STUDIES ON THE ADSORPTION OF MOLYBDENUM BY PURE FORM OF SOME SOIL CONSTITUENTS AND DIFFERENT TYPES OF SOIL

A THESIS SUBMITTED TO THE
BIDHAN CHANDRA KRISHI VISWAVIDYALAYA

FOR THE AWARD OF THE DEGREE OF
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1985

Dedicated

to

my beloved brother

'PRADIP'

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This is to certify that the work recorded in the thesis entitled "STUDIES ON THE ADSORPTION OF MOLYBDENUM BY PURE FORM OF SOME SOIL CONSTITUENTS AND DIFFERENT TYPES OF SOIL", for the award of the Degree of Doctor of Philosophy in Agricultural Chemistry and Soil Science of B. C. K. V. , is the faithful and bonafide research work carried out under my personnel supervision and guidance. The results of the investigation reported in the thesis have not so far been submitted for any other Degree or Diploma. The assistance and help received during the course of investigation have been duly acknowledged.

Biswanath Das.

(Biswanath Das)

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The Dated 25th Jan. 1985.

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CHAPTER -I

INTRODUCTION

1.1. General Introduction :

Molybdenum is an essential micronutrient element for plants, playing important role in nitrogen metabolism and atmospheric nitrogen fixation by bacteria. Striking variations exist in the plant availability of soil borne molybdenum. Application of molybdenum fertilizer in molybdenum deficient soil results dramatic increase in yield; on the other hand, excess molybdenum absorbed by plants results deleterious to the healthy ruminants, causing molybdenosis disease. These seemingly conflicting situations result from i) the relative ease with which the soluble molybdenum is absorbed by plants, ii) the comparatively low levels of the element that can be tolerated by ruminants and iii) the very pronounced influence of soil properties upon the availability of soil and fertilizer molybdenum to plants.

It is widely held that the adsorption of the element as molybdate ion ($HMoO_4^-$ or MoO_4^{-2}) in soil occurs through anion exchange, primarily with surface OH^- groups of soil materials. The adsorption reaction is dependent on the pH and iron oxide concentration in the soil and is accompanied by an increase in pH upon the addition of molybdate in solution to soil suspension (Borsad *et al.* 1951, Jones 1957).

Variable change minerals, such as iron and aluminium oxides are important in the reaction of many ions with soil. Anions are strongly adsorbed by these compounds. The adsorption of anions by iron and aluminium sesquioxide components is an important phenomena in soil system. In the tropical and sub-tropical areas, where many soils contain significant amount of hydrous iron oxides and aluminium hydroxides, severe deficiencies of phosphate, sulphate and molybdate in plants have been observed. Several workers have used iron and aluminium oxides with well defined surfaces to study ion adsorption. This has stimulated much further research and has led to the development of a general model for ion adsorption on hydrous oxides surfaces which takes account of the pH dependent charge on the surface and the charge of the adsorbing ion. (Bowden _et_ _al_. 1977).

Formation of precipitated form of $AlPO_4$ and $FePO_4$ is also known in soil in the reaction of phosphate with the ions of Fe and Al in solution or in adsorbed phase. These precipitated forms of $AlPO_4$ and $FePO_4$, may also contribute surface for adsorption of molybdate on it.

From the agricultural and environmental stand points, the need for understanding, factors of ion partition across solid-liquid interfaces is of great importance. Nutrient cations and anions held on the soil surfaces as exchangeable ions, reach the plant root zone through the soil solution by exchange phenomena, The ions of the soil solution is always at equilibrium with the exchangeable ions on the solid phase.

An adsorption isotherm describes the equilibrium relationship between the amounts of adsorbed and desorbed species at a given temperature. The adsorption equations developed by Freundlich and Langmuir to quantitatively described the gas adsorption by solids have been used with some success in solid-liquid systems and the determination of adsorption isotherm is also one of the most useful experimental procedures in the study of interaction of anions with hydrous oxides, clays and soils.

Molybdate sorption on soil has been used as an index of a soil's potential for decreasing the availability of molybdenum to plants (Wells 1956, Barrow and Spencer 1971). The behaviour of the labile nutrient ion in soil is dominated by the sorption and desorption processes. An index for general characterization of the phosphate or molybdate relationship of soils, should therefore reflect their sorption properties. To realistically measure, the capacity of a soil to sorb fertilizer molybdenum, sorption characteristics should be analysed at low equilibrium concentration of molybdenum. Sorption sites on soil particle surfaces undoubtedly exhibit a wide range of affinities for Mo. A portion of the sorbed molybdenum become unavailable to the plant, while the remainder is in equilibrium with the soil solution.

The rate of desorption of an adsorbed anion will give an indication of the energy of adsorption. The amount desorbed and the mechanism of desorption is relevant to the uptake of nutrients by plants. The availability of nutrient anion is dependent on the characteristics of desorption isotherm. Crank showed (1956) that diffusion coefficient of the ions which react with the adsorbent are related to the slope adsorption isotherm.

Considering the Langmuir's parameter like adsorption maxima, the relative bonding energy one can predict the nature of adsorption reaction. From the Langmuir intercept, the K-value or equilibrium constant, related to bonding energy can be computed. With the help of the various thermodynamic constants computed from the Langmuir isotherm, the nature of adsorption can be ascertained. Adsorption curve in association with desorption curve will give an indication about the strength of adsorption and behaviour of the adsorbed anion in soil system.

Competition is a very common phenomena in nature. Competitive adsorption is of interest in relation to solute transpart in soil, because adsorption has a profound influence on the movement of chemicals. In acid soils, three plant nutrient anions - phosphate, sulphate and molybdate may be adsorbed by mineral surface. The availability for each of these anions is much affected by this competition for adsorption. When comparing adsorption of anions by soils, it is convenient if the reaction of the anion with a given soil can be characterised by a single value such as for example the adsorption maxima, calculated from the Langmuir Curve. The comparison can also be done by considering the single value characteristics, obtained from the adsorption at particular equilibrium concentration, e.g. for molybdate it is 0.1 ppm, for phosphate it is 0.2 or 0.5 ppm. From the comparison, the relative ease of desorption by addition of another anion can be ascertained.

Adsorption - desorption isotherms along with the various thermodynamic constants, are the useful tools for assessing the nature of adsorption reaction, release of the adsorbed anion, possible deficiency of the applied nutrient anion or in more detail for assessing the fertilizer requirement and it's fate in a particular soil. Similar studies with various soil constituents in pure form have been found to be of much help in avoiding ambiguity in interpreting the results of study with the heterogeneous soil systems.

1.2. Scope and objective of the present investigation:

Anionic nutrient ions like phosphate and molybdate participate in various soil-chemical reactions and are found to maintain a solution concentration at equilibrium between the solid surface and soil solution. Heterogeneous nature of soil having different state of energy level makes the assessment of the nature of involved reactions, a difficult problem possible interpretations in this regard are also likely to be ambiguous. Under such conditions the importance of the study of adsorption is obvious so far as immobilization, mobilization, deficiency and toxicity of nutrients ion are concerned. Soil scientists have tried to do the same under a lot of limiting conditions.

Adsorption isotherm study is an important tool, which can tell, to some extent, the nature of the adsorption reaction. But most obligation arises, in using Langmuir equation for assessing the adsorption isotherm is the hetero-energy state of the soil surface. Even though every body is using this equation as because, it will give some useful information like bonding energy, adsorption maxima, change in the free energy, enthalp~~h~~y and entrop~~h~~y of the reaction.

Various workers have tried to fit Langmuir equation by using hetero surface adsorbent. They have over come the problems by some approximation.

In the present investigation Langmuir equation has been used for computation of the adsorption data.

Molybdate anion, which is an important micronutrient element of the plants, goes through lot of chemical reactions in soil, at the same time deficient to the plants as well as toxic to the ruminants. So assessment of the reaction, in order to quantify the fertilizer requirement, is essential. So for this, it needs much more idea regarding its nature of transformation and diffusion in soil system.

As because, the adsorption sites for molybdate, are mainly the hydrous oxides of Fe and Al, and their coatings on soil and clay surfaces, the experiments were carried out on the precipitated form of pure Fe and Al hydroxides gel. On the other hand the more or less similar behaviour of the phosphate and molybdate in soil reaction particularly in acid soils, there may be some possible sites for molybdate on Fe and Al phosphates. Al- and Fe phosphates are the likely product of the acid soil, on application of phosphatic fertilizers as reported by Bache and others (1963). Their chemical nature exhibit some sort of exchange reaction with other anions similar to phosphate. So molybdate, more or less similar to phosphate can go through adsorption or exchange reaction on the precipitated form of Al and Fe phosphate. Accordingly, in the present investigation, adsorption of molybdate on Fe and Al phosphates as adsorbent has been considered.

Calcium carbonate is an important soil constituents of the calcarious soil, as well as used as soil amendment, may contribute surface area for anion adsorption. As literature reveals that phosphate adsorption study on calcite but with little study for other anion adsorption. In the present investigation it is taken as an adsorbent for molybdate adsorption.

Rock phosphate, a product of geo-chemical reaction, also used as fertilizer may take part in the adsorption of of molybdate in soil. The similar behaviour of phosphate and molybdate, in acid solution may result some adsorption of molybdate on the surface of rock phosphate. Keeping this view, the rock phosphate of 80 mesh size was taken as adsorbent for the study.

Adsorption experiments carried out on pure compounds were expected to give an idea, which may be consistent with the results of the soil adsorption study, particularly in soils, where the particular constituent is dominant. By simple comparison, it would be easy to interprete the dominant adsorption sites of the soil. In the present investigation all the pure compounds used for adsorbent are of precipitated form except $CaCO_3$ and rock phosphate. Precipitated form of pure compounds are selected, keeping in view that in the natural soil system the compounds are the likely product of various soil-chemical reaction, where at the initial stage precipitation is the major reaction product.

Clays, the most reactive component of the soil systems were also taken as important adsorbents on which the detailed study was done. Two reference clays, Kaolinite and Bentonite were taken with saturated cations of H, Al, Fe and Ca. On the homoionic clays the adsorption experiments were carried out under two level of pH of the system. The major cations controlling the soil reactions are Fe, Al, Ca, H, Na and K, out of which, as literature reveals, Fe, Al, Ca and

H are important so far as the adsorption of molybdate ion is concerned. As anion adsorption is a pH dependent phenomena, two levels of pH were selected for comparison and in order to assess its influence, particularly on the adsorption in homoionic clays.

In order to assess the nature of molybdate adsorption on soils adsorption isotherm, studies were undertaken with different soils - native, organic matter free and free from oxides of ion and aluminium.

Different workers have used higher concentrations of molybdenum in the adsorption study. In order to avoid possible polymerization of molybdate ions, the experiments were carried out at a concentration lower than $3x10^{-4}M$ where no polymerization is likely to occur. While selecting the concentration range, the concentration of molybdenum in soil solution was also taken into consideration, in order to make consistent the possible interpretation with the natural system.

In order to study the influence of temperature, particularly for assessing the physical or chemical nature of sorption, the experiments were carried out at two isotherm conditions. Study of isotherm at two temperature levels, 20° and $40^{\circ}C$ ($\pm 1^{\circ}$) was undertaken in order to find out changes in enthalpy and entrophy of the adsorption reaction which can be computed from the equilibrium constant, calculated from the Langmuir intercept.

Adsorption-desorption isotherm studies in association were expected to provide the hysterosis of the curves, which in turn, would indicate the reversibility and irreversibility of the adsorption reaction. The nature of desorption curves and the relative bonding energy values can also reflect their conformity of the release curves of the adsorption.

For determination of actual sha-King time required for reaching equilibrium condition in respect of adsorption a set of experiment was also conducted in order to avoid conflicting reports on the subject.

As phosphate and molybdate ions are very similar in their behaviour in the soil system, so far as adsorption phenomena is concerned, competition of adsorption between these two anions is expected. With this view the present investigation considers one experiment on co-adsorption of molybdate and phosphate from the solution on different soils. The comparisons were being made, considering the adsorption of molybdate and phosphate at 0.1 ppm and 0.5 ppm equilibrium concentration respectively.

Most of the works carried out so far, regarding anion adsorption were confined among phosphate and sulphate with little study of molybdate. Keeping in view that the scanty study of molybdate adsorption on Indian soils and on homoionic clays, the present investigation were undertaken.

With a view to get some new information on the adsorption of molybdate, the present investigation considered the adsorption studies on the precipitated form of strengite, variscite, $CaCO_3$ and rock phosphate.

CHAPTER - II

REVIEW OF LITERATURE

2.1. Soil chemistry of Molybdenum :

Molybdenum is a curious element, chemically in that its properties are very different from those of its near neighbouring in the periodic Table. The Mo content in the lithosphere is estimated at 2.3 ppm, which provides $10^{-3.68}$(M), if it were to dissolve completely in the soil solution at 10% moisture. It has been estimated by Chatterjee and Dakshinamorthy (1962) that the total Mo content of Indian soils ranges from 0.6 to 1.34 ppm of which, available amount is from 0.012 to 0.34 ppm.

Amin and Joham (1958) reported that oxides of both Mo and Mn react as acids or bases depending upon their valence. Oxides of the same metal react more acidic as the valence or positive oxidation state of the metal increases and conversely more basic as it decreases. MoO_3 in which the metal is hexavalent acts as an acidic oxide and readily combines with the oxides of Na, Mg and K, to form soluble molybdates. MoO_2 and hemi penta oxide, on the other hand, act as bases and are quite insoluble in alkaline solution. So, oxidation process in soil would tend to make Mo more available and conversely reduction process less so.

2.1.1. Anionic nature of Molybdenum : - In its compounds, Mo exhibits many oxidation states. The lower valency (+4) is practically limited to the most abundant Mo minerals. The chemistry of Mo in near surface environment is a chemistry of its anions. Solubilities of different Mo containing minerals estimated by Vlek and Lindsay (1977) show a general decrease in the order, Cu $MoO_4 >$ Zn $MoO_4 > MoO_3 >$ H $MoO_4 >$ $CaMoO_4 >$ Pb MoO_4.

They also estimated the solubility of Mo from soil by the following equation.

$$\text{Soil-Mo} \rightleftharpoons MoO_4^{=} + 0.8H^+$$
$$[\ \log K^o = -12.4\ ]$$

The expression for solubility of molybdates in soils covers the pH range of 5.3 to 8.0.

The chemistry of molybdates is complex because of polymer formation in solution. It is generally accepted that basic solution of molybdate contains only simple tetrahedral $MoO_4^{=}$ ions. Upon acidification, two reactions occur. First the molybdate ions become protonated forming monomeric H MoO_4^- and H_2MoO_4 and after protonation, condensation begins forming a series of iso or hetropoly molybdates. However recent research has shown that concentration affects polymer formation so that polymeric forms do not exist in solution having a Mo (VI) concentration less than 10^{-4}M [Averton et al.(1963), Chojnacki (1963), Jenkin (1963) Rohwer (1955)]. Lavy (1964) studied the saturation extracts of several Indian soils, in which the concentration of Mo varied from 2 to 8×10^{-8}M; hence polymeric form would not exists in such soil solution.

The literature reveals, however, that the exact form(s) of the acid condensation product remains in considerable doubt. According to Scharqzenbach and Meir (1958), an intermediate monomeric form of molybdate in acidic solution is Mo $(OH)_6$ or $MoO_3.3H_2O$. This form an easily polymerize by forming an oxobridge with the elimination of water. Carpeni (1947) further concluded that only monomeric molybdate ions exist in solution of less than $3x10^{-4}M$ MoO_3 i.e. approximately 29 ppm Mo at all pH values.

The form of Mo in solution varies with pH. Rohwer _et al_ (1964) found that most of the Mo was present as unionised Mo $(OH)_6$ at pH-2.5. Chojnacki (1963) reported that in very dilute solution ($10^{-5}M$ to $10^{-8}M$), $MoO_4^{=}$, $HMoO_4^{-}$, disappear add cationic forms appear. From pH 2.5 to 4.5, the species in solution generally decrease in the order.

$$MoO_4^{=} > HMoO_4^{-} > H_2MoO_4^{\circ} > MoO_2(OH)^{+} > MoO_2^{++}$$

Since most of the soils have a pH above 5.0, the $MoO_4^{=}$ would be the predominant form in soil. The available evidences also indicate that only monomeric forms would be adsorbed (Reyes _et al_. 1967, Barrow 1970), from solutions on the soil colloids.

2.1.2. Reactions of Molybdenum in Soil : - Mo exists in combination with both the organic and inorganic fractions of soil (Davies 1956). Wells (1956) found that iron stone nodules of Newzealand soils contained as much as 10 ppm of

Mo, whereas nodules contained less than 1 ppm, which suggests a strong affinity of Mo by iron and its compounds. Evidence of the greater affinity of Mo for Fe_2O_3, xH_2O than Al_2O_3, xH_2O has been reported by Jones (1957).

The availability of Mo to plants is closely related to the kinds and amount of Fe compounds in soil has been shown by Williams and Moore (1952), Rabinson and Edington (1948), Wells (1956) and others.

Several workers have shown that -

i) the amount of Mo sorbed by soils, clays and the hydrous oxides decreases with increasing pH to about 7.5, above which no sorption virtually takes place;

ii) The amount sorbed Mo, increases with successive increments of $MoO_4^=$ added in soil;

iii) The sorption of $MoO_4^=$ ions by soil colloids results in an increase in the pH of the system;

iv) The precipitates of Ferric-molybdates, have minimum solubility at pH 2.7, in contrast to Al-molybdates having minimum solubility at pH 4.8.

The nature of the products formed on sorption of molybdates by Fe_2O_3, xH_2O was investigated by Reimenaur *et al.* (1962) by quantitative determination of the release of OH^- and water. The equation of the reaction involved may be written.

$$Fe_2O_3 + 3H_2O \rightleftharpoons 2\,Fe\,(OH)_3$$

$$2Fe(OH)_3 + 3Na_2MoO_4 + 6\,HCl \rightleftharpoons Fe_2\,(MoO_4)_3 + 6\,NaCl + 6H_2O.$$

Schlichting (1960) reported that there was a close relationship between the reserve Fe and of 'P' or 'Mo' in soils containing bog iron.

Trobisch *et al*. (1963) reported that there was a close relationship between the amount of Mo and soluble iron in soil; low amount of Fe-extracted with oxalate of low concentration or with EDTA, were accompanied by low amount of Mo.

Results suggest that Mo is fixed by Fe in soil by way of sorption and/or formation of crystalline compounds of the two.

Jorrel and Dowson (1978) reported that Fe-oxides which are extracted with $(NH_4)_2\,C_2O_4$, at pH 3.3 can be considered to play the major role in Mo sorption.

2.2. Adsorption of Molybdenum :-

In the recent years there has been an increasing volume of literature dealing with the topic of anion adsorption by soils and soil materials, including the Fe and Al sesqui oxide components. Posnor, Qurick and Co-Workers (1971) have used Iron and Aluminium Oxides with well defined surface of study the ion adsorption. This has stimulated much further research and has led to the development of a general model for ion adsorption on hydrous oxide surfaces, which takes account of the pH dependent charge on the surface and the charge of the adsorbing ion (Bowden *et al*.1977). It has become apparent that the adsorption behaviour of many anions, in particular the important nutrients phosphate, sulphate and molybdate is very similar (Barrow 1970). In the following discussions an attempt has been made to review the works with soil, clay minerals and various soil components including the hydrous oxides of Iron and Aluminium with particular reference to adsorption behaviour, various models and mechanism of adsorption of molybdates from solution.

2.2.1 Techniques for the study of Adsorption :-

There are different techniques of study the adsorption reactions of anions. They are as follows :-

a) Infrared spectroscopy,
b) Kinetic study,
and c) Adsorption isotherm.

Infrared spectroscopy can be used to study both the nature of the adsorbing surface and the mechanism of adsorption, on these surface. (Little 1966 and Hair 1967). Information on the co-ordination of anions to surfaces and their mechanism of adsorption can be obtained by comparing their spectra of OH- groups and OD groups before and after anion exchange.

A study of the Kinetics of anion adsorption can be used to gain information about the mechanism of adsorption reaction. The data are usually presented to show the change in adsorption with time or the change in concentration with time. A study of the effect of pH, temperature or the successive addition of anions may give further useful information about reaction mechanisms or rate limiting steps but it is very difficult to interpret kinetic data without some reasonable theory. The studies of kinetics of isotopic exchange led Atkinson *et.al.*(1972) to postulate that phosphate formed a bridging complex on Goethite. Mattingly (1975), have got useful information about the nature of labile phosphate in soils.

The third technique, study of adsorption isotherm, being more versatile and more frequently used one is discussed in greater detail in the next section.

2.2.2. Adsorption Isotherms :

Theoretical consideration :- The relationship between the amount adsorbed of an absorbate by an adsorbent and pressure (concentration) of the adsorbate at constant temperature is called adsorption isotherm. This variation of adsorption with concentration (pressure) is often expressed as

$$\frac{x}{m} = K.P^{1/n}$$

Where xg of adsorbate is adsorped by mg of adsorbent at pressure P., so that $^x/_m$ denotes the amount of adsorbate per unit weight of adsorbent. The terms K and n are constants, depending upon the nature of adsorbate and adsorbent; n is always greater than unity, meaning that adsorption does not increase as the pressure. Taking the logarithm of both sides,

$$\log {}^x/_m = \log K + {}^1/_n \log P.$$

This is the equation for Freundlich adsorption isotherm. The graphical representation of log $^x/_m$ against log P, should give a straight line. But practically at low temperature there is deviation from this linearity and the equation is considered to be an approximate one, and is suitable for small ranges of pressure concentration.

In 1916 Langmuir deduced an adsorption equation. According to the Langmuir model, the fraction 'Θ' of the surface of an adsorbent covered by an adsorbate is given by

$$\Theta = \frac{KC}{1 + KC}$$

Where C = equilibrium concentration of the adsorbate and K is the constant related to the adsorption energy. Again, $\Theta = {}^{x/m}/_{xm}$, where xm is the sorption maxima and x/m is the amount of ion adsorbed per unit weight of the adsorbent.

On considering the above two relationship the adsopption equation may be written in linear form

$C/_{x/m} = C/_{xm} + \frac{1}{Kxm}$ and a plot $C/_{x/m}$ against C should give a straight line of slope $1/xm$ from which x/m may be calculated and the constant K is obtained from intercept.

The Temkin equation can be derived from the Langmuir equation (Bache and William 1971) by inserting the condition that the energy of adsorption decreases linearly with increasing surface coverage. The equation is :

$$x/_{xm} = \frac{RT}{b} \ln AC$$

where A and b are constants. A plot of X against log C should give a straight line.

2.2.3. Adsorption isotherm - its application and limitation to soil system:

The adsorption equations developed by Freundlich and Langmuir to quantitatively described gas adsorption by solids have been used with some success in solid-liquid system, even though no rigorous theoretical treatment has been developed for the latter system.

Although Freundlich equation is often considered to be purely empirical in nature, a justification for its application to adsorption from dilute solution has been presented by Kipling (1965). As pointed out by many investigators a major advantage of the Langmuir equation is that it is possible to calculate an adsorption maxima and a relative bonding energy term for adsorption of adsorbate.

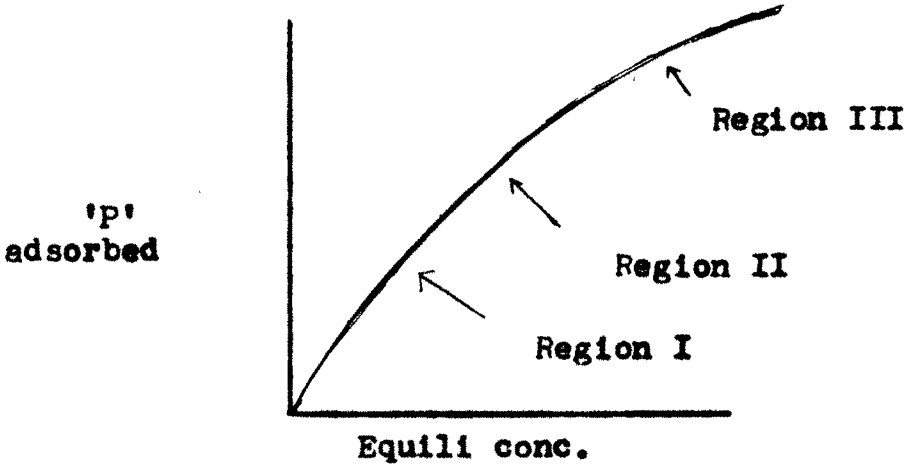
The determination of adsorption isotherm is one of the most useful experimental procedures in the study of the interaction of anions with hydrous oxides or soils. Most of the adsorption isotherm reported in the literature belong either High-affinity type as defined by Gibbs el al. (1960) or Langmuir type.

In the Langmuir model derived for the adsorption of gases on the solid surfaces, it is assumed that the adsorption is restricted to a monolayer and the energy of adsorption does not vary with surface coverage. Thus the sites must be isolated and uniform and the adsorbed molecules must not interact with each other.

Over wider concentration ranges (Bache and Williams 1971) the adsorption plots were however curved. This curvature indicates that the bonding energy is not in fact constant and that there is no well defined maximum. The Longmuir equation can nevertheless be used to characterize the sorption over limited concentration ranges.

The failure of the simple Langmuir model to describe anion adsorption at solid solution interfaces has led to the use of two or three term Langmuir equations which give much better description of experimental data (Muljadi et al. 1966a, Holford et al.1974, Rajon 1975 C, Rayden et al. 1977b).

While describing the two or three surface adsorption isotherms, Muljadi et al.(1966) reported that the adsorption isotherms have been devided into three destinct regions. It was suggested that these were related to the affinity of phosphate for at least 3 energetically different reactive sites. It was suggested that under the condition in the adsorption experiments; where the concentration of phosphate was reduced drastically, the adsorbed phosphate may undergo a phase change. The true irreversibility is considered to exists only if the isotherm lies on y-axis. If the isotherm is dependent of time and does not lie on y-axis, then each point of region I, II and III of the isotherm should be microscopically reversible with respect to concentration.



Argument based on the thermodynamic reversibility should therefore be applicable to both adsorption and desorption limbs when considered separately. This suggests the existence in each soil of two or more populations of sites which have a widely differing affinity for adsorbing anions. As a consequence equation (Langmuir) may be rewritten as follows for two population of sites.

$$x/m = \frac{K_1{}^{II}K_2{}^{II}C}{1 + K_1{}^{I}C} + \frac{K_1{}^{II}K_2{}^{II}C}{1 + K_1{}^{II}C}$$

where K_2 = y-intercept and K_1 is the gradient^{-1}, I and II referring to Part I (straight line for lower C value) and Part II (straight line corresponding to higher C value), respectively.

Syers et al.(1973) reported that it can be shown that the equilibrium phosphate concentration at which the straight line intersect (breaks) are inversely related to the ability of the soil to sorb added inorganic phosphate.

Holford et.al.(1974) used the method of least square for calculation of bonding energy for two different regions. For this they have used the Rathamsted Maximum Likelyhood computer programme, developed by Ross (1973).

Attempts to use the Langmuir equation for phosphate adsorption on synthetic goethite have not been *successful*

(Bowden *et al.*1974), although synthetic goethite crystals have only one site available for anion adsorption (Parfitt *et al.*1976). Bowden *et al.*(1977) also reported that the Langmuir model is also inadequate when adsorption condition such as pH or salt concentration are changed, because the factors effect both Km and K.

Hartel *et al.*(1977) reported that the deviation of Langmuir equation in the soil system is due to the concommitant desorption of another species. When a second species is desorbed, reaction of the adsorbate with the surface will be altered depending upon the concentration at equilibrium C_2, they developed the equation

$$\frac{C_1/C_2}{(x/m)_1} = \frac{b_2}{b_1K_1} + \frac{1}{K}\;{}^{C_1}/_{C_2}$$

According to them it is familiar liner form. But difficulty arises in the estimation of C_2, which is very very low enough and many reactions are not sufficiently characterized to even know what ions are being replaced.

The Langmuir equation has been preferred to the Freundlich equation because its parameters have physicochemical significance, representing the extensive (adsorption capacity) and intensive (affinity) properties of the adsorbent for the adsorbate. However Adamson (1967) has suggested that the Freundlich parameters may be roughly interpreted in the same way. Fitter and Sutton (1975), apparently regarded the exponent as an extensive property when correlating the exponent with exchangable Ca or Al. Apparently there is some confusion in how to interpret the Freundlich parameters and perhaps as a consequence of this, there have been few attempts to demonstrate their utility in soil adsorption studies (Fitter and Suttan 1975, Barrow 1980).

Unfortunately some of the research applying the Langmuir equation to soil phosphate was vitiated by failure to recognize the limitation of the Langmuir equation (Holford _et al._ 1974) and by exclusion of native adsorbed phosphate from adsorption measurement. (Holford 1980).

The two surface Langmuir equation gives a meaningful estimates of phosphate adsorption capacity (Holford 1974), which is under estimated by simple Langmuir equation. Holford and Mattingly (1976) have got the significance of the affinity parameter in the uptake of labile phosphate or the release of adsorbed phosphate. It has been found that the release is decreased with increasing value of parameter.

The Langmuir equation may be used to provide a single sorption characteristic sorptivity from the product of the two constants. This parameter which is maximum slope of the sorption isotherm, as solution concentration tends to zero, is an excellent index of potential immobilization or unavailability of labile phosphate in soil (Holford 1974).

2.2.4. Free energy change in Adsorption from equilibrium constants :

The chomical reactions proceed until the free energy of such a system reaches a minimum, then the system is at equilibrium. The standard free energy change of reaction is related to the equilibrium constant of that reaction by the relationship.

$$\Delta G_r^o = - RT\ln K^o$$

where K^o is the activity equilibrium constant and T the absolute temperature.

The transfer of a solute from a solution phase to solid is a heterogenous reaction, which may be treated in terms of the changes in "Gibb's free energy" or "useful energy" involved (Alexandar and Johnson 1949). At equilibrium the standard free energy of the reaction ΔG^o is given by

$$\Delta G^o = -RT \ln \left(\frac{a_{solid}}{a_{solution}}\right)$$, where 'a' indicates the activity of the solute in the phase indicated and

$$\frac{a_{solid}}{a_{solution}} = K ,$$

Where K is the equilibrium constant for the reaction. The activity of the solute in the solid (surface) phase is normally measured in terms of moles of sorbed solute per unit surface area, but it is unlikely that the phosphate sorbed on to sexquioxide surface will all remain in equilibrium with solution and the measurement of the amount of surface phosphate by isotopic exchange would be a better estimate. However the figures of the total solid phosphate sorbed by one mineral (surface area constant) can be combined with the total phosphate concentration (activity coefficient are constant at constant ionic strength used), to give an approximate functions of the sorption energy

$$\triangle G' = \log_{10} \frac{P_{sorbed}}{P_{in\ solution}}$$

It is reported by Alexandar and Johnson (1949), that $\triangle G'$ is not constant but varies with the solute present. It is suggested that solid phase component of the reaction is not likely to be constant. However, this free energy function may provide a valuable method for characterizing the solid solution system.

K, the equilibrium constant can be estimated from the intercept and the adsorption maxima of the Langmuir curve. The value of K, obtained from Langmuir curve can also be directly computed by using the relationship -

$K = \frac{\theta}{C(1-\theta)}$ where θ is the fraction of surface covered and C is the equilibrium concentration. Value of θ is obtained as the ratio of amount adsorbed/maximum adsorption.

Enthalpy of adsorption ($\triangle H^o$) can be calculated from the value of K at two different temperatures with the help of Causius-Clayeyrou equation.

$$\text{Log} \left[\frac{C_2}{C_1} \right]_0 = - \frac{\Delta H^\circ}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where C_1 and C_2 are the equilibrium concentration at T_1 and T_2 respectively.

The above equation can be written in the following form

$$\log \frac{K_1}{K_2} = \frac{-\Delta H^\circ}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Entropy change (ΔS°) can be calculated from

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ.$$

Rayden et al(1977b) have used the approach to calculate ΔG° for three regions of isotherm for phosphate adsorption. In this approach the free energy of adsorption (ΔG ads) is separated in to three component. ΔG coul, the coulombic component and ΔG int, the interaction component, ΔG chem - the chemical component, thus,

$$\Delta G \text{ ads} = \Delta G \text{ coul} + \Delta G \text{ chem} + \Delta G \text{ int}$$

In different ions such as nitrate are adsorbed only on positively charged surfaces and ΔG coul is significant but ΔG chem is low. If an ion is adsorbed out of proportion to its activity in solution because of the size and polarizability of the ion, ΔG int is also important. Potential determining ions and ligand exbhange ion can be adsorbed on a surface of like charge or zero charge and ΔG chem is significant.

2.2.5. Importance of Adsorption isotherm study in soil system:

Soil systems due to its heterogenous characteristics can undergo a lot of reactions. Adsorption isotherm can sometimes be used to give an indication of different types of such reaction as well as the nature of adsorption. The shape of the adsorption isotherm having three distinct regions, suggesting that there are three different adsorption mechanisms (Parfitt et al. 1977a). For phosphate adsorption Ryden et al. (1977a) used five Langmuir equations which then were reduced to three equations by successive approximation thus dividing the isotherm into three regions. The nature of adsorption in region I and II is largely chemical, where as physical adsorption may occur in region III. Rajon (1976) and Parfitt et al.(1976) suggested that OH_2^+ and OH^- participate in exchange reaction with phosphate in region I and II.

The behaviour of labile inorganic phosphate in soil is dominated by sorption and desorption processes. The slope of the sorption isotherm expresses the buffer capacity of the soil with respect to phosphate (Mattingly 1965).

Ozanne and Shaw (1968) used phosphate sorption curves to estimate the amount of P required for wheat. They also reported that when the values of 'P' are plotted against log 'P', a straight line is obtained. The slope of the curve gives the information about the 'P' buffering capacity of the soil.

Wild (1967) reported that the intercept at zero phosphate sorption is an estimate of the amount of phosphate in soil solution, which is related to plant growth than'P' potential.

Fox and Kamprath (1970) also used the sorption isotherm for evaluating the phosphate requirement of soil.

Bache and William (1971) have tried to deduce lot of sorption indices which may be necessary for the evaluation of plant nutrient status of the soil.

Wells (1956) and Barrow and spencer (1971) reported that Mo sorption on soil can be used as an index of a soil's potential for decreasing the availability of Mo. Jarrel and Dowson (1978) reported that Mo added to soil as fertilizer will be relatively less available to plants in soils which sorb relatively high amount of Molybdenum.

Moody (1979) reported that 'P' sorbed at a particular supernatant solution 'P' concentration should be a function of PBC (Phosphate Buffering Capacity) of the soils at the concentration and the 'P' status of the soil.

Bache and Williams (1971) developed a single point 'P' sorption index which was highly correlated with PBC, at various supernatant solution 'P' concentration of a range of soils.

2.2.6. Desorption isotherm study - its importance in soil system.

Desorption of the adsorbed ions is an important study, in characterizing the adsorption phenomena in soil system. The rate of desorption of an adsorbed anion will give an indication of the energy of adsorption. The desorption of adsorbed anion from the soil exchange complex is generally studied because the amount of desorption and the mechanism of desorption is relevant to uptake of neutrients by plants. Crank (1956) has shown that diffusion coefficient of ions which react with adsorbent are related to the slope of the adsorption isotherm and this has been elaborated by Nye (1966) with respect to ion movements in soil. Clearly, the desorption study is relevant to isotherm rather than the adsorption, so that any meaningful analysis of ion transport must take into account.

Hingston _et al_.(1974) were able to show that small amounts of phosphate could be desorbed from Goethite, where as fluride could be desorbed completely.

The desorption of OH^- ions during anion adsorption has also been studied but it is usually difficult to interpret these results unambiguously (Rajon 1975).

Ray and Das (1974) reported that desorption isotherms can reflect the hysterisis, which highlight irreversibility or reversibility of adsorbed ion with respect to ionic concentration in solution.

2.2.7. Influence of different factors in attaining equilibrium condition in adsorption study of soils :-

i) Ionic strength of the medium :- In the study of adsorption, several supporting media have been used but the rationalisation for the choice of the media has rarely been justified. Schefield (1955) suggested the use of 0.01 M $CaCl_2$ on the basis that cation exchange is minimised by the use of Ca^{+2} and at this concentration Ca^{+2} has no specific replacing power. This support medium has been used subsequently in numerous studies (White and Beckett 1964; Taylor and Kunerh 1971). Other support media have included KCl (Mattson et al.1950), NaCl (Syers et al. 1970), distilled water containing phosphate and associated cations (Shapiro and Fried 1959).

According to Volkweiss et al.(1973) and Barrow (1972) the use of support medium should be selected on the concepts of solubility of the adsorbent compounds.

Ryden and Syers (1975) suggests that if an equilibrium condition is to be attained, the support medium is of practical and not theoretical concern. Where a rapid reaction rate desirable, a support medium of high ionic strength and containing a divalent cation is desirable. They added that to avoid high concentration of divalent cations and the possible precipitation of sparingly soluble phosphate, in such systems at high 'P' concentration, however, a support medium containing cations of soluble phosphate may be preferred (e.g. 0.01M NaCl).

Ryden and Syers (1977) also reported that in three surface adsorption reaction the sorption maxima for Region I and II were virtually independent of matrix solution used. The sorption maxima for Region III however, was markedly dependent on the matrix solution.

Singh and Tabatabai (1977) reported that the Langmuir adsorption constant calculated from results of obtained in the presence of $CaCl_2$ were from 7 to 27 fold higher than those in absence of salt.

Barrow and Shaw (1979) reported that desorption was faster in 0.01M $MgCl_2$ than in 0.01 $CaCl_2$ and faster in 0.03M NaCl than either $MgCl_2$ or $CaCl_2$.

ii) Soil-solution ratio :- The relationship between adsorbed phosphate and solution concentration may be influenced by solution-soil ratio. There are conflicting reports about the effect of soil-solution ratio. The results of Fordham (1963), Barrow <u>et al</u>.(1965) and White (1966) indicate that adsorption was favoured by a high solution soil ratio. Hope and Syers (1976) found that adsorption was lowest at high solution-soil ratio.

Barrow and Shaw (1979) found that with gentle shaking, there was no effect of solution-soil ratio with any method of shaking.

iii) Equilibrium time :- Adsorption of anions by soil appeared to continue for long time (Barrow 1970). The adsorption of Molybdenum is rapid at first and then continue to decreasing rate.

Gonzalez et al.(1974) reported that regarding equilibrium time 1 to 4 hours were sufficient to attain equilibrium. At least 70% of the total Molybdenum was adsorbed in the first few minutes.

Barrow (1970) used 24 hours shaking time for attaining equilibrium time.

According to Fox and Searle (1978) standard methods are prerequisite to an evaluation of the diversity of 'P' sorption by soils. The methods used should ensure that that equilibrium has continued until the initial fast reaction between phosphate and soil colloids has subsided.

Rajon (1972) reported that 85% phosphate adsorption was completed in 24-48 hrs, but reasonably stable levels of 'P' in solution were attained only after 6 days.

Kothandaraman and Krishnamurthy (1978) found that initial fast reaction follow slow process of phosphate adsorption and the equilibrium was attained after 6 days.

2.3. Sites of Adsorption and Adsorption Reactions in Soil and Mineral Surface :

2.3.1. Adsorption sites on mineral surface :

The surfaces of ion and aluminium oxides and hydrous oxides usually consists of mixtures of OH^- ion and water molecules, which are co-ordinated to Fe^{+3} or Al^{+3} ion directly below the surface. In the ideal structure the surface is assumed to have no net charge and therefore a freshly cleared surface OH^- and water molecules replace the structural O^{2-} and OH^- ions, which become exposed. The OH^- ion may be in one, two or three-co-ordination to the metal ion of which in the one-co-ordinated form (A-type) it is able to take part in ligand exchange reactions (Parfitt et al.(1976). Under acid condition they adsorb proton, giving positively charged $-OH_2^+$ ion, which is readily exchanged with other ligands.

Mott (1970) has got the opinion that Lewis acid sites occur where water molecules are co-ordinated to metal ions exposed at a surface and in the presence of OH^- ions a proton may be lost from these $M-OH_2$ sites to give $M-OH^-$ at the surface.

The important sites of adsorption are the M-OH and $M-OH_2$, which may become charged in the presence of excess H^+ or OH^- ions. Potentiometric titration in indifferent electrolytes are used to give information on the charge characteristics of these surfaces, as because the charge is pH-dependent. The pH, where the titration curves cross over is referred to as the pH of the point of zero charge (PZC). The

PZC for Fe and Al-oxides occur at pH 7.5 and 9.0 respectively (Hingston et al.(1974)).

The sites that accept proton are modified when ligand exchange occurs and the PZC usually shifts to lower pH as surface become more acidic and therefore accept fewer protons at any one pH. Hingston et al.(1972), Parfétt and Atkinson (1976), show that the negative charge added to the surface when ligand exchange takes place on Goethite was -0.38 eq. mol^{-1} of silicate, -0.7 eq. mol^{-1} of selenate and -1.0 eq. mol^{-1} of phosphate.

2.3.2. Adsorption sites on soil :-

The reactive sites for anion adsorption in pure system are the singly co-ordinated Al-OH and Fe-OH groups, which are exposed at surfaces. The groups are present at the edges of clay minerals as well as on the surfaces of hydrous oxides and therefore, they are present in most soils (Mott, 1970). The nature and distribution of reactive iron and Al-compounds in soils, have been described else where (Jones and Uchara, 1973; Rich, 1968; Greenland, 1971, Wada and Harward, 1974).

The OH- sites in two-cc-ordinated Al (OH)-Al do not normally take part in ligand exchange reactions in pure system, although they can form H-bonds. The Lewis acid sites $Al-OH_2$ and $Fe-OH_2$ also occur on the edge of minerals. Under certain conditions they can react with Lewis bases such as NH_3 to give $Fe-NH_3$ and $Al-NH_3$, although under soil conditions water is held more strongly than ammonia. At high pH these sites become negatively charged.

$$Al - OH_2 + OH^- \longrightarrow Al - OH^- + H_2O$$

The sites that adsorb protons at low pH are probably the one-co-ordinated Al-OH and Fe-OH groups which give $Al-OH_2^+$ and $Fe-OH_2^+$.

On some oxides and oxyhydroxides Fe-O groups may also be exposed at the surface and they may become protonated to $Fe-OH_2^+$ at low pH.

Krishnamurthy et al.(1966) reported that iron and aluminium components of soil organic matter are also important in the adsorption of anionic surfactants by soil.

Many workers have correlated exchangable Fe and Al in soils with anion adsorption sites. Extraction by Tamm's acid-oxalate reagent has been widely used. Buffered dithionite have been used to serve this purpose. But dithionite is not completely specific, for extraction of Iron from soil, since aluminium and silicons are also brought into the solution (Habibullah et al. 1972).

According to Greenland (1971) and Colombera et al.(1971), surface coatings of iron and aluminium hydroxides of clay minerals can adsorb anions. However, it has been shown by

Sree Ramulu et al.(1967) and Huang (1975 b) that similar material in 2:1 clay interlayers is not active in anion adsorption.

Weir and Soper (1963) reported that humic acid containing ferric iron is able to hold 'P' in solution at higher pH. Alekasondroua (1954) reported that part of'Al' that reacted with humic acid was exchangable and could adsorb phosphate and other anions.

2.3.3. Adsorption sites on clay minerals :

Some clay minerals have a pH dependent charge which occurs at the edge of the crystals where Al (OH), H_2O groups are exposed. The Al(OH) groups are the sites that accept proton at low pH to become $AlOH_2^+$ (Schofield 1949, Balland et al. 1976), Kellay and Midgley (1943), Mehlich (1964), reported that the mechanism of adsorption is by exchange of phosphate with Al-OH groups on the edge sites of clay minerals. Kaf Kafi (1967) suggested that some phosphate could be fixed on kaolinite as binuclear complex. Kuo and Lolse (1972) suggested that anion exchanged with Al-OH_2 groups on kaolinite rather than Al-OH, since a) adsorption increased with decrease in pH and b) no release of OH was observed. These effects can now be explained by considering surface-OH_2^+ groups.

Pissardies et al.(1968) showed that the exchangable cations influenced the amount of anion that could be adsorbed on the edge site of clay minerals and on Na-montmorillonite, there was negative adsorption owing to diffuse double layer effects. Parfitt (1972) reported that negative adsorption also occurs if Al is present on the exchange sites.

2.3.4. Adsorption by Goethite (α-FeOOH) :

Hingston <u>et al</u>. (1968a, 1971, 1974) studied the adsorption of $SO_4^{=}$, $H_3S_2O_4^{-}$, $H_2PO_4^{-}$, $MoO_4^{=}$, $SeO_3^{=}$, $H_2AsO_4^{-}$ and F^{-} on Goethite showed that these anions were selectively adsorbed in the presence of Cl^{-}. It was suggested that the anions were specifically adsorbed on Goethite and Gibbsite by ligand exchange with surface OH or OH_2^{+} groups. Parfitt and Russel (1977) supported this and found that OH groups are replaced during the reaction. Bowden <u>et al</u>.(1974) reported that anions of fully dissociated acids were adsorbed if the surface carries a positive charge and adsorbed on the acid side of PZC. The anions of incompletely dissociated acids however, can also be adsorbed on the alkaline side of the PZC. They also added that maximum adsorption occurs at pH close to the pK of the acid, where the surface potential and the concentration of the hydrolysable ions are optimal.

2.3.5. Adsorption by Hematite (α-Fe_2O_3):

Although the oxygen within hematite crystals is present as oxide, the ideal surface is composed entirely of hydroxide ions in one and two co-ordination (Parfitt <u>et al</u>.1974).

Reyes and Jurinak (1967) reported that molybdate adsorption on hematite is very complex and the paramolybdate probably forms on the surface at high concentration. They also reported that two distinct reactions took place on the iron oxide surface at pH-4.0 and the first surface reaction was insensitive to temperature change. The second surface reaction was endothermic process. They also found that adsorption of molybdate by hematite was 5 times greater than at pH-4 than 7.5. The adsorption of molybdate in the alkaline system was also insensitive to temperature change. It was suggested from the experimental data that lack of temperature dependence of the first surface reaction indicates, a definite fixed site adsorption, which indeed, is one of the assumption of the Langmuir isotherm. The temperature dependence indicated by the second adsorption reaction, is considered to be the result of the on set of monomeric condensation, which enhanced by high molybdenum concentration and increased temperature. Unlike pH-4, the adsorption reaction at high pH 7.5 was one surface, as because, at high pH, no condensation occur in the absence of protonation.

Jurinak and Buran (1967) showed that the surface energy of hematite was lower after molybdate adsorption.

2.3.6. Adsorption by other iron oxides :

The crystal structure of Lepidocrocite (γ-FeooH) consists of rows of one, two or three co-ordinated OH ion on its surface (Wells 1962). The crystal structure of akagancite

(β-FeOOH) consists of multiple octahectral chains. It probably has rows of OH ions in one, two and three co-ordination exposed at the surface (Gallagher 1970; Parfitt *et al.* 1975).

Infrared spectroscopy has shown that both phosphate and sulphate are adsorbed as binuclear bridging complex on lepidocrocite and akagancite. (Parfitt and Smart 1978).

Jones (1957) reported that the affinity for molybdenum of Fe_2O_3, xH_2O was more than that of Al_2O_3, xH_2O. Reisenaur *et al.*(1962) showed that the reaction of molybdate with Fe_2O_3, xH_2O involves the replacement of two hydroxyl group for each molybdate reacting. They also reported that molybdate sorption by Fe_2O_3, xH_2O at a given pH follows the Freundlich adsorption isotherm but do not fit the Langmuir equation over the range of Mo concentration studied.

2.3.7. Adsorption by Gibbsite and other Aluminium oxide surfaces :

The mechanism of anion adsorption on Al-hydroxides is less well understood than that on iron oxides, because the surfaces were less well defined. According to Bragg and Claringbull (1965), the crystal structure of Gibbsite consists of well ordered hexgonal crystals and although the (001) face predominates, the edge faces contain the reactive sites (Parfitt 1977 b). Russel *et al.*(1974) found that five different types of surface OH on the (001) face could be detected by infrared spectroscopy. But Parfitt *et al.*(1977b) added that none of these surface OH- groups are exchangeable with phosphate and oxalate.

Hingston et al.(1972, 1974) reported that adsorption of selenite, molybdate and silicate on gibbside are consistent with ligand exchange reaction.

Rajon (1976) suggested that at pH-4, $H_2PO_4^-$ was adsorbed initially on $AlOH_2^+$ sites and with increasing phosphate coverage Al-OH react to form monodentate complexes $Al\text{-}H_2PO_4^0$.

Rich (1968) has reviewed the literature and concluded that interlayer hydroxy-aluminium does not take part in anion exchange reaction in the interlayer surface region of expansible layer silicates.

Greenland (1971) and Colombera (1971) pointed out that hydroxy aluminium on the illite surfaces probably involved in ligand exchange reactions.

2.3.8. Adsorption by Amorphous hydroxides :

Amorphous iron and aluminium hydroxides have less well defined surfaces than the crystilline hydrous oxides.

Reaction that have been studied includes the adsorption with silicic acid (Beckwith, 1963), Phosphate (De-1961, Bache 1964; Ryden and Syers 1975a) and molybdate (Jones 1957; Reisenaur et al.1962) and the results are consistent with ligand exchange. Parfitt and Smart (1978) have shown that phosphate and sulphate are adsorbed on amorphous $Fe(OH)_3$ and both form a binuclear bridging complex.

Rajon and Perrot (1975) showed that at low concentration of phosphate were adsorbed by ligand exchange on silica-alumina and soil allophanes. At higher concentration hydroxy-aluminium polymers were disrupted and structural silicate was displaced (Rajon and Watkinson 1970).

2.3.9. Adsorption by Calcite :

Cole*et al.*(1953), Kuo and Latse (1972), Holford and Mattingly (1975b) studied the phosphate adsorption on calcite and described by Langmuir equation. Latior and Bolt (1963) showed that the calcite surface was modified by dissolved components from soil solution, suggesting that calcite in soil will have different surface properties from pure calcite.

Santa *et al.*(1982) reported that three distinct adsorption sites of phosphate on calcite. Singh and Sekleon (1978) studied the adsorption of NO_3^- and $SO_4^=$ on $CaCo_3$. They found that NO_3^- adsorbed on $CaCO_3$ surface fitted the Langmuir model well. $SO_4^=$ ion when present in the displacing fluid seemed to desorb NO_3^- ions from the surface of $CaCO_3$. Cl^- ion had little effect on it.

Literature reveals no or little study of adsorption of molybdate on calcite.

2.4. Factors governing adsorption reactions of molybdate by soil and soil components.

The following discussion made on the adsorption characteristics of molybdate and other anions by soil.

2.4.1. pH :

pH is the determining factor for the anionic molybdate, which ultimately determines the size of the anion formed at a particular pH. It is generally accepted that basic solution of Mo, contain only tetrahedral $MoO_4^{=}$, below pH-6 $MoO_4^{=}$ becomes protonated forming monomeric $HMoO_4^{-}$ and H_2MoO_4. Jones (1957) reported that on increasing pH, adsorption falls and none is adsorbed above pH 8.0. Adsorption of molybdate by Fe_2O_3 is highly pH dependent (Jones 1956). Reyes and Jurinak (1967) reported that the adsorption maxima of $MoO_4^{=}$ on hematite was found to reduce by 80% if the pH was changed from 4.0 to 7.75. Reisenauer et al.(1962) reported that the sorption by hydrous oxides and soils increases exponentially with the equilibrium Mo concentration at constant pH and decreases exponentially with OH^{-} ion concentration at constant Mo concentration.

For soil system, they developed the relation

$$\text{Mo solubility} = \frac{\text{Mo Sorbed}}{(\text{wt of soil})} \times \text{pH}$$

Vlek and Lindsay (1977) representing the equation in following way.

$$\text{Soil-Mo} \rightleftharpoons MoO_4^{=} + 0.8H^{+}$$

$$[\log K^{o} = -12.4]$$

Gonzalez (1974) reported that the effect of pH on Mo adsorption, where the general trend is, that adsorption decreases as pH increases with a distinct change in slope occuring approximately at pH 5.5. This pH is close to the pKa value of the molybdic acid. Hingston (1972) reported that with incompletely dissociated acids, specific anion adsorption (ligand exchange) can also take place at more alkaline to ZPC, provided the pH is close to pKa value of the molybdic acid.

2.4.2. Organic matter :

Aleksodroca (1954) reported that part of the aluminium of the humic acid-Al complexes, was exchangeable and could adsorbed phosphate and other anions. Krishnamurthy _et al_. (1966) and Appett _et al_.(1975b) reported that iron and aluminium components of soil organic matter are important in the adsorption of anionic suspectants by soils.

NGSK and Bloomfield (1962) reported that co-precipitation of molybdenum with ferricoxide may be inhibited by organic matter.

Szilagyii (1971) reported that the humic acid have the ability to reduce anionic $MoO_4^{=}$ to cataionic Mo^{+5}, the latter can be fixed by humic acid and rendered unavailable to plants.

Karimian and Cox (1978) reported that adsorbed molybdenum was highly correlated with organic matter content.

Mishra and Mishra (1972) found that application of glucose under permanent water logged condition increase the retention of applied molybdenum.

2.4.3. Iron and Aluminium :

Affinity for molybdenum on Fe/Al containing surfaces, have been reported by several workers (Wells 1956; Reyer and Jurinak 1967; Jones 1957, Reisenaur et al.(1962).

Jones (1957) and Reisenaur et al (1962) showed that formation of ferric and aluminium molybdate on reaction with molybdenum on Fe/Al compounds. As soils contain coatings of these oxides, they also adsorb molybdate in similar fashion.

It has been reported by several workers (Jones, 1957; Reisenaur et al.1962; Trobish and Schilling, 1963; Smith Leeper, 1969; Cheng and Outllette, 1973) that adsorbed molybdate of soils can be released after treatment with dithionite or oxalate, which is consistent with ligand exchange iron and aluminium surfaces. Similar results have also been obtained in volcanic ash soils by Theng (1971) and Gonzalez et al. (1974). They also reported that high adsorbtion of these soils is due to the presence of allophane and amorphous Al, Si and Fe compounds.

Jorrel and Dowson (1978) found that adsorption of molybdenum on soils was related to ammonium oxalate extractable Fe but not other fractions of extractable Al form.

Kariman and Cox (1971) reported that adsorbed molybdenum was positively correlated with Fe oxides. Mishra and Mishra (1971) studied the adsorption of Mo on soils and concluded that the order of decreasing Mo retention with respect to soil type was red > alkali > Black soil. Application of Fe_2O_3 generally increase the retention capacity of Mo by soils.

2.4.4. Clay minerals :

Jones and Milne (1956) studied the adsorption of molybdate on solids. They found the relative ability of solids, used for molybdate sorption, in the acid side of the order

ferric oxide > Boehmite > metahalloysite > nontronite

It has been found that large amounts of molybdate were adsorbed from Na- molybdate solution at pH-4.0 to 5.5 by boehimite and halleysite, with the formation of Al-molybdate within the mineral.

Gallego and Jolin (1960) reported that adsorption of $MoO_4^{=}$ was greatest at pH 2.0. They added, that the adsorption of $MoO_4^{=}$ was in the order

hydrated halloysite > Bentonite > Kaolinite.

Bentonite and Kaolinite ceased to adsorb molybdenum at pH 7.53 and 8.1 respectively.

Teng (1971) studied the adsorption isotherm of molybdate adsorption on crystalline and amorphous soil clays. It has been found that adsorption isotherm for the allophane [illegible] clays obey the Langmuir equation but the isotherms for the Kaoline and illite clay show two distinct region of adsorption. They also reported that the molybdenum adsorbed by all 3 clays were reduced by treatment with dithionite citrate and it was found that after this treatment the isotherm of Kaolinite and illite become linear.

2.4.5. Presence of other anions :

It has become apparent that the adsorption behaviour of many anions, in particular the important nutrients phosphate, sulphate and molybdate is very similar. (Barrow 1970).

Molybdate can be desorbed from soils by phosphate or sulphate (Stout _et_ _al_. 1951; Barrow 1973b). It has been reported by Barrow (1973) that desorption of molybdate with phosphate is increased with pH. It is also found that phosphate was more effective than hydroxide at pH-7 but at pH above 9, hydroxide ion alone was nearly as effective as phosphate.

Gorlach _et_ _al_.(1969) reported that with the increase of phosphate ion conentration, the sorption of molybdate is reduced but $SO_4^=$ ion has no effect on the sorption of molybdate in the soil. They also added that the effect with phosphate decreased with time, which shows that molybdate is more strongly adsorbed after initial adsorption. Barrow(1974) has got the same results and concluded as the proportion converted was not affected by level of addition of molybdate solution within the range tested, the conversion does not involve diffusion in solution phase molybdate from one kind of site to another. The rate of conversion was increased by increasing the temperature from 10°C to 40°C.

Barrow (1970) studied the comparison of the adsorption of molybdate, phosphate and sulphate at 0.1, 0.2 and 20 ppm equilibrium concentration respectively and found that with decreasing pH from 6 to 4, the ratio of SO_4/PO_4 adsorption increased by 3-fold and that of MoO_4/PO_4 adsorbtion increased 20 fold. This relationship between sorption and pH is consistent with the hypothesis that adsorption occured in the simultaneous presence, at the interface of the adsorbing phase with the solution ions capable of adsorbing and donating proton. He also found that adsorption of all the three nutrients is highly correlated with exchangeable Al and suggests that similar soil constituents are involved in the adsorption of all three anions.

Pisarev <u>et</u> <u>al</u>.(1980) reported that systematic application of 'P' fertilizer to podzolic soil increased the labile 'Mo' content in soil and its uptake by plants.

Gonzalez <u>et</u> <u>al</u>. (1974) reported that Cl^- and $SO_4^=$ did not compete with molybdate for the adsorption sites. The higher adsorption of Mo for highest concentration of Cl^- (Mo : Cl^- = 1:10) may be associated with the increasing ionic strength of the equilibrium solution. Adsorption of Mo was decreased by the presence of 'P' in equilibrium solution when the ratio of Mo/P was 1:10.

According to Gonzalez et al.(1974) competition between anions would depend on their relative ability to increase the negative charge of the surface and that the effects of the anions specifically adsorbed are complementary rather than additive.

2.4.6. Saturated Cations :

Lal and De (1974) studied the effect of different cationic saturation (H^+, NH_4^+, K^+, Ca^{+2} and Mg^{+2}) on the sorption of $MoO_4^=$ and observed that the sorption of homoionic soil was greatest for H^+ soil and least for Ca^{+2} and Mg^{+2} soils.

Paricha and Randhawa (1972) found marked increase in molybdate sorption in soils saturated with Fe^{+3} and Al^{+3}. The amount of $MoO_4^=$ adsorbed followed in the order

Fe^{+3}-Soil $>$ Al^{+3}-Soil $>$ Ca^{+2}-Soil $>$
Original Soil $>$ K^+-Soil $>$ NH_4^+-Soil.

2.5. Phosphate adsorption by soils :

Phosphate adsorption by soils has been the subject of extensive reviews. Most reviewers have dealt with the precipitation mechanism and the adsorption mechanism of phosphate. Some paper suggests that in acid soils, phosphate is associated with hydrous oxides of Fe and Al and it is unlikely that discreate crystalline iron and aluminium phosphate persist in soil. (Bache 1963, 1964).

However, in the immediate vicinity of phosphate fertilizer particles, there are local conditions of low pH and high phosphate concentration, which may cause dissolution of clays and reprecipitation of phosphate. Later work suggests that basic aluminium phosphate may form in acid soils even at low phosphate concentrations (White and Tailor 1977, Van Reemsdijk et al.1975,1977).

Many workers have determined the phosphate adsorption isotherm on soils and then attempted to fit the results to a Langmuir or Frendlich equation. Straight lines are obtained when the results from a limited concentration range plotted according to Langmuir equation. In some cases the data can best be fitted with two straight lines and this has been taken to indicate two different phosphate adsorption sites (Syers et al.1973, Karim et al.1973, Juo and Maduakar 1974, Rajon and Fox 1975).

Holford et al.(1974) used a two surface Langmuir equation and obtained a quite good agreement with experimental data.

Ryden et al.(1977 b) used five Langmuir equation, which then were reduced to three equations by successive approximation into three regions. Muljadi et al.(1966a) suggested that in Region I and II, the adsorption is largely chemical and for Region III, it is physical.

Rajon (1976) suggested that OH_2^+ is exchanged in Region I and OH^- is exchanged in Region II. Of course Parfitt and Atkinson (1976) suggested that both OH_2^+ and OH^- participate in Region I and II. Ryden and Syers (1977) suggested that in Region III, phosphate is adsorbed through ligand exchange, as the surface coverage is greatly reduced, which is readily desorbed and obviously important for plant growth.

Many workers, often using a single point on the isotherm, have correlated the phosphate adsorption capacity with other soil factors.

Most results show that phosphate adsorption is better correlated with extractable Al than with Fe (Williams et al. 1958; John 1972; Evans et al.1976). However, some results show that either Al or iron alone is correlated with phosphate adsorption (Schwertmann 1973; Myszka and Jonowska 1977).

It has been reported by Frankline and Reisenaur (1960) and Fitter and Sutton (1975), that phosphate adsorption in soil is correlated with exchangeable Al when pH is less than 5, but it is correlated with exchangeable Ca, when pH $>$ 5.0.

Several workers have found that the significant correlation with soil organic matter Fakin and Singha (1970) suggested that some phosphate is adsorbed by the iron and aluminium ion, which are also chelated by large organic molecules in soil such as humic acid or fulvic acid. However, Fox and Kamprath (1971) showed that phosphate is weekly held on organic soil and can be removed by leaching. Thus phosphate adsorbed at different energy level by ferric and aluminium ions, which are held by organic matter.

Hashimats and Takaryane (1971) and Moshi et al.(1974) reported that soil organic matter can block sites on iron and Al hydrous oxides and reduce phosphate adsorption by soil.

Hudecova and Kavarava (1969) found that by removing organic matter with H_2O_2, results the formation of oxalate; which block more sites and further reduce phosphate sorption.

Rajon and Fox (1975) found that phosphate displaced sulphate and silicate during legand exchange, but at high phosphate concentrations structural silicate was displaced.

Fox and Searle (1978) reported that the order of increasing 'P' sorption is quartz-organic matter $<$2:1 clay $<$1:1 clay $<$desillicated volcanic ash.

Fox et al.(1971) found that high sorption maxima in soils containing hydrated Al and Fe oxides.

Cajuste (1979) found that 'P' sorption follows the Langmuir isotherm and adsorption maxima significantly correlated with exchangeable aluminium.

CHAPTER III

STUDIES ON ADSORPTION OF MOLYBDATE BY SOME HYDROUS OXIDES, PHOSPHATES AND CARBONATE

In the present investigation, experiments were carried out on the adsorption of molybdate by some pure compounds like ferric hydroxide gel, aluminium hydroxide gel, ferric phosphate, aluminium phosphate, calcium carbonate and rock phosphate. As these compounds are likely products of different soil chemical reactions, in the soil system, these compounds are expected to play some role in the anion adsorption phenomena. With this idea, an attempt has been made to find out the nature and degree of reaction of these species with molybdate.

3.1. Materials and Methods :

In the following section a short description of the adsorbent used and the methods of their preparation are given.

3.1.1. Materials :

i) Aluminium Phosphate - Aluminium phosphate or variscite was prepared by mixing dilute solution of $AlCl_3$, $6H_2O$ and NaH_2PO_4 in the mole ratio Al/P = 0.4, adjusting the pH-4, with NaoH solution and digesting at 90°C for 14 days. The precipitate was washed twice with 1% NaCl solution at pH-4 to remove adsorbed phosphates and then with 90% ethanol until free from chlorides. The material was finally washed with acetone and dried at 100°C. The product of this procedure was a crystallime powder, having particle size $\sim 5\mu$ and composition $Al_2O_3\ (P_2O_5)_{1.02}(H_2O)_{4.45}$ and X-ray diffraction powder diagram similar to variscite but perhaps containing a small amount of amorphous materials (Cole and Jackson, 1950).

ii) Iron Phesphate - Iron phesphate or strengite was prepared by an essentially similar method, using $Fe_2(SO_4)_3$ and NaH PO_4 solutions, but adjusting to pH-3 and washing the crystallised precipitate first with dilute H_3PO_4 to remove amorphous materials. The product of this procedure was a very pale cream crystalline powder, having particle size $\sim 5\mu$ and composition $Fe_2O_3\ (P_2O_5)_{1.01}(H_2O)_{4.45}$ and X-ray diffraction pattern identical to a natural simple strengite (Cole et.al, 1959).

iii) Hydrous ferric oxide - Hydrous ferric oxide was prepared by the method of Schuylenborgh and Arens (1950). A solution of 405 g of Fe $(NO_3)_3$, $9H_2O$, in one litre of water was run slowly into a solution of 3.5(M)NH_3 in 1 lt of water, stirring vigorusly all the while. Precipitate, from the hydroxide was then freed from extra electrolytes by dialysis.

iv) Hydrous Aluminium Oxide - Boehmite $Al(OH)_3$, was prepared by the method of Schuylenborgh (1951) by adding 820 ml of 2(M) NH_3 to a solution of 50 g. $AlCl_3$ in 200 ml of water at temperature of 18°C. Precipitated form of Boehmite was then freed from electrolytes by dialysis.

v) Calcium Carbonate - Precipitated powder of AR grade, was used as adsorbent for the adsorption study of molybdate on its surface.

vi) Rock Phosphate - Rock phosphate, taken for adsorption experiments, was collected from Calcutta Mineral Supply Corporation, Calcutta, West Bengal. Minerals of 80 mesh size was used in this investigation.

3.1.2. Methods :

a) Methods for the study of Adsorption :

Adsorption studies of molybdate were conducted by equilibriating the suspension of the pure compounds, with appropriate quantities of molybdate, ranging from 0.1 to 1 ppm of molybdenum as molybdic acid in 50 ml 0.01 M $CaCl_2$ solution, with a constant solid-solution ratio at two different constant temperature levels. For the experiments, the following conditions were maintained.

i) Solid-Solution ratio - For adsorption of molybdate $AlPO_4$ and $FePO_4$, the ratio were 1:50. For $Fe(OH)_3$ gel, the solid-solution ratio for the experiment was 1:5000, where solid amount was reported as Fe_2O_3,xH_2O, which was obtained by heating the gel suspension at 900°C for 3 hours to get Fe_2O_3, xH_2O. For $Al(OH)_3$ gel suspension, the ratio was 0.7 : 5000. Here also the solid was in the form of Al_2O_3, xH_2O, which was obtained by heating the gel at 900°C for 3 hours. In both the cases, suspension of the gel was used for the experiments as adsorbent.

ii) Equilibrium Time - It has been found that, in the present investigation, in order to reach equilibrium of the solid-solution system a shaking period of 5-6 hours followed by 40 hrs incubation at constant temperature, was sufficient.

iii) Equilibriating Temperature - In the present investigation, experiments were carried out at two different temperature, one at 40°C and another at 20°C. For this, incubation was carried out after necessary shaking in BOD incubator, adjusted to 40 ± 1°C and 20 ± 1°C, respectively.

iv) pH of the equilibriating solution - For adsorption of molybdate on $Al(OH)_3$ and $Fe(OH)_3$ gel, the pH of the equilibriating solution was maintained at constant pH of 7, by using 0.1(M) NH_4O AC solution.

v) Ionic strength of the equilibriating solution - For maintaining a constant ionic strength of the equilibriating solution a 0.01(M) $CaCl_2$ solution was used.

b) Procedure :

Considering the above conditions the adsorption experiments were carried out. 2-3 drops of choloroform was added in each of the equilibriating solution, for inhibiting microbial activity, if any. Immediately after completion of incubation, the suspensions were filtered, through Whatman No-42 filter paper. After discarding 5-6 ml of the first filtrate, the filtrate was taken for estimating the equilibrium concentration of molybdenum. Each set of adsorption experiment was conducted in duplicate and the data obtained from the two were found to be more or less concordant.

c) Methods of Analysis of Molybdenum :

The estimation of molybdenum from the equilibrium solution, was done by formation of an amber-coloured compound of ferrous-molybdenum-thiocyanate complex in organic medium. The complex has maximum adsorption at 465 nm. The method used in the analysis was adopted from the procedure developed by Arkley and Jhonson (1954).

d) Interpretation of adsorption data :

In the present investigation, adsorption data of molybdate have been computed, in order to study the nature of adsorption, by using Langmuir equation, in the following form -

$$C/x = \frac{1}{K} \cdot \frac{1}{xm} + \frac{C}{xm}$$

Where xm is the adsorption maxima, K, a constant related to bonding energy of molybdate ion and C is the equilibrium concentration.

Thermodynamic constants were usually calculated from the K-value of the Langmuir curves.

3.2. Results and Discussion :

3.2.1. Adsorption of molybdate by $AlPO_4$ and $FePO_4$:

Adsorption isotherms at 40°C and 20°C of the precipitated form of $AlPO_4$ and $FePO_4$, at various concentration of molybdate in solution are shown in Fig.1A(a) and 1A(b). The adsorption curves are characterised by gradual rise, followed by flattening of the curves. No distinct regions are found. The adsorption isotherms $FePO_4$ and $AlPO_4$ followed the Langmuir equation, as depicted in the Fig. 1B(a) and 1B (b). The Correlation coefficient values of the Langmuir curves are given in the Table-1(A) and the Langmuir adsorption maxima and K-values are given in the Table-1(B).

It is observed from the data the $FePO_4$ adsorbs much molybdate than $AlPO_4$. This is in conformity with the results reported by Jones (1957) that affinity for Mo of iron compounds are much more than that of Al-compounds.

Adsorption maxima, for the adsorbent are found to be higher at lower temperature compare to higher temperature.

Regarding K-value, related to bonding energy, it is observed that in case of $FePO_4$, it is much higher than that of $AlPO_4$. Though both the adsorbents adsorb higher molybdate at lower temperature, but exhibit higher K-values at higher temperature.

Gibb's free energy change in the adsorption of molybdate on these compounds are negative, indicating spontaneous

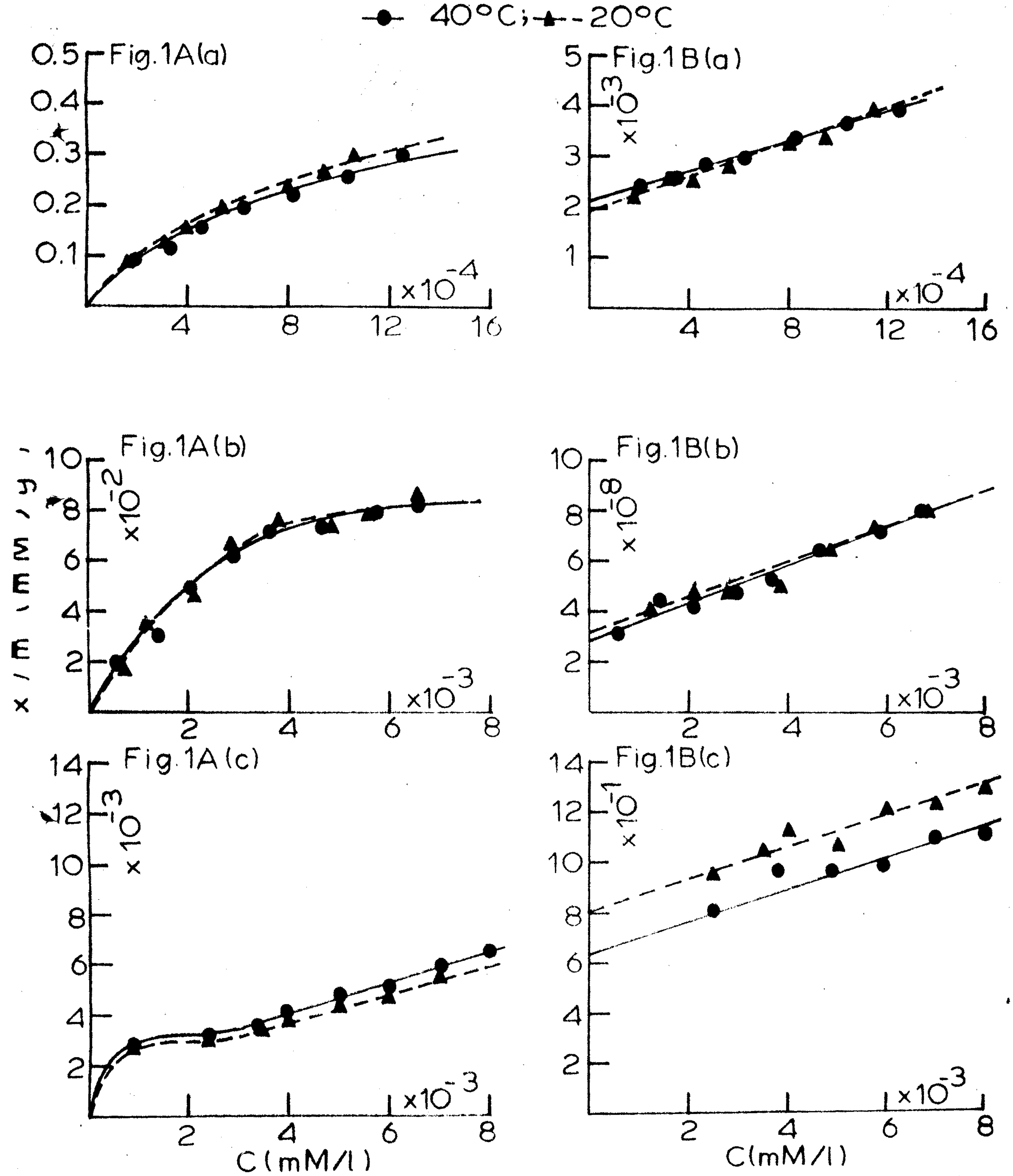


Fig.1A. Molybdate adsorption on a) $FePO_4$, b) $AlPO_4$ and c) $CaCO_3$ at different temperature levels.

Fig.1B. Langmuir plot of molybdate adsorption in a) $FePO_4$, b) $AlPO_4$ and c) $CaCo_3$ at different temperature levels.

adsorption. The Table-1(B) shows, a higher negative value of ΔG^{o} for adsorption of molybdate on $FePO_4$. It is also higher at higher temperature level.

It is evident from the data, that adsorption of molybdate on $FePO_4$ is chemical in nature and $AlPO_4$ adsorbs molybdate rather weakly.

Since precipitated form of $FePO_4$ and $AlPO_4$ contribute large surface area for adsorption and molybdate and phosphate, are more or less similar in their behaviour. Molybdate ions exchange with and adsorbed by phosphate on the surface of $AlPO_4$ and $FePO_4$, to form ultimately molybdates of iron and aluminium. As reported by several workers, Fe-containing compounds have greater affinity for Mo, compared to Al-compounds.

Considering the ΔH^{o} value of the adsorption which is positive in case of $AlPO_4$, indicating endothermic nature of reaction, though $AlPO_4$ adsorbs higher amount at lower temperature. On the other hand $FePO_4$ exhibits negative ΔH^{o} value, indicating exothermic nature of adsorption.

Regarding the value of ΔS^{o} it is observed that greater positive value of ΔS^{o} for adsorption on $FePO_4$ than $AlPO_4$.

The thermodynamic parameters derived from the study clearly indicate that ferric phosphate which is obviously related to the stronger bonding of molybdate by the former material.

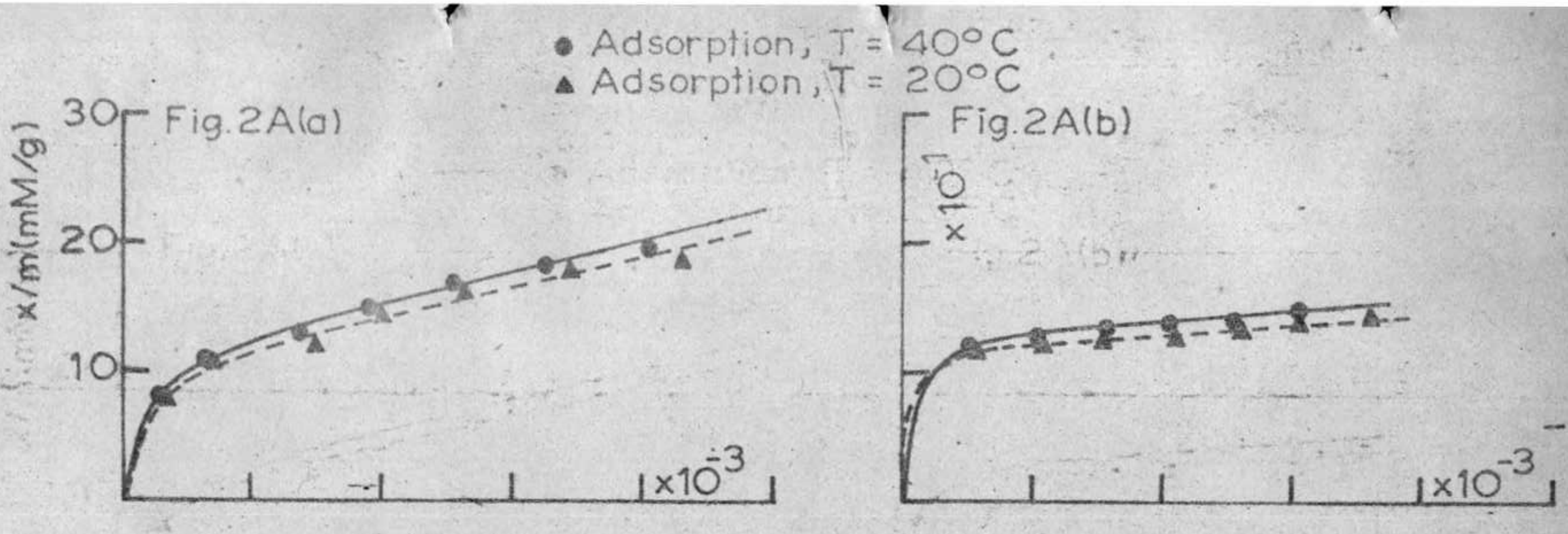
3.2.2. Adsorption of molybdate by hydrous iron and aluminium oxide gel :

Adsorption isotherms of molybdate on hydrous oxides of Fe and Al at 40°C and 20°C, at various concentrations of molybdate in solution are shown in Fig.2A(a) and 2A(B).

The three distinct regions of adsorption (I, II and III) occured at this pH level. The region I is characterised by the occurrence of initial steep rise of the curve, which bends (region II) and finally flattens out (region III), at higher concentration of molybdate in solution.

In both the cases adsorption isotherms followed the Langmuir equation, as depicted in the Fig.2B(a) and 2B(b). The correlation coefficient values of the Langmuir curve are given in the Table I(A). However in case ferric hydroxide gel, the break in the Langmuir curve is observed, which indicates second surface reaction on the surface of hydroxide get. The Langmuir parameters calculated from the more dominant second surface adsorption. The Langmuir adsorption maxima and K values are given in the Table-I(B).

From the data it is clear that Fe-hydroxide possess a higher adsorption capacity for molybdate compare to Al-hydroxide gel, at both the temperature studied. Adsorption maxima of the hydroxide surfaces reveal 3 times greater adsorption of molybdate by ferric hydroxide than Al-hydroxide gel at the pH level of 7. In both the cases, however, greater adsorption of molybdate occurs at higher temperature.



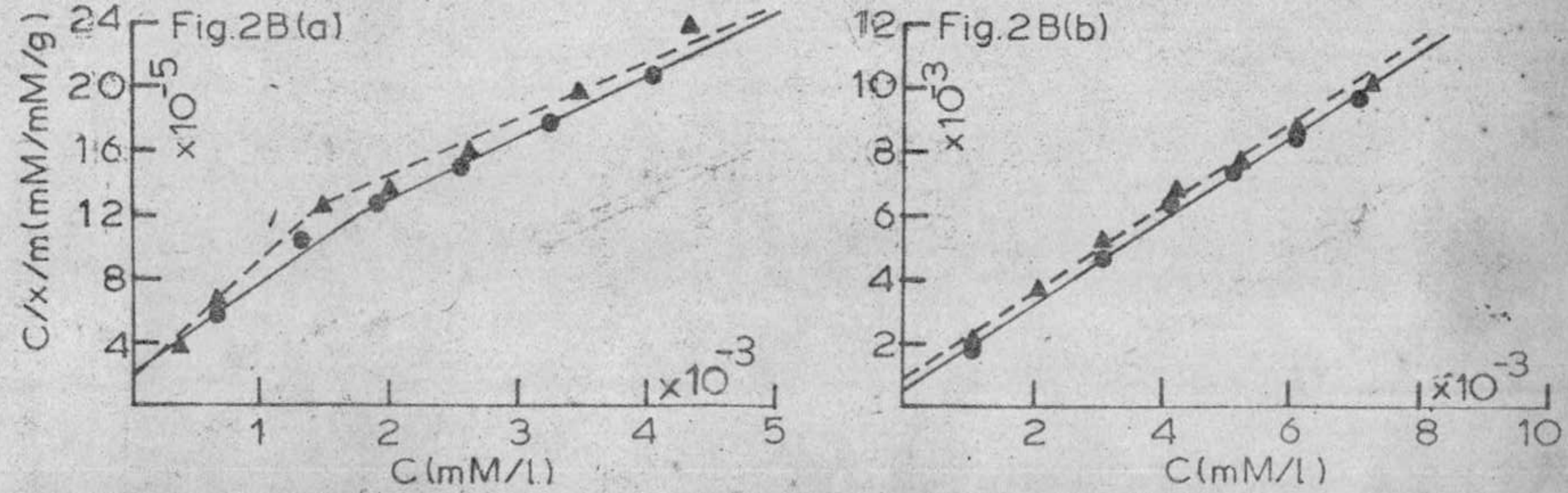


Fig.2A. Adsorption of molybdate on (a) hydrous oxide of Fe (b) hydrous oxides of Al at different temperature levels.

Fig.2B. Langmuir plot of molybdate adsorption on (a) hydrous oxides of Fe (b) hydrous oxides of Al at different temperature levels.

TABLE -I(A) : <u>Correlation Coefficient values of the Langmuir Curve for the adsorption of molybdate by pure compounds.</u>

Adsorbent	*r values for 40°C	*r values for 20°C
$FePO_4$	0.9533	0.9533
$AlPO_4$	0.9771	0.9451
Fe_2O_3, xH_2O (pH-7).	0.9470**	0.9364**
Al_2O_3, xH_2O (pH-7).	0.9897	0.9896
$CaCO_3$	0.9971	0.8789

* Significant at 1% level.

** Values from more dominant second surface adsorption at higher absorbate concentration.

TABLE-I(B) : Langmuir Parameters for the adsorption of molybdate by pure compounds.

Adsorbent	Adsorption maxima (m M/g)		K-value or Equilibrium constant ($x10^3$ M^{-1})		$-\Delta G^o$ (K Cal / mole)		ΔH^o K Cal/ mole	Mean ΔS^o (Cal/deg/ mole)
	40°C	20°C	40°C	20°C	40°C	20°C		
$FePO_4$	0.555	0.714	923.07	673.67	8.54	8.34	-2.87	0.037
$AlPO_4$	0.132	0.153	265.36	199.08	7.77	7.10	+2.61	0.015
Fe_2O_3, xH_2O (pH-7.0)	25.77*	24.22*	923.80*	951.15*	8.54*	8.01*	-0.265*	0.028*
Al_2O_3, xH_2O (pH-7.0)	8.00	7.87	1882.50	1395.60	8.98	8.24	+2.72	0.019
$CaCo_3$	0.010	0.008	203.29	307.37	7.60	7.35	-3.76	0.061

* Calculated from more dominant second surface adsorption.

Considering the value of K which is related to bonding energy, it can be said that hydrous aluminium oxide adsorbs molybdate with greater strength. The second surface adsorption of molybdate at higher equilibrium concentration of molybdate at higher equilibrium concentration of molybdate) in solution on hydrous oxide of Fe, seem to be take place with little strength compare to other cases.

Change in Gibb's free energy for adsorption of molybdate, as given in the Table-I(B), shows a greater negative value of ΔG^{o} for hydrous aluminium oxide adsorbent in comparison to Fe-hydroxide gel. The negative value of ΔG^{o} in both the cases indicate spontaneous nature of molybdate adsorption, on the hydrous oxide gels.

Iso steric heats of adsorption i.e. ΔH^{o} as given in Table I(B) show positive value of ΔH^{o} for adsorption on hydrous Al- oxide on the other hand negative ΔH^{o} value is observed in case of adsorption on hydrous ferric oxide. As observes in case adsorption of molybdate on $FePO_4$ negative ΔH^{o} value, indicates the iron compounds exhibit exothermic nature of adsorption, on the other hand Al-compounds exhibit endothermic nature of adserption.

Higher ΔS^{o} value is observed in case of adsorption on hydrous ferric oxide gel compared to hydrous Al- oxide gel.

3.2.3. Adsorption of molybdate by $CaCO_3$ and Rock Phosphate:

From the experiments on molybdate adsorption by $CaCO_3$ and rock phosphate in the present investigations it has been found that there is little or almost no adsorption of molybdate by rock phosphate on equilibriating for 6 hours followed by 40 hours incubation at isotherm condition.

$CaCO_3$ on the other hand shows a little adsorption of molybdate. The adsorption isotherm curves of the $CaCO_3$ at various concentrations of molybdate in solutions are shown in the Figs. 1A(C). The adsorption curves follow the Langmuir equation. The correlation coefficient values of the Langmuir curves are given in the Table-I(A).

The data indicate the little adsorption of molybdate by $CaCO_3$. The K value related to bonding energy is also of low value, indicating a much weaker strength of adsorption.

Unlike phosphate, molybdate adsorption on $CaCO_3$ is not upto the mark or quite significant. Though both are anionic in nature, reaction of molybdate on the $CaCO_3$ surface is not at all prominent. Phosphate is known to be adsorbed by $CaCO_3$ by chemisorption through precipitation of insoluble calcium phosphates on its surface but molybdate has not been found to so. The high pH of the $CaCO_3$ surface appears to inhibit the molybdate anions to be adsorbed on it. Unlike phosphate, molybdate does not react with Ca^{+2} ion readily, also due to relatively higher solubility of $CaMoO_4$ compared to that of Calcium phosphate.

Rock phosphates have little affinity for molybdate. Usual 6 hrs shaking followed by 40 hrs of incubation under isotherm condition, fails to make adsorption of molybdate on the mineral surface of rock phosphate, analytically detectable. From the study it is quite clear that rock phosphate has practically no power for the adsorption of molybdate anions on its surface very strong energy of bonding for phosphate in rock phosphate structure may be the reason for this lack of adsorption of molybdate by any chemical force on the rock phosphate surface.

3.2.4. Comparison of adsorption of Molybdate by different pure compounds.

From the thermodynamic parameters given in the Table-I(B), it is clear that adsorption of molybdate by these compounds is mostly chemical. More or less physical adsorption appears to occur only in case of $AlPO_4$ and $CaCO_3$.

The comparison of the Langmuir adsorption maxima indicates that the molybdate adsorption on these pure compounds at both the temperatures increases in the order

$$\underset{\text{(pH-7)}}{\text{Fe-hydroxide gel}} \gg \underset{\text{(pH-7)}}{\text{Al-hydroxide gel}} \gg FePO_4 \gg AlPO_4 \gg CaCO_3$$

The values of bonding energy for adsorption followed in the order at 40°C, $Al_2O_3, xH_2O > Fe_2O_3, xH_2O \simeq FePO_4 > AlPO_4 > CaCO_3$

At 20°C, the order is

$Al_2O_3, xH_2O > Fe_2O_3, xH_2O > FePO_4 > AlPO_4 > CaCO_3$.

Positive heat of adsorption is found in case of adsorption on Al- compounds and negative heat of adsorption is observed in case of adsorption on Fe- compounds and $CaCO_3$.

CHAPTER IV

STUDIES ON ADSORPTION OF MOLYBDATE BY SOME PURE HOMO IONIC CLAYS.

This chapter deals with adsorption and desorption studies of molybdate on homo ionic bentonite and kaolinite clays at two pH and temperature levels, with a view to derive the degree of adsorption and related thermodynamic parameters which will help in understanding the nature and strength of its binding with the clay surfaces.

4.1. Materials and Methods :

4.1.1. Materials

a) Reference clay minerals -

i) Bentonite - Bhavanagore, Sourashtra (Gujarat).

ii) Kaolinite - Singhbhum (Bihar).

The samples were obtained from the Calcutta Mineral Supply Corporation, Calcutta.

b) Separation of clays - Pure clays were separated from the reserve materials following the international method. Chemical composition of the standard clays given in the following Tables - II(a) and II(b).

TABLE-II(a) : Chemical composition of the standard clay minerals (expressed as percentage on oven dry basis) (Lala, ScC. 1959).

Clay	SiO_2	R_2O_3	Fe_2O_3	Al_2O_3	Mgo	K_2O	CaO
Kaolinite	48.10	45.58	0.98	44.60	-	-	0.29
Bentonite	60.58	27.00	3.99	23.01	2.43	0.19	-

TABLE -II(b) : Molar ratio of reference clay minerals.

Clay Minerals	SiO_2/R_2O_3	SiO_2/ Al_2O_3	Al_2O_3/Mgo	Al_2O_3/K_2O
Maolinite	1.81	1.83	Infinity	Infinity
Bentonite	4.03	4.47	3.03	110.20

c) Preparation of Homo ionic clays of Ca, Fe and Al - Homo ionic Bentonite and Kaolinite with respect to Fe^{+3}, Al^{+3} and Ca^{+2} ions were prepared by repeated equilibration of the clays with 1(M) solution of the respective chlorides. Excess electrolytes were removed by repeated washing and centrifugation with 60% ethanol until the solid ~~id~~ phase was chloride free and finally with acetone. In case of iron and aluminium clays the solutions in contact were kept at pH-3, in order to prevent hydrolysis of these cations. The homo ionic clays were then dispersed and density of their well dispersed suspensions were determined, so that desired quantities of clay could be taken from volume measurement.

In order to ascertain the complete saturation, the saturated homoionic clays were taken for estimation of adsorbed cations. It has been found that the amount of adsorbed cation (meg/100 g) was more or less equivalent to the CEC of the respective clays, as shown in the following Table.

TABLE III : CEC and amount adsorbed of homoions on the homoionic clays.

Clay Minerals	CEC (Ca+Mg) meq/100g	Adsorbed Ca^{+2} on Ca-clay (meq/100g)	Adsorbed Fe^{+3} on Fe-clay (meq/100 g)	Adsorbed Al^{+3} on Al-clay(meq/100g)
Kaolinite	8.53	8.54	8.2	8.0
Bentonite	73.00	72.56	72.0	72.1

d) Preparation of H-clays :- Suspension of 2μ, H-saturated bentonite and Kaolinite were prepared by the use of sulfonic acid type cation exchange resin, Amberlite IR-120. Each 500 ml of Bentonite and Kaolinite suspensions (2%) were agitated with a gentle reciprocating motion in the column for 30 minutes and then left for over night in contact with resin. To separate the clay from the resin a gentle suction was applied to the suspension in such a way as to remove from the H-clays the resin column as much as possible (Kalovoulos, 1960).

4.1.2. Methods :

a) Study of Adsorption Isotherm :-

The adsorption experiments of molybdate on homoionic clays were carried out at two different temperatures under the following conditions -

i) Solid-solution ratio - For the H-clays the solid-solution ratio employed was 1:100 and for the metal clays it was 1:300.

ii) pH of the suspension - The experiments were carried out at two pH levels - one at 4.0 and another at 7.0. For maintaining constant pH of the system respective suspensions were titrated to the desired pH level, prior to the addition of buffer solution. Buffers used for this experiment were for pH-4.0, NaoH-acetic acid buffer and for pH-7.0, 0.1(N) NH_4O AC buffer. 5 ml of the respective buffer solutions were added to each sample in equilibriating solution, in which 0.01(M) $CaCl_2$ and desired molybdic acid concentration were maintained.

iii) Concentration of Adsorbate - In order to get isotherm curves, the experiments were carried out at eight different concentrations of molybdate in solution, ranging from 0.1 to 1 ppm. Higher concentration were not used in order to avoid any polymerization of molybdate ions. Available evidence indicates that only monomeric form would be adsorbed and according to Carpeni (1947), only monomeric form of molybdate exists in solutions of less than 3 x 10^{-4}M MoO_3, at all pH values. Keeping this idea into consideration, experiments were carried out by employing the concentrations as specified.

iv) <u>Equilibrium Time</u> - In order to ascertain the equilibrium time the suspensions were shaken for several hours, followed by incubation at isotherm condition for 40 hours. It was found that 3 to 5 hours shaking in rotating shaker, followed by incubation for 40 hours was sufficient to attain equilibrium for all adsorbents taken in this investigation, as depicted in Fig.3. Gonzalez <u>et al</u>.(1974) also used the same shaking time for equilibriation.

vi) <u>Temperature</u> - The experiments were carried out at two isotherm conditions viz. at 40°C and 20°C. The incubation were carried out at the respective temperatures (± 1°C), using a BOD incubator for the purpose.

Considering the above conditions, the adsorption experiments were carried out by 6 hours shaking followed by 40 hours incubation. 2-3 drops of chloroform were added for inhibiting possible microbial activity in the system. Immediately after completion of incubation, the suspensions were then centrifused at 8000 rpm for 20 minutes. The clear supernatant liquid was obtained and taken for analysing the equilibrium concentration of molybdenum in solution.

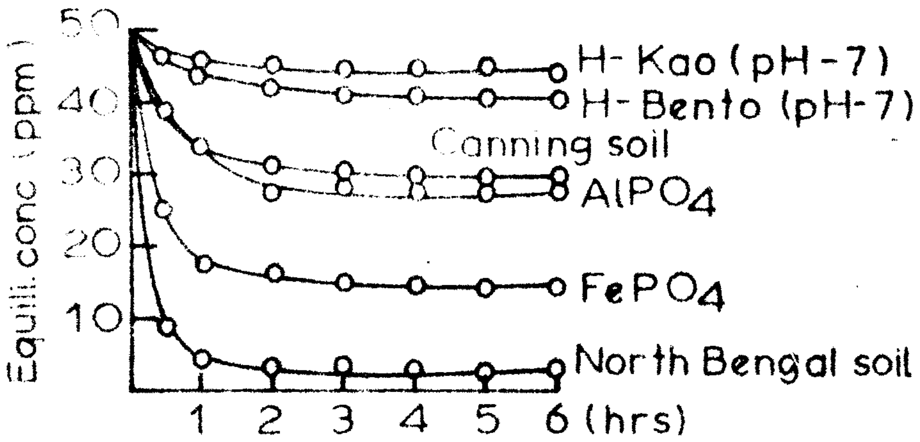


Fig. 3 Equilibrium concentration of molybdenum after hours of shaking.

b) Study of Desorption Isotherm :-

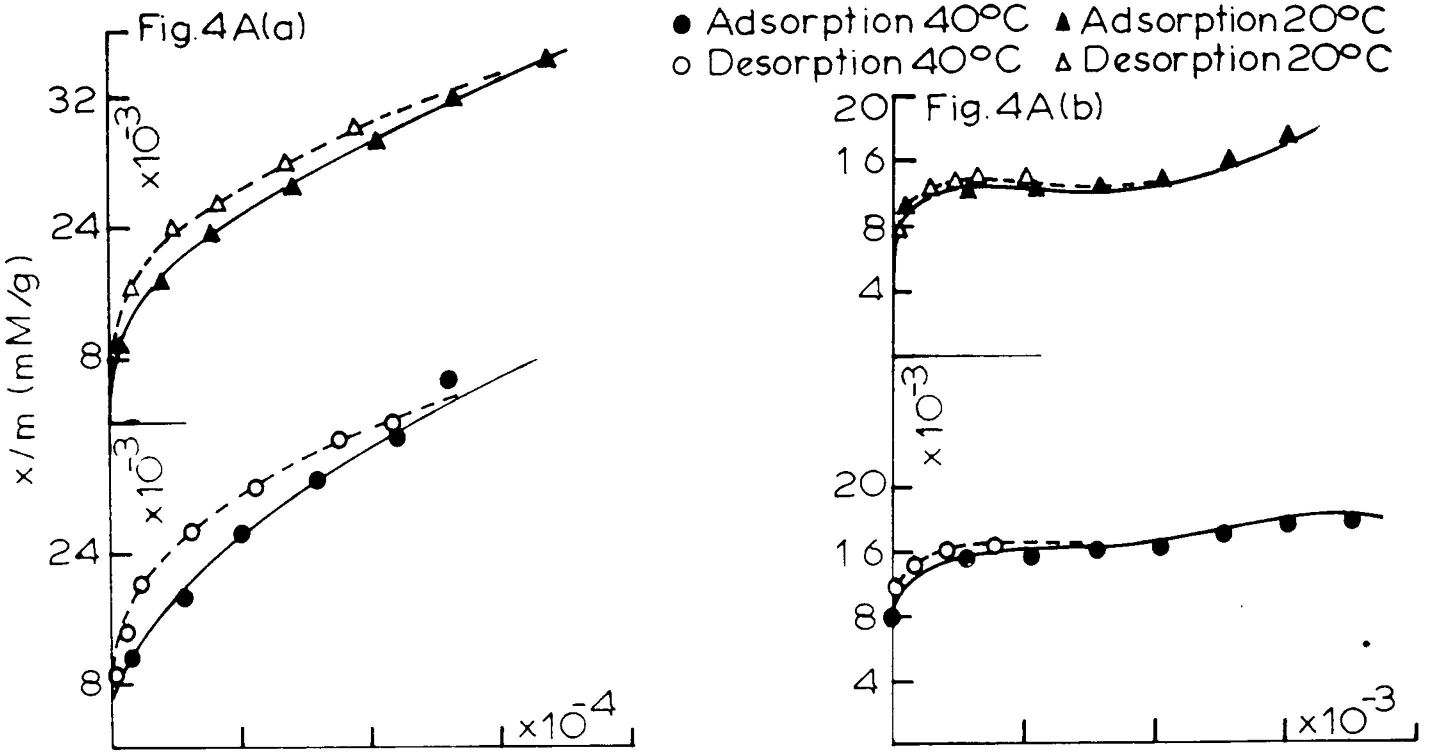
After completion of absorption, as described in the previous section, the suspensions were centrifused. The solid portion, the adsorbent after adsorption, was then washed with 2 ml of distilled water and again centrifused. The solid portion left in the centrifuse tube was then transferred to a conical flask by using 50 ml of 0.01M $CaCl_2$ associated with respective buffer solution. The suspensions were then shaken for one hour and kept for over night under the respective isotherm conditions. The suspensions were then centrifused and supernatant liquids were collected for estimation of desorbed molybdenum, from the adsorbed phase.

As mentioned earlier, the Langmuir equation has been used to study the adsorption isotherms. The adsorption data were computed for drawing adsorption-desorption curves and also the release curves.

4.2. Results and Discussion :

4.2.1. Adsorption of molybdate by H-clays :

The adsorption isotherm of the H-clays at two different pH (4 and 7) levels and at two temperature (40°C and 20°C) levels are shown in Fig.4(A) and 5(A). Except for the H-Kaolinite at pH-7, all the isotherm curves show three distinct regions of adsorption (I, II, III). The region I is characterised by initial steep slope of the isotherm, which bends



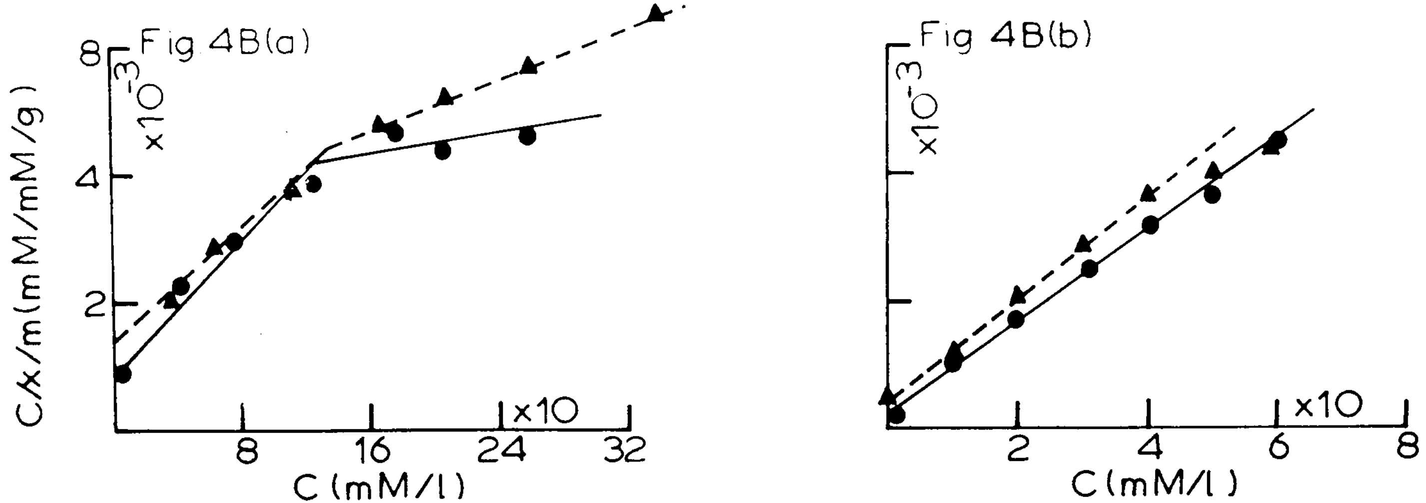


Fig.4A. Molybdate adsorption and desorption in H-Kaolinite at a) pH-4 and b) pH-7 at different temperature levels.

Fig.4B. Langmuir plot of molybdate adsorption in H-Kaolinite at a) pH-4 and b) pH-7 at different temperature levels.

(region II) and finally flattens at (region III), at higher solution concentration of molybdate. Adsorption isotherm for H-Kaolinite at pH-7.0, shows a quite different nature from others. This curve is characterised by initial steep rise followed by flattening of the curve which is more or less horizontal to the x-axis, which is an indication of completion of adsorption at the lower concentration level of molybdenum in solution. Gradual rise of the adsorption curve is observed in case of H-Bentonite at pH-7.0 level. At pH-7.0, unlike H-Kaolinite, adsorption of molybdate continues on the H-Bentonite as the concentration of molybdate in solution increases.

The adsorption isotherm follow the Langmuir equation, [Depicted in Fig. 4(B) and 5(B)]. The correlation coefficient values of the curves are given in the Table-IV (A). However, break in the Langmuir curve is observed in case of adsorption at pH-4.0 level in both the H-clays, indicating a second surface adsorption on this homoionic clays. The Langmuir adsorption maxima (xm) and K-values related to bonding energy are given in the Table-IV(B).

It is observed from the Table-IV(B) that adsorption of molybdate on H-Bentonite is always higher than that of H-Kaolinite at all pH level and temperature. Quite inconsistent result has been observed in case of H-Bentonite at pH-7.0, where exceptionally higher amount of molybdate is adsorbed at high temperature. Considering the Langmuir

TABLE IV(A) : Correlation Coefficient values of the Langmuir curves for the adsorption of molybdate by H-clays.

Adsorbent	* r value for 40°C	*r value for 20°C.
H-Kaolinite (pH-4.0)	0.9532**	0.9779**
H-Kaolinite (pH-7.0)	0.9992	0.9981
H-Bentonite (pH-4.0)	0.9756**	0.9946**
H-Bentonite (pH-7.0)	0.9104	0.9400

* Significant at 1% level.

** Values from more dominant first surface adsorption at lower adsorbate concentration.

TABLE IV(B) : Langmuir Parameters for the adsorption of molybdate by H-clays.

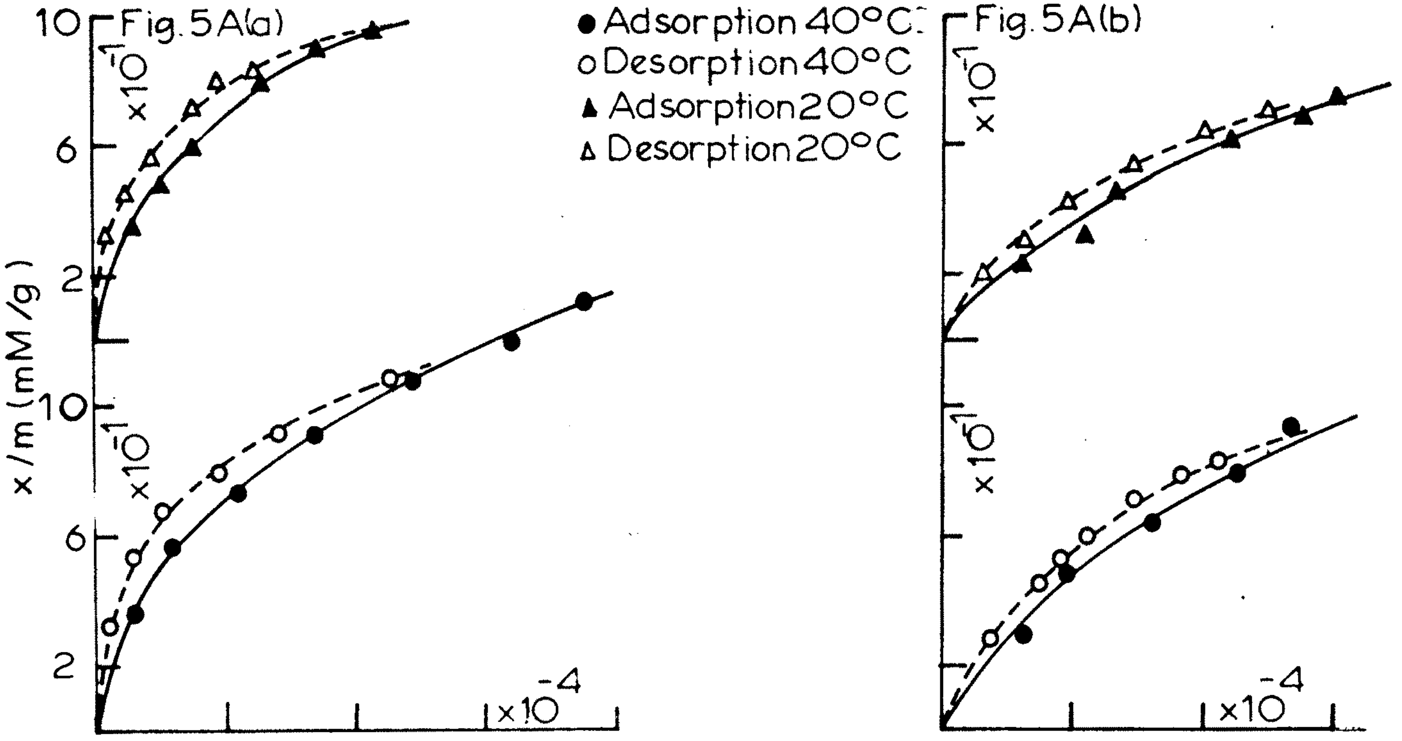
Absorbent	Adsorption maxima (mM/g)		K-value (x10^{3}) M^{-1}	
	40°C	20°C	40°C	20°C
H-Kaolinite(pH-4.0)	0.66*	0.50*	1062.6*	1611.2*
H-Kaolinite(pH-7.0)	0.14	0.13	3406.6	2145.7
H-Bentonite(pH-4.0)	1.84*	1.33*	3188.2*	6097.8*
H-Bentonite(pH-7.0)	4.64	2.86	62.5	81.9

*Values for the first surface adsorption.

isotherm curve for H-Bentonite at pH-7.0, no specific information about the adsorption maxima can be obtained. At lower temperature, higher amount of adsorption is also found. This result may be due to greater adsorption surface of Bentonite clays. Besides this, H-Bentonite may possess some Fe- ions on its surface, which may come from the mineral structure due to entrance of H ion in the system. The higher capacity of iron to adsorb molybdate subsequently results in the higher adsorption capacity of the H-Bentonite compared to H-Kaolinite.

Higher amount of molybdate adsorption by H-Kaolinite is found to occur at pH-4.0 rather than at pH-7.0. This may be due to protonation of the exposed-OH groups of Kaolinite at lower pH values, which results in higher adsorption of the molybdate. Adsorption on H-Kaolinite at pH-4.0, however, shows a two surface adsorption as indicated by the Langmuir curve. It is possibly due to adsorption of molybdate by two different on H-Kaolinite- one through more or less chemical bonding by protonated -OH groups and the other through ligand exchange by free OH^- groups on the clay surface. The influence of pH on the adsorption of molybdate by H-clays is thus found to be quite conspicuous.

Regarding the effect of temperature on molybdate adsorption, it is found that significant difference is only found in case of H-Bentonite. On the other hand H-Kaolinite does



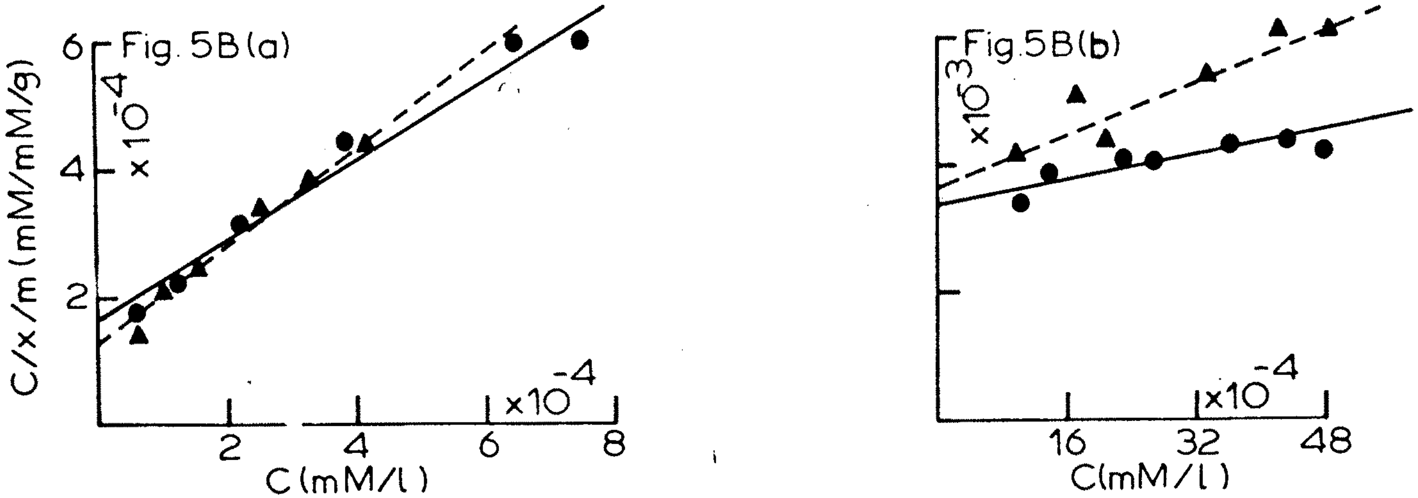


Fig.5A. Molybdate adsorption and desorption in H-Bentonite at a) pH-4 and b) pH-7 at different temperature levels.

Fig.5B. Langmuir plot of molybdate adsorption in H-Bentonite at a) pH-4 and b) pH-7 at different temperature levels.

not show any major difference in this respect. Most of the adsorption reaction of molybdate on H-Kaolinite takes place through exchange with OH^- ions, while reaction of molybdate with surface Fe^{+3} of H-Bentonite may occur to form insoluble ferric molybdate with in the latter case.

The K-value related to bonding energy of adsorption, calculated from Langmuir curve indicates a greater strength of adsorption of molybdate by H-Bentonite at pH-4.0. H-Bentonite at pH-7.0, adsorbs higher amount of molybdate, but with less strength. On the other hand, H-Kaolinite at pH-7.0 though adsorbs little amount of molybdate, it does it with greater strength. He-Kaolinite at pH-4.0 level adsorbs higher amount of molybdate with higher bonding energy. The bonding energy decreases in the order H-Bentonite (pH-4) $>$ H-Kaolinite (pH-7) $>$ H-Kaolinite (pH-4.0) $\gg$ H-Bentonite (pH-7.0).

Though the effect of temperature on molybdate adsorption in H-clays is not prominent, but as value of K-indicates greater strength of adsorption at lower temperature, which is only found in case of H-Bentonite. On the other hand, at high temperature level, strength of adsorption is to some extent higher in case of H-Kaolinite. Quite inconsistent result, in this regard, fails to interpret the actual nature of adsorption although it can be concluded that H-Bentonite shows a greater affinity for molybdate compared to H-Kaolinite.

4.2.2. Desorption of the adsorbed molybdate by H-clays:

The desorption isotherms shown in association with their respective adsorption ones in Fig. 4(A) and 5(A), at different pH and temperature levels highlight reversibility or irreversibility of the adsorption. It is found from the curve, in all the cases, except for H-Bentonite at PH-7.0, hysterosis of the curve is occured. In all the cases, desorption curve merges with adsorption curve at the higher concentration of molybdate in solution. At higher pH level of H-Bentonite, greater reversibility of the adsorption is indicated. Hence, it can be concluded that at pH 4.0 level, molybdate ion can be adsorbed on the H-clays with greater strength. H-Kaolinite at pH-7.0, though adsorbs lowers amount of molybdate, shows irreversibility at the lower concentration level. The result is consistent with the value of K, which is more or less higher for the cases specified.

From the release curves, shown in Fig.12, it is observed that slower release of molybdate is occured in case of H-Bentonite and H-Kaolinite at pH-4.0 level. On the other hand, H-Bentonite releases molybdate with higher rate at higher concentration of molybdate. The result is consistent with the adsorption-desorption curve, where greater reversibility is indicated by the merger of the curves.

H-Kaolinite at pH-7.0, also releases small amount of molybdate, as because it originally adsorbed very little amount of it.

4.2.3. Change in free energy, enthalpy and entropy for molybdate adsorption by H-clays :

The values of ΔH^o, ΔS^o and ΔG^o, as calculated from the equilibrium constant, obtained from Langmuir intercepts, are given in the Table VII. It is found that H-Kaolinite shows a greater change in ΔG^o, but H-Bentonite at pH-7, shows a lower change in ΔG value. In case of H-Bentonite (pH-4) and H-Kaolinite (pH-4 and 7) the ΔG^o values are more or less same. In all the cases the values are negative, indicating spontaneous adsorption of molybdate on these clays. Greater $-\Delta G^o$ value is also found at higher temperature compared tolower temperature level.

Regarding the value of ΔH^o, it is observed that except in the adsorption of molybdate on H-Kaolinite at pH 7.0, negative, indicating exothermic nature of adsorption on these H-clays. On the other hand H-Kaolinite at pH 7.0 exhibits endothermic nature of adsorption.

Higher mean ΔS^o value is observed in case of adsorption of molybdate at lower pH-level on H-clays compared to at higher pH level.

4.2.4. Adsorption of molybdate by Fe-clays :

The adsorption isotherms of the Fe-clays at two different pH levels (pH-4 and 7) and at two temperatures (40°C and 20°C) are shown in Fig.6(A) and 7(A), from which it becomes evident that Fe-saturation increases molybdate adsorption in the clay minerals, compared to other homoionic clays. The isotherms are characterised by steady rise of the curve, indicating adsorption of molybdate on single surface with similar state of energy level in Fe-Kaolinites at all level of pH values. But in case of Fe-Bentonite, the isotherm curves are characterised by different adsorption regions. Initial steep rise of the isotherm (region-I), which bends (region-II) and finally flattens out (region-III), at higher concentration of molybdate in solution.

The break in the Langmuir adsorption curve [Fig.6(B) and 7(B)] observed in case of Fe-Bentonite at all pH levels, indicating a second surface reaction of molybdate on Fe-Bentonite. The correlation coefficient values of the Langmuir curve are reported in the Table-V(A). The Langmuir adsorption maxima (Xm) and K-values are given in the Table-V(B).

It is observed from the Table V(B) that the adsorption maxima of Fe-Bentonite is much higher than that of Fe-Kaolinite. High cation exchange capacity of Bentonite results in high amount of adsorbed Fe^{+3} (i.e. 9 times more than that of adsorbed Fe^{+3} on Kaolinite), contribute large

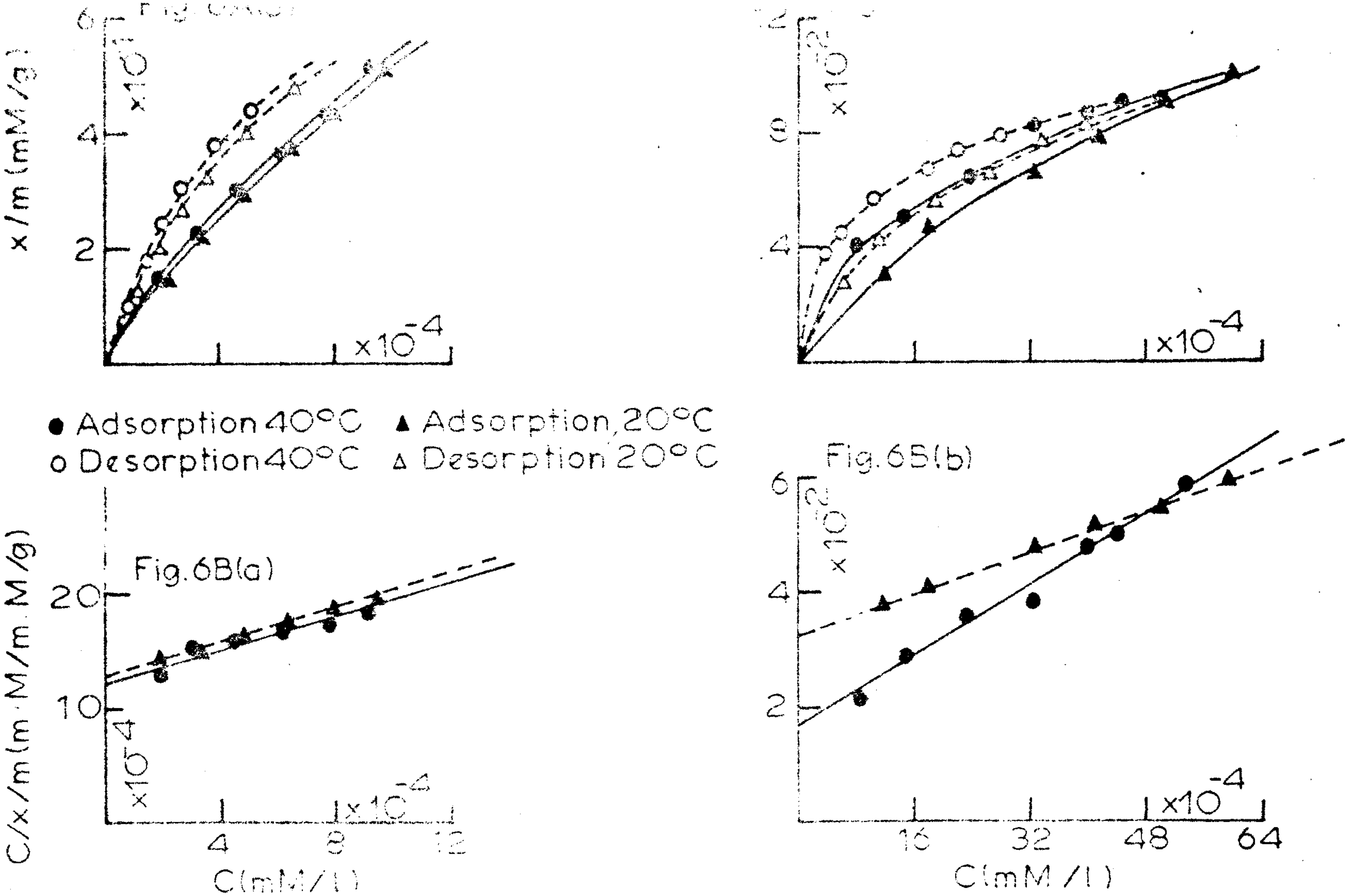


Fig 6 A. Molybdate adsorption and desorption in Fe-Kaolinite at a) pH-4 and b) pH-7 at different temperature levels.

Fig 6 B. Langmuir plot of molybdate adsorption in Fe-Kaolinite at a) pH-4 and b) pH-7 at different temperature levels.

TABLE-V(A) : Correlation coefficient values of Langmuir curves for the adsorption of molybdate by H-clays.

Adsorbent	r*value for 40°C	r*value for 20°C
Fe-Kaolinite (pH-4)	0.8151	0.9983
Fe-Kaolinite (pH-7)	0.9447	0.9979
Fe-Bentonite (pH-4)	r_1=0.9937 r_2=0.9759	r_1= 0.9824 r_2= 0.9937
Fe-Bentonite (pH-7)	r_1=0.9992 r_2=0.9989	r_1= 0.9987 r_2= 0.9991

* Significant at 1% level.

TABLE-V(B) : Langmuir parameters for the adsorbtion of molybdate by Fe-clays.

Adsorbent	Adsorption maxima(m^M/g		K-value(X10^3)M^{-1}	
	40°C	20°C	40°C	20°C
Fe-Kaolinite (pH-4)	2.55	1.38	285.4	585.3
Fe-Kaolinite (pH-7)	0.13	0.23	266.6	127.5
Fe-Bentonite (pH-4)	3.47* 4.83**	4.73* 4.90**	5764.7* 3103.4**	3266.2* 2982.4**
Fe-Bentonite (pH-7)	2.66* 2.85**	2.53* 2.50**	220.5* 200.0**	225.7* 245.3**

* Values for the first surface adsorption.

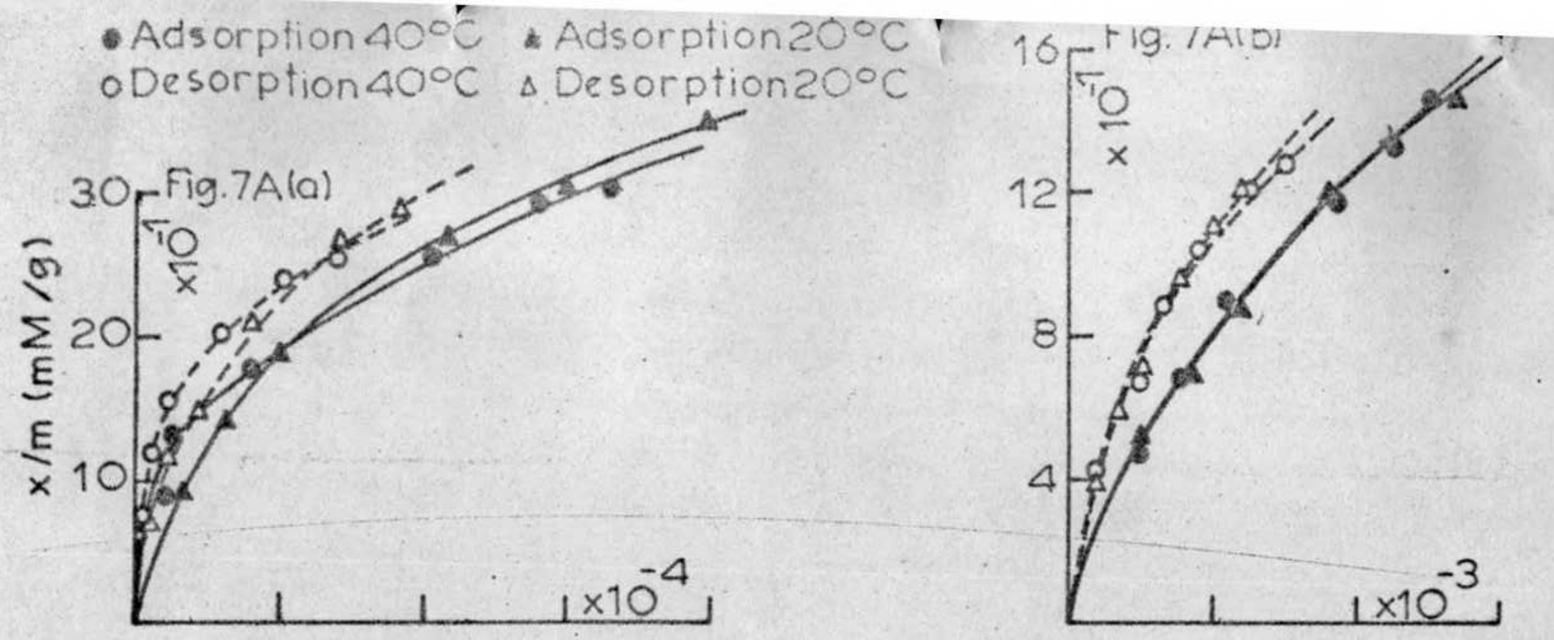
** Values for the second surface adsorption.

reactive surface area for molybdate adsorption. Very high adsorption of molybdate on Fe-saturated clays is obvious as because high affinity for molybdate anions of Fe-containing components as reported by Reyes and Jurinak (1967) and Reisenaur *et al*.(1962).

Effect of pH on molybdate adsorption in Fe-clays is very much obvious. At low pH level, the adsorption was higher. In case of Fe-saturated Kaolinite, the effect is more prominent, as increase in pH from 4 to 7, results drastic-reduction in the adsorption of molybdate. In case of Fe-Bentonite, effect of pH is also prominent but much less than that of Fe-Kaolinite.

Break in the Langmuir curve, indicates two-surface reaction of Fe-Bentonite with molybdate, which is consistent with the nature of the adsorption curve.

Effect of temperature on the adsorption of molybdate is also prominent. Higher amount of molybdate at high temperature occurs only at lower pH level in both the clays. On the other hand, reverse observation is found in both the clays at higher pH level. It may be generalised that at lower pH, the adsorption is mostly chemical. But in all the cases greater K-values have been obtained at higher temperature, which means adsorption of molybdate by the iron clays is largely chemical. It can be further seen that Fe-Bentonite adsorbs molybdate with greater strength than that of Fe-Kaolinite. However higher K-value is observed in case of Fe-Kaolinite at pH-4.0.



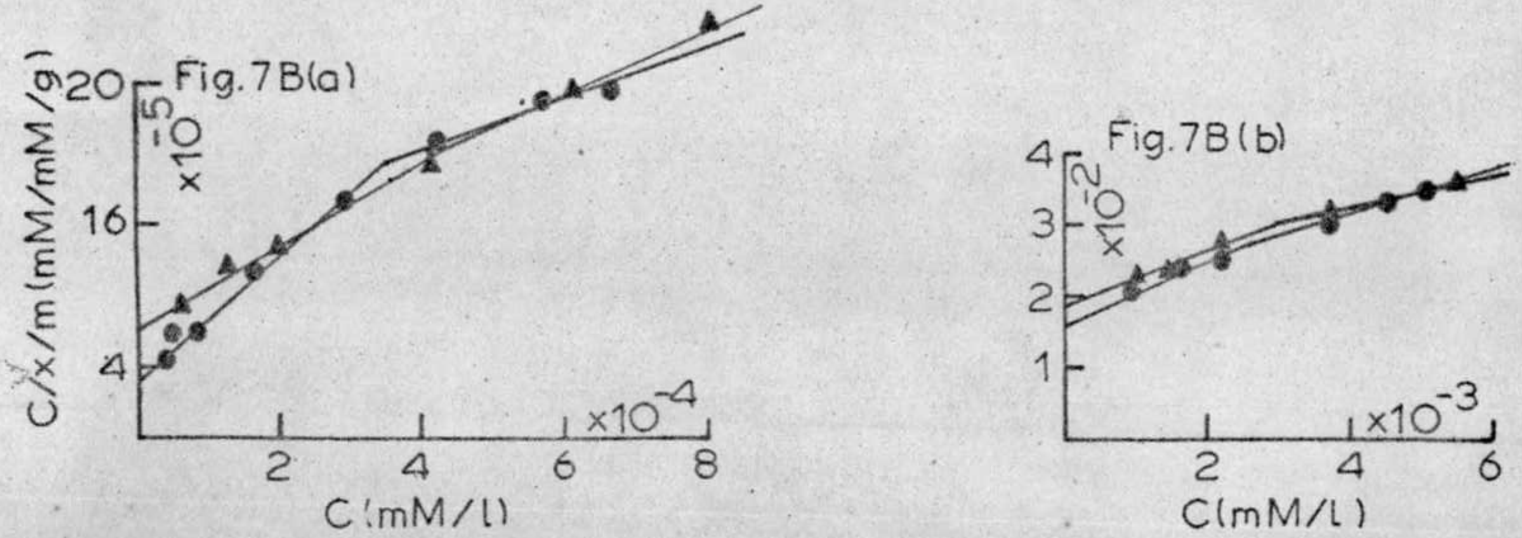


Fig. 7A. Molybdate adsorption and desorption in Fe-Bentonite at pH (a) 4.0 and (b) 7.0 levels at different temperatures.

Fig. 7B. Langmuir plot of molybdate adsorption in Fe-Bentonite at pH (g) 4.0 and (b) 7.0 levels at different temperatures.

4.2.5. Desorption of the adsorbed molybdate by Fe-clays:

The adsorption isotherms shown in association with their respective adsorption ones in Fig.6(A) and 7(A) at different pH and temperature levels, highlight a marked irreversibility of the adsorbed molybdate with respect to its ionic concentration in solution. The desorption curve have reflected a strong hysterosis irrespective of pH of the system except at pH-7.0 for Fe-Kaolinite. For this case, desorption curve merges with the adsorption curve at higher concentration of molybdate in solution, indicating reversibility of the adsorbed molybdate in this region. The nature of desorption curve in case of Fe-Kaolinite at pH-7.0 is very much consistent with value obtained from the Langmuir curve. As K-value related to bonding energy is lower in this case, after desorption practically no molybdate remains in the adsorbed phase.

Release curves, as shown in Figs.12, also indicate the nature of release of the adsorbed molybdate from the Fe-saturated clays. It is evident from the curves, that the release is gradual as slope of the curve is lower, which is also in conformity with the higher bonding energy of the adsorption, signifying little release of the adsorbed molybdenum.

It may be generalised from the above discussion that the molybdate ions adsorbed on the surface of Fe-clays undergo certain transformation that gives it a stronger affinity to the surface, particularly when their concentration is low.

Results of several workers (Jones, 1971; Reisenauer *et.al*, 1962) are in consistent with the present work, regarding the strong affinity of Mo with the Fe-coatings of soil and clay surfaces.

4.2.6. Change in free energy, enthalpy and entropy for Molybdate adsorbtion by Fe-clays :

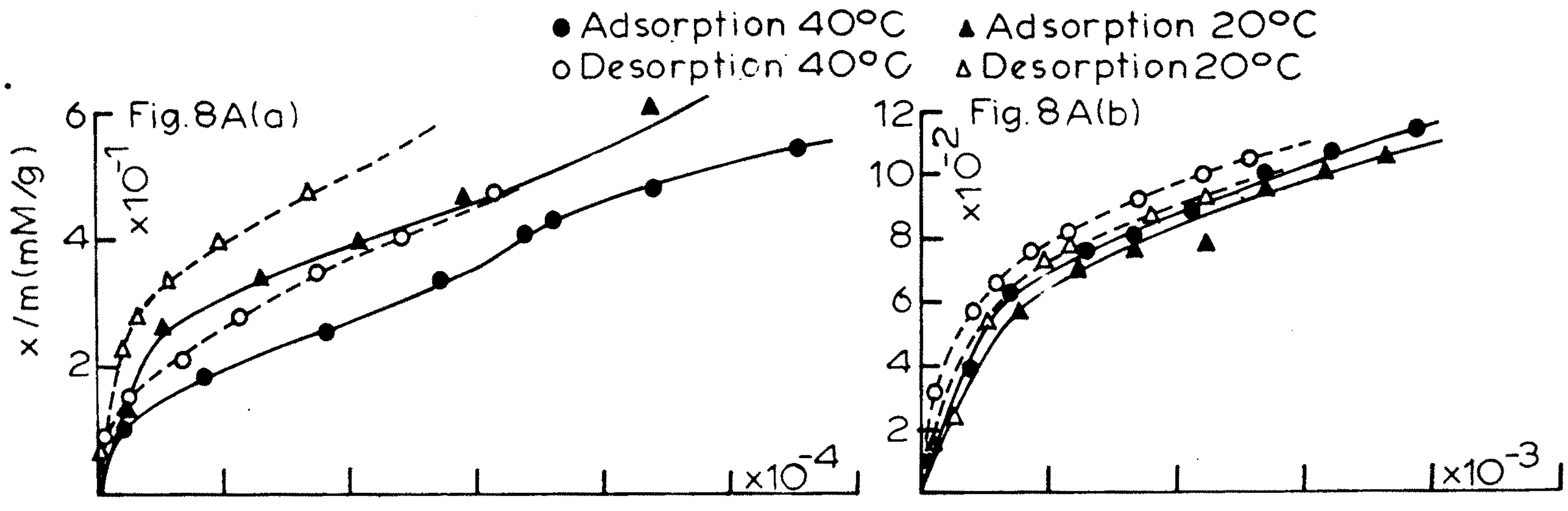
As reported in the Table-VIII it is found that ΔH^o values for adsorption of molybdate by Fe-clays are positive but at pH-4.0 negative values of ΔH^o are observed, only in case of Fe-Kaolinite. Lesser positive values of ΔH^o are obtained in case second surface adsorption of molybdate on Fe-Bentonite. Higher ΔS^o value is observed in case of adsorption by Fe-Kaolinite at pH-4.0 level. The ΔS^o value increases in the order Fe-Kaolinite (pH-4.0) $>$ Fe-Bentonite (pH-7.0) $>$ Fe-Bentonite (pH-4.0) $>$ Fe-Kaolinite (pH-7.0).

Change of free energy (ΔG^o) as reported in the Table-VIII, is found in all the cases to be negative, indicating spontaneous reaction of the molybdate with Fe-clays. Higher negative ΔG^o is observed in case adsorption at pH-4.0 level in both the temperatures. The ΔG^o change increases in the order, at 40°C temperature level. Fe-Bentonite (pH-4) $>$ Fe-Kaolinite (pH-4) $>$ Fe-Kaolinite (pH-7) $>$ Fe-Bentonite (pH-7.0). But the order increases at 20°C, Fe-Kaolinite (pH-4) $>$ Fe-Bentonite (pH-4.0) $>$ Fe-Bentonite (pH-7.0) $>$ Fe-Kaolinite (pH-7.0).

4.2.7. Adsorption of Molybdate by Al-clays :

The adsorption isotherms of molybdate for Al-clays at two pH levels are shown in Figs.8(A) and 9(A), from which it becomes evident that Al^{+3} saturation increases molybdate adsorption like Fe^{+3} saturation. The isotherms are characterised by different adsorption regions. Region I and II have been observed in all the Al-clays at all pH and temperature levels, which indicate two different sets of energy level for molybdate adsorption on Al-clays. The region I is characterised by initial steep slope of the isotherm which bends (region II) and finally flattens out (region III) at higher solution concentration.

The adsorption isotherms follow the Langmuir equation as evident from the correlation coefficient values, given in the Table VI(A). The break in the Langmuir adsorption curves [Fig.8(A) and 9(A)] obviously indicate either precipitation or a second surface reaction of molybdate with this clay. The Langmuir adsorption maxima (Xm) and K-value of the Al-clays are given in the Table VI(B). Al-Kaolinites, though exhibit two surface adsorption, the present investigation considers the more dominant second surface adsorption at pH 4-0 level and first surface adsorption at pH-7.0 level.



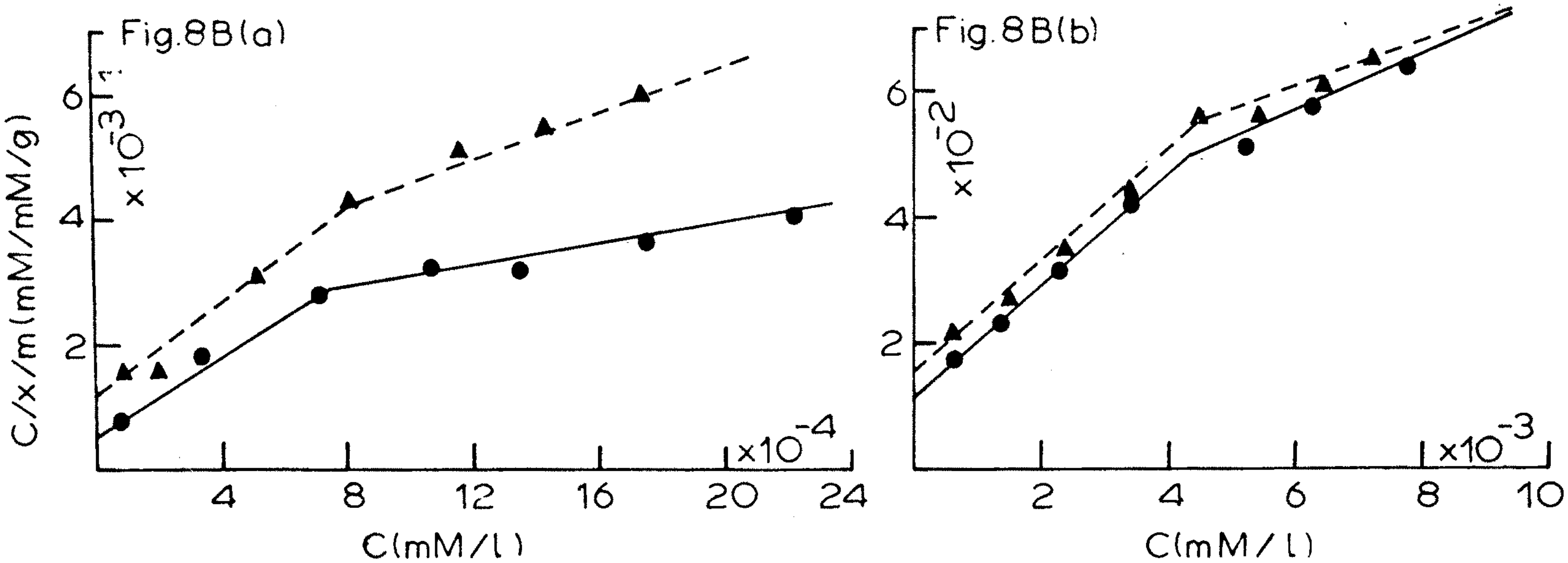


Fig. 8A. Molybdate adsorption and desorption in Al-Kaolinite at pH (a) 4.0 and (b) 7.0 levels at different temperatures.

Fig. 8B. Langmuir plot of molybdate adsorption in Al-Kaolinite at pH (a) 4.0 and (b) 7.0 levels at different temperatures.

TABLE-VI(A) : Correlation coefficient values of the Langmuir curves for the adsorption of molybdate by Al-clays.

Adsorbent	r*value for 40°C	r*value for 20°C
Al-Kaolinite (pH-4)	r_2=0.9443	r_2=0.9983
Al-Kaolinite (pH-7)	r_1=0.9972	r_1=0.9969
Al-Bentonite (pH-4)	r_1=0.9518 r_2=0.8728	r_1=0.9986 r_2=0.9837
Al-Bentonite (pH-7)	r_1=0.9837 r_2=0.9841	r_1=0.9841 r_2=0.9867

* Significant at 1% level.

r_1 and r_2 stand for correlation coefficient values for first and second surface adsorption respectively.

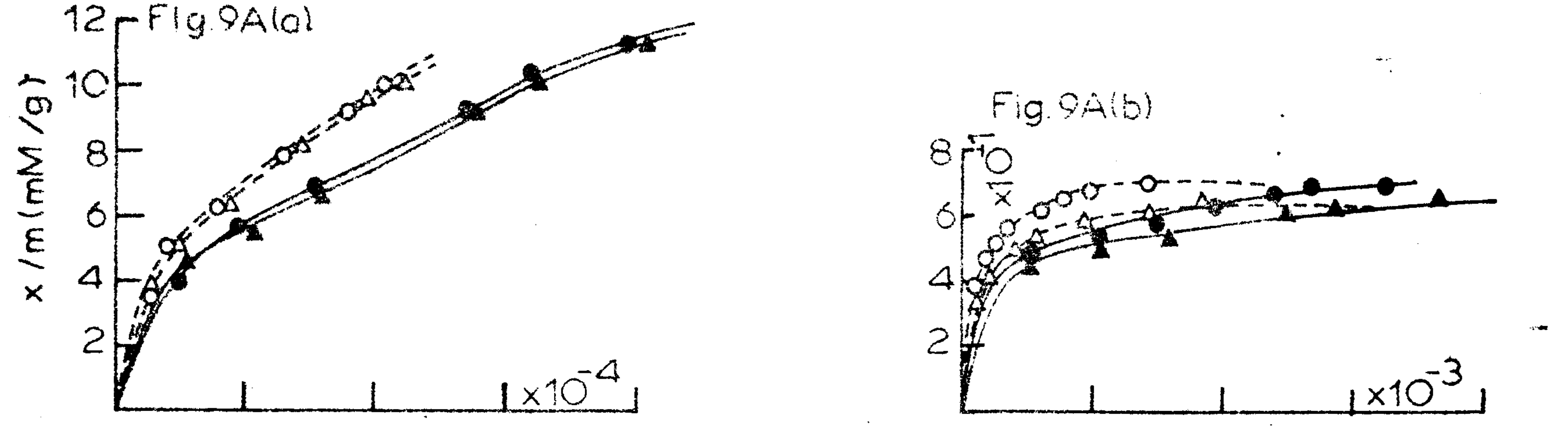
TABLE-VI(B): Langmuir parameters for the adsorption of molybdate by Al-clays.

Adsorbent	Adsorption maxima (mM/g)		K-value ($\times 10^3$)-M^{-1}	
	40°C	20°C	40°C	20°C
Al-Kaolinite (pH-4)	0.724**	0.714**	1078.9**	1021.8**
Al-Kaolinite (pH-7)	0.144*	0.140*	451.4*	407.7*
Al-Bentonite (pH-4)	1.081* 2.140**	0.977* 1.420**	1185.8* 253.8**	1320.0* 298.6**
Al-Bentonite (pH-7)	0.781* 1.647**	0.729* 1.231**	1226.0* 170.9**	1014.8* 234.6**

* Values for first surface adsorption.

** values for second surface adsorption.

Fig.9A. Molybdate adsorption and desorption in Al-Bentonite at pH (a) 4.0 and (b) 7.0 levels at different temperatures.



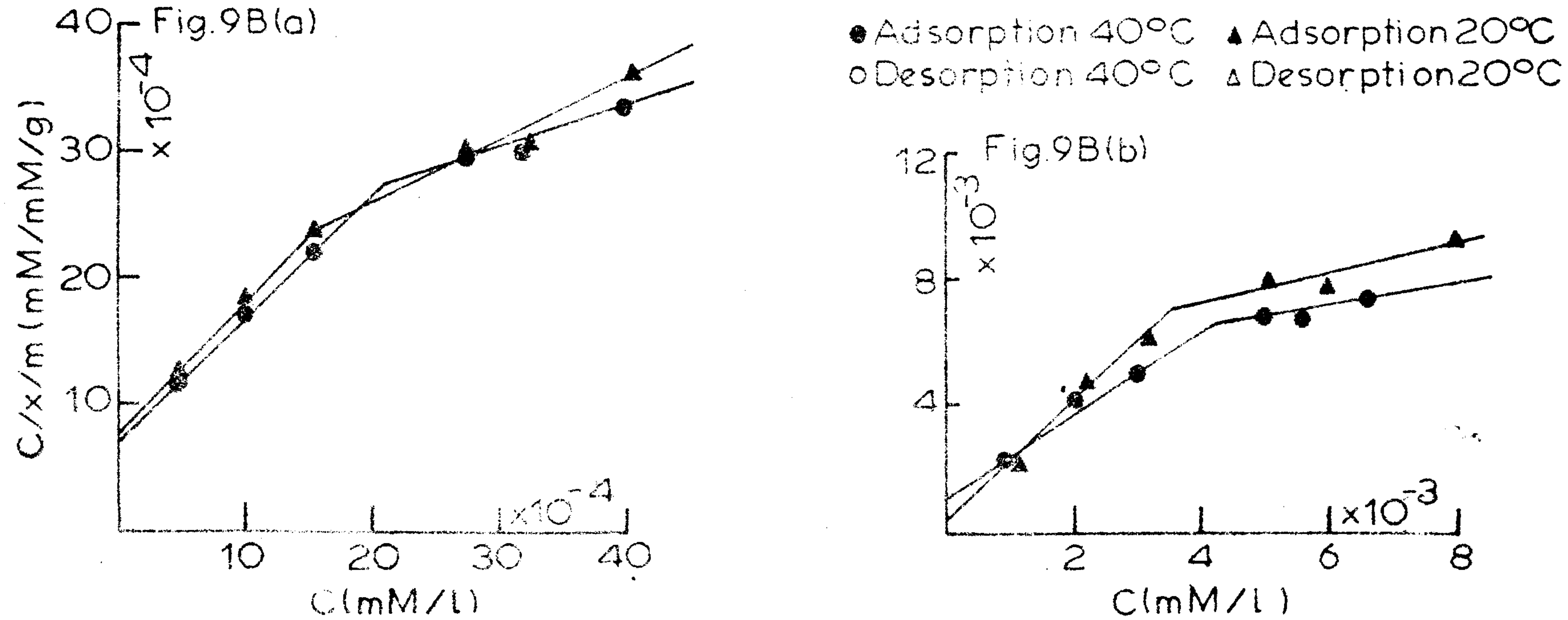


Fig.9B. Langmuir plot of molybdate adsorption in Al-Bentonite at pH (a) 4.0 and (b) 7.0 levels at different temperatures.

It is observed from the data cited in the Table VI(B) that Al-Bentonite adsorbs higher amount of molybdate than Al-Kaolinite. It is due to the high CEC of Bentonite, which adsorbs higher amount of Al^{+3}, resulting in greater reactive sites for molybdate adsorption. At pH 7.0 adsorbed Al^{+3} ions however remain in the form of hydrous oxides, which are the sole agent for molybdate adsorption.

In all the cases, break in the Largmuir curve is observed. Greater amount of molybdate adsorption occurs at higher concentration of molybdate in solution, but with lesser strength. Reverse result has been found in the adsorption of molybdate at lower concentration of Mo, in solution.

Significant effect of pH on molybdate adsorption is observed in both the clays. At lower pH level greater amount of molybdate is adsorbed. The observed effect of pH on molybdate adsorption is related to the reactivity of the aluminium, which is higher at low pH.

As observed, temperature imperts little effect on the adsorption of molybdate on Al-clays at both pH levels. But the effect is prominent to some extent in the second surface reaction. So, at low concentration level of Mo in solution, temperature plays little role. So mostly physical nature of adsorption may occur at first surface adsorption, on the other hand greater chemical reaction at the second surface is expected in Al-clays.

Considering the K-value, it can be said that on the first surface reaction molybdate ion is adsorbed with greater strength. At the lower pH values, molybdate is adsorbed with greater strength compared to higher pH in these clays, however, Al-Bentonite at pH-7.0 adsorbs molybdate with greater strength. On the other hand Al-Kaolinite, at this pH level adsorbs molybdate weakly. With the exception of Al-Bentonite at pH-4.0 all the Al-saturated clays adsorb molybdate with greater strength at higher temperature. However, second surface adsorbtion on Al-Bentonite, shows relatively greater strength of adsorption at lower temperature.

The comparison of the Langmuir adsorption maxima indicates that the degree of molybdate adsorption by the Al-clays follow the order.

Al-Bentonite (pH-4.0) > Al-Bentonite (pH-7.0) >
Al-Kaolinite (pH-4.0) > Al-Kaolinite (pH-7.0)

The adsorption of molybdate by Al-clays is thus found to be, more or less chemical in nature. Observations are in conformity with the report of Jones and Milne (1956) which indicates the formation of Al-molybdates on clay surfaces. Reyes and Jurinack (1967) also reported that there is a strong affinity for Mo by Al-containing surfaces.

4.2.8. Desorption of adsorbed molybdate by Al-days :

The desorption isotherms shown in association with their respective adsorption ones in Figs.8(A) and 9(A) ; at different pH and temperature levels, reflected strong hysterosis effect, irrespective of pH. This shows that adsorption of molybdate ions by Al-clays is irreversible with respect to its ionic concentration in solution. The curves indicate greater hysterosis at pH 4.0 level reflecting stronger bonding energy of the molybdate ion to the adsorbate. On the other hand desorption curve merges with the adsorption curve in case of pH-7.0 of the system, at higher concentration of molybdate in solution (region III), indicating greater irreversibility of the adsorbed molybdate in this region. It is also evident from K-value obtained from the second surface adsorption, where the value is much lower than that of K-value obtained from the first surface adsorption. So molybdate adsorbed with little strength on this region, is reversible in nature, indicating largely physical adsorption.

According to release curves, shown in Figs.12, the amount of adsorbed molybdate, coming out due to desorption, is enhanced with the increase in molybdate saturation status of the clay surface. It is observed from the curves, that the rate of release is higher at higher pH of the system which must be due to the increasing concentration of OH^- ions in the solution, competing for the active sites, particularly when the concentration of molybdate in solution is decreased due to dilution. At low pH, the molybdate ions are released with greater strengh.

4.2.9. Change in free energy, entropy and enthalpy in the adsorption of molybdate by Al-clays:

The different thermodynamic parameters for molybdate adsorption on Al-clays, are given in the Table VIII. It is observed from the Table that ΔG^{o} value in all the cases are negative, greater negativity being observed in the first surface adsorption reaction. Negative value of ΔG^{o}, clerly indicates that the adsorption is spontaneous.

The ΔG^{o} (negative) value for the adsorption of molybdate on Al-clays increases in the order.

Al-Bentonite (pH-7) $\not>$ Al-Bentonite (pH-4) $>$
$>$ Al-Kaolinite (pH-4.0) $>$ Al-Kaolinite (pH-7).

Change in enthalpy (ΔH^{o}) as calculated from first surface adsorption, are positive in all the cases except in the adsorption on Al-Bentonite at pH 4.0 of the system.

Entropy change ΔS^{o} values are found to be positive in all the cases. The value increases in the order
Al-Bentonite (pH-4.0) $>$ Al-Kaolinite (pH-4.0) $>$
Al-Kaolinite (pH-7.0) $\not>$ Al-Bentonite (pH-7).

4.2.10. Adsorption of Molybdate by Ca-clays :

The adsorption isotherms of the Ca-saturated Kaolinite and Bentonite at various concentrations of molybdate in solutions and at different pH levels and two isotherm conditions (40°C and 20°C) are shown in Figs.10(A) and 11(A). Two distinct regions of adsorption of molybdate by Ca-clays are observed particularly at lower pH values. The region I is characterised by initial relatively steeper slope of the isotherm, which finally flattens out (region II), at higher concentration of molybdate in solution. The adsorption isotherms follow the Langmuir isotherm, as indicated by the Correlation Coefficient values, reported in the Table-VII(A) and depicted in the Figs.10(B) and 11(B). However break in the Langmuir curve is observed in case of adsorption at pH 4.0 of the system, indicating second surface adsorption by Ca-clays at pH 4.0, The Langmuir parameters, as obtained, are given in the Table-VII(B).

Adsorption maxima as reported, indicate that Ca-clays have very little adsorption capacity compared to other homoionic clays. Ca-Bentonite adsorbs higher amount of molybdate at both the pH-level, compared to Ca-Kaolinite. Higher surface area may be the cause of it. Effect of pH on the molybdate adsorption is obvious in the adsorption by Ca-clays. At lower pH levels, adsorption occurs on different regions, which is again observed in the Langmuir

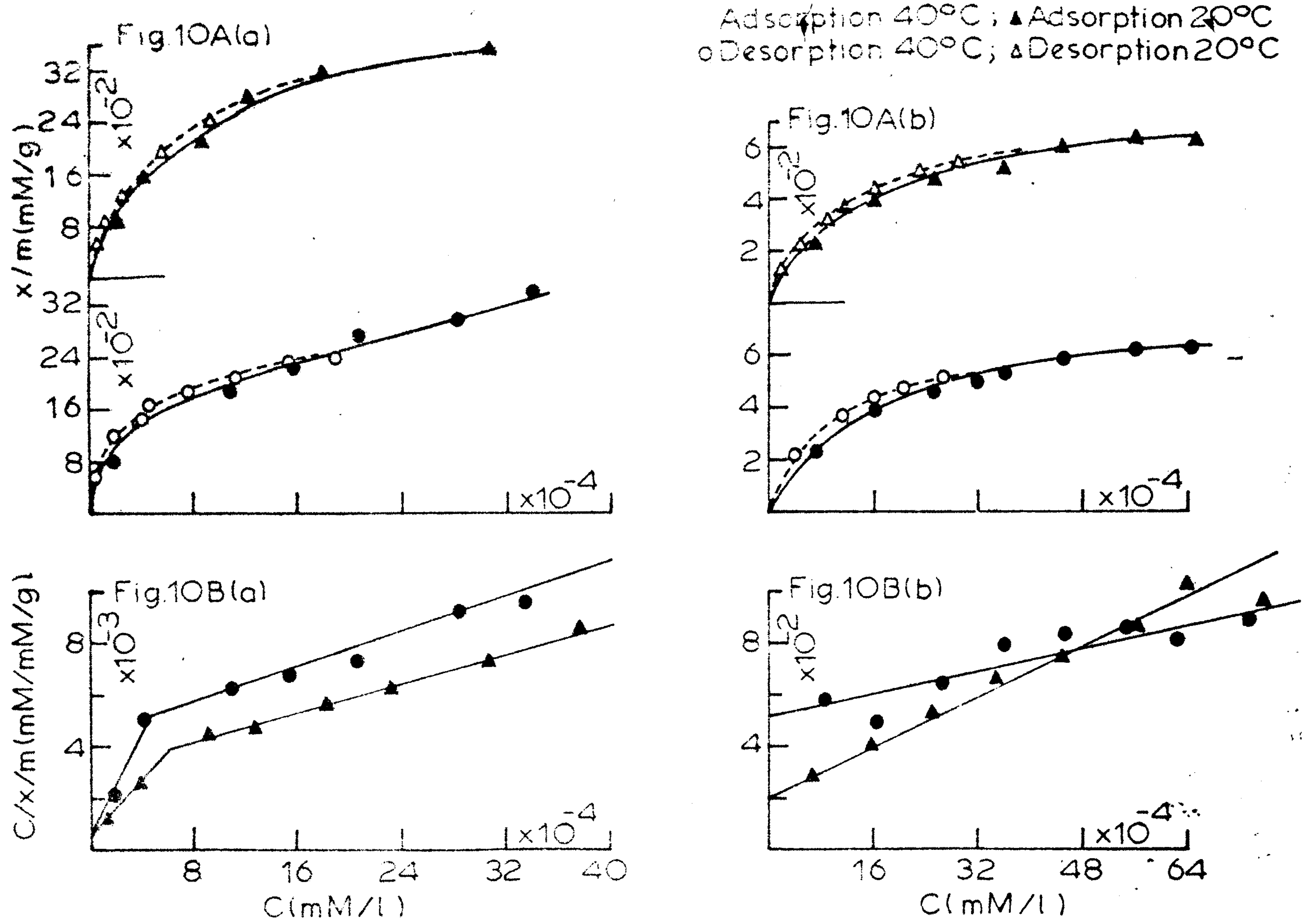


Fig.10A. Molybdate adsorption and desorption in Ca-Kaolinite at pH (a) 4.0 and (b) 7.0 levels at different temperatures.

Fig.10B. Langmuir plot of molybdate adsorption in Ca-Kaolinite at pH (a) 4.0 and (b) 7.0 levels at different temperatures.

TABLE -VII(A) : Correlation Coefficient values for the molybdate adsorption by Ca-clays.

Adsorbent	r*values for 40°C	r*values for 20°C
Ca-Kaolinite (pH-4.0)	0.9768**	0.9933**
Ca-Kaolinite (pH-7.0)	0.9806	0.8353
Ca-Bentonite (pH-4.0)	0.9879***	0.9497***
Ca-Bentonite (pH-7.0)	0.9971	0.9981

* Significant at 1% level.

** Calculated from more dominant second surface adsorption.

*** Calculated from more dominant first surface adsorption.

TABLE-VII(B): Langmuir Parameter for adsorption of molybdate by Ca-clays.

Adsorbent	Adsorption maxima (mM/g)		K-value($\times 10^3$)M^{-1}	
	40°C	20°C	40°C	20°C
Ca-Kaolinite (pH-4)	0.416	0.558	995.8	908.6
Ca-Kaolinite (pH-7)	0.166	0.081	123.7	417.6
Ca-Bentonite (pH-4.0)	0.892	0.847	978.0	937.0
Ca-Bentonite (pH-7.0)	0.364	0.353	1014.8	1194.0

*(For Ca-Kaolinite (pH-4), values are calculated from second surface adsorption and for Ca-Bentonite (pH-4) values are calculated from first surface adsorption).

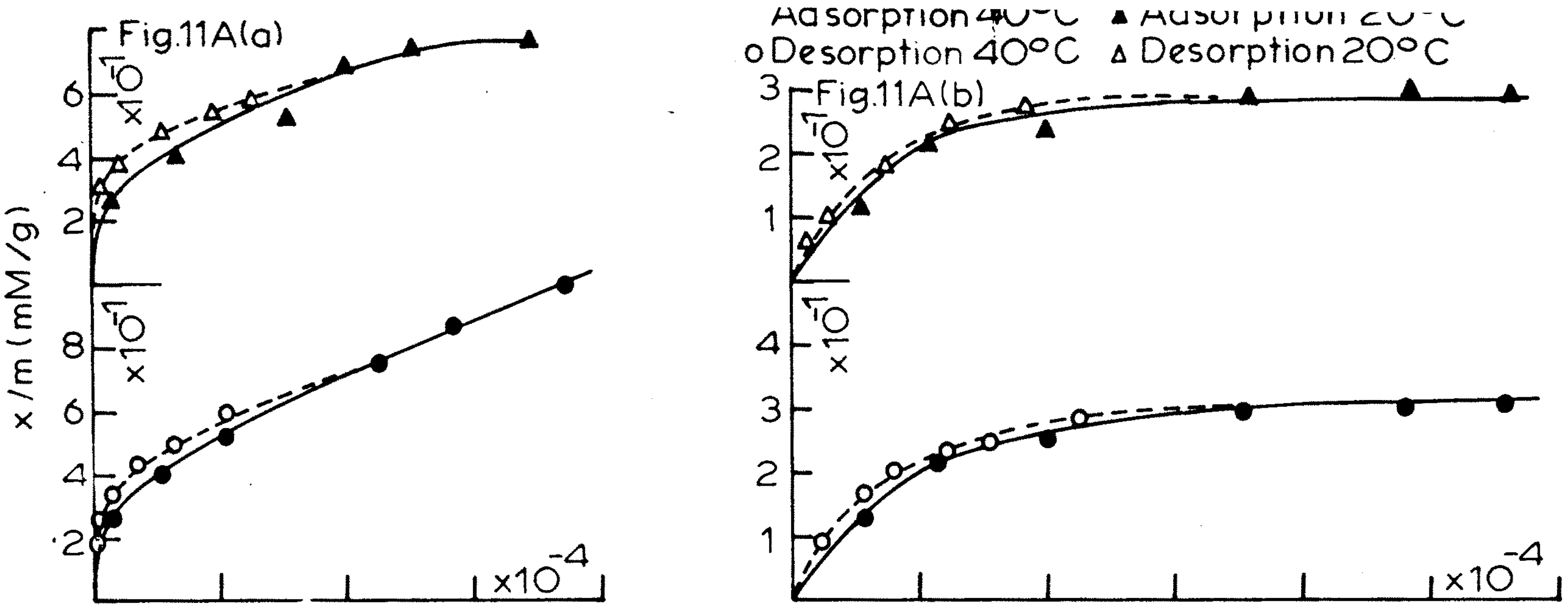
curve. The effect of temperature on the molybdate adsorption by Ca-clays is found significant, particularly in case of Ca-Kaolinite at both the pH level, studied. Greater amount adsorption occurs at lower temperature by Ca-Kaolinite at pH-4.0 level unlike other Ca-clays.

The K-value related to bonding energy is observed higher at higher temperature only at lower pH value. On the other hand relatively higher strength of adsorption is found at higher pH-level of the system.

It can be generalised from the observation that Ca-saturation decreases molybdate adsorption due its contribution of higher pH values at the close of its surface, which results little anion adsorption, of course with the exception of phosphate anion, in which largely chemical precipitation takes place. As with the adsorption of molybdate on $CaCO_3$, Ca-clays also found to be very little affinity for molybdate. The little amount molybdate which is adsorbed at different pH levels on Ca-clay surface seems to be physical in nature particularly at higher pH value. At lower pH value to some extent chemical adsorption may take place with the formation of $Ca\,MoO_4$ on its surface.

4.2.11. <u>Desorption of adsorbed molybdate by Ca-clays:</u>

The desorption isotherm shown in association with their respective adsorption curves in Figs.10(A) and 11(A) at



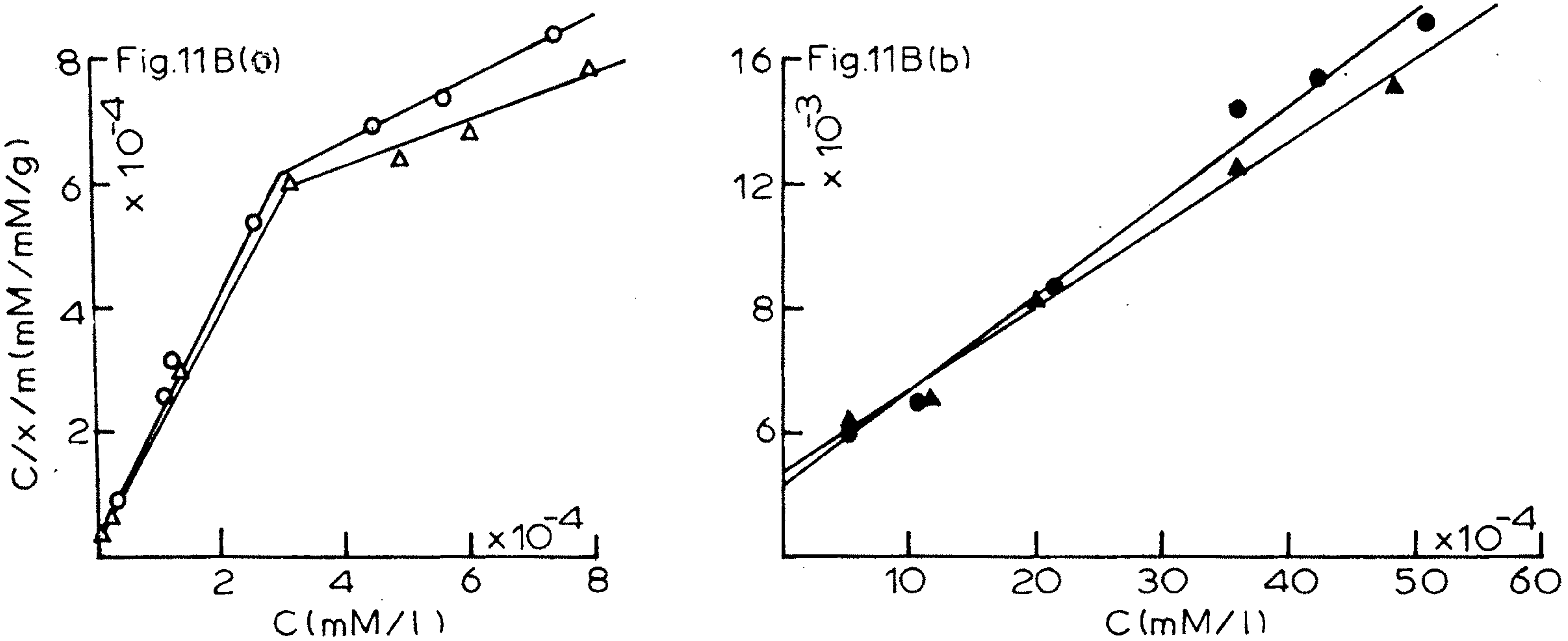


Fig.11A. Molybdate adsorption and desorption in Ca-Bentonite at pH (a) 4.0 and (b) 7.0 level at different temperatures.

Fig.11B. Langmuir plot of molybdate adsorption in Ca-Bentonite at pH (a) 4.0 and (b) 7.0 levels at different temperatures.

different pH and temperature levels, highlight marked reversibility of the adsorbed molybdate with respect to its ionic concentration in solution. The curves indicate some hysterosis only at pH 4.0 of the system. Thus at this pH, molybdate adsorption, is to some extent irreversible. It is also observed that desorption curves merge with adsorption curves at higher concentration of molybdate in solution, indicating the presence of only a few active sites on the Ca-clays available for molybdate adsorption.

4.2.12. Change in ΔG^{o}, ΔS^{o} and ΔH^{o} in the adsorption of molybdate of Ca-clays :

The ΔG^{o}, ΔH^{o} and ΔS^{o} values derived from the adsorption of melybdate by Ca-clays, are given in the Table VIII. It is observed that ΔG^{o} are negative in all the cases, indicating spontaneous reaction. Greater negative ΔG^{o} is observed in case of adsorption at lower pH values.

Regarding the value of ΔH^{o}, it is found that positive ΔH^{o} value for adsorption at pH-4.0 and negative ΔH^{o} value for adsorption at pH 7.0 level by Ca-clays, indicating exothermic nature ef molybdate adsorption by Ca-clays at pH-4.0, on the other hand endothermic nature of adsorption occurs at pH 7.0 level.

With the exception of Ca-Kaolinite at pH 7.0, all adsorbent of Ca-system exhibit more or less same ΔS^{o} value, where as Ca-Kaolinite at pH-7.0, shows higher ΔS^{o} value compared to others.

The entropy data thus demands a smaller degree of molybdate adsorption at higher pH, which is in conformity with greater release of molybdate by clays on Ca-saturation.

4.2.13. Comparison of Adsorption of molybdate among different homo ionic clays:

Results of the adsorption of molybdate at different pH and temperature level on different homo-ionic Kaolinite and Bentonite clays have been discussed in the earlier sections. It is obvious from the discussion, that the adsorption pattern of molybdate differs according to nature of the clays, nature of saturated cations, pH and temperature.

The comparison of the Langmuir adsorption maxima indicates that molybdate adsorption by different homo-ionic Kaolinite increases in following order under different pH and temperature level.

At pH 4.0 and $T = 40^{\circ}C$.

Fe > Al > H > Ca

At pH 4.0 and $T = 20^{\circ}C$

Fe > Al > Ca > H.

At pH 7.0 and $T = 40^{\circ}C$

Al > Fe > Ca > H.

At pH 7.0 and $T = 20^{\circ}C$

Al > Fe > H > Ca.

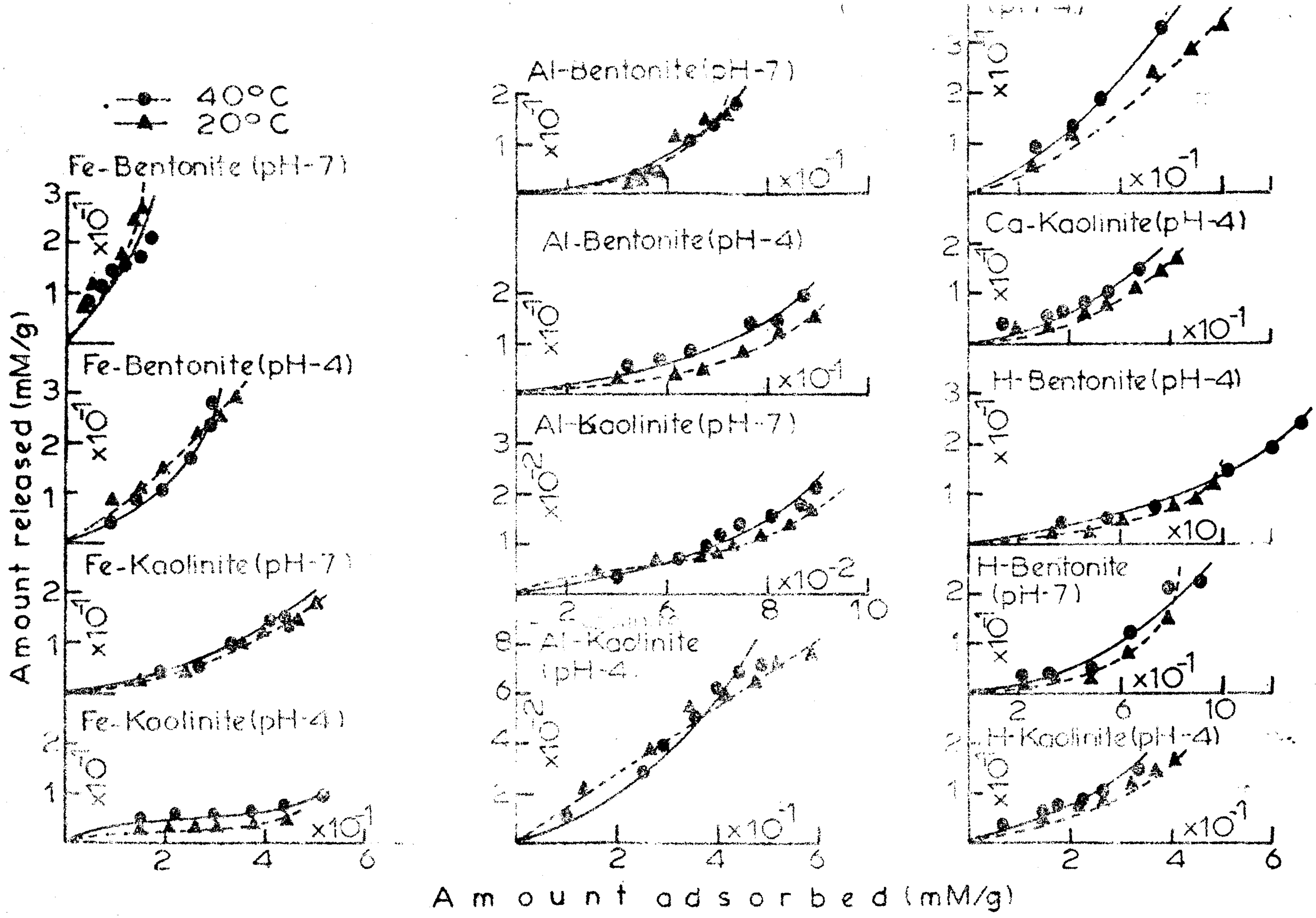


Fig.12. Molybdate release curves of different homoionic Kaolinite and Bentonite at different pH and temperature levels.

The comparison of the Langmuir absorption maxima among different homo-ionic Bentonite minerals shows that adsorption of molybdate increases in the following order under different pH and temperature level.

At pH-4.0 and T = 40° and 20°C

Fe > H > Al > Ca

At pH-7.0 and T = 40° and 20°C

H > Fe > Al > Ca.

The comparison of the K-value for molybdate adsorption in different homo ionic Kaolinite, shows the following order of increase under different pH and temperature level.

At pH 4.0 and T = 20°C and 40°C

H > Al > Ca > Fe.

At pH-7.0 and T = 20°C

H > Ca > Al > Fe

At pH-7.0 and T = 40°C

H > Al > Fe > Ca.

The comparison for K-value of molybdate adsorption among different homo-ionic Bentonite, shows following order of increase at different pH and temperature level.

At pH-4.0 and T = 40°C

Fe > H > Al > Ca

At pH-4.0 and T = 20°C

Fe > H > Ca > Al.

At pH-7.0 and $T = 40^{\circ}C$

$Al > Ca > Fe > H$

At pH-7.0 and $T = 20^{\circ}C$

$Ca > Al > Fe > H$.

It is observed from the above series of homo-ionic clays, regarding the order of increase in adsorption maxima and K-value for molybdate adsorption, quite conflicting particularly in the adsorption of molybdate on Ca-system.

Fe and Al saturation results greater variation of adsorption of molybdate on clay surface, with respect to pH and temperature of the system. H-clays also plays dominating role, depending on the pH of the system.

It can be generalised from the various observation, mostly chemical nature of adsorption takes place on Fe and Al saturated clay surfaces.

TABLE-VIII : Values of change in free energy, enthalpy and entropy in the adsorption of molybdate by Homoionic clays at different pH and temperature levels.

Adsorbents with pH of the system	-△ G° K Cal/mole 40°C	-△ G° K Cal/mole 20°C	△ H° K Cal/mole	△ S° Cal/deg/mole
H-Kaolinite (pH-4.0)*	8.63	8.32	-3.79	0.040
H-Kaolinite (pH-7.0)	9.35	8.49	4.21	0.015
H-Bentonite (pH-4.0)*	9.31	9.09	-5.91	0.049
H-Bentonite (pH-7.0)	6.87	6.58	-2.45	0.030
Fe-Kaolinite(pH-4)	7.81	7.73	-6.54	0.047
Fe-Kaolinite(pH-7.0)	7.81	7.73	+6.69	0.002
Fe-Bentonite(pH-4.0)*	9.78	8.73	+6.63	0.008
Fe-Bentonite (pH-4.0)**	9.30	8.68	+0.36	0.028
Fe-Bentonite (pH-7.0)*	7.65	7.17	+0.59	0.022
Fe-Bentonite (pH-7.0)**	7.59	7.22	+0.45	0.025
Al-Kaolinite (pH-4.0)**	8.64	8.05	0.49	0.026
Al-Kaolinite (pH-7.0)*	8.10	7.52	0.92	0.022
Al-Bentonite (pH-4.0)*	8.70	8.20	-0.97	0.031
Al-Bentonite (pH-4.0)**	7.74	7.34	-1.48	0.029
Al-Bentonite (OH-7.0)*	8.72	8.05	+1.72	0.021
Al-Bentonite (pH-7.0)**	7.49	7.20	+0.35	0.023
Ca-Kaolinite (pH-4)**	8.59	7.99	+0.83	0.024
Ca-Kaolinite (pH-7)	7.29	7.53	-11.13	0.061
Ca-Bentonite (pH-4)*	8.58	8.00	+0.397	0.028
Ca-Bentonite (pH-7.0)	8.60	8.14	-1.48	0.022

* Values for first surface adsorption.

** Values for second surface adsorption.

CHAPTER V

STUDIES ON ADSORPTION OF MOLYBDATE BY SOILS

Soil systems can undergo a lot of reactions due to heterogeneous nature of soils, it is usually difficult to trace the nature of such reactions. Still adsorption isotherm can sometimes be used to have an indication about such types of reactions. Molybdate anion like most of the other anions can be adsorbed on soils with diverse degree and strength, according to their nature or composition. To have an idea, on this aspect, experiments were carried out by using different types of soils in their native forms, as well as free from organic matter or free oxides of Fe and Al as adsorbents for studying adsorption of molybdenum.

5.1. Materials and Methods :

A brief description of the different adsorbents and methods used in the present investigation are given in the following sections.

5.1.1. Materials : The soils used in this investigation were collected from different agricultural farms of West Bengal studied in different agroclimatic zones. The detailed informations about the collected soil samples are given below.

Agro climatic zones	Place of collection	Probable class in the old system	Probable class in the new system	Nick name used in this investigation
Norther West Bengal	Dhupguri farm	Alluvial (acidic)	Spodosol	Dhupguri soil
Coastal West Bengal	Canning farm	Alluvial (saline)	Inceptisol	Canning soil
Gangetic allivial of Nadia, (W.B.)	Kalyani seed farm	Alluvial (Neutral)	Intisol	Kalyani soil
Lateritic tract of Midnapore (W.B.)	Jhargram farm	Laterite	Oxisol	Laterite soil

The soil samples collected from different farms, represent a composite of 10 randomly collected surface soils (0-6"). The samples after collection were air dried, ground by wooden mortar and seived through a nylon 80-mesh seive. The various physico-chemical properties of the soil samples are given in the Table IX.

The samples of different soils were then subjected to different treatments, in order to get organic matter free soil and free oxides free soil. The preparation of such samples of soils is described below :

<u>Organic matter free soil</u> :- The 80 mesh soil samples were treated with 30% H_2O_2 for several times for destruction of organic matter present in the soil. It was done until the soils did not evolve gaseous bubbles any longer. More or less equal amount of H_2O_2 was added in all soils. The soils

TABLE -IX : Physico-chemical properties of soil.

Physico-chemical Properties		Dhupguri soil	Laterite soil	Kalyani soil	Canning soil
Texture	Sand %	33.2	67.5	39.1	16.2
	Silt %	35.6	21.4	20.5	49.3
	Clay %	20.3	3.9	17.9	27.0
Dominant clay Mineral		Illite and cholorite[1]	Illite & cholorite with traces of Kaolinite[2]	Montmorilonite and Illite[3]	Montmorilonite and Illite[4]
pH (1:2.5)		4.6	5.25	7.0	7.0
Org.Carbon %		1.34	0.26	0.66	1.11
Exch. Cations meq/100 g					
	i) $Ca^{+2}+Mg^{+2}$	Trace	1.340	3.780	5.460
	ii) Fe^{+3}	0.048	0.039	Trace	0.068
	iii) Al^{+3}	0.196	0.028	0.017	0.015
	iv) K^{+}	0.153	0.256	2.430	1.025
Oxalate extractable (ppm).	i) Mo	0.025	0.019	0.020	0.029
	ii) Fe	1140	1700	1540	1620
	iii) Al	5.0	3.5	2.5	2.5
Dithiomite extractable (ppm)	i) Fe	240	320	288	304
	ii) Al	27.5	29.2	13.4	12.7
CEC (meq/100g)		11.39	8.88	15.84	32.84
AEC (,,)		0.36	0.08	0.05	0.32
Fe_2O_3%		0.48	1.54	0.58	0.99
$CaCO_3$ %		Trace	0.005	0.040	0.041
Total N%		0.153	0.043	0.090	0.139

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[1] Ghosh and Dutta (1974)

[2] Sahu and Das (1972)

[3] Sahu and Das (1974)

[4] Dalui and Roy (1979)

were then subsequently air dried and ground. The amount of organic matter remaining with the soils after H_2O_2 treatment was estimated by Walkley and Black's method as done also for the native soils. The amount of organic matter present in the soils before and after H_2O_2 treatment are shown in the following Table.

Soils	% org C before H_2O_2 treatment	% org C after H_2O_2 treatment
Dhupguri	1.349	0.342
Laterite	0.264	0.097
Kalyani	0.665	0.048
Canning	1.114	0.136

Oxides free soil :- The soils were freed from oxides by treating a portion of the organic matter free soil with 1(N) Na-acetable, Citrate-bicarbonate and dithionite at 70°C. Immediately after treatment, the soils were centrifuged and washed with distilled water for several times for removal of excess electrolytes. The oxide free soils were then air-dried, ground and taken for adsorption experiments.

5.1.2. Methods :

a) Study of Adsorption Isotherm :- Experiments were carried out, considering the following conditions.

i) Soil-solution ratio :- For the soils and other treated soils, the solid-solution ratio employed for the adsorption experiments was 1:25 (2 gm soil in 50 ml 0.01 M $CaCl_2$ solution).

ii) Concentration of adsorbate :- Same concentration, as used for adsorption on clays, described in the previous chapter (Chapter IV).

iii) Equilibrium Time and Temperature :- 5-6 hrs. shaking followed by 40 hrs incubation at 40°C and 20°C. The determination of time required for equilibriation of the system was done, as described in the Chapter IV.

b) Study of Desorption :- The methodology for the study of desorption of molybdate from soil samples after its adsorption was the same as employed for desorption study of molybdate on clays depicted in the Chapter-IV.

c) Methods of Analysis :

i) Estimation of Molybdenum :- Mo was estimated spectrophotometrically, according to the procedure developed by ArKley and Johnson (1954).

ii) Estimation of Phosphorus :- 'P' was estimated by chloro-stanous-reduced molybdophosphoric acid blue colour method, developed by Dickman and Bray (1940).

iii) Determination of pH :- pH of the soils and other systems were measured in 0.01M $CaCl_2$ solution with the help of a pH meter. The pH of the native soils were determined by pH meter using soil-solution ratio 1 : 2.5.

iv) Determination of C.E.C.:- CEC of the soils were determined with 1(N) NH_4OAC (pH-7) solution, according to the procedure developed by Jackson (1967). CEC for clays were estimated by using Ca and Mg solution, according to the procedure described by Jackson (1967).

v) Determination of Anion Exchange Capacity of Soils :- AEC of the soils were determined by using $NH_4H_2PO_4$ at pH-4.0, according to the procedure developed by Piper (1942).

vi) Determination of exchangeable Fe and Al :- Exchangeable Al and Fe were estimated by washing the soils with 1(N) KCl solution according to the procedure described by Jackson (1967).

vii) Determination of free iron oxide :- Free iron oxide of soils was estimated by dithionite extraction according to the procedure of Kilmer (1960).

viii) Determination of oxalate extractable Fe and Al :- Iron and aluminium extraction was done by shaking the soil with 0.1(M) oxalic acid and 0.775 (M) NH_4-oxalate solution, for 4 hours with a soil solution ratio of 1:50. From the extractants the Fe and Al were estimated colorometrically according to the procedure described by Jackson (1967).

ix) Determination of available Mo :- Available Mo of soil was estimated by extraction with Tamm's solution (oxalic acid and ammonium oxalate, pH 3.3), according to the procedure of Grigg (1953).

x) Estimation of organic carbon :- Organic carbon of soil was estimated by Walkley and Black's method.

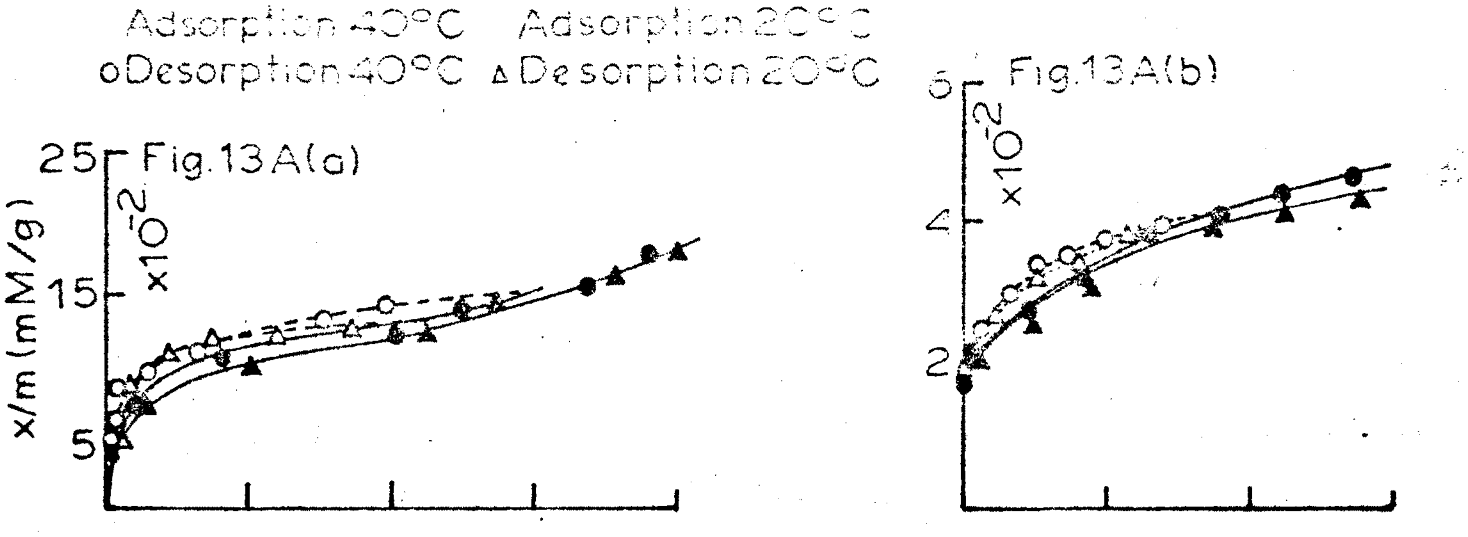
vi) Estimation of Exchangeable Ca^{+2} and Mg^{+2} :- Exchangeable Ca^{+2} and Mg^{+2} were determined with 1(N) NH_4O AC extraction, according to the procedure described by Jackson (1967).

5.2. Results and Discussion :

The results of investigation on adsorption of molybdate by different native soils, organic matter free soils and oxide free soil are discussed in the following sections.

5.2.1. Adsorption of molybdate by native soils :

The isotherms for adsorption of molybdate on different soils at various concentrations of molybdate in solution under constant temperature levels are shown in Fig.13(A), 14(A), 15(A) and 16(A). The adsorption curves usually



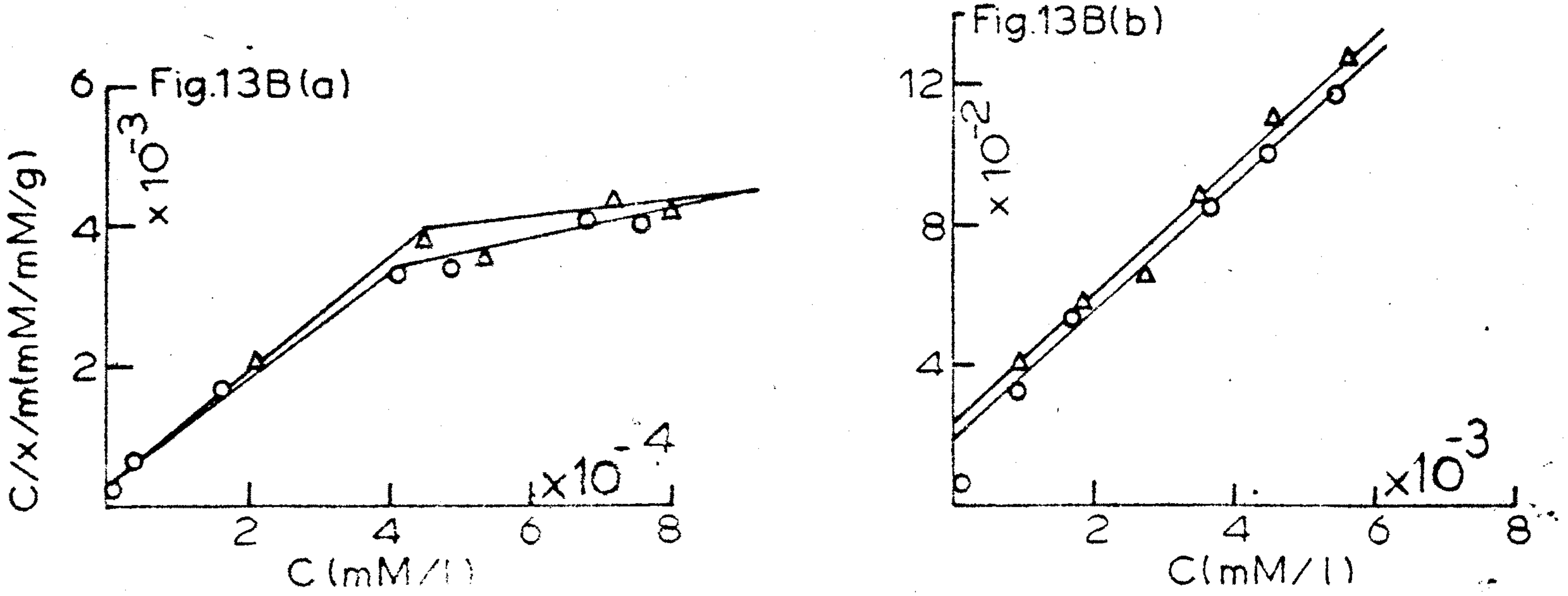


Fig.13A. Molybdate adsorption and desorption in a) Native Dhupguri soil and b) O.M. free Dhupguri soil at different temperatures.

Fig.13B. Langmuir plot of molybdate adsorption in a) Native Dhupguri soil and b) O.M. free Dhupguri soil at different temperatures.

consist of three regions, characterised by initial steep slope (region I), which bends (region II) and finally flattens out (region III) at higher solution concentration of molybdate. Such regions are, however less characterised in Canning and Kalyani soils. Relatively higher pH and low content of Fe, Al and their free oxides seem to be the reasons for this.

Adsorption isotherm characterised by more than one region in Dhupguri as well as Laterite soils, is an indication of multiphase adsorption of molybdate on soil surface. Each phase has a different set of energy level.

The adsorption isotherms of different soils derived from the present investigation followed the Langmuir equation. The correlation coefficient values for this, is reported in the Table-X(A). The Langmuir curves of the respective adsorption have been depicted in the Figs.13B(a), 14B(a), 15B(a). Break in the Langmuir curve is observed only in case of Dhupguri soil, indicating the second surface reaction of molybdate on this soil. As because the Dhupguri soil contains high exchangable Al, the results are in conformity with the results obtained in case of Al- clays. Hence it is clear that in soil adsorbents with Al as a reactive phase undergo a more or less two surface adsorption reaction of molybdate.

Among the four soils investigated Kalyani and Canning soils show least capacity to adsorp molybdate.

The adsorption maxima and K-value related with bonding energy and other thermodynamic parameters, as calculated from the Langmuir equation are given in Table-X(B).

It can be seen from the Table X(B) that Dhupguri and Laterite soils have higher capacity to adsorb molybdate. High exchangeable 'Al' content of Dhupguri soil and high free oxide content of the Laterite soil and lower pH value of these soils result in greater adsorption of molybdate by these soils. On the other hand, Kalyani and Canning soils, having very little exchangeable Al and Fe and relatively higher pH, adsorb low amount of molybdate.

It is observed that a little higher amount of molybdate is adsorbed at lower temperature compared to that at higher temperature in all the soils except in Kalyani soil. Of course there is less significant difference in adsorption maxima between the two temperatures, in all the soils, studied.

The correlation coefficients of Langmuir parameters with different physico-chemical properties of the soils are given in the Table-XI. It is observed from the data that the Langmuir adsorption maxima for molybdate adsorption on soil is negatively correlated with pH of the soil. Significant positive correlation coefficient are obtained between Langmuir adsorption maxima and oxalate extractable Al and Fe, exchangeable Fe and Al content and free iron oxides of soil. Non-significant negative correlation is

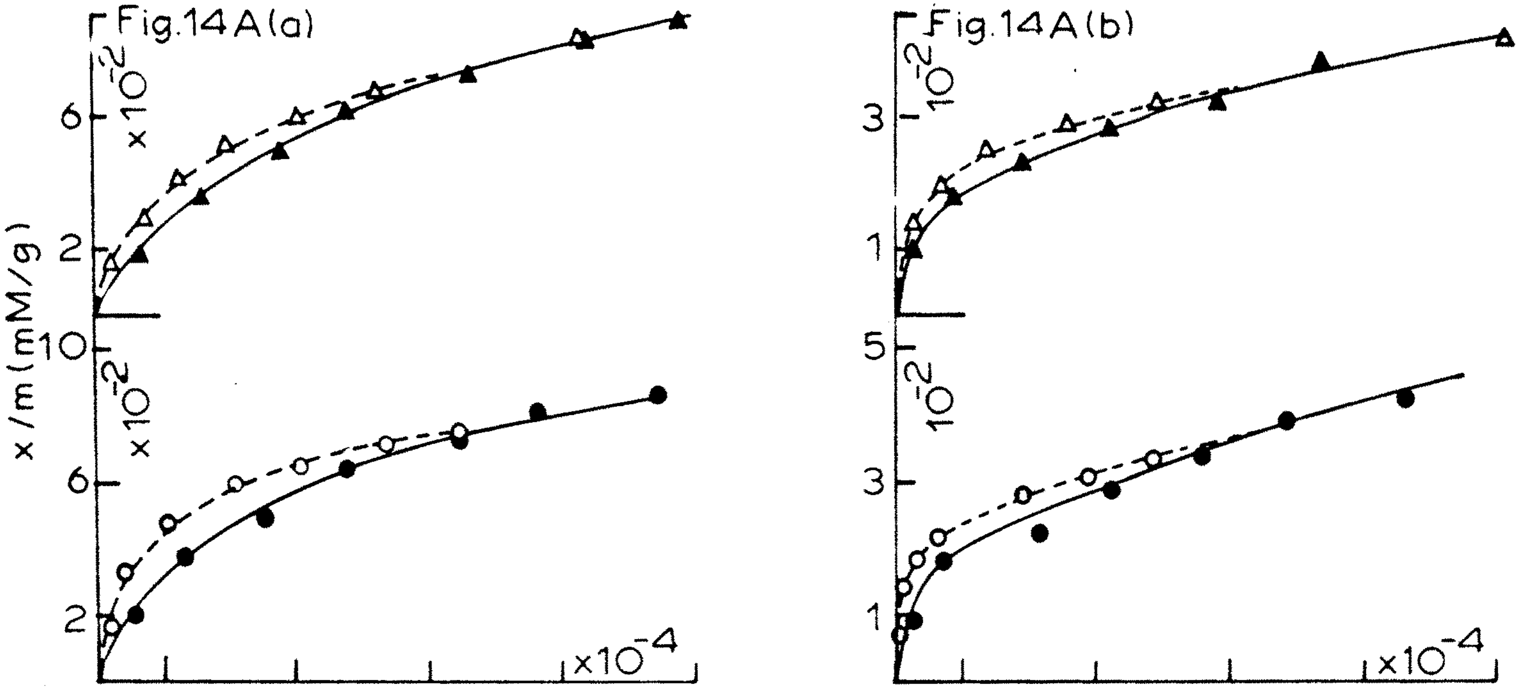


Fig.14A. Molybdate adsorption and desorption in a) Native Laterite soil and b) O.M. free Laterite soil at temperatures.

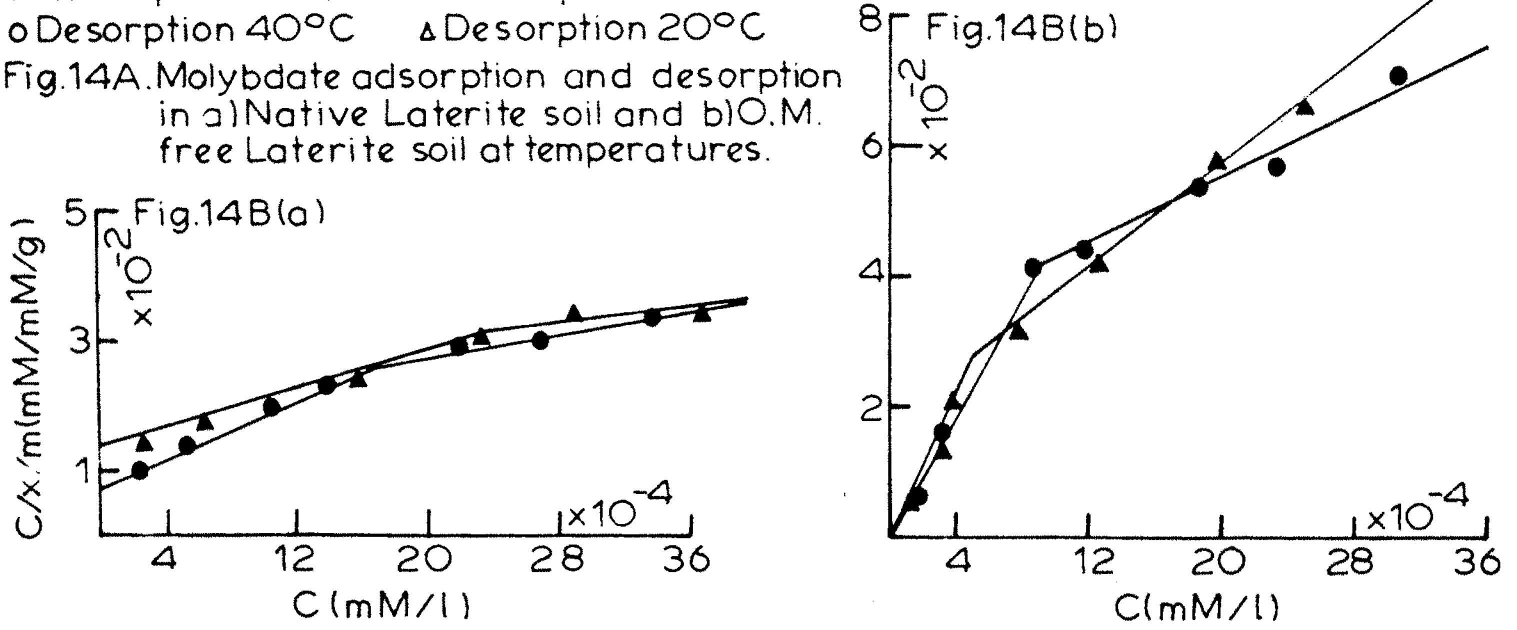


Fig.14B. Langmuir plot of molybdate adsorption in a) Native Laterite soil and b) O.M. free Laterite soil at different temperatures.

TABLE -X(A) : Correlation Coefficient values for Langmuir curves for the adsorption of molybdate by soils.

Adsorbents	r Walues (Significant at 1% level)	
	$40^{\circ}C$	$20^{\circ}C$
Dhupguri Soil	0.9839*	0.9511*
Laterite Soil	0.9903**	0.9899*
Kalyani Soil	0.9849	0.9472
Canning Soil	0.9655	0.9030
Org. matter free Dhupguri soil	0.9838	0.9937
Org. matter free Laterite Soil	0.9761**	0.9884**
,, Kalyani Soil	0.9841	0.9843
,, Canning Soil	0.9923	0.9523
Oxide free Dhupguri Soil	0.9816**	0.9703**
,, Laterite soil	0.9841**	0.9973**
,, Kalyani Soil	0.9537	0.9943
,, Canning Soil	0.9774**	0.9582**

* Indicates r value for more dominant first surface adsorption.

** Indicates r value for more dominant second surface adsorption.

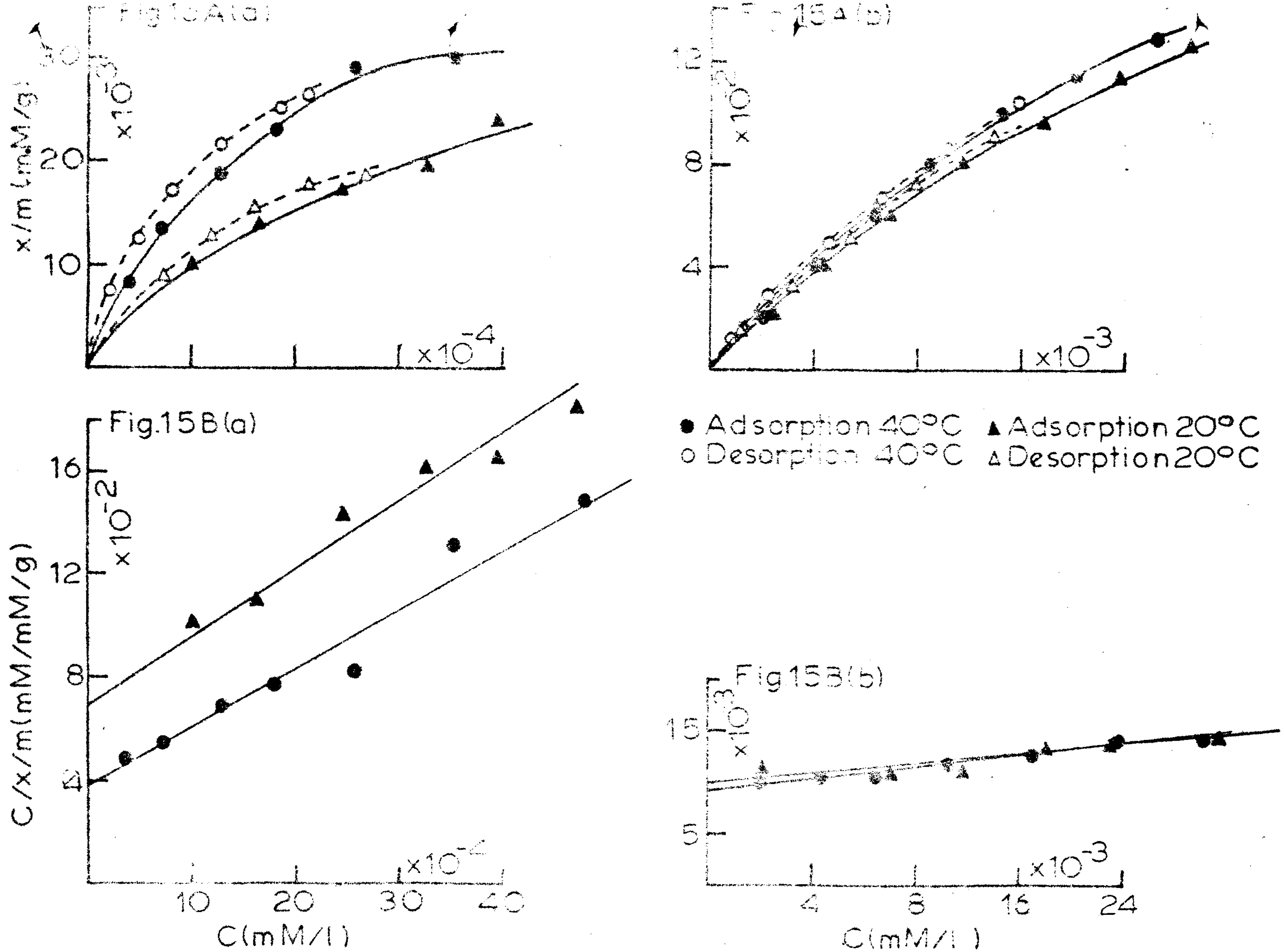


Fig.15A. Molybdate adsorption and desorption in a) Native Canning soil and b) O.M. free Canning soil at different temperatures.

Fig.15B Langmuir plot of molybdate adsorption in a) Native Canning soil and b) O.M. free Canning soil at different temperatures.

TABLE -X(B) : Langmuir Parameters for the adsorption of molybdate by Soils.

Soils	Adsorption Maxima (mM/g)		K-value $(X10^3)M^{-1}$		$-\triangle G^o$ K Cal/mole		$\triangle H^o$ (KCal/mole)	Mean $\triangle S^o$ Cal deg/mole
	40°C	20°C	40°C	20°C	40°C	20°C		
Dhupguri Soil (*)	0.189	0.191	9547.9	7539.7	9.99	9.22	+2.15	0.024
Laterite Soil(**)	0.135	0.144	623.7	506.5	8.30	7.65	+1.89	0.020
Kelyani Soil	0.011	0.009	190.1	344.9	7.56	7.42	-5.42	0.042
Canning Soil	0.036	0.058	949.3	185.9	8.56	7.06	+1.48	0.020
Organic matter free Dhupguri Soil	0.049	0.048	1705.5	1443.5	8.92	8.25	+1.52	0.023
,, Laterite Soil (**)	0.047	0.053	1651.9	1120.4	8.90	8.11	+3.53	0.016
,, Kalyani Soil	0.006	0.004	197.8	245.4	7.58	7.22	-1.96	0.030
,, Canning Soil	0.363	0.578	298.9	163.2	7.84	6.99	+5.51	0.006
Free Oxide free Dhupguri Soil(**)	0.008	0.007	276.10	342.3	7.99	7.42	-1.95	0.031
,, Laterite Soil(**)	0.014	0.015	141.7	102.0	7.38	6.71	+2.99	0.013
,, Kalyani Soil	0.003	0.003	239.4	191.8	7.70	7.08	+2.02	0.017
,, Canning Soil (**)	0.012	0.013	230.7	193.0	7.68	7.09	+1.53	0.019

* Indicates values for more dominant first surface adsorption.
** Indicates values for more dominant second surface adsorption.

TABLE-XI : Simple correlation coefficients for the correlation between Adsorption maxima and various soil characteristics.

Soil Characteristics	r value	
	40°C	20°C
pH	-0.9906	-0.9615
CEC	-0.6282	-0.5391
AEC	+0.3774	+0.4592
Organic Carbon	+0.1924	+0.2122
Dithiomite extractable		
i) Fe	0.4817	0.5853
ii) Al	0.8098	0.7726
Oxalate extractable		
i) Fe	0.8792	0.8301
ii) Al	0.9565	0.9280
Exchangeable Al	0.9313	0.9421
Exchangeable Fe	0.9437	0.9549
Fe_2O_3 %	0.8831	0.8872

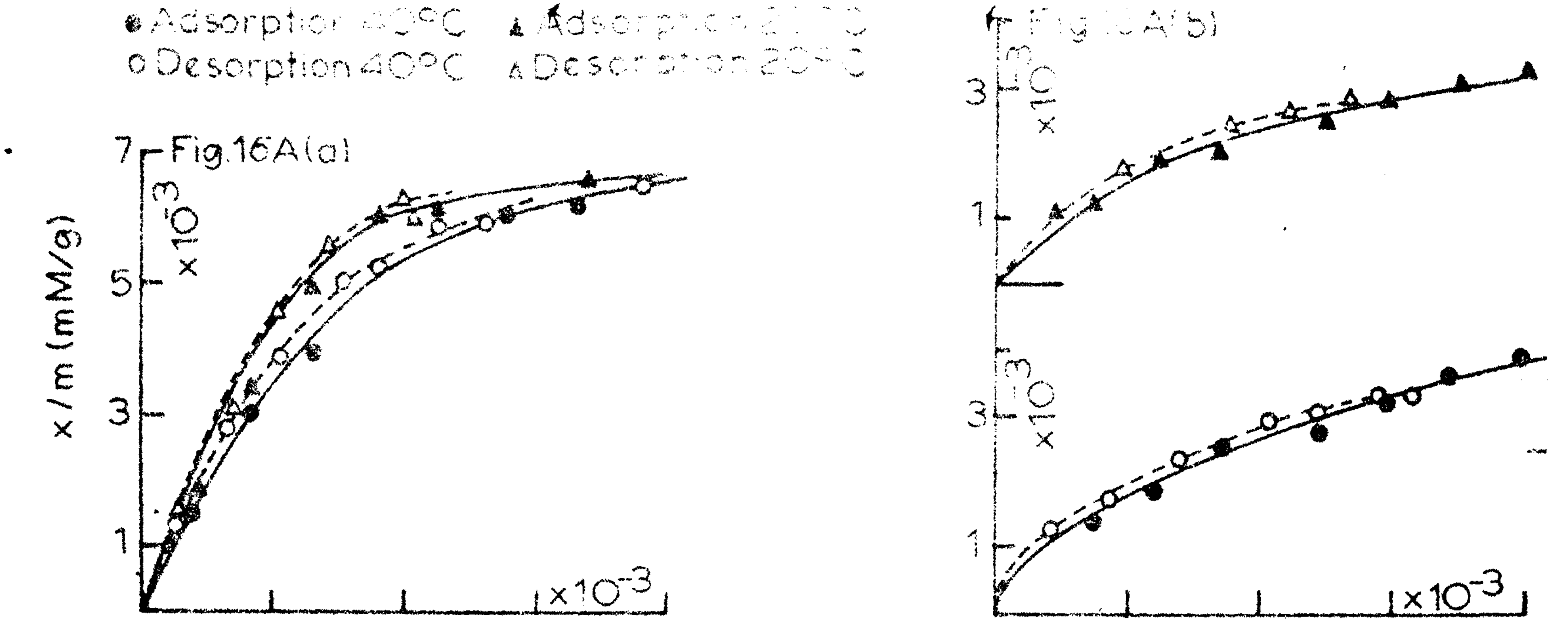
(Table value at 1% level = 0.8783).

observed with CEC of the soils and non-significant positive correlation is observed with anion exchange capacity of the soils, organic carbon content of the soil and dithionite extractable Fe and Al content of the soils. As reported by many workers (Jones and Uchara 1973; Wada and Harward 1974), the reactive sites of anion adsorption are iron and aluminium compounds of the soil. Correlation Coefficient values for these soils constituents obtained in the present investigation are also in conformity with those reports.

It is obvious from the results of the study that adsorption of molybdate by soil is primarily due to the presence of exchangeable Fe and Al content of the soils Free iron oxides present in soil and organic matter content of the soils also play important roles in the anion adsorption phenomena in soil, as obtained for molybdate adsorption in the present case.

5.2.2. Desorption of adsorbed molybdate from the soil surface.

Desorption isotherm for adsorbed molybdate from the soils are shown in association with their respective adsorption isotherms in Figs.13A(a), 14A(a), 15A(a) and 16A(a). The curves indicate a stronger hysterosis in case of Dhupguri and Laterite soils. On the other hand, little hysterosis is found in case of Kalyani and Canning soils. Greater hysterosis in the former cases is obviously due to low pH of the soils and higher content of Al, Fe, On



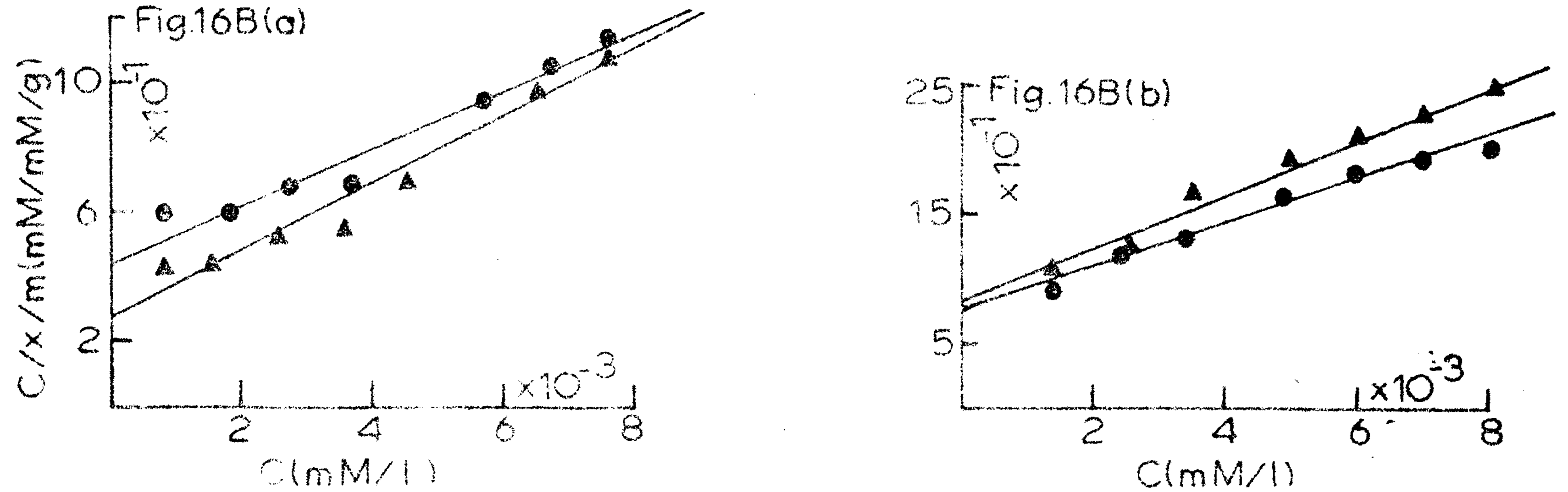


Fig.16A. Molybdate adsorption and desorption in a) Native Kalyani soil and b) O.M. free Kalyani soil at different temperatures.

Fig.16B. Langmuir plot of molybdate adsorption in a) Native Kalyani soil and b) O.M. free Kalyani soil at different temperatures.

the surface of the soils. At higher concentration of molybdate in solution, it is found that the desorption curve merges with adsorption curve, indicating greater reversibility of the adsorption reaction at higher solution concentration of molybdate.

Release curves, as shown in Fig.19 reveal, higher slopes for Kalyani and canning soil compared to Dhupguri and Laterite soils, which is in conformity with higher bonding strength of the molybdate with the latter soils. The K-values and adsorption maxima for those soils in respect of molybdate adsorption also in consistent with the slope of the corresponding release curves.

5.2.3. Bonding energy of adsorption and other thermodynamic parameters of the molybdate adsorption on soil.

The K-value related to bonding energy for molybdate adsorption as reported in the Table X(B), indicate that molybdate is adsorbed on Dhupguri soil with greater strength than that by other soils used in this investivation.

Relatively greater strength of adsorption is observed at higher temperature in all the soils, except in Kalyani soil, indicating greater chemical nature of adsorption of molybdate on these soils.

The change in free energy for molybdate adsorption in all the cases is found to be negative, indicating spontaneous adsorption of molybdate on these soils, which increases in the following order at 40°C level, Dhupguri $\rangle$ Canning $\rangle$ Laterite $\rangle$ Kalyani, however, at 20°C level, the order is Dhupguri $\rangle$ laterite $\rangle$ Kalyani $\rangle$ Canning.

Quite inconsistent result in bonding energy and free energy change is observed in case of Canning soil, particularly at higher temperature, fails to interpret the nature of molybdate adsorption by this soil.

Regarding the ΔH^o value of the adsorption, it is observed that except in Kalyani soil, all are exhibiting positive ΔH^o value,. Greater positive ΔH^o is observed in case of Dhupguri and laterite soils. The ΔS^o value for the adsorption increases in the order

Kalyani $\rangle$ Dhupguri $\rangle$ Canning $\simeq$ Laterite.

5.2.4. Adsorption of molybdate on organic matter free soils.

The adsorption isotherms for the organic matter free soils of Dhupguri, Laterite, Kalyani and Canning, at various concentrations of molybdate in solution are shown in Figs. 13A(b), 14A(b), 15A(b) and 16A(b).. The curves usually consist of more than one region but unlike the native soils there are no quite prominent regions. However in case of organic matter free Dhupguri and Laterite soils, the regions are somewhat prominent. Occurrence of more than one region with varying slopes in the isotherm curve, as already poin out, is an indication of multi surface adsorption on the adsorbents as happened with the latter samples.

The adsorption isotherms of different organic matter free soils, followed the Langmuir equation. The correlation coefficient values for this, is reported in the Table X(A). The Langmuir curves of the respective adsorption have been depicted in the Figs.13A(b),14B(b),15B(b) and 16B(b). However in case of organic matter free Laterite soil [Fig.14B(b)], a break in the Langmuir curve is observed, indicating a second fixation reaction at higher concentration of molybdate ions in solution. This observation, unlike the native Laterite soil, seems to be due to the exposure of adsorbent surface on removal of organic matter. On the other hand native Dhunguri soil showing break in its Langmuir curve [Fig.13A(A)] due to high organic matter, fails to show any break when the soil is freed from organic matter. This type of result for the Laterite soil is due to its high free oxide content on its surface, which on removal of organic matter become the reactive sites for adsorption. On the other hand organic matter and Al forming complexes suitable for adsorption of anions, as reported by Krishnamoorthy *et al*.([illegible]), may also contribute the surface of the adsorbent for secondary adsorption reaction. On removal of organic matter this soil shows no break in the Langmuir curve.

The Langmuir parameters and different thermodynamic values calculated thereof for organic matter free soils are given in the Table X(B).

In all the cases, except in case of Canning soil the removal of organic matter, decreased the adsorption of molybdate. However, exceptional rise of molybdate adsorption is observed in case of Canning soil. The observed increase is obviously due to increase in the number of adsorption sites on the clay surface, some of which are blocked by the formation of clay-organic matter complexes in this soil.

The increase of adsorption maxima of the organic matter free soils follows the order :

Canning Soil > Dhupguri Soil > Laterite Soil > Kalyani Soil.

It is further observed that more or less same value of adsorption maxima at both the temperature level in case of Dhupguri and Laterite soils. However, relatively greater amount of molybdate adsorption is observed in the case of Kalyani soil at higher temperature, on the other hand Canning soil adsorbs greater amount of molybdate at lower temperature.

5.2.5. Desorption of adsorbed molybdate from organic matter free soil.

Desorption isotherm of molybdate for the organic matter free soils are shown in association with the adsorption isotherm is Figs. 13A(b), 14A(b), 15A(b) and 16A(b). The curves indicate marked hysterosis, reflecting stronger bonding energy of molybdate ions to the adsorbent in case of Laterite and Dhupguri soils. On the other hand, Kalyani and Canning soils show little hysterosis in this respect indicating greater reversibility of the molybdate adsorption reaction by these soils. Marked irreversibility of the reaction is, however observed in case of organic matter free Laterite and Dhupguri soils. Desorption curve merges with adsorption curve at higher concentration of molybdate in solution, in case of Dhupguri soil, indicating greater reversibility of the adsorption at this region of adsorption.

Though organic matter free Canning soil exhibits exceptional high amount of molybdate adsorption very little hysterosis of the adsorption-desorption curve is noted for this soil.

Slope of the release curve (Fig.19), is found to be higher in case of organic matter free Kalyani and Dhupguri soils, at higher concentration level. The release curve of the canning soil, also exhibits greater slope, indicating higher rate of release of the adsorbed molybdate. Laterite soil on the other hand, releases molybdate at a slower rate.

Removal of organic matter of Dhupguri soil results reversibility of the reaction at high concentration of molybdenum and also higher slope of the release curve at higher concentration. The finding may be largely due to the presence of considerable amount of organic - Al complex which takes part in the adsorption reaction of the anions like molybdate in this soil, which is known to be a Spodosol.

The removal of organic matter from Canning soil, however, results in greater adsorption of molybdate but with little strength. Freshly exposed surface of free oxides of iron may be partly responsible for enhanced adsorption in this soil.

The Laterite soil, where organic matter might protest the adsorbed phase by surface coatings, greater adsorption of physical nature, could be observed from which molybdate is released only slowly.

5.2.6. Bonding Energy of adsorption and other thermodynamic parameters of the molybdate adsorption on organic matter free soil:

The values of K, which is related to bonding energy of the adsorption and calculated from the Langmuir equation, are given in the Table X(B). The results indicate that K-values of all the soils except Laterite soil, have been reduced by the removal of organic matter of the soils. Hence organic matter of the soils, shows an additive effect on the strength of adsorption by contributing more sites of adsorption. Laterite soil, on the other hand adsorbs molybdate with greater strength, on removal of its organic matter.

Conflicting results, however, is observed in case of Canning soil, where greater amount of adsorption occurs after removal of organic matter but with weaker strength, than it was in original native soil. It is also found that greater adsorption of molybdate in case of Canning soil at lower temperature, which reveals that adsorption is mostly physical in nature. This result is in conformity with the nature of adsorption - desorption curve and release curve, where little hysterosis and greater slope are observed.

Kalyani soil also adsorbs molybdate with greater strength at lower temperature, indicating more or less physical adsorption of molybdate which is also the case with corresponding native soil.

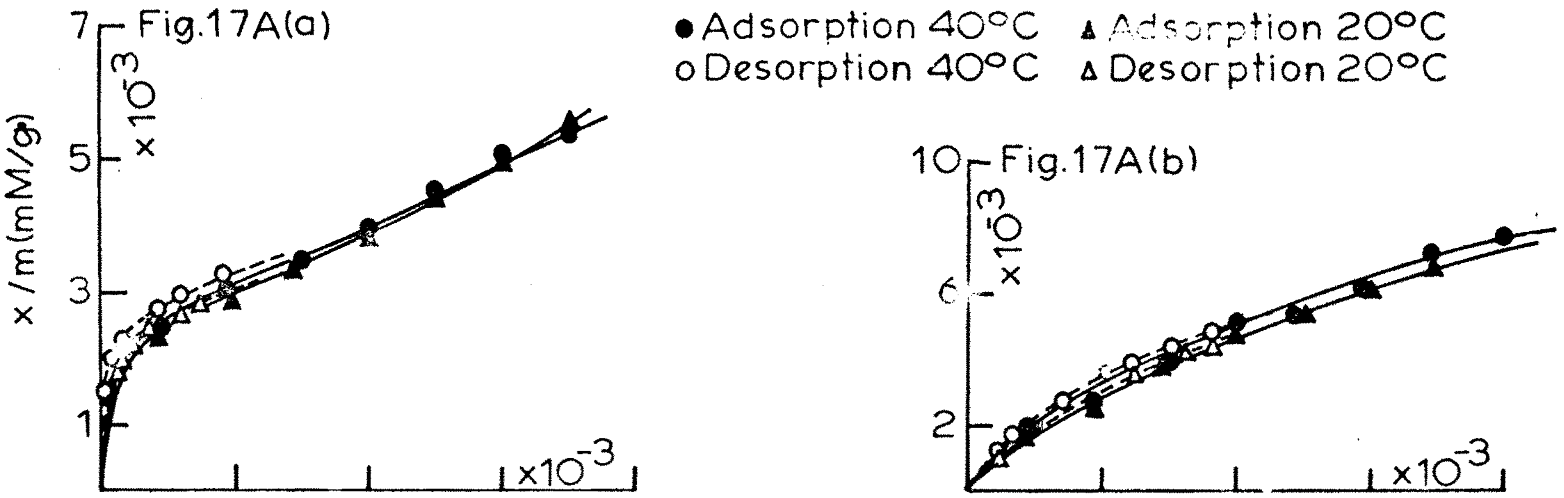
Regarding change in free energy, it is obvious from the Table-X(B) that the values are less negative compared to the original soils, however, signifying less spontaneous nature of the adsorption. Only the Laterite soil shows a slight increase in the negative value of ΔG^o on removal of organic matter from it.

Regarding the value of ΔH^o, it is observed that like the native soils, Organic matter free Dhupguri, Laterite and Canning soils exhibit positive ΔH^o values. On the other hand Kalyani soil exhibits negative ΔH^o value both in case of native and organic matter free soil. As regards entropy it can be seen that greater values for Kalyani and Dhupguri soils and relatively lower values for Laterite and Canning soils.

5.2.7. Adsorption of molybdate in free oxide free soils :

The adsorption isotherms of free oxide free soil of Dhupguri, Laterite, Kalyani and Canning at two temperature levels, are shown in the Fig.17A and 18A. It is observed that on treatment with dithionite, soils adsorb little molybdate. The isotherm curves, which are characterised by initial gradual rise (region I), which finally flattens out (region II). The adsorption isotherm of dithionite treated soils followed the Langmuir equation. The correlation coefficient values for the same, have been reported in the Table X(A) and Langmuir curves have been depicted in Figs. 17B and 18B. However, in case of Dhupguri, Laterite and Canning soils, break in the Langmuir curves, is observed, indicating second surface adsorption at higher concentration of molybdate in solution. The Langmuir adsorption maxima and K-value are calculated from the more dominant second surface adsorption. The related data have been reported in the Table XB. The data shows that in all the cases removal of oxides on treatment with dithionite results drastic decrease in molybdate adsorption. The order of decrease of the adsorption capacity as follows -

Dhupguri soil $>$ Laterite soil $>$ Canning Soil $>$ Kalyani Soil.



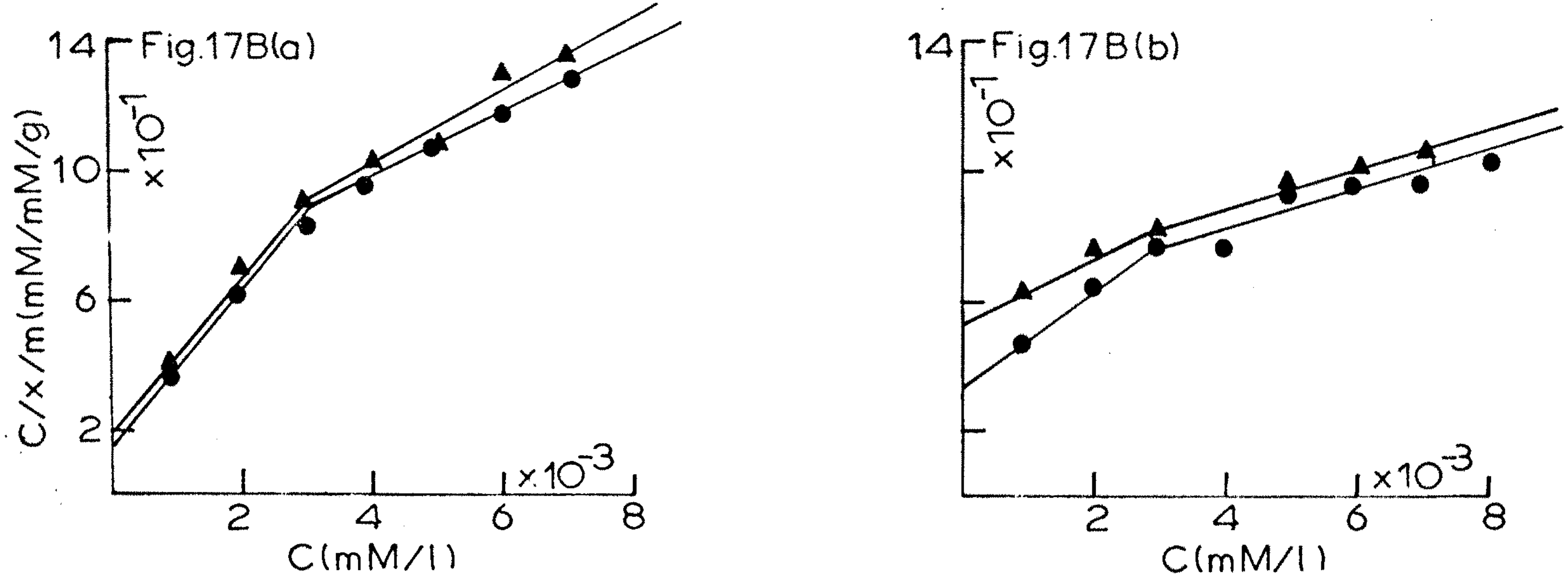


Fig.17A. Molybdate adsorption and desorption in oxide free a) Dhupguri and b) Laterite soils at different temperatures.

Fig.17B. Langmuir plot of molybdate adsorption in oxide free a) Dhupguri and b) Laterite soils at different temperatures.

As the free oxide coatings on the soil surface are the major adsorption sites of anion, removal of the coatings results in a drastic decrease of the adsorption capacity of molybdate by the soil. As Laterite and Dhupguri soils contain large amount of the oxides, greater decrease of the adsorption capacity is observed for these.

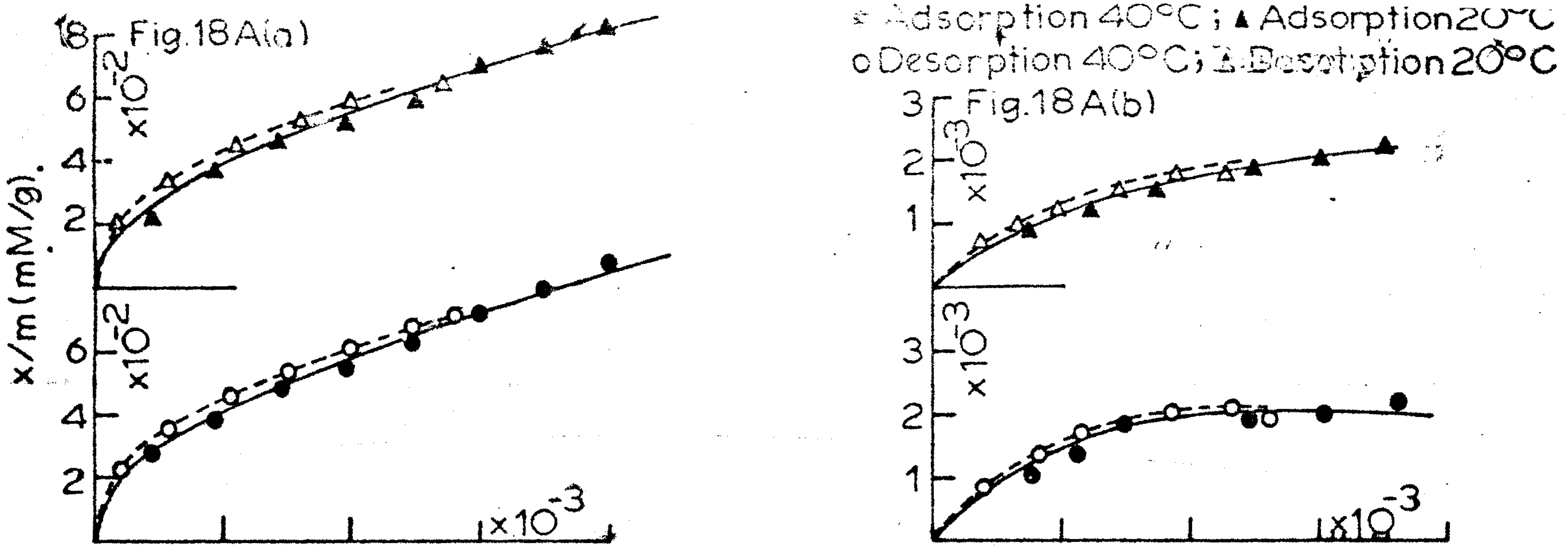
In case of Laterite soil exposure of clay minerals particularly Kaolinite, is largely responsible for the second surface adsorption of molybdate. It is also found in case of Dhupguri and Canning soil.

More or less same amount molybdate is adsorbed at both the temperature level in all the oxides free soil, with the exception of oxides free Dhupguri soil, where relatively greater amount is being adsorbed at higher temperature.

5.2.8. Desorption of adsorbed molybdate from oxide free soils :

The desorption isotherms of the oxide free soils shown in association with their respective adsorption isotherms in the Figs. 17A and 18A, highlight little hysterosis of the isotherm curve, indicating the reversibility of the adsorption reaction.

Greater reversibility of the adsorption coupled with slightly greater adsorption of molybdate at lower temperature level, reveal that adsorption of molybdate on oxide



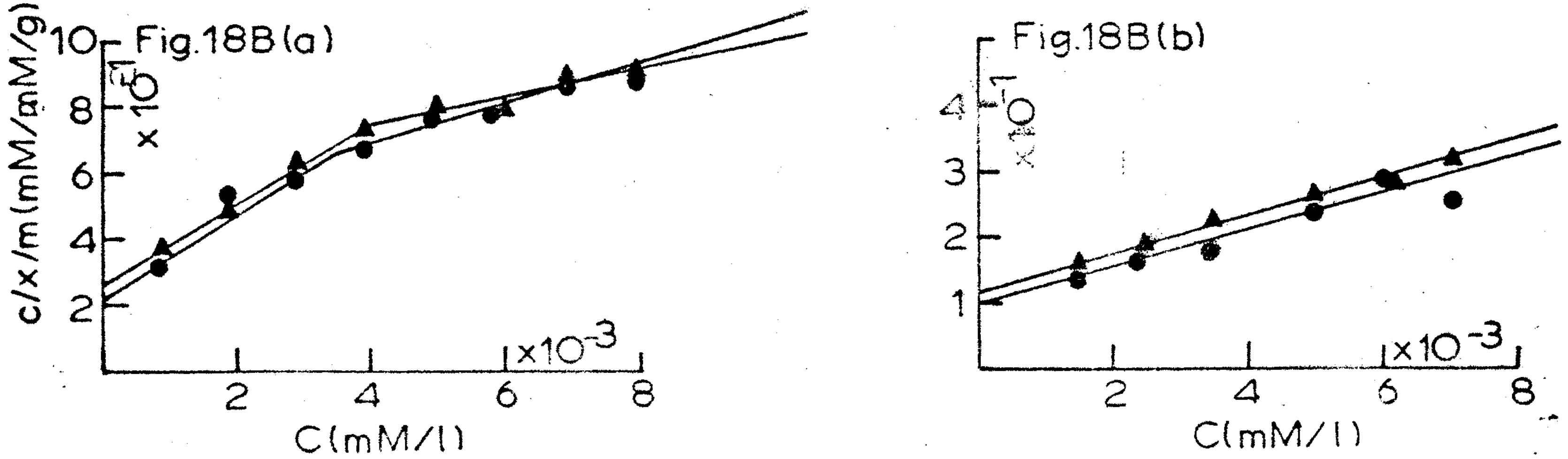


Fig.18A. Molybdate adsorption and desorption in oxide free a) Canning and b) Kalyani soil. at different temperatures.

Fig.18B. Langmuir plot of molybdate adsorption in oxide free a) Canning and b) Kalyani soil at different temperatures.

free soil is mostly physical in nature.

Release curve (Fig.19) of these oxide-free soils, also show the steep slope, indicating rapid release of the adsorbed molybdate from the adsorbent.

5.2.9. Bonding energy and other thermodynamic parameters of molybdate adsorption on Free Oxide free soils:

The value of K which is related to bonding energy and change in Gibb's free energy are given in the Table XB. It is found that the removal of free oxides not only decrease the adsorption capacity but also reduce the K-value, in all the soils. Greater decrease of the K-value is observed in case of Dhupguri and Laterite soils. On the other hand Kalyani soil exhibits little reduction rather little increase of the K-value.

In all the cases change in Gibb's free energy, calculated from K-value, are negative, indicating spontaneous nature of adsorption of molybdate on such soil samples. More or less similar ΔG^{o} value is observed in all the oxide free soils, particularly at higher temperature.

Regarding the value of ΔH^{o}, it is found that, in all the cases, with the exception of oxide free Dhupguri positive ΔH^{o} value for molybdate adsorption. Negative ΔH^{o} is being found only in case of oxide free Dhupguri soil. Somewhat higher positive value of ΔH^{o} is observed in case of Laterite and Kalyani soil.

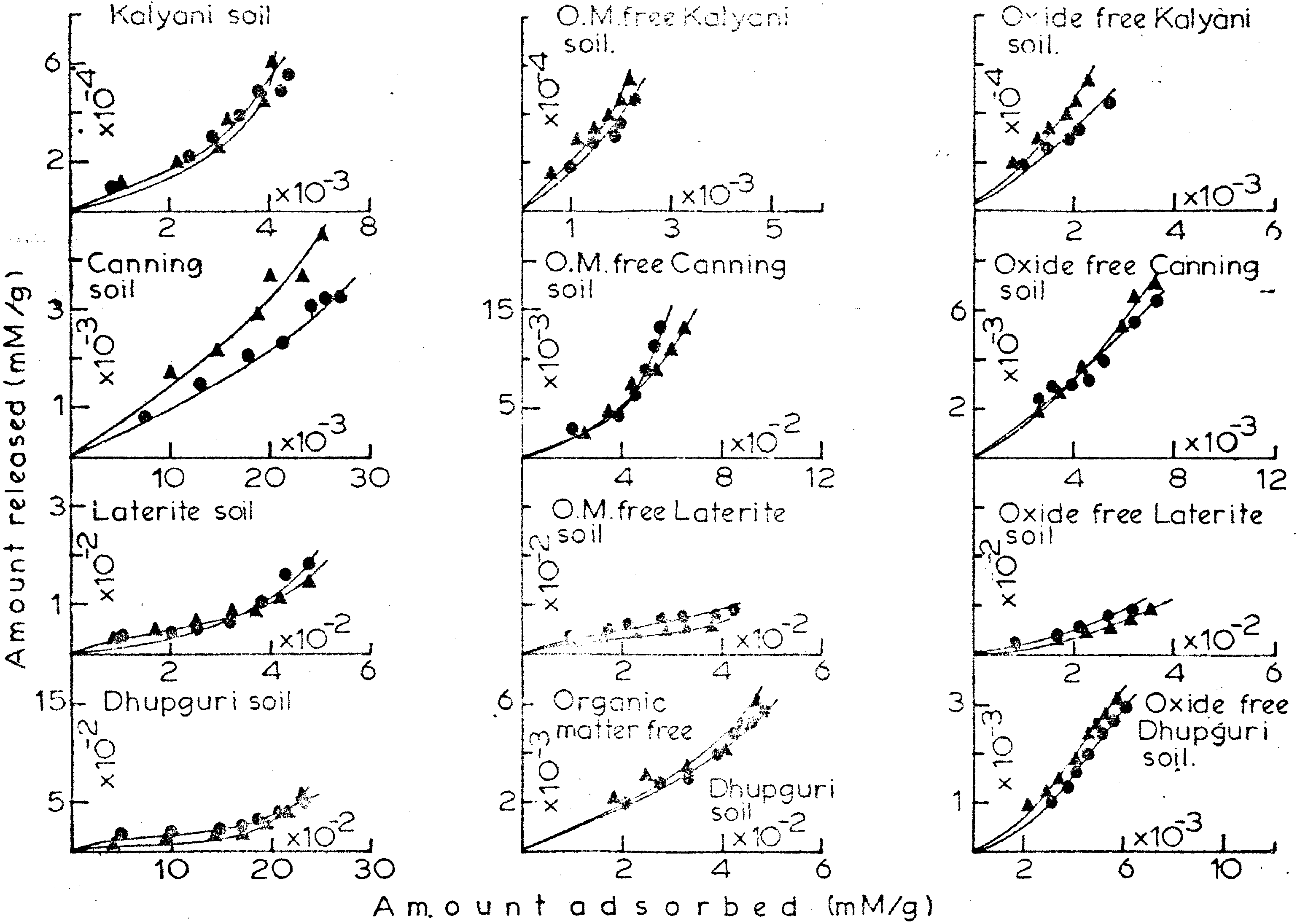


Fig.19. Molybdate release curves of different native soils, organic matter free soils and oxide free soils at different temperatures.

Entropy change values are found to almost same in case of oxide free Laterite, Canning and Kalyani soil. Slightly higher value is obtained in case of oxide free Dhupguri soil.

CHAPTER VI

STUDIES ON ADSORPTION OF PHOSPHATE AND COMPETITIVE ADSORPTION OF PHOSPHATE AND MOLYBDATE ON SOILS :

Phosphate and molybdate anions are similar in their behaviour in many reaction due to their anionic nature. As reported by Barrow (1970) adsorption behaviour of phosphate and molybdate is similar in soil. Hence competition between these two anions for the adsorbent sites may be an useful information regarding the relative case of release of the one anion on addition of another. In order to assess such behaviour, in the present investigation experiments are carried out on phosphate adsorption and co-adsorption of phosphate and molybdate on soil surface.

6.1 Materials and Methods :

Experiments on phosphate adsorption and co-adsorption of phosphate and molybdate were carried out on soils of four different agroclimatic zones of West Bengal. The type of soil and their different physiochemical properties have been reported in the previous chapter.

To have an idea regarding the co-adsorption of these two anions from the same solution, it is necessary to assess the nature of individual anion adsorption on the soil sample used. Accordingly, like the molybdate adsorption a study on adsorption of phosphate was also under taken, the methods for which are depicted below.

6.1.1. i) Methods of phosphate adsorption study : Phosphate adsorption study was conducted by shaking 2.0 gm of soil with 50 C.C. 0.01M $CaCl_2$ containing different phosphate concentration in the equilibriating solution ranging from 20 to 70 ppm. For attaining equilibrium, the soil suspension were shaken for 6 hours, followed by 40 hours incubation at 40°C. 2-3 drops of chloroform was added for inhibiting microbial activity, if any. Immediately after completion of incubation, the soil suspensions were centrifuged at 8000 rpm for 20 minutes. The clear supernatant liquid was obtained and taken for analysis of equilibrium concentration of phosphate.

ii) Desorption of phosphate:- Desorption experiments for phosphate was done, according to the procedure used for molybdate desorption study.

iii) Adsorption isotherm of phosphate :- For the adsorption data, adsorption isotherms were drawn and Langmuir equation was used for it. Desorption data were computed from desorption isotherm, for assessing any hysterosis in the adsorption - desorption isotherm curve in association.

6.1.2. Methods of co-adsorption study of molybdate and phosphate on soil :

In order to determine the relative ability of soil to adsorb phosphate and molybdate, it is convenient, if the reaction of each anion with a given soil, can be characterised by a single value. However, for comparison, Langmuir adsorption maxima should not be taken, as because the controversy over the Langmuir curve under more than one anion system. The procedure for adsorption was according to the procedure of Barrow (1970). For each anion, solution concentration was chosen and the quantity of adsorbed ion in equilibrium with the concentration in solution was interpolated from the adsorption data as shown in Fig.21.

For molybdenum the concentration was 0.1 ppm. According to Barrow (1970), the primary reason for this choice was that it is a convenient concentration for analysis but an addition reason was that measurements were made at this concentration by Reisenauer, Tabikh and Stout.

Though Barrow's choice for 'P' concentration was 0.2 ppm, in the present investigation, the choice of adsorption for 'P' is 0.5 ppm, Considering the usual ratio of 'Mo' and 'P' concentration soil solutions.

In order to get different set of adsorption data, the four soils were equilibriated with 1:1, 1:10, 1:30, 1:40 and 1:50, molybdate : phosphate concentration in solution ranging for Mo 0.2 to 1 ppm and for phosphate 0.2 to 100 ppm.

2.0 gms of soils were incubated for 40 hours at 40°C after 6 hours shaking with 0.01M $Cacl_2$ and respective molybdate- phosphate concentration in different ratios, as mentioned above. Immediately after completion of incubation, the samples were filtered and after discarding the first 5 C.C. filtrate subsequent filtrates were taken for analysis of phosphate and molybdate. From the adsorption data, different adsorption curves were drawn and at the chosen equilibrium concentration by interpolation, the data were obtained for necessary comparison.

6.2. Results and Discussion

6.2.1. Adsorption of phosphate by soil :

The adsorption isotherms of the four different soils at various concentrations of phosphate in solution are shown in Figs. 20(A). The curves usually consist of three regions, characterised by initial steep rise (particularly in case of Canning and Dhupguri soils) of the isotherm, which bends and finally flattens out. The regions are I, II and III, which are prominent in case of Bhupguri, Laterite and Canning soils. Adsorption isotherms for these soils are characterised by more than one regions, clearly indication multiphase adsorption, with each phase having a definite set of energy level, in case of these adsorbents.

In all the soils, isotherm curves follow the Langmuir equation. The correlation coefficient values for the same

Fig.20A

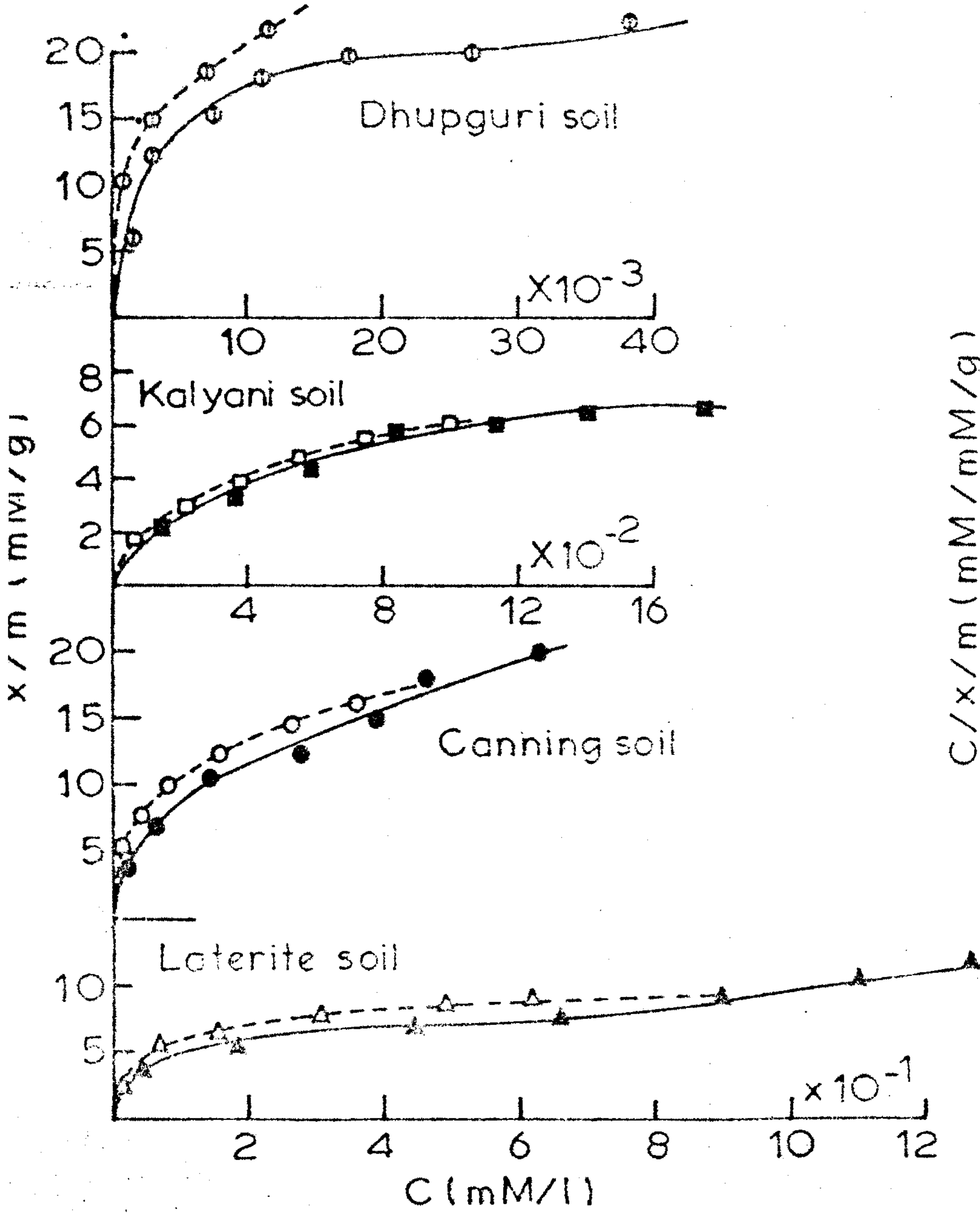


Fig. 20(A). Phosphate adsorption and desorption in different soils.

Fig.20B

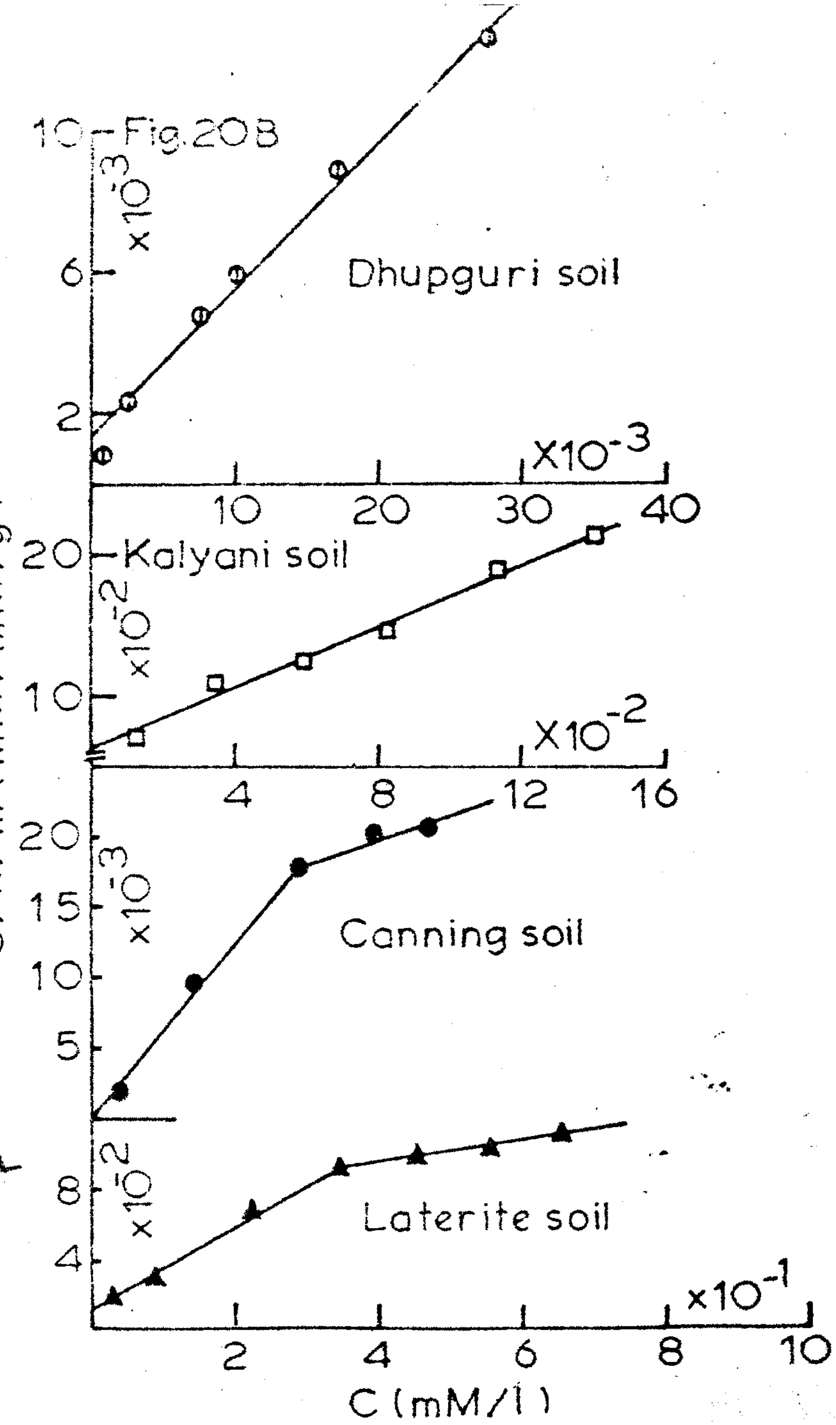


Fig. 20(B). Langmuir plot of phosphate adsorption in different soils.

are given in the Table-XII. The Langmuir curves are depicted in the Fig.20(B). It has been found that break in the Langmuir curves occured in case of Canning and Laterite soils. The adserption maxima and K-value (related to bonding energy) and change in Gibb's free energy for the adsorption, derived thereof, are giv n in the Table XII.

TABLE-XII : Correlation Coefficient values for Langmuir Curves and Langmuir Parameters for the adsorption of phosphate by soils.

Soils	'r'* values	Adsorption maxima (mM/g)	K-value $x10^{-3}(M^{-1})$	$-\Delta G^{o}$ (K cal/mole)
Dhupguri	0.8562	28.49	16.55	15.61
Laterite (1st surface)	0.9946	6.85	42.26	17.11
Laterite (2nd surface)	0.9829	25.83	0.24	8.86
Canning (1st surface)	0.9985	10.90	65.97	17.83
Canning (2nd surface)	0.9496	32.05	2.64	12.66
Kalyani	0.9829	8.40	2.28	12.42

* Significant at 1% level.

It is clear from the table that adsorption maxima of Laterite, Dhupguri and Canning soils are higher than that of

Kalyani soil. Two surface adsorption occurs in case of Laterite and Canning soil. High adsorption of phosphate in Laterite and Dhupguri soils may be ascribed to the exchangeable 'Al' of Dhupguri soil and high free iron oxide content of Laterite soil respectively. High adsorption of Canning soil appears to be due to high pH and high exchangeable 'Ca' content of this soil. Kalyani soil on the other hand, though of high pH, adsorbs very little phosphate mainly due to low AEC and relatively low Ca and Fe content of this soil. High adsorption of phosphate of Canning soil appears also due to the high organic matter content as well as high anion exchange capacity of this soil.

While comparing the K-value related to bonding energy of adsorption it is found that Canning and Laterite soils bind phosphate with higher strength at the first surface adsorption compared to Dhupguri and Kalyani soils. However, these two soils adsorb higher amount of phosphate at the second surface adsorption, with very little strength. Dhupguri soil adsorbs phosphate with greater strength, on the other hand Kalyani soil adsorbs phosphate weakly.

Regarding change in free energy, it is observed that the value ΔG^{o} (negative) increases in the following order, considering the first surface adsorption of Canning and Laterite soil,

Canning $>$ Laterite $>$ Dhupguri $>$ Kalyani.

From the observation it can be concluded that in Dhupguri, Laterite and Canning soil, the adsorption is mostly chemical. However, in the second surface adsorption of phosphate on canning soil is mostly physical. Kalyani soil exhibits mostly physical nature of adsorption. The change of ΔG^{o} clearly indicates that the nature of phosphate adsorption by Dhupguri, Canning and Laterite soils, is mostly chemical. Chemical precipitation of phosphate on free oxide of Al and Fe present in these soils may be the principal cause of phosphate adsorption by Dhupguri and Laterite soil rather low pH of these soils.

6.2.2. Desorption isotherm of Adsorbed Phosphate by Soil :

The desorption isotherms for the adsorbed phosphate by the soils, are shown in association with adsorption isotherm in Fig.20(A). The figures high light marked irreversibility of phosphate adsorption in Dhupguri soil. Desorption isotherms of Laterite and Canning soils show irreversibility of adsorbed phosphate at lower phosphate concentration in solution but merging of the curve at higher concentration of phosphate with the adsorption curve, indicating greater reversibility at higher concentration levels of of phosphate in solution. Kalyani soil on the other hand exhibits little hysterosis, indicating a general reversibility of the adsorption. This observation is consistent with the K-value obtained for this soil. As Canning soil adsorbs higher amount of phosphate with lower strength at higher concentration of phosphate in solution, maximal amount of phosphate gets desorbed from the surface, on the other hand Dhupguri and Laterite soil adsorb phosphate with greater strength, desorbing very little amount of phosphate from the surface.

6.2.3. Comparison of the adsorption of molybdate and phosphate by soils :

The adsorption isotherms of phosphate and molybdate adsorption from the binary anion system of phosphate and molybdate of the equilibriating solution by different soils are shown in Fig.21. Adsorption isotherm for molybdate from the binary system in which molybdate to phosphate ratios, Mo : P ranging from 1 : 1 to 1 : 50 show that increase in phosphate concentration in the solution results in a decrease of molybdate adsorption by different soils. The results are given in the Table XIII.

It is observed from the Table that adsorption of molybdate decreases, as the concentration of phosphate increases in the system. With fifty times addition of phosphate to molybdate in solution, the magnitudes of decrease are 35.3%, 51.6%, 60% and 77% in Dhupguri, Laterite, Kalyani and Canning soils respectively.

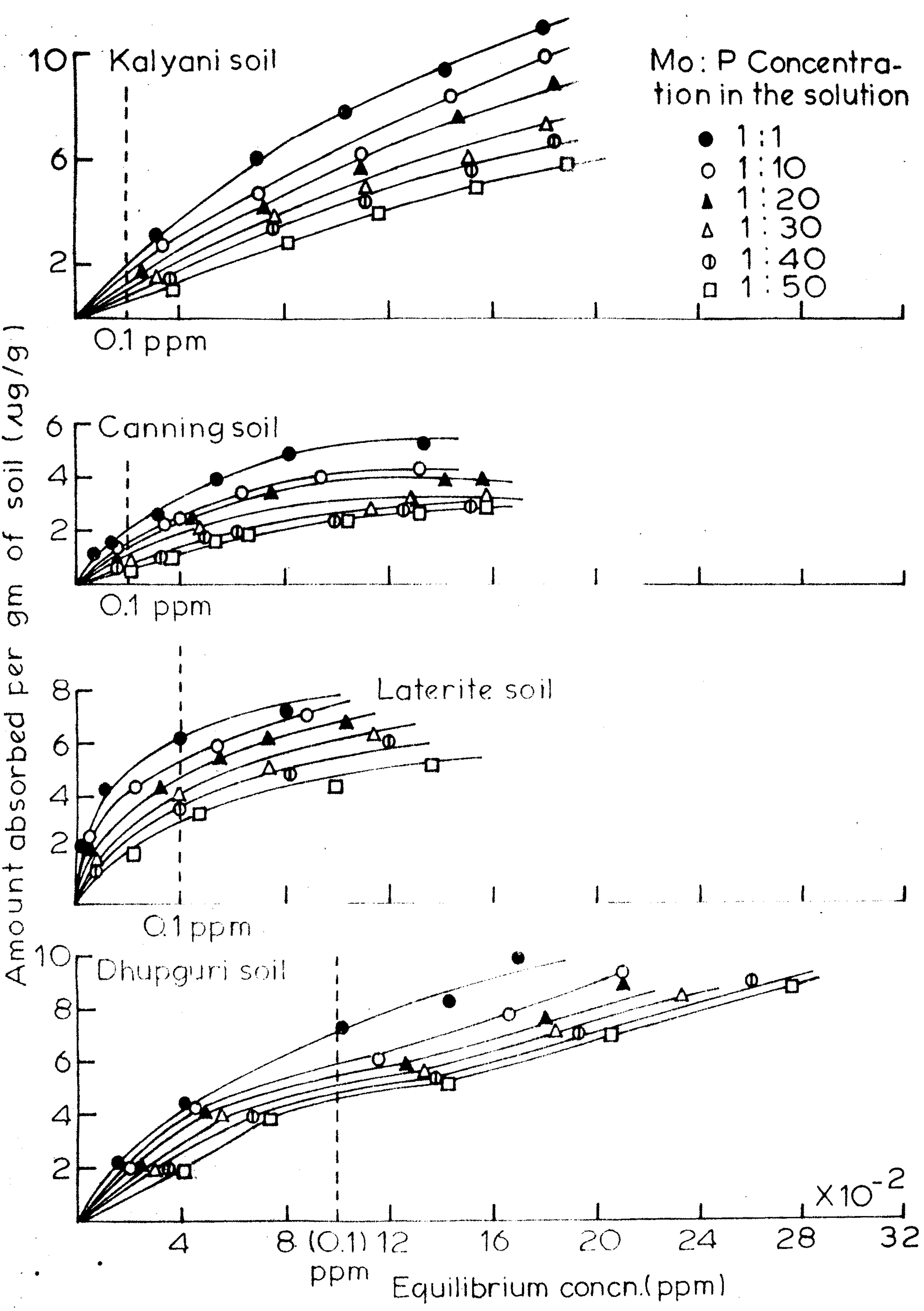


Fig. 21. Adsorption of molybdate from the binary system of phosphate and molybdate at different ratios.

TABLE-XIII : Molybdate adsorption ($\mu g/g$) from the binary system of Mo and 'P' at different ratios.

Soil	Molybdate adsorbed for Mo : P ratio					
	1:1	1:10	1:20	1:30	1:40	1:50
Dhupguri	7.4	6.0	5.6	5.2	5.0	4.8
Laterite	6.2	5.2	4.7	4.0	3.6	3.0
Canning	1.8	1.5	1.2	0.9	0.5	0.4
Kalyani	0.2	0.15	0.12	0.10	0.09	0.08

The adsorption of molybdate by Kalyani and Canning soils, thus drastically reduced due to the addition of phosphate in solution. On the other hand, though Dhupguri and Laterite soils have high capacity for phosphate adsorption as well as can adsorb molybdate with higher strength, adsorption of molybdate is decreased on application of phosphate as a general observation. But it is not so conspicuous as with Kalyani and Canning Soils. Relatively high amount of free oxides or organic complexes of Fe and Al present in Dhupguri and Laterite soils adsorb molybdate mostly by chemical forces from which desorption of molybdate, on application of phosphate can not be expected upto the mark as is observed in case of Canning and Kalyani soils.

Considering the relative ability of molybdate and phosphate adsorption by these soils, it can be generalised that the Canning and Kalyani soils possess greater affinity for phosphate compared to that for molybdate. Kalyani and

Canning soils go through mostly physical adsorption of phosphate and molybdate, resulting in a much higher decrease in molybdate adsorption in presence of greater amount of phosphate in equilibriating solution.

When comparing the phosphate adsorption at 0.5 ppm equilibrium concentration of phosphate, it is found that there is no significant effect on the adsorption of phosphate by adding a small amount of molybdate in solution. The effect of co-adsorption is not observed due to the small amount of molybdate compared to phosphate present in solution.

CHAPTER VII

SUMMARY AND CONCLUSION

In the present investigation, adsorption studies have been carried out with the anion molybdate as the adsorbate and some hydrous oxides, phosphates, and carbonate, some clays in their homo-ionic forms and some soils belonging to diverse agroclimatic zones of West Bengal, as adsorbents. A study on phosphate adsorption as well as phosphate-molybdate competitive adsorption by soil has also been made.

Among the two precipitated phosphates used, $FePo_4$ has been found to adsorb much more molybdate than $AlPO_4$ at both the temperature (40°C and 20°C), used for the study. In both the cases Langmuir equation was followed and it is revealed from the K-value, derived from Langmuir isotherm and related to bonding energy, that molybdate adsorbed by $FePO_4$ with greater strength at both the temperatures. The free energy ΔG^o value indicates spontaneous nature of adsorption by both the adsorbents. Higher positive values of ΔH^o have been observed in case of $FePO_4$, Entropy change ΔS^o has also been calculated and found to be more positive for $FePO_4$.

Among the two hydrous oxide gels Fe_2O_3, xH_2O is found to possess a higher adsorption capacity for molybdate and corresponding Langmuir curve indicates a two-surface reaction. The hydrous Al_2O_3, xH_2O has been found to adsorb less molybdate at both the temperature used (20°C and 40°C). The ΔG^o

value is much more negative for Al_2O_3, xH_2O than for Fe_2O_3, xH_2O which signifies more spontaneous nature of molybdate, by the former as also greater strength of adsorption. Negative heat of adsorption in case of Fe_2O_3, xH_2O signifies exothermic nature of reaction by the adsorbent, whereas a positive ΔH^o value for Al_2O_3, xH_2O is observed. ΔS^o value is found to be higher in case of Fe_2O_3, xH_2O.

$CaCo_3$ exhibits very little adsorption of molybdate but rock phosphate has been found to show practically no adsorption of this anion.

From the various thermodynamic parameters derived for the adsorption of molybdate by the above inorganic materials it can be concluded that except possibly by $CaCo_3$, the adsorption is largely chemical. The order of the degree of adsorption is Fe_2O_3, $xH_2O \gg Al_2O_3$, $xH_2O \gg FePO_4 > Al\ PO_4 \gg CaCO_3$.

The study on the adsorption isotherm of molybdate by different homo-ionic Kaolinite and Bentonite at two pH levels (4 and 7) and at two temperatures (20°C and 40°C) was carried out. Among the H-clays, it is found that at pH-4.0, the break in the Langmuir curve corresponds to a two-surface adsorption. The adsorption maxima calculated from the more dominant first surface adsorption indicate higher amount by H-Bentonite than H-Kaolinite at both the temperatures used. Higher amount of adsorption is observed at higher temperature but K-values related to bonding energy are found to be higher at low temperature in both the cases at this pH-level. At pH-7, the adsorption is much less by H-Kaolinite but degree of adsorption also higher at higher temperature, signifying mostly physical nature of adsorption of molybdate by the clays.

Desorption isotherms studied reveal irreversible nature of adsorption by the clays except by H-Bentonite at pH-7.0. Slower release of adsorbed molybdate is observed at pH-4.0 level compared to at pH-7.0 in all cases.

Higher negative ΔG^o values, are obtained in case of adsorption by all the H-clays except for H-Bentonite at pH-7.0, indicating greater spontaneity of the molybdate adsorption, by the clays. In general, a greater affinity for molybdate on H-Bentonite compared to H-Kaolinite has been observed.

Adsorption study of molybdate on Fe-clays at different pH and temperature levels, reveals that lower pH value enhances greater adsorption of molybdate with higher strength, by these homo-ionic clays. Langmuir isotherm indicates two-surface adsorption of molybdate by Fe-Bentonite in all cases. In the first surface, adsorption is much higher, with greater strength compared to adsorption on the second surface. Increase in pH, results in a decrease in molybdate adsorption drastically on Fe-Kaolinite, which is also observed in case of Fe-Bentonite but to a smaller extent. Adsorption is higher at higher temperature in all the Fe-clays except for Fe-Kaolinite at pH-7.0.

Desorption isotherms show greater irreversibility of the adsorption reaction on Fe-clays, irrespective of pH and temperature but at pH-7.0, Fe-Kaolinite exhibits reversibility at higher concentration of molybdate in solution. Release of the adsorbed molybdate is gradual which is inconformity with the bonding energy of adsorption as well as hysterosis effect of desorption isotherm.

Change in free energy is negative in all the cases, indicating spontaneous nature of adsorption with Fe-clays. ΔH^{o} values for adsorption in all the cases are positive except for the adsorption of molybdate on Fe-Kaolinite at pH-4.0, which is negative.

From the observation it can be concluded that adsorption of molybdate on Fe-clays is largely chemical in nature.

Adsorption studies on molybdate with Al-clays indicate a two-surface adsorption of molybdate at both pH and temperature levels studied. Greater amount of adsorption by both the Al-clays at lower pH level, has, however, been observed. Temperature change has little effect on the adsorption of molybdate on Al-clays, except for the adsorption on the second surface of the Al-Bentonite, indicating appreciable chemical nature of adsorption on this surface.

The desorption isotherms indicate strong hysterosis in all the cases of Al-clays, reflecting irreversibility of the reaction. However, at higher pH level, reversibility of adsorption can be seen at higher concentration of molybdate in solution, which is inconformity with lower bonding energy, at the second surface adsorption. Release curves also indicate higher rate of release at higher level of molybdate in solution as well as at the higher pH.

Change in free energy ΔG^o for the adsorption is found to be negative, indicating spontaneous nature of adsorption of molybdate by the Al-clays. In all the cases ΔH^o is positive, except in the adsorption of molybdate on Al-Bentonite at pH-4.0, Entropy change is higher at pH-4.0 level than at pH-7.0.

Adsorption isotherm of molybdate on Ca-clays at two pH levels and temperatures followed Langmuir equation at pH 7.0. Ca-Bentonite at pH-4.0, however, follows Langmuir curve only at lower concentration level of molybdate. At lower pH values, greater amount of molybdate is adsorbed by the Ca-clays, of which Ca-Bentonite adsorbs greater amount of molybdate with greater strength. Except Ca-Kaolinite at pH 4.0, higher amount of molybdate is adsorbed by Ca-clays, at higher temperature at both the pH level used.

Change in Gibbis free energy is higher in case of adsorption on Ca-Bentonite and is relatively higher at higher pH level also. Heat of reaction ΔH^o value is positive in both the Ca-clays at pH 4.0 level but negative at pH-7.0 level, indicating exothermic nature of adsorption at higher pH level.

Desorption isotherms of Ca-clays, indicate reversibility of the adsorption reaction at pH 7.0 level but irreversibility at pH 4.0 level.

Considering all the homo-ionic clays it is observed that Fe and Al play dominating role in the adsorption of molybdate by chemical force and with higher strength. Lower pH value enhances adsorption in all the cases and at pH 4.0 the degree of adsorption follow the order

Fe-Bentonite > H-Bentonite > Al-Bentonite > Ca-Bentonite
Fe-Kaolinite > Al-Kaolinite > H-Kaolinite > Ca-Kaolinite

At pH 7.0, the order is found to be slightly modified as :

H-Bentonite > Fe-Bentonite > Al-Bentonite > Ca-Bentonite
Fe-Kaolinite ≃ Al-Kaolinite > H-Kaolinite > Ca-Kaolinite.

Adsorption studies of molybdate on the four different soils show that the adsorption isotherm is characterised by different regions, indicating multiphase adsorption. The adsorption maxima calculated from the Langmuir curve indicate greater adsorption of molybdate on Dhupguri and Laterite soils. The adsorption increases in the order :

Dhupguri soil > Laterite soil ≫ Canning soil > Kalyani soil.

More or less same amount of adsorption has occured at both the temperature (20°C and 40°C), except in Canning soil, where greater adsorption at lower temperature is observed. The break in the Langmuir curve is observed in case of Laterite, and Dhupguri soils. Except Kalyani soil, in all the cases higher bonding energy at higher temperature, reveal the chemical nature of adsorption. The presence of high amount of exchangeable Al in Dhupguri soil and free ferric oxide in Laterite soil appear to be the reason for this.

Organic matter has been found to play an important role in the molybdate adsorption, as its removal from the soil results in drastic reduction of molybdate adsorption in all the soils, except in Canning soil. Interesting observation is found in Canning soil, where highest amount of molybdate has been adsorbed on removal of organic matter, although with little bonding energy. Higher adsorption of this organic matter free soil is found at lower temperature. In other cases, adsorption is higher at higher temperature. Organic matter free Kalyani and Canning soils adsorb molybdate with lesser strength. Laterite soil, on the otherhand, adsorbs molybdate with greater strength after removal of organic matter.

Removal of free oxides from the soil decreases molybdate adsorption, which is more prominent in case of Laterite and Dhupguri soil. The removal of active sites from soil, results in reduction of molybdate adsorption. The K-value related to bonding energy of adsorption on oxide free soils, are also lower in both the temperatures, indicating weaker strength of adsorption.

Desorption isotherms of native and organic matter free Dhupguri and Laterite soil, highlight greater irreversibility of the adsorption, on the other hand little or no hysterosis is observed in case of Kalyani and Canning soil. Though organic matter removal causes higher adsorption of molybdate in Canning soil, the little hysterosis in desorption curve is observed, which is inconformity with the lesser strength of adsorption, indicating some what physical nature of adsorption.

Removal of oxides also results in complete reversibility of the adsorption of molybdate on soil which also confirms the physical nature of adsorption.

Adsorption maxima of the soil for molybdate adsorption is significantly correlated negatively with pH of the soil and positively with oxalate extractable as well as exchangeable Fe and Al in soil. Adsorption maxima is also correlated positively with free Fe_2O_3 content of the soils.

In all the cases negative ΔG^{o} value has been obtained indicating spontaneous nature of adsorption at both the temperatures. Greater negative values are found in Dhupguri and Laterite soil. These are also higher in case of organic matter free Dhupguri and Laterite soil.

Regarding change in ΔH^{o} value it is observed that except Kalyani soil, in all the cases it is positive, indicating endothermic nature of adsorption, on the other hand negative ΔH^o of Kalyani soil is an indication of exothermic reaction. Same observation is also noted in case of adsorption on organic matter free soils.

From the thermodynamic parameters and nature of adsorption curves, it can be concluded that more or less chemical adsorption of molybdate takes place on native and organic matter free Laterite and Dhupguri soils, whereas all the oxide free soils, show some what physical nature of adsorption. From the Correlation value it can also be concluded that the adsorption of molybdate by these soils is primarily due to the presence of Fe_2O_3, and exchangeable Fe and Al content of the soils.

Studies on phosphate adsorption on different soils show that the adsorption isotherms at 40°C are characterised by three distinct regions, indicating multiphase adsorption with each phase having a definite set of energy level. In all the cases isotherm curves follow the Langmuir isotherm. Breaks in the Langmuir curves are observed in case of Laterite and Canning soil, indicating two-surface adsorption of phosphate on these soils. The degree of adsorption of phosphate by soils is found to increase in the order :

Canning(second surface) $>$ Dhupguri $>$ Laterite (second surface) $>$ Kalyani.

K-values related to bonding energy indicate greater strength of adsorption in case of Dhupguri and Canning soil. Canning and Laterite soils adsorb smaller amount of phosphate on the first surface but with higher bonding energy. Kalyani soil, on the other hand, adsorbs phosphate with little strength.

Gibb's free energy change (ΔG^{o}) for phosphate adsorption, increases in the order :

Canning > Laterite > Dhupguri > Kalyani.

Desorption isotherms of phosphate highlight marked irreversibility of the adsorbed phosphate in Dhupguri soil. Laterite and Canning soils show reversibility at higher concentration of phosphate in solution but irreversibility at lower concentration, indicating physical nature of adsorption at the second surface adsorption, whereas Kalyani soil show little hystorosis in the isotherm curve, indicating a general reversibility of the adsorption. Hence, it can be concluded that adsorption of phosphate on the Dhupguri, Laterite and Canning soils is mostly chemical in nature.

From the studies on the comparison of adsorption of molybdate and phosphate on soils from the binary system it is observed that the adsorption of molybdate decreases as concentration of phosphate increases in the solution. The order of decrease is found to be as follows :

Canning soil > Kalyani soil > Laterite soil > Dhupguri soil.

Considering the relative ability of molybdate and phosphate adsorption by these soils, it can be generalised that the canning and Kalyani soils possess greater affinity for phosphate compared to molybdate. However, no significant effect of phosphate adsorption on the adsorption of molybdate at 0.5 ppm of phosphate in solution at equilibrium is found in the binary system, by adding a small amount of molybdate in solution.

CHAPTER VIII

FUTURE SCOPE OF RESEARCH ON THE ADSORPTION

In the present investigations most of the experiments were carried out for assessing the nature and degree of molybdate adsorption by various adsorbents, on the basis of Langmuir parameters. Emphasis was given on the affinity of molybdenum for several soil constituents, as formulated previously by various Scientists. In order to make it more fruitful and practical one, it is necessary to study the molybdate adsorption over a wide range of soils as well as other soil constituents. The important factors which are conducive for molybdenum adsorption, have to be located on the various soils. The nature of adsorption and desorption curve would have to be correlated with the various availability indices and adsorption with respect to plant.

The various equations, formulated by several workers, for overcoming the limitation of Langmuir model in soil system have also to be taken into consideration, for more fruitful and scientific computation of the adsorption data.

The important parameters obtained from Langmuir equation i.e. K-value related to bonding energy and adsorption maxima, have to be correlated with the availability of the applied molybdenum, if there is any possibility for assessing the fertilizer requirement of soils by this consideration. The constants obtained from the equation for soils of diverse class and different agro-climatic zones may provide useful informations for assessing the fertilizer requirement and this necessiates the investigation of sorption indices with the better physico-chemical basis.

As a soil is enriched or depleted in molybdate, there are changes in both solution and supporting pool of labile molybdate. The manner in which they change, however, differs from soil to soil according to the slope of the sorption isotherm, which express the buffering capacity of the soil with respect to molybdate. This slope may be a much more permanent soil characteristic than either the existing molybdate content, which varies the manurial treatment or the amount sorbed from a given solution. Further research on all these aspects is necessary from the practical point of view.

Regarding the competitive adsorption of with other anion, it needs further investigation on co-adsorption with sulphate, silicate, borate and chloride. Suitable equations for computing the co-adsorption are required to be formulated in order to estimate the various thermodynamic parameters. Particularly for this purpose, equation developed by Harter and Baker (1977) can be taken into consideration. In this aspect also, the sorption indices have to be estimated for assessing the nutrient interaction in soil solution and absorption by plants.

The effect of organic matter on molybdate adsorption, needs further research, particularly on the nature of compounds formed after adsorption of molybdenum on various organic or clay-organic surfaces.

The formation of heteropoly anions such as phosphomolybdate, silicomolybdate etc, as well oxy-cations of molybdenum also need some consideration if molybdate adsorption in soil is to be more fully understood.

The adsorption of molybdate on precipitated form of $FePO_4$ and $AlPO_4$ needs a more detail study for finding out the nature of adsorbed compounds.

BIBLIOGRAPHY

Adamson, A.W.; Boyo, G.E.(1967) Exchange adsorption of ions from aqueous solution by organic zeolities. J.Am.Chem. Soc. 69 : 2818-2829.

Aleksandrova, L.N. (1954). Poehuovdenic I (14-29).

Alexander, A.E. and Johnson, P (1949) Colloid Science, Oxford.

Amin, J.V., Joham, N.E. (1958). A molybdenum cycle in the soil. Soil Sc.85 : 150-160.

Appett, H; Coleman, N.T.; Pratt, P.F. (1975 b). Soil Sc. Am. Proc. 39 : 628-630.

Arkley, T.H. and Johnson, C.M. (1954). Determination of Mo in Plant tissue. Anal. Chem 26 : 572-573.

Atkinson, R.J.; Posner, A.M.; Quirk, J.P. (1972). J. of inorg, Nucl Chem. 34 : 2201-2211.

Agerton, J; Anaeker, E.W. and Johnson, J.S.(1963) Hydrolysis of Mo (VI). Ultra Centrifugation, acidity measurements and Roman Spectra of Paramolybdates. Inorg. Chem. 3 : 735-746.

Bache, B.W. (1963). Solution and Hydrolysis of varicite and strengite. J. Soil. Sc. 14 : 113-123.

Bache, B.W. (1964). J. Soil. Sc 15 : 110-116.

Bache, B.W.; Williams, E.G. (1971). A phosphate sorption index of soils. J. Soil. Sc. 22 : 289-301.

Barrow, N.J. (1970) Comparison of the adsorption of Molybdate, Sulphate and Phosphate by Soils. Soil. Sc. 109 : 282-288.

Barrow, N.J. and Spencer, K (1971) Fectors in the Mo and P status of soils on Dorrigo Plateau of New South Wales. Aust. J. Exp. Agric. Anim. Proc. Husb. II : 670-676.

Barrow, N.J. (1972) Influence of solution concentration of Ca on the adsorption of phosphate, sulphate and molybdate by soils. Soil. Sc 113 : 175-180.

Barrow, N.J.(1973) On the displacement of adsorbed anions from soil. I. Displacement of molybdate by phosphate and by hydroxides. Soil Sc. 6 : 423-431.

Barrow, N.J. (1974) On the displacement of adsorbed anions from soil I. Displacement of molybdate by phosphate and by hydroxide. Soil Sc. 116 : 423-431.

Barrow, N.J. and Shaw, T.C. (1979) Effects of ionic strength and nature of the cation on desorption of phosphate from soil. J. of Soil. Sc 30 (1) : 53-65.

Barrow, N.J. (1980) Difference among a wide ranging collection of soils in the rate of reaction with phosphate. Aust. J. soil. Res. 18 : 215-224.

Beckwith, R.S; Lave, R (1963) Aust. J. Res. I : 157-168.

Bolland, M.D.A; Posner, A.M; Quirk, J.P (1976). Aust. J. of Soil Res 14 : 197-216.

Bowden, J.W; Bolland, M.D.A; Posner, A.M; Quirk, J.P (1974) Trans. Int. Congr. Soil. Sc.10th Vol II : 29-36.

Bowden, J.W; Posner, A.M; Quirk J.P.(1977) Aust. J. Soil. Res. 15 : 121-136.

Borsad, I (1951) Factors affecting the Mo content of pasture plants 1) Nature of Soil Mo growth of plants and soil pH. Soil SC. 71 : 297-313.

Bragg, W.L; Claringbull, G.F (1965) The crystalline state IV: 118.

Cajuste, L.J (1979) Phosphate adsorption in some Mexican soils of volcanic origin and its relationship with some soil components. Agrociencia. Mexico 36 : 137 - 144.

Carpeni, G (1947) Su La constitution des solutions aqueus d' acide molybique et. de. molybdates alcalins IV. Bull. Soc. Chim Fr 14 : 501-503.

Catani, R.A; Alcarde, J.C; Furlani, P.R (1970) Anions de Escola superior de Agricultura Luiz. de Queiroz 27 : 223-233.

Chatterjee, R.K. and Dakshinamurthy, C (1962) Available MO status of some Indian soils. J.Sc. Indust. Res. 21 : 597.

Cheng, B.T; Quellette, G.J (1973) Soil Ferti. 36 :207-215.

Chojnacki, J. (1963) Influence of pH on the ionic mobilities of molybdate isopolyacids. Recz Chem 37 : 259-272.

Cole, C.V and Jackson, M.L (1950) Colloidal phosphates of Al and Fe. J. Physic. Chem. 54 : 128-142.

Cole, C.V; Olsen, S.R; Scott, C. (1953) Soil Sc. Am. Proc. 17 : 352-356.

Colombera, P.M; Posner, A.M; Quirk, J.P (1971) Soil Sc. 22: 119-128.

Crank, J (1956) The mathematics of ion diffusion. Clarendon Oxford 3 :213-216.

Davies, E.B (1956) Factors affecting Mo availability in soils. Soil Sc 81:209-223.

De, S.K (1961) Kolloid Z. 172 : 134-140.

Dolui, A.K and Roy, B.B (1979) Clay minerology of some alluvial soils of W.B (India) Indian Agric. 23 (2) :57-66.

Evans, J; Smillie, G.W (1976) Jr. J. Agril. Res. 15 : 65-73.

Fitter, A.H; Sutton, C.D (1975) The use of Freundlich isotherm for phosphate sorption data. Soil Sc 26 : 241-246.

Fordham, A.W (1963). The measurement of Chemical Potential of phosphate in soil suspension. Aust. J. Soil Res 1 : 144-156.

Fox, R.L; Kamprath, E.J (1970) Phosphate sorption isotherm for evaluating the phosphate requirements of soils. Soil Sc. Am. Proc 34 : 902-907.

Fox, R.L; Kamprath, E.J (1971) Soil Sc. Am. Proc. 35 :154-156.

Fox, R.L; Hasan, S.M; Junes, R.C(1971) Phosphate and sulphate sorption by Latosols. Proceedings, international symposium on soil fertility evaluation. New Delhi. Ind. Soc. of Soil Sc.1 : 857-864.

Fox, R.L; Searle, P.G.E(1978) Phosphate adsorption by soils of the tropics. In Diversity of soils in the Tropics. USA. American Society of Agronomy Special Publication 34 : 97-119.

Frankline, W.T and Reisenauer, H.M (1960) Soil Sc.90 :192-200.

Gallego, A.R; Jolin, B.T (1960). Studies on adsorption of the molybdate ion by clays. Ciencias 25 (4) :983-988

Ghosh, S.K. and Dutta, N.P. (1974) X-ray investigation of clay minerals in the soils of W.B. Proc. Indian. natn. Sci. Acad. 40 : 138-150.

Gonzalez, B.R; Arpett. H ; Schalascha, E.B; Bingham, F.T(1974). Molybdate adsorption characteristics of volcanic ash derived soils in chile. Soil Sc. Soc. of Am. Proc. 38 (6) : 903-906.

Gorlach, E; Gorlach, K. and Compala, A (1969). Sorption and desorption of molybdate in the soil. Agrochimica 13 : 506-510.

Greenland, D.J. (1971). Soil Sc. 111 : 34-41.

Greenland, D. J (1965) Soil Fert. 28 (415-425).

Hair, R (1967) The mechanism of $SO_4^{=}$ adsorption on Iron Oxides Soil Sc. Soc. Am. Proc. 42 : 48-51.

Harter, D.R. and Dale, E.B. (1977) Application and Misapplication of the Langmuir equation to soil Adsorption phenomena. Soil Sc. Soc. of Am. J. 41 (6) : 1077-1080.

Hingston, E.J; Posner, A.M; Quirk, J.P. (1972) Anion adsorption by goethite and gibbsite I. The role of proton in determining adsorption envelops. J. Soil Sc. 23 (177 -193).

Hingston, E.J; Posner, A.M; Quirk, J.P. (1974). J. Soil Sc. 25 (16-26)

Holford, J.C.R; Weddarburn, R.W.M; Mattingly, G.E.G (1974). J. Soil Sc. 25 : 242-255.

Holford, J.C.R; Mattingly, G.E.G. (1975 b) Geoderma 13: 257-264.

Holford, J.C.R.; Mattingly, G.E.G. (1976) Plant Soil 44:219-229.

Holford, J.C.R. (1980) Adsorbed phosphate in soils and sediments. Soil Sc. Soc. Am. J44:441-442.

Hope, G.D; Syers, J.K (1976). Effect of solution soil ratio on sorption by soils. J. Soil Sc.27 : 301-206.

Huang, P.M.(1975b) Soil Sc. Am. Proc. 39 : 271-274.

Jarrell, W.A; Dowson, M.D.(1978) Sorption and availability of Molybdenum in soils of Western Soil Sc. Soc. of Am. J. 42 (3) : 412-415.

Jenkin, I.L. and Wain, A.G. (1963) Mo species in acid solution, J.Appl. Chem.(London) 13 : 561-564.

John, M.K.(1972) Factors affecting the adsorption of tagged phosphorus by soils. Communications in soil Sc. and Pl. Analysis **3** (3) : 197-205.

Jones, L.H.P; Milne, A.A. (1956) Aluminium molybdate and its formation in clay minerals. Nature. Land **178** : 1115.

Jones, L.H.P.(1956) Interaction of molybdenum and iron in soils. Science **123** : 116.

Jones, L.H.P.(1957). The solubility of Mo in simplified system and Aquous soil suspension. J. Soil. Sc. **8**:313-317.

Jones, R.C; Uchara, G. (1973) Soil Sc. Am. Proc. **38** :792-798.

Jurniak, J.J; Burau, R.G(1967) Soil Sc. Am.Proc.**31**:732-756.

Juo, A.S.R; Moormann, F.R; Maduakar, H.P(1974) Geoderma **11**: 167-179.

Kafikafi, U; Posner, A.M; Quirk, J.P. (1967) Soil Sc. Am. Proc. **31** : 348-352.

Karimain, N; Cox, F.R.(1978) Adsorption and extractability of Mo in relation to some chemical properties of soil. Soil Sc.Soc.Am.J. **42** (5): 757-761.

Karim, M; Ahmed, F; Islam, A.(1973) Geoderma **9**:221-227.

Kaolovoulos, J.M.(1960) The aging of H-clay suspensions. Trans. 7th Int.Cong.Soil Sc.**7**:492-498.

Kelley, J.B; Midgley, A.R.(1943) Soil Sc. **55**:167-176.

Kathandaraman, G.V; Krishnamoorthy, K (1978) Influence of reaction time on phosphate adsorption. J. of Ind. Soc. Soil Sc. 26(3): 274-277.

Krishnamurthy, G.S.R; Volk, V.V; Jackson, M.L.(1966) Soil Sc.Am.Proc. 30 : 685-688.

Kuo.S; Lotse, E.G.(1972) Kinetics of Phosphate adsorption by Ca Co_3 and Ca-Kaolinite. Soil Sc.Am.Proc. 36:725-729.

Lal, S; De, S.K; Rao, N.S.(1974) Sorption of Molybdenum soluble in water. Pochvovedenie 5 :65-68.

Langmuir, I.(1918) The adsorption of gases on plane surface of glass, mica and platinum. J.Amer.Chem.Soc. 40: 1361-1403.

Lavy, T.L. and Barber, S.A.(1964) Movement of Mo in the soil and its effect on availability to the plant. Soil Sc. Soc. Am.Proc. 28 : 93-97.

Little, P. (1966) The mechanism of phosphate adsorption on Geethite Can J. Soil Sc.46 : 315-317.

Mattingly, G.E.G.(1965) The influence of intensity and capacity factors on the availability of soil phosphates. Soil phosphorus. Min. Agric. Teach. Bull. 13 : 1-9.

Mattingly, G.E.G.(1975) Soil Sc. 119 : 369-375.

Mattson, S; Williams, E.G; Erikson, E. and Vohtras, K(1950) Phosphate relationship of soils and plant II soil-soil-solution equilibria and phosphate solubility. Lantbr. Hogsk. Ann. 17 : 64-91.

Mehlich, A. (1964) Soil Sc. Soc. Am. Proc. **31**: 46-50.

Mishra, K.C; Mishra, S.G.(1971) Molybdenum reaction in soils in presence of free iron oxide and $CaCO_3$. Technology **8** (1) : 42-45.

Mosni, A.O; Wild, A; Greenland, D.J.(1974) Geoderma **11**:275-283.

Moody, P.W.(1979) Prediction of 'P' requirements of *Desmodium intortum* Green leaf using a 'P' sorption index and extract 'P'. Commun Soil Sc and Anal. **10**(8):1127-1139.

Muljadi, D; Posner, A.K. and Quirk, J.P. (1966) The mechanism of phosphate adsorption by Kaolinite, Gibbsite and pseudo-beomite part I. The isotherms and the effect of pH on adsorption. J.of Soil Sc. **17** : 214-217.

NG.SK; Bloomfield, C. (1962) The effect of flooding and aeration on the mobility of certain trace elements in soils. Plant and soil **16** : 108-135.

Nye, P.H.(1966) The mechanism of ion diffusion in soils, J. of soil Sc. **17** : 16-23.

Ozanme, P.G; Show, T.P. (1967) Aust. J. Agril Res. **18**:601-612.

Parfitt, R.L.(1972) Soil Sc.**113** : 417-421.

Parfitt, R.L; Atkinson, R.J; Smart, R.S.(1975). Soil Sc. Soc. Am. Proc. **39**: 837-841.

Parfitt, R.L; Atkinson, R.J.(1976) J.Chem. Soc. Faraday, Trans. **I.78**: 2834-2842.

Parfitt, R.L. and Russell, J.D.(1977) Soil Sc. Am.J.**41**: 1064-1067.

Parfitt, R.L; Fraser, A.R; Russell, J.D; Farmer, V.C.(1977b)

J.Soil Sc. 28:40-47.

Parfitt, R.L. and Smart, R.S.(1978) The mechanism of $SO_4^{=}$ adsorption on Iron Oxides. Soil Sc. Soc. Am. Proc. 42 : 48-51.

Pasricha, N.S. and Randhawa, N.S.(1972) From a review of micronutrient Research in soils and plants in India. I.C.A.R.

Piper, G.G.(1942) Soil and Plant Analysis. Uni of Adelade.

Rajon, S.S.S.(1975b) J. of Soil Sc.26 : 250-256.

Rajon, S.S.S.(1975b) Newzealand, J.Sci.18:93-101.

Rajon, S.S.S; Fox, R.L.(1975) Phosphate adsorption by soils II. Reactions in tropical acide soils. Soil Sc. Am. Proc. 39:846-851.

Rajon, S.S.S. and Perrot, K.W.(1975) J.Soil Sc. 26:257-266.

Rajon, S.S.S; Watkinsen, J.H.(1976) Soil Sc. Am. 40:51-54.

Ramuln, U.S; Pratt, P.F; Page, A.L. (1967) 'P' Fixation by soils in Relation to Extractable iron oxides and Minerological composition soil Sc. Am. Proc. 31: 193-196.

Reisenauer, H.N; Tabikh, A.A; Stout, P.R.(1962) Molybdenum reactions with soils and the hydrous oxides of Iron, Aluminium and Titatinum. Soil Sc. Soc. Am. Proc. 26 : 23-27.

Reyes, E.D. and Jurnak, J.J(1967) A mechanism of Molybdate Adsorption on α Fe_2O_3. Soil Sc. Soc. Am.Proc. 31 : 637-641.

Rohwer, E.F.G.H. and Cruywagen, J.J.(1964). The first protonation constant of monoeric molybdic acid. J.S. African, Chem. Inst. 17 : 145-148.

Roy, S.C. and Das. S.C. (1974). Adsorption and Desorption of Phosphate in clays and clay constituents in Relation to pH and phosphate concentration in solution. Part I. Clay minerals-Hydrogen and Aluminium clays. Indian Agri. 18 (3): 235-247.

Ryden, J.C; Mclanghlin, J.R; Syers, J.K.(1977) Mechanism of Phosphate sorption by soils and Hydrons Ferric Oxide gel. J. of soil Sc. 28 : 72-92.

Ryden, J.C; Syers, J.K.(1978). Rationalization of Ionic strength and cation effect on phosphate sorption by soils. J. of soil Sc 26 (4): 395-406.

Ryden, J.C; Syers, J.K; Mclanghlin, J.R. (1977). Effects of ionic strength on chemicorption and potential determining sorption of phosphate by soils J. of soil Sc. 28 (1): 62-71.

Ryden, J.C. and Syers, J.K.(1977) Origin of labile phosphate pool in soils. Soil Sc. 123: 353-361.

Sahu, S.S. and Das, S.C.(1974) Study of electro chemical and physicochemical properties of clay minerals and mixtures and some soil clays to characterize their their∠clay mineral. Proc. Indian natn. Sci. Acad. B-40 3: 235-248.

Sahu , S.S. and Das, S.C.(1972). Study of electrochemical and viscus properties and surface area of clay minerals and some of soil clays (W.B.) to Characterize their minerology. Indian J. Appl. Chem. 35 (2).

Sanata, C.F; Bolarin, M.C; Roig, A; Caro, M.(1982). Phosphate adsorption by $CaCO_3$. Soils and Ferti **45** (6): 6742.

Schlichting, E.(1960) The fixation of phosphate and molybdate in soil profiles containing bog iron Z. pfl Ernahr. Diing.**90**: 204-208.

Schofield, R.K.(1949) J. Soil. Sc. **I**:1-8.

Schofield, R.K.(1955) Can a precise meaning be given to available phosphate. Soils Fertil **18** : 373-375.

Schuylenborgh, J. Van and Arens, P.L.(1950) The electro Kinetic behaviour of freshly prepared and α Fe-OOH. Res. Trav. Chim. Pays. Bas **69** : 1557-1565.

Schuylenborgh, J.Van (1951) The electrokintic behaviour of freshly prepared γ-AlooH, α-and γ-$Al(OH)_3$. Res. Trav. Chim. Pay. Bas **70** : 985-988.

Schwarzenbach, G. and Meier, J. (1958) Formation and investigation of unstable protonation and deprotonation products of complexes in aquous solution J. Inorg. Nucl. Chem. **8** : 302-312.

Shapiro, R.E; Fried, M. (1959) Soil Sc. Am. Proc. **23**:195-198.

Singh, B. and Sekhon, G.S.(1978) Leaching of nitrate in calcarious soil as influenced by its adsorption on $CaCO_3$ Geoderma **20** ( ):271-279.

Singh, B. and Tabtabai, M.A.(1977) Effect of soil properties on phosphate sorption. Commun in soil sc and plant Analysis **8**(2): 97-107.

Smith, B.H; Leeper, G.W.(1969). The fate of applied molybdate in acidic soil. J. Soil Sc. **20** : 246-254.

Stout, P.R; Meagher, W.R; Pearsan, G.A. and Johnson, C.M.(1951) Mo nutrition of Crop Plants I. The influence of phosphate and So$_4^{=}$ on the adsorption of Mo from soil and solution culture. Plaintx and soil **3** : 51-87.

Syers, J.K; Browman, G; Smille, W; and Corney, R.B.(1973) Phosphate sorption by soils Evaluated by the Langmuir Adsorption equation. Soil Sc. Soc. Am. Proc. **37** : 358-361.

Syers, J.K; Murdock, J.T. and Willaims, J.D.(1970) Adsorption and desorption of phosphate by soils. Soil Sc. Plant Anal. **1** : 57-62.

Szilagyi, M. (1967) Sorption of molybdenum by humus preparations. Grokhimiya **12** : 1489-1492.

Teng, B.K.G.(1971) Adsorption of molybdate by some crystalline and amorptions soil clays. Newzealand J. of Sc. **14**(4):1040-1056.

Trobisch, S. and Schilling, G. (1963) Mo Fixation by arable soils in Thuringia. Chem. d. Erde. 23:91-103.

Vlek, P. L. G. and Lindsay (1977) Thermodynamic solubility and solubility of Mo mineral in soils. Soil Sc. Soc. Am. J. 41 (1) : 42-46.

Wade, K; and Harward, M.E.(1974) Adv. Agron. 26:211-260.

Wells, N. (1956) Soil Studies, using sweet vernab to assess element availability. Part II Molybdate ion fixation. Newzealand J. Sci. Technol. 37 : 482-502.

White, R.E.(1966) Studies on the phosphate potentials of soils IV. The mechanism of the soil/solution ratio effect. Aust. J. of Soil Res. 4:77-85.

White, R.E. and Beckelt. P.H.T. (1964) Studies on the phosphate potentials of soils I. The measurements of phosphate potential Pl. Soil 20 : 1-6.

White, R.E. and Taylor, A.W.(1977) Reaction of soluble phosphate with acid soils- the interpretation of adsorption- desorption isotherms. J of soil Sc 28(2): 314-328.

Wild, A. (1967) Soluble phosphate in soil and uptake by plants. Nature (London) 203 : 326-327.

Williams, C.H. and Moore, C.W.E. (1952) The effect of stage of growth on the Cu, Zn, Mn and Mo contents of Algerian Oat grown on 13 soils. Aust. J. Agro. Res. 3: 343-361.