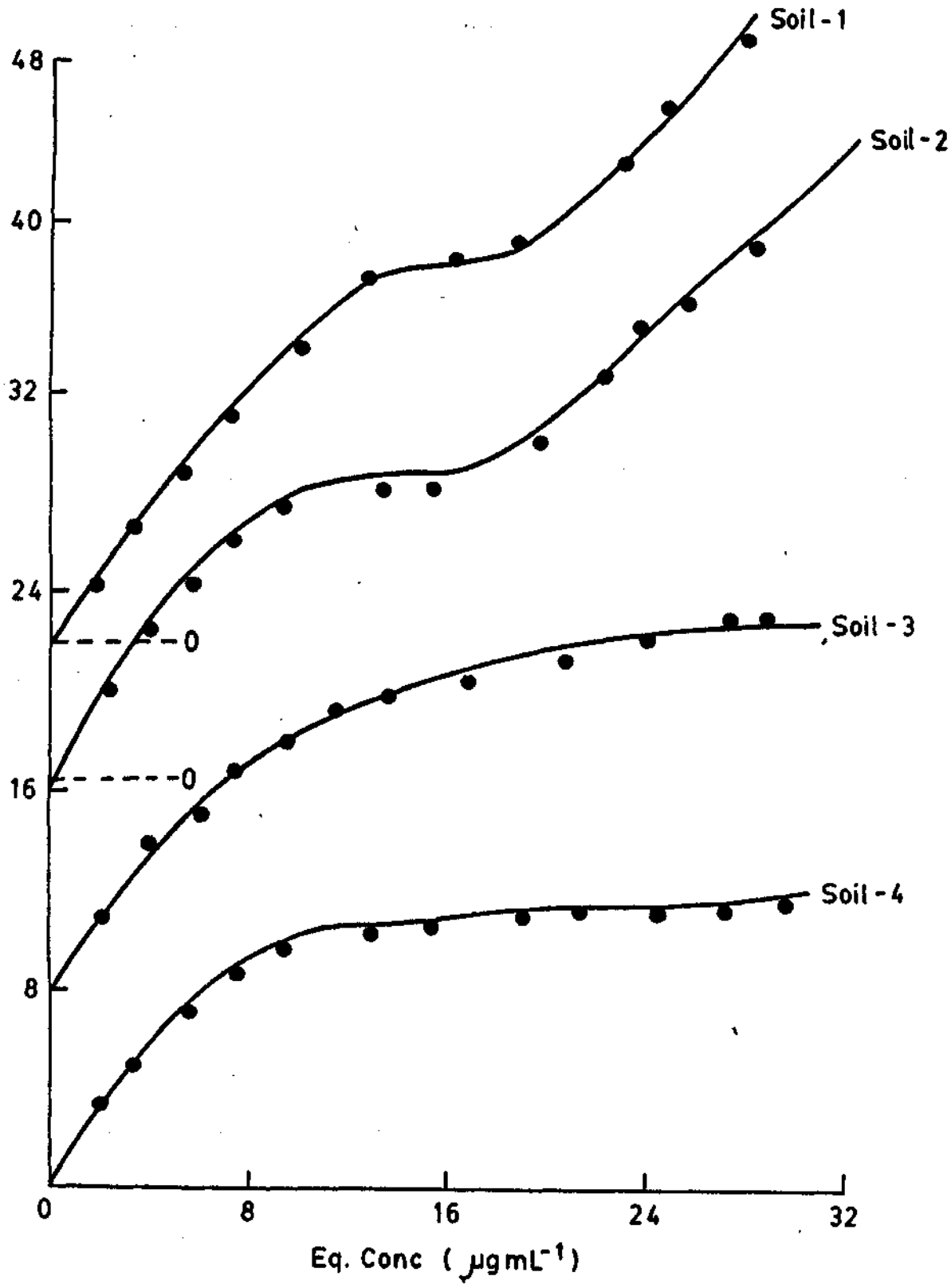


FIG. 13 : ADSORPTION ISOTHERMS OF METOXURON ON 2mm SOIL FRACTIONS

adsorbed varied from 3.6 to 26.9 µg/g in soil-1, 2.9 to 35.0 µg/g in soil-2, 1.8 to 19.07 µg/g in soil-3 and 3.7 to 17.2 µg/g in soil-4. Adsorption isotherms of metoxuron on < 50 µ fractions are given in Fig.14. These isotherms were S-shaped in all the cases with an initial plateau followed by steep rise. Surface saturation was not attained in the concentration range studied. The amount adsorbed on < 50 µ fractions are given in Table 14. The amount adsorbed varied from 17.3 to 120.0 µg/g for soil-1 4.1 to 144.0 µg/g for soil-2, 7.2 to 115.1 µg/g for soil-3 and 17.0 to 133.7 µg/g for soil-4.

The adsorption data fitted well to Freundlich model and the Freundlich constants, K and α are given in Table 15. Freundlich 'K' varied from 0.12 to 7.00 in 2 mm fractions and from 0.12 to 2.20. For < 50 µ fractions the 'K' varied from 1.10 to 1.67 and α from 0.76 to 1.18.

The amounts of tebuthiuron adsorbed for each initial concentration for 2 mm fractions are given in Table 16 and on < 50 µ fractions in Table 17. Adsorption isotherms for 2 mm fractions are given in Fig.15. These indicated a tendency for S-shape in the initial stages of adsorption. The adsorption isotherms for < 50 µ fractions are given in Fig.16.

Table 14 : Adsorption of metoxuron on < 50 µ soil fractions

Initial concentration µgmL^{-1}	Soil-1		Soil-2		Soil-3		Soil-4	
	Eq.C (µgmL^{-1})	A.A (µg/g)	Eq.C (µgmL^{-1})	A.A (µg/g)	Eq.C (µgmL^{-1})	A.A (µg/g)	Eq.C (µgmL^{-1})	A.A (µg/g)
2.5	2.06	17.37	2.41	4.17	2.31	7.21	2.07	17.04
5.0	4.16	33.44	2.65	13.77	4.49	20.04	4.31	27.54
7.5	6.65	34.42	6.81	27.21	6.86	35.24	6.95	23.63
10.0	8.66	53.44	8.73	50.48	8.77	48.90	8.71	53.03
15.0	11.99	120.00	11.38	144.60	12.12	115.10	11.65	133.78

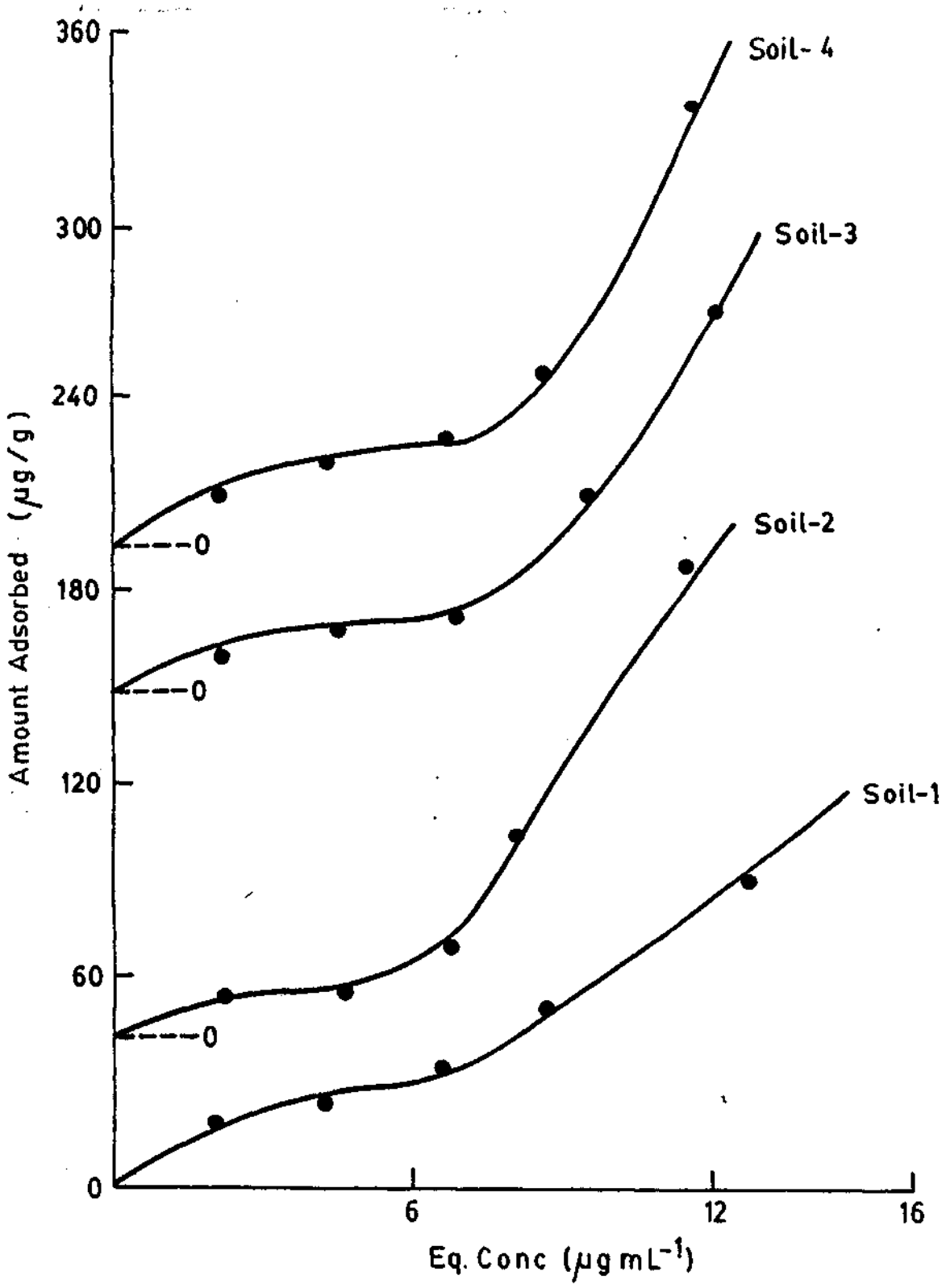


FIG. 14: ADSORPTION ISOTHERMS OF METOXURON ON - 50µ SOIL FRACTIONS.

Table 15 : Freundlich constants of metoxuron on 2 mm and < 50 µ fraction of soils

Freundlich constant	2 mm fractions				<50 µ fractions			
	Soil 1	Soil 2	Soil 3	Soil 4	Soil 1	Soil 2	Soil 3	Soil 4
α	0.12	1.30	1.90	2.20	1.11	1.18	0.76	0.76
K	7.00	0.12	3.90	2.50	1.11	1.67	1.11	1.43

Table 16 : Adsorption of tebuthiuron on 2 mm soil fraction

Initial concentration μgmL^{-1}	Soil 1		Soil 2		Soil 3		Soil 4	
	Eq.C (μgmL^{-1})	A.A ($\mu g/g$)	Eq.C (μgmL^{-1})	A.A ($\mu g/g$)	Eq.C (μgmL^{-1})	A.A ($\mu g/g$)	Eq.C (μgmL^{-1})	A.A ($\mu g/g$)
4	3.61	3.87	3.54	4.54	3.31	6.81	3.31	6.81
8	7.31	6.86	7.27	7.27	6.51	14.05	6.72	12.72
12	11.01	9.95	9.70	22.95	9.45	20.45	10.40	15.90
16	13.38	26.13	12.79	32.84	13.26	27.27	13.27	27.27
20	16.79	32.04	15.86	41.36	16.81	31.72	16.54	34.54
24	19.74	42.49	19.27	47.27	20.24	37.27	19.81	41.81
28	23.04	49.54	23.02	49.56	23.63	42.72	23.36	46.36
32	26.34	56.59	26.43	61.49	26.72	52.72	27.00	50.00
36	28.50	74.99	26.25	77.32	30.01	59.90	29.94	60.45
40	30.31	98.81	32.22	77.72	33.17	68.13	33.18	69.54
50	39.63	103.63	39.49	104.99	41.94	80.45	41.17	88.17

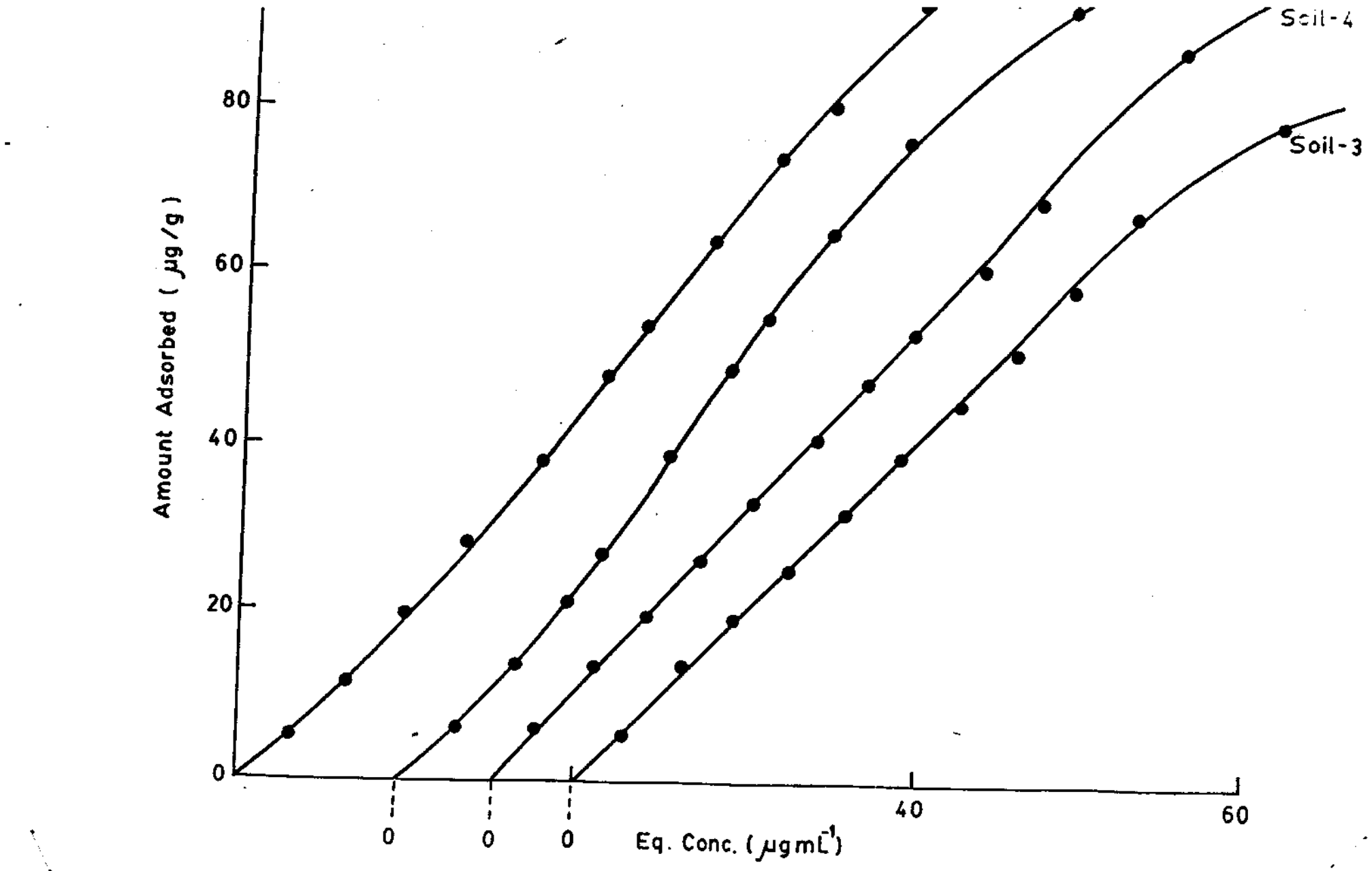


FIG. 15 : ADSORPTION ISOTHERMS OF TEBUTHIURON ON 2mm SOIL FRACTIONS.

Table 17 : Adsorption of tebuthiuron on < 50μ soil fractions

Initial concentration μgmL^{-1}	Soil-1		Soil 2		Soil 3		Soil 4	
	Eq.C (μgmL^{-1})	A.A ($\mu g/g$)	Eq.C (μgmL^{-1})	A.A ($\mu g/g$)	Eq.C (μgmL^{-1})	A.A ($\mu g/g$)	Eq.C (μgmL^{-1})	A.C ($\mu g/g$)
4	3.40	23.63	3.47	20.92	3.54	18.18	3.52	18.96
8	6.59	56.36	6.54	58.15	7.09	36.36	7.34	34.74
12	10.47	60.90	10.34	66.36	10.00	80.00	10.20	71.84
16	14.22	70.90	15.20	61.81	13.18	112.72	13.30	107.76
20	17.86	85.70	17.99	80.00	16.18	127.27	16.54	138.40
24	21.61	85.45	21.86	85.45	19.00	200.00	19.62	174.92
28	25.36	105.45	25.38	104.95	20.63	294.55	20.83	286.56
32	28.43	142.72	29.02	119.09	24.45	301.82	24.34	306.16
36	31.27	189.09	32.43	142.72	25.81	407.27	25.46	421.56
40	34.79	208.18	36.52	149.09	28.81	447.27	29.02	438.88
50	44.22	231.06	43.58	166.36	35.63	574.55	36.34	546.16

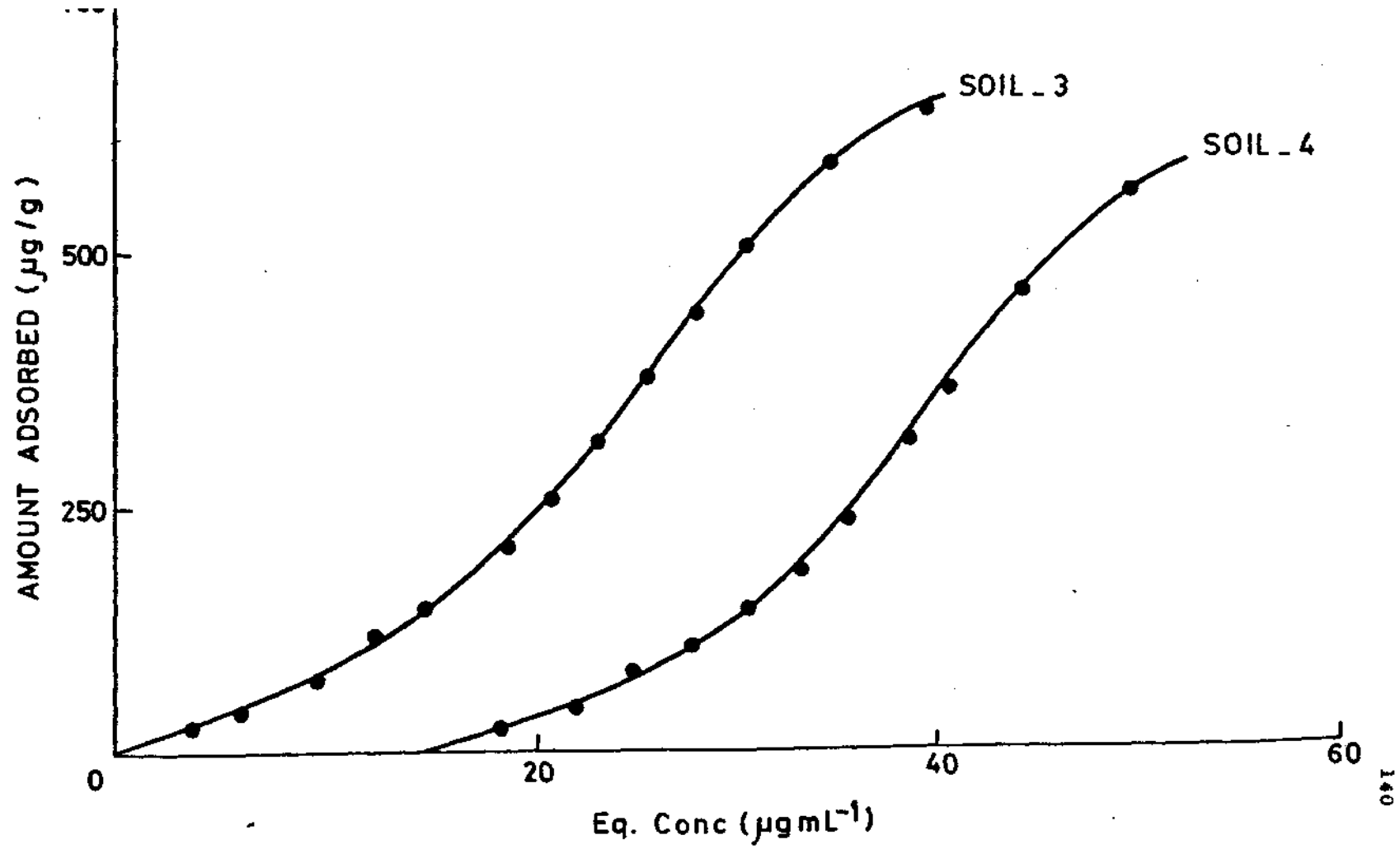


FIG. 16: ADSORPTION ISOTHERMS OF TEBUTHIURON ON <50µ SOIL FRACTION.

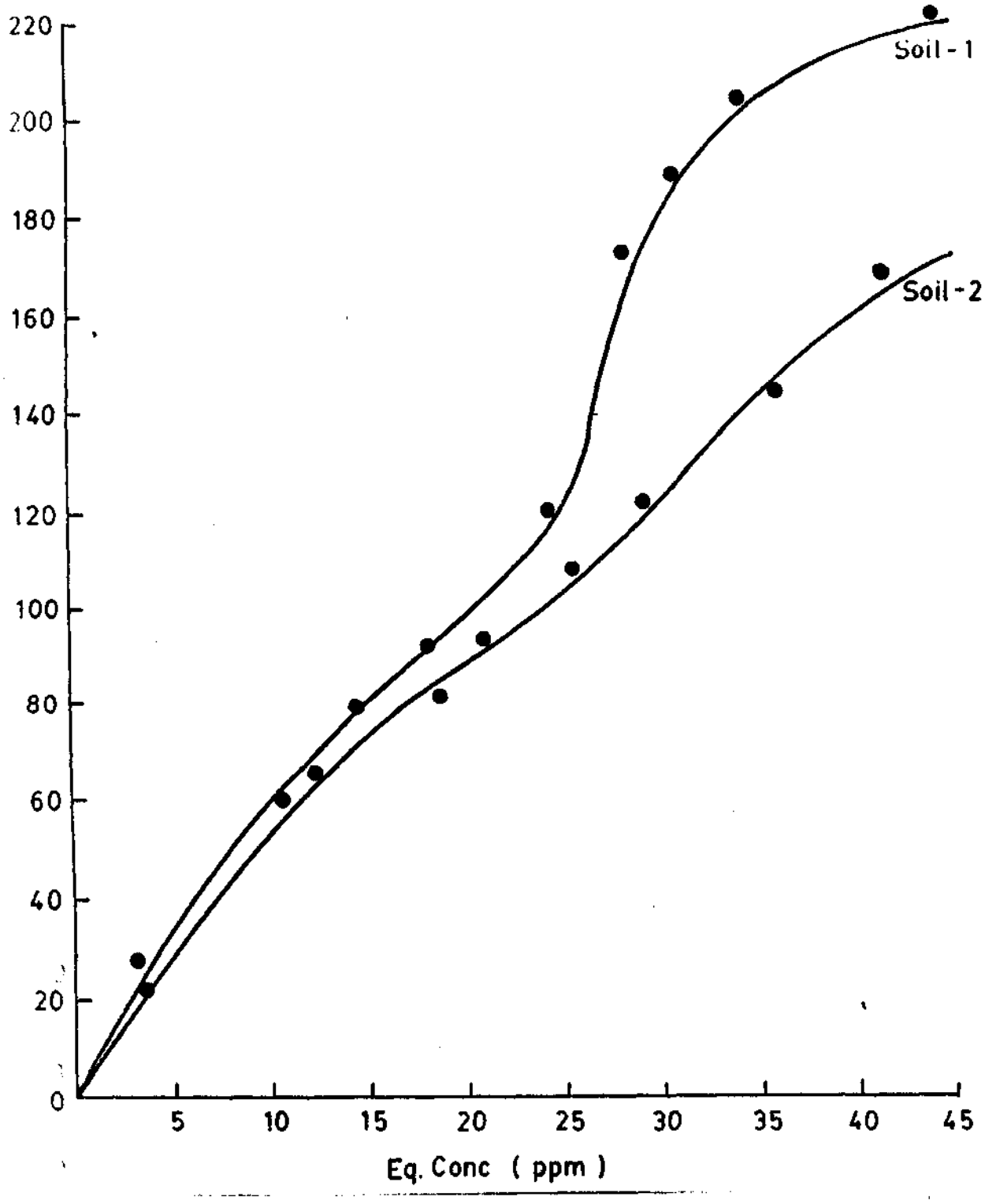


FIG. 16 Contd : ADSORPTION ISOTHERMS OF TEBUTHIURON ON - 50 μ SOIL FRACTIONS

Table 18 : Freundlich constants of tebuthiuron on 2 mm and <50 µ soil fractions

Freundlich constant	2 mm fractions				< 50 µ fractions			
	Soil 1	Soil 2	Soil 3	Soil 4	Soil I	Soil 2	Soil 3	Soil 4
K	1.14	1.21	2.34	2.18	15.13	7.07	4.46	2.63
α	1.64	1.33	0.93	1.04	0.59	0.84	1.35	1.48

The data was analysed by Freundlich equation. The values of K and α are given in Table 18. Freundlich K varied from 1.14 (Soil-1) to 2.34 (Soil-3) and α from 0.93 (Soil-3) to 1.64 (Soil-1). For < 50μ fractions the value of K varied from 2.63 (Soil-4) to 15.13 (Soil-1) and α from 0.59 (Soil-1) to 1.48 (Soil-4).

4.2.2 Adsorption of metoxuron and tebuthiuron on Humic Acid :

The amount of metoxuron and tebuthiuron adsorbed on humic acid is given in Table 19. The adsorption isotherm of metoxuron is given in Fig.17 and of tebuthiuron in Fig.18. These isotherms were L-shaped in contrast to 2 mm and 50μ fractions. These were analysed by Freundlich model. The Freundlich constants K and α for metoxuron were 22.43 and 0.92 respectively. These constants were 28.84 and 0.88 for tebuthiuron.

4.3 POLYMALEIC ACID (PMA) AS A MODEL FOR SOIL FULVIC ACID :

The results of the investigation with PMA are presented under the following heads :

1. Preparation and properties of PMA
2. Interaction of PMA with homoionic montmorillonites.

Table 19 : Adsorption of Metoxuron and tebuthiuron on Humic Acid

Metoxuron			Tebuthiuron		
Initial concentration μgmL^{-1}	Eq.C μgmL^{-1}	A.A. $\mu g/g$	Initial concentration μ	Eq.C μgmL^{-1}	A.A. $\mu g/100mg$
2.5	1.48	565.9	4	3.21	78.18
5.0	3.33	831.9	8	6.54	145.45
7.5	4.67	1413.9	12	10.09	190.90
10.0	6.94	1528.6	16	13.54	245.45
15.0	11.07	1916.5	20	16.72	327.27
			24	19.09	409.09
			28	23.09	490.90
			32	26.67	578.18
			36	29.99	609.09
			40	33.54	645.45
			50	43.54	645.45

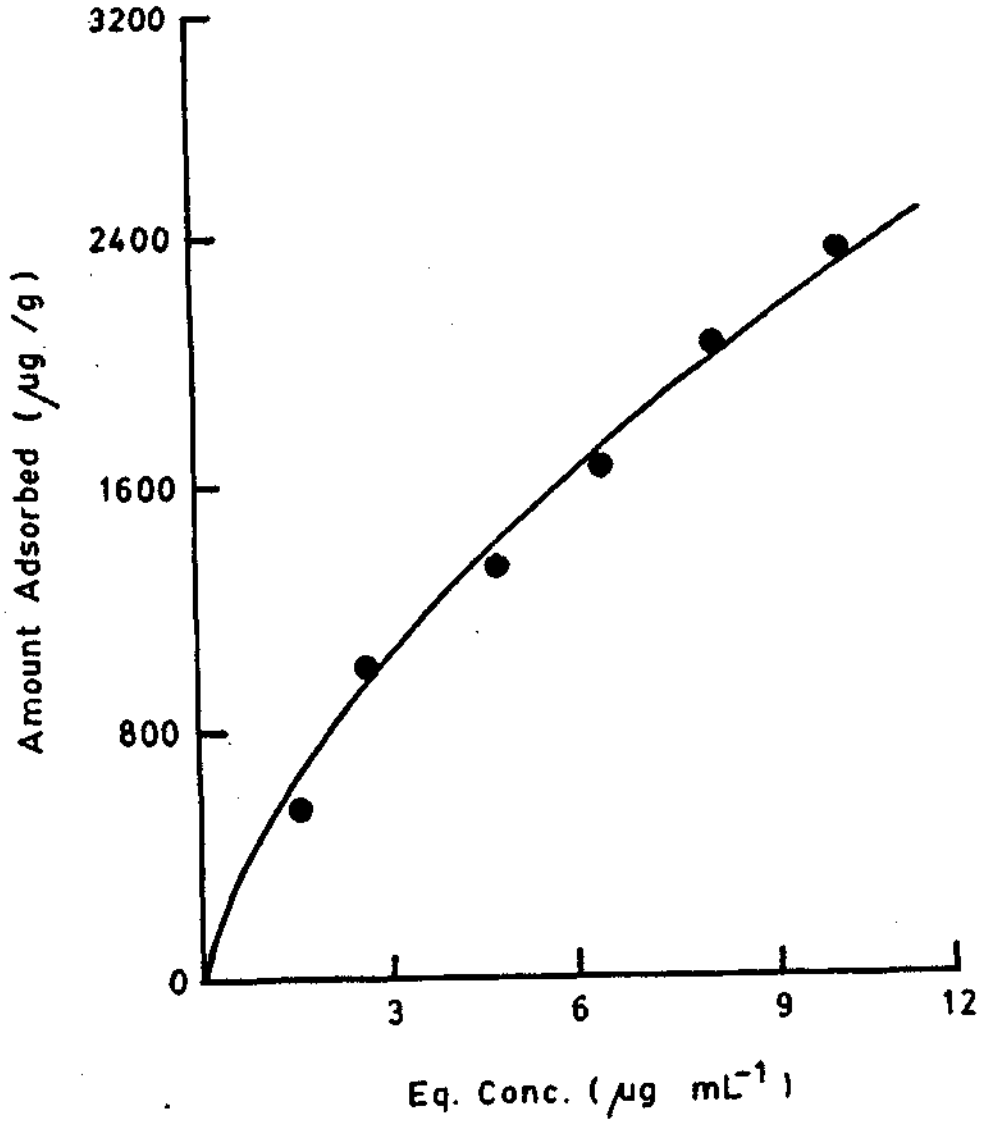
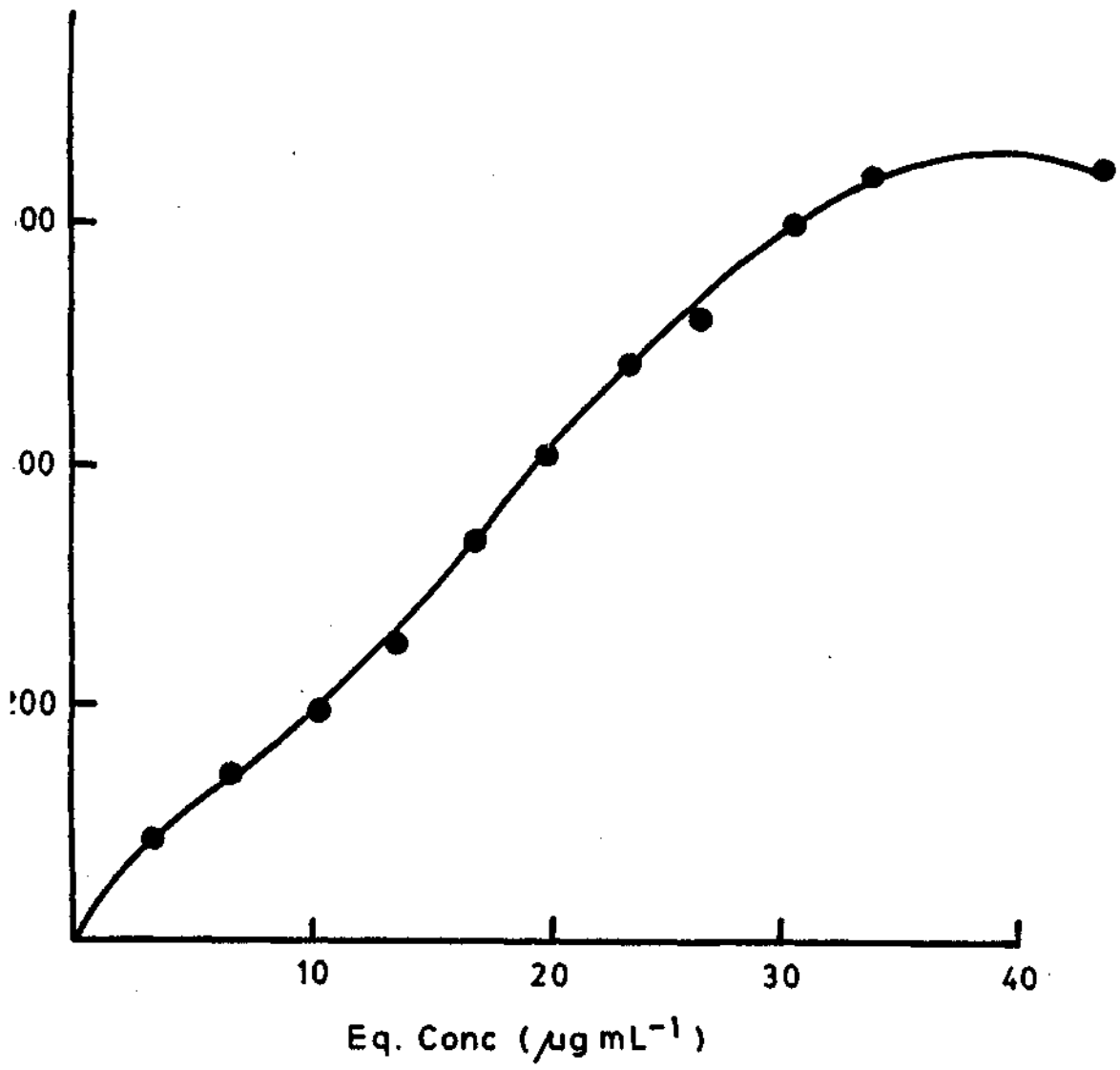


FIG. 17 : ADSORPTION ISOTHERM OF METOXURON ON HUMIC ACID



G.18: ADSORPTION ISOTHERM OF TEBUTHIURON ON HUMIC ACID

3. Adsorption of PMA on cation saturated IR-120 resin.

4. Comparative adsorption of metoxuron and tebuthiuron on homoionic montmorillonites and the corresponding clay-PMA complexes.

4.3.1 Preparation and properties of Polymaleic Acid:

Polymaleic acid was prepared by the polymerisation of maleic anhydride as given in 'Materials and Methods' and was characterised for functional group analysis and spectral properties. It was dark brown in colour and soluble in water.

4.3.1.2 Functional group analysis :

Functional group analysis provide information about the type of reactive sites on PMA. The method has already been discussed in Materials and Methods. The total acidity as determined by $Ba(OH)_2$ method was 11.43 me/g. The carboxyl content of PMA was 7.82 me/g and phenolic hydroxyl group content was 3.61 me/g PMA. The contribution of - COOH and phenolic OH groups towards total acidity thus was 68.4 and 31.6 per cent respectively. Thus, the contribution of -COOH group towards total acidity was almost twice as that of phenolic OH groups.

4.3.1.3 Potentiometric titration :

The potentiometric titration curve of PMA with standard NaOH is shown in Fig.19. There was a gradual rise in pH with the addition of base, thus attesting to the high buffering capacity of PMA. This shows that PMA behaves as weak acid polyelectrolyte like FA and HA. A fairly sharp break occurred at 1.87 meq of NaOH thus corresponding to 9.35 meq of titratable acidic groups per gram of PMA. Potentiometric titration was also carried out in the presence of 10^{-2} M, 10^{-1}M and 1M KCl to notice if there is a shift in acid-base equilibrium. These curves are given in Fig.20. The pKa of PMA was calculated from the potentiometric titration data as explained under 'Materials and Methods' using Henderson-Hesselbalch-equation

$$pH = pKa + \log \frac{[A^-]}{[HA]}$$

From the plot of $\log \frac{[A^-]}{[HA]}$ vs pH the pKa was taken as the intercept on X-axis (Fig.21) and was equal to 5.48.

4.3.1.4 Conductometric titrations :

Conductometric titration curve of PMA with standard NaOH is depicted in Fig.22. From the curve it can be seen that with the addition of NaOH, conductance

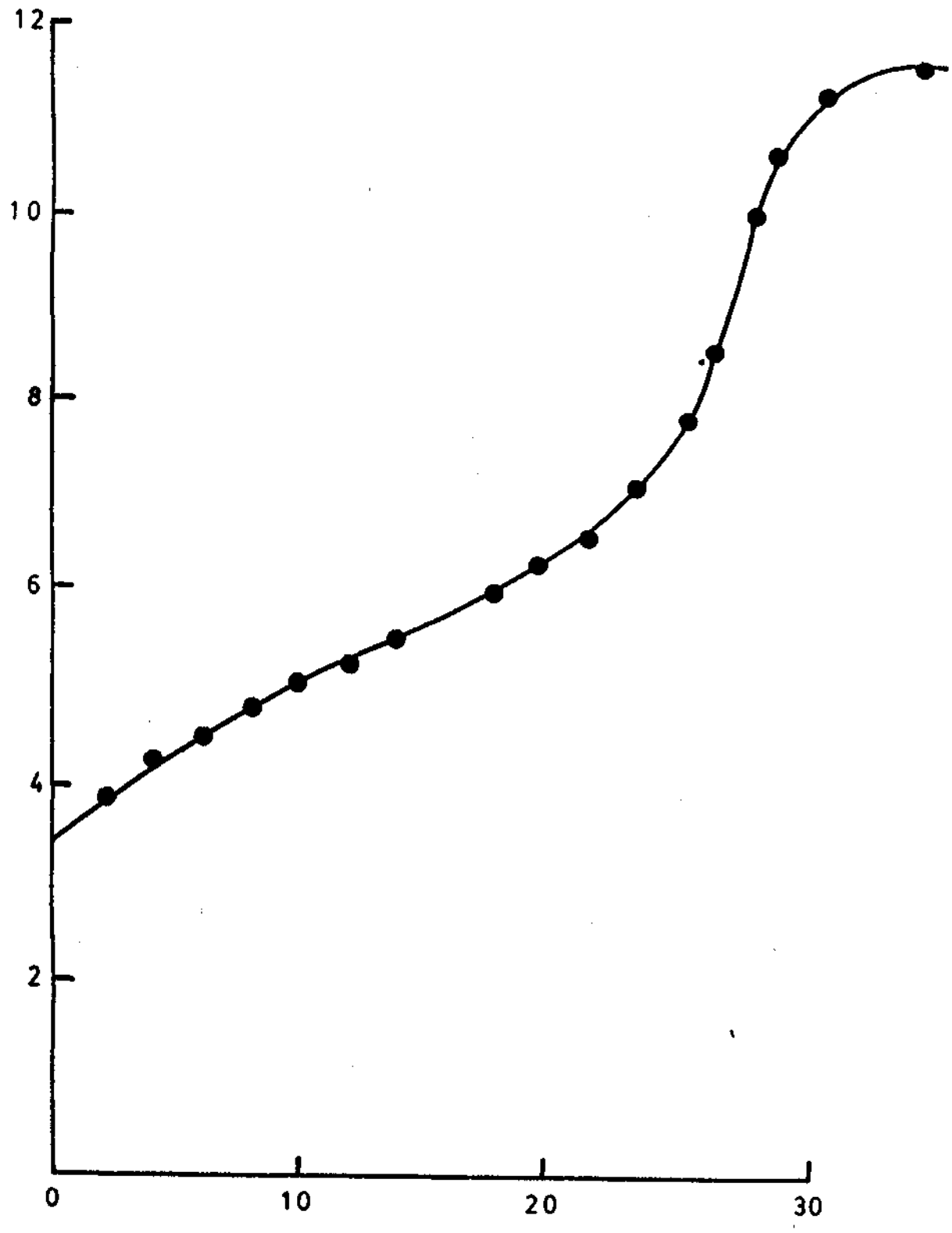


FIG. 19: POTENTIOMETRIC TITRATION CURVE OF PMA WITH STANDARD NaOH (1.04N)

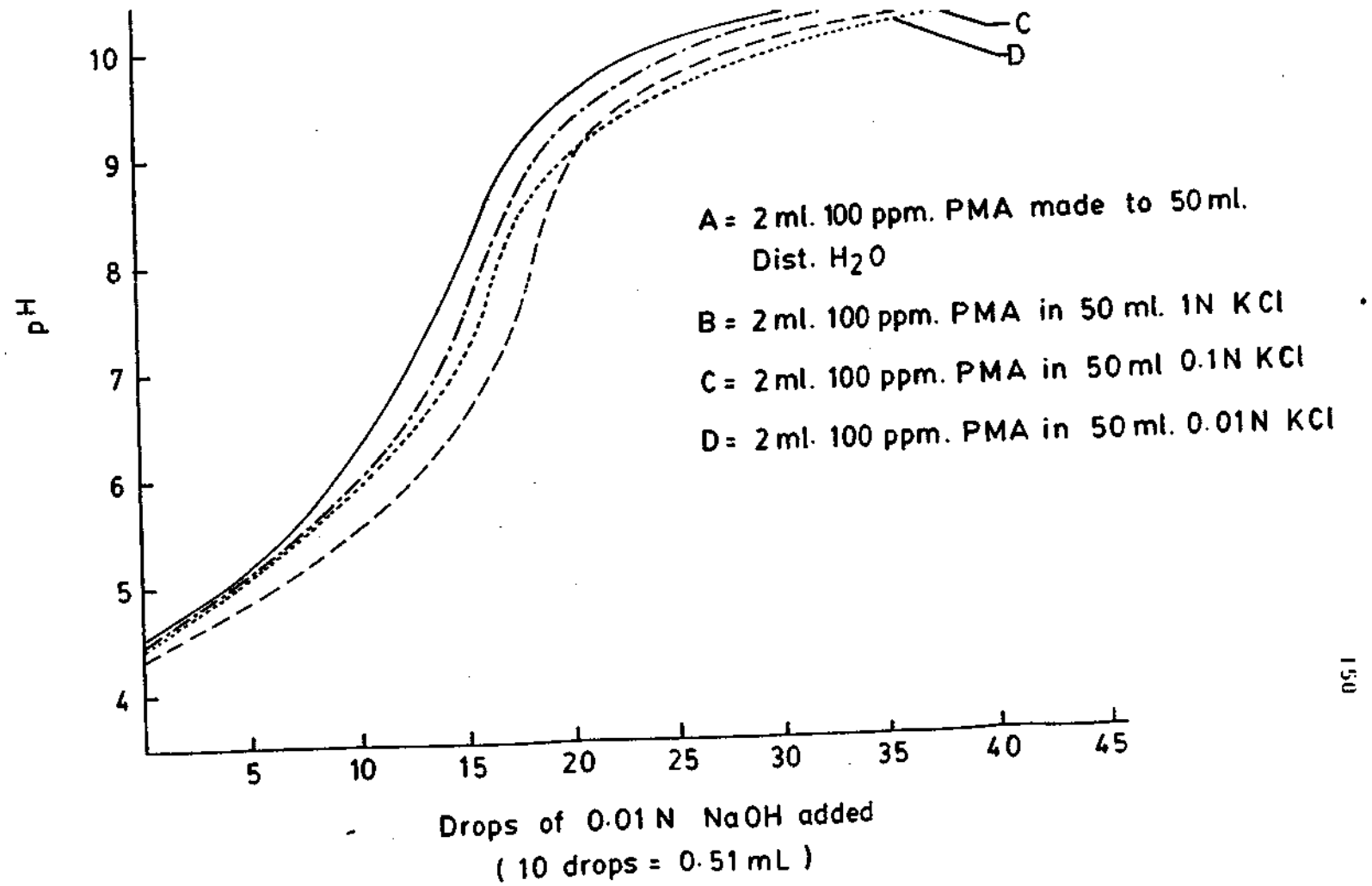


FIG. 20: EFFECT OF ELECTROLYTE CONC. ON POTENTIOMETRIC TITRATION OF PMA WITH STANDARD NaOH (0.01 N)

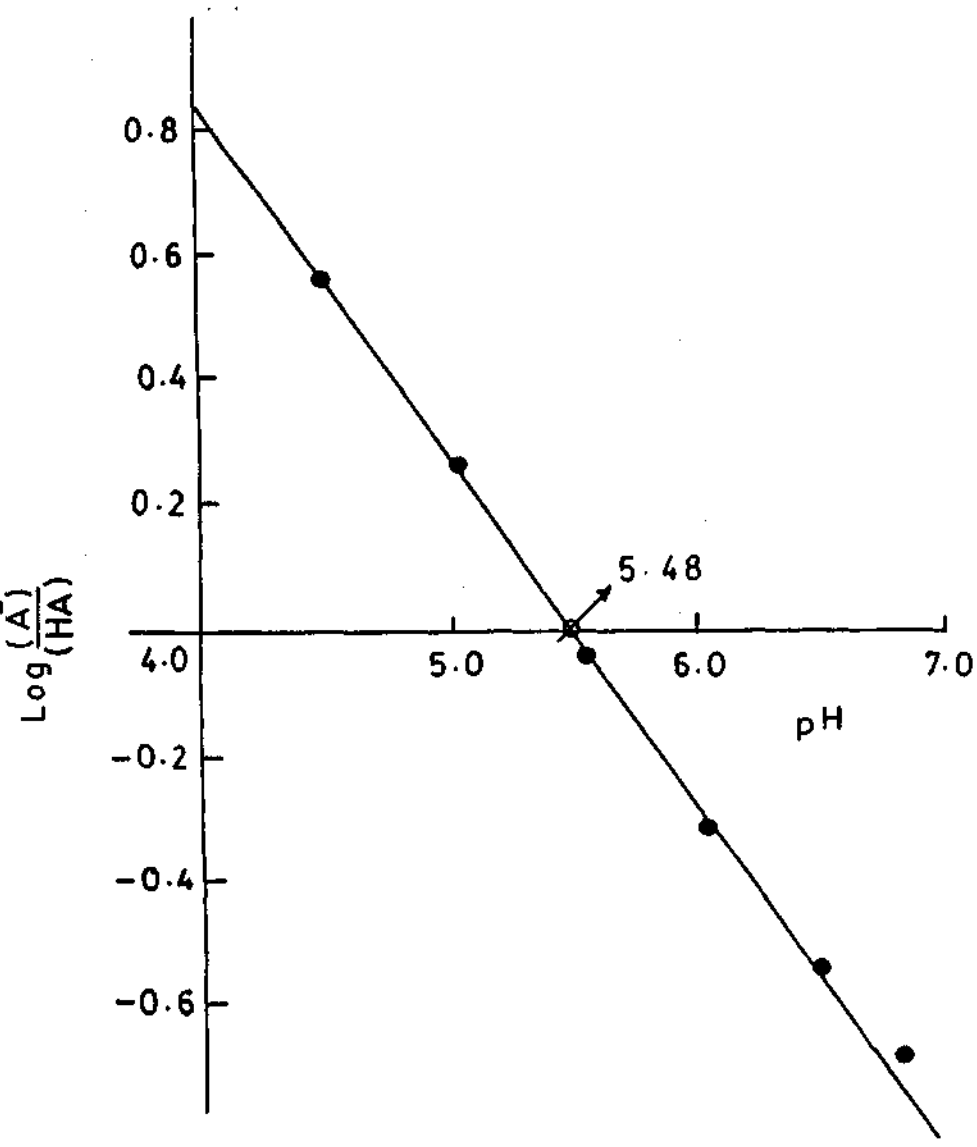


FIG. 21. PLOT OF LOG $\frac{(A^-)}{(HA)}$ vs pH

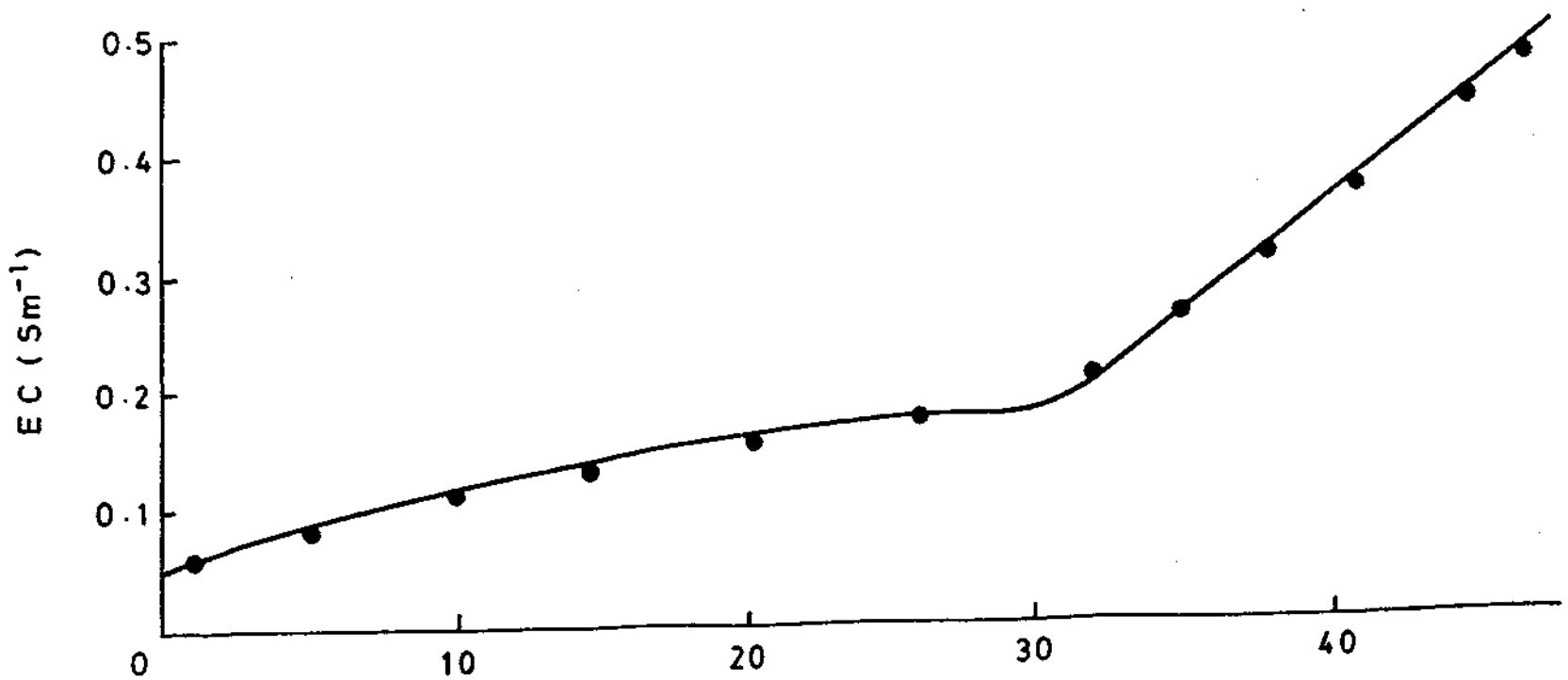


FIG :22. CONDUCTIMETRIC TITRATION OF PMA WITH STANDARD NaOH (1·04N)

increased very slowly in the beginning followed by a sharp rise. The end point was obtained at 1.54 me NaOH. This corresponds to 7.7 me/g of -COOH groups and is close to the value obtained by the $Ba(OH)_2$ method.

4.3.1.5 Spectral properties :

Ultravoilet spectrum of PMA scanned from pH 1 to 10 showed a well defined peak at 255 nm till pH (Fig.23).

A plot of absorbance vs concentration of PMA in the range of 10 to 100 μgmL^{-1} (Fig.24) followed a straight line and obeyed Beer-Lambert's law. The standard curve had a slope of 0.0135 absorbance units per μgmL^{-1} of PMA. The concentration of PMA in the experiments on resins and montmorillonites was determined with reference to this factor.

4.3.1.6 Infrared Spectrum :

Infra-Red spectroscopy provides information regarding the nature, reactivity and structural arrangement of oxygen containing functional groups. Infrared spectrum of PMA obtained in KBr pellet is presentedin Fig.25. The spectra showed a number of bands at various wavelengths. The assignment of various peaks in

2. " " " " pH 2·0
3. " " " " " 3·0
4. " " " " " 4·0
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8. " " " " " 8·0

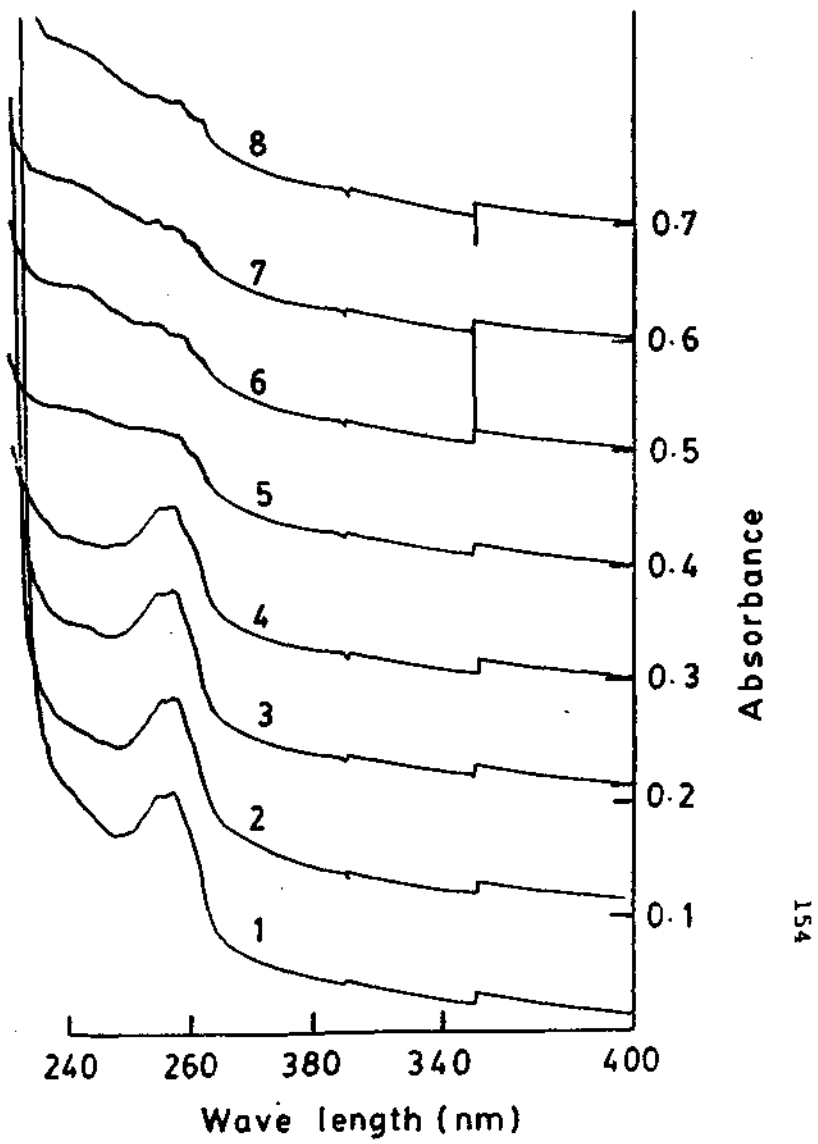

FIG. 23: SPECTRUM OF PMA

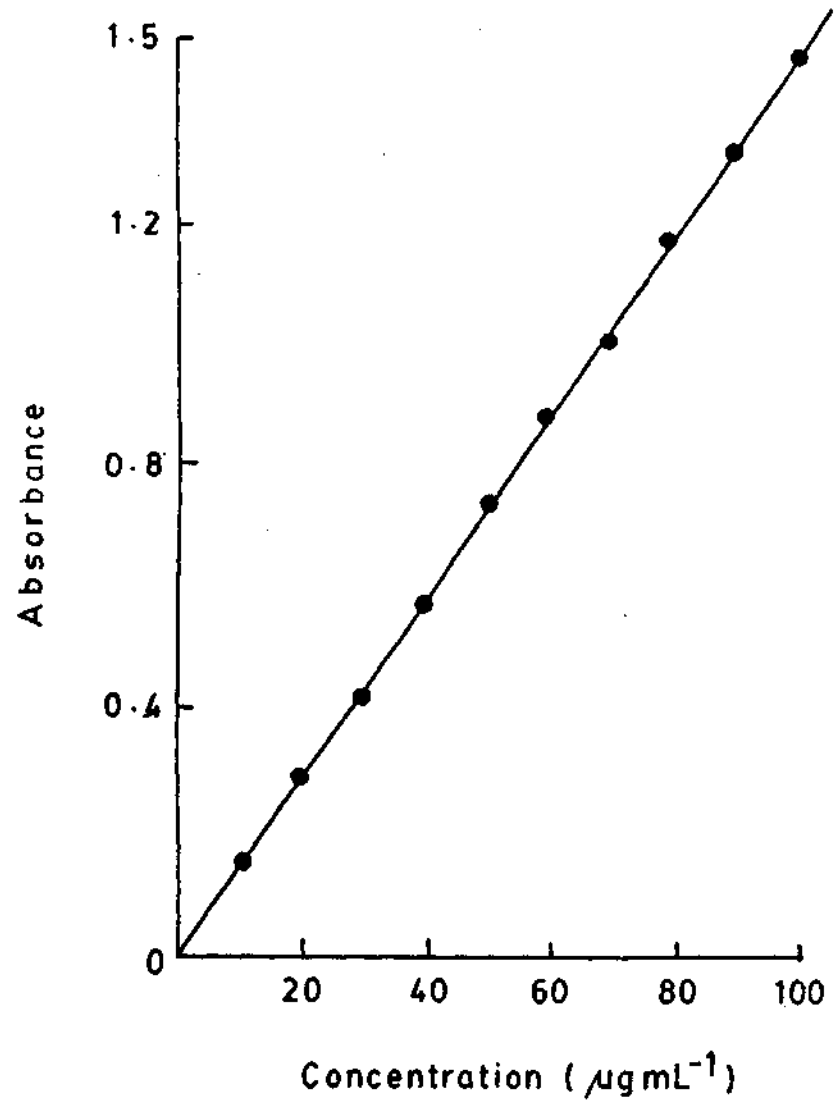

FIG. 24 : STANDARD CURVE FOR PMA (255 nm)

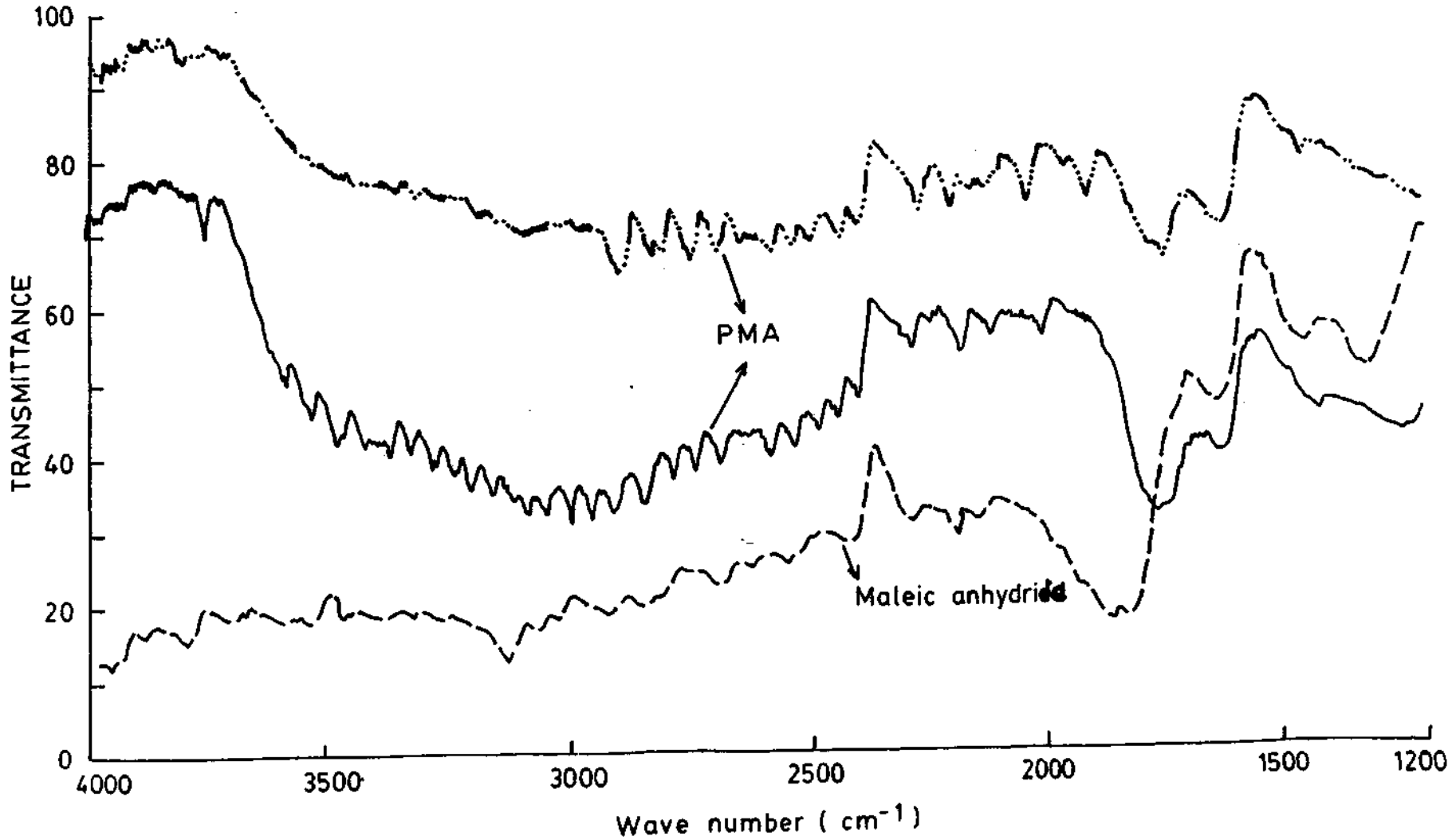

FIG. 25: INFRARED SPECTRUM OF PMA

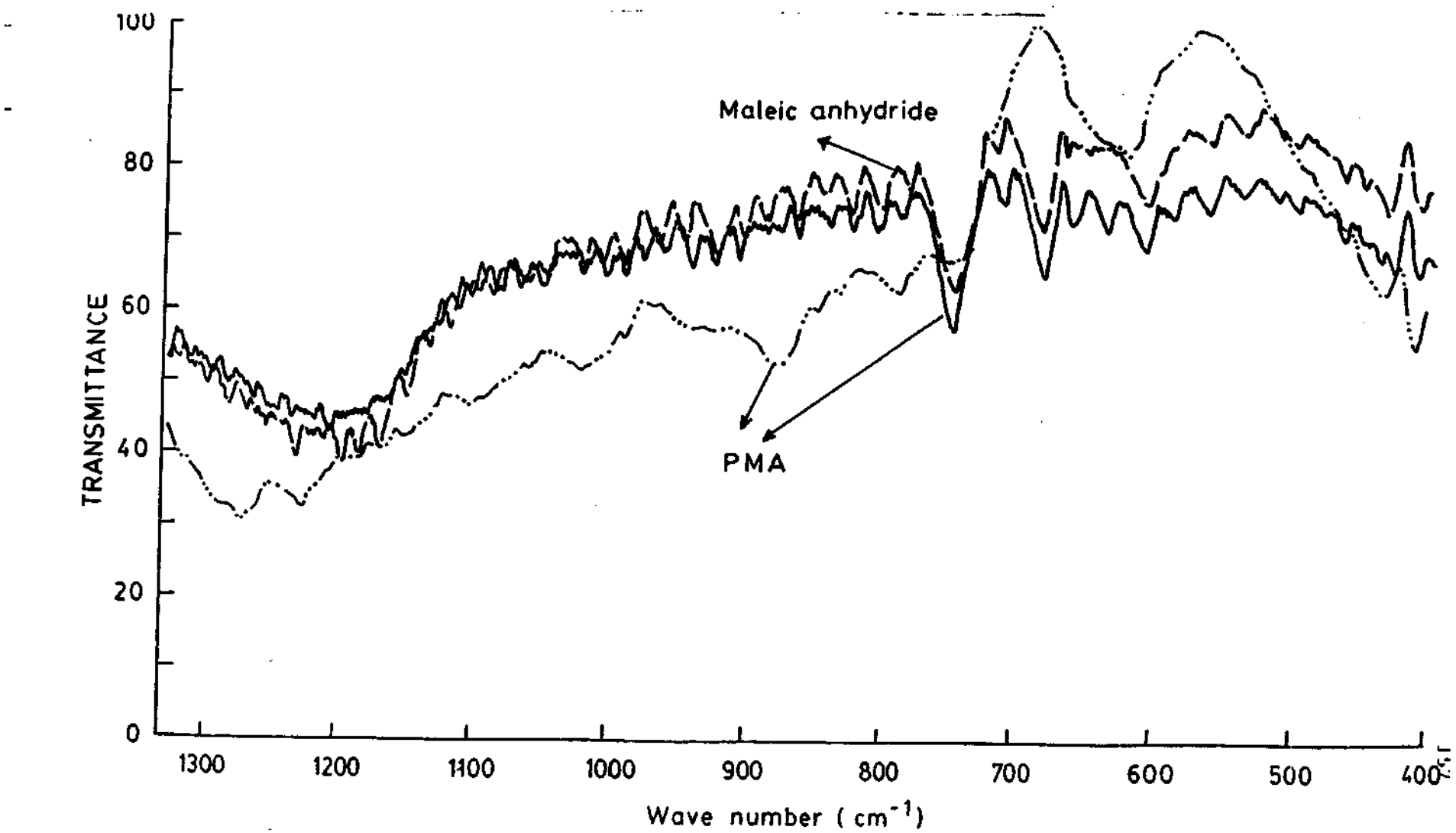

FIG.25: INFRARED SPECTRUM OF PMA

the spectrum was done with the help of data available in the literature. In general, the spectra showed the presence of aromatic ring with phenolic, carboxyl and carbonyl substituents. The spectrum showed shoulders at 1780 and 1850 cm^{-1} due to cyclic anhydrides. The spectra exhibited a number of bands at 1640 cm^{-1} (medium, C = C stretch of olefin or pyridine derivative), 1490 cm^{-1} (medium, C = C stretch of aromatic ring), 755 cm^{-1} (medium, C-H out-of-plane deformation of alkyl pyridine) and 680 cm^{-1} (pyridine derivative). The presence of these bands have been reported by Spiteller and Schnitzer (1983) also.

4.3.2 Adsorption of PMA on homoionic montmorillonites:

Adsorption of PMA was studied on aqeous suspensions of homoionic montmorillonites saturated with Fe-, Al-, Ni-, Cu-, Zn-, Co-, Ca-, Ba-, Mg-, Na-, NH_4- and K-. Five mL of suspension (containing ~50 mg clay) was equilibrated with initial concentration of PMA ranging from 10 to 100 μgmL^{-1}. After equilibration for 24 h at 27°C and centrifuging, the amount left in supernatant was determined spectrophotometrically at 255 nm. The amount of PMA adsorbed on different homoionic montmorillonites fell into four distinct groups : trivalent > transition 3d ions> alkaline earth ions > monovalent, as in the case of

adsorption of metoxuron and tebuthiuron on metal montmorillonites and resins.

For trivalent ions the amount of PMA adsorbed varied from 261.7 to 2132.8 µg/100 mg for Fe-M, 76.5 to 1425 µg/100 mg for Al-M.

Transition metal ions followed Fe-M in amounts adsorbed and were of the order 116.1 to 1125.3 µg/100 mg for Ni-M, 259.1 to 673.8 µg/100 mg for Co-M and 73.3 to 851.1 µg/mg for Cu-M.

Alkaline earth metal ions followed the transition metal ions and the amounts adsorbed varied from 57.4 to 277.8 µg/100 mg for Mg-M 82.5 to 256.7 µg/100 mg for Ca-M and 67.9 to 252.6 µg/100 mg for Ba-M.

For monovalent ions, the extent of adsorption was 83.8 to 340.6 µg/100 mg for NH_4-M, 29.5 to 165.1 µg/100 mg for K-M and 9.5 to 141.1 µg/100 mg for Na-M (Table 20). Adsorption isotherms were mostly L-shaped (Fig.26). Adsorption increased with increase in initial concentration and tend to reach saturation. A slight S-character was seen in the initial stages of adsorption for Co-M and Na-M.

The adsorption data was fitted to Freundlich equation. The Freundlich constants, K and α, the value of $(C_{0.5})^{-1}$ which corresponds to binding constant

Table 20 : Adsorption of PMA on Al-, Fe-, Ni-, Cu-, Zn-, Co-, Ca-, Mg-, Ba-, K-, NH_4 -Montmorillonite

Initial concentration $\mu g\ mL^{-1}$	Al-		Fe-		Ni-		Cu-		Zn-		Co-		Ca-		Mg-		Ba-		K-		Na-		NH_4	
	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)	Eq.C ($\mu g\ mL^{-1}$)	A.A (μg /100 mg)
10	4.27	76.53	0.77	261.76	4.50	116.18	5.44	73.34	4.94	88.12	8.51	25.92	5.46	82.58	6.66	67.47	5.97	67.94	7.75	29.58	9.23	9.59	6.96	83.8
20	6.03	251.77	3.08	476.45	9.15	226.28	11.41	138.17	8.77	191.54	14.92	86.24	14.72	93.72	15.16	76.62	14.09	99.07	15.45	60.78	17.98	25.18	14.20	145.5
30	11.46	406.23	4.16	727.19	12.12	373.27	14.49	250.91	12.69	295.80	20.91	157.15	22.34	122.41	25.92	86.41	20.87	147.54	23.95	82.57	25.46	56.74	21.93	203.9
40	14.41	459.51	5.44	973.30	15.72	506.76	19.12	327.66	12.62	467.57	22.20	307.87	32.24	150.10	33.70	104.94	29.37	178.38	31.67	109.94	32.75	90.66	30.68	238.6
50	19.34	599.56	9.80	1187.69	20.43	617.33	24.34	412.76	16.82	566.54	29.01	355.24	38.34	167.06	42.22	127.71	37.54	206.94	40.12	130.56	41.23	108.51	38.62	291.7
60	31.03	598.28	15.29	1335.62	30.62	617.75	35.70	678.61	28.90	736.52	42.39	472.51	57.78	301.48	60.74	166.87	55.15	241.74	58.12	180.36	58.20	83.61	60.51	320.7
80	38.28	884.48	26.23	1784.57	35.72	924.13	35.14	715.52	33.46	795.33	49.84	610.75	65.96	231.73	68.51	191.35	64.83	252.66	68.40	168.10	66.70	141.13	68.24	322.7
90	38.80	1410.0	22.34	1885.69	39.63	1052.32	40.91	791.44	39.37	865.31	54.51	697.57	74.41	246.59	75.92	265.45	74.83	252.66	78.35	163.80	78.70	141.13	78.27	340.69
100	48.94	1425.7	24.27	2132.83	46.08	1125.47	47.09	851.17	44.98	940.80	60.20	673.59	83.55	256.79	83.33	277.73	84.83	252.66	88.41	165.10	88.70	141.13	88.03	340.69

Eq.C = Equilibrium concentration; A.A. = Amount Adsorbed

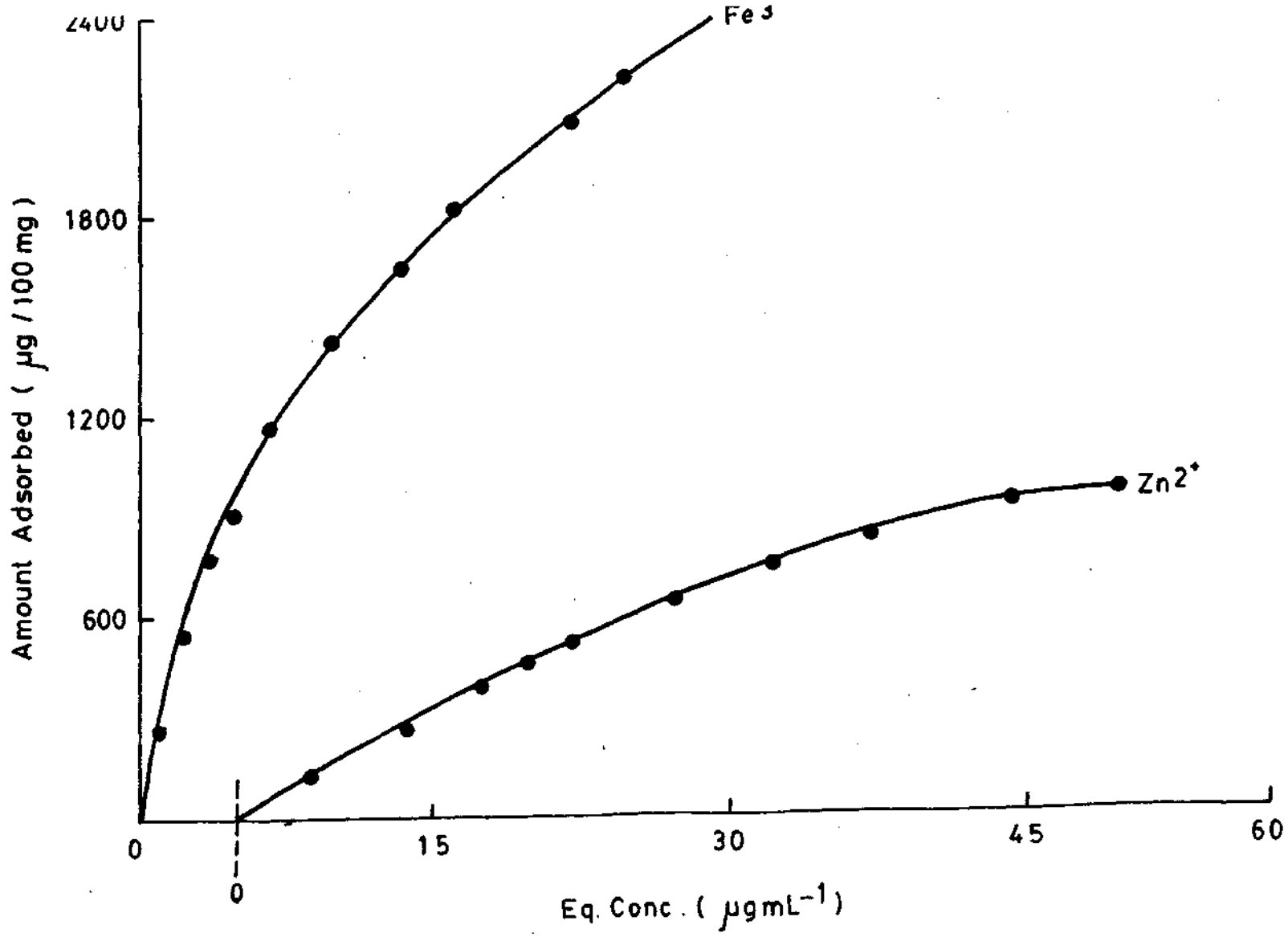

FIG. 26: ADSORPTION ISOTHERMS OF PMA ON HOMOIONIC MONTMORILLONITES

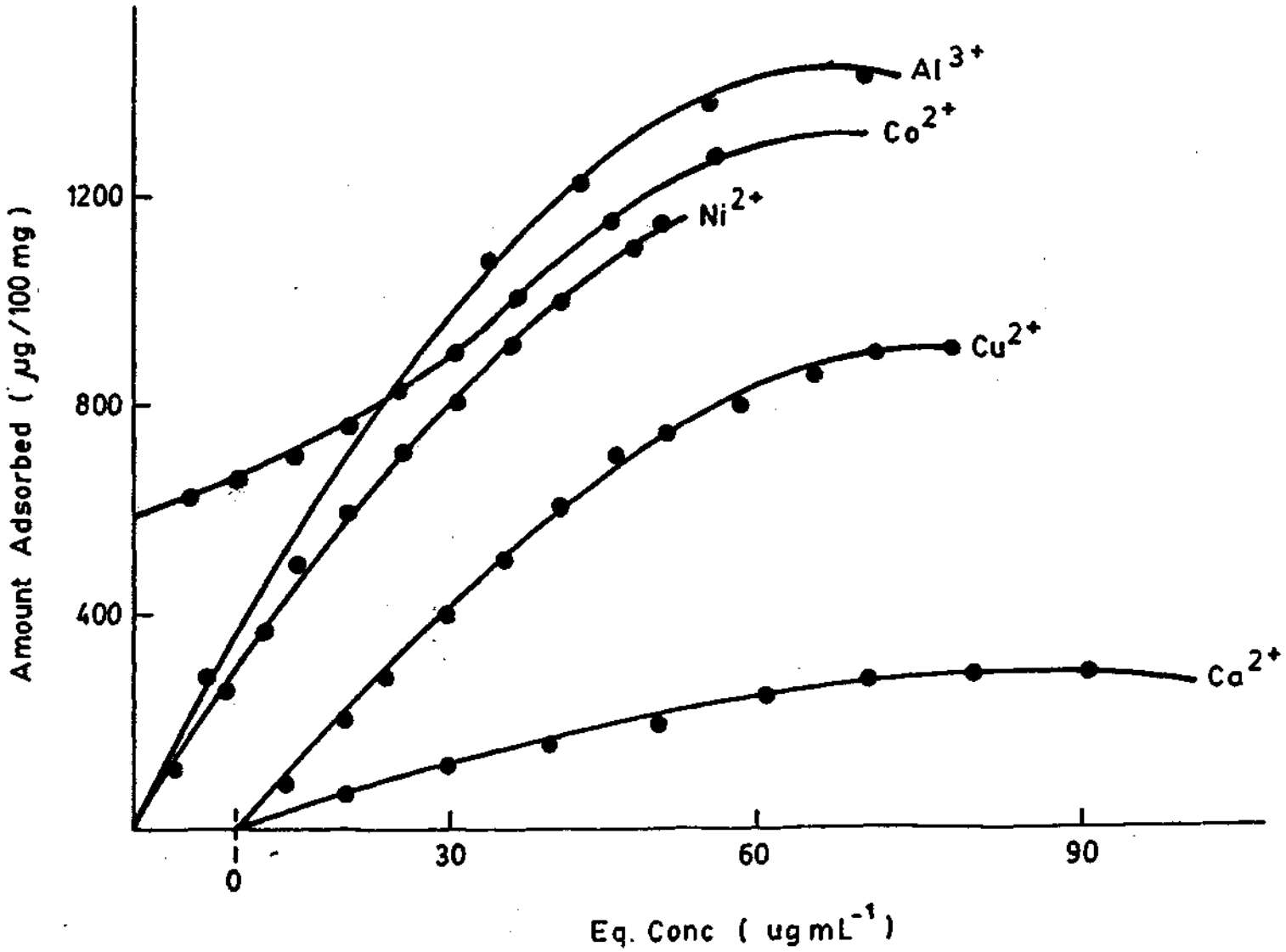

FIG. 26 : ADSORPTION ISOTHERMS OF PMA ON HOMOIONIC MONTMORILLONITES

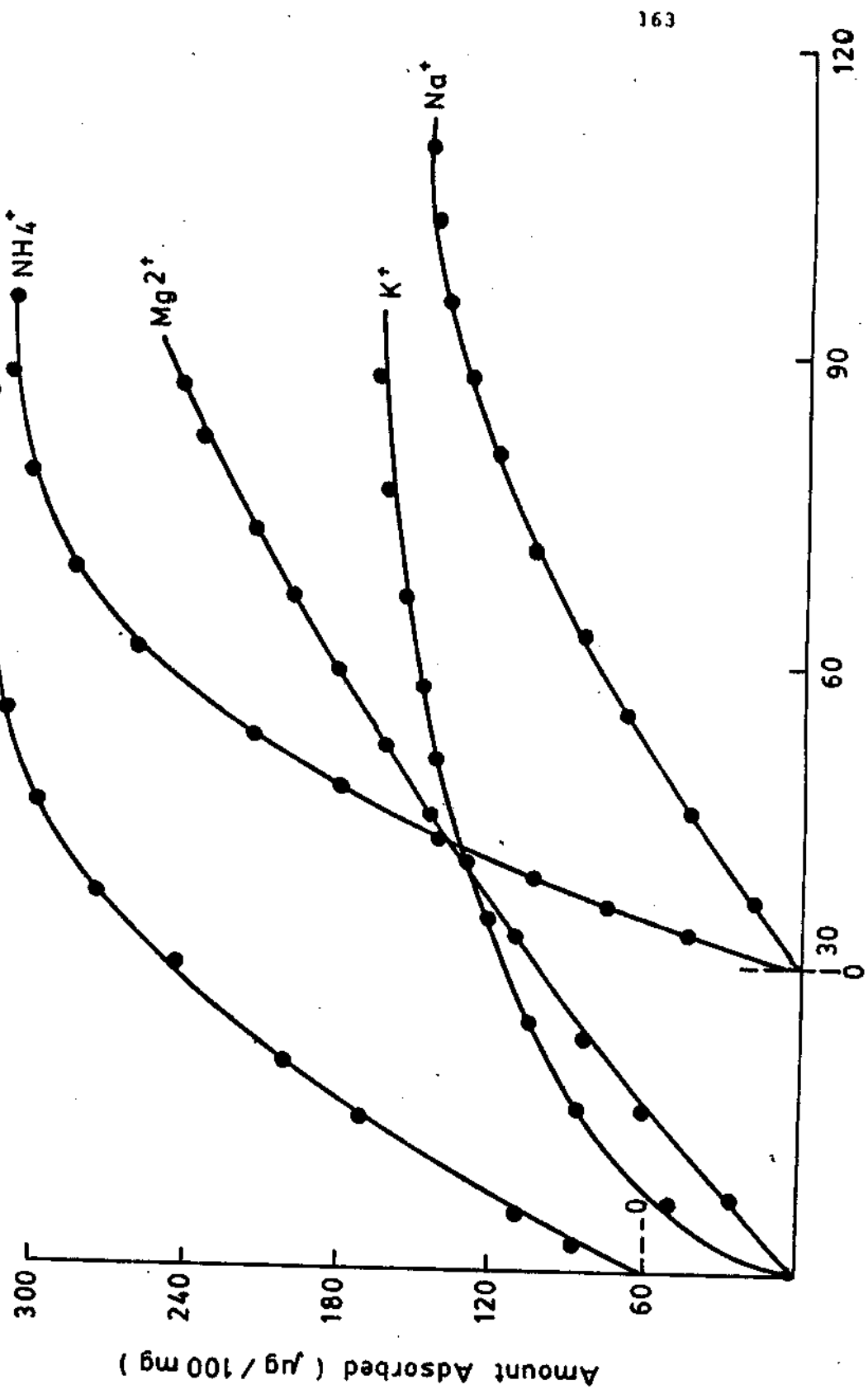

FIG. 26 : ADSORPTION ISOTHERMS OF PMA ON HOMOIONIC MONTMORILLONITES.

Table 21 : Freundlich constants, maximum adsorption and K_L of PMA on homoionic montmorillonites

Ion saturating the Complex	Freundlich constants		Maximum Adsorption (µg/ 100mg)	K_L $\mu g^{-1}mL$
	K	α		
Al-	27.23	0.60	1420	0.0714
Fe-	199.52	0.78	2200	0.1430
Ni-	29.51	0.96	1150	0.0541
Cu-	2.09	0.81	900	0.0435
Co-	2.30	0.76	710	0.0294
Zn-	14.79	0.85	950	0.0556
Ca-	23.44	0.54	270	0.0400
Mg-	10.35	0.73	260	0.0253
Ba-	21.30	0.60	260	0.0571
NH_4-	25.11	0.64	310	0.0714
Na-	6.09	0.88	145	0.0317
K-	1.15	0.92	105	0.0435

K_L of Langmuir equation calculated from the isotherms, along with maximum adsorption are given in Table 21. Freundlich constant 'K' was highest for Fe-M (199.50) and was lowest for K-M (1.15) and α was highest for Ni-M (0.96) and lowest for Ca-M (0.54).

4.3.3 Adsorption of PMA on Homoionic resins :

Adsorption was studied on the same set of representative cations as in the case of metoxuron and tebuthiuron. Surface saturation was attained with much larger concentration of PMA and hence the initial concentration range used was 0 - 500 μgmL^{-1}.

The amount of PMA adsorbed on different ion saturated resins are presented in Table 22. The amount adsorbed decreased in the order

trivalent	>	divalent 3d transition metal ions	>	divalent alkaline earth metal ions	>	monovalent ions

The amount adsorbed was highest for Fe-R, Al-R and H-R and varied from 69.4 to 1068.9 μg/100 mg, 85.5 to 910.3 μg/100 mg and 100.6 to 983.8 μg/100 mg respectively. Transition metal ions closely followed trivalent ions and the amounts adsorbed varied from 27.5 to 962.0 µg/100 mg (Cu-R), 44.8 to 951.7 µg/100 mg (Ni-R),

Table 22 : Adsorption of PNA on homoionic resin (IR-120) saturated with different cations

Initial concentration $\mu g\ mL^{-1}$	H-		Al-		Fe-		Cu-		Co-		Zn-		Ni-	
	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)
50	39.99	100.65	41.37	85.57	42.57	69.48	47.24	27.58	44.82	51.72	44.82	51.72	45.58	44.82
100	80.46	195.15	83.53	163.59	91.37	86.20	85.68	143.11	77.24	227.58	84.82	151.73	85.86	141.37
150	127.17	228.34	128.93	211.54	132.75	172.41	125.34	246.56	116.89	331.03	114.13	358.62	122.06	279.31
200	147.79	344.79	170.03	297.58	171.54	280.75	164.51	358.62	156.10	417.24	160.68	393.10	156.55	434.48
250	204.10	458.58	208.96	410.34	203.44	465.51	199.51	504.63	203.10	466.89	200.34	496.55	204.82	451.72
300	250.55	494.79	253.60	484.06	251.72	482.75	238.27	617.24	253.10	466.89	248.17	548.27	252.41	675.51
350	290.96	592.51	296.62	513.79	294.75	655.17	270.75	792.42	286.81	693.10	290.03	592.65	288.10	817.48
400	327.10	725.59	334.56	651.57	320.68	793.10	307.24	927.58	322.06	779.31	333.03	649.65	315.17	865.51
450	358.03	894.82	374.48	785.17	363.82	896.55	356.41	935.51	366.85	881.03	376.20	737.91	365.98	940.14
500	401.90	993.89	408.96	910.34	393.10	1068.96	403.79	962.06	413.17	848.27	417.58	824.13	404.82	951.72

Contd..

Table 22 (Contd..

Initial concentration $\mu g\ mL^{-1}$	Ca-		Mg-		Ba-		K-		Na-		NH_4-	
	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)	Eq.C (µg/mL)	A.A. (µg/100 mg)	Eq.C (µg/mL)	A.A. (µg/100 mg)	Eq.C (µg/mL)	A.A (µg/100 mg)
50	45.17	45.25	44.30	51.68	48.95	10.25	49.48	5.17	49.31	6.98	49.31	6.84
100	87.41	125.86	86.20	139.65	87.15	128.27	95.68	43.10	96.46	34.48	95.98	41.37
150	130.51	194.84	130.20	200.80	130.95	189.65	144.75	58.96	145.68	34.46	145.81	41.72
200	171.03	289.65	173.10	268.96	173.21	267.58	194.19	68.96	196.55	34.48	195.18	41.72
250	212.41	375.86	200.80	493.10	207.23	422.68	239.79	112.06	244.87	50.28	240.91	78.66
300	250.34	496.55	248.34	527.60	260.48	477.68	288.38	114.78	294.85	50.49	292.06	83.37
350	302.31	476.68	302.75	492.40	306.69	475.86	337.93	120.68	344.82	51.72	341.68	96.44
400	350.68	493.37	347.10	527.58	358.58	477.75	387.98	120.38	393.10	68.96	390.37	110.34
450	388.27	612.41	393.75	560.08	399.48	501.89	437.93	120.68	442.10	68.20	439.37	106.20
500	436.20	637.94	441.72	582.03	448.10	572.06	486.20	137.93	493.10	68.20	487.41	125.86

57.7 to 848.2 µg/100 mg (Co-R) and 57.7 to 824.1 µg/100 mg (Zn-R).

Alkaline earth metal ions followed transition metal ions and the amounts adsorbed were 45.2 to 637.9 µg/100 mg for Ca-R, 51.6 to 582.0 µg/100 mg for Mg-R, and 10.2 to 512.0 µg/100 mg for Ba-R. Monovalent ions showed least adsorption and varied in the order 5.1 to 137.9 µg/100 mg (K-R) 6.8 to 125.8 µg/100 mg (NH_4-R) and 6.8 to 68.2 µg/100 mg (Na-R).

Adsorption isotherms for different homoionic resins are presented in Fig.27. Adsorption isotherms were parabolic showing a tendency to reach surface saturation within the concentration range studied. There was some S character in almost all the isotherms in the initial stages. The adsorption data was fitted to Freundlich equation. Freundlich constants 'K' and α alongwith the values of maximum adsorption, K_L are given in Table 23.

4.3.4 Comparison of adsorption of metoxuron and tebuthiuron on homoionic montmorillonite and metal montmorillonite-PMA complexes :

Montmorillonite-PMA complexes were prepared by treating suspensions of homoionic montmorillonites with PMA and washing free the excess PMA with distilled water. Adsorption was carried out under identical

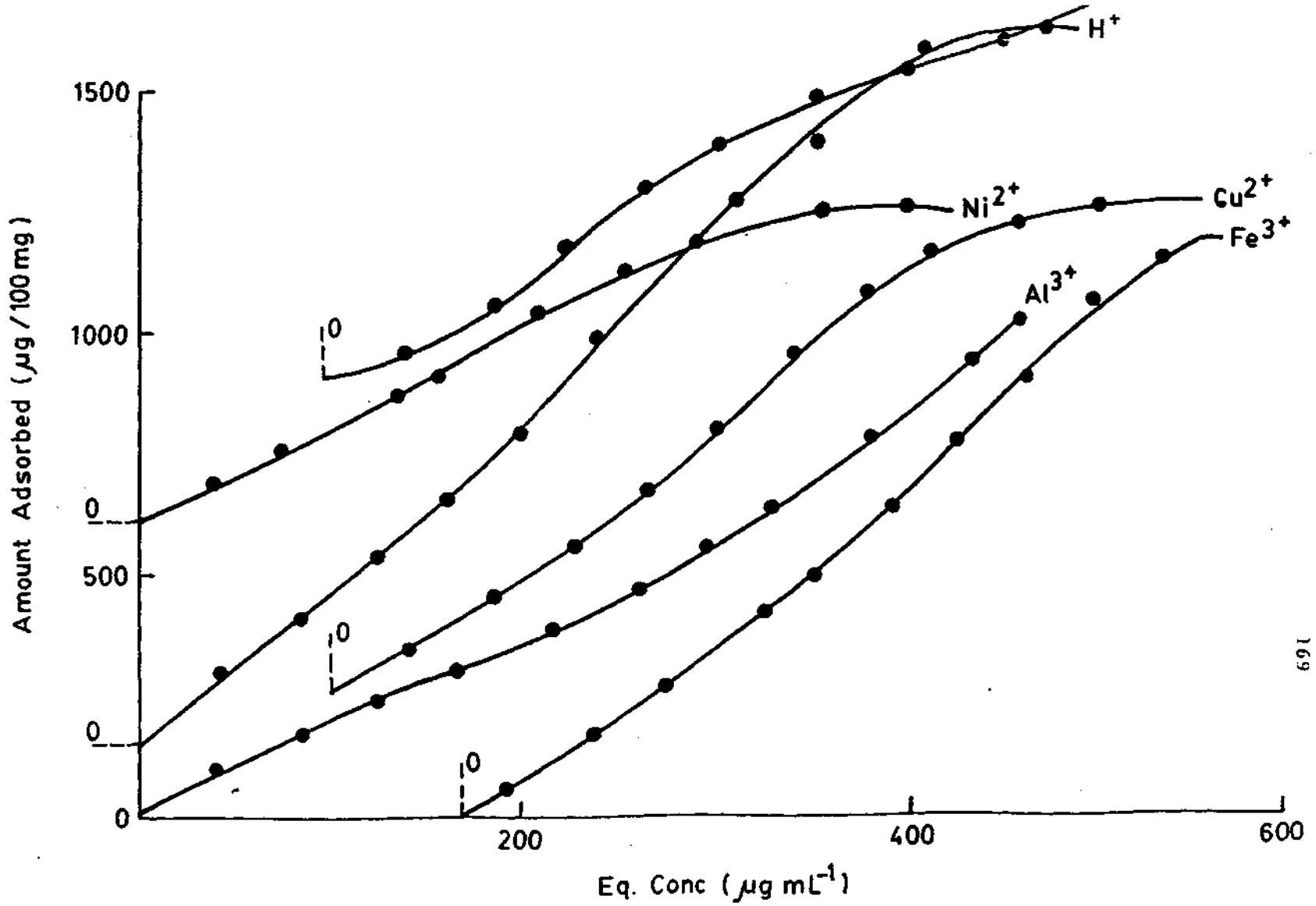

FIG.27: ADSORPTION ISOTHERMS OF PMA ON HOMOCATIONIC (IR-120) RESIN.

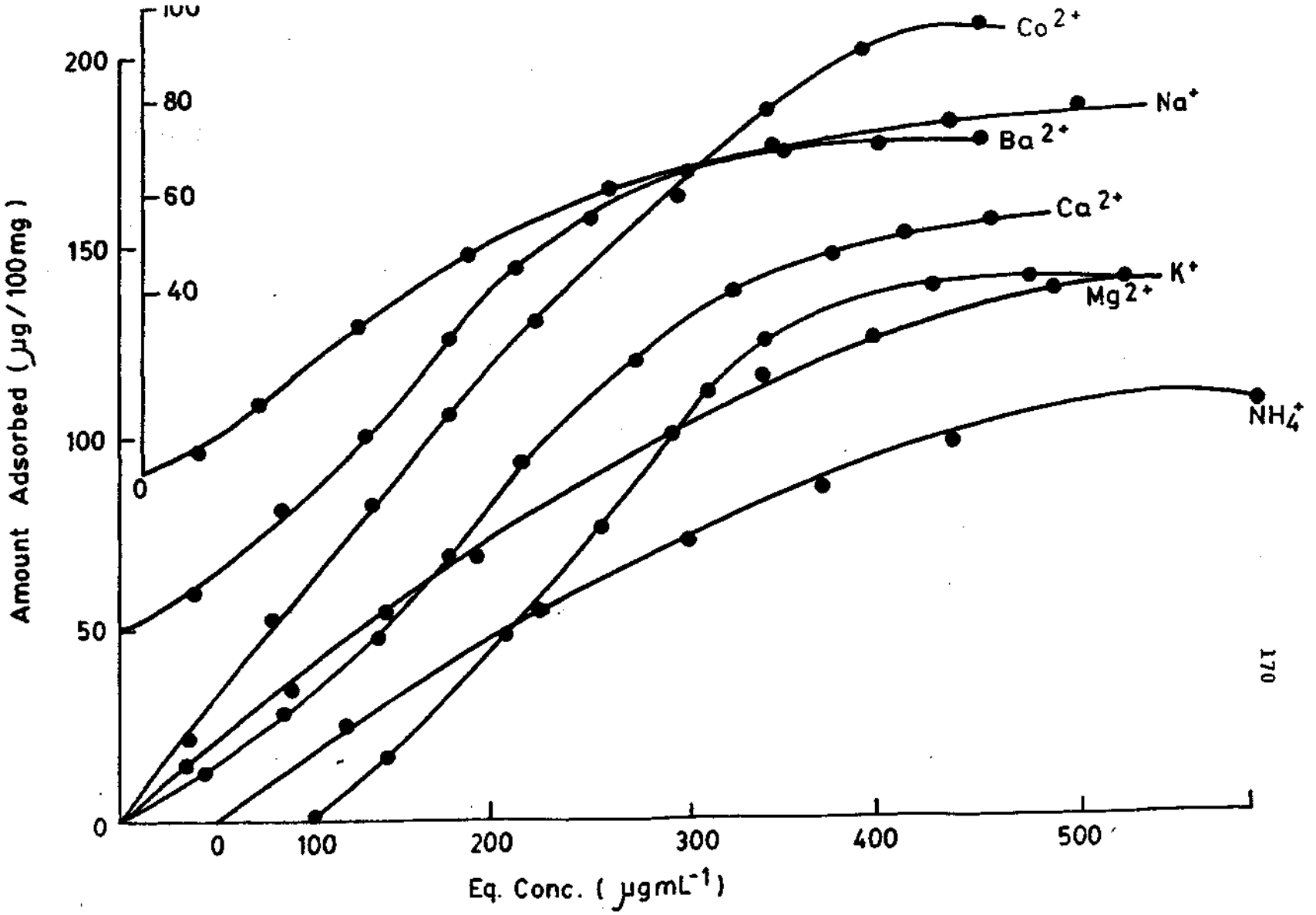

FIG. 27: Contd: ADSORPTION ISOTHERMS OF PMA ON HOMOCATIONIC (IR-120) RESINS.

Table 23 : Freundlich constants, maximum adsorption and K_L of PMA on homoionic resins

Ion saturating the resin	Freundlich constants		Maximum Adsorption (µg/100 mg)	K_L $\mu g^{-1}mL$
	K	n		
H-	1.74	0.98	1040	0.0038
Al-	2.24	0.91	1020	0.0035
Fe-	1.01	1.60	1200	0.0036
Ni-	1.12	1.29	960	0.0050
Cu-	1.04	1.48	990	0.0052
Co-	1.19	1.19	855	0.0057
Zn-	1.07	1.37	830	0.0057
Ca-	1.07	1.31	640	0.0054
Mg-	1.17	1.17	565	0.0057
Ba-	1.19	1.07	520	0.0063
Na-	1.16	0.81	65	0.0100
K-	1.22	0.93	135	0.0053
NH_4^-	1.25	0.75	110	0.0055

conditions as explained under 'Materials and Methods' with 20 and 50 μgmL^{-1} initial concentration of metoxuron and tebuthiuron. The amount adsorbed on metal clays and corresponding metal clay-PMA complexes is given in Table 24. There was consistent increase in amount adsorbed on clay-PMA complexes as compared to corresponding metal clays. The per cent increase in adsorption on clay-PMA complexes is given in Table 25. In order to derive information about the role of exchange cations on the shape, extent and mechanism of adsorption of metoxuron, tebuthiuron and PMA on resins and clays, relevant adsorption parameters like maximum adsorption, Freundlich K, Langmuir K and free energy of adsorption were analysed qualitatively and quantitatively with respect to ionic properties like crystalline ionic radius (CIR), crystalline ionic potential (CIP), hydrated ionic radius (HIR), hydrated ionic potential (HIP), and charge on the ions and are presented in Table 26. The results are summarised for individual adsorbents and adsorbates as follows :

4.3.5 Adsorption of metoxuron and tebuthiuron on homoionic montmorillonites ;

The adsorption isotherms constructed for all samples (Fig.7 and 10), indicated that these isotherms were mainly S-shaped in nature with a tendency to reach surface saturation within this concentration

Table 24 : Adsorption of metoxuron and tebuthiuron on montmorillonite-PMA complexes

Metal ion	20 μgmL^{-1}				50 μgmL^{-1}			
	Metoxuron		Tebuthiuron		Metoxuron		Tebuthiruon	
	Clay	Clay-PMA complex	Clay	Clay-PMA complex	Clay	Clay-PMA complex	Clay	Clay-PMA comples
Al-	80.45	83.52	68.88	78.73	203.24	216.26	142.56	155.89
Fe-	69.87	79.09	64.14	80.28	170.25	195.86	94.32	118.79
Ni-	78.69	86.34	33.59	44.58	174.83	208.16	57.51	74.50
Cu-	56.65	60.91	24.58	29.44	153.24	164.62	72.84	85.91
Co-	40.63	46.33	29.51	33.54	102.53	135.55	78.51	94.59
Zn-	44.75	54.18	28.96	34.36	155.64	189.95	66.07	66.98
Ca-	47.57	57.27	24.66	29.49	150.98	161.76	53.18	64.15
Ba-	34.94	60.37	25.02	28.60	132.72	149.25	60.07	69.31
Mg-	42.91	54.02	26.59	29.58	114.55	148.29	46.59	52.63
NH_4-	41.87	44.52	9.52	11.25	135.34	146.38	23.12	29.32
Na-	35.28	40.02	8.97	10.06	42.57	57.61	21.12	25.46
K-	22.23	26.66	7.10	9.21	62.53	79.48	21.05	28.61

Table 25 : Per cent increase in Metoxuron and Tebuthiuron by montmorillonite - PMA complexes

Ion saturating the resins	Metoxuron % increase at		Tebuthuiruon % increase at	
	20 μgmL^{-1}	50 μgmL^{-1}	20 μgmL^{-1}	50 μgmL^{-1}
Al^{3+}	3.8	3.8	14.3	9.3
Fe^{3+}	13.0	14.7	25.1	21.2
Ni^{2+}	9.7	19.0	32.7	29.5
Cu^{2+}	6.9	7.5	19.7	18.0
Co^{2+}	14.0	32.1	13.6	20.3
Zn^{2+}	21.0	19.9	18.6	1.3
Ca^{2+}	20.3	17.8	19.5	20.7
Ba^{2+}	9.8	13.0	14.0	15.6
Mg^{2+}	25.8	29.3	11.2	12.9
NH_4^+	6.3	16.8	18.2	26.8
K^+	19.9	26.4	29.7	36.1
Na^+	13.4	35.2	12.0	20.9

Table 26 : Correlation coefficients of various adsorption parameters with ionic properties

Crystalline ionic radius (CIR)

Parameter	Metoxuron on montmorillonites	Tebuthiuron on montmorillonites	PMA on montmorillonites	Metoxuron on Resins	Tebuthiuron on Resins	PMA on resins
1	2	3	4	5	6	7
			OVERALL RELATIONSHIP			
Maximum Adsorption	-0.3284	-0.7563**	-0.5528	0.7382**	0.7192**	-0.7998**
K_F	-0.1892	-0.4724	-0.2492	-0.3524	-0.1293	-0.2366
K_L	0.5293	-0.1338	-0.2613	0.3368	-0.3468	0.2692
k	0.1224	0.1983	-	-	-	-
Log K_F	-0.0678	-0.4749	-0.1123	-0.3274	-0.0701	-0.1731
Log K_L	0.5278	-0.1843	0.2433	0.3634	-0.3314	0.1423
			ALKALI AND ALKALINE EARTH IONS			
Maximum Adsorption	-0.1035	-0.1892	-0.0832	-0.0092	-0.5142	-0.1273
K_F	0.3262	-0.5894	0.1296	0.3629	0.4198	0.3345
K_L	0.9215**	0.1158	-0.8991*	-0.2334	-0.7398	0.3378
k	0.2692	0.0734	-	-	-	-
Log K_F	0.2378	-0.5173	-0.1678	0.4099	0.4123	0.3257
Log K_L	0.9403**	-0.0102	-0.8514*	-0.2263	0.6963	0.3075

Contd..

Table 20 (Contd..)
Crystalline ionic potential (CIP

1	2	3	4	5	6	7
			OVERALL RELATIONSHIP			
Maximum Adsorption	0.6667*	0.9645**	0.8740**	0.8901**	0.8355**	0.8576**
K_F	0.3568	0.8149**	0.4756	0.6448*	0.0154	0.5350
K_L	-0.4380	0.1869	0.5179	-0.3515	-0.0493	-0.8170
k	-0.3267	-0.0057	-	-	-	-
Log K_F	-0.3237	0.8265**	0.3986	0.6176*	-0.0136	0.4672
Log K_L	-0.4304	0.2340	0.4843	-0.3438	-0.0672	0.0021
			ALKALI AND ALKALINE EARTH IONS			
Maximum Adsorption	0.7897	0.8131*	0.7815	0.7438	0.8387**	0.8177*
K_F	0.3523	0.9849**	0.4540	-0.4062	-0.5671	-0.3978
K_L	-0.7048	0.4554	0.5525	-0.3685	0.3148	0.4066
k	-0.9695**	0.3456	-	-	-	-
Log K_F	0.4365	0.9812**	0.6141	-0.4269	-0.5599	-0.3919
Log K_L	-0.7128	0.5295	0.5138	-0.3653	0.2400	0.4013

Contd..

Table 26 (Contd..)
Hydrated ionic radius (HIR)

1	2	3	4	5	6	7
			OVERALL RELATIONSHIP			
Maximum Adsorption	0.4375	0.3487	0.0836	0.4548	0.2545	0.3578
K_F	0.0781	0.4356	0.3361	0.2618	-0.2056	0.1932
K_L	-0.4373	0.4003	0.3667	-0.2118	-0.2012	0.0811
k	-0.7515**	0.1483	-	-	-	-
Log K_F	0.2533	0.6025*	0.5469	0.2515	-0.2151	0.1599
Log K_L	-0.4453	0.4543	0.2811	-0.0191	-0.2582	0.1329
			ALKALI AND ALKALINE EARTH IONS			
Maximum Adsorption	0.9373**	0.9575**	0.9065*	0.8785*	0.8279*	0.9183**
K_F	0.6158	0.9023*	0.8246*	-0.1274	-0.7294	-0.4869
K_L	-0.4079	0.7375	0.6211	-0.3206	-0.6469	-0.4686
k	-0.9513**	0.6167	-	-	-	-
Log K_F	0.7065	0.9394**	0.8421*	-0.1479	-0.7246	-0.4826
Log K_L	-0.5968	0.7921	0.1865	-0.3102	-0.3505	0.4384

Contd..

Table 26 (Contd..)
Hydrated ionic potential (HIP)

1	2	3	4	5	6	7
			OVERALL RELATIONSHIP			
Maximum Adsorption	0.3639	0.7431**	0.6727*	0.7758**	0.7206**	0.8206**
K_F	0.3907	0.3312	0.2701	0.0692	0.2616	0.1551
K_L	0.1874	0.1189	0.2185	-0.5429	0.0343	0.0761
k	0.2910	0.0228	-	-	-	-
Log K_F	0.2622	0.2721	-0.0254	0.2488	0.2217	0.0977
Log K_L	0.1977	0.0985	0.1584	-0.5396	0.0375	0.2275
			ALKALI AND ALKALINE EARTH IONS			
Maximum Adsorption	-0.2210	-0.3458	0.1003	-0.0504	-0.2712	-0.1041
K_F	0.0457	-0.4293	-0.1369	-0.0180	0.8173*	0.1489
K_L	0.9617**	-0.2662	0.0420	-0.5657	-0.5640	0.4468
k	0.4439	0.0276	-	-	-	-
Log K_F	-0.0195	-0.4009	-0.5052	-0.0003	0.8145*	0.1311
Log K_L	0.9521**	-0.4036	0.1084	-0.5654	-0.5206	0.5009

* Significant at 5% level; ** Significant at 1% level

range. There was an S-character only in the initial stages of adsorption. However, the adsorption isotherms of metoxuron on H-, Fe- and Al- montmorillonites did not exhibit any tendency for surface saturation. For the other ions there was a prominent S-character in the initial stages of adsorption particularly for the adsorption of tebuthiuron. The capacity for adsorption was consistently dependent on the charge of the ions and fell into four distinct groups. Thus for the adsorption of both metoxuron and tebuthiuron on clays, the order observed was

H^+ > trivalent > divalent 3d transition ions > alkaline earth metal ions > monovalent ions. Within each group of ions, the extent of adsorption was very similar and thus dependent only on the charge of ions and not so much on their individual characteristics. The transition metal ions formed a separate group by themselves and the adsorption for these was higher than divalent alkaline earth ions. There was an overall negative correlation between the maximum amount adsorbed and the crystalline ionic radius of the cations and a positive correlation with the crystalline ionic potential (Fig.28 and 29), for both metoxuron and tebuthiuron. The correlation coefficients were 0.607** and 0.964** for metoxuron and tebuthiuron respectively.

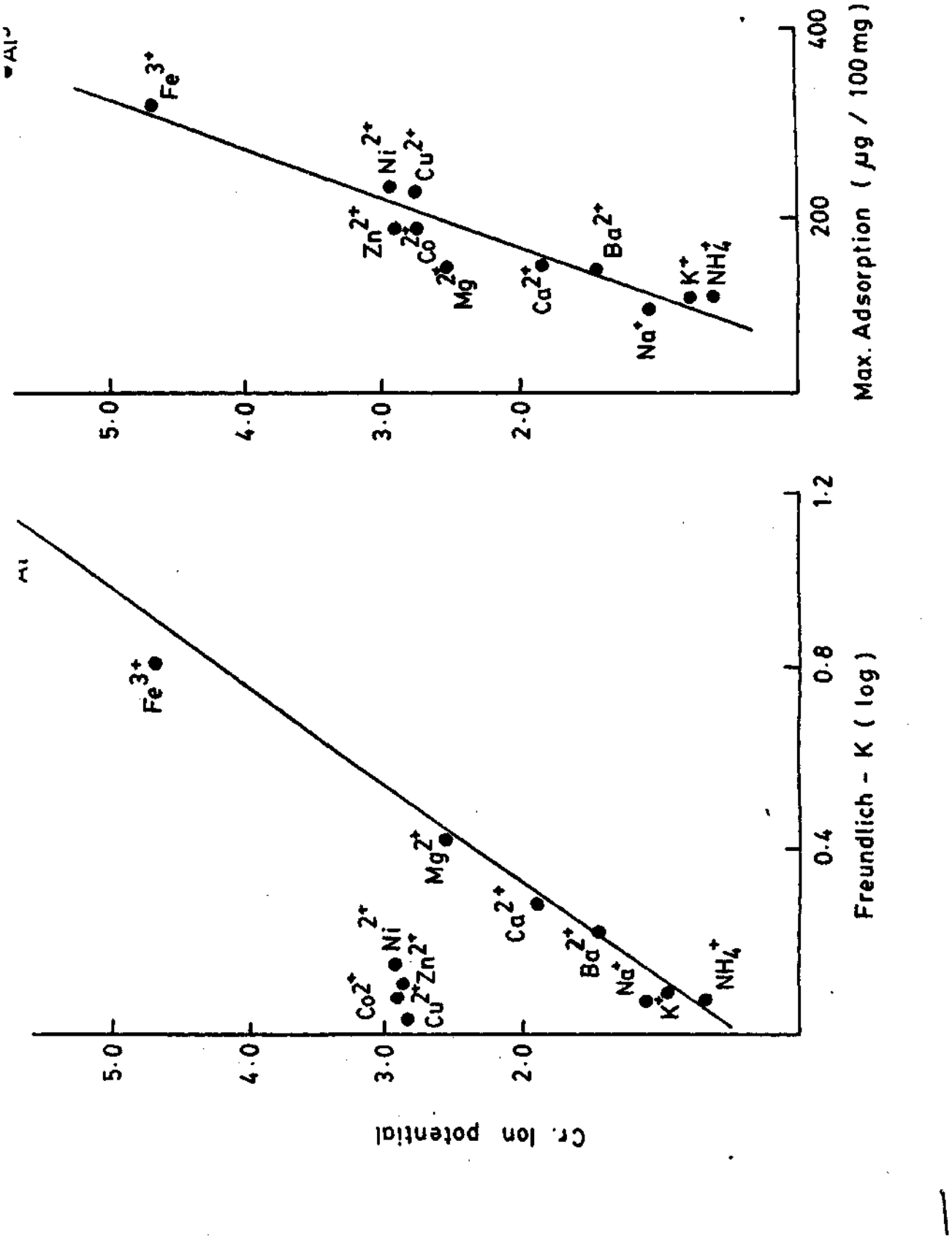

FIG: 28. CORRELATIONS BETWEEN (FOR TEBUTHIURON)

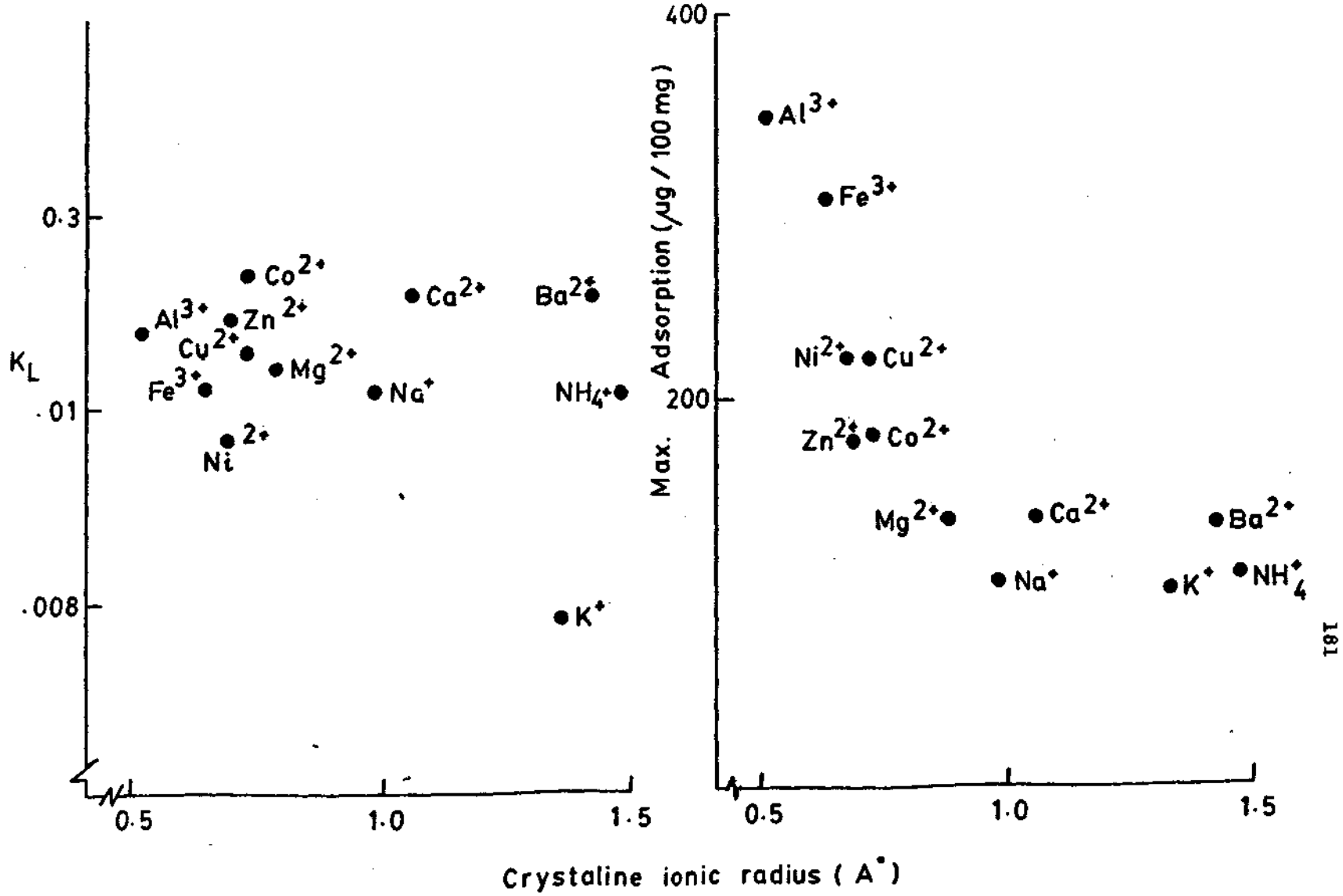

FIG. 29: CORRELATION BETWEEN (FOR TEBUTHIURON)

Since the differences within each group of ions was insignificant, there was no purpose in correlating the amount adsorbed with ionic properties within each group. The variation within the transition metal ions was however much steeper than in the other groups.

It was found that the maximum adsorption varied positively with hydrated ionic radius and inversely with hydrated ion potential for alkali and alkaline earth ions put together. Since the concept of hydrated ionic radius is not well suited for easily hydrolysable Fe^{3+} and Al^{3+} and since for transition metal ions, the precise values were not available, the overall analysis of the adsorption parameters with respect to these properties is not meaningful and hence not reported.

Freundlich constant (K_F) which is an indicator of adsorption capacity and strength of binding also gave a consistently negative and positive overall correlation with CIR and CIP respectively (Fig.30). The correlation (Fig.31) was however significant only for tebuthiuron (0.814**). The correlation with respect to HIR and HIP was again positive and negative respectively when the group of alkali and alkaline earth ions were considered (Fig.31). The correlation was however

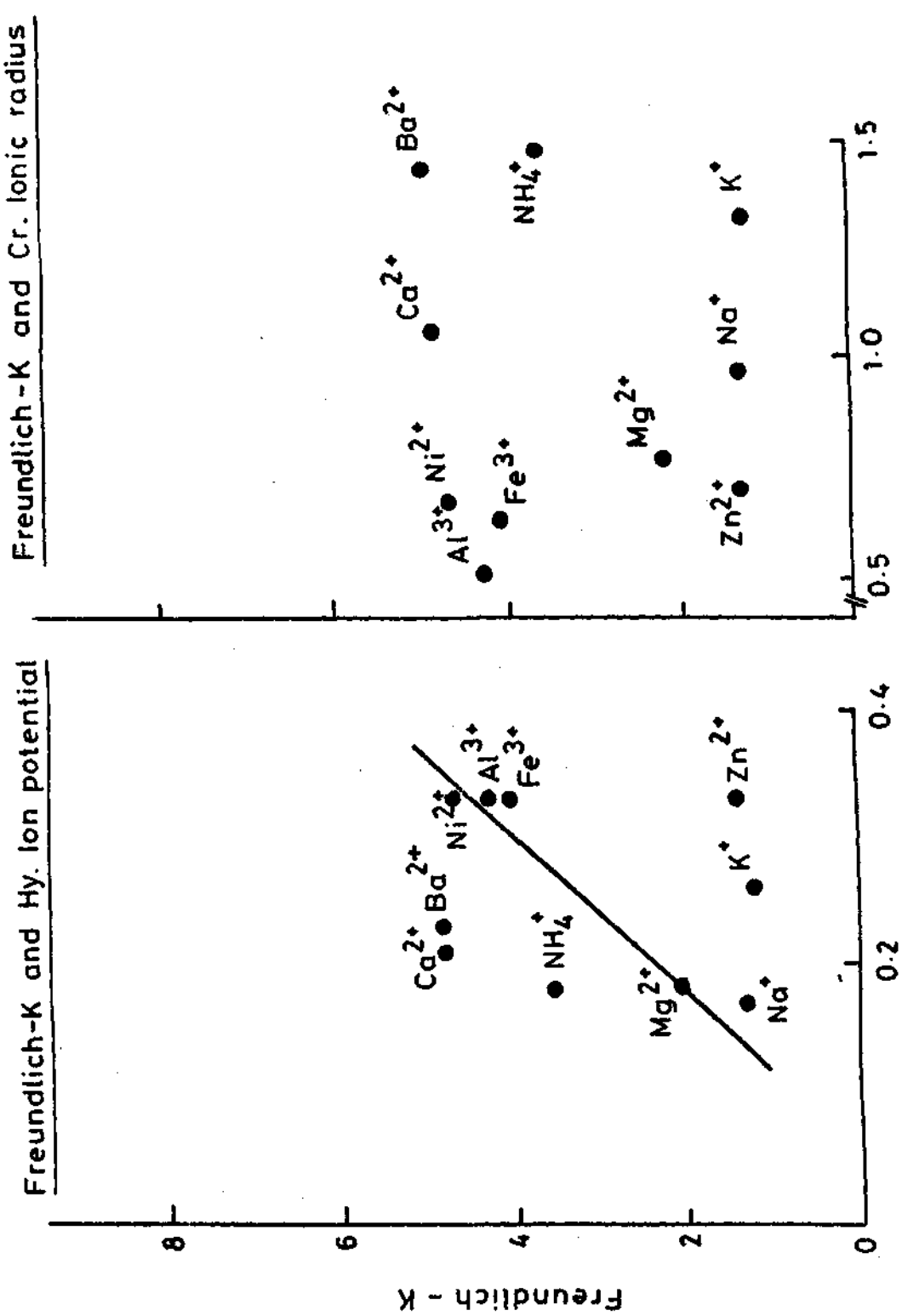

FIG. 30 : CORRELATIONS BETWEEN (FOR METOXURON) FREUNDLICH - K AND HYDRATED ION POTENTIAL AND CR. IONIC RADIUS

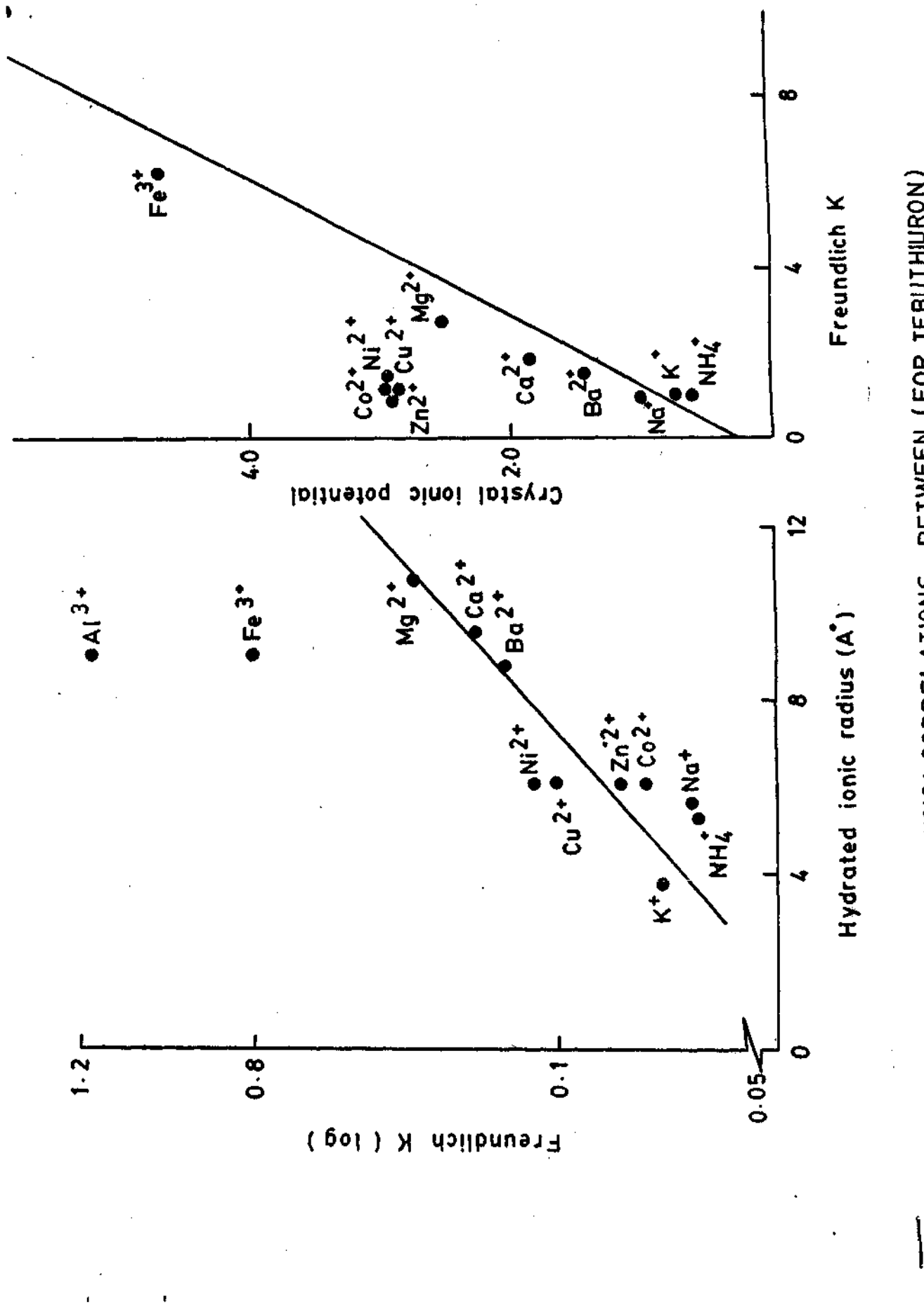

FIG:31 CORRELATIONS BETWEEN (FOR TEBUTHIURON)

not significant.

The Langmuir K, (K_L) which in this study was calculated only at 50 per cent surface saturation, also followed the same qualitative trends (Figs.29 and 32) with respect to CIR, CIP, HIR and HIP as in the case of K_F. The correlation coefficients were however not significant in any of the above cases.

The constant k which describes the specific rate of change of adsorption with increase in equilibrium concentration (Saroja Raman, 1981) showed exactly the reverse relationship with CIR, CIP for both metoxuron and tebuthiuron and was thus positive and negative respectively for CIR and CIP. For the alkali and alkaline earth group ions put together, K varied positively and negatively with respect to HIR and HIP respectively.

The free energy functions, $-RT\ln K_F$ and $-RT\ln K_L$, were also correlated to CIR and CIP of the entire range of ions. They correlated negatively to CIR and positively to CIP for both metoxuron and tebuthiuron (Fig.28, 30, 31 and 33). The correlation coefficient was significant only for tebuthiuron and CIP ($r = 0.8265^{**}$) and tebuthiuron and HIR (Table 26).

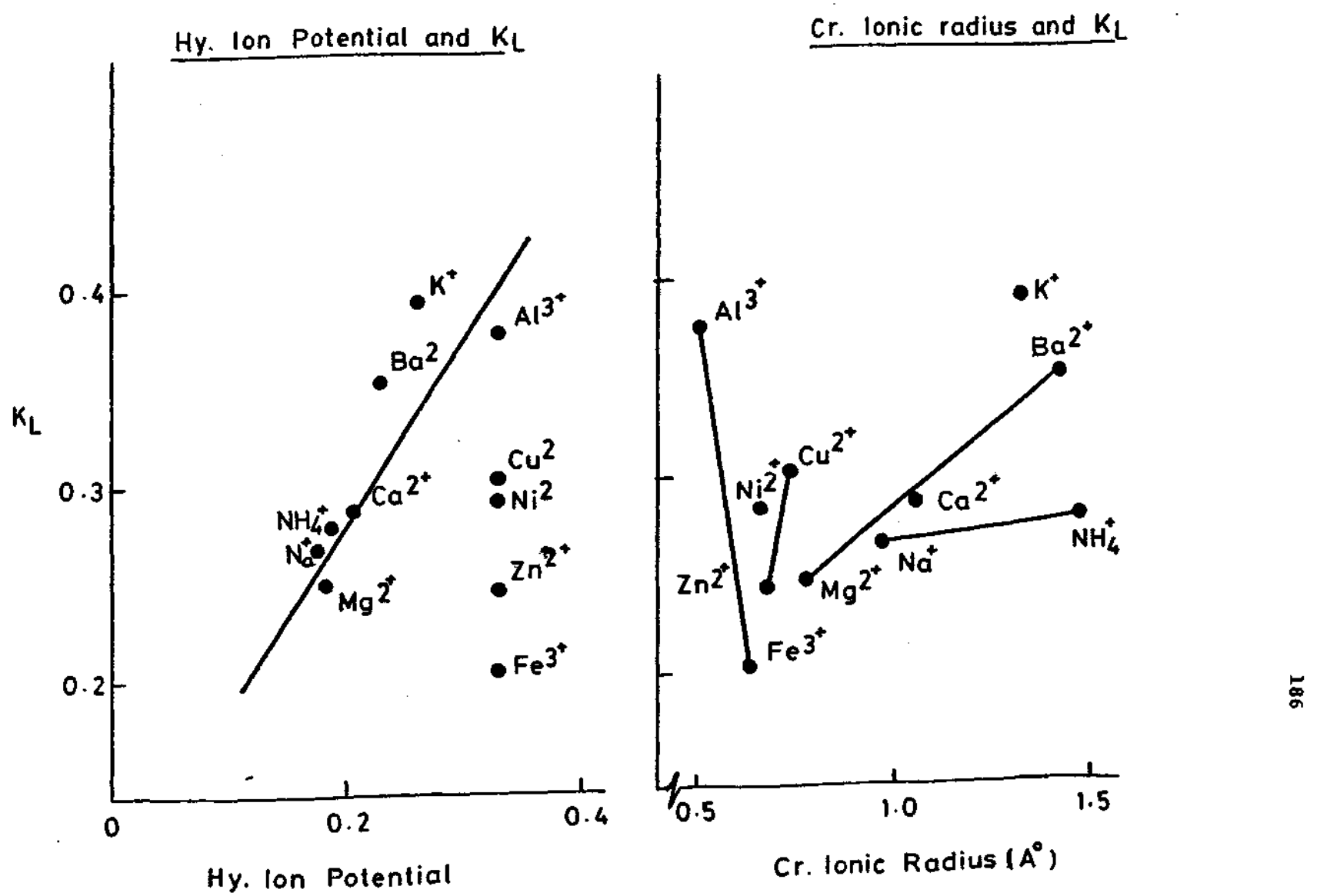

FIG. 32: CORRELATION BETWEEN (FOR METOXURON) AND LANGMUIR CONSTANT (K_L)

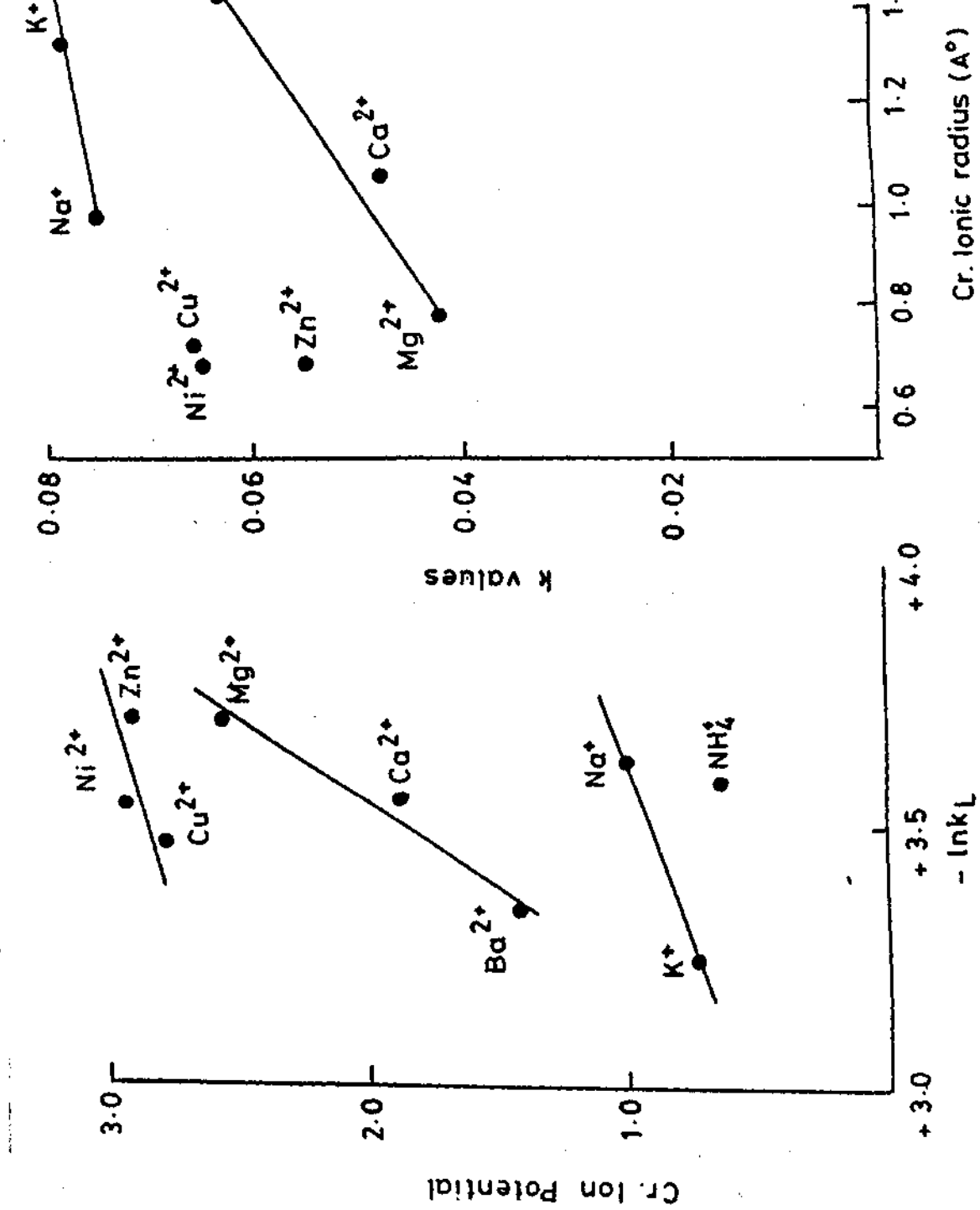

FIG:33. CORRELATIONS BETWEEN(FOR METOXURON)

The variations in all these properties within the same group were very small except for trasition metal ions.

4.3.6 Adsorption of metoxuron and tebuthiuron on homoionic (IR-120) resins :

Adsorption isotherms of metoxuron and tebuthiuron on ion saturated resins (Fig.9 and 12) exhibited a tendency to reach surface saturation and were parabolic in nature. The variation in adsorption parameters with respect to ionic properties, for the adsorption of metoxuron and tebuthiuron on homoionic IR-120 resins was similar to the adsorption of these chemicals on homoionic montmorillonites. Thus, the maximum adsorption fell into four distinct groups as : trivalent and H-> transition metal ions > Alkaline earth ions > Alkali metal ions. The variations within each group was very minor here also except for transition metal ions. Thus the overall correlation of the maximum adsorption to CIR and CIP was negative and positive respectively for both metoxuron and tebuthiuron. The correlation coefficients were also significant for these parameters.

The qualitative trends for K_F, K_L and the corresponding free energy functions also followed the same trend as that of adsorption but were not

significantly correlated.

4.3.7 Adsorption of PMA on homoionic montmorillonites and homoionic (IR-120) resins :

The adsorption isotherms were mostly L-shaped (Fig.26) with a tendency to reach surface saturation within the concentration range studied. The extent of adsorption was dependent mainly on the charge and polarizing power of the cation and followed the same order as that obtained for adsorption of metoxuron and tebuthiuron. The overall relationship between the adsorption characteristics and ionic properties followed the same trend as that for the herbicides. The correlation coefficients were however not significant in any of the cases.

Adsorption isotherms of PMA on homoionic (IR-120) resins were mainly L-shaped (Fig.27) with a tendency to reach saturation of the surface within the concentration range studied. The maximum adsorption of PMA was significantly and positively correlated to CIP and CIR respectively. Freundlich K_F (K_p) and K_L also followed the same trend. For alkali and alkaline earth ions however, the relationship was negative for adsorption and positive for all others with respect to HIP. The maximum adsorption was significantly correlated to HIR only.

4.4 PERSISTENCE OF METOXURON AND TEBUTHIURON IN AN ALFISOL AND A VERTISOL AND EVALUATION OF PHYSICAL AND MATHEMATICAL MODELS TO PREDICT RESIDUES UNDER FIELD CONDITIONS :

The period during which a pesticide remains intact and biologically active is of importance in determining the efficacy of pesticide, its effect on subsequent crops, environment and ecology. It is called the time of residence of the chemical in soil. In addition to specific microbial population, moisture and tempera ture are the two important environmental factors influencing persistence and degradation of soil applied posticides. An alfisol (Soil-5) and a vertisol (Soil-6) were selected for studying the persistence of metoxuron and tebuthiuron. As explained earlier, 10g portions of the herbicide treated soils, incubated at 10 $\pm$ 1°C and 27 $\pm$ 1°C under three moisture regimes were extracted with methanol at different time intervals. The amount of methanol extractable metoxuron and tebuthiuron at different time intervals is given in Tables 27 and 28 respectively. The quantity of herbicide exrtracted was plotted against time for the different experimental conditions and these are given in Fig.34 and 35 for metoxuron and tebuthiuron respectively. Thus, the persistence curves consist of two distinct phases and suggested that the disappearance of the herbicides took place at two different

Table 27 : Amount of metoxuron extracted at different time intervals for vertisol (Soil-a) µg

30 ± 1°C

Moisture levels	DAYS OF INCUBATION																	
	0	4	8	12	16	20	24	28	32	36	40	48	56	64	72	80	95	110	125
Saturation	203.9	196.7	192.3	183.7	170.9	156.4	131.4	111.0	105.3	96.2	79.7	74.9	66.9	65.0	62.4	62.5	59.4	61.5	45.6
Field capacity	204.6	198.8	192.9	189.4	179.1	168.5	142.1	135.7	117.3	105.3	94.3	81.4	72.1	68.1	66.6	62.6	61.4	35.7	36.6
50% field capacity	203.8	199.3	196.1	190.3	179.0	172.4	146.5	139.3	129.4	108.4	95.2	75.4	75.4	67.4	66.5	58.1	60.1	49.9	49.6
								27 ± 1.1°C											
Saturation	203.9	198.9	196.7	193.8	184.2	177.0	155.1	142.3	134.4	124.5	104.4	99.5	81.5	69.8	65.5	61.3	58.5	47.6	46.4
Field capacity	204.6	199.5	192.9	185.3	177.2	164.5	154.6	136.5	131.5	112.2	97.5	92.4	69.5	68.6	48.5	46.5	41.1	39.6	39.5
50% field capacity	205.7	202.1	195.1	189.2	176.4	168.4	164.5	131.4	123.4	104.3	99.3	87.5	66.5	61.3	57.5	45.6	41.2	41.4	40.1

Cor

Table 27 : Amount of metoxuron extracted at different time intervals for Alfisol (Soil-5) µg

30 ± 1°C

Moisture levels	DAYS OF INCUBATION																		
	0	4	8	12	16	20	24	28	32	36	40	48	56	64	72	80	95	110	125	155
Saturation	213.6	194.2	173.3	170.0	164.8	124.2	122.2	113.7	103.4	99.3	96.3	86.4	84.4	79.4	76.4	64.4	59.4	57.4	48.4	45.6
Field capacity	203.4	196.8	171.1	170.0	167.7	128.3	124.2	110.8	101.4	95.8	92.7	83.4	83.8	72.4	71.4	69.4	59.5	53.5	51.5	49.4
50% field capacity	202.9	200.7	176.5	170.2	168.7	125.8	122.2	117.3	101.4	99.3	96.2	87.3	80.3	80.4	75.4	74.4	63.4	51.5	45.6	39.6
25% field capacity	205.9	196.4	183.5	181.9	168.1	148.4	148.3	143.9	110.2	96.4	90.3	76.4	65.3	64.3	62.3	60.4	59.6	56.5	57.5	47.4

27 ± 1°C

Saturation	213.6	194.2	173.3	170.0	164.8	124.2	122.2	113.7	103.4	99.3	96.3	86.4	84.4	79.4	76.4	64.4	59.4	57.4	48.4	45.6
Field capacity	205.3	194.4	181.5	180.1	169.6	155.3	146.4	139.3	136.3	134.3	108.3	100.4	91.9	83.9	74.4	68.5	65.6	63.1	60.6	54.1
50% field capacity	204.1	198.3	194.4	182.1	167.5	162.3	152.4	150.3	145.3	134.4	123.4	112.3	106.4	106.4	83.5	75.4	71.9	62.5	60.6	59.1

Table 28 : Amount of Tebuthiuron extracted at different time intervals for Alfisol (Soil-5) (µg)
10 ± 1°C

Moisture levels	DAYS OF INCUBATION																			
	0	4	8	12	16	20	24	28	32	36	40	48	56	64	72	80	95	[illegible]	125	155
Saturation	204.2	178.0	166.0	161.0	145.3	138.7	130.9	125.9	122.1	119.2	115.1	117.9	109.2	103.3	98.7	91.7	84.2	78.3	62.5	62.4
Field capacity	207.0	185.2	178.4	171.2	165.3	152,7	143.2	131.1	118.8	108.1	106.1	93.4	78.9	70.6	64.0	59.8	50.4	47.1	36.8	33.6
50% field capacity	199.2	180.1	168.4	161.7	159.2	153.3	145.8	137.1	128.3	118.9	115.4	127.1	110.7	103.0	96.7	91.3	84.7	77.3	55.8	40.5

Amount of tebuthiuron extracted at different time intervals for Vertisol (Soil-6) (µg) at 27 ± 1°C

Saturation	208.1	201.7	194.4	190.4	190.0	184.4	176.0	171.8	172.7	170.4	161.1	160.3	150.4	136.2	130.2	127.7	101.8	94.1	84.7	72.8
Field capacity	205.1	200.1	191.6	185.9	181.4	176.1	171.4	165.8	161.2	156.0	152.3	143.6	137.1	124.3	112.7	104.2	96.6	84.7	80.9	64.6
50% field capacity	198.2	194.2	190.8	183.3	180.5	174.7	169.8	165.2	160.3	156.0	152.0	150.9	143.6	138.7	108.4	117.8	113.4	101.4	97.2	91.2

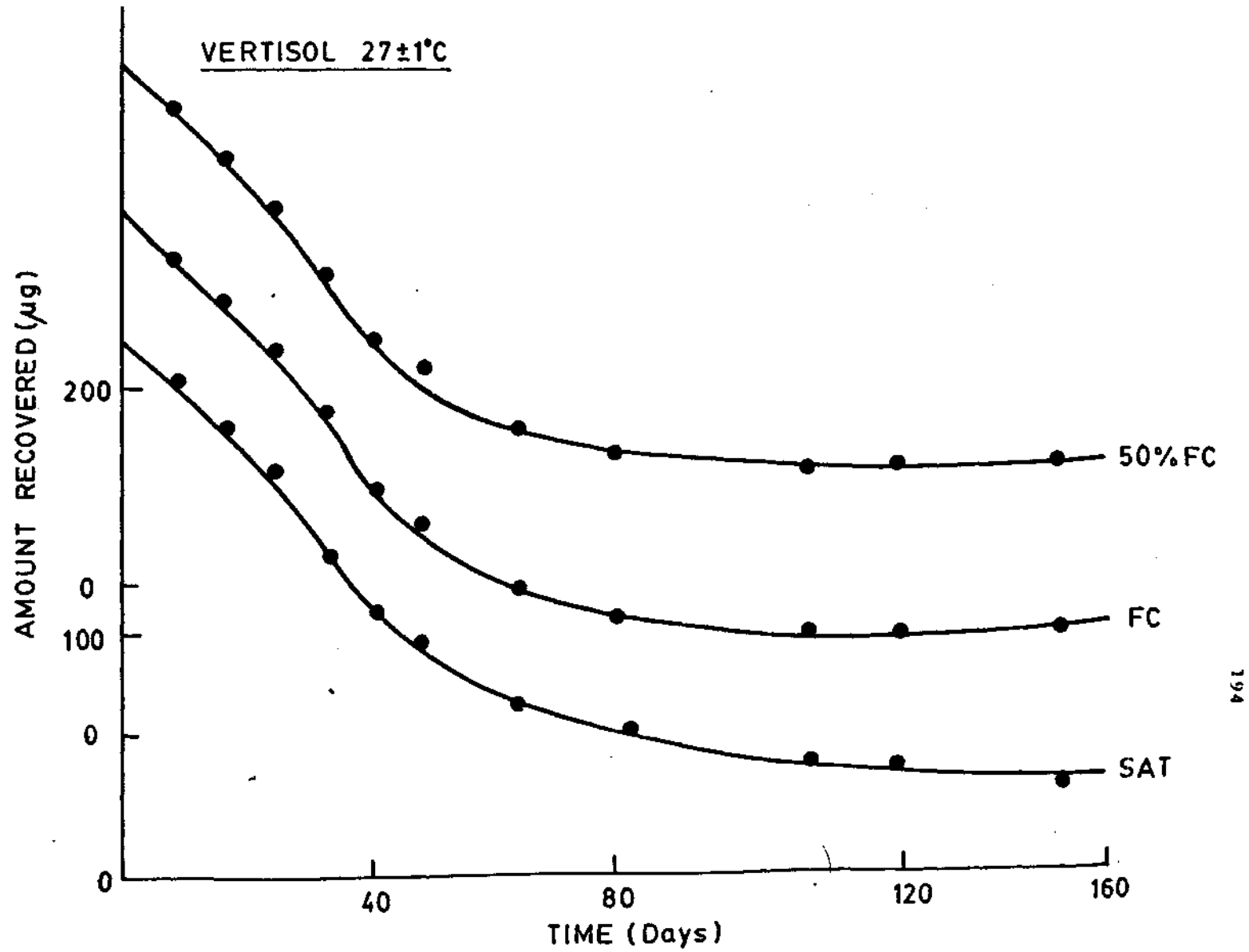

FIG. 34: AMOUNT OF METOXURON EXTRACTED AT DIFFERENT TIME INTERVALS

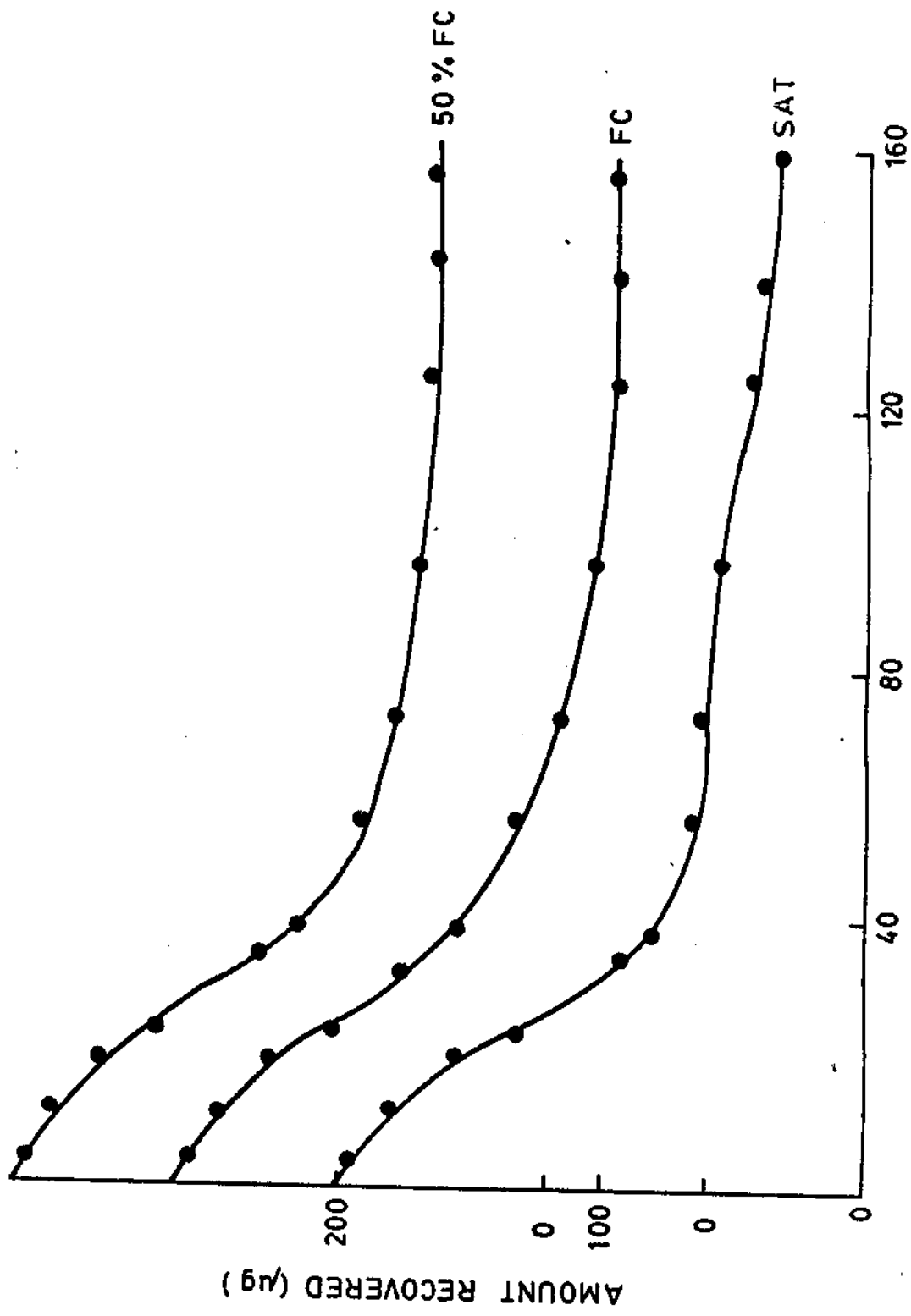

FIG. 34 : AMOUNT OF METOXURON EXTRACTED AT DIFFERENT TIME INTERVALS

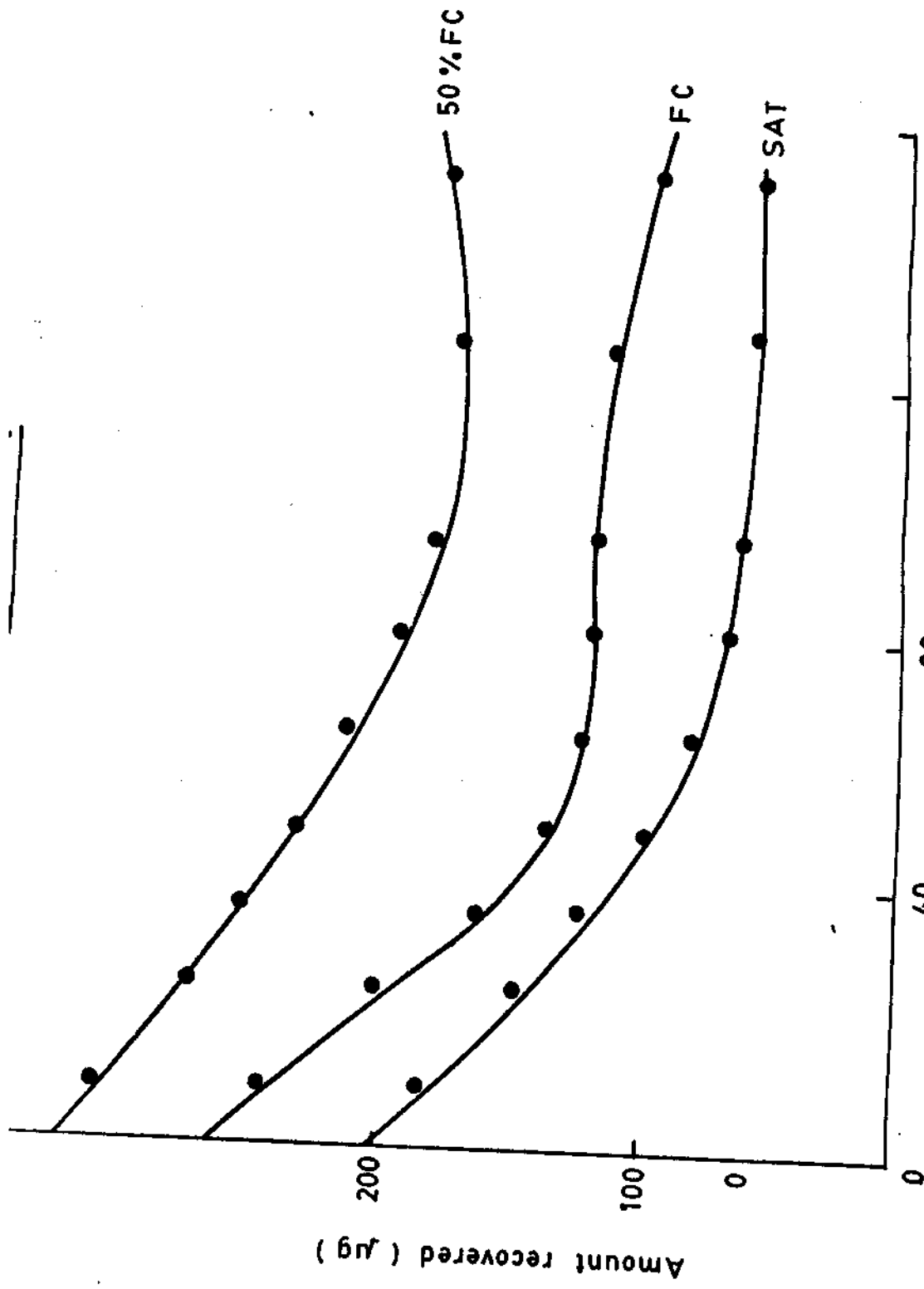

FIG. 34: AMOUNT OF METOXURON EXTRACTED AT DIFFERENT TIME INTERVALS

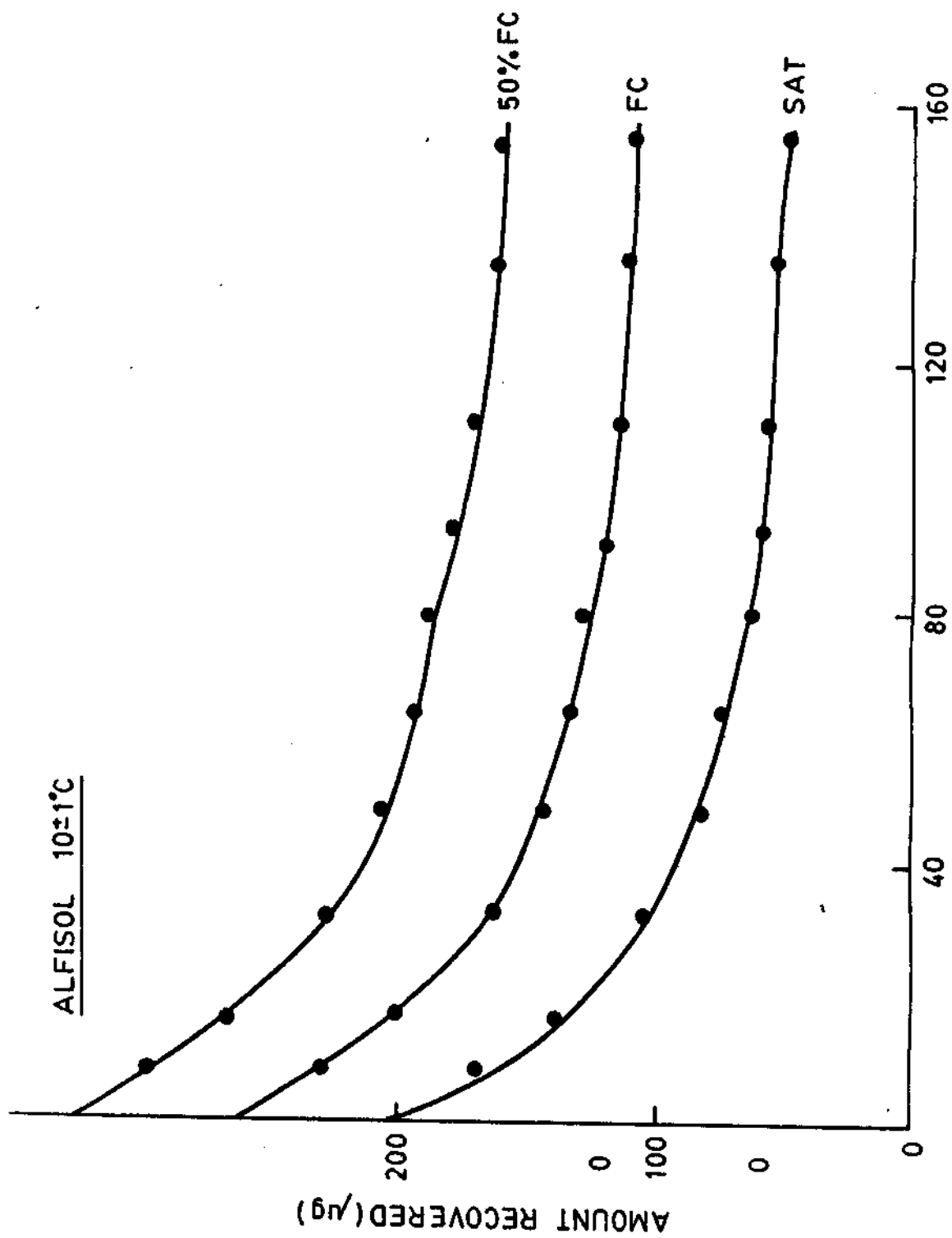

FIG. 34 : AMOUNT OF METOXURON EXTRACTED AT DIFFERENT TIME INTERVALS

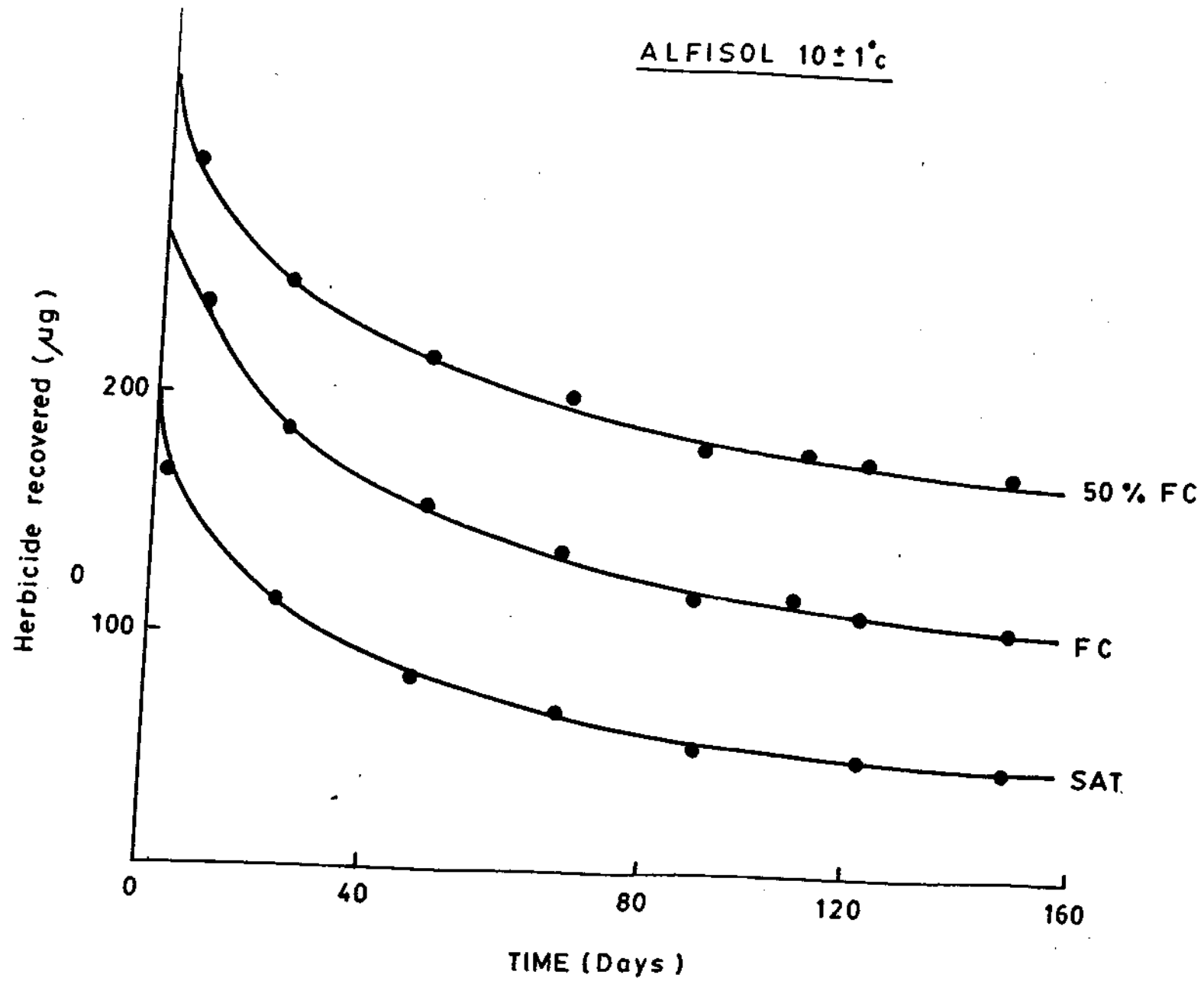

FIG. 35 : AMOUNT OF TEBUTHIURON EXTRACTED AT DIFFERENT TIME INTERVALS

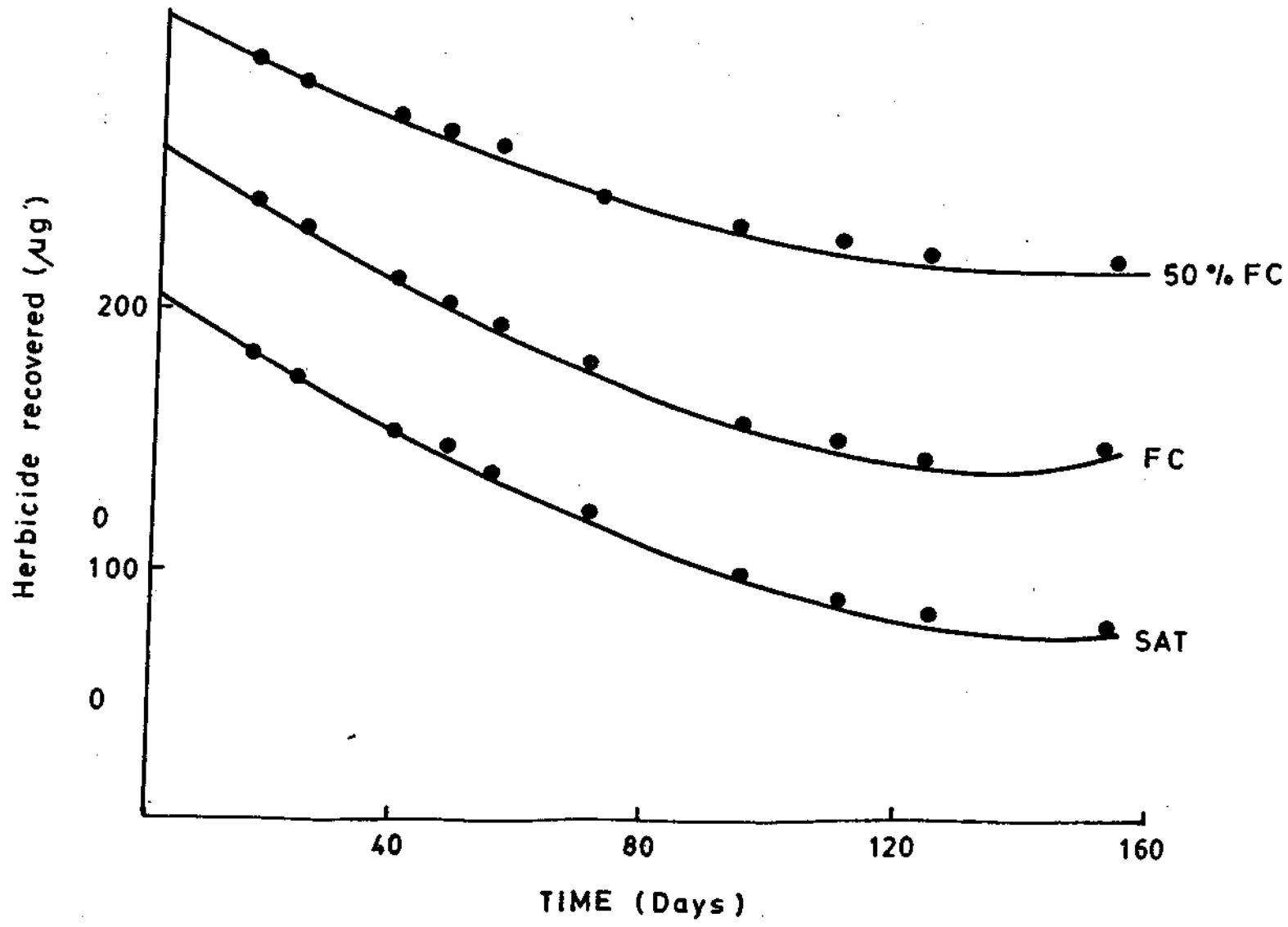

FIG. 35 : AMOUNT OF TEBUTHIURON EXTRACTED AT DIFFERENT TIME INTERVALS

rates viz., an initial faster rate and followed by a slower and more gradual disappearance. This indicated two different pathways for disappearance of herbicide.

To calculate the rates of disappearance, the data was treated according to first order kinetics by plotting the logarithm of concentration vs time. These are given in Fig.36 for metoxuron and Fig.37 for tebuthiuron. The first order kinetic plot confirmed two distinct rates of disappearance. The faster mode of disappearance continued only till about 40 days whereas slower rate of disappearance continued till the end of study. The specific reaction rates or rate constants for these steps were calculated by resolving the fast and slow steps of disappearance as explained under 'Materials and Methods'. As a first approximation, as defined by Hamaker and Goring (1976), the rate of reentry into labile pool was considered negligible and the faster rate and slower rates of disappearance were calculated as explained earlier. A finer refinement was later attempted to include the rate of reentry of pesticide into labile pool. Thus k and k_1 correspond to the rate of entry of herbicide into bound pool (non-extractable) and the rate of decomposition of the herbicide respectively. A complete analysis of the persistence data was carried out for resolving the constants k, k_1 and k_{-1} according

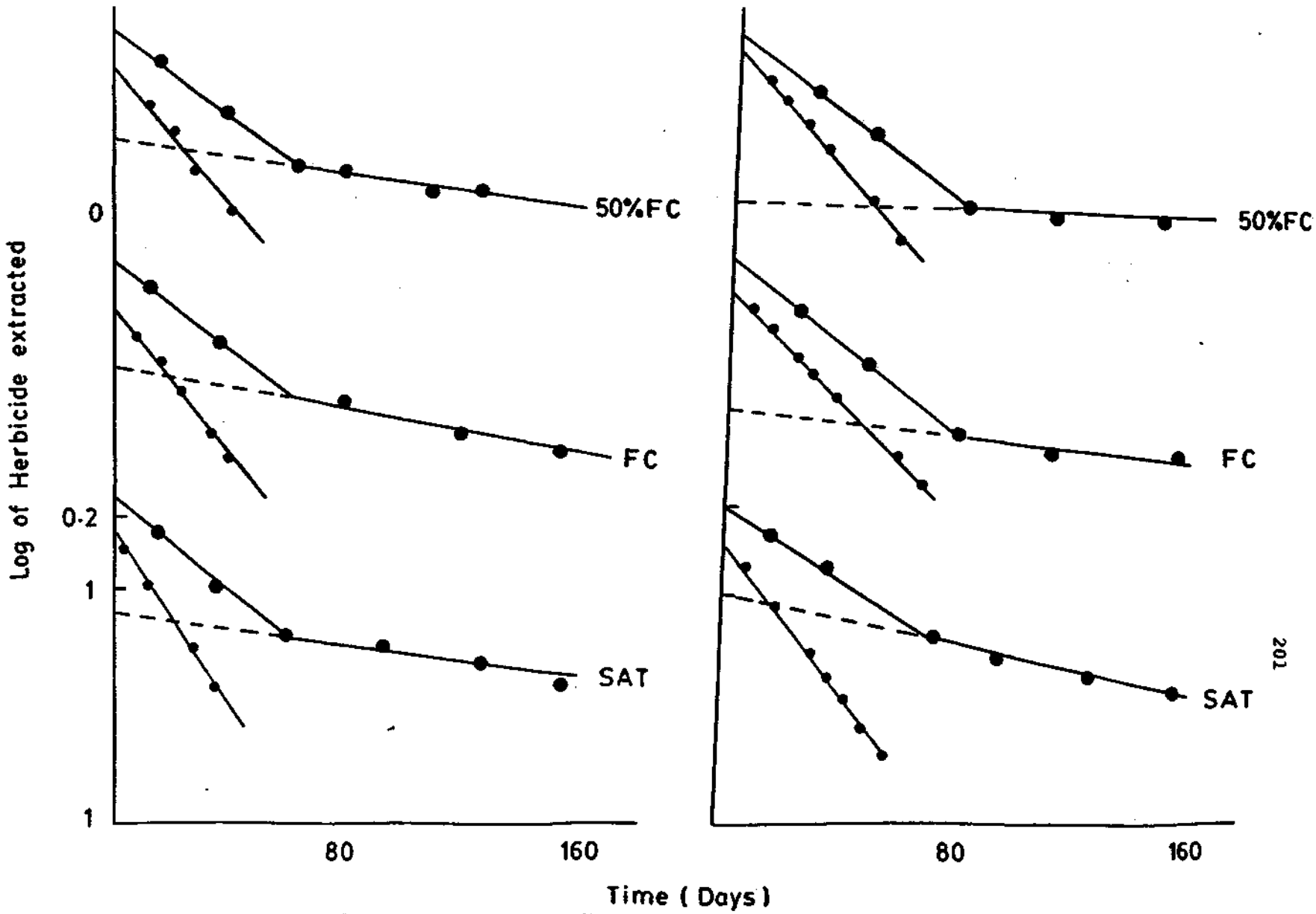

FIG. 36: SEMI - LOG PLOT OF METOXURON EXTRACTED vs TIME

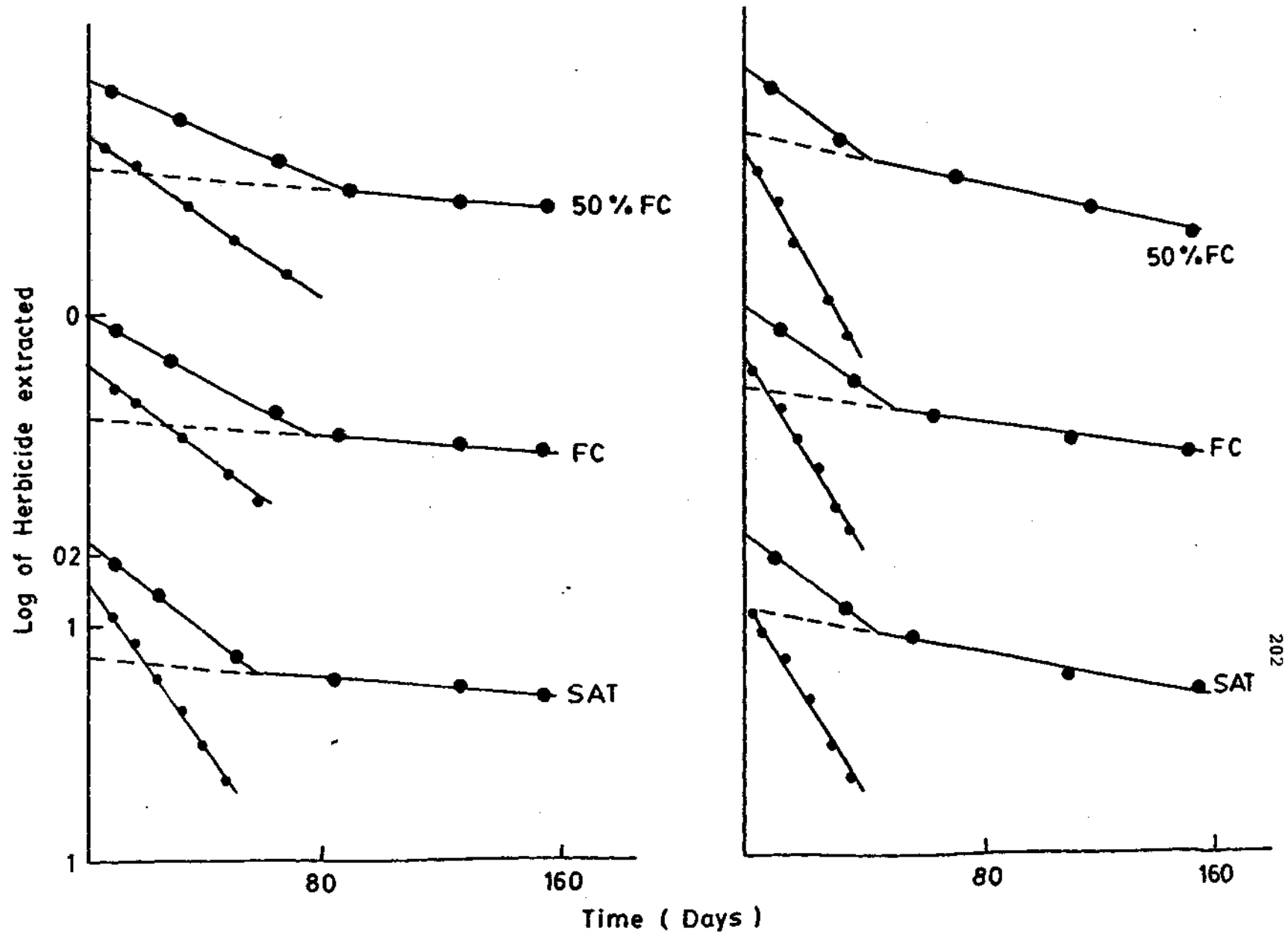

FIG. 36 : SEMI-LOG PLOT OF METOXURON EXTRACTED vs TIME

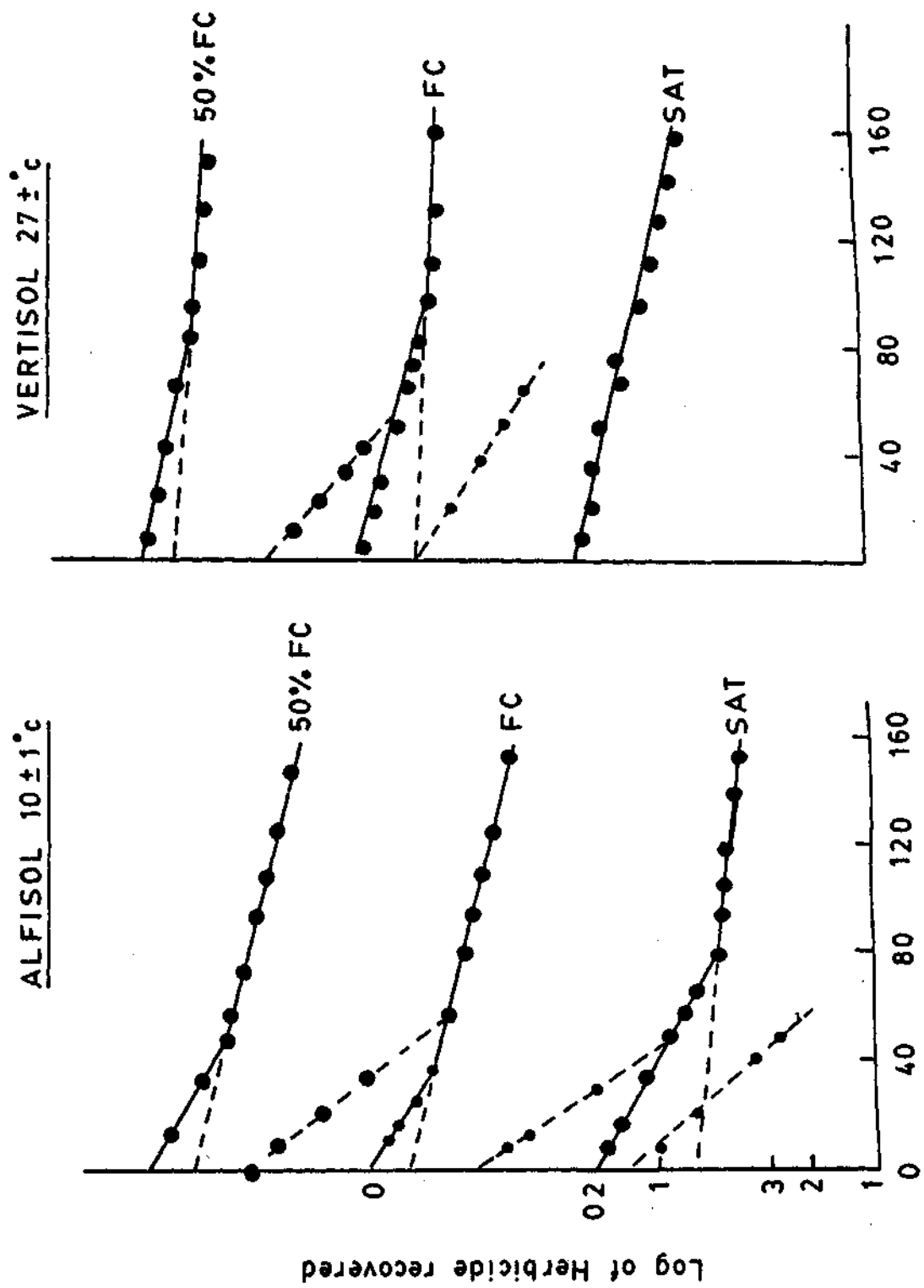

FIG. 37 : SEMI - LOG PLOT OF TEBUTHIURON EXTRACTED vs. TIME.

to the method given by Hamaker and Goring (1976) and explained in 'Materials and Methods'. The detailed values are given in Table 29 for metoxuron and Table 30 for tebuthiuron.

The activation energy was also calculated for all the rate constants, in the case of metoxuron, from the Arrhenius equation :

$$Ea = R \times \left[\ln \frac{k_1}{k_2} \right] \left[\frac{T_2 \times T_1}{T_2 - T_1} \right]$$

where k_1 and k_2 are the rate constants at temperatures T_1 and T_2 and R is the gas constant and Ea is the energy of activation in kJ $mole^{-1}$. These values are also given in Table 29.

Table 39 : Specific reaction rates (Days^{-1}) and energy of activation (kJoules Mole^{-1} day^{-1}) for different steps for metoxuron

Soil	Temperature	MOISTURE LEVELS															
		Saturation				Field capacity				50% Field capacity				Pooled values			
		k	k_1	k_{-1}	m	k	k_1	K_{-1}	m	k	k_1	k_{-1}	m	k	k_1	k_{-1}	m
Alfisol (Soil-5)	10°C	0.0386	0.0219	0.0044	0.0027	0.0215	0.0081	0.0022	0.0040	0.0199	0.0067	0.0078	0.0033	0.0267	0.0124	0.0063	0.004
	27°C	0.0451	0.0271	0.0098	0.0058	0.0457	0.0351	0.0010	0.0053	0.0503	0.0164	0.0119	0.0083	0.0470	0.0260	0.0110	0.006
	Activation energy	14.0	8.8	33.6	7.6	31.4	60.9	62.8	2.8	38.3	36.8	17.4	4.2	27.9 ±9.1	35.5 ± 17.8	37.9 ±36.5	4.7
Vertisol (Soil-6)	10°C	0.0346	0.0225	0.0102	0.0072	0.0080	0.0022	0.0327	0.0024	0.0327	0.0123	0.0047	0.0033	0.0346	0.0126	0.0057	0.009
	27°C	0.0477	0.0297	0.0179	0.0066	0.0312	0.0102	0.0127	0.0085	0.0346	0.0111	0.0073	0.0048	0.0376	0.0181	0.0090	0.006
	Activation energy	7.7	1.6	6.8	1.02	5.4	14.1	57.1	12.6	2.3	21.1	17.8	2.4	5.1 ± 1.7	12.8 ± 6.7	47.6 - 26.8	3.9

Table 30 : Specific reaction rates of tebuthiuron ($Days^{-1}$)

Soil	Temperature	MOISTURE LEVELS															
		Saturation				Field Capacity				50% Field capacity				Pooled values			
		k	k_1	k_{-1}	m	k	k_1	k_{-1}	m	k	k_1	k_{-1}	m	k	k_1	k_{-1}	m
Alfisol (Soil-5)	10°C	0.0363	0.0258	0.0160	0.00833	0.0493	0.0809	0.0224	0.00763	0.0396	0.0455	0.0334	0.00701	0.0417	0.0413	0.0169	0.00766
Vertisol (Soil-6)	10°C	0.0381	0.0275	0.0175	0.0243	0.00499	0.0187	0.0242	0.0163	0.00254	0.0231	0.0122	0.0370	0.0025	0.0186	0.0102	0.0183	0.00835

DISCUSSION AND CONCLUSIONS

CHAPTER V

DISCUSSION AND CONCLUSIONS

Herbicide behaviour in soils is complicated by numerous interactions between the solid, liquid and gaseous phases of soil and between living and inanimate components. The complexity of the system is a hindrance to understanding the precise nature of these interactions. The key to precise understanding of herbicide behaviour in soils should lie in resolving the various factors involved, into simpler and unitary steps which dominate the overall interactions. As explained earlier, the objectives of present investigations are based mainly on the presumption, that, a better understanding of these fundamental processes occurring in soil components, is a prelude to cracking the more complicated picture that is usually present in soils. Thus, detailed quantitative and mechanistic aspects of the adsorption of metoxuron and tebuthiuron were studied on the two adsorption-intense colloid fractions of soil viz., clays and organic matter.

Since expansible clays like smectites and vermiculites are the most active sites of pesticide interaction, fairly pure samples of montmorillonite

were selected for the adsorption studies. Emphasis has been laid on understanding the role of exchange cations in clay suspensions which are nearer to actual field conditions, in contrast to most of the earlier attempts which were related to low moisture status. Predictive modelling for herbicide residue problems have also been attempted.

The complex role of FA and HA on the fate of herbicide has been sought to be simplified with the help of well defined and simpler model, PMA. Thus, systematic investigation on the properties of PMA and its interaction with homoionic clays have been carried out. Synthetic montmorillonite-PMA complexes have been tested as model simulants for naturally occurring clay-organo complexes, which are difficult to characterise.

Persistence of soil applied chemicals is a very important environmental, ecological and economic factor and predctive modelling incorporating the effect of various environmental factors for the estimation of residue levels has to replace the existing cumbersome and repititive empirical measurements. Thus kinetic studies on the persistence of metoxuron and tebuthiuron under controlled conditions have been taken up. With the above lack dropof the importance of the experiments carried

out, actual discussion of the results obtained is taken up in subsequent parts of this chapter. For convenience and cojency, the sequence observed is similar to that followed for results, with necessary integration and cross-linking, wherever necessary.

5.1 ADSORPTION OF METOXURON AND TEBUTHIURON ON HOMOIONIC MONTMORILLONITES :

Montmorillonites are typical of the soil clays which affect the adsorption of chemicals significantly. The effect of exchange cations on the nature, extent and mechanisms of adsorption was emphasised in the study because, adsorption in general has constantly been postulated to occur through these centres with or without the mediatory effect of sorrounding water molecules. As mentioned before, this is a first comprehensive and systematic attempt made in understanding the mechanism of adsorption on clays in suspensions.

Cations selected for the study belonged to a very wide range with respect to ionic properties like charge, ionic potential, size of hydration, electron configuration and tendency for complexation so that a systematic analysis of these properties could be made to arrive at specific bonding mechanisms. Similarly the most important adsorption characteristics that yield clues to the possible bonding mechanisms like

the shape of adsorption isotherms, presence or absence of tendency for maximum adsorption, extent of adsorption and adsorption constants like Freundlich constant (K_F), and Langmuir constant (K_L) which are thermodynamic indicators of the binding strength and are directly related to free energy of adsorption (-RT ln K) were studied systematically.

In order to facilitate overall comprehension of the role of ionic parameters, the relationship between adsorption parameters and ionic properties were individually analysed, as already discussed under 'Results'. The idea was that the interaction between the adsorption parameters and ionic properties should throw light on mechanism of adsorption.

Adsorption isotherms (Fig.7) for metoxuron on homoionic clays were predominently S-shaped in character whereas, the adsorption isotherms for tebuthiuron (Fig.10) were more parabolic in nature with a subdued S-character confined mostly to the initial stages of adsorption. However the adsorption isotherms of metoxuron on H-, Al-, and Fe-montmorillonites (Fig.7) did not exhibit surface saturation in the concentration range studied. Similar S-shaped isotherms were reported by Bansal (1983 and 1985) for the adsorption of oxamyl and dimecron on homoionic montmorillonites and by

Saroja Raman and Ranga Rao (1984) for the adsorption of methabenzthiazuron on some soils of Hyderabad low in OC. The tendency for S-shaped character indicates stronger initial competition of water molecules to clay surface as compared to the herbicide. The observed S-character for adsorption on clays is legitimate as exchange cations have a strong tendency for hydration and would exclude the organic molecule from their immediate vicinity until the intermolecular attraction of the adsorbed molecules become favourable for further adsorption. The S-shape thus reflects the initial resistence to the adsorption of herbicides, overcome later by the cooperative effect of adsorbed molecules. The S-shaped isotherms were also observed for the < 50 μ fractions of the soils used in the study. Saroja Raman and Ranga Rao (1984) postulated that soils low in organic carbon have a tendency to give S-shaped isotherms on account of their hydrophilic nature as compared to soils much high in organic carbon which tend to be hydrophobic. This has been reasonably corraborated by Weber et al. (1986) also.

The extent of adsorption of herbicides was dependent largely on the charge of the exchange cations and followed the order : trivalent > divalent > monovalent. H-montmorrillonite was an exception and expressed

high adsorption capacity. Within this overall classification, the ions could further be grouped as trivalent > divalent 3d ions > alkaline earth ions > monovalent ions. The divalent 3d ion saturated montmorillonites had a much higher capacity for adsorption as compared to montmorillonites saturated with alkaline earth ions. The differences in maximum adsorption in the alkaline earth group and alkali group was very small, except for NH_4-in the case of metoxuron. The traisition metal ions showed much larger differences within the group. Within each group, the extent of adsorption was in the order :

H >

Al- > Fe-

Ni-> Zn-> Cu-

Mg-> Ca-> Ba-

NH_4-> K$\approx$ Na

For tebuthiuron, the extent of adsorption was similar and was

Al-> Fe-

Cu-$\approx$ Ni-> Co-> Zn-

Mg-$\approx$ Ca-$\approx$ Ba-

NH_4 > K-$\approx$ Na-

Although no reference exists in literature, where such a detailed and a systematic study of the effect of exchange cations has been made, observations

recorded by several studies agree quite well with our observations. Thus a similar sequence was recorded for the adsorption of linuron on bentonite (Hance, 1971), and montmorillonite (Khan, 1974). Kausalya et al. (1982) also reported similar trend for terbutryne on homoionic montmorillonites. The work of Bansal (1983 and 1985) on adsorption of oxamyl and dimecron and that of Purkayastha and Misra (1985) on the adsorption of methabenzthiazuron also indicated the distinct role of charge on the exchange cations. As seen earlier there was an overall positive and significant correlation between the maximum adsorption capacity of the homoionic montmorillonites and CIP of exchange cations, for the adsorption of both metoxuron and tebuthiuron (Fig.28). This is a categorical confirmation that the adsorption capacity of metal clays are primarily dicated by the polarizing power of the cations. Thus, the role of cations as bridges between the clays and organic chemicals is vindicated for the adsorption of metoxuron and tebuthiuron on montmorillonite.

Maximum adsorption capacity of homoionic montmorillonite was also positively related to HIR and negatively to HIP for the group of alkali and alkaline earth ions put together. The reasons for trying out the relationship between the adsorption and their ionic properties is that the alkali and

alkaline earth ions are extensively solvated and exhibit a well identified and quantified solvation sphere. Further, these ions in general interact with organic molecules through their polarizing power as well as the ease with which the solvated water molecules can be displaced. Since the relationship of adsorption capacity with CIR and CIP were opposite of HIR and HIP, it can be reasonably concluded that it is the polarizing power of the cations, that are more important in the binding of metoxuron and tebuthiuron on montmorillonites, consistent with this observation is the fact that the adsorption of metoxuron and tebuthiuron varied positively with CIP of the ions (Fig.28) and negatively with CIR (Fig.29). The correlation coefficients however were significant only for maximum adsorption ($r = -0.756^{**}$), CIP with maximum adsorption ($r = 0.964^{**}$): CIP with K_F ($r = 0.814^{**}$) for tebuthiuron, CIP with maximum adsorption ($r = 0.666^{*}$) for metoxuron (Table 26).

The fact that overall correlation coefficients were small and that the ions mainly fell in terms of Fe-, Al-, transition metal ions, alkaline earth ions and monovalent ions, which clearly show that ion potential is not the sole parameter governing adsorption. The poor and inconsistent relationship between CIP and adsorption within each group is a further confirmation of this fact.

The observation that position of transition group of elements was much higher and different from alkaline earth ions is likewise an indication of the involvement of other factors in the binding of metoxuron and tebuthiuron. The variation in maximum adsorption within this group was sharp although valency and polarizing power of these group of ions were quite similar. This referred to the strong possibility of formation of coordination bonds between these metal ions and the herbicide.

Falling in line with the adsorption capacity were the adsorption parameters K_F, K_L, k and the corresponding free energy functions $-RT\ln K_F$ and $-RT\ln K_L$. Thus the correlation of all these parameters with CIR and CIP were negative and positive respectively. Likewise, the reverse trend was observed for the HIR and HIP of the alkali and alkaline earth group of cations.

As seen from the 'Results', these relationships are at best qualitative, because the correlation coefficients were not significant in most of the cases except for maximum adsorption with CIR ($r = -0.756^{**}$; with CIP ($r = 0.964^{*}$; with K_F ($r = 0.814^{*}$); with $RT\ln K_F$ ($r = 0.826^{**}$) for tebuthiuron and CIP with maximum adsorption for metoxuron ($r = 0.666^{*}$) (Table 26).

It is however significant to note that all the above adsorption parameters also fell into distinct groups like H-, Fe- and Al-, transition metal ions, alkaline earth ions and monovalent ions, as in the case of maximum adsorption. However within each of these subgroups, no quantitative or qualitative inference could be drawn primarily due to the fact that variables in each group of ions were limited and more significantly the differences in adsorption within each group itself is limited and the estimated experimental errors preclude attaching too much significance to these.

Detailed analysis of the relationship between the various ionic and adsorption parameters, should help in understanding the mechanism of binding of herbicides with homoionic clays. The poor overall correlation between any of the adsorption parameters except maximum adsorption and ionic properties, distinctly brings out the differences in the nature of bonding in the case of different ions. A straight forward simple type of bonding would have manifested itself in a clean and significant relationship between the ionic and adsorption constants. Further, in almost all the cases, the ions fell into some distinct slots mainly dictated by their charge and electron configuration as discussed earlier. This is very strong evidence that ions within the respective groups should have

similar bonding mechanisms, although individual differences between its members may be too small or smothered by other effects like solvation.

It has been suggested earlier that metal ions present on the clay surface, especially in the case of smectites, are responsible for adsorption of organic molecules either directly or through water bridges (Farmer and Mortland, 1965; Farmer and Ahlrichs, 1969; Mortland, 1966; Theng, 1979).

Specific mechanisms of bonding between exchange cations and the adsorbed organic molecules have been verified especially through IR techniques in systems containing little water. Such studies have shown that ions can bind with the adsorbate either directly or through the limited sphere of highly perturbed water molecules of hydration (Green, 1974; Mortland, 1970).

However, it is difficult to come to definite conclusions regarding the nature of interactions in dilute suspensions on account of the dominating and mediatory role of water molecules solvated to these cations. In these cases, indirect coulombic interactions between the cations and organic molecules or the weak forces like dipole-dipole, ion-dipole or ion-induced

dipole types of interactions through the participation of water molecules will be expected. The pH of the clay suspensions in this study varied from 5.5 to 6.4. Since metoxuron and tebuthiuron remain neutral in this pH range, ion-dipole type of interactions due to protonation of the herbicide are not considered likely. On the other hand, the presence of carbonyl group and -NH groups on the herbicide make dipole-dipole type of interaction and H-bonding most probable (Fig.38). Thus in the case of monovalent and alkaline earth ions, it can be inferred that electrostatic forces by way of dipole-dipole and H-bonding through water molecules may be the main forces binding metoxuron and tebuthiuron to the clays. These ions have a stable, rare gas electronic configuration and do not form strong complexes as explained later for transition metal ions. The effect of CIP and DEP on the adsorption parameters of these ions are consistent with this explanation.

The mechanism of adsorption of metoxuron and tebuthiuron to H-, Al- and Fe- montmorillonites needs to be looked at differently from that of alkali and alkalineearth ions, although their high polarizing power, manifested in the form of their large CIP, may still be the dominant force. Special and specific types of bonding between these ions and organic chemicals

have already been postulated. Thus, Dixon (1977) observed that substituted ureas are more readily adsorbed on acid mineral surfaces quite possibly due to protonation or hydrogen bonding. Thus H-clays have strong tendency to adsorb organic molecules and the mechanism may be entirely different from simple electrostatic bonding as in the case of alkali and alkaline earth ions. The high charge and ion potential of Fe- and Al- coupled with their tendency to form polyhydroxy complexes offers scope for hydrogen bonding with the adsorbed organic molecules.

The unique grouping of transition metal ions and abnormally high variation in adsorption parameters with ionic properties within this group, unlike other groups of ions which vary only minimally, point very categorically to more specific and stronger interactions than the general coulombic type of interactions. Thus, there is a possibility of direct ion-dipole type of interactions. Transition metal ions have vacant 'd' orbitals and tend to form very strong complexes with ligands, resulting in intricate orbital overlaps. It is not easy to get direct evidence of complex formation in suspensions, where the cations are surrounded by thick sheath of water molecules. However, the unique variation in the adsorption properties for

these metal ions can be deemed as indirect evidence for such an intimate interaction in suspensions also. The preferential stabilization of complexes of transition metal ions with neutral ligands like thiourea and ethylene diamine on clay surface has been shown to occur (Pleysier, 1976). This is probably an indication that complex formation between pesticides and transition metal clays can take place.

Some inference could also be drawn regarding the adsorption sites from the amount of metoxuron or tebuthiuron adsorbed on homoionic clays. The maximum amount of metoxuron and tebuthiuron adsorbed on homoionic clays was about 10 to 15 me/100 g which is much less than the CEC of montmorillonite which indicates that these herbicides are adsorbed on the edges and surface and do not penetrate the interlayers.

In the end, it must be added that apart from enthalpy considerations which go with various types of bonding, change in entropy during adsorption may also be very critical. It is well known that, the water molecules in the immediate vicinity of cations are highly perturbed and structured (Sposito, 1984; Geissing, 1975) and immediate presence of organic molecules, which in general are structure makers, may induce effects opposing or reinforcing coulombic

effects. Since acccording to Barclay and Butler principle (Franks, 1973), entropy and enthalpy effects generally oppose each other, the overall free energy effect of cations which is the balance of entropy and enthalpy factors may not be sharp and may be more difficult to perceive.

5.2 ADSORPTION OF METOXURON AND TEBUTHIURON ON ION SATURATED RESINS :

The effect of cations saturating the exchange sites of IR-120 resin, on the adsorption of metoxuron and tebuthiuron has been analysed under 'Results'.

The adsorption isotherms showed a tendency for surface saturation. The adsorption isotherms of metoxuron (Fig.9) were parabolic in nature. However the isotherms on Cu^{++}, H^{+} and NH_4^{+} saturated resins indicated an S-shaped character. The isotherms of tebuthiuron (Fig.12) were S-shaped in nature. In both the cases the extent of adsorption was high for H-, Fe-, and Al-, followed by divalent 3d ions and alkaline earth ions whereas monovalent ions showed the least adsorption indicating that the adsorption was dependent on charge and polarizing power of the cations. Hance (1971) and Khan and Mazurkewitch (1974) observed that the adsorption of linuron on cation saturated peat, IR-120 resin, bentonite, montmorillonite and humic

acid followed the order Fe-> Al-> Cu-> Ni-> Ca. This order is in confirmity with the suggestion made referring to the polarizing power of cations as the main factor governing the adsorption of organic molecules. One of the major differences between homoionic montmorillonites and IR-120 resin was that the adsorption of both metoxuron and tebuthiuron was much higher on the resins. The maximum adsorption capacity of the resins however was also largely dictated by the charge of cations on the resin. Thus, the adsorption followed the order : Il-and trivalent > transition metal ions> Alkaline earth ions > monovalent ions. Thus, the formation of discrete clusters based on charge is seen in this case also.

The capacity for adsorption as well as other adsorption parameters like K_F, K_L and free energy functions - $RT\ln K_F$, $-RT\ln K_L$ were all negatively related to CIR and positively to CIP as in the case of homoionic montmorillonites (Table 26). Thus, the polarizing power of ions, was seen to be the major factor influencing the adsorption of both metoxuron and tebuthiuron on homoionic resins. The effects of HIR and HIP were also in line with this trend, as in the case of montmorillonites.

Apart from qualitative relationship, no significant correlation was found with any of the

adsorption parameters and ionic properties, when all the ions were considered together. Within groups of ions, neither the variable differences, nor the number of ions were large enough for a quantitative treatment.

Thus, the effect of exchange ions on the resins, are very similar to the effect of cations on montmorillonites. The effect of ionic parameters like crystalline ionic potential and crystaline ionic radius on the maximum adsorption and Freundlich constant (K_F) was studied by Shalali (1986). Negligible correlation was obtained with respect to CIR but significant and positive correlation was obtained with CIP thus establishing the importance of polarizing power of cations in adsorption of atrazine.

There is however, a basic difference between the exchange resins and clays. In resins, the exchange cations are adsorbed on an intricate organic network as the backbone on which the polar groups are present. This is very distinct from the clays on which the substitution in silicate and Aluminium hydroxY network create the charge centres. The organic network is capable of interacting with the herbicides through a large number of forces especially Vander Waal's forces. The silicate and Aluminium hydroxide network

in clays have been shown not to interact with the organic chemicals (Dixon, 1977) as originally suspected. Thus the greater adsorption on resin may be attributed to the large organic network. In this respect, a resin serves more like metal humate/fulvate. It is thus possible that, on account of this, the effect of cation may be considerably clouded or attenuated. Even so, the results have made it clear that the cations have a specific role to play as in the case of montmorillonites.

The bonding mechanisms to the cations, may thus be considered to be similar to that found for homoionic montmorillonites. Thus, weak electrostatic forces like H-bonding and dipole dipole bonds mediated through water molecules in case of alkali and alkaline earth ions, specialised bonds due to hydrolytic nature of Fe- and Al- and ligand exchange or coordinate bonds with transition metal ions, are indicated.

A figure depecting the various mechanisms of bonding between metoxuron and tebuthiuron on homoionic montmorillonites/resins is presented in Fig.38.

5.3 CHARACTERISATION OF POLYMALEIC ACID :

Polymaleic acid was suggested as a synthetic model for soil fulvic acid by Anderson and Russell (1977) and Linehan (1977).

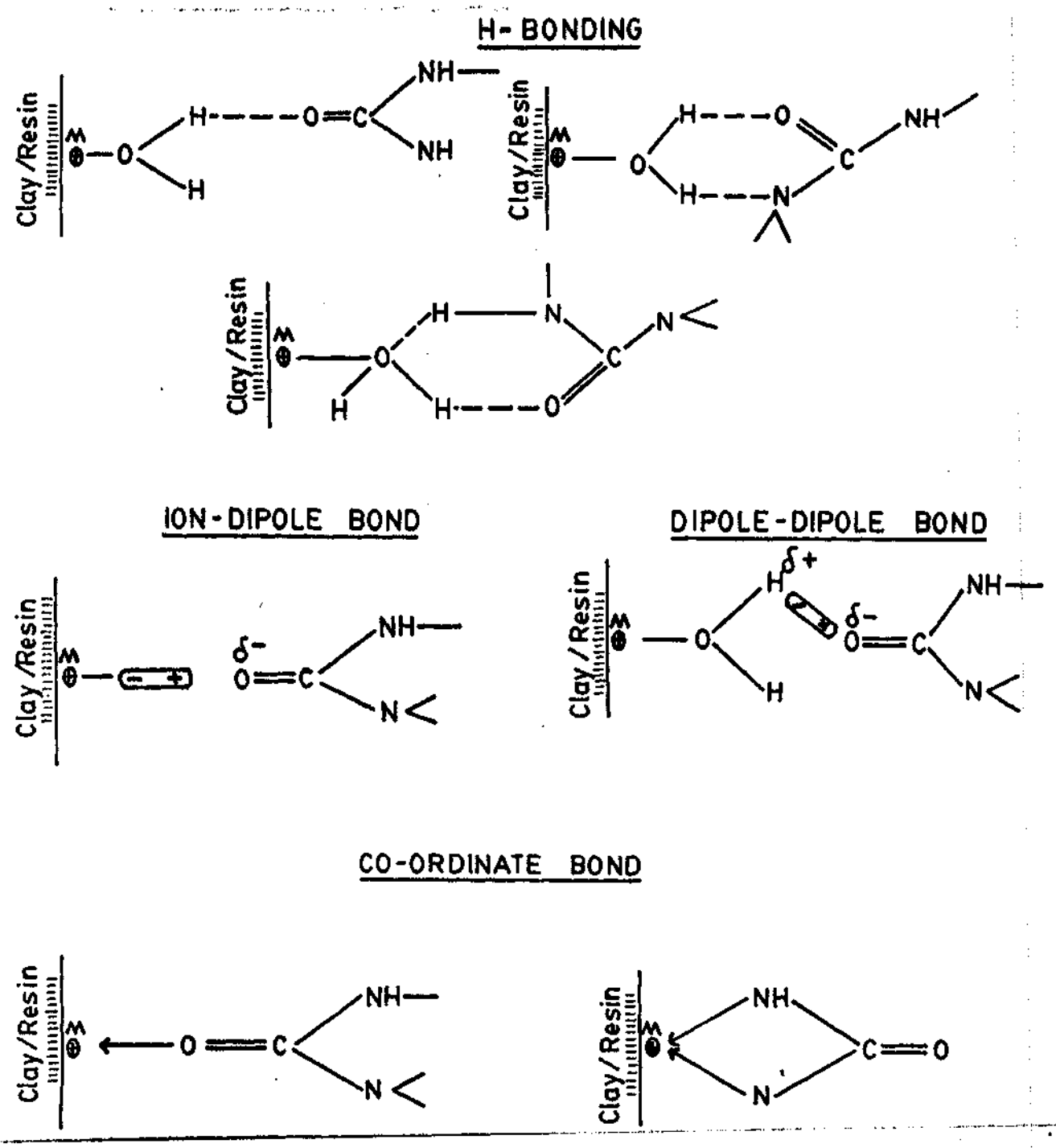

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FIG: 38. BONDING MECHANISMS OF METOXURON / TEBUTHIURON ON HOMOIONIC MONTMORILLONITES / HOMOIONIC (IR-120) RESINS

Its synthesis and special characteristics were studied by us. It was taken up as a model compound for studying the interaction of soil organic colloids with clays.

The sample of PMA, agreed well with the general characteristics of the polymer reported by Spiteller and Schnitzer (1983) and functional group analysis corraborated the presence of several functional groups and bonding considerations present in FA.

It was rich in -COOH and phenolic OH, the former contributing to 68.4% of the total acidity. The infrared spectrum of PMA was quite complex and suggests the presence of several vibrational modes. Some of the observed trends have been tentatively identified on the basis of literature available earlier. Thus, the band at 1640 cm^{-1} is assigned to C = C stretching of olefin or pyridine origin. The medium band at 1490 cm^{-1} is attributed to C = C stretch of the aromatic ring, small band at 1060 and 1040 cm^{-1} may be due to = C - O - C = and 755 cm^{-1} to C-H out of plane deformation of pyridine ring. Adsorption at 3020 and 2910 cm^{-1} indicate olefin HC = CH and aliphatic C-H stretching. The vibrational modes are quite similar to those reported for FA (Spiteller and Schnitzer, 1983), and justify the choice of PMA as a model for

FA. The absorption in the UV region spectrum had a well defined peak at 255 nm, which was attributed to the incorporation of a small quantity of pyridine in the polymer. Other than this, the UV-visible spectrum of PMA was quite uncharacteristic like the soil organic colloids.

The absorption in the UV region (200-300 nm) is mainly due to atomic and electrostatic vibrations and involve elevation of electrons from σ , π or non bonding orbitals to higher energy orbitals. Molecules containing non-bonding electrons on oxygen, sulfur etc., and systems containing conjugated C = C double bonds often undergo such transitions. PMA being a complex molecule is expected to show a series of such overlapping transition in the region which results in a rather uncharacteristic spectrum.

Potentiometric and conductimetric titrations were carried out for the first time and they reflected several features similar to FA. Thus, PMA has a high buffering capacity which is consistent with the concept of its being a weak acidic polyelectrolyte. The titration curve clearly indicated the presence of a series of ionising groups with closely varying ionisation constants, consisting of COOH group of low pKa to phenolic -OH group of high pKa which do not dissociate until the pH is quite high.

The average pKa as shown earlier is 5.48 (Fig.21). Both conductimetric and potentiometric titrations agreed quite closely and gave a value of 106.8 for its equivalent weight. An important feature of the potentiometric titration curve was its shift with a change in ionic strength (Fig.20).

5.4 ADSORPTION OF PMA ON HOMOIONIC MONTMORILLONITES AND THE FORMATION OF MODEL CLAY ORGANO COMPLEXES

The interaction of organic substance with clay has a magnitude of consequences that are reflected in the physical, chemical and biological properties of the soil matrix. The importance of clay-organic interactions in predominently inorganic soils, was pointed out by Greenland (1965) who showed that 52 to 98 per cent of organic carbon in these soils was associated with the clay fraction. Weathering and soil formation are largely affected by clay-organo complexes (Mortland, 1970). Stabilisation and immobilisation of soil enzymes are known to take place on soil clay-organo complexes (Ladd, 1985; Boyd and Mortland, 1985). Thus, a more adequate knowledge of the synthesis, stability and characteristics of clay-organo complexes would be of great value in a better understanding of the physical, chemical and biological properties of soil.

No report exists concerning the adsorption of PMA on homoionic montmorillonites. Our aim was to compare the behaviour of these better defined models with that of soil humic and fulvic acids, specially the latter.

As seen from the 'Results' the adsorption isotherms of PMA on homoionic montmorillonites (Fig. 26) were mainly parabolic in nature with a tendency to reach surface saturation in the concentration range studied in contrast to the adsorption isotherms of metoxuron and tebuthiuron on metal clays which were mainly S-shaped. However S-shaped character was seen in the case of adsorption isotherm of PMA on Co-montmorillonite. Adsorption isotherms were mostly L-shaped indicating a relatively high affinity between PMA and the clays. Linear isotherms were obtained by Levy and Francis (1976) for montmorillonites saturated with Na-, Ca-, Al- and Fe- ions. However Evans and Russell (1959) obtained L-shaped curve for adsorption of HA on K-montmorillonite. The extent of adsorption of PMA on homoionic clays was much higher in comparison to the adsorption of metoxuron and tebuthiuron on metal clays. The effect of saturating cation was similar to that of metoxuron and tebuthiuron and depends on the charge of cation. Thus the adsorption decreased in the following order : trivalent > divalent > monovalent.

Also, the adsorption on transition metal saturated montmorillonite was higher as compared to the alkaline earth metal ions. The detailed differences in the adsorption brought about by cations can be summerized as

(Fe-> Al-) > (Ni-> Zn-> Co-> Cu-) > (Ca-> Mg- $\simeq$ Ba)> (NH_4- > K- > Na-)

The adsorption parameters for PMA were analysed with respect to ionic properties as explained earlier for metoxuron and tebuthiuron. Qualitatively, the adsorption increased with charge and polarizing power of the ion. The maximum adsorption, thus was inversely related to CIR ($r = -0.552$) and positively and significantly related to CIP as shown in (Fig. 39 ($r = 0.874^*$). The relationship between maximum adsorption and HIR was positive and significant for alkali and alkaline earth ion group. The variation in adsorption was negative with respect to HIP for this group. Thus, the trend for maximum adsorption was similar to the adsorption of metoxuron and tebuthiuron on montmorillonites.

The variation of other adsorption parameters like K_F, K_L and the free energy factors log K_F and log K_L were also essentially similar to that of metoxuron and tebuthiuron. K_F was even significantly and positively correlated to HIR for alkali and alkaline earth group cations.

Fig. 39 previous ?

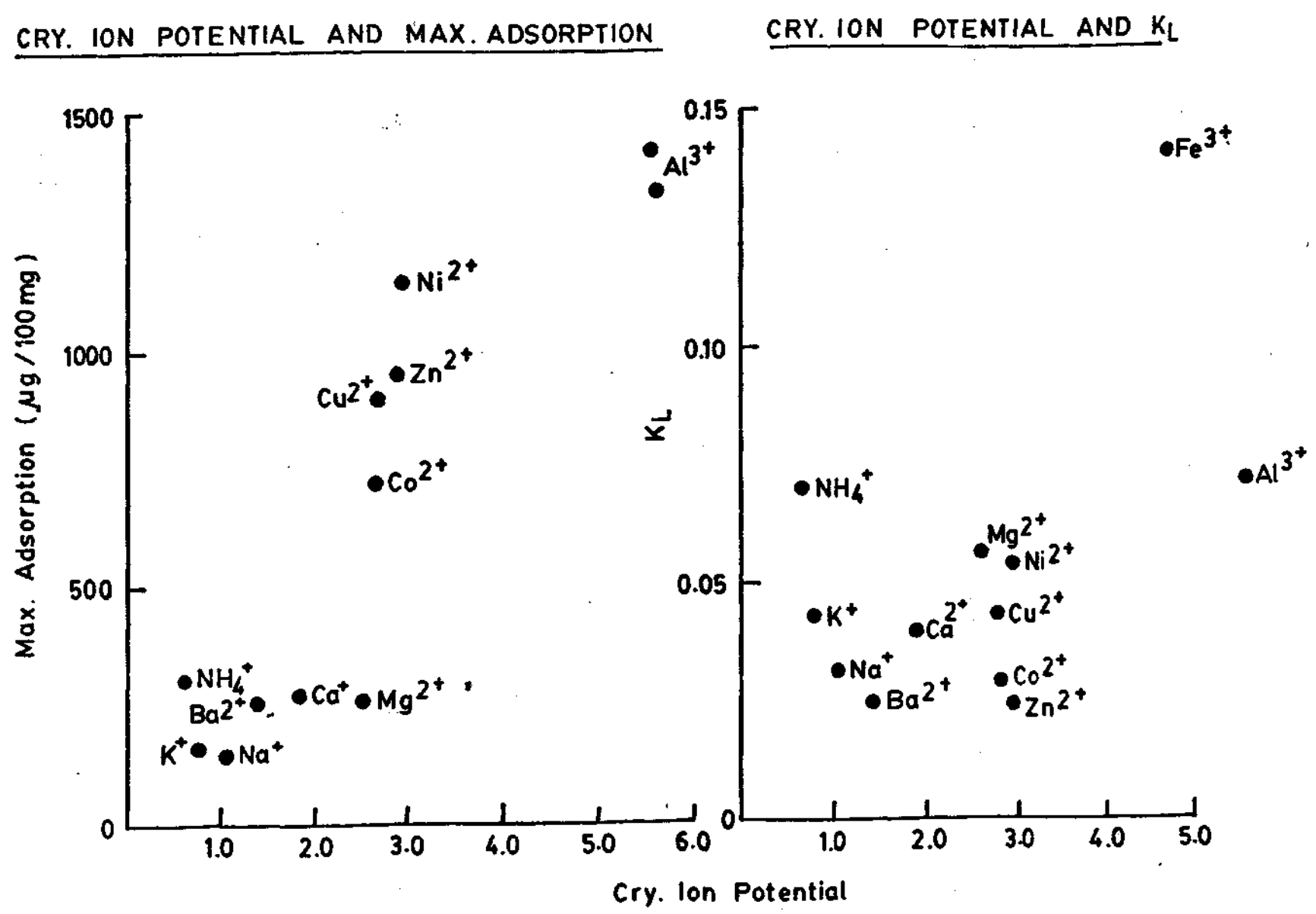


FIG.39: CORRELATION BETWEEN (FOR PMA)

Quantitative relationship within each group and on the whole, were also attempted although they do not hold much significance for the reasons explained for metoxuron and tebuthiuron.

The main points to be considered in arriving at bonding mechanism between PMA and homoionic montmorillonite are discussed below. PMA is a polymer of fairly low molecular weight (< 1000) and contains -COOH and phenolic OH groups. The -COOH groups have a wide range of pKa with an average p^{Ka} = 5.48. The pH of clay suspensions in the adsorption experiments varied generally between four and five and hence the dominant fraction of PMA existed in uncharged form. The large quantity of PMA adsorbed on homoionic montmorillonite was in tune with this, because negatively charged species would be repelled by the clay surface. The polyvalent cations may however, effect the adsorption of some of the negatively charged fraction also as they can maintain neutrality at the surface by neutralising the charges both on clay and PMA.

Polymaleic acid being a polyanion, contains more than one polar centre, which can be solvated by water and which can also interact with the clay surface. Thus, a multi centred interaction with clay surface would be anticipated. The high adsorbability of PMA to the clays supports this presumption.

The possible types of interaction between the active centres of PMA and homoionic clay are summed below : crystalline ion potential was found to be positively related to almost all the adsorption parameters. This leads to the possible conclusion that in the case of alkali and alkaline earth ions, the forces between PMA centres and cations are mainly ion-dipole and H-bonding as suggested for metoxuron and tebuthiuron. The large abundance of water molecules in clay suspension, leads one to logically conclude that these interactions should be mainly taking place through the mediation of water molecules. The fact that K-clay adsorbed more PMA than Na-clay however, suggests that there may be a possibility of direct ion-dipole interaction between PMA and the cations in this case as suggested by Theng (1979) for HA and FA. Theng and Scharpens eel (1975) found such order for the adsorption of HA. The low hydration energy of alkali cations, can result in displacement of water of hydration from around these ions by the polymeric species like PMA, FA and HA. In the case of the divalent ions, where the hydration energy is high, the solvating water molecules are important. The higher charge and polarizing power of Fe- and Al-montmorillonites, together with their tendency to form polyhydroxy complexes at mineral surfaces offer scope for H-bonding with the PMA.

Transition metal ions adsorbed much more than alkaline earth ions and this can be explained by the formation of ligand exchange. Transition metal ions have vacant d orbitals which can accept electrons from PMA acting as a ligand. Further, these metal ions can also accept π electrons from ligands as postulated by Theng and Scharpenseel (1975) for HA. PMA has an extensive network of electrons as well as functional groups like - COOH, -OH, C = O etc., which can coordinate with these metal ions.

The importance of polyvalent cations in the adsorption of humic substances have been emphasized (Dixon, 1977; Evans and Russell, 1959; Kodama and Schnizer, 1967; Theng and Scharpenseel, 1975). Among these cations, Fe (III) - was particularly effective in promoting adsorption because Fe (III) tends to form polyhydroxy complexes at the mineral surface, offering scope for bonding mechanism other than cation and water bridge formation to occur. Similar results were obtained for adsorption of HA on homoionic montmorillonite by Theng and Scharpenseel (1975) and by Obulpathy (1977) for the adsorption of FA on homoionic clays.

In the end it is important to note that apart from ion-PMA interaction, the role of entropy

generation which has been shown to be of the foremost importance in polymer adsorption, needs to be considered also. These arise from the dislodging of water molecules in the secondary and successively higher hydration shells around the exchangeable cations by polymer molecules. It has been shown that in the case of polyethylene oxide and polyvinyl alcohol (Glass, 1968) that the loss of entropy on adsorption of polymer due to freezing of a translational degree of freedom is more than offset by the entropy of hydration arising from the release of solvated water molecules from the polymer due to the entropy of dilution of the interphase. The entropy factor may be the reason for the reversal of ion potential effects in the case of alkali metal ions. Such effect was shown for polyethyleneglycol adsorption of homoionic montmorillonites containing Cs- Na-, Co-, and Al- (Parfit and Greenland, 1970).

In the end the question of penetration of interlayer by PMA needs to be considered also. Although negatively charged species will not be able to penetrate the interlayer space, the preponderance of unionised molecules of PMA under the pH conditions of experiment allows the possibility of entry of the clay interlayers by neutral PMA molecules. The large adsorption of PMA on homoionic montmorillonite indicates the possibility

although no direct proof for this was obtained.

The effect of exchange cations saturating the exchange sites of IR-120 resin, on the adsorption of PMA has been analysed under 'Results'.

The adsorption isotherms (Fig.27) were mainly parabolic in nature with a tendency to reach surface saturation within the concentration range studied. There was a slight S-shaped character in the initial stages of adsorption. The adsorption isotherm of PMA on Cu-Resin indicated an S-shaped isotherm. The extent of adsorption was high for H-, Fe- and Al- followed by divalent transition metal ions and alkaline earth ions and it was least in monovalent ions. The extent of adsorption was largely governed by the charge and polarizing power of the cations on resin and followed the order H- and trivalent > transition metal ions > alkaline earth ions > alkali metal ions.

The positive correlation of the maximum adsorption and other adsorption parameters to CIP and negative correlation to CIR indicated that the CIP or the polarizing power of ions was the major factor governing the adsorption of PMA on ion saturated resins. Apart from the this relationship, no significant correlation could be obtained for any of the adsorption parameters with ionic properties, when all the ions

were considered together. The effect of exchange ions on the resins, were similar to the effect of cations on the clays. As explained for the adsorption of metoxuron and tebuthiuron on ion saturated resins, the exchange cations are adsorbed on an intricate network as the backbone which is capable of interacting with PMA through a large number of forces especially Van der Waal's forces. The adsorption on resin may be attributed to this the large organic network. It is thus possible that the cationic effect may be clouded on account of this organic network.

The bonding mechanisms to the cations may be considered similar to that found for homoionic montmorillonites. Hence, ion-dipole and H-bonding for alkali and alkaline earth ions, coordination bonds through ligand exchange for transition metal ions and formation of hydroxy bridges for Fe- and Al- are possible. The possible mechanisms of bonding of PMA on homoionic montmorillonites/resins is depicted in Fig.40.

5.5 EFFECT OF CLAY-PMA COMPLEXES IN THE ADSORPTION OF METOXURON AND TEBUTHIURON :

The intimate association of organic matter with clay may cause some modification of their adsorption capacities, or they may complement one another in

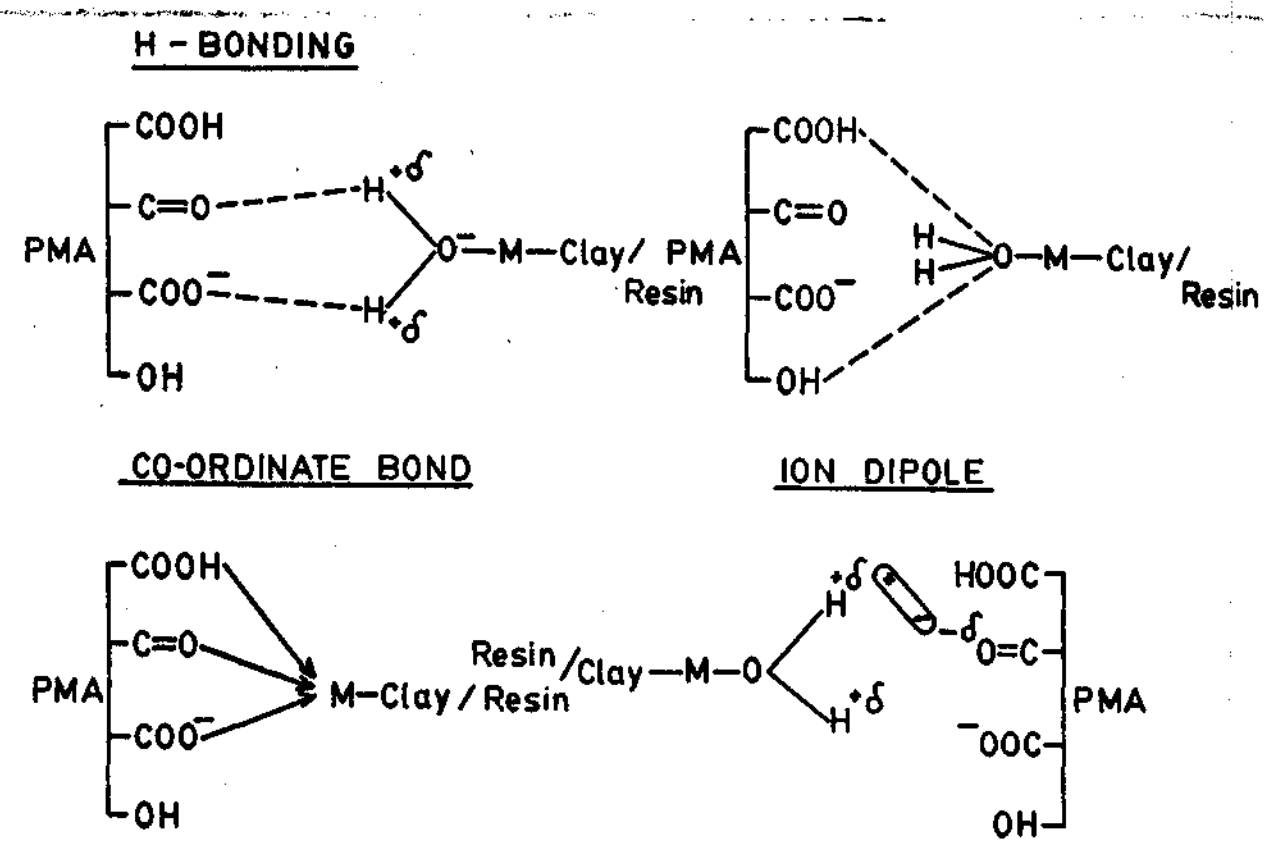


FIG.40: BONDING MECHANISMS OF PMA ON HOMOIONIC MONTMORILLONITES / RESINS

the role of pesticide adsorption (Pierce et al., 1971; Burns et al., 1972; Boyd and Mortland, 1985). Burns (1972) pointed out that a humus-clay microenvironment is a site of high biological and non-biological activity and opined that there is need to look for the basic information concerning soil pesticide interactions. Hance (1969) suggested that, in soil, clay and organic matter associate in such a manner, that, little of clay mineral surface will the accessible for pesticide adsorption. Although there is no direct evidence so far, the adsorption of soil applied chemicals is likely to be controlled by these complexes. Mortland (1970) opined that clays upon treatment with organic matter fractions are likely to facilitate the adsorption of pesticide at levels, beyond that observed in pure clay systems.

The complexit y of these naturally occuring clay organo complexes and the difficulty in isolating them, have precluded their characterisation and the study of their possible role in adsorption. Hence for this purpose a simple model system viz., clay PMA complexes was selected, to test how the adsorption of metoxuron and tebuthiuron was affected when homoionic montmorillonites are converted to their organo complexes.

Adsorption of PMA on homoionic montmorillonite (as reported earlier) was shown to attain surface

saturation and the adsorption followed the order:

Fe->Al-> Ni-> Zn-> Cu->Co-> NH_4-> Ca-> Mg-> Ba-> K-> Na-

The amount of metoxuron adsorbed by homoionic clays decreased in the order:

Al-> Ni-> Fe-> Zn-> Cu-> Ca-> Ba-> Mg-> Co-> NH_4-> K-> Na->

The amount of metoxuron adsorbed by model clay PMA complex also followed the same trend as that of homoionic clay and decreased in the order :

Al-> Ni-> Fe-> Zn-> Cu-> Ca-> Ba-> NH_4-> Ca-> K-> Na->

Similar observation was recorded for adsorption of tebuthiuron also. In the case of homoionic clays the order was :

Al-> Fe-> Co-> Cu-> Zn-> Ba-> Ni-> Ca-> Mg-> NH_4-> K-> Na-

and on model clay-PMA complex the order was identical except for a small change in the case of Zn- and Ni-

Al-> Fe-> Co-> Cu-> NI-> Ba-> Zn-> Ca-> Mg-> NH_4-> K-> Na-

Thus the adsorption of metoxuron and tebuthiuron on both homoionic clays and their corresponding clay-PMA complexes, was governed by the charge on the ions.

The per cent increase in adsorption by model clay-PMA complexes over the corresponding homoionic clays was calculated from the difference between the adsorption of herbicide on clay -PMA complex and

pure metal clays. The monovalent ions showed a high increase in per cent adsorption upon treatment with PMA followed by alkaline earth metal ions whereas it was low in case of Al- and Ni- (Table 24). These results clearly indicated that there was a consistent increase in adsorption when the clays were converted to their clay-PMA complexes. This seems to be the first time that a systematic study of the adsorption on clay organo complexes has been effected. These results agree with Mortland's (1970) opinion that clays upon interaction with organic compounds present in organic matter may facilitate and stabilise the adsorption of pesticides at levels higher than those observed in pure clay systems. Apart from the general increase in adsorption, two specific effects were evident: 1) the nature of saturating cations and 2) the relationship between the amount of PMA adsorbed by the homoionic clays and per cent increase in the adsorption brought about.

The role of cations acting as bridges in the interaction of organics with clays, especially montmorillonites is well accepted (Green, 1974, Mortland, 1970; Theng, 1979). The most interesting point that emerges was that the alkali and alkaline earth cations, which generally exert a weak binding of organic chemicals,

and which adsorb less PMA than the trivalent cations like Fe- and Al- brought about a larger increase in adsorption of metoxuron and tebuthiuron, when converted to their PMA complexes. To test the effect of actual PMA adsorbed by the homoionic clays, percentage increase in adsorption was plotted against the amount of PMA adsorbed (Fig.41). A fairly good inverse relationship was found between the percentage increase in adsorption and PMA present on the clay complex for alkali and alkaline earth metal ions. The transition metal ions fell into a separate group by themselves. Al- and Fe- (III) were also very different. Thus, the less adsorbing cations, seem to be more effective in enhancing adsorption when complexed with PMA.

Although these observations are very interesting and constitute a beginning into the role of clay-organo complexes, more extensive and systematic work needs to be carried out, before specific categorical and unequivocal conclusions can be drawn. Though not directly related to this work, the results of Boyd and Mortland (1985) on the role of clay-organics on the adsorption and properties of soil enzymes like urease and phosphatase has opened up exciting poossibilities of the role of clay-organo complexes.

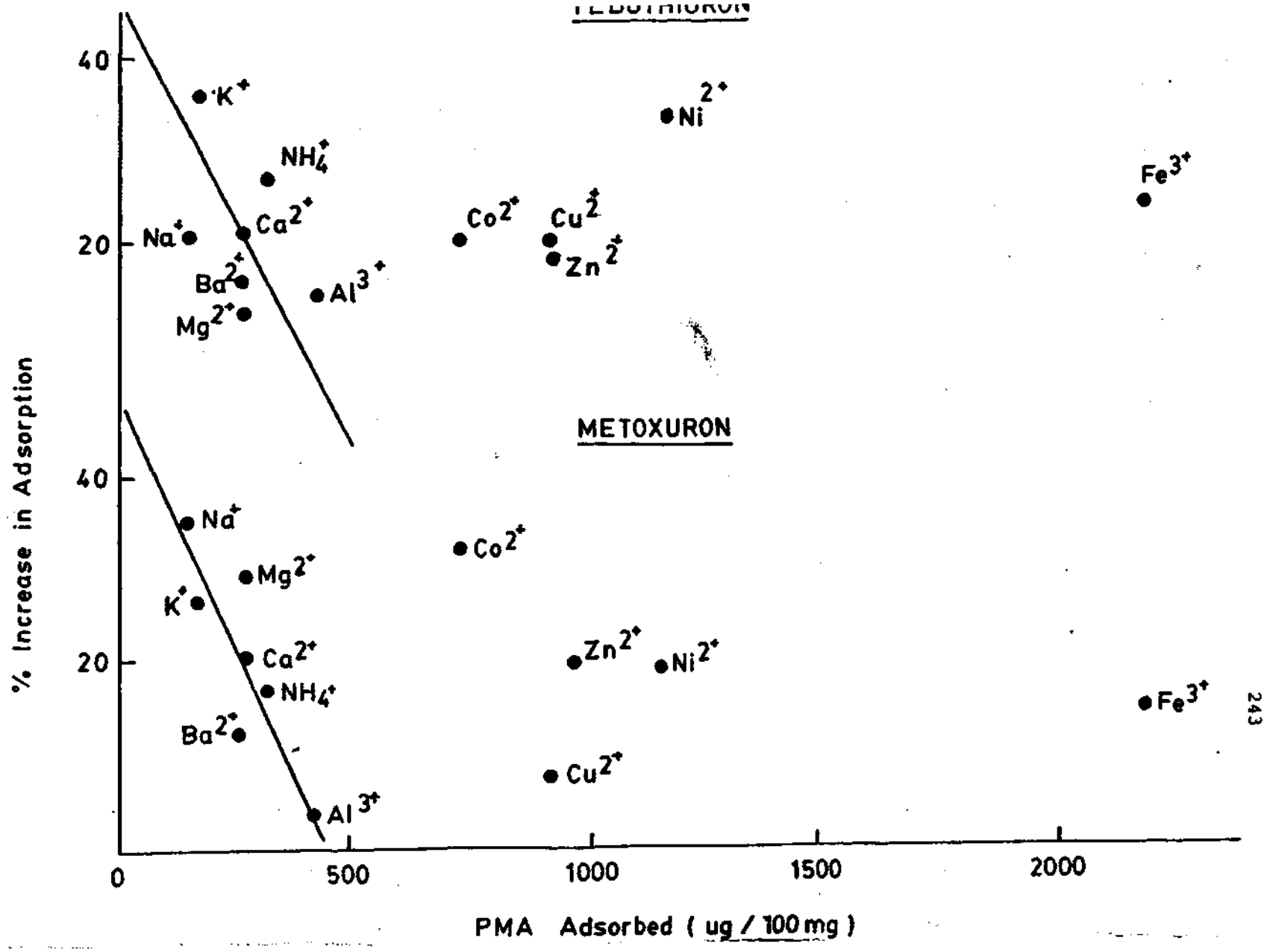


FIG:41. PLOT OF % INCREASE IN ADSORPTION OF METOXURON AND TEBUTHIURON AND AMOUNT OF PMA ADSORBED

The observation that transition metal ions have once again taken up a unique position in contrast to alkali and alkaline earth ions, fortifies our earlier stand that there is indeed a substantial difference in the bonding characteristics of these ions. Repeated evidence of their singular behaviour is a clear verdict of the decisive involvement of their unique electronic configuration with vacant low level d orbitals, with those of ligand molecules like metoxuron, tebuthiuron and PMA, even in clay suspensions. A number of cases have been reported recently which support this stand. Thus cation-neutral ligand complexes can be exchanged against hydrated metal cations adsorbed by clays (Allen and Metijevic, 1975; Laura and Cloos, 1970; Theng, 1974). Maes et al. (1977) found that ethylene diamine complexes of Cu-, Ni-, Zn-, Cd- and Ag- can replace Ca- easily, the selectivity coefficient of Cu-complex being 10^3 times higher as compared to free Cu^{2+}-ions. The ion exchange affinity of silver thiourea (AgTU) complex for clays was high indicating increased stability of AgTU which shows drastic stabilisation of 10^3 units and can displace Na-, Ca-, and Al- in Kaolinite, montmorillonite or vermiculite (Pleysier and Crammers, 1975). This suggests that the displacement of water molecules from metal ion-coordinating sphere of uncharged ligands occur more favourably on a clay surface than

in bulk. This may result in the more frequent formation of stronger complexes between exchange cations and pesticides than hitherto predicted.

5.6 SOIL PERSISTENCE OF METOXURON AND TEBUTHIURON:

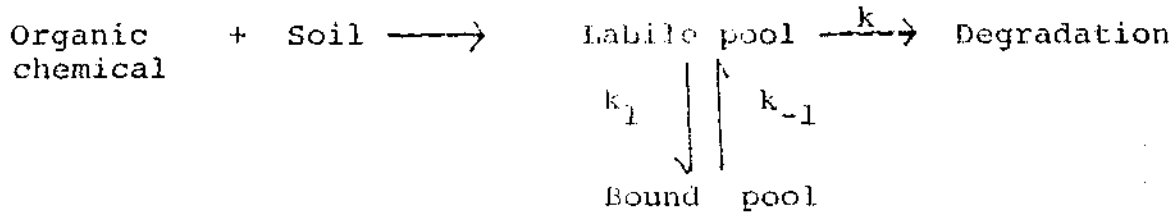
Herbicides may persist in soil when initial dosage is large or when repeated doses exceed the rate of degradation. The persistence of herbicides is influenced by interaction of a number of factors including soil type, clay content, plant uptake and environmental factors like moisture and temperature. There are marked differences in the degree of persistence of various substituted urea herbicides. As clarified earlier, the direct monitoring of residue levels in fields through cumbersome and repititve analytical procedures need to be replaced by predictive mathematical models, which, with the help of components can simplify the matter to a large extent. An attempt has been made by Walker and Coworkers through computer simulation models for prediction of persistence levels in soils incubated under controlled temperature and moisture conditions (Walker, 1974 and 1976; Walker and Barnes, 1981; Walker and Zimdahl, 1981; Zimdahl and Clark, 1982).

The present study aims at quantifying the effect of temperature, moisture and some soil properties,

on the persistence of metoxuron and tebuthiuron. As explained under 'Results', the disappearance of these herbicides was studied in soils incubated at controlled temperature and moisture status. The results indicated that there is atleast a two phase kinetics with which metoxuron and tebuthiuron disappeared. Initially, there was a very sharp decrease in the methanol extractable portion of the herbicides, which was followed by a much slower decrease. The kinetic pattern was similar to that observed by Katan et al. (1976) for the disappearance by ^{14}C- parathion treated under field conditions, by Liechtenstein et al. (1977) for ^{14}C- parathion, fonofos, dieldrin and DDT, by Khan et al. (1981) and Bhatadt (1986) for the degradation of atrazine.

The persistence kinetics in the case of metoxuron and tebuthiuron could be explained quantitatively in terms of the model suggested initially by Hamaker and Goring (1976). According to this model, a soil applied chemical distributes itself into two compartments which could be termed labile and bound. The labile pool consists of the fraction of chemical dissolved in soil solution and extractable in suitable organic solvents under mild conditions. The bound pool consists of the herbicide adsorbed strongly on more restricted sites in soil and unlike labile pool,

it cannot be desorbed by solvents. The scheme of events that take place during the interaction of herbicide can be pictured as



Where 'k' is the rate constant for degradation of chemical, k_1 for entry into bound pool, k_{-1} for reentry into labile pool.

Hamaker and Goring (1976) published a complete graphical method for the analyses of all the rate constants viz., k, k_1 and k_{-1} from the kinetic data as explained under 'Materials and Methods'.

As a valid approximation, for metoxuron and tebuthiuron, the rate of reentry of herbicide from bound pool to labile pool was considered negligible compared to the other rates, over the time period under study. Thus first order kinetics was used for the entry into bound pool and the disappearance from labile pool as explained under 'Materials and Methods'. These values are given in Tables 31 and 32 for metoxuron and tebuthiuron respectively.

Complete mathematical analysis was also carried out for resolving all the kinetic rate constants

Table 31 : Rates of disappearance of metoxuron (d^{-1})

Soil	Temperature °C	Saturation		Field Capacity		50% Field capacity		Pooled values	
		k	m	k	m	k	m	k	m
Alfisol	10°C	0.0386	0.0027	0.0215	0.0040	0.0199	0.0053	0.0267	0.0040
	27°C	0.0451	0.0058	0.0457	0.0053	0.0503	0.0081	0.0470	0.0064
Vertisol	10°C	0.0346	0.0072	0.0080	0.0024	0.0327	0.0033	0.0346	0.0043
	27°C	0.0417	0.0065	0.0312	0.0085	0.0346	0.0043	0.0378	0.0064

Table 32 : Rates of disappearance of tebuthiuron (d^{-1})

Soil	Moisture content	k	m
Alfisol	Saturation	0.0363	0.00833
	Field Capacity	0.0493	0.00763
	50% Field Capacity	0.0396	0.00701
	Pooled value	0.0417	0.00966
Vertisol	Saturation	0.0080	0.00499
	Field capacity	0.0187	0.00254
	40% Field Capacity	0.0231	0.00251
	Pooled value	0.0156	0.00385

including the rate of reentry of herbicide from bound pool to labile pool as detailed by Hamaker and Goring (1976) and explained under 'Materials and Methods'. The rate constants of metoxuron increased with an increase in temperature from 10°C to 27°C and followed the order $k > k_1 > k_{-1}$. The rate of degradation was higher in alfisol as compared to vertisol and increased with increase in temperature. Poku and Zimdahl (1980) reported a slightly faster degradation of dinitramine in sandy loam soil than in clay loam soil. Majka and Lavy (1977) observed similar temperature effects on diuron, which degraded in the order 35 > 5°C. The rate of entry into bound pool was higher for vertisol than for alfisol and was higher at higher temperature. It decreased with soil moisture in the order : Saturation> Field capacity > 50% Field capacity. However the clay content and organic matter content of vertisol was high (62.5 per cent clay and 0.59 per cent organic carbon). Thereby herbicide may be adsorbed more strongly on these sites in soil and can not be desorbed by organic solvents. From the rate constants it can be seen that there was higher rate of disappearance at 27°C than at 10°C. From the rate constants at two temperatures the activation energy was calculated and presented in Table 29. These values were lower than those reported by Walker and Zimdahl (1981). It may be pointed out here that they did not consider

the existence of two rates of disappearance, but fitted the whole data to first order kinetics. This may be the reason for higher predicted levels for residues, in comparison to the actual field levels. Higher activation energy was obtained in alfisol as compared to vertisol. Similar results were reported by Shalali (1986) for the disappearance of atrazine.

The rate of degradation of tebuthiuron from labile pool was high at higher soil moisture levels in both the soils and followed the order saturation> Field capacity > 50 per cent Field Capacity. Similar results were reported by Zimdahl and Clark (1982). The rate of degradation was higher for alfisol as compared to vertisol. Hollist and Foy (1971) studying on the interactions of trifluralin with soil constituents, suggested that increasing soil moisture content blocked the adsorptive sites for trifluralin, thereby increasing the amount available for degradation in soil solution.

The rate of entry into bound pool was higher for vertisol as compared to alfisol and tended to decrease with soil moisture. The higher rate of entry into bound pool for vertisol as compared to alfisol may be attributed to higher clay and high OM content.

Complete mathematical analysis carried out for resolving all the kinetic rate constants including

the rate of reentry from bound pool to labile pool as detailed by Hamaker and Goring (1976) for metoxuron, showed that this calculation involves a number of inherent approximations and cumulative errors due to experimental constraints as well as method of calculation, and hence undue emphasis should not be attached to the absolute values of these rate constants. Nevertheless, some distinct trends could be observed for both metoxuron and tebuthiuron.

The results of this study are significant as they clearly brought qualitatively and quantitatively, the concept of herbicides being partitioned into bound pool and labile pool. There are not too many cases where the two have been established firmly. Although the concentration in labile pool has all along been considered more important in bioactivity of chemical, recent investigation have focussed the importance of bound pool as well. Kearney (1976) opined that bound residues may be considered both as hidden residues capable of subsequent release and long term bio-activity and also as a process of deactivation helping to avoid long term effects. The description of bound residues being chemically unidentifiable and as a part of soil matrix has undergone revision since Khan and Hamilton (1980) used a new technique involving high temperature distillation to detect intact bound residues of prometryne from

treated field and laboratory incubated soil samples. This clearly shows that atleast a part of unextractable portion of herbicide comprises of parent molecule.

The biological role of bound residues is also a matter of differing opinion. Suss and Gramp (1973) showed that unextractable ^{14}C- linuron could be taken up by mustard plants. On the other hand Katan et al. (1976) showed that ^{14}C- parathion would be taken up from soil by earthworms and oats. This shows that the soil bound herbicides are not excluded from environmental reactions.

In the end, it is relevant to point out that Walker's model for predicting the persistence of pesticides did not take into consideration, the possibility of the pesticide applied to soil being retained in the bound fraction. The model suggested by him assumed a straight forward one phase kinetics for disappearance of pesticides involving first order kinetics. This is certainly a lacuna and a correction for partitioning into bound pool is necessary, because there is overwhelming evidence now that this happens in a large number of cases. Thus, it is possible that the reasons for obtaining higher values for pesticide residues through predictive modelling equations by Walker and his coworkers was actually due to this

factor. Thus a two phase kinetic pattern of disappearance of soil applied chemicals was observed by Katan et al. (1976) for the disappearance of ^{14}C-parathion, Liechtenstein et al. (1977) for ^{14}C-parathion, fonofos, dieldrin, by Khan et al. (1981) and Saroja Raman et al. (1987) for degradation of atrazine.

5.7 ADSORPTION OF METOXURON AND TEBUTHIURON ON SOILS AND THEIR CONSTITUENTS :

Adsorption studies were taken up in four soils from Hyderabad region, as explained earlier, to study the effect of actual mineral and organic colloids present in these soils and to see if any of these could be, integrated to explain the behaviour of the whole soils. The 'Results' of adsorption on the silt + clay (<50 μ), humic acid and 2 mm fraction of the soils were explained under 'Results'.

Mainly two types of adsorption isotherms were observed in the present investigation.

a) L shaped isotherms exhibiting a tendency to reach saturation of surface, observed for soils 3 and 4 and HA.

b) S-shaped isotherms with an initial plateau followed by a fairly steep rise for soils 1 and 2, < 50 μ fractions. No saturation was seen in the range of concentrations studied for the latter.

It was observed that adsorption of metoxuron and tebuthiuron in all the soils under the same conditions of temperature decreased in the order:

Humic Acid > < 50 μ fraction > 2 mm - sieved soil.

In order to see if any meaningful correlation exists between the amount adsorbed on soil and the adsorption intense humic acid, clay and silt components, the adsorption was calculated on the basis of individual contributions of these components. It was found that adsorption for the whole soil was lower than that calculated on basis of the colloidal components. The reasons for this primarily seem to be due to less specific surface area of 2 mm sieved soil as compared to the above fractions. This clearly proves that the soil as a whole is not just a mixture of the constituents but is a more intricate system involving newer and more complex features and hence a one to one correlation based on its constituents is untenable. It may be stated here again that in soil the organic and mineral colloids exist in a very intricate manner and, thus, the role of organo-mineral complexes may be dominating the process of adsorption and other events.

The major conclusions that can be drawn from the present investigation can be summed as :-

1) The adsorption isotherms obtained for metoxuron and tebuthiuron (with the exception of Fe-, Al and H-) on homoionic montmorillonites were parabolic in nature with an S-character in the initial stages of adsorption indicating a stronger competition of water molecules to clay surface as compared to the herbicide.

2) The extent of adsorption was dependant largely onthe valency and polarizing power of cations and followed the order H and trivalent > Divalent > Monovalent. The divalent transition 3d-ions had a much higher tendency for adsorption as compared to alkaline earth ions

3) With a view to understand the mechanisms of bonding between the herbicides and homoionic montmorillonites in suspensions the analysis of adsorption parameters with ionic properties was carried out. The overall relationship was poor, distinctly bringing about the difference in the nature of bonding in the case of different ions. In almost all the cases the ions fell into four distinct groups i.e., monovalent, divalent alkaline earth ions, transition 3d ions and trivalent and H.

4) Since metoxuron and tebuthiuron remained neutral in the pH range of clay suspension (5.5 to 6.4),

the ion-ion type of interactions due to protonation are not considered likely. The presence of -CO and $-NH_2$ groups on herbicide make dipole-dipole, H-bonding, ion-dipole or ion-induced dipole most probable.

5) In the case of monovalent and alkaline earth ions, electrostatic forces in the form of dipole-dipole interactions mediated through water molecules may be the main forms of bonding of metoxuron and tebuthiuron to clays. The unique grouping of transition metal ions point to the formation of coordination complexes. In the case of Fe- and Al-, charge, higher ion potential coupled with their stronger tendency for hydrolysis and formation of hydroxy bridges may be important in addition to electrostatic forces of attraction.

6) Apart from enthalpy considerations which go with various mechanisms of bonding, change in entropy during adsorption may also be very critical.

7) The amount of metoxuron/tebuthiuron adsorbed on homoionic clays was about 10 to 15 me/100 g which is much less than CEC of montmorillonites which indicates that these herbicides are adsorbed on the edges and do not penetrate the interlayer of crystal lattice.

8) From the analysis of adsorption parameters with various ionic properties for the adsorption metoxuron/ tebuthiuron on homoionic resins indicate that ion saturated resins also behave similarly to homoionic clays. However because of extensive organic network present on them the adsorption was much higher and involves Van der Waal's types of forces. The silicate, Aluminium hydroxy network of clays are fundamentally different from the organic network. Hence the effect of exchange cation may be overshadowed or suppressed.

9) Polymaleic Acid, a synthetic polymer resembling soil fulvic acid was prepared and analysed for functional groups, potentiometric and conductimetric titrations were carried out for the first time. These reflected the structural features similar to soil fulvic acid.

10) The interactions between PMA and homoionic montmorillonites were accomplished by studying the adsorption of PMA on homoionic montmorillonites. The extent of adsorption was much more than that of metoxuron or tebuthiuron. The effect of saturating cation was similar to that of metoxuron or tebuthiuron.

11) Ion potential or the polarizing power of cation is the most important for alkali and alkaline earth ions. The possible mechanisms of interactions

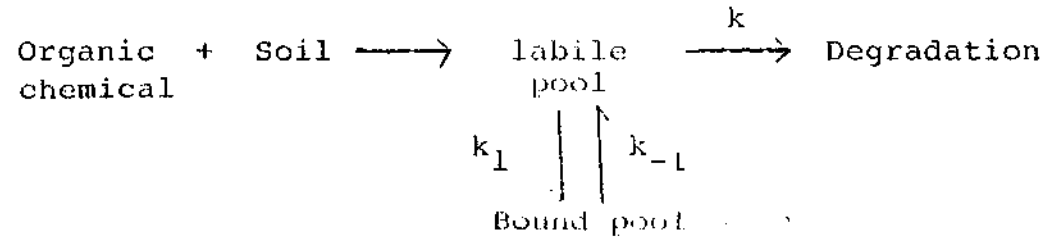
can be grouped as ion-dipole including cation-bridge, water bridge, ligand exchange, H-bonding and Van der Waal's forces.

12) The role of entropy generation was also shown to most important in the case of PMA adsorption, arising from dislodging of water molecules in the secondary and successively higher hydration shells around the exchange cation by the polymer molecules. The extent of adsorption of PMA does not rule out interlayer penetration.

13) From the studies on adsorption of metoxuron and tebuthiuron on model clay-organo complexes, it was found out that there was a consistent increase in the adsorption of both metoxuron and tebuthiuron on clay-PMA complexes as compared to pure metal clays. The alkali and alkaline earth ions which exert a weak bonding on organic chemicals and which adsorb less PMA than the trivalent ions like Fe- and Al- brought about larger increase in adsorption of herbicides when converted to their PMA complexes.

14) From the studies on the persistence of metoxuron and tebuthiuron in laboratory incubated soils under well defined conditions as affected by moisture and temperature, indicated that there are two distinct pathways for disappearance, a faster

one and a much slower one. The scheme of events that take place during the interaction of soil applied chemical can be pictured as



where k is the rate constant for degradation rate of chemical, k_1 for entry into bound pool and k_{-1} for reentry into labile pool. As a finer refinement, the rate of reentry of herbicide from bound pool was considered negligible compared to the other rates, over the time period understudy. Thus first order kinetics was used for the entry into bound pool and disappearance from labile pool. In both the soils at different moisture and temperature levels, these constants for metoxuron varied in the order

$$k > k_1 > k_{-1}$$

The rate of degradation was higher in alfisol compared to vertisol and increased with increase in temperature. The energy of activation was calculated for the rate constants and these values were lower than that reported in literature.

15) Specific rate of entry of tebuthiuron into bound pool was higher for vertisol than alfisol and

tended to decrease with decrease in soil moisture. The rate of degradation from labile pool was distinctly higher for higher soil moisture. The rate of entry into bound pool was higher for higher organic matter and clay content. The rate of degradation of tebuthiuron from labile pool was high at higher soil moisture levels in both the soils and followed the order Saturation > field capacity > 50 per cent field capacity. The rate of degradation was higher for alfisol as compared to vertisol.

16) Mainly two types of adsorption isotherms were obtained for adsorption of metoxuron and tebuthiuron on four soils, their 50 μ fractions (consisting of silt + clay) and Humic acid extracted from soil-1.

a) Isotherms exhibiting a tendency to reach saturation of surface.

b) Isotherms with an initial plateau followed by a steep rise.

The adsorption of metoxuron and tebuthiuron per g of adsorbent decreased in the order

Humic Acid > 50 μ fraction > 2 mm soil.

The adsorption for whole soil was lower than 50 μ fraction and Humic acid. This may be due to less specific surface area in 2 mm fraction as compared to the other two fractions.

SUMMARY

CHAPTER VI

SUMMARY

Use of herbicides has become an integral part of modern agricultural production. It has not only eliminated the drudgery of manual weed removal, but has assured stabilised yields and guaranteed income to farmers. Herbicides constitute 50 per cent of agricultural chemicals, although only 10 per cent of these chemicals are said to be used in developing countries. In India, the use of herbicides is picking up fast. Most of these herbicides are applied to the soil where they interact with soil constituents and the prevailing environmental factors. The adsorption of these chemicals with soil colloidal constituents i.e., clay and OM fractions is the most important factor in deciding the fate of these chemicals. Among the inorganic colloids expanding lattice minerals like montmorillonites are important in the interaction of these herbicides because of their large specific surface area and charge. In addition, the nature of cation on the exchange complex plays an important role in deciding the nature and extent of binding of herbicides.

The complexity of natural OM precludes clear understanding of interactions between the clays and

OM. Hence, model polymers like polymaleic acid were considered useful in getting more fundamental information about these interactions. Conventional methods of quantifying persistence through periodical analysis of samples is combersome and does not lead to unified concepts of possible precasts. The work initiated by Walker and coworkers to deduce simple mathematical models based on experiments with soils incubated in the laboratory under well defined conditions to predict pesticide residues under field conditions holds great promise.

The present investigation lays emphasis on the factors mentioned above, and experiments were carried out to 1) study in detail the adsorption of metoxuron and tebuthiuron, two urea herbicides on homoionic montmorillonites with a view of identify the mechanism of adsorption, 2) prepare and characterise PMA, as a model for soil FA and study its interaction with clays, 3) prepare model clay-organo complexes from montmorillonite and PMA and to evaluate its role in adsorption of metoxuron and tebuthiuron and 4) to quantify the persistence of metoxuron and tebuthiuron under well defined conditions in the laboratory.

The experiments conducted and the results obtained are summarised below :-

1) Clay samples (predominently montmorillonitic, obtained from Srirangapur clay deposit, A.P.) were fractionated to < 2 μ fraction. Homoionic montmorillonites were prepared by saturating suitable amounts of these fractions with 1N solutions of chlorides or nitrates of respective ions for 24 h and washing them free of excess ions with distilled water. These were resuspended in distilled water and used for adsorption studies. Homo cationic resins were prepared by equilibrating suitable amounts of IR-120 resin in similar manner and were shade dried. The cations chosen belonged to a wide range of properties with respect to charge, radius, ionic potential, ease of hydration, tendency for complexation etc. These could be grouped as trivalent - Fe- and Al-, divalent 3d ions- Cu, Ni, Co, and Zn- Alkaline earth ions- Ca- Ba-, Mg- and monovalent ions - NH_4-, K-, Na-, and H-. Adsorption studies were conducted by equilibrating clay suspensions (containing approximately 50 mg. of clay) with initial concentration of metoxuron/tebuthiuron ranging from 0 - 100 ug $ml.^{-1}$ and 0 - 200 $\mu g ml.^{-1}$ respectively; for 24 h at 27°C and centrifuged. The amount of metoxuron/tebuthiuron was determined in the supernatant at 240 nm and 254 nm respectively. Similar studies were conducted by equilibrating 100 mg. of ionic resins with 0 - 500 $\mu g\ ml.^{-1}$ of metoxuron/

tebuthiuron and the amount adsorbed calculated as explained earlier. Adsorption isotherms were constructed and the adsorption data was analysed by Freundlich equation and a new mathematical equation was employed as described by Saroja Raman (1981) for the analysis of S-shaped isotherms.

2) Model synthetic polymer - polymaleic acid resembling soil fulvic acid was prepared by the polymerisation of maleic anhydride in pyridine and washed free of excess pyridine with acetone and chloroform. It was characterised for functional groups. Potentimetric and conductimetric titrations were carried out for the first time and its interactions with homoionic montmorillonites were studied by conducting the adsorption experiments with initial concentration of PMA ranging from 0 - 100 µg m_L^{-1} as explained in the case of metoxuron/tebuthiuron. Similar studies were conducted by equilibrating 100 mg of homoionic resins with 0 -500 µg m_L^{-1} of PMA. Adsorption isotherms were constructed and the adsorption data was analysed by Freundlich equation and Langmuir equivalent was calculated.

3) Preliminary investigation was carried out to understand the role of clay-organo complexes in the adsorption of metoxuron and tebuthiuron. Model clay-PMA complexes were prepared by saturating homoionic

montmorillonites with PMA through adsorption. Metoxuron/ tebuthiuron was adsorbed from aqueous solutions containing 20 and 50 µg m_L^{-1} under identical conditions on homoionic montmorillonites and clay-PMA complexes.

4) The effect of moisture (saturation, field capacity, 50% field capacity) andtemperatures on the persistence of metoxuron and tebuthiuron was studied in an alfisol and vertisol. The soils treated with metoxuron and tebuthiuron at the rate of 20 µg g^{-1} soil were incubated from 0 - 155 days, they were sampled at intervals of 4 days for 40 days, at 8 days for 80 days, at 15 days till 125 days and at 30 days till 155 days. At each incubation interval, the soil samples were shaken successively with two 20 mL portions of methanol for 30 minutes and filtered. The amount of herbicide was assayed spectrophotometrically after correcting for soil blanks.

5) The adsorption studies were conducted by equilibrating 2 mm fractions, <50 µ fractions of four soils from Hyderabad and on humic acid extracted from one of the soils.

The experimental findings of the investigation carried out are summarised below :

1) Adsorption isotherms obtained for metoxuron (with the exception H-, Fe, and Al-) and tebuthiuron on homoionic montmorillonites were parabolic in nature with a S-shape character in the initial stages of adsorption indicating a stronger initial competition of water molecules to the clay surface as compared to herbicide.

2) The extent of adsorption was dependent largely on the valency and polarising power of exchange cation and followed the order trivalent > divalent > monovalent. H-montmorillonite being an exception. The transition metal ions had a much higher tendency for adsorption as compared to alkaline earth ions. The analysis of various adsorption parameters with ionic properties indicated a poor overall relationship between these two thereby distinctly bringing about the differences in the nature of binding in the case of different ions. In almost all the cases the ions fell into 4 groups i.e., monovalent, divalent, transition 3d ions and Fe- and Al-. Crystalline ion potential was found to be positively correlated to almost all the adsorption parameters for metoxuron and tebuthiuron mainly in the case of alkali and alkaline earth ions. Thus possible mechanisms of bonding include dipole dipole, ion-dipole, ion-induced dipole interactions. Since, metoxuron and tebuthiuron remain neutral in the pH range of clay suspension (5.5 - 6.4), the ion-

ion type of interactions due to protonation of the herbicide are not considered likely. Hence, the interaction may be assumed to be through the mediating effect of solvated water molecules, and these ions. The water molecules in the vicinity of these ions are in a highly polarised state and can result in dipole-dipole and hydrogen bonding. The unique grouping of transition metal ions and abnormally high variation in adsorption parameters point to the formation of co-ordination complexes. It is not easy to get direct evidence of complex formation in suspensions, where the cations are surrounded by water molecules. The unique variation in adsorption properties for these metal ions may be deemed as an indirect evidence for such an intimate interaction in suspensions also. In the case of Fe and Al charge, higher ion potential coupled with their strong tendency for hydrolysis and formation of OH bridges may be important inaddition to electrostatic forces of attraction.

3) Apart from enthalpy considerations, change in entropy during adsorption is also critical. The water molecules in the immediate vicinity of cations are highly perturbed and structured and the presence of organic molecules may induce effects opposing or reinforcing coulombic effects. Enthalpy and entropy

effects generally oppose each other, the overall free energy effect of cations which is the balance of entropy and enthalpy factors may not be strong and may be more difficult to percieve.

4) The amount of metoxuron, tebuthiuron adsorbed on homoionic montmorillonite was about 10 - 15 me/100g which is much less than the CEC of montmorillonite which indicate that these herbicides are adsorbed on the edges and do not penetrate the inter-layer of crystal lattice.

5) The analysis of adsorption parameters with ionic properties for adsorption of metoxuron/tebuthiuron on homoionic resins indicated that the ion saturated resins are more akin to ion saturated organic matter because of extensive organic network present on them. Hence, the effect of cations may be suppressed or over shadowed. The exchange cations are likely to be involved in similar types of bonding as in the case of montmorillonites.

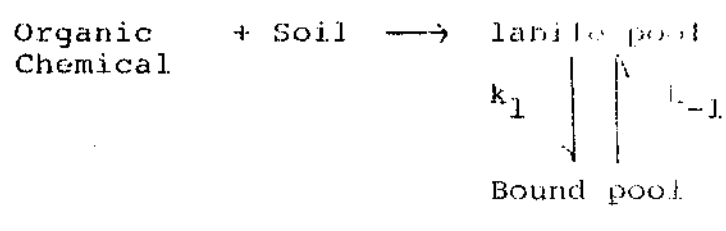
6) The characterisation of PMA for functional group analysis, the potentiometric and conductimetric titrations, carried out for the first time reflected the structural features similar to soil FA.

7) The interactions of PMA with homoionic clays, with the object of comparing the behaviour of better defined models with those of soil FA indicated that the extent of adsorption much higher than those observed on metoxuron and tebuthiuron. The possible mechanisms of interactions can be grouped as ion-dipole interactions including cation bridge, water bridge, ligand exchange, hydrogen bonding and Van der Waal's forces of attraction. Ion potential or the polarising power of cation is the most important for alkali and alkaline earth ions. The role of transition metal ions is unique and point to the formation of coordination complexes. For Fe- and Al-, hydrogen bonding may be possible. The role of entropy generation was also considered to be the most important in the case of polymer adsorption. The extent of adsorption does not rule out the interlayer penetration.

8) The studies on the adsorption of metoxuron and tebuthiuron on model clay-organo complexes was attempted for the first time to evaluate the role played by the naturally occuring clay-organo complexes in the adsorption of herbicides. There was a consistent increase in the adsorption of metoxuron and tebuthiuron on clay-PMA complexes over the corresponding metal clays. The alkaline and alkali earth ions which exert weak binding on organic compounds and which adsorb less PMA than trivalent ions like Fe & Al brought

about larger increase in adsorption of metoxuron and tebuthiuron when converted to their PMA complexes.

9) From the studies on the persistence of metoxuron and tebuthiuron in laboratory incubated soils under well defined conditions as affected by moisture and temperature, indicated that there are two distinct pathways for disappearance, a faster one and a much slower one. The scheme of events that take place during the interaction of organic-chemicals can be pictured as :



where k is the rate constant for the degradation of chemical, k_1 for entry into bound pool and k_{-1} for re-entry into labile pool. These were calculated from the first order kinetic plot. In both the soils at different temperature and moisture levels these constants varied in the order $k > k_1 > k_{-1}$. As a finer refinement, the rate of reentry of herbicide from bound pool was considered negligible compared to other rates. First order kinetics was used for entry into bound pool and disappearance from labile pool.

10) The rate of degradation was higher in alfisol as compared to vertisol and increased with increase

in temperature. The energy of activation was calculated from the rate constants and these values were lower than that reported in literature.

11) In the case of tebuthiuron, rate of entry into bound pool was higher for vertisol than for alfisol and tended to decrease with decrease in soil moisture. The rate of degradation from labile pool was distinctly higher for higher soil moisture in both the soils and followed the order saturation > field capacity > 50 per cent field capacity. The rate of degradation was higher for alfisol as compared to vertisol. The rate of entry into bound pool was higher for higher organic matter and clay content.

12) Mainly two types of adsorption isotherms were observed for adsorption of metoxuron and tebuthiuron on four soils, their 50 μ fractions (consisting of silt + clay) and Humic Acid (extracted from soil-1):- a) isotherms exhibiting a tendency to reach saturation of surface, b) Isotherms with an initial plateau followed by a steep rise.

The adsorption of metoxuron and tebuthiuron per g of adsorbent decreased in the order: Humic Acid> 50 μ fractions > 2 mm soil. The adsorption for whole soil was lower than for Humic and 50 μ fractions. This may be due to less specific surface area in 2 mm fraction and compared to the other fractions.

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* Original not seen.