SORPTION OF HEAVY METALS BY MODIFIED KAOLINITIC CLAYS

THESIS SUBMITTED TO THE
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by

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STATEMENT

I hereby declare that the matter embodied in this thesis is the result of the investigations carried out by me at the Clays and Clay Minerals Unit of the Regional Research Laboratory, Trivandrum, under the joint guidance of Dr. M. Lalithambika and Dr. C.S.P. Iyer and the same has not been submitted elsewhere for a degree.

In keeping with the general practice of reporting scientific observations, due acknowledgment has been made wherever the work described is based on the findings of other investigators.

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CERTIFICATE

Certified that the work embodied in this thesis entitled **Sorption of Heavy Metals by Modified Kaolinitic Clays** has been carried out by Mr. G. Suraj under our joint supervision and the same has not been submitted elsewhere for a degree.

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PREFACE

River basins are dominant features of the earth's surface. Human settlements, industrial development, agriculture and deforestation have significantly altered the physical and ecological features of many river basins; introducing nutrients, metals and synthetic chemicals to the hydrologic cycle. Kerala has 41 west flowing rivers with the Western ghats forming the watershed. The study of textural and chemical composition of the Periyar river, which is the second largest river in Kerala having numerous industries along side, leads to the observation that heavy metals are being concentrated on the fine sediments of this river basin, which is contributed by the ion-exchange property of the clay minerals present in these sediments. Kaolinite being the dominant clay mineral in the region and has the least cation exchange capacity, efforts were made to improve its exchange capacity. Various physical and chemical modification procedures were tried on pure kaolinite sample. It was finally observed that, a significant enhancement in metal uptake could be achieved by the chemical alteration procedure.

In this thesis, the first chapter gives an overview of the literature available on sediment / water interface reactions. A brief description regarding the role of clay minerals present in the sediments on the uptake of metal ions, in the context of its structure is presented.

In order to understand the role of clay minerals as a scavenger of heavy metals in a fluvial environment, it will be appropriate to study the exchange properties of a particular metal from its solution on to a river sediment sample. In the second chapter, fluvial sediments obtained from the Periyar River were characterized and their exchangeability of metal ions, giving particular reference to cadmium and nickel, was studied.

As an attempt to improve the exchange capacity of natural kolinite sample, the third chapter discusses the chemical modification procedure wherein pure kaolinite mineral was acid activated to release metal ions thereby increasing their sorption capacity.

A physical modification procedure was also tried on the kaolinite structure and the details are discussed in chapter four. Structural modification was achieved by micronization of kaolinite sample which produces vacant sites in the lattice structure, which can accommodate metal ions from solution, thereby increasing their sorption capacity.

Fifth chapter describes a structural alteration procedure, where the structure of kaolinite is transformed into a mixture of zeolite like sodalite, Na-X, zeolite 4A and analcime along with some unreacted material. This material could accommodate more metal ions in its structure thereby improving the sorption capacity.

CONTENTS

CHAPTER 1

INTRODUCTION

Clay is one of the most widespread and earliest mineral substances utilized by man. The term clay is applied to the earthy substances, consisting chiefly of aluminium silicates, which with colloidal materials and specks of rock fragments; plastic when wet and stone-like when fired. These properties give clay their usefulness, since they can be moulded into any form which they retain after firing. Wide spread accessibility, ease of extraction and adaptability to many uses has resulted in the products of clay, entering the wide ramification of modern industrial civilization. In domestic life, clay is used in pottery, earthenware, china cookingware, vases, ornaments, plumbing fixtures, tiles, linoleum, wall paper, scouring soap, etc. It even finds a place as filler in foods and medicine. The mineral kaolin, which is discussed in this work, is used mainly as a coating and filling pigment in the paper industry. Their application in the ceramic industry extends to many different sectors, viz. tableware, sanitaryware, wall tiles, floor tiles, electrical and industrial porcelains, etc. Polymer industries (paints, plastics, rubber, etc.) use kaolinite as extenders and fillers. Chemical and pharmaceutical industries use them as catalysts and fillers. Moreover, they find uses in modern fine or engineering ceramics, cordierite catalysts used in car exhausts and are converted to a form of zeolites which replaces phosphates in detergents. A new field of research has introduced clay minerals as scavengers of pollutants form waste waters. The work done in this field, with a special emphasis to kaolinite is reviewed in a later section.

1. COMPOSITION AND PROPERTIES.

Clay is not a mineral but an aggregate of minerals and colloidal substances. The constituents are so fine that, until the use of X-ray and electron microscope for mineral determination, its exact composition was unknown. Residual clay is often called kaolin (after *'Kau-ling'*, in Jiangxi Province in China, where firing of ceramicware was done) but this is now recognized as one variety of clay. It was formerly thought that kaolin was composed of the mineral kaolinite. It is now known that, although kaolinite contains considerable kaolinite, other clay minerals are also constituents. Some of the commonly encountered clay minerals are

Group	Composition	Origin	Occurrence
A. Kaolinite			
1. Kaolinite	$Al_2Si_2O_5(OH)_4$	H, W	China clays,
		H	Under clays, soils
2. Dickite	$Al_2Si_2O_5(OH)_4$	H	Wallrocks
3. Nacrite	$Al_2Si_2O_5(OH)_4$	H	Wallrocks
4. Anauxite	$Al_2Si_2O_5(OH)_4$	W	Soils
5. Halloysite	$Al_2Si_2O_5(OH)_4$	H, W	Soils
6. Endellite	$Al_2Si_2O_5(OH)_4 . 2H_2O$	W	Soils
B. Montmorillonite			
1. Montmorillonite	$Mg_2Al_{10}Si_{24}O_{60}(OH)_{12}[Na_2,Ca]$	H, W	Soils, bentonite, Fuller's earth
2. Nontronite	$Fe'''Si_{22}Al_2O_{60}(OH)_{12}[Na_2, Ca]$	H	Veins
3. Saponite	$Mg_{18}Si_{22}Al_2O_{60}(OH)_{12}[Na_2]$	H	Veins
4. Beidellite	$Al_{13}Si_{19}Al_5O_{60}(OH)_{12}[Na_2]$	H	Veins
5. Hectorite	$Li_2Mg_{16}Si_{24}O_{60}(OH)_{12}[Na_2]$	W	Clays
C. Hydrous micas (illite)	$(OH)_4K_2(Si_6 . Al_2)Al_4O_{20}$	W	Soils, marine clays, underclays
D. Miscellaneous			
1. Palangorite	$Mg_5Si_8O_{20}(OH_2)_4 . 4H_2O$	W	Fuller's earth
2. Sepiolite-like	$Mg_6Si_8O_{20}(OH)_4 . nH_2O$		
3. Allophane	$Al + SiO_2 + H_2O$	W	Clays, soils

W = weathering; H = hydrothermal; square brackets surrounds exchangeable bases

Table 1-1 Composition and occurrence of clay minerals

2. FORMATION OF CLAY MINERALS

Replacement of the primary rock forming minerals by clay minerals generally involves both physical and chemical process; biological agencies are also important in the zone of weathering. The clay minerals are stable under a wide range of conditions. Clay containing earth materials may be subdivided into two groups, the residual and the transported. Soils formed by weathering are the most common residual clay containing material though some hydrothermal material belongs to this category. Transportation may be affected by gravity, water, ice and wind.

During physical processes, the mechanical breakup of the parent material allows water and active solution to gain access into the rock, aided by the disintegration process which leads to an increased surface area. A major class of chemical reaction in which one solid is converted into another involves an intermediate stage in which the reactions are in true or colloidal solution. There are three major types of such reaction. These are; interaction between acids and bases as for example in carbonation and hydroxylation; electron transfer as in oxidation and reduction; and free radical interaction. Clay mineral formation by a solution mechanism has been proposed by many authors which include methods such as hydration and hydrolysis, surface reaction, oxidation followed by removal of cation in solution, etc. and are discussed by Gillott (1968).

3. CLAY AND ENVIRONMENT

Environmental pollution has become a grim reality in the last part of the twentieth century. Nowhere are the signs of pollution so clearly visible as in the aquatic environment. One of the typical properties of an industrialized and affluent society is its relatively high consumption of various materials. As a general practice, waste products generated by industrialized societies have not been disposed of according to scientific reasoning, but rather in response to economic pressure or merely by the most convenient method. As a result, many waste products have been dispersed at elevated concentrations over wide areas, through atmospheric and aquatic reservoirs.

One of the main objectives of environmental chemistry has been to describe the behaviour of elements in natural systems based on knowledge of their fundamental physico-chemical properties. Development of sophisticated analytical techniques for the measurement of trace quantities of metal ions has greatly helped in assessing their impact on ecosystems due to anthropogenic activities. As a result, strict environmental regulatory standards have been promulgated and tremendous technological advances have been made to minimize their adverse effects. In many natural systems, the behaviour of metals is profoundly affected by the presence of particle surfaces. Krauskopf [1956] has shown experimentally that adsorption of heavy metals on suspended solids is probably responsible for their considerably undersaturated concentration in the marine environment as compared to their point of origin. Several trace metals, including mercury, are strongly concentrated in the finer size fractions of sediments than in the coarser ones (Parks, 1975).

Generally more than 90% of the heavy metal load in aquatic systems is bound on particulates like suspended matter and sediments. Natural particles in rivers, lakes and sea consist of clay minerals, iron and manganese oxyhydroxides, carbonates, organic substances (e.g. humic acid) and biological materials (e.g. algae and bacteria). The type and stability of heavy metal bonding on these solid compounds are decisive factors for the potential mobility and their bio availability. The physico-chemical and bio-chemical conditions in the aquatic system and sediment are determined by the two master variables viz. pH and redox potential, respectively, which together with the suite of inorganic and organic ligands present, control the mobilization of heavy metals from the sediment (Calmano et al. 1988; Forstnov et al. 1989).

Metals with atomic number greater than 20 are considered as heavy metals (but are often used as connotations of toxicity). Heavy metals earlier were defined as those metals having a density of at least five times greater than that of water(Kumaraguru 1995; Tare and Chaudhari 1995). Introduction of metals into aquatic systems include both (1) Natural sources of metals due to weathering of soils and rocks and volcanic eruptions and (2) Human activities including mining, processing and use of metals and substances that contain metals. Some metals, such as Mn, Fe, Cu, and Zn are essential for living beings in small quantities and hence known as micronutrients or essential elements/metals. On the other hand, metals such as Hg, Cd and Pb are not required even in small quantities by any organism and hence denoted as non-essential elements/ metals. Heavy metals like Hg, Cd and Pb show greater affinity for sulfhydryl(-SH) group and exert its toxic effects largely by combining with such groups present in proteins which result in disruption of enzyme mediated processes in the cells (Laws 1981).

A solute may react with a existing solid phase by three main processes; adsorption (the accumulation of matter at an interface without the development of a three dimensional molecular arrangement),absorption (the diffusion of an aqueous chemical species into a solid phase) and surface precipitation. The generic term used here to describe the general removal of a solute from the solution phase to a contiguous solid phase is sorption (Honeyman and Santschi 1988).

Adsorption occurs as a result of a variety of binding mechanisms. Most of the solids in the aquatic environments are electrically charged, and some adsorption of ionic species would be expected to occur through electrostatic attraction. Other than electrostatic attraction, changes in hydration state of the solid or the adsorbate, interaction between the adsorbate molecule and ions themselves and covalent, van der Waals' or hydrogen bonding between the adsorbate and the solids etc. will also contribute to adsorption.

4. ROLE OF CLAY MINERALS

Clay colloids present in the suspended sediments and soil profiles interact with heavy metal pollutants, which occur as cationic and anionic species in solution. It is well known that clay particles have charged surfaces and edges which contribute to their ion-exchange and adsorption properties. Isomorphous replacement, broken bonds and lattice defects are responsible for the net negative charge on clay particles which contribute to their Cation Exchange Capacity (CEC). Among clay minerals, commonly present in the soils and sediments, montmorillonite shows the highest CEC in the range 0.8-1.5 $mol_c kg^{-1}$ (Carroll 1959) whereas kaolinite shows the least of 0.02-0.15 $mol_c kg^{-1}$. [Unit for CEC are $mol_c kg^{-1}$(moles of charge per kilogram) and earlier used to represent the number of chemical equivalents per unit weight of dry clay quoted normally in milliequivalents per hundred gram; 1meq per 100g = 0.01$mol_c kg^{-1}$]. This difference is primarily due to the nature and location of exchange sites on the clay lattice, as montmorillonite contributes both surface and interlayer sites but kaolinite has its exchange sites restricted to the surface. Except under extremely acidic conditions, the layer charge is predominantly negative (Swartzen-Allen and Matijevic 1974). The principal origin of negative charge in montmorillonite is isomorphous substitution of cations with layer charge, e.g. the substitution of aluminium for silicon in the tetrahedral sheet and magnesium and/or ferrous iron for aluminium, or sometimes lithium for magnesium in the octahedral layers. Their exchange cations are mainly between the adjacent tetrahedral layers. Other clays have much less isomorphous subtitution and correspondingly lower CEC values. It has been suggested that broken bonds at particle edges may also contribute to exchange capacity, particularly for clays of the kaolinite groups (Hall 1987).

	Approximate surface area ($m^2\ kg^{-1}$)	Approximate CEC ($mol_c\ kg^{-1}$)	Approximate surface charge denisty ($umol_c\ m^{-2}$)	Dominant negative charge
Kaolinite	$(1\text{-}2) \times 10^4$	0.02 - 0.06	1 - 6	pH dependent
Illite	1×10^5	0.3	3	permanent
Smectites	8×10^5	1.0	1	permanent
Fe & Al oxides	3×10^4	0.005	0.2	pH dependent
Humic acid	9×10^5	3.0	3	pH dependent

Table 1-2: Surface properties including cation exchange capacity (CEC) at pH 7 of the relative soil components (Wild 1993).

5. CHEMISTRY OF CLAY MINERALS

Clay minerals are aluminosilicates that predominates in the clay fraction of soils at the intermediate to advanced stages of weathering. These minerals, are sandwiches of silica tetrahedra and alumina octahedra sheet structure. The pattern of combination classifies them into three layer types and further into five groups, differentiated by the kinds of isomorphous cation substitution. The 1:1 layer type consists of one tetrahedral and octahedral sheet. eg., kaolinite group, with general chemical formula $[Si_4]Al_4O_{10}(OH_8)$. nH_2O, where the cation enclosed in the square bracket is in tetrahedral coordination and *n* is the number of moles of hydration water[ie., 0 for kaolinite and 4 for halloysite].

The 2:1 layer type consist of an octahedral sheet sandwiched between two octahedral sheets e.g. illite, vermiculite and smectite where the layer charge decreases in the order illite> vermiculite> smectite. Another 2:1 layer type with hydroxide interlayer is represented by dioctahedral chlorites in soil clays. A description of various clay minerals and their chemical structure is given in the Table 1-1.

The crystal structures and chemical compositions of the clay minerals and their associated minerals are extensively discussed by various authors; the pioneers being Blindly and Brown (1980); Brown et al. (1978); Deer et al. (1966).

5.1. Sorption and sorption sites on kaolinite

Kaolinite is 1:1 dioctahedral clay with 7 Å spacing that has no structural charge in its pure stoichiometric form (Grim 1968). Kaolinite exposes singly coordinated –OH groups on the freshly broken edge surfaces (Fig. 1-1).

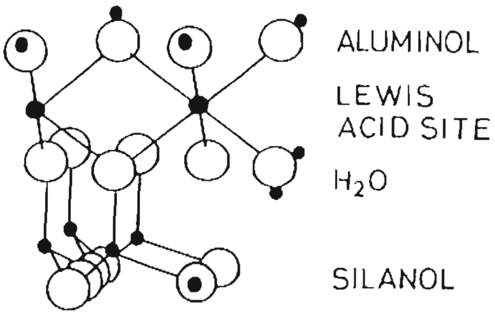

Fig.1-1 Surface hydroxyl groups on the kaolinite surface showing the Lewis acid site, Al(III) .H_2O, aluminol and silanol groups.

At the edge of the octahedral sheet, –OH groups which are singly coordinated to Al^{3+} cations and which bind as well as dissociate protons are termed aluminol. Where as –OH groups which are singly coordinated to the

Si^{4+} cations, due to the greater valence of silicon tend only to dissociate protons are termed silanol. The plane of oxygen atoms on the surface of 2:1 layer silicate is called a siloxane surface (Sposito 1989).

Amphoteric reactions at oxygen sites on aluminol and siloxane surfaces contributing to the sorption of aqueous species and development of surface charge are conceptually similar to surface reactions on oxide minerals (Sposito 1984). Natural kaolinite do, however, have small cation exchange capacities (Table 1-2) and thus, the surface properties of kaolinite share characteristics with both oxides and smectites. A weak sorption capacity displayed by kaolinite is generally attributed to two factors: either isomorphic substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet giving rise to a negative structural charge or due to the contamination by small amounts of 2:1 phyllosilicate minerals (Bolland et al 1976,1980; Ferris and Jepson 1975; Sposito 1984; Wieland and Stumm 1992).

Studies of divalent metal cation uptake on kaolinite shows that fractional uptake from solution is low at lower pH conditions, rises rapidly in a narrow pH range, and then exceed 95% below the pH of precipitation of a stable hydroxide (O'Day et al 1994). Solution uptake experiments and potentiometric titrations classify the uptake of cations, anions and/or protons from solutions onto kaolinite, as a function of pH, on two sites: (1)non specific adsorption/ion-exchange sites which adsorb background electrolyte cations through weak bonds (outersphere complexes) and (2) specific adsorption at amphoteric surface hydroxyl sites (e.g. Al OH, Si OH) which are strongly bound to surface oxygen (innersphere complexes) (Farrah et al 1980; Carroll-Webb and Walther 1988). In otherwords, if no water molecule is interposed between the surface functional group and the ion or molecule it binds the complex is innersphere. If at least one water molecule is interposed between the functional group and the bound ions or molecules, the complex is outersphere.(Sposito 1989; Carroll-Webb and Walther 1988; Singh and Mattigod 1992; Wieland and Stumm 1992; Xie and Walther 1992).

An evaluation on the surface sites on kaolinite that may take part in sorption can be made by considering the ideal kaolinite structure and way in which O atoms and -OH groups are coordinated to Al and Si atoms (Sposito 1984; O'Day et al 1994). In kaolinite, there are O atoms in six structurally unique sites (Fig. 1-2).

(1)Non-bridging (single bonded) Al OH exposed at the edges of the aluminol sheets (surface OH).

(2)Non-bridging Al-OH in between the aluminol and siloxane sheets (inner-OH).

(3)Non-bridging Si-O exposed at the edges of siloxane sheets .

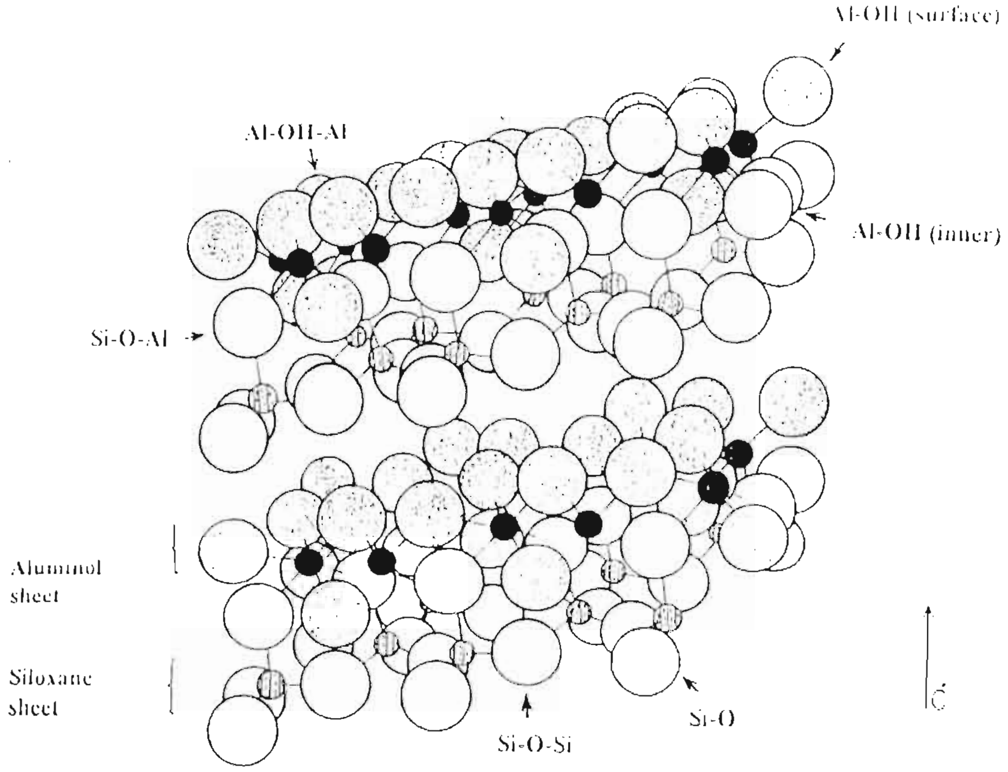

Fig. 1-2 Kaolinite crystal structure showing the aluminol and siloxane sheets forming 1:1 layers, and surface oxygen atoms exposed on faces that may act as reactive surface sorption sites. Atoms: Al - solid; Si - hatched; O - open; OH - shaded

(4)Bridging Al–O–Si between the aluminol and siloxane sheet exposed at the edges.

(5)Bridging Al–OH–Al exposed on (001) faces of the aluminol sheet .

(6)Bridging Si–O–Si exposed on (001) faces of the siloxane sheet.

Among these, non-bridging Al–OH (inner and surface) and Si–O exposed on the edges, have long been regarded as the most reactive surface sites that can sorb metal ions and protons(Sposito 1984; O'Day 1994). Al–O–Si is usually not considered in the sorption reactions and Si–O–Si sites on the (001) faces are considered unreactive (Sposito 1984). There is a general disagreement over whether or not, bridging Al–OH–Al sites in the (001) alumina planes react significantly as kaolinites being a dioctaherdal clay, stoichiometric Al vacancies in this sheet may give rise to localized negative charge and the reactivity of oxygen atoms exposed at the particulate surface affected by the vacancy is unclear. Finally, the ditrigonal siloxane cavity functions as a soft Lewis base, where there is no isomorphous substitution to create local positive charge in the underlying layer; and can complex only neutral, dipolar molecules such as water molecules (eg. easily reversible entrapment of water molecule having one of its hydroxyl groups directed into cavity perpendicular to the siloxane surface). Even though isomorphous substitution in the underlying sheet results in an excess negative charge produces stronger complexes with metal ions but its reactivity in uncharged kaolinite particles is considered low (Sposito 1989; O'Day et al. 1994).

6. ADSORPTION

Adsorption, or some kind of surface limited association, must play an important role in the distribution of trace constituents between water and solids and between different solids. Adsorption occurs as a result of a variety of binding mechanisms (Gardiner 1974). The reasons for adsorption are varied and complex. Except in simple systems, surface charge is unlikely to be a reliable guide, to adsorption behaviour (Parks 1975). Adsorption is the net accumulation of matter at the interface between a solid phase and an aqueous solution phase. It differs from precipitation because it does involve the development of three-dimensional molecular structure, even if such a structure grows on the surface (denoted surface precipitate). Thus the matter that accumulates in the two-dimensional molecular arrangements at an interface is the adsorbate and surface on which it accumulates is the adsorbent.

Adsorption on the solid particle surfaces can take place via. three mechanism: (1)The innersphere surface complexes are those in which metal ion complexed directly with the surface functional group, with no water molecules interposed between them. (2)The outersphere surface complexes involves cation hydration shell in which at least one water molecule get interposed between the functional group and the bound ion or molecule. (3)diffuse ion swarms where the solvated ion does not form a complex with the charged surface functional group, but instead neutralizes surface charge only in a delocalized sense (Sposito 1989).

Adsorption is studied experimentally by means of two basic methods: (1)reaction of clay mineral with a metal solution of known concentration at fixed temperature and pressure for a prescribed period of time and (2)chemical analysis of the reacted clay mineral, the clay solution or both, to determine their components. The reaction in step 1 can take place either with solution mixed uniformly with clay particles (batch process) or with the solution in uniform motion relative to a column of clay (flow-through process).

6.1. Adsorption equilibria

When a solution is in contact with a solid adsorbent, molecules of adsorbate transfer from the liquid to the solid until the concentration of the adsorbate in solution is in equilibrium with the adsorbate on the solid. The equilibrium data is usually represented by an adsorption isotherm, which is the relationship between the quantity adsorbed per unit mass of solid and the concentration of adsorbate in solution (Sundstrom and Klei 1979). The isotherm derived by Langmuir (1918) for adsorption of a solute from a liquid solution is

$$q_e = \frac{q_m k_A C_e}{1 + K_A C_e} \qquad (1 - 1)$$

where q - mass of solute adsorbed at equilibrium time / mass adsorbent (mg/g).
q_m - mass of solute adsorbed / mass adsorbent for a complete monolayer (adsorption capacity)
C_e - equilibrium concentration of solute in solution, mass / volume (mg/l)
K_A - constant related to enthalpy of adsorption

This equation is based on the assumption that: (a)adsorption is related to single layer of solute molecules; (b)adsorbed molecules are not free to move on the surface; and (c)the enthalpy of adsorption is the same for all molecules. The above equation can be rearranged to the following linear form

$$\frac{C_e}{q_e} = \frac{1}{K_A q_m} + \frac{C_e}{q_m} \qquad (1 - 2)$$

or

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{K_A q_m}\right)\frac{1}{C_e} \qquad (1 - 3)$$

By plotting C_e/q_e vs C_e, the constants K_A and q_m can be evaluated from the slopes ($1/q_m$) and intercept ($1/K_A q_m$).

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L (Hall et al. in Namasivayam and Ranganathan 1995) which is defined by

$$R_L = \frac{1}{1 + K_A C_0} \qquad (1 - 4)$$

where C_0 = initial metal ion concentration (mg/l)

Freundlich developed an empirical equation for the adsorption isotherm:

$$q_e = K_F C_e^{1/n} \qquad (1 - 5)$$

This equation can be rearranged to a linear form as:

$$\log q_e = \log K_F + 1/n \log C_e \qquad (1 - 6)$$

where C_e is the equilibrium concentration (mg/l), q_e is the amount adsorbed (mg/g) at equilibrium time, K_F and n are Fruendlich constants and $n > 1$, n gives an indication of the favourability and K_F, the capacity of adsorbent [mg/g (l/mg) ^{n}]. A linear plots of log$C$ vs log$q$ is used to calculate n and K_F from the slope ($1/n$) and intercept (log K_F). This equation is most useful for dilute solutions over small concentration ranges.

Kinniburgh (1986) suggests that non linear regression should be used while fitting adsorption isotherm equations to experimental data, since this enables Langmuir and Fruendlich isotherms to be fitted directly. According to him the Tóth, modified Dubinin-Radushkevich and multisite Langmuir isotherms has greater flexibility as they can describe competitive adsorption (binary exchange) reactions and are well suited for heterogeneous exchanges such as soils and sediments.

7. ADSORPTION OF SOIL SYSTEMS - A REVIEW

Elements present in the sediments in minor concentrations were of great interest in environmental studies because of their detrimental effects on natural environment (Fuller et al. 1990; Pardo et al. 1990).

An interaction between the soil particles and contaminated waste water have been dealt in great detail. The distribution of metal ions depends upon the soil characteristics: ie. mineral composition,specific surface area, cation exchange capacity, organic matter and clay content (Vertacnik et al. 1995). In land, the upper soil is found to act as a chemical filter which prevents ground water pollution. But they can reach the running water through surface processes, where the soil particles have the role of chemical traps. Anthropogenic activities are a source of heavy metals in the aquatic sediments.

An excellent review on the structure and dynamics of ions in water was presented by Ohtaki and Kadnai (1993). This work discusses the method for the determination and structure of hydrated ions, their structural aspects of ionic hydration and finally their dynamic aspects. Another excellent review on the radius (ionic radii) of metals in aqueous environment was discussed by Marcus (1988). The residence time of a metal in an aquatic environment and modeling the processes that takes place, predicted by laboratory experiments was critically reviewed by Honeyman and Santschi (1988).

7.1. Soils

The immobilization of metal pollutants in the land was studied in great details by soil scientists. Sorptive properties of soils was critically discussed by Wild (1993). A review on the experimental evidence of competitive adsorption in a soil system was presented by Murali and Aylmore (1983). Both inorganic and organic cations are capable of competing for adsorption sites with cations like calcium, lead, magnesium, sodium and zinc, on a whole variety of soils, such as kaolinite, montmorillonite, hematite, goethite, gibbsite, pseudoboehmite, etc. The competition was clearly influenced by factors such as pH, solution concentration and nature of competing species. Wilson (1975) reviewed the mechanism and products of weathering of feldspars, micas and ferromagnesian minerals in residual soil profiles where unambiguous mineral transformations have been observed directly and from experimental work in the laboratory.

Atanasova (1995) measured the adsorption and desorption of Cu on two soils and their clay fractions and found to be fully reversible on one soil whereas it was largely irreversible for the other. Batch techniques were used to investigate adsorption of Cu and Zn on several soils as a function of background Ca, Mg, and K concentrations. Ca and Mg competed for exchange sites on the solid surface inhibiting Zn adsorption more than Cu adsorption (Zhu and Alva 1993). But thermodynamic studies of K-Ca and Mg-Ca exchange reactions on a kaolinitic soil revealed greater affinity for potassium in a K-Ca system but calcium was preferred on a Mg-Ca system, as evidenced by the free energy and enthalpy changes (Udo 1978). Aringhieri et al. (1985) investigated the kinetics of adsorption of Cu^{2+} and Cd^{2+} on an organic soil and explains the dependency of internal diffusion which produce a decrease in the specific rate of adsorption as a function of time or the amount of Cu^{2+} and Cd^{2+} adsorbed.

Mann and Ritche (1995) tried to reduce the mobility of cadmium when a sandy soil was supplemented with soil containing either organic or inorganic fraction that were better sorbents for Cd where the effectiveness depended on the type of soil added, the pH and the rate of Cd addition. Hooda and Alloway (1994) compared the ability of some semi-arid and temperate soils to sorb Pb and Cd when mixed with sewage sludge. The application of waste water sludge significantly increased the amount of Cd and Pb retained in most soils, except for those from the semi arid regions that showed a decrease in Pb sorption. Lamy (1993) also found that soluble organic matter in the sludge increased the mobility of Cd as a loam soil based on laboratory and field studies. Sanchez-Martin and Sanchez-Camazano (1993) studied the influence of soil properties on the mobility of Cd on 22 uncultivated soils using batch isotherm and thin-layer chromatography methods and found that the uptake amount is related to the CEC, exchangeable Ca content and sum of bases. Basta and Tabatabai (1992 a&b)also noticed the influence of soil pH and base saturation on the sorption of Cd, Cu, Ni, Zn, and Pb while analyzing soils from two different long term cropping systems.

The adsorption behaviour of cadmium, both as Cd^{2+} and complexed as $CdEDTA^{2-}$ was reported on four different soils by Elliott (1983). The pH-dependent adsorption of Cd^{2+} was nearly identical for the four soils. But complexed $CdEDTA^{2-}$ preferred positively charged soil, suggesting chelation does not hinder substantial metal adsorption.

Cd sorption isotherm were measured for 16 soils and a general scheme based on reaction surface type was proposed for characterizing Cd sorption capacity (Schulte and Beese 1994). Ca was also found to be competing strongly with Cd as described using a Langmuir model by Boekhold (1993). The effect of pH and Cd complexation by Cl was also discussed. A modified Freundlich expression was developed to describe Cd sorption as a function of soil pH and organic matter content. Good agreement was noted between the results of column experiments and prediction made using parameters measured by batch studies. (Boekhold and van der Zee 1992).

The mobility of chlorocomplexes of Cd(II), Cu(II) and Ni(II) through soil columns was investigated using 0.1, 0.2, 0.3 and 0.5M NaCl or $NaClO_4$ solutions, each containing 10μg/ml of metal (Doner 1978). Metal mobility was found to be more in chloride solution (1.1 to 4 times greater) than perchlorate solution, which is not known to form metal complexes. The results showed that Cl^- has a marked effect on the mobility of Cd(II) than Cu(II) and Ni(II).

Young and Phadungchewit (1993) evaluated the problem of varying species of heavy metals in relation to selectivity on retention in four different soils as influenced by pH and observed that soils are highly pH sensitive as regarded with soil attenuation. According to them, at high pH, precipitation dominates (as hydroxides or as carbonates) while at lower pH, cation exchange become dominant. A selectivity of Pd > Cu > Zn > Cd is observed at pH values above 4 or 5, when precipitation prevails for illite, montmorillonite and natural clay soils. At lower pH, the selectivity order obtained by is given as Pb > Cd > Zn > Cu, as displayed by kaolinite and montmorillonite. Behaviour similar to that of other hydrolyzable metals was noted for the adsorption of Cu onto geothite when examined as a function of pH, concentration, surface area and ionic strength (Kooner 1992).

The retention and release of Pb^{2+} in a silty loam and a fine sandy loam was examined by Carriere et al. (1995). A faster sorption kinetics and complete removal was observed for 10 and 100 mg / L solution than the 1000 mg / L, which could display only partial removal. Surface precipitation was predicted to be the reason.

According to them, the release of lead using $CaCl_2$ washes was less than those released using EDTA and HCl. The adsorption of Pb from a land fill leachate onto clays was investigated over a range of pH where an increased pH did not increase the sorption of Pb. Majowe (1993) explain this could be due to the changes in the free Pb concentration as the pH was increased.

Zinc adsorption by mineral soils of Finland was studied by Ylihalla and Loeppert (1995) and found to obey Fruendlich isotherm. Hg sorption was studied in batch experiments involving geothite and soil systems and found that the role of pH and chloride concentration are differing significantly relative to other heavy metals (Barrow and Cox 1992 a&b.).

Laboratory experiments of cation removal using air-dried clayey kaolinitic soil from acid solutions was examined primarily to assess the proportion of cation removal to the proton concentration of the acidic input solution and then to find the effective charge balance of the major cations after termination of acid input (Liu et al. 1990). The application of acid (HCl) solution definitely accelerated leaching losses of cations from the forest soil.

A theoretical treatment of the behaviour of soil columns, as a model for a soil profile followed by experimental confirmation of the work to indicate the degree of validity of the theory was attempted during the early years by Rible and Davis (1955). Experimental-model comparison were used by Hoins (1993) to conclude that sulphate adsorption reduced surface potential and increased Cd adsorption where ternary surface complex was found important. Selim (1992) presented a multi-component model incorporating equilibrium ion-exchange, as well as reversible and irreversible kinetic sorption, for adequately explaining Cd transport in two soils. A multisite model was found to provide a good description on batch sorption of Cd to the unseparated utisols (Cowan et al. 1992).

Regression analysis was used to examine the relationship between CEC and clay minerals and their organic matter for 170 profiles of 49 New Jersey soil series (Drake and Motto 1982). They concluded that 59% of the variation in the CEC could be explained by variation in clay and organic matter contents (where the clay is having a CEC of 35 and organic matter 217 meq./100 g). An earlier work of similar kind using clay rich soils from the lowlands of Quebec, Canada, containing illite, chlorite, smectite and vermiculite together with quartz and feldspars as impurities revealed (as calculated by multiple regression equations) that the CEC values of organic matter increased with depth while that of total clay and fine clay decreased (Martel et al. 1978). Variations in mineralogical composition, although small, will sufficiently explain nearly 50% of the variations in the CEC and the contribution of clay is 3.5 to 5 times greater than that of organic matter.

Multiple regression models were utilized to high-light the discharge source and distribution of metal contaminants that are found in the sediments along the continental shelf near Sydney, Australia (Schneider and Davey 1995). Oceanic flux of metals through organic sediments was studied by Reinfelder (1993).

7.2. Fluvial sediments

High concentrations of Pb, Hg, As and Cd were a severe pollution factor in the gold mining area near Los Andes, Southern Columbia, South America which resulted in their transportation downstream followed by enrichment in food causing a possible threat to humans (Grosser 1994). Gumgum (1994) observed very high concentrations of Co, Cu, Ni, Pb, V and Zn in the Tigris river sediments. The temporal variations in the distribution of Cu, Pb, and Zn in the sediments of Botany bay, Australia were investigated by Morrisey (1994). Fifty year record of metal pollution was monitored by Carignan et al. (1994) in the fluvial lake sediment at St. Lawrence, Canada and concluded that metal pollution is much higher in the 1960's and 1970's than they are now. While studying mobilization of Cu, Pb, Zn, and Cd at different redox- and pH- condition on contaminated sediment from Hamburg Harbour, it was observed that Cd and Zn are strongly released at lower pH (result of oxidation) as compared to Cu and Pb (Calmano et al. 1994). The surface properties of sorption of trace metals as suspended sediment matter from Ebro River delta, Spain was investigated (Garnier 1993). Metal distribution in differing size fractions were studied in the Mahanadi River, India by Chakrapani and Subramanian (1993). Heavy metals in sediments of the Baltic bay were observed to decrease after installation of a tertiary waste water treatment plant (Blonquist 1992). Smectite containing soil displayed strong pH and ionic strength dependencies during Cd exchange experiments. Relations between heavy metals and varying sediment particle size were discussed while evaluating pollution of torrential rivers of Basque country, Spain (Ruiz and Romero 1992). The role of sediment fractions in the accumulation of ^{137}Cs, Pb, Zn and Cu in the Bombay harbour bay was studied by Pillai et al.(1987).

The exchangeability of Cd was studied on a bulk bottom laccustrine sediment from Caminada bay, Louisiana, containing 50% clay-sized material (poorly crystallized smectite, illite, kaolinite and chlorite), 8% organic debris, and the remainder being quartz, using different exchange solution like N $NaNO_3$, N NaOAc, N NH_4OAc, and 2N $CaCl_2$ and found to replace Cd as arranged in an increasing order. They observed that sodium nitrate has produced better results in exchangeability as compared to other solutions, especially when a sparesely solute solid complex such as octavite (cadmium carbonate) is involved. Octavite is easily soluble in acetate solutions which lead to improper quantification of Cd content. Chloride solution produces complex hydroxyl chloride salt, which has also made the Cd values obtained too high (Farell and Price 1978).

Maran (1995) tried mathematical models of heavy metal and non metal fluxes at the sediment water interface developed from benthic chamber experiments and successfully applied to Ba, Co, Fe, Pb, Mn, and Cu. Fu and Allen (1992) developed a model that predicts cadmium adsorption of oxic sediment for pH 4.5-7.0. Another model described the chemical process of cobalt adsorption onto Gulf coast sediment (Hansen 1992). Isotopic lead sedimentation was studied using a revised model and their lower mixing coefficients and total deposition values were derived (Joshi 1992). Heijin et al. (1995) tried to correlate the pore-water velocity influence on zinc sorption by a clay-bearing sand.

7.3. Anthropogenic influence

A baseline study of metal deposition in Cardiff Bay, U.K. was found to be due to heavy anthropogenic influence (Hitchcock and Thomas 1992). But the studies in the River Goksu and Tosuku Delta, Turkey found that metal depositions in the delta depends on geological factors rather than anthropogenic inputs to the river (Sanin 1992). William (1992) was also of this opinion, as his desorption study in Loch Ba, Scotland, showed strong influence of subsurface redox rather than anthropogenic influences. A large coastal segment of Guipuzcoa, Spain, also was studied to determine the extent of anthropogenic pollutions (Legorburu and Canton 1992). A similar study of the Italian coast revealed metal concentration higher in harbours with heavy shipping activities compared to less industrious harbours (Giordano 1992). A large area near the large industrial harbour of Hellshire, Jamaica, was sampled to determine if a local reef was being affected (Greenway and Rankine Jones 1992).

A multi elemental analysis of about 20 elements was conducted in total sediment and clay size fractions collected from Lake Superior and the harbour of Duluth, Minnesotta, and Superior, Wisconsin, to evaluate trace element concentration in these sediments thereby assessing anthropogenic inputs of these elements (Helmke et al. 1977).

7.4. Oxides

Kooner (1995) calibrated a triple layer model for adsorption of Cu, Pb, and Zn onto geothite as a function of pH, dissolved metal concentration, surface area and ionic strength. Boron sorption by hydrous Al-oxide indicated two mechanism of adsorption (1) physical sorption of boric acid, and (2) chemisorption by borate, both onto the oxide surface. The reaction was found to obey Langmuir type equation at pH values below 7.2 (boric acid was the only species in solution) with maximum sorption at pH 8.5 (Debussetti et al. 1995). The effect of EDTA addition on Ni sorption by hydrous ferric oxide (HFO) was discussed in the light of evidence that the complexing agent can dissolve the HFO surface (Nowack and Sigg 1995).

Papelis et al. (1995) tried to model the rate of Cd and Se sorption on micro and mesoporous alumina using a diffusion model, assuming solute diffusion in a sphere from limited volume, and suggested Cd and Se sorption takes place through intra particle mass transfer. A modified two stage rate model was used to analyze experimental data gathered from the sorption of Cd and Zn onto aluminium oxide surfaces (Lo and Leckie 1993). Another model developed by Palm (1994) simulated Cd transport influenced by non-linear isotherm. The effect of component hydroxide and oxide interaction on Cd^{2+} and SO_4^{2-} adsorption to $Al(OH)_3$ / SiO_2 was modeled using triple layer models (Meng and Letterman 1993a.). Changes in surface potential caused by the formation of $Al(OH)_3$ on SiO_2 enhanced Cd^{2+} adsorption compared to individual surfaces. In another study, aqueous solution of mixed oxide solid phases $Al(OH)_3$ / SbO_2 and $Fe(OH)_3$ / SiO_2 were used to study the effect of interaction between hydroxide and silica on the uptake of Cd^{2+} and Ca^{2+} from solution. Here also enhanced sorption of Cd^{2+} and Ca^{2+} occurred on SiO_2 surface partially covered by $Al(OH)_3$ compared with sorption on either component surface (Meng and Letterman 1993b.).

Ainsworth (1994) tried the sorption experiments of divalent metal ions on ferric oxide as a function of oxide ageing and residence time and concluded that Cu and Cd were incorporated into the oxide structure via recrystallization. But Pb was seen to remain in the surface. The removal of Cu from waste water using iron oxide-coated sand filter was studied by both batch and column method and was found to be rapid (Lai et al. 1994).

The effect of "solids concentration" in adsorption studies was reviewed and experimentally verified by McKinley and Genne (1991). Adsorption of cadmium by iron oxyhydroxides was experimentally quantified at pH 7.00 at equilibrium cadmium concentration and suspended iron oxyhydroxide concentrations and concluded that the reported "solid concentration" effect, excluding those which are admittedly caused by experimental artifacts, are due to inappropriate experimental design or errors of data interpretation.

Cadmium sorption onto iron oxides in the presence of Ca, Mg, Sr, and Ba as competing ions was studied by Cowan (1991). In the binary-element sorption experiments, Cd-Ca proved competitive and increased with Ca concentration which was suggested to occur via. mass action on mutually accessible surface sites. Adsorption of Cd, Zn, Cu and Pb onto amorphous iron-oxide was measured as a function of pH, metal ion concentration and adsorbent concentration by Benjamin and Leckie (1981). Their results suggests that in no case, the adsorption density attain a maximum limiting value and the absorbing surface is composed of many groups of binding sites, where the strength of binding between a metal and the site varies from one site to the another. At small adsorption densities, all types of sites were available in excess, describing Langmuir isotherm, however at higher adsorption densities, the availability of stronger adsorption sites diminishes. Sorption of Cu^{2+} and Pb^{2+} on amorphous hydrous ferric oxide was also studied by Swallow et al. (1980), analyzing the effect of ageing of solids, ionic strength and electrolite concentration, and found unaffected by ageing of the solid over several days, by variation in ionic strength from 0.005 to 0.5, or by changing background electrolyte from $NaClO_4$ to a complex artificial sea water mix. (Pb^{2+} sorption slightly decreased because of the complexation by Cl^- at high concentration). Effect of Fe^{2+} and Cu^{2+} competition in an oxygen-free system with large excess of Fe^{2+}, leads to quantify the total adsorption sites by accounting one site per Fe atom. But Cu^{2+} and Pb^{2+} ions precipitated as corresponding metal hydroxide, even before the saturation of the surface of the surface with either metals.

X-ray absorption fine structure spectroscopy was used to examine the local structure of chromium sorbed onto silica and the influence of surface and reaction conditions on chromium sorption was explored by using several molecular level experiments (Fendrof and Sparks 1994 a&b).

Cadmium uptake by calcite (pure calcite crystals cleaved from pre-cleaned Iceland spar) from aqueous solution containing various concentrations of Cd^{2+}, CO_3^{2-}, ClO_4^- and / or Cl^- was studied using techniques sensitive to the near-surface : X-ray photo electron spectroscopy (XPS), low-energy electron diffusion (LEED), and Auger electron spectroscopy (AES). The study suggests that solid-state diffusion may play a role in the rate and extent of uptake of certain trace metals from solution and probably leads to the formation of solid-solution in calcite and other carbonate minerals. They also suggest that the process of solid-state diffusion has to be given due consideration on hydrogeochemical models that intend to simulate and predict trace metal mobility in carbonate terrains (Stipp et al. 1992).

Water-rock interaction experiments involving laterites and soil clays and solutions containing Pb and Ni ions indicate that iron hydroxides/oxides present in the laterite provides excellent sites for positively charged heavy metal ions in aqueous systems (Chandrasekharam and Ushakumari 1987). Humic acids found associated with laterite induces a charge reversal on their surface, thereby contributing to the adsorption property. Presence of anions (such as PO_4^{3-}) are also known to enhance the metal adsorption capacity by providing more sites with negative charge. Maximum metal adsorption was observed between pH 4.8 to 5.0 and the metal ions adsorbed can easily be recovered.

*7.5. **Role of clay minerals***

A general review with 20 references on the utilization of natural minerals (zeolites, bentonites, diatomite, kaolinite, perlite, magnetite, etc.) for removal of various kinds of suspended and dissolved pollutants from water which suggests that the minerals can be introduced at various stages of water purification, such as coagulation, floatation, sedimentation, adsorption, mechanical filtration, ion exchange, etc. (Lin and Spevakova 1994). Ramahasay (1987) compared clay minerals for pollution control and observed that clayey soils could act as barriers against dispersion of toxic metals, detergents, and dyes. An excellent review with 380 references covering the structure of clay minerals, interactions at the clay surface and their colloidal stability was discussed by Swartzen-Allen and Matijevic (1974)

Ticknor (1994) studied the effects of [Ca], [Mg], and pH while monitoring Ni sorption (59Ni) from solutions onto various geological materials such as granite, biotite, K-feldspar, quartz, hematite, and kaolinite. In general, sorption was greatest on hematite and least on quartz regardless of solution composition. Increased [Ca] and [Mg] and lower pH generally resulted in lower Ni sorption. Ni was found to sorbed by a combination of ion exchange and surface complexation, depending on the nature of the sorbing solid. Taylor (1994) included kaolinite with plagioclase feldspar, small amounts of mica, serpentine, and optional magnetite to produce a catalytic material capable of reducing pollution in combustion gases generated from an internal combustion engine (Taylor 1994). Mn-Ca exchange equilibria was evaluated for kaolinite and illite clays as a function of pH where Mn selectivity by illite clay mineral was much greater than that by kaolinite (Wang 1993).

Chabazite, vermiculite, montmorillonite, hectorite, and kaolinite were used to remove Pb, through ion - exchange from 0.01M aq. $Pb(NO_3)_2$ solutions. These minerals contained 27 (Na-chabazite), 16, 9, 9, and 0.4 wt% of Pb, respectively after equilibration with the solutions. Ion exchange reached equilibrium within 24 hrs. for Na-chabazite and vermiculate but in < 5 min. for montmorillonite and hectorite. Ca impurities present on the clay mineral precipitated Pb as cerussite ($PbCO_3$) (Liang and Sherriff 1993). According to them, all the clay minerals have a similar inter layer site which is available for cation exchange, at least by lead. Moreover lead ions could replace most of the Na^+ in one single exchange experiment. Lead and cadmium exchange onto clinoptilolite has been studied under different grain size and temperature conditions. Size of the zeolite does not affect the actual metal uptake toward equilibrium point, but is greatly affected at short contact times. At higher temperature both Cd and Pb shows better exchangeability and higher size fractions shows a preference to Pb. Kinetic studies displayed a selectivity for Pb ions compared to Cd (Maliou et al. 1992). Zamzow and Murphy (1992) analyzed twenty four zeolite samples by X-ray diffraction and inductively coupled plasma analysis for the uptake of metal cations like Cd, Cu and Zn. Phillipsite proved to be most efficient while mordenite had the lowest uptakes. Sodium was the most effective exchangeable ion for exchange of heavy metals. Clinoptilolite was tried to treat multi-ion waste water collected from an abandoned copper mine in Nevada and found that Fe^{3+}, Cu^{2+} and Zn^{2+} could be removed to below drinking water standards while Mn^{2+} and Ni^{2+} were not. Calcium and NH_4^+ interfered with the uptake of heavy metals. Moreover the adsorbed metal ions could be eluted using 3% NaCl solution upto thirty fold relative to waste solution. Anions were not being adsorbed by zeolites.

Singhal and Gupta (1978) studied the effect of pH time and temperature on the interaction of zinc with acid and base saturated dickite. They found that adsorption process increased with pH, and more rapidly during the initial period of interaction.

The metal adsorption sites of natural (untreated) kaolinite, montmorillonite and synthetic mordenite were elucidated by comparing the pH values of their adsorption edges with those of Si and Al oxides (Schulthess and Huang 1990). They are of the opinion that cation adsorption by these clays is strongly inflenced by the Si/Al ratio, steric effects of inter layers or channels, Lewis acid strength of the metal and the pH of the medium. Using nickel they observed an additive adsorption behaviour on kaolinite by the Si and Al oxide surfaces with well defined boundaries. Modernite showed adsorption edges at low pH values assigning stable nickel ions inside the channels. Montmorillonite displayed an additional adsorption edge at low pH values, attributed to its interlayer structure. They further went on to suggest that Al sites having stronger affinity than Si sites for Ni adsorption on kaolinites.

The effect of exchange kinetic methodology on adsorption rate coefficient (*Ka*) and activation energy (*Ea*) were investigated on Ca-saturated kaolinite, a Chester soil and vermiculite by K-adsorption (Ogwada and Sparks 1986a). The *Ka* values were highest for kaolinite and chester soil showed an intermediate property of kaolinite and vermiculite. Among different methods tried, equilibrium was attained during K-adsorption, in the order: static > miscible displacement > batch > stirred > vortex batch. They concluded that in colloids, where more significant intraparticle diffusion occurs, the batch or stirring technique employed was ineffective in eliminating the influence of diffusion. They further went on to study the rate limiting steps for K^+ adsorption on the clay minerals and soils. For kaolinite and Chester soil, film diffusion was the rate limiting step whereas for vermiculite, both film diffusion and intraparticle diffusion determines the rate limiting step (Ogwada and Sparks 1986b).

Identification of a new inorganic sorbent material (HSORB), which is a combination of ferrihydrite along with akermanite (a crystalline silicate phase) in close proximity was reported to sorb metal ions (Cd, Ni, Pb, Cu, and Zn) by Gao et al. (1995). The simultaneous presence of akermanite and ferrihydrite in a single particle had a synergistic effect on the sorption process: while akermanite helps neutralize aqueous phase hydrogen ions by producing hydroxyl ions through incongruent hydrolysis reaction (thus enhancing sorption capacity of ferrihydrites), neighbouring sorption sites in ferrihydrites quickly removed dissolved heavy metals, thus avoiding precipitation. MacKinnon (1994) developed a low cost kaolinite amorphous derivative having a porous lattice structure which they claim to have extraordinary affinity for heavy metal waste.

The use of kaolinite clay (Gim clay, Nigeria) as an adsorbent for the removal of lead from water as a function of contact time, concentration, temperature and pH was investigated by Orumwense (1996). The results show that lead removal is favoured by low concentration, high temperature and acidic pH. An attempt to assess the toxic pollutants in an Urban storm water, their sources and treatability was done by Pitt et al. (1995). Adsorption studies of Zn from zinc acetate solution on kaolinite clay were made under varying conditions of time and pH (Khattak et al. 1995). Increase in pH was found to have a significant positive effect with the isotherm data obeying Langmuir and Freundlich equations. Equilibrium was also found to be established within two hours with 50 ppm solution.

Saiers and Hornberger (1996) studied the role of colloidal kaolinite in the transport of cesium through laboratory sand columns. Two types of intercalation complexes were identified by Lapides et al.. (1995) during their intercalation studies on kaolinites by CsF. First complex seem to be an hydrated CsF intercalation complex whereas the other a water intercalation complex, probably containing H_3O and F^-.

Kaolinite was used to control Pb aerosol formed from a surrogate Pb-containing waste of a 17 kW laboratory downflow combuster and found that commercial kaolinite could sorb 99% of the metal (Scotto, et al., 1992). When Co^{2+} (60Co), Zn^{2+} (65Zn), and Ba^{2+} (133Ba) was sorbed on alumina, kaolinite and magnetite, two stages of kinetics were displayed, with slower process dominating. Highest sorption was observed for alumina and the system was found to obey both Freundlich and Dubinin-Radushkevich type isotherm (Erten and Gokmenoglu 1994). The effectiveness to remove airbone lead and cadmium was examined by inorganic aluminosilicate sorbents (alumina and kaolinite) from a simulated waste incinerator was studied by Chun and Hall (1994). Complexation by dissolved organic matter was observed to play a key role in metal transport during sorption experiments of Cd, Pb, and Cu from a landfill leachate-contaminated ground water to kaolinite (Holm and Zhu 1994).

The sorption of Cd and Pb from an incinerator fly-ash sample onto kaolinite and illite and the effect of chloride complexation was looked into by Roy et al. (1993). At pH 5-9, chloride complexation reduced the sorption. At pH 6.85, dissolution of Cl and Ca essentially eliminated Cd sorption because of complexation and cationic competition. At extremely alkaline condition (pH 12) Cd was essentially insoluble and lead, precipitated as anionic lead hydroxide.

O'Day et al. (1994), gives an excellent reference to the exchange sites in kaolinite giving emphasis to the sorption of Co using X-ray absorption spectroscopy. Zhou and Gunter (1992), tried to evaluate the nature of surface changes on kaolinite and observed that ionization of edges alone cannot explain the magnitude of the changes in the CEC and net surface proton charge density as basal surface must also contribute to these changes. According to them, the charges on the basal surface will be always negative but the magnitude is pH dependent.

Singh and Mattigod (1992) tried to model Boron adsorption on kaolinite using both phenomenological equations and surface complexation reactions. Data on three kaolinites show that cesium was preferentially sorbed by kaolinites in NaCl and $CaCl_2$ solutions. While desorption studies shows that 0 - 0.5% was strongly held to kaolinite and correlated well with the nature of impurities (Komameni 1978).

McBride (1978), tried to study the factors influencing adsorption by giving various treatments on the kaolinite surface and adsorbing Cu^{2+} on kaolinites. Cu^{2+} shows better preference for Na^+ exchanged form of kaolinite but natural kaolinite showed weak affinity. Adsorption of Cu^{2+} by kaolinite is generally accompanied by proton release to solution, due to Cu^{2+}- H_3O^+ exchange at low concentration and hydrolysis of Cu^{2+} at higher Cu^{2+} concentration. In an earlier study, they investigated the origin and position of exchange sites on kaolinite using electron spin resonance spectroscopy (McBride 1976) It was observed that divalent metal ions are 11-12 Å apart on kaolinite surfaces and that planar $Cu(H_2O)_4^{2+}$ ions are oriented parallel to the surfaces. The evidence seem to eliminate edge sites as being active in cation exchange, at least in the acidic range of pH and leads to suggests that most exchange sites on kaolinites arise from ionic substitutions or mineral impurities.

Ferris and Jepson (1975), critically examined the concepts of cation and anion exchange capacity of kaolinites and concluded that contrary to classical ideas, new data show no evidence for any definite cation exchange capacity. The cation uptake depends upon the cation chosen, the electrolyte concentration, solution pH, and solvent used. Their data do not support the simple model of isomorphous substitution / basic/ edge sites rather suggest complex ion exchange reactions on heterogeneous -SiOH and -AlOH sites.

Bolland et al. (1976) reported that positive surface charges of kaolinite, which is thought to be due to exposed alumina, was found to increase with decreasing pH or sometimes with increasing ionic strength. They also observed that aluminium was found to dissolve out from kaolinite at pH values below about 6.5 and found to dissolve with decreasing pH and time. When Na^+ is the index cation, these aluminium could replace some of these Na^+ balancing the negative surface charge. They further conclude that the pH independent negative and net negative surface charge is due to the isomorphous substitution, together with some pH dependent charge due to exposed SiOH sites. The exchangeable form of aluminium on kaolinite was investigated by Smith and Emerson (1976), and found the isomorphous replacement charge to be 8.4 meq. /100 g.

Dillard and Koppelman (1982) used X-ray Photoelectron Spectroscopic (XPS) studies of cobalt on kaolinite surface and provided experimental evidence that the chemical nature of the cobalt-clay interaction changes with pH. They identified satellite intensity and energy separation from main photo peak which is related to the extent of covalent bonding in the metal compound and their results suggest Co(II) to be more covalently bound to the clay at lower pH (pH 5) than at higher pH values.

ESR and IR evidence of chromium in two natural kaolinites(Gey and Milo, formed in a hydrothermal environment in Sonoma County, California) was presented by Mosser, et al., (1993). EDX analysis shows richer Cr distribution in Gey than Milo where ESR spectroscopics indicate that Cr^{3+} is present in the octahedral positions of both these samples.

Bishop et al. (1994) studied the nature of adsorbed water in montmorillonite by infrared spectroscopic studies and found variable moisture environment associated with exchanged metal ions (H, Na, Ca, Mg, and Fe^{3+}). Absorption near 3620 cm^{-1} and 3550 cm^{-1} was assigned to water band directly to cations (inner sphere) and surface water, while bands at 3450 cm^{-1} and 3350 cm^{-1} are assigned to physisorbed water molecules. Strong dependence of the adsorption and desorption processes on the ionic strength of Pb at pH > 7 on montmorollonite was observed by Ulrich and Degueldre (1993) whereas, at higher pH values, this dependence totally disappears. They also found that the adsorption of Pb is highly reversible.

The alkali cation selectivity and surface charges of 2:1 clay minerals were studied using a hard and soft acid and base (HSAB) model by Xu and Harsh (1992) and quantitatively predicted their alkali cation selectivity from the net tetrahedral and octahedral charge of the minerals and the absolute electronegativity, and softness of the exchangeable cation. Adsorption of Co^{2+} and Cd^{2+} on Wyoming montmorillonite was studied by batch equilibration technique as a function of salt concentration, pH, adsorbate concentration and presence of complexing ions. He found that adsorbability of Cd was much lower from chloride solutions than nitrate solutions. In noncomplexing medium the adsorbability of Cd and Co increases with pH and the distribution coefficient of Cd and Co decrease with increasing salt concentration whereas it decreases with increasing loading of the clay (Egozy 1980).

Chemical interaction of trace metals with ligands and surfaces and competition among metals of natural waters at a pH range of 6.2 - 8.0 are examined by chemical modeling (Vececta and Morgan 1978). Investigations include the response of a body of oxic fresh water containing major cations (Ca, Mg, K, Na), nine trace metals (Cu, Pb, Cd, Co, Ni, Zn, Hg, Mg, Fe), eight inorganic ligands (CO_3, SO_4, Cl, F, Br, NH_3, PO_4, OH) and an adsorbent surface with the characteristics of SiO_2 (s). Pb(II) tends to exist as free metal ions below pH 7.1 and as Pb-CO_3 above this range. Cd precipitated as $CdCO_3$ (s) above pH 6.9 and Hg remained mainly as chloro complexes (below pH 7.1) or as hydroxo complexes (above pH 7.1).

Boron adsorption behaviour on the clay minerals kaolinite, montmorillonite and illite was investigated by Goldberg and Glaubig (1986). It was assumed that boron adsorbs by means of a ligand exchange mechanism with aluminol groups at the edges of the clay particles and a constant capacitance model could describe boron adsorption onto kaolinites over the entire pH range studied (i.e. pH 3-12). Silicon release to solution increased in the order: kaolinite << illite < montmorillonite showing a minimum at pH 8-9. By adding silicate, boron exchange onto kaolinite got slightly lowered whereas it remained unaffected on montmorillonite.

The effect of changes in pH and the presence of ligands on the uptake of copper ions by kaolinite, illite, and montmorillonite was investigated by Farrah and Pickering (1976). According to them, the clay suspension (both kaolinite and illite) acts as a nucleation center for the hydroxy-bridged copper species [general formula $Cu_n(OH)_{2n-2}(H_2O)_4$] considered to be formed as the pH is increased above 6. But the presence of ligands is to 'mask' this precipitation reaction. Here the adsorption process appears to be the formation of the polymeric hydroxy species attached to particular sites on clay whereas in montmorillonite ion-exchange process dominates with all positively charged solution species competing for the available sites. They went on to suggest that uncharged and negatively charged complex species are not adsorbed to any measurable extent by kaolin. Finally, the adsorptive capacity of the clay for cations increases with pH upto a limiting value of about pH 7.

McBride and Mortland (1974), observed that the properties of Cu (II) on montmorillonite surfaces are dependent largely on its strongly held ligand water, and the ion behaves much like other divalent ions on clays. The solvation property of calcined clay varied with ethanol than with water. Dehydration of exchangeable Cu(II) allows these ions to become embedded in hexagonal cavities of the silicate structure or penetrate into the empty octahedral positions and lower layer charge. Resolvation allows these metal ions to move out from the hexagonal cavities but not from octahedral layers.

Swahney (1964), studied the sorption and fixation of microquantities of Cs by six minerals and found that montmorillonite and kaolinite sorbed more Cs in the presence of K and similar monovalent elements than in the presence of Ca and similar divalent elements but micas and vermiculate preferred the presence of Ca. While micas and vermiculate fixed large proportion of the Cs sorbed, montmorillonite and kaolinite did not. Cs sorption of clays were found to be electrostatic while in micas, they are governed by the size and hydration, rather than valence of the competing cation. Micas particularly exhibited a large fixation of Cs.

Koppelman and Dillard (1977) examined the mode of bonding of Cu(II) and Ni(II) ions to the clay minerals (kaolinite, chlorite, and illite) and suggested that Ni (II) is probably bound as the aquo ion while Cu (II) may be adsorbed as $Cu(OH)^+$. The adsorption of Cu and Co from aqueous solution onto illite and other substrates was studied as a function of pH, solution composition and solid phase composition and the results were interpreted in terms of a model whereby the trace metals are absorbed in exchange for surface bound H^+ ions. Cu^{2+} was found to be two orders of magnitude more reactive towards solid surfaces than Co^{2+} and also found that Mg^{2+} interferes with adsorption by competing with trace metals for surface sites. According to them at constant pH, there will always be a tendency toward desorption as salinity increases. Hence the corresponding pH gradient has to be given importance in a river mouth while evaluating the fate of heavy metals as they are carried across salinity gradients (O'Conor and Kester 1975).

7.6. Structural studies

Infrared study of influence of temperature as clay minerals (kaolinite in particular) to identify the thermal transformation occurring between 30 - 1000°C (Ramaswamy and Kamalakannan 1995).

Trapped holes located on Al–O–Al bands in kaolinite were studied by electron paramagnetic resonance spectroscopy (EPR) at 9.3 and 35 GHz and concluded that the hole is probably trapped on oxygen center atom flanked by two octahedral aluminium (Clozel et al. 1995). While reviewing the crystal chemistry of kaolinite and Fe - Mn oxides using spectroscopic [X - ray absorption (XAS) and Electron paramagnetic resonance (EPR)] methods, Muller et al. (1995) deduced that the defect centers and paramagnetic impurities are effective fingerprints of kaolin origin. i.e. the presence of Mn^{2+} outersphere and vanadyl innersphere complexes provide clues to their formation from laterites and sediments respectively.

A good account on the publication on the DTA of montmorillonites starting with the first experiments of Le Chatelier and ranging up to present was made in the review by Fajnor and Jesenak(1996).

Activation method was tried on a natural clay containing 51% kaolinite, 46% montmorillonite and 3% illite, and having a specific surface area of 65 m^2/g, to improve its Ni sorption capacity from waste waters. Natural clays was treated with different activators e.g. HCl, NaCl, and H_2O_2 but HCl treatment did not bring in any significant improvement in adsorption relative to untreated clay while NaCl and H_2O_2 displayed 16.0% and 23.2% greater efficiency. A comparison with activated carbon displayed 216.9%, 204.2%, and 176.1% more exchangeability for H_2O_2 activated, NaCl activated and natural clay, respectively (Hawash et al. 1992).

Wieland and Stumm (1992) studied the dissolution kinetics of kaolinite in acid solutions and interpreted the process in terms of surface complexation model. Their three site model incorporating solid-solution equilibria at aluminol groups of the edge and gibbsite surfaces and at negatively charged XO groups of the siloxane surface describes the protonation of kaolinite platelets in acidic solutions. According to them the dissolution of kaolinite is nonstoichiometric in the pH range 2-6.5 with a preferential release of silicon. This is due to the readsorption of aluminium on distinct surface sites, after detatchment from the lattice structure, occurring simultaneously during the dissolution process causing experimental nonstoichiometry. Stoichiometry of the dissolution is however achieved in the presence of oxalate and salicylate as Al-complexing ligands (as they can form surface complexes only with Al centers) thereby promoting the release of both Al and Si centers during the dissolution process. The proton-promoted dissolution of kaolinite occurs at the edge surface (pH <6.5) and the gibbsite surface (pH<4).

Xie and Walther (1992) also observed a similar (as observed by Wieland and Stumm) dissolution behaviour for kaolinites with Al dissolution rates greater than Si at pH <4 and Si dissolution rate greater than Al at 4<pH<11. An analysis of the surface site density by potentiometric titration indicates that the surface area of kaolinite and other clay minerals available for surface complexation and sites for cation detachment are sufficiently larger than those measured by standard gas adsorption models (using Kr), attributing this to the penetration of H^+ and OH^- between the layers of sheet silicates.

The constant dissolution rates, *Kr*, of kaolinite was determined at 25°, 60° and 80°C, are dependent on solution pH and temperature. For all three temperatures, *Kr* decreases from acid to near neutral pH and increases from near neutral to alkaline pH (Carroll and Walther 1990). They identified three consecutive periods of dissolution for kaolinite at 25°C and 60°C: an initial period of incongruent dissolution where Al is preferentially removed over Si at pH <6.0 and pH >9.3 at 25°C and at pH <4.5 and pH >12.0 at 60°C and the reverse occurs between pH 6.0 and 9.3 at 25°C and between pH 4.5 and 12.0 at 60°C. Their dissolution studies on corundum at 25°C showed a decreased rate with increasing pH upto pH 8.0 and increased thereafter. They also accounted that kaolinite dissolution is a complex function of H^+ and OH^- ion adsorption to >AlOH and >SiOH surface reaction sites (Carroll-Webb and Walther 1988).

Predictive equations for a system containing three heterovalent cations (Ca^{2+}, Mg^{2+} and Na^{+}), as compared to the commonly used two cation system, are derived using solid phase activity coefficients and thermodynamic equilibrium constants for the three binary systems obtained from experimental data (Wiedenfeld 1978). Interaction between two cations as they affect the exchange behaviour of a third cation are also predicted. The applicability of this method to systems containing any number of heterovalent cations is claimed.

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CHAPTER 2

METALS IN THE FLUVIAL ENVIRONMENT

The Kerala region is a geologically important narrow strip of land bound by the Western ghats on the east and the Arabian sea on the west, and constitutes a part of the Indian craton. Geologically the study area forms a part of the Precambrian shield. Rao (1976) recognizes five major phases of tectonogenesis of which the fifth phase is related to the development of the western coast of India during Cretaceous- Eocene times. The upper Cretaceous faulting separated the SW part of the Indian subcontinent from Madagascar, deriving a coastline running parallel to the escarpments of the Western ghats (Nair, 1988).

1. GEOLOGY

The rock types found in the region can be grouped into (i) the Precambrian crystallines (ii) the Tertiaries and (iii) Quaternary and Recent to subrecent sediments (Soman, 1980; Raha et al., 1983). The eastern part of the area under study is occupied by Precambrian rocks with patches of Tertiaries overlying them. Both the Tertiaries and Crystallines have been extensively lateritised enabling them to be considered as yet another rock type in the region. To the west of this lies the coastal plain occupied by Quaternary and Recent sediments.

1.1 Precambrian:

The Crystallines (Precambrian) have been intensively lateritised / kaolinised and fresh outcrops are restricted mostly to quarries and wall sections. They comprise chiefly Charnockites, Khondalites, granitic gneiss, Dharwar schist's and granites traversed by pegmatite's and basic dykes (Resource Atlas of Kerala, 1984).

The Charnockites are characterized by the presence of rhombic pyroxene-hypersthene. The charnockites with narrow bands of pyroxene granulite, magnetite-quartzite and calc granulite form the most widespread group in the state. Many of the hornblende and biotite gneiss are considered to be the retrograded equivalents of charnockites.

The Khondalite group include a group of light coloured, fine to medium grained, foliated / granulitic rocks comprising garnet-sillimenite gniess with or without graphite, garnet-biotite gniess, garnet-quartzofeldspathic gneiss or granulite and quartzite. These are the predominant rock types of south Kerala. Lenticular bands of crystalline limestone associated with calc-granulite are also seen in these rocks. A narrow zone of cordierite gneiss is seen around Konni, Thiruvalla and Kottayam.

The quartz-mica schist, quartz-schist, fuchsite quartzite and tremolite-chlorite-talc schist forms the narrow belt of Dharwar schist's (covering parts of Kasargode, Kannur and Wayanad districts). Later studies in Karnataka necessitated the sub-division of Precambrian group into (i) Sargurs - which represents the lower (older) members of the Dharwar (Viswanatha and Ramakrishnan, 1976) and (ii) Dharwars - represents the younger members of the same.

There are numerous dolerite and gabbro dykes traversing the crystallines. Bodies of granites, granophyres, syenites, anorthosites and pyroxenites were also recorded.

1.2 Tertiaries

The Tertiary formation which lies unconformably above the Precambrians extents as a narrow belt along a major part of the Kerala coast. Their landward extension contains essentially Neogene and Quaternary sediments comprising a series of variegated sandstones and clays with lenticular lignitic seams (Warkalai formation) which are underlain by more compact sand, clays and thin beds of limestones (Quilon formation) (Paulose and Narayanaswami, 1968).

But the recent classification considers Warkalai as a group which contains Quilon formation overlain by Ambalapuzha formation (Warkalai formation) and underlained by Mayyanad formation (Vaikom formation). Warkallai group lies above the weathered crystalline rocks which are inturn overlained by Quaternary Vembanad formation (Raha, et al., 1983). A recent lithostratigraphic classification of the Cenozoic sedimentary sequence of Kerala coastal region is given in Table 2-1.

1.3 Quaternary and Recent formations

The coastal plain, to the west of the lateritic highland comprises white sand, brown sand, white silica sand, silty clays and black silty clays of Quaternary and Recent age. Among these, the white and brown sands occupy major part of the coastal area and occur as alternate zones intervening mud flats and marshes which are almost parallel to the present coastline and varies in width from 0.5 to 3.5 kms extending upto 20 kms length. White sand comprises mainly of white coloured quartz which are mostly sub-rounded to sub-angular varying in size from 0.125 to 0.500 mm. Brown sands contain quartz as the dominant mineral together with some amount of mafic minerals, mostly ilmenite and magnetite. They are mostly sub-rounded to sub-angular varying in size from 0.1 to 0.5 mm. Recent shell fragments are generally seen in this

MALABAR SUPER GROUP		Vembanad formation	Soil and alluvium Beach and dune sands, lime-shell deposits, older red 'Teri' sands, marine and estuarine deposits, sands, peat and black steaky and sandy calcareous clays Gravel beds with laterite gravels at places
		Unconformity (marked by laterite)	
	Warkalai group	Ambalapuzha formation	Pebbly and coarse sand with peat and variegated and mottled clay Grey sand and white plastic steaky clay and lignite Alternation of sand and steaky grey and carbonaceous clay often with lignite beds, with coarse pebbly sand near the base
		Quilon formation	Limestone with bands of calcareous clay and sand in various proportions, grey fossiliferous and calcareous clay near the base
		Mayyanad formation	Coarse to medium grained sandstones with interbedded grey and white clay and lignite beds. Facies grades laterally to sandy clay alternations with lignitic bands towards the central part of the basin.
		Unconformity	
		Basement	(Gneiss, Charnockites, Leptynites, etc.)

Table 2-1. Lithostratigraphic classification of the Cenozoic sedimentary sequence of Kerala coastal region (after Raha et al., 1983).

sand. At places, there are raised sand beaches, composed of fine grained reddish sandy loam known as '*teris*' which are of aeolin origin. Mud banks, locally known as '*chakaras*', which are high sediment load suspension in water, occuring in patches along the Kerala coast, are also considered recent deposits. Black sticky clay is seen below the white sand zones at places which appears to have been deposited in the local depression.

The quaternary formation is separated from the Tertiary rocks by a polymict pebble bed comprising predominantly of quartz and quartzite pebbles and cobbles and is seen almost throughout Kerala

2. GEOMORPHOLOGY

Kerala has a coastline of about 560 km in length extending from Manjeshwaram in the north to Poovar in the south, being 14 km in length per 100 sq.km of land territory. The drainage pattern of the region is in conformity with the physiographic divisions, with the summit of the Western ghats forming the watershed between the drainage systems of the west coast and that of the Tamilnadu plains. There are 41 west flowing rivers in the Kerala region, the majority of which are drained by sixth order master streams.

Physiographically the Kerala region is referred into four longitudinal zones, viz. the highlands, the midlands, the lowlands and the coastal plains. The hilly region of the highlands form the catchment area of these rivers and the midland and lowland act as the transfer zones. One of the characteristic features of the rivers in the Kerala region is their almost straight courses in the high lands and midlands. Two major knick points were observed for these rivers; one at an elevation of 500 - 800 m corresponding to the boundary between the highlands and the midlands and another at an elevation of 90 - 150 m indicating the boundary between the midlands and the lowlands. These factors suggests that the drainage pattern is controlled to a great extent by the tectonic forces (Sinha and Mathai, 1979). The drainage is generally of dendritic type but in some cases a trellis pattern is observed to have superimposed with the dendritic type.

Though straight over a greater part of the length, Kerala coast is a highly broken one with varied and contrastic features like sand bars, creeks, lagoons, estuaries, raised beaches and cliff sections which could mostly be due to the earth movements along and across the coast in the geologic past and the erosional and depositional activities that have taken place in the Quaternary to the Recent times (Jacob, 1976).

The backwater lagoons, generally running parallel to the coast are locally known as '*kayals*', vary in width from a few hundred meters to more than 10 kms. The actual extent of *kayals* might have been greater than at present and the gradual siltation of these backwater tracts gave rise to agricultural encroachment and left the present structure as the remnants of once greater lagoons that have not yet been silted up.

Kayals are generally described as a body of brackish, marine or hypersaline water, impounded by a sandy barrier and having an inlet connecting with the open ocean. Numerous perennial rivers debouch into the *kayal* and with the influence of tidal currents and monsoonal variations, they act as the exchange sites of fluvial debris to the ocean.

The river Periyar, the second largest in Kerala (244 km) gets divided into two channels to the north of Aluva (10°7'N, 76°21'E). The major distributary viz. the northern one, takes a meandering course of about 14 km until receiving Chalakudi river from the north. Even before the main bifurcation, distributary-like channels of significant proportions are seen branching off from the main river, at least at two points, and meandering to the right as that by the main river. These in turn receive minor streams from the north and finally join back the northern branch. Down from the first point of branching off at Vadakkumbhagom, the main channel of Periyar is in a braided form having disproprotionately large braids (*thuruths*) which are thickly populated and are developed lands. The Chalakudi river flows from the north through a meandering course to the right (unlike R. Periyar having a meandering to the left) and joins Periyar to the south of Puthenvelikkara. The lower reaches of the Chalakkudi river is also braided and receives numerous minor streams flowing in from the north. The southern channel of Periyar takes a westward course and join the backwaters having a general meandering to the right. The mouth portion of the Periyar river is wide and straight for a distance of about 5 km from Kottapuram to Munambam. The Tottapalli river, a tidal channel extending from the backwaters in the south, joins Periyar to the west of Chennamangalam. However at the debouching point, the river mouth is narrowed down by a sizable sand spit extending from the northern bank. Starting from Aluva, the whole of the stable lands within the immediate basin of Periyar, particularly those lying between the two main branches of the river have been designed to its present stage suggesting deltaic occurrence. Generally, there has always been the coupling action of marine and fluvial processes in carving the morphology of this portion.

2.1 The Cochin estuarine system

The Cochin estuarine system receives industrial effluents from various large scale and small scale industries located in the region. Toxic heavy metals form the major group of pollutants that reach the ocean through rivers. These potentially hazardous and non essential metals are biologically non-degradable and tend to accumulate in marine organisms and ultimately reccur in the food chain. Since clays are charged particles, they can contribute to ion-exchange and adsorption properties resulting in the uptake of these toxic elements (Sposito, 1989). Knowledge about the rate of uptake of these hazardous pollutants by clay particles present in the aquatic systems is necessary for any critical evaluation of pollution by toxic heavy metals. Thus knowledge of the clay minerals present in the region would give a clearer picture as to how effectively they can trap the pollutants from water and prevent defericative of the marine environment.

Clay minerals represent an important group in the particulate matter and since clays are charged particles, they can contribute their sorption properties resulting in the uptake of these toxic elements (Sposito, 1989). Information regarding the rate of uptake of these hazardous pollutants by the clay particles present in the aquatic system is vital for any critical assessment. Rivers and estuaries serve as indicators for pollution. The amount of pollutants that reach the estuary, once they are discharged into the hydrosphere, depends on the quantity and quality of the particulate matter present in the region.

A thorough knowledge of the clay minerals present in the region will give a clearer picture of how effectively these sediments can trap these pollutants from the river water before they are finally discharged into the oceans. It is known for the past several years that some of the rivers of Kerala, viz. Chaliar, Periyar, Chitrapuzha, Kallada, etc. Have polluted the estuarine flora and fauna. This chapter tries to characterize the clay minerals present in the fluvial sediments of the Periyar River basin and the rate at which these heavy metal pollutants are being sorbed onto them.

3. EXPERIMENTAL

3.1 Sampling

Sampling of sediments was done at seven different locations along the Periyar river course, starting from a meander zone at Cheranalloor-Chowara region and

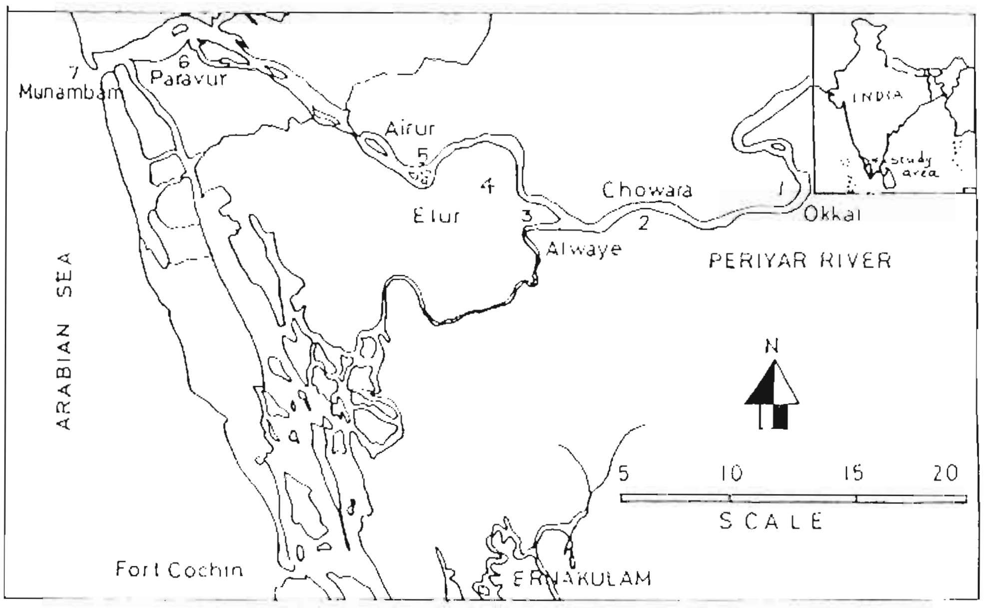

Fig.2-1 Location map of the Periyar river (1-7 indicate the sampling points).

extending down to Munambam ferry region, the former representing a comparatively non-polluted area and the others of progressively increasing pollution. About 250 g of the sample was collected from each point using a Van -Veen grab sampler, dried at room temperature and mixed thoroughly. The sediment samples are mostly iron-stained silty sand and coarse sand in the higher reaches. The lower reaches contain good amount of organic matter. Sub-sampling was done by coning and quartering. The fraction <45 µm, separated by wet -sieving was used for further investigations.

3.2 Preparation of sample

3.2.1 Removal of organic impurities:

Each 1g sample of clay was treated with 10 ml of 30% H_2O_2, slightly warmed for 1 hour, centrifuged, washed and dried at 60°C.

3.2.2 Removal of iron oxides:

External ferruginous impurities were removed using sodium dithionite [$Na_2S_2O_4$] solution, buffered at neutral pH with sodium bicarbonate [$NaHCO_3$] and sodium citrate is added as a complexing agent to assist in keeping the iron in solution (Subramanyam and Mohanachandran, 1990).

3.3 Instrumentation

3.3.1 X-ray diffraction studies

X-ray diffraction is undoubtedly the most widely used technique for identification and characterization of clay minerals. As a reference work, Brindley and Brown (1980) published a monumental work in the most complete form as a monograph incorporating every detail on X-ray diffraction information on clay minerals. Later, Moore and Reynolds (1989) also presented an excellent review on the identification of clay minerals using X-ray diffraction technique and the analysis of the obtained data.

Clay minerals are composed of tiny crystals made up of ordered array of atoms which are arranged in a periodic and repetitive pattern. When an incident X-ray beam falls upon such an array, general scattering occurs, where these scattered waves interfere and destroy one another. But in certain specific directions, however, scattered waves are in phase with one another and combine to form new wave-fronts. This constructive interference is known as diffraction whose direction depends upon the size and shape of the unit cell of the crystal, whereas the intensity of diffraction is governed by the atomic organization or the nature of the crystal structure.

This phenomenon can more conveniently be visualized as a reflection of incident beam by parallel, closely spaced planes of atoms within a crystal and can be well described using Bragg's equation:

$$n\lambda = 2d\sin\theta$$

where n is an integer which indicates the order of reflection, λ is the wave length of X-rays, θ is the glancing angle of incidence and d is the interplanar spacing of the crystal.

Copper radiation is used almost universally and is also used for this study because it will give higher radiation intensity. Inorder to obtain a low-background and high quality pattern, monochromated radiation was used by introducing a nickel foil (0.017mm thick) into the primary beam (between the source and sample), which can effectively filter the shorter wavelength $K\beta$ radiation and allows the longer wavelength $K\alpha$ radiation to pass through. The clay samples for this study were usually scanned through an angle of 3 to 60° 2θ, at the rate of 2° 2θ/min. Ni filtered Cu $K\alpha$ radiation was used at 40 KV and 20 mA on a Rigaku X-ray diffractometer.

3.3.1.1 Sample preparation

(*a*) Oriented mounts - A thick slurry of clay sample was made using water and pipetted onto a microscopic glass slide and allowed to air dry at room temperature or oven dried at 50°C. For quantitative analysis, the dry clay powder was stuffed into a specially designed glass slide having a groove of standard dimension (1.5 x 1.5 x 0.2 cm) which will enable us to compare equal quantity of different samples.

(*b*) Randomly oriented preparation - Dried sample was allowed to fall freely from a sieve into a sample holder smeared with vacuum grease. This will definitely reduce preferred orientation but does not eliminate it. Drying an acetone-clay suspension onto a glass slide was also tried which yields the same result.

(*c*) Glycolation - A drop of ethylene glycol was mixed thoroughly with a finely dispersed clay suspension and the resultant slurry was allowed to air-dry on a glass plate. This technique was extensively used to confirm the presence of smectite group of clay minerals, wherein the organic molecules are entrapped within their basal cleavages, thereby altering their characteristic basal spacing.

(*d*) Heating experiments - Minerals like kaolinite which normally has crystalline peaks in the X-ray patterns gets converted to an amorphous metakaolin on heat treatment at 500-600°C for one hour. The X-ray pattern of this metakaolin lacks characteristic kaolinite peaks in their spectra which enables us to confirm their availability in a mixture containing both kaolinite and chlorite, where peaks due to chlorite persists.

(*e*) Acid treatment - The sample is treated with 6N HCl at 90°C for 30 min., and washed free of chloride ions using distilled water. This method is used as a confirmatory test for chlorite (and serpentine) in the sample. Nearly all the commonly encountered chlorites (and serpentines) can be easily decomposed by HCl. It is usually difficult to separate the 001 kaolinite and 002 chlorite reflections on the X-ray diffractogram at ~7.1Å. But the second order reflection of kaolinite at ~3.57Å and the fourth order of chlorite form a distinct, easily separable double peak system, but unfortunately this observation does not hold for all kaolinite / chlorite mixtures.

3.3.2 Scanning electron microscopy.

Scanning electron microscope (SEM) is considered indispensible for the study of clay mineral configuration, fabric, texture and growth mechanisms. A portion of the sample devoid of organic matter and iron mineral coating are made into a thin solution using distilled water and allowed to air dry atop a brass-stud at room temperature, followed by oven drying at 50°C, overnight. The brass-studs are highly polished for better background image. For non-conducting specimens like clay samples, the surface is sputter coated with a very thin layer of gold (using gold - palladium alloy) which will not alter the surface morphology and conduct away the excess charge build up. The clay samples for this study was done using JEOL scanning electron microscope with an accelerating voltage of 15 KV.

3.3.3 Thermal analysis.

Thermal analysis involves a group of techniques in which the physical property of a substance and/or its reaction products is measured as function of temperature by subjecting the substance to precisely controlled temperature program.

3.3.3.1 Differential Thermal Analysis (DTA)

The physical parameter measured in DTA is ΔT, the difference in temperature between the sample and a reference material (Alumina) while both are simultaneously subjected to controlled temperature. The difference in temperature ΔT is plotted on the ordinate with endothermic peak pointing downwards while time required or temperature of the sample will be plotted on the abcissa.

3.3.3.2 Thermogravimetric analysis (TG)

The change in mass with an increase in temperature is the parameter measured in TG. Weight loss encountered in the sample is plotted against time or temperature of the specimen. The differentiation of the obtained data gives the derivative thermogravimetric (DTG) curve.

In order to elucidate fully the thermal behavior of the clay mineral, both DTA and TGA are performed simultaneously in a single run, using SEIKO TG/DTA 320 simultaneous analyzer at the rate of 10°C min^{-1} in air (N_2 was used whenever an inert atmosphere was required). The temperature is attained using a resistively heated electric furnace in which the output from the temperature sensor (Platinum / Platinum - Rhodium (13%) thermocouple placed at the base of platinum crucibles) inside the furnace is compared with a ramp signal corresponding to the predetermined temperature program (null point method). The μv output from the differential thermocouple pair is plotted against temperature during DTA measurements. For TG analysis, where the measured parameter is the mass of the sample, the change in mass with temperature is sensed by an electrobalance assembly with the sample pans held horizontally at the tip of ceramic beams which encloses the thermocouple. A slight change in mass is readjusted by applying a counter force (null method) and this restoring force is monitored and recorded.

Oven-dried clay samples were finely disaggregated by light dry-grinding in an agate mortar inorder to achieve a similar particle distribution with that of the reference material so as to enhance base line performance. In some soil clays, organic matter is attached to the crystal structure and can undergo oxidative decomposition between 200-500°C. This can result in large exothermic peaks which can obscure the intrinsically weaker endothermic peaks and hence has to be removed earlier using 20% H_2O_2.

3.3.4. Surface area analysis

The specific surface area of the fluvial sediment samples are measured using Micromeritics GEMINI 2360 surface area analyzer using extra pure nitrogen as the adsorbate gas. This instrument uses the flowing gas technique in which the nitrogen flows into a sample tube containing sediment sample and a reference (balance) tube, simultaneously; both the tubes have same internal volume and are maintained at identical temperature conditions. Nitrogen gas was introduced into both tubes simultaneously, which are maintained at isothermal conditions by immersing in a liquid nitrogen bath, and the pressure imbalance produced between the sample and the reference tube, caused due to the adsorption of nitrogen onto the sample, is measured. Free space correction was made using helium in order to avoid any slight differences between the two tubes.

3.4 Chemical analysis

Classical chemical analysis forms the oldest and most established determinative methods used to study clay minerals. A full chemical analysis gives the composition in terms of elements and is generally expressed as oxides on a percentage basis. There are a variety of methods whereby this information is obtained. The procedure involves dissolving the sample by fusing in sodium carbonate or sodium hydroxide or heating with HF and H_2SO_4 and estimating the elements gravimetrically. A more rapid procedure has been developed by Shapiro and Brannock (1952, 1975). In this work, classical scheme of analysis reported by Bennet and Reed (1971) was followed.

3.4.1 *Loss on ignition.*

Loss on ignition of the sample was determined by slowly heating 1 g of the sample in a platinum crucible to 1025 ± 25°C in a muffle furnace. Normally 60 min. ignition was sufficient and the loss in weight corresponds to the ignition loss of the material.

3.4.2 *Estimation of silica*

0.5 g of the predried and cooled clay sample was fused with about 2 g of 1:1 mixture of Na_2CO_3 and K_2CO_3. The melt after cooling was extracted with 1:1 HCl to which a few drops of H_2SO_4 was added. The silicic acid precipitated was dehydrated initially on a water bath followed by heating at 110±10°C for 4-5 hrs. The residue was digested with hot dilute HCl and this hot slurry is filtered through Whatman No. 40 filter-paper. The residue is then washed with hot dilute HCl followed by hot distilled water, until the filtrate is chloride free. Filter-paper along with the residue was heated in a pre-weighed platinum crucible at about 1000°C till it weighed constant. The residue corresponds to the silica content. As a double check, the residue was heated with HF and a few drops of conc. H_2SO_4 and evaporated to dryness. After heating at 1000°C, the remaining weight of the crucible with residue was found out. The difference in weights gives the silica content of the sample.

Clay on fusion with Na_2CO_3 and K_2CO_3 gets converted to sodium and potassium salts as silicates and aluminates and are water soluble. On acid addition, the silicates precipitate as silicic acid and is evaporated and baked to get silica. HF treatment volatalises silica as hydrofluorosilicic acid leaving behind impurities and the change in weight represents the amount of silica.

3.4.3 *Solution preparation for the estimation of Al_2O_3, Fe_2O_3 and TiO_2.*

0.5 g of clay sample was weighed accurately in a platinum dish. 1 ml of 1:1 H_2SO_4 and 20 ml of 48% HF are added and is evaporated to dryness on a sand bath followed by addition of another 20 ml HF and reheating the contents to dryness. This dried residue was heated with potassium pyrosulphate; the melt after cooling, was extracted with 3% H_2SO_4 and the solution made up to 250 ml.

Here, clay during HF treatment in the presence of H_2SO_4, removes entire silica from the sample and the residue on fusion with potassium pyrosulphate, become water soluble. Extraction with 3% H_2SO_4 makes the resultant solution slightly acidic (pH ~ 4).

3.4.4 Estimation of alumina (Volumetric method).

20 ml of the sample solution was pipetted into a conical flask together with 25 ml of EDTA and a drop of methyl orange indicator. Dropwise addition of NH_4OH will change the colour of the solution from red to yellow. 10 ml of pH 5.3 buffer was added and heated to boiling for 5 min. Followed by titration with 0.02 N zinc acetate using xylenol orange indicator; the end point is marked by a colour change from yellow to orange. 1 g of sodium fluoride was added and boiled the solution for 5 min., cooled and buffered to pH 5.3, followed by titration with 0.02 M zinc acetate (A).

$$\% \text{ of alumina} = \left(\frac{A \times x \times 100}{W} - 0.6378T \right)$$

where, x = equivalent Al_2O_3 in g/ml of zinc acetate solution; W = the weight of the sample in 20 ml of the stock solution and T = percent titania in the sample.

To the sample solution containing aluminium, a known excess of EDTA was added and heated after adjusting the pH to 5.3. Aluminium forms stable complex with EDTA; the excess free EDTA was titrated with zinc. This solution was then heated with sodium fluoride to liberate Al from the Al-EDTA complex producing AlF_3. The EDTA thus liberated was titrated with zinc solution, which corresponds to the amount of aluminium in the sample

3.4.5 Estimation of iron (Colourimetric method).

An aliquot of the sample solution was pipetted out into a standard flask, followed by 1-2 drops of p-nitrophenol indicator and 10 ml of 10% tartaric acid. Drop wise addition of 1:3 NH_4OH changes the colour of the solution to yellow, which disappears on acidification with dilute HCl. 2 ml of 10% hydroxylamine hydrochloride solution was added, followed by 10 ml of 0.1% 1,10 phenanthroline solution. The characteristic colour will develop in 5 min. The contents are then mixed and made up to 100 ml and the absorbance was measured at 510 nm. A calibration curve was prepared using standard iron (i.e. 0.2, 0.4, ... , 1.0 ppm) solution and the unknown concentration of the sample solution was matched with this calibration curve.

Hydroxyl ammonium chloride added to the sample solution will convert all of the iron present in the solution to a ferrous state. Ferrous iron (Fe^{2+}) forms an orangish red complex with 1,10 phenanthroline, the intensity of which was measured at 510 nm (visible range).

3.4.6 Estimation of TiO_2.

10 ml aliquot of the sample solution was pipetted into a 100 ml standard flask, 10 ml of 6% H_2O_2 was added and made up to 100 ml. Optical density was measured at 410 nm against a reference solution. Calibration curve was also prepared using 0, 1, 2, ... , 10 ppm of standard Ti solution. In acidic medium (H_2SO_4), titanium forms an yellow complex with H_2O_2.

3.4.7 Estimation of Na_2O and K_2O.

0.1 g of the sample was digested with HF and a few drops of conc. $HClO_4$ over a sand bath to remove silica. The residue was dissolved in 5 ml of 1:1 HCl (metals are converted to their chloride forms) and made upto 100 ml. The amount of sodium and potassium present in the sample solution was measured using flame photometer by comparing it with solutions of known concentration.

When chlorides of Na and K are introduced into a flame, the valence electrons of the elements are exited on absorption of energy, which is released on deexitation. This is related to the amount of Na and K present in the system.

3.5 Cation exchange capacity (CEC)

0.2 g of the sediment sample was weighed into a centrifuge tube and is shaken with about 1 *N* NH_4OAc solution (pH 7) and left overnight. After centrifuging, clear leacheate was decanted and a drop of very dilute HCl was added and the slurry was washed with 90% alcohol until the leachate is free of chloride ions. This washed residue was transferred quantitatively into a distilling flask connected to a distilling condenser and diluted to ~100 ml. 0.5 g of MgO (AR) powder was added and heated. About 10 ml of saturated boric acid solution was mixed with a few drops of mixed indicator (Bromocresol green / methyl red) and the tip of the condenser tube was immersed into the boric acid solution, so that the evolved gas was collected and absorbed into it indicated by a colour change from pink to blue. This distillate was titrated against standard HCl (standardized using Na_2CO_3) and the end point was indicated by a colour change from green to pink.

4. RESULTS AND DISCUSSION

Texturally the river sediments are coarse grained, silty sand and varying towards downstream to fine grained clayey silt in the reaches (Table 2.2). This lowering of the grain size in the sediments is attained due to the energy condition in the gradient of the river. Moreover, grain size proves to be an important controlling factor in the distribution of heavy metals in the sediments. The major clay minerals identified in the region was kaolinite together with small amounts of illite and chlorite (Fig. 2-2).

Sample location	Sand (%)	Silt (%)	Clay (%)	Texture	Kaolinite + Chlorite (%)	Illite (%)	Smectite (%)
Okkal	55	33	12	silty sand	85	13	2
Chowara	62	24	14	silty sand	82	16	2
Aluva	46	29	25	silty sand	83	14	3
Elur	43	33	24	silty sand	79	17	4
Airur	45	37	18	silty sand	81	16	3
Paravur	23	52	24	clayey silt	73	17	10
Munambam	38	41	20	silty sand	77	16	7

Table 2-2 Particle size distribution and clay size percentages of Periyar river sediments.

Smectite is also observed in traces. Among the non-clay minerals, quartz is an ubiquitous mineral in the region followed by feldspars, amphiboles and gibbsite. The minerals are highly covered by organic matter, especially those in the lower reaches where stagnant conditions prevail and are found associated with organic debris. Iron-oxide coating in the minerals explains their traverse through laterite terrain. Hence removal of such coatings had to be employed to get better XRD and SEM details. The X-ray diffractogram shows a dominant peak at 3.35 Å followed by 4.27 Å and 2.46 Å confirming the presence of quartz. The peaks at 3.26, 3.20 and 2.99 Å represents feldspar in the sample. The reflection at 8.5 Å is due to amphibole. Another peak at 4.87 Å depicts the presence of gibbsite and is later confirmed by thermal studies as well (Fig.2-3). On acid treatment, partial destruction of structure lowered the gibbsite peak intensity (Fig. 2-2.B). The peaks at 7.20 and 3.58 Å are of

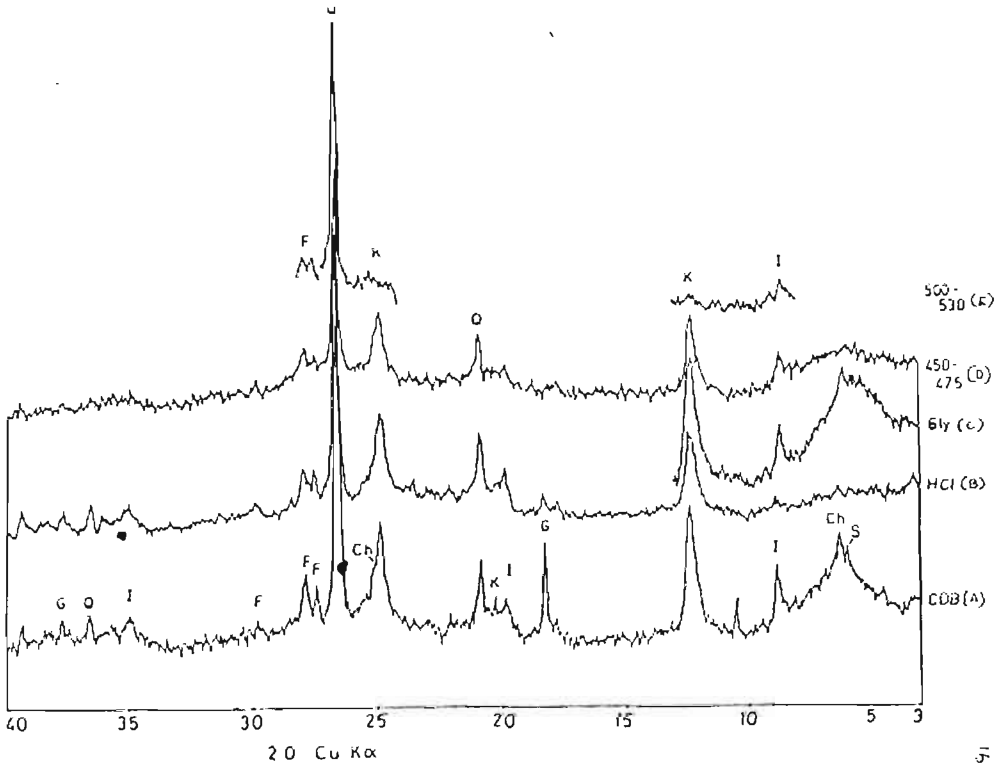

Fig. 2-2 X-ray diffraction pattern of a representative sample.
(Ch - chloride; F - feldspar; G - gibbsite; I - illite; K - kaolinite; Q - quartz; S - smectite)

kaolinite (001) and (002) planes respectively. The presence of mineral chlorite with their (002) and (004) reflections at 7.00 Å and 3.54 Å in the sample will complicate their identification in presence of kaolinite (Biscaye, 1964). Another refection at 14.23 Å represents the basal reflection of chlorite and suggests its presence. Here the doublet at 3.50 Å is very helpful which identifies chlorite with its (004) reflection at 3.58 Å as a shoulder peak at the fast scan conditions. The presence of chlorite is further confirmed by acid treatment which decomposes the same thereby evicting the representative peak from the XRD pattern (Fig.2-2.B) (Wilson, 1987; Biscaye, 1964). On heating the sample at 450-475°C, the basal reflection of chlorite at 14 Å is expected to remain unaffected but a low intensity broad peak persisted (Fig. 2-2.D). This leads us to believe that chlorite was present interstratified with smectites in the sample, which upon heat treatment, loses their interlayer water giving rise to a collapsed structure (Wilson, 1987). The presence of smectite is also indicated in the XRD pattern with a small peak at 14.98 Å, adjoining that of chlorite (Fig. 2-2.A). The shifting of this peak to 15.78 Å during glycolation, which is an intermediate position between chlorite (14.23 Å) and fully expanded smectite (16.90 Å) suggests the possibility of a randomly interstratified chlorite-smectite (Fig. 2-2.C; Wilson, 1987). On calcining the sample at 450-475°C, a broad peak in the region (~14.5 Å) observed can be due to the collapsed structure of chlorite interstratified with smectite. The presence of illite is confirmed by the persistence of the characteristic peak at 10.14 Å, even at 530°C (Fig. 2-2.E). But their absence in the acid treated sample suggests the leaching out of Na and K ions during the process and affecting their structure.

A semiquantitative treatment was carried out on the clay minerals in the sample by measuring the relative peak areas of these minerals above the background response using the X-ray diffractogram of the iron-oxide removed and glycolated sample (Table 2-2). This was under the assumption that kaolinite, chlorite, illite and smectites together constitute hundred percent of the minerals in the sample. Peak areas of clay minerals were multiplied by a weighing factor 2, 4 and 1 respectively for kaolinite plus chlorite, illite and smectite, as suggested by Biscaye (1964).

An initial weight loss event observed in the thermogravimetric plot (Fig. 2-3) represents the physically sorbed water, due to the highly disordered nature of kaolins, which forms the bulk of the samples (Earnest, 1988). A highly crystalline kaolinite shows very little weight change during this process. XRD patterns also support the highly disordered nature of kaolin mineral in the region. For well crystallized kaolinites, almost all of the physically adsorbed moisture will be removed at ~110°C whereas for poorly crystallized kaolinites, this temperature stretches upto 200°C. This is indicated by an endothermic peak in the region which represents the removal of inter-planar water entrapped between the leaflet parallel to the c-axis (Todor, 1976). DTG shows a peak at ~300°C due to the burning of carbonaceous impurities and organic matter together with thermal dehydration of iron oxyhydroxides and gibbsite. About 9 - 10% of weight loss was observed during this event. A shoulder peak was seen attached to this peak in the DTG patterns at ~320°C in the samples collected from higher reaches of Periyar river and was found shifting to 343°C towards estuary. This peak represents boehmite [AlO(OH)] formation of gibbsite mineral due to the partial

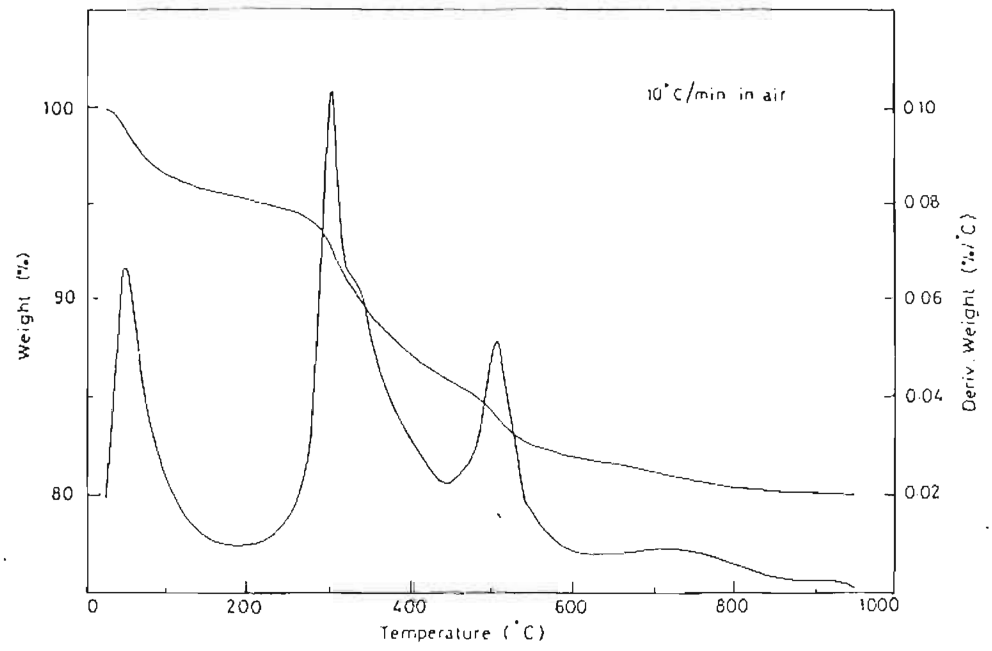

Fig. 2-3 DTA and TG of a representative sediment sample

removal of -OH groups from the $Al(OH)_3$ lattice, which at a later stage, dehydroxylates to form γ-alumina. The following reactions takes place during this process.

$$\underset{\text{gibbsite}}{Al_2O_3.\,3H_2O} \xrightarrow{\sim 250^{\circ}C} \underset{\text{boehmite}}{\gamma\text{-}Al_2O_3.\,H_2O} + 2H_2O$$

$$\gamma\text{-}Al_2O_3.\,H_2O \xrightarrow{\sim 300^{\circ}C} \underset{\text{diffusent gibbsite remaining}}{\gamma\text{-}Al_2O_3\,(aq) + H_2O}$$

$$\gamma\text{-}Al_2O_3.\,(aq) \xrightarrow{450\text{ - }580^{\circ}C} \gamma\text{-}Al_2O_3 + (aq)$$

The shifting in the gibbsite peak from 320 to 343°C can be attributed to the quantity of the mineral present as well as the particle size characteristics of the sample.

The final weight loss event as marked by the DTG peak at ~500°C is due to the dehydroxylation of the minerals present in the sample, recording 16 - 22% of weight loss. For kaolinites, removal of hydroxides takes place from 450 to 700°C (Todor, 1976) where the crystalline kaolinite will get transformed to an amorphous metakaolin resulting in the decrease in the particle size and crystallinity.

$$Al_2O_3\,.2SiO_2\,.2H_2O \xrightarrow{500\text{ - }700^{\circ}C} \underset{\text{metakaolinite}}{Al_2O_3\,.2SiO_2} + 2H_2O$$

$$2(Al_2O_3\,.2SiO_2) \xrightarrow{900\text{ - }1000^{\circ}C} \underset{\text{silicon spinel}}{2Al_2O_3\,.3SiO_2} + SiO_2$$

$$3(Al_2O_3\,.3SiO_2) \xrightarrow{\text{about }1250^{\circ}C} \underset{\text{mullite}}{3Al_2O_3\,.2SiO_2} + \underset{\text{crystobalite}}{SiO_2}$$

But poorly crystalline kaolinites will shed their hydroxyls more easily (Refer Chapter 4) than a well crystallized one. Hence the weight loss at ~500°C can be due to the dehydroxylation of poorly crystallized (well fractionated) kaolin minerals present in the samples. Moreover, the presence of small hexagonal platelets of kaolin mineral together with the filamentous illite particles observed in the scanning electron microscope (Fig. 2-4) explains and confirms their presence in sediment samples.

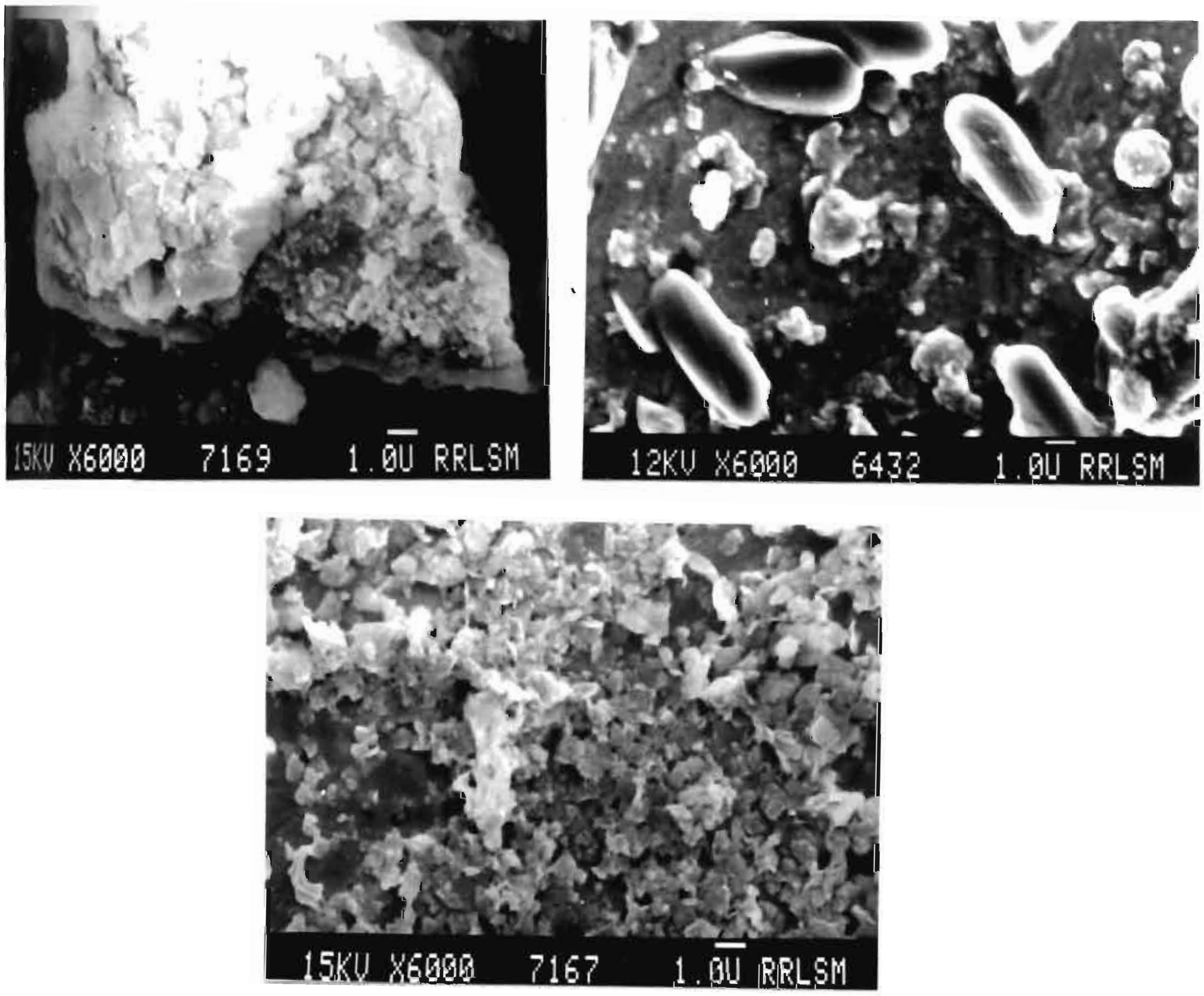

Fig. 2-4. Scanning electron micrographs of a representative sample showing very small amounts of illite and other minerals.

Sample No	Loss on Ignition	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O
1	23.14	42.86	6.98	21.98	0.55	0.42	1.10	0.77	1.52
2	21.17	42.07	10.00	23.06	0.60	0.47	1.01	0.65	1.41
3	19.25	42.13	8.98	25.56	0.75	0.81	1.28	0.63	1.18
4	19.17	43.17	6.93	25.37	0.79	0.82	1.02	0.53	1.19
5	22.04	44.05	7.46	22.92	0.75	0.30	0.96	0.51	1.22
6	19.87	44.52	8.07	20.98	0.74	1.00	2.83	0.41	0.96
7	21.68	42.05	8.04	21.08	0.83	1.09	2.83	0.47	1.20

Table: 2-3a Chemical analysis of the samples for major elements in percentage

Sample No	Mn	Ni	Zn	Cd	Pb	Cu	Co
1	40	15	35	0.1	2.8	8	1.5
2	70	10	70	0.1	4.4	9	0.8
3	25	30	255	4.0	4.0	5	0.3
4	50	10	80	0.1	2.4	11	1.5
5	60	25	135	2.0	2.8	5	0.2
6	25	25	20	0.1	3.2	4	1.0
7	20	-	85	0.1	3.2	31	0.8

Table 2-3b: Chemical analysis of the samples for trace elements (ppm)

The chemical analysis in Table 2-3 shows that the sample is mainly aluminosilicate with good amounts of iron and contains titanium to a certain extent. Considerable amounts of organic matter in the samples accounted for their high loss on ignition. Cation exchange capacity does not vary much among these samples which ranges from 177.6 $mmol_c$ kg^{-1} for sample 4 to 233.8 $mmol_c$ kg^{-1} for sample 3. Surface area also displayed similar trend ranging from 15.25 m^2 g^{-1} for sample 1 to 20.16 m^2 g^{-1} for sample 7 (Table 2-4).

Sample No	Location	CEC mmol$_c$ kg^{-1}	Surface area (m^2 g^{-1})
1	Okkal	186.5	15.25
2	Chowara	189.9	15.90
3	Aluva	233.8	18.16
4	Elur	177.6	14.88
5	Airur	184.9	16.07
6	Paravur	202.7	17.65
7	Munambam	201.8	20.16

Table 2-4 Cation exchange capacity (CEC) and surface area of fluvial clays from different locations

4.1 Origin of clay minerals.

A large area of the drainage basin of the Periyar river passes through laterite and red soil terrains, which are formed due to the weathering of basement rocks under tropical climatic conditions. The charnockites, khondalites and gneissic rocks which constitute the basement rocks of the drainage system, contain high proportion of iron and magnesium which are favorable for the formation of clay minerals (Russell, 1962; Harder, 1977). According to Harder (1977), amorphous hydroxides of iron, aluminium and other elements in the parent rock from laterite terrain can adsorb with it silica in a very under saturated concentration thereby enriching in the precipitates, which upon diagenesis, can produce clay minerals. Morey et al. (1964), observed that the solubility of silica from the parent rocks of laterite profiles (feldspars and ferromagnesian minerals) was much higher (~140 ppm) than that from quartz (~ 6 ppm). Harder (1977) suggests an optimum concentration of 10-60 ppm SiO_2 in the pore water as favorable for the formation of clay minerals. But later, Garrels and Christ (1965) considered an equilibrium concentration between 1.5 and 3 ppm in soil water could produce kaolinite, gibbsite and halloysite in a partly altered feldspar grain. This condition can easily be attained on a tropical environment where the pH condition required for the formation of clay minerals could easily be achieved by the precipitation and percolation of ground water. The dominance of kaolinite in the region can be due to the acidic conditions prevailing in the soils aided by the presence of organic compounds in higher amounts (Harder, 1977; Huang et al., 1970).

Kaolin is believed to have derived from three principal sources : (1) The resilication of gibbsite in the higher acidity saprolitic soil away from the rock weathering front (2) the kaolinization of feldspars and (3) the pseudomorphic alteration of biotite (Rebertus, 1986).

Gibbsite is produced as a by-product during kaolinite synthesis and found as a left over in laterite terrains where all of the SiO_2 and Fe_2O_3 have been leached down by percolating water (Carroll, 1970). But kaolin is known mainly to have derived from feldspars. Feldspars are the most abundant constituent in the parent rock and various combinations of secondary alteration minerals have been suggested; for example, K-feldspar to illite-muscovite (Eggleton and Buseck, 1980); to kaolinite and illite (Loughnan, 1969); to smectite (Wilson et al., 1971); to smectite, kaolinite and gibbsite (Tardy et al., 1973; Carroll, 1970); to kaolinite and gibbsite (Anand et al., 1985) and to gibbsite (Lodding, 1972). Plagioclase grains are generally more altered than associated alkali feldspars. Sutter et al. (In Eggleton and Buseck, 1980) concluded that kaolinite originates from feldspar under humid conditions, whereas smectite forms in semi-arid climates; the difference resulting from more complete flushing of K^+ ions under humid weathering. Tsuzuki and Kawabe (1983) suggested that a dissolution-reprecipitaion mechanism may be responsible for the entire sequence from feldspars to kaolinite. Access of solution to the feldspar surface is probably controlled by defects, cleavages, twin-planes and cracks. Dissolution appears to proceed by preferentially attacking at energetically favoured sites, producing solution pits (etch pits) located at dislocations, and on twin planes and cleavages in otherwise unaltered plagioclase (Banfield and Eggleton, 1990). The alteration of feldspars pass through a transitory stage cell-textured protocrystalline material having variable composition and limited crystal order and their existence with clay suggests that the protocrystalline material was a precursor of clay (Banfield and Eggleton, 1990). According to them, the assemblage of clay mineral formed by the alteration of feldspars (and muscovite) include halloysite and platy kaolinite, suggesting a mineralogical pathway involving the replacement of feldspar by protocrystalline material, smectite, and a second protocrystalline material, and halloysite or kaolinite, depending upon the environment of formation. But Anand et al. (1985) observed various mixtures of kaolinite, halloysite and gibbsite from the clay minerals that fills the etch pits on feldspar surface. Here, kaolinite plus halloysite dominates the lower (deeper) profiles but contains gibbsite as well in the shallow profiles. Many attempts have also been made to support the above theory on the basis of phase diagrams for the formation of smectite and kaolinite from plagioclase (Loughnan, 1969). Similar predictions were also made by Garrells (1984) in which muscovite will alter to form illite, smectite and kaolinite.

Thin section studies in amphibolite and charnockites in the region show that muscovite and biotite alters to an aggregate containing kaolin. Stoch and Sikora (1976) give a detailed picture of the transformation of biotite and muscovite present in the granite and gneisses to kaolinite. Even though the transformation of muscovite to kaolinite is a direct process, some authors suggest the formation of an intermediate hydromuscovite which was later identified to be an intergrowth of kaolinite and muscovite, coexisting within the original planes of mica (Stoch and Sikora, 1976). Dioctahedral montmorillonite was also rarely observed as a product of muscovite weathering. The muscovite to kaolinite transition follows the equation

$$\underset{\text{muscovite}}{2KAl_2[Si_3AlO_{10}](OH)_2} + 2H^+ + 3H_2O = \underset{\text{kaolinite}}{1.5Al_4[Si_4O_{10}](OH)_8} + 2K^+$$

(But Rausell-Colom and co-workers (in Banfield and Eggleton, 1990) indicate the removal of K^+ from muscovite as extremely difficult and strongly dependent on the K content of the solution.)

Weathering of biotite to kaolinite can occur through two different steps depending upon the concentration of K^+, H^+, Al^{3+} and Mg^+ ions in the immediate surroundings. (1) The transformation of trioctahedral mica (biotite) to dioctahedral mica (muscovite) followed by kaolinite, will require high Al^{3+} concentration (Konta et al., 1972). Hence this process takes place at a lower part of the weathering profile, close to potash feldspars and (2) a direct conversion of trioctahedral mica to kaolinite due to the low K^+/H^+ ratio. Transformation of trioctahedral to dioctahedral mica involves an exchange of cations of the octahedral layers by aluminium according to the equation

$$\underset{\text{biotite}}{KMg_3[AlSi_3O_{10}](OH)_2} + 2Al^{3+} = \underset{\text{muscovite}}{KAl_2[AlSi_3O_{10}](OH)_2} + 3Mg^{2+}$$

Muscovite thus formed will eventually gets replaced by kaolinite through a transitory stage dominated by smectites (Banfield and Eggleton, 1990).

Illite, another clay mineral in the sediment samples, are also known to have derived as an alteration product of feldspars and mica (Deer et al., 1976; Rao and Raman, 1979; Banfield and Eggleton, 1990; Eggleton and Buseck, 1980).

The presence of non-clay minerals such as quartz and feldspars are due to the recent weathering of the parent rocks. Another non-clay mineral, gibbsite, owes its origin from the plagioclase present in the parent rock (Macías, 1981). He refers to two kinds of origin for gibbsite: the first, a rapid process occurring in the initial weathering of various aluminosilicates, where gibbsite will be one of the first crystalline products of neoformation during plagioclase weathering (Tazaki, 1976). The second mechanism involves a long period of weathering where the kaolinite type phyllosilicates undergoes desilicification (secondary gibbsite) (Clarke and Keller, 1984). Gibbsite may have formed in better-drained region within grains formed due to random cracking where the circulation of water was most rapid. Another theory on the origin of gibbsite was postulated as they are the byproduct of kaolinite synthesis from organic complexes (eg. humic complexes) (Linares and Huertas, 1971; LaIglesia et al., 1978) and is found as a leftover in lateritic terrain where all of the SiO_2 and Fe_2O_3 have been leached down by percolating water (Carroll, 1970). In certain cases, under favorable conditions, resilicification of gibbsite reconverts gibbsite back to kaolinite. The condition responsible for this resilicification process is best achieved around the undulating water table of a laterite terrain.

Eventhough smectite was also expected to be present in the sediment sample as discussed above, only traces of the same could be detected in the samples collected upstream, as compared to the higher concentration of kaolinite (Table 2-2). But a better availability of smectite was recorded on the fluvio-estuarine samples (Paravur, Munambam). This could be due to the fact that smectites are transported in suspension because of their smaller grain size and swelling nature (Gibbs, 1977; Rao et al., 1983).

4.2 Adsorption studies.

All the clay samples were sodium saturated by exchanging overnight in a 1M NaCl solution, maintaining the solid-liquid ratio of 1:50 (Maliou et al., 1992). The supernatant solution was decanted and this process was repeated twice using fresh solutions of NaCl. This sample was then thoroughly washed free of chloride ions using double distilled water, oven-dried at 60°C, gently crushed and stored over saturated NaCl solution on a desiccator.

A 0.2 g of this homoionic sample was equilibrated with 25 ml of 1 mg/ml metal solution (~0.009M $CdCl_2 \cdot 2\frac{1}{2}H_2O$ and ~0.017M $NiSO_4 \cdot 7H_2O$) with varying periods of contact time upto 300 min. 10 ml aliquots of the well mixed slurry was collected at definite intervals and filtered using 0.1μm filter paper. The filtrate was further analyzed for the remaining metal concentration using an ECIL Atomic Absorption Spectrophotometer (AAS), from which the amount of metal ion exchanged was calculated. A bentonite sample procured from Ashapura Mining Company, Gujarat, was also compared, giving prior conversion to homoionic sodium form, under the same experimental conditions as cited above. Bentonite sample was chosen because of its relatively high ion-exchange capacity (Wilson, 1987; Hsia et al., 1992) and have high iron content making it comparable with the iron-stained fluvial sediments in the region.

All the experiments were conducted at room temperature (27±2°C) and maintaining a pH between 5.5 and 6.0 for the system. Also <45μm fraction of the sample, retaining the organic matter was used, so as to simulate natural conditions. The metal ions were selected because of their toxic nature and included in the priority pollutant list by the Environment Protection Agency (Keith and Telliard, 1979).

Eventhough the kaolinite is the dominant mineral in the region, the sediment samples shows higher exchangeability than that expected for a kaolinite mineral which is 10-30 $mmol_c\ kg^{-1}$. Kaolinite posses two types of surface charges; first is a pH dependent negative charge due to the exposed broken edges (silica and alumina bonds) and the second type, a pH independent (permanent) negative charge due to the isomorphous subtitution of Al^{3+} for Si^{4+} (Bolland et al., 1980). Lim et al. (1980) suggests the presence of impurities in small amounts such as 2:1 clay minerals (smectites and illites) which can also contribute to the permanant negative charge. For montmorillonite, most of the substitution takes place in the central alumina sheet where Mg^{2+} is being substituted for Al^{3+} and for micaceous impurities like illite and chlorite, Al^{3+} is isomorphously replaced by Si^{4+} in the silica tetrahedra (Farrah and Pickering, 1976), but some replacement of Al^{3+} for Mg^{2+}, Fe^{2+} and Fe^{3+} are also observed in the octahedral positions. The importance of organic matter (humus)-kaolin complex in the sorption of heavy metal contaminants have also been widely discussed (Huang and Yang, 1995; Dalang et al., 1984). Amorphous iron-oxides and oxyhydroxides are also known to improve the sorption capacity of sediments (Swallow, et al., 1980; Benjamin, 1983; Hsia et al., 1992; Benjamin and Leckie, 1981).

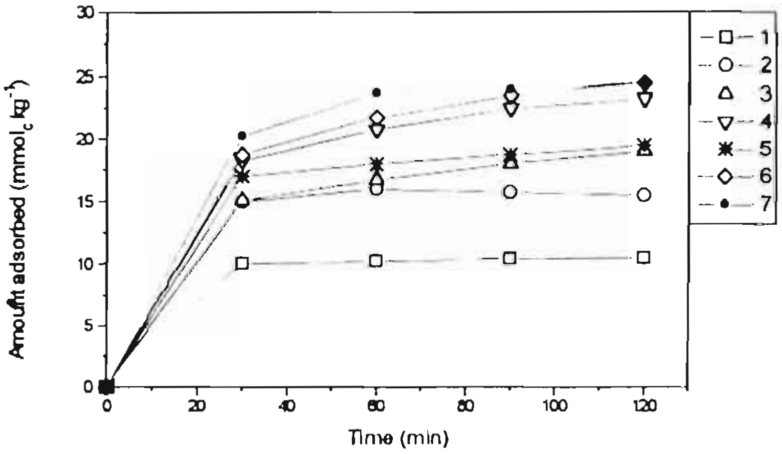

Fig. 2-5 Cd/Na exchange kinetics for fluvial samples

. It is seen from Figs. 2-5 that the samples marked 4, 6 and 7 show higher uptake of Cd as compared to others (ie. 23.0, 24.5 and 28.0 mmol$_c$ kg^{-1}). Similar observations are also made for Ni. (ie. 47.3, 48.5, and 49.0 mmol$_c$ kg^{-1}). At Elur, the samples were collected from a meandering region where stagnant water conditions prevail. The higher clay content in these samples (with comparatively higher smectite concentration) brought in by the stagnant condition can be the reason for the observed high sorption capacity. The differential flocculation caused by the mixing of fresh water and salt water (samples 6 and 7) derive more suspended particles in the region and explains their improved sorption. From the chemical perspective, an estuary is a region where sea-water of high ionic strength (0.6 mol l^{-1}) is diluted by river-water (ionic strength 1-4 x 10^{-3} mol l^{-1}), leading to axial salinity gradients and the formation of fresh water / sea water interface, which is frequently a region of elevated concentrations of suspended particulate matter, which is caused and maintained by tidal energetics (Millward, 1995).

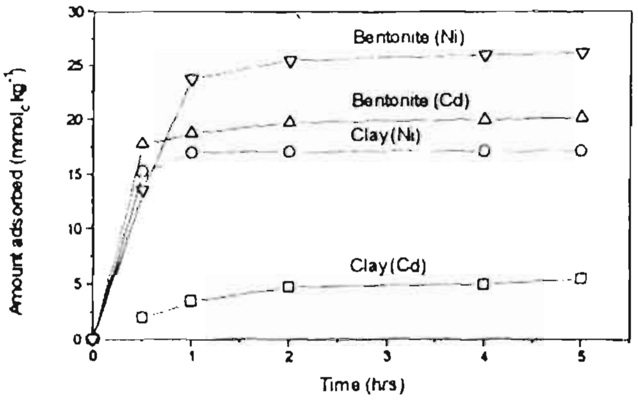

Fig. 2-6 Ni/Na and Cd/Na exchange kinetics of a fluvial sample and a bentonite

Eventhough smectites have higher exchangeability (700-1500 mmole$_c$ kg^{-1}) bentonite sample used for this study could exchange only small amounts of metal ions, may be due to the low concentration of metal solution used and the short duration of contact time (Fig. 2-6). Moreover, kaolinite shows better kinetics compared to smectites, as most of the metal ions are sorbed within the first 30 minutes of contact time. Since sorption of metals into smectite layers involves diffusion into the sheets, the kinetics are fairly slow when compared to that of kaolinite. It was also observed that nickel shows better exchangeability (clay - 17.25 mmol$_c$ kg^{-1}; bentonite - 25.75 mmol$_c$ kg^{-1})as compared to cadmium (clay - 5.00 mmol$_c$ kg^{-1}; bentonite - 20.00 mmol$_c$

kg^{-1}). Cadmium chloride complexes formed in solution are comparatively stable and will adsorb into the clay mineral with difficulty.

5. CONCLUSION

Clayey sediments collected from the Periyar river sediments shows kaolinite as the dominant clay mineral, followed by illite, chlorite and smectite. Other minerals include quartz, feldspar and gibbsite. Cation exchange capacity and surface area did not vary much among the samples. On assessing the metal exchange capacity of these samples revealed selectivity of these clays to nickel than cadmium.

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CHAPTER 3

CHEMICAL MODIFICATION

1. INTRODUCTION

Ion-exchange is one of the important processes which controls the distribution of elements between solution and particulate phases, thus regulating the availability of trace metal pollutants in the hydrosphere. Adsorption by various substances such as hydrous manganese and iron-oxides, apatite, clay and organic matter is an important factor which is responsible for maintaining low concentrations of trace metals in the sea water (Gao et al. 1995; Osman et al. 1995; Rao and Bandyopadhyay 1995; Xu et al. 1994; Suzuki et al. 1994).

Owing to their cation exchange properties, zeolites, ion-exchange resins, activated carbon, etc. could technically solve the pollution problem but are often too expensive to be utilized for the removal of heavy metal's from waste waters (Maliou et al. 1992; Mazidji et al. 1992) Montmorillonite variety of clay mineral is reported to have cation exchange capacity much higher than that of kaolinite (Egozy 1980; Velghe 1977). But the latter is more abundant in the catchment areas and the rivers of Kerala, India.

Although kaolinite exhibits the least exchangeability among clay minerals, several studies have confirmed the potentiality of natural kaolinite for the adsorption of metal ions from solution. Using X-ray spectroscopy, O'day et al. (1994) observed that Co(II) is bound to the kaolinite as Co-complexes (both inner sphere complexes and outer sphere complexes). Boron adsorption on kaolinite was studied by Singh and Mattigod (1992). Cs was preferentially sorbed by kaolinites from NaCl and $CaCl_2$ solutions (Komarneni 1978) of which 0-3.5% was found to be strongly held. McBride (1978) observed the strong preference, for the Na^+ exchanged form of kaolinite over raw kaolinites, for copper ions. Exchange capacity (both cation as well as anion) of kaolinites and their relation with homoionic counterparts with Na^+ was critically examined by Ferris and Jepson (1975). The adsorption of Ni^{2+} and Cu^{2+} onto the clay minerals kaolinite, chlorite and illite, has been investigated by Koppelman and Dillard (1977). They observed that kaolinites adsorb Cu(II) ions to the least, at pH 5. McBride (1976), tried to locate the exchange sites on kaolinite using ESR spectroscopy and suggested that divalent ions are distributed 11 - 12Å apart on kaolinite surfaces, whereas planar $Cu(H_2O)_4^{2+}$ ions are oriented parallel to the surfaces, suggesting that the concept of exchange sites on the edges are invalid, at least in the acidic pH range. At relative humidity between 75 and 100%, these hydrated copper complexes possess solution like mobility on kaolinite surfaces, supporting this theory with conclusions derived from ESR studies of Cu^{2+}-saturated talc and pyrophyllite.

Cd-exchange property of sediment samples are reported in the literature (Gagon et al. 1992; Boal et al. 1989) but those related to the Cd exchange on kaolinites are less numerous. The uptake of trace metals (Pb, Zn, Cu, Cd and Hg) on calcite, kaolinite and bentonite was studied in Krka river water by Bilinski et al. (1991) where Cd is practically not adsorbed at salinity of 38 ppt on kaolinite and bentonite. Petersen et al. (1993) observed that 0.1mmol of FeOOH coated on the kaolinite (1g) can adsorb upto 95% of the added Cd.

MacKinnon (1994) has recently reported that kaolinite amorphous derivative (KAD) absorbs heavy metals and could solve the problems of toxic metal pollution in water. The porous lattice of the collapsed crystalline structure of KAD can absorb a large amount of metallic ions such as Pb, Cd and Cu from waste waters. The present work reports the development of amorphous kaolinite derivatives made by thermal modification, followed by acid activation, which could improve the exchangeability of natural kaolinite.

2. EXPERIMENTAL

Mainly, this chapter concentrates on two natural kaolinitic clays, viz. one from Thonnakkal region of Trivandrum district (south Kerala, India) supplied by M/s. English Indian Clays Limited, Trivandrum, India, which is a well crystallized clay containing >90% kaolinite of which ~87% fall below <2μm size fraction (TK). Another sample is obtained from the Madai region of Kannur district (north Kerala, India) supplied by M/s. Kerala Mineral Exploration and Development Corporation Limited, Trivandrum, India, which contained kaolinite as the major component and mica and quartz as the major impurities (MK). Thus, an evaluation on the exchangeability of a well crystallized and poorly ordered kaolinite samples with Hinkley crystallinity indices of 0.91 and 0.75 respectively will also be made.

Thonnakkal clay was supplied in a purified form and no further processing was carried out before analysis. The Madai clay was washed with distilled water to remove soluble impurities and wet sieved through 350# (45μm) sieve, homogenized and <45μm sample was collected for adsorption studies. The clay samples were divided into three portions. One portion was retained as the raw sample, whereas the other two portions were heated to 350°C and 600°C, respectively, for one hour . Portions of all these samples were then subjected to acid treatment by refluxing with 2 *M* HCl at 80°C for 20 minutes, and washed free of chloride ions using double distilled water. These samples were characterized as follows. The chemical assay of the samples were carried out following the classical wet chemical analysis method (Bennet and Reed, 1971). Samples were subjected for X-ray diffraction studies on a Rigaku Geigerflex X-ray diffractometer using Ni filtered Cu-Kα radiation (40KV 20mA). The samples were made into a thick slurry, transferred onto a glass plate and air-dried at room temperature. Thermogravimetric analysis was done on a simultaneous DTA-TGA analyzer (Sieko TG/DTA 320) at a heating rate of 20°C/in in air. Surface area measurements were carried out on a Micromeritrics Gemini 2360 surface area analyzer using BET equation and N_2 as the adsorbate and at -196°C after degassing at 120°C. Pore-size distribution was obtained by a Carlo Erba Milestone 100 porosimeter using N_2 as the adsorbate. Infra-red spectra was recorded on a Nicolet Impact 400D FT-IR spectrophotometer in the region 4000 - 400 cm^{-1}, using KBr sample pellets on a KBr detector giving 100 scans per analysis.

To convert into a homoionic sodium form, these samples were saturated with sodium ions by shaking overnight in a 1000 mg/l NaCl solution (1 : 5 ratio), repeating the procedure 4-5 times in order to attain the maximum saturation. This process gives effective saturation of sodium ions compared to those using higher concentration of the solution with lesser contact time. These sodium saturated samples were used for adsorption studies.

Heavy metals like Cd, Pb, Cu, Zn and Ni were selected for adsorption studies considering their contribution as toxic metals in the environment. AnalaR grade of $CdCl_2.2\frac{1}{2}H_2O$ (Polskie Odczynniki Chem-Gliwice), $Pb(NO_3)_2$ (Merck), $CuSO_4.5H_2O$ (BDH), $ZnCl_2$ (BDH) and $NiSO_4$ (BDH) were used for the studies. 100ml of 1.5×10^{-4} *M* metal solution was equilibrated with 0.2 g of the clay sample for 20, 40, 60, 120, 180, 240 and 300 minutes of contact time. After centrifugation, the suspended solution was analyzed for the concentration of the metal in solution, using AAS (ECIL, AAS 4127)and the amount adsorbed on the clay mineral was calculated. Another known quantity of the clay sample was equilibrated with 50 ml of 1.5×10^{-4} *M* metal salt solution for 3 hrs. at temperatures of 30°, 40°, 50° and 60°C in a constant temperature water-bath and the amount adsorbed by the clay mineral was calculated as described above. Effect of concentration on the metal uptake was also looked into using metal solutions of equally varying initial concentrations. pH was maintained at 6.0±0.5 through out the experiment.

To study the effect of solution pH on metal uptake, TK alone was used by equilibrating with 5 x 10^{-4} *M* metal solution.

3. RESULTS AND DISCUSSIONS

3.1. Chemical composition

Chemical compositions of both TK and MK were similar (Table 3-1). The elemental distribution was found to vary with calcination temperature for the modified kaolinite samples and their acid treated counterparts (calcined to 600°C - TK/MK 600A). The alumina/silica ratio decreased with calcination temperature. LOI values, eventhough decreased with calcination temperature shows an increasing trend upon acid activation. A small increase in the iron and potassium concentration in MK sample is due to the presence of muscovite mica as the major impurity.

. Sample	SiO_2	Al_2O_3	(Al_2O_3/SiO_2)	Fe_2O_3	TiO_2	Na_2O	K_2O	LOI at 1025±5°C
TK raw	47.05	36.98	0.78	0.34	0.53	0.12	0.08	14.31
TK 350	47.75	36.82	0.77	0.36	0.54	0.13	0.07	14.16
TK 600	55.35	36.85	0.70	0.61	0.70	0.14	0.13	3.45
TK rawA	45 66	38 20	0 84	0.36	0 49	0 09	0 03	1515
TK 350A	46.68	36.90	0.79	0.39	0.25	0.05	0.01	14.60
TK 600A	59.56	22.35	0.37	0.39	0.18	0.08	0.01	17.17
MK raw	46.01	34.27	0.75	1.26	220	0.15	1.45	14.40
MK 350	46.26	34.53	0.75	1.28	2.24	0.16	1.48	14.31
MK 600	54.83	36.10	0.66	1.44	2.23	0.15	1.45	3.21
MK rawA	46.13	35.54	0.77	1.00	2.29	0.01	0.05	14.96
MK 350A	46.06	37.53	0.86	0.92	1.01	0.01	0.05	14.40
MK 600A	60.52	20.20	0.33	1.01	0.96	0.01	0.07	17.20

Table 3-1 : Chemical composition of raw and modified samples (in percentage).

TK - Thonnakkal kaolinite MK - Madai kaolinite Number indicate temperature (°C)
A - acid activated samples.

An increase in the elemental distribution with calcination temperature can be attributed to the weight loss incurred during the process. On heating the sample, due to the escape of organic matter and adsorbed water molecules, an increased elemental concentration is expected on that sample. On comparing the sample with and without acid treatment, for eg. RawA and Raw, an increase in the percentage of alumina and a decrease in all other elements (with slight variations in some elements) were observed and similar trend was displayed by both TK and MK. The decrease in the elemental values is due to their leaching by acid. But the increase in the alumina values can be due to reprecipitation of the leached alumina on the kaolinite structure. Carroll-Webb and Walther (1988) observed a nonstoichiometric dissolution with preferential release of aluminium over silicon at pH < 6. Similar nonstoichiometric dissolution was reported by earlier workers (Chou and Wollast 1984, 1985; Casey et al. 1988). This theory was later supported by Xie and Walther (1992). Sabu et al. 1993, verified the removal of aluminium from TK by 2M HCl. Wieland and Stumm (1992) described the observed nonstoichiometry as due to the adsorption of alumina back into the kaolinite layers. Hence the observed increase in the alumina concentration can be attributed to the secondary precipitation of alumina. An increase in the Al/Si ratio upon acid activation for raw sample (TK/MK raw) and the one heated to 350°C (TK/MK 350) indicates the enrichment of alumina compared to silica in the kaolinite structure, whereas the decrease in the ratio for the metakaolin upon acid activation (as half) indicates that the destruction of layers enable the acid to leach out more alumina than silica.

The acid activated metakaolinite sample showed a high silica concentration but all other elements displayed a decreasing trend. During metakaolinization, the escape of hydroxyl groups from the lattice structure will transform the crystalline kaolinite to an amorphous form. This amorphous metakaolin is more prone to acid attack than the crystalline phase and this explains the observed reduction in the elemental concentration. Silica is also being leached out during this process but not to the same extent. The contribution of physically adsorbed moisture by the amorphous structure describes the observed increased in the LOI value of the metakaolinite sample.

3.2. X-ray diffraction studies:

X-ray diffractograms of the TK raw samples (Fig. 3-1a; raw)and their acid activated counterparts (raw.A) are similar indicating that there are no apparent changes taking place in the clay structure due to acid activation. Similarly, no significant change was observed among the diffractograms of the raw sample and the one calcined to 350°C (raw and 350°C.A). On further calcining the samples to 600°C, all the peaks in the

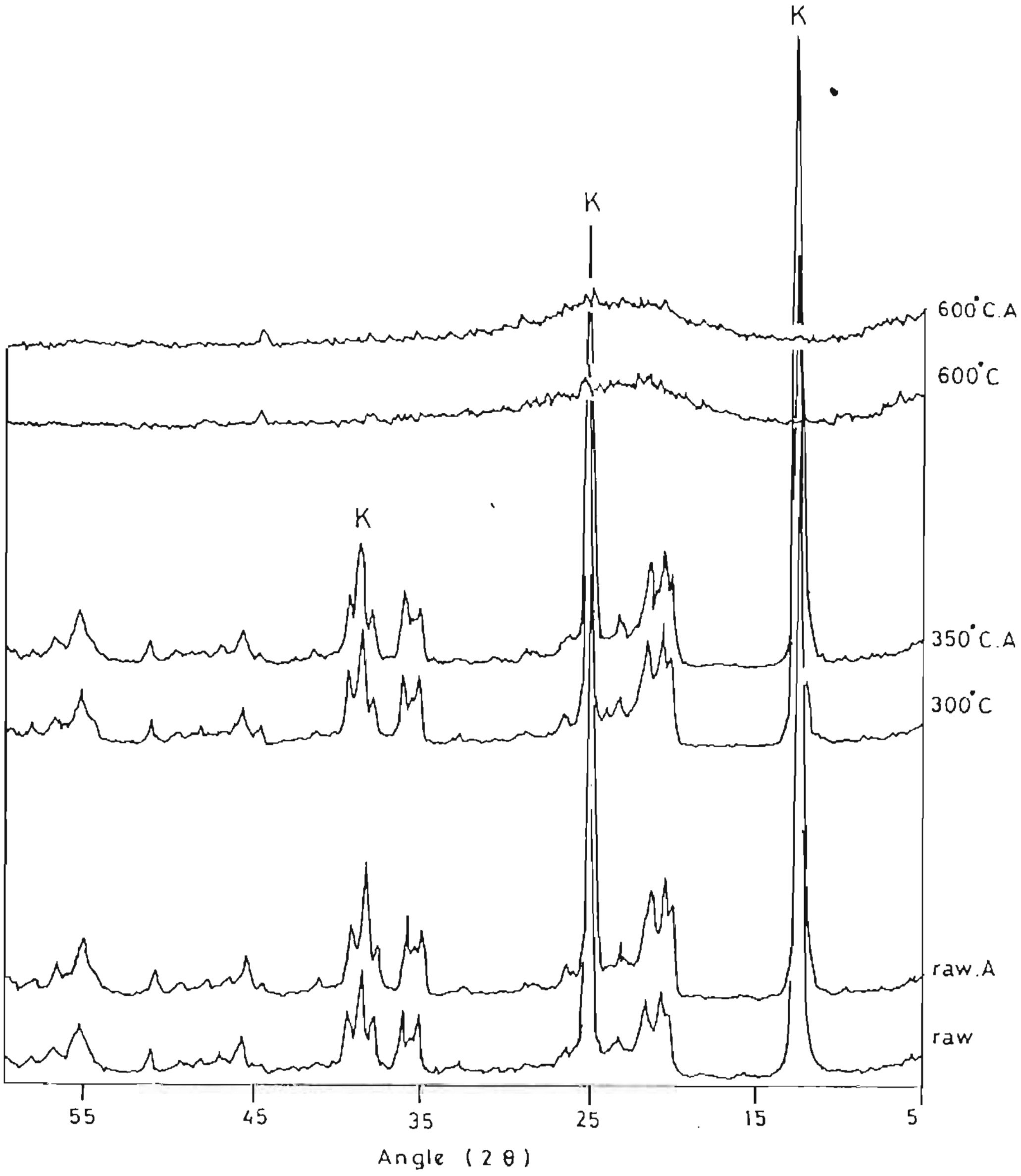


Fig. 3-1a X-ray diffraction patterns of the pretreated Thonnakkal clay samples.

Fig. 3-1b X-ray diffraction patterns of pretreated Madai clay samples

diffractogram due to kaolinite disappear indicating its transformation to amorphous metakaolinite (600°C and 600°C.A). Certain peaks due to quartz and mica remained in the X-ray patterns of MK sample (Fig 3-1b) which persists even on the metakaolinite samples (600°C and 600°C.A). This indicated that among the X-ray detectable minerals, only the kaolinite samples were affected by the thermal treatment. For all these samples (ie. the raw sample and those heated to 350°C and 600°C) a similarity was observed with their acidtreated counterparts (designated -.A in the figure) indicating that their physical structure are being affected the least by this acid leaching procedure (For legends, see Table 3-1).

3.3. Infra-red spectroscopic studies:

The infra red spectra of the sample TK is shown in Fig. 3-2. Sample MK also gives a similar IR-spectra, and hence not discussed in this paper. The spectra of the raw sample as well as the one heated to 350°C were similar (Fig. 3-2). But the metakaolinite sample (600) presented a broad spectra suggestive of a highly distorted structure. In the structure of kaolinite, a layer of octahedral $Al[O(OH)]_6$ group is superimposed on a network of SiO_4 tetrahedra. In metakaolinites (dehydroxylated kaolinites), the alumina layer becomes a network of AlO_4 tetrahedra (Percivial et al. 1974). A detailed description on the structure of metakaolin was described by MacKenzie et al. (1985).

The vibration intensities at 3695 and 3620 cm^{-1} represent the surface -OH stretching and inner -OH stretching vibrations respectively (Wilson 1987), which is characteristic of the kaolinite group in general. The 3669, 3654 cm^{-1} doublet denotes the crystallinity of the sample. The spectral bands at 1115, 1098 and 1034 cm^{-1} represents Si - O bending vibrations whereas the one at 701 cm^{-1} represents Si - O stretching vibration. The bands at 470 and 431 cm^{-1} also represent Si - O vibrations. The Al - OH bending vibrations are denoted by bands at 942 and 915 cm^{-1}. The compounded vibrations due to Si - O - Al^{iv} is represented by the bands at 796 and 756 cm^{-1}, whereas the one at 542 cm-1 represents Si - O - Al^{vi} vibrations (Kristóf et al. 1993; Suraj et al. 1997).

A merging of the shoulder peak at 942 cm^{-1} was noticed in the sample heated to 350°C, when compared to that of the raw sample. The rest of the peaks remained same. This merging of the 942 cm^{-1} peak indicates the release of hydroxyl groups loosely attached to the alumina layer. On further calcining the sample to 600°C, a broad spectrum

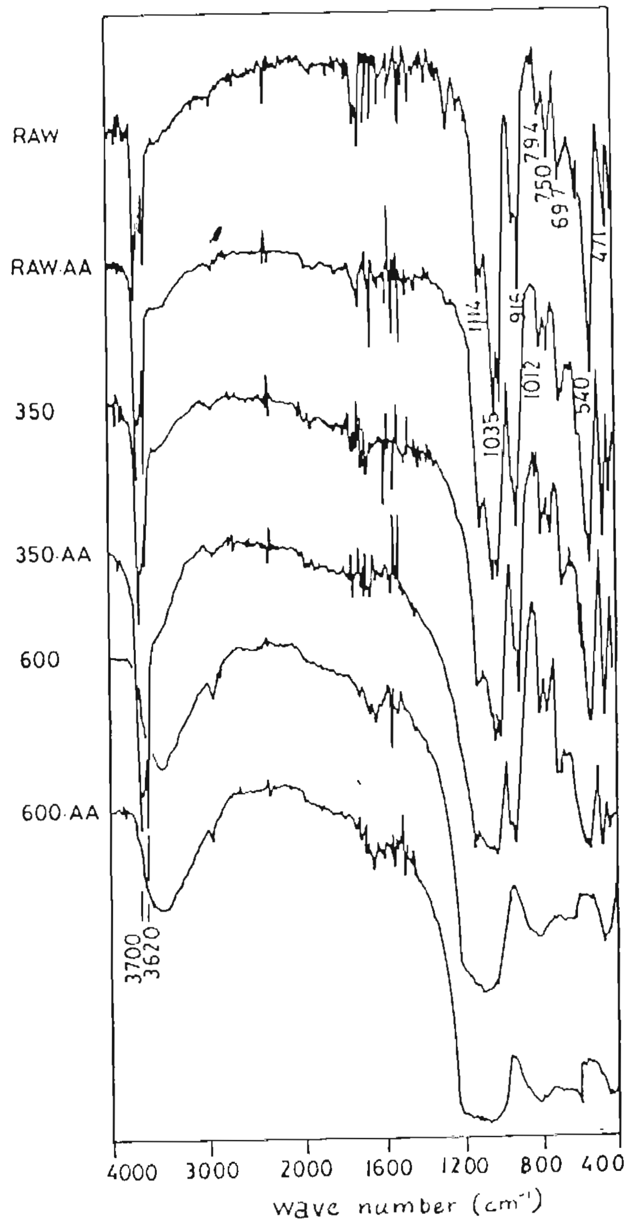


Fig. 3-2 Infrared spectra of the Thonnakkal kaolinite at various treatment conditions.

was obtained, indicating a merging up of individual peaks in their respective region. The transformation of the crystalline kaolinite to amorphous metakaolinite is confirmed by the absence of detectable Al - OH bands in the spectrum (600) i.e. those at 942, 915, 796, 756 and 542 cm^{-1}. Furthermore the presence of a broad new band at 807 cm^{-1} confirms the formation of metakaolin (Percival et al. 1974). The change in symmetry of the silica layer upon dehydroxylation of kaolinite explains the absence of 701 and 756 cm^{-1} SiO_4 kaolinite bands in the metakaolin spectrum (Percival et al. 1974).

Even though chemical analysis revealed the leaching out of metal ions from the kaolinite structure, little or no difference was observed between the spectrum of the acid activated samples and their non-acid activated counterparts (Fig. 3-2). Carroll-Webb and Walther (1988) observed a preferential dissolution of Al over Si at acid pH. But Wieland and Stumm (1992) observed preferentially dissolution of Si over Al in acid solutions. In kaolinites, Al and Si cations are bound to a common oxygen anion. Considering the former, the initial faster detachment of an aluminium cation, results in the breaking of Al - O bond where the oxygen is being shared by silicon also. This increases the probability of the detachment of the silicon cation as well. Brady and Walther (1989) suggested that the exposed sites due to the detachment of Al have lowered the activated site energy due to decreasing oxygen coordination, thereby allowing bond weakening at the silicon site aiding its dissolution. This simultaneous release of Al and Si will expose fresh surfaces, which behaves as the original mineral and thus the observed similarity in the ir-spectrum.

3.4. Pore size distribution:

The pore size distribution plots (Figs. 3-3a&b) indicates that when the samples were calcined to 600°C the Dv / Dr ratio (ratio of the change in volume to the change in radius) decreases when compared to the raw sample and on acid activation, they tend to increase. Eventhough the decrease in Dv / Dr ratio is not prominent for the

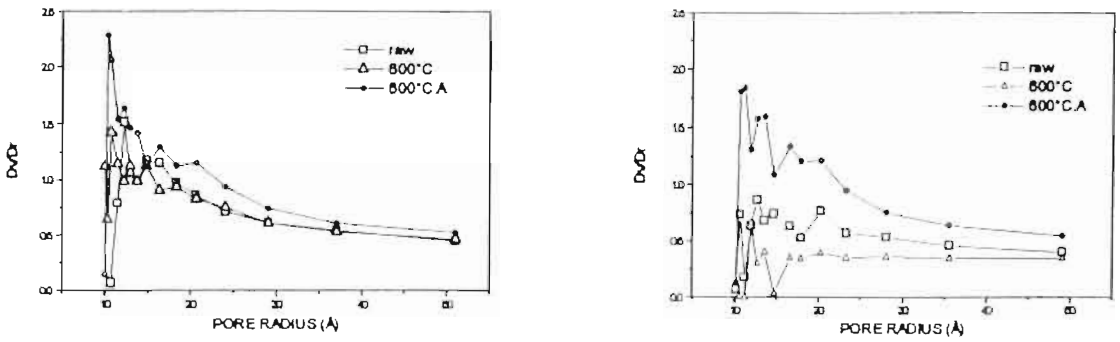


Fig.3-3 Pore size distribution plots of (a) Thonnakkal and (b) Madai kaolinites (A-acid activation)

TK sample (from 1.51 to 1.42 at 10.34 Å) after acid activation, a prominent increase was observed (2.28 at 10.34 Å). MK sample clearly shows a decrease in Dv/Dr ratio on calcination (from 1.17 to 0.67 at 11.93 Å) and an increase on acid activation of this calcined sample (1.84 at 11.22 Å). This clearly indicates that the distribution of particles with smaller pore radius decreases in the case of calcined samples whereas their acid activated form shows an increased distribution.

3.5. Cation exchange capacity

In order to assess the exchangeability of the clay samples, the cation exchange capacity (CEC) measurements were carried out using ammonium as the cation. The CEC values of various pretreated samples are given in Table 3-2. From this table, it is clear that the sample heated to 600°C has the least CEC. When it is acid activated, the exchange capacity shows an enormous increase (479.8 $mmol_c\ kg^{-1}$ for TK and 487.1 $mmol_c\ kg^{-1}$ for MK). But the amount of metals removed by the kaolinite samples in our adsorption studies does not comply with the observed CEC values. One should keep in mind that ion exchange is affected by both the affinity of the ions for the surface and the aqueous metal ion concentration. The isotherms in our study (Fig. 3-24 to 3-28) showed increased metal uptake with increasing aqueous concentration. Note, however, that CEC measurements generally use 1 *M* NH_4OAc; the highest initial concentration used in the present study is 5×10^{-4} M . Further more, CEC measurements conveniently use a monovalent cation and the hike in exchange capacity is due to the saturation of all available exchange sites using ammonium ions.

	Thonnakkal kaolinite(TK)		Madai kaolinite(MK)	
Sample	CEC ($mmol_c\ kg^{-1}$)	Surface area ($m^2\ g^{-1}$)	CEC ($mmol_c\ kg^{-1}$)	Surface area ($m^2\ g^{-1}$)
raw	134.89	16.87	138.53	11.77
350°C	127.90	14.32	128.45	12.29
600°C	60.06	14.77	96.05	11.90
raw.A	126.56	20.30	123.65	19.16
350°C.A	187.41	20.80	182.75	16.13
600°C.A	479.88	22.72	487.07	32.91

Table 3-2: Cation exchange capacity and surface area values of modified clay samples.

Adsorption studies:

The exchange kinetics of metal ions, viz. Cd, Pb, Cu, Zn and Ni onto various treated clay mineral samples was monitored as a function of equilibration time, temperature, pH and metal concentration. It was observed that in general, all metal ions are attaining equilibrium within the first one hour of equilibration.

On kaolinites, the sorption of aqueous species and development of surface charge are controlled mainly by amphoteric reactions at oxygen sites on aluminol and siloxane surfaces, that are conceptually similar to surface reactions on oxide surfaces (Sposito, 1984). Natural kaolinites possess a small cation exchange capacity, generally 0.02 - 0.06 $mol_c\ kg^{-1}$. Eventhough, the electrical nature of the kaolinite surface are still somewhat uncertain, evidence suggests of a permanent negative charge over the whole pH range in the siloxane surface due to the isomorphic substitution of Si by Al (Sposito, 1989). The silica face of the kaolinite structure is also known to possess an additional negative charge due to the variable charge which is significant only at high pH. Rand and Melton (1977) reports the point of zero charge pH_{zpc} of the aluminol group to be about 7.2. Williams and Williams (1978) calculated the value of point of zero net proton charge (PZNPC) as 7.3 for the edge surface. Therefore, above pH 7.2, the edges and aluminol surface will become negatively charged. >SiOH is the dominant Si site species at pH < 6 (Xie and Walther, 1992). Furthermore the surface charge on the kaolinite layer is also contributed by the contamination with small amounts of 2:1 phyllosilicates (Ferris and Jepson, 1975; Bolland et al., 1976; Lim et al., 1980; Wieland and Stumm, 1992). Swartzen-Allen and Matijevic (1973) adds up lattice imperfection and broken bonds at the edges for this charge on the clay lattice. But during metakaolinization, the collapse of the lattice structure containing tetrahedral aluminium, which upon acid activation, will contain more exchange sites.

Studies on divalent metal cation uptake of kaolinite show that fractional uptake from solution is low at low pH, rises rapidly in a narrow pH range and exceed 95% below the pH of precipitation of a stable hydroxide (O'Day, et al., 1994). Figure 3-4 also shows a similar trend. Farrah and Pickering (1976) tried to explain this as at low pH, the positively charged edges and negatively charged faces of the particles link to form an extended card house structure. As the pH is increased, adsorption of hydroxyl ions will increase the negative potential of the faces, resulting in increased electrostatic repulsion and subsequent expansion of the aggregates. Dillard and Koppelman (1982) in their studies on the adsorption of cobalt on kaolinites, assumes a reduction in surface concentration at kaolinite faces due to the competition with the aluminium released from kaolinite crystal for surface exchange sites, at low pH conditions, as responsible for the lower sorption of metal ions. At higher pH, a significant uptake of Co was explained as the reversal of charge at the edge surfaces and at pHs above about 7.5, hydrolysis of $Co(H_2O)_6^{2+}$ produces a surface coating on face and edge surfaces, resulting in large increase in adsorption. More convincing explanation was provided by Schulthess and Sparks (1989) and Schulthess and Huang (1990). At low pH, the H^+ competitively exchanges with the metal cation whereas at high pH values, the Na^+ (or conjugate acid to the base used for the alkaline pH adjustments) competes with the metal cation for the surface sites. More specifically each metal varies in its ability to compete with protons for the surface sites.

$$\text{surface-O}_n\text{Metal} + nH^+ = \text{surface-(OH)}_n + \text{Metal}^{n+}$$

Each sudden adsorption increase at various pH values corresponds to a threshold H^+ concentration value when the aqueous proton is no longer able to compete with the aqueous metal ion for adsorption by a particular site on the clay surface. This competitive adsorption of H^+ ions reduces the metal exchange capacity of the sample at low pH conditions.

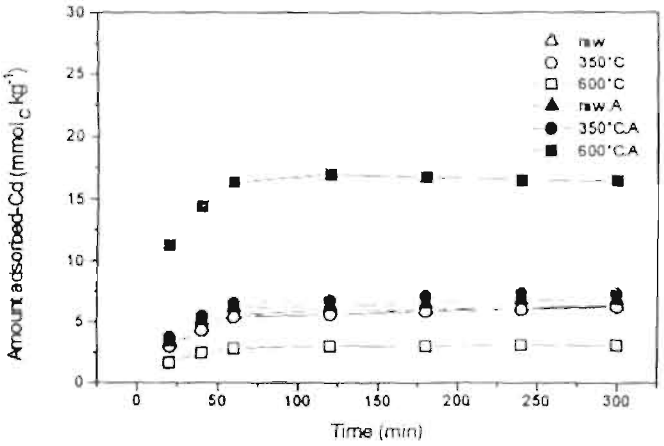


Fig. 3-4 Cd exchange kinetics for modified TK samples

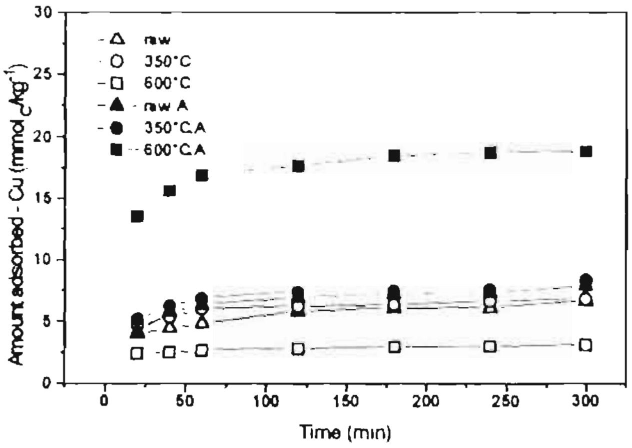


Fig. 3-5 Cu exchange kinetics for modified TK samples

Increasing the initial metal concentration obviously increased the uptake of metal ions. The increased metal uptake observed with their increased distribution in the solution emphasizes the competition taking place in the solid / solution interface.

3.6.1 Thonnakkal kaolinite:

The exchange kinetics of TK for various metals with time are given in figures 3-4 to 3-8. Fig. 3-4 show the uptake of Cd with equilibrium time. It was observed that, generally, the equilibrium was attained within the first 60 min. of equilibration time. Garcia-Miragaya and Page (1976) also observed that one hour was sufficient to attain equilibrium for Cd from sodium salt solution at pHs between 6.5 - 7.0. Similar behaviour or very little change was observed between the exchangeability of Cd on to the raw sample and the one heated to 350°C. It has to be noted that the additional room created by the release of physisorbed water was not contributing to the increase in cation exchange

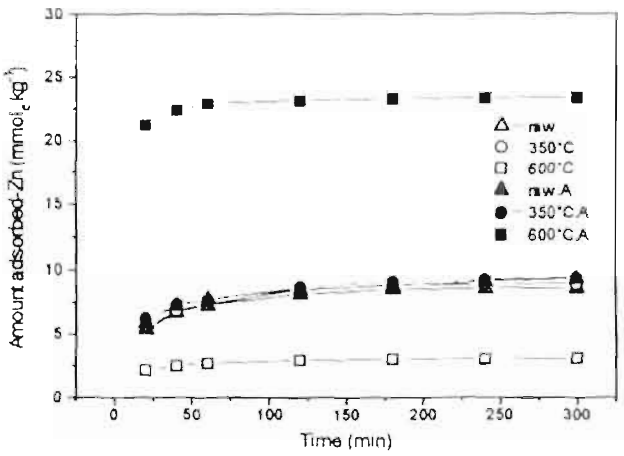


Fig. 3-6 Zn exchange kinetics for modified TK samples

capacity. Further calcining the sample to 600°C lowers the exchangeability of Cd (from 6.34 to 3.08 mmol$_c$ kg^{-1}). Slight improvement in the Cd exchangeability was displayed by the acid activated counterparts of the raw sample and the one heated to 350°C (i.e. from 6.34 to 6.76 mmol$_c$ kg^{-1} (raw sample) and 6.18 to 7.29 mmol$_c$ kg^{-1} (350°C heated sample)). But the acid activated metakaolinite sample showed an appreciable improvement in the uptake of Cd; i.e. from 3.80 to 13.36 mmol$_c$ kg^{-1}. Similar trend was also followed by the other metals studied. For Cu (Fig. 3-5) the exchangeability decreased from 6.06 to 3.06 mmol$_c$ kg^{-1} with calcination but upon acid activation, improved to 18.80 mmol$_c$ kg^{-1}. For Ni (Fig. 3-6), the values were 6.35, 2.55 and 20.40

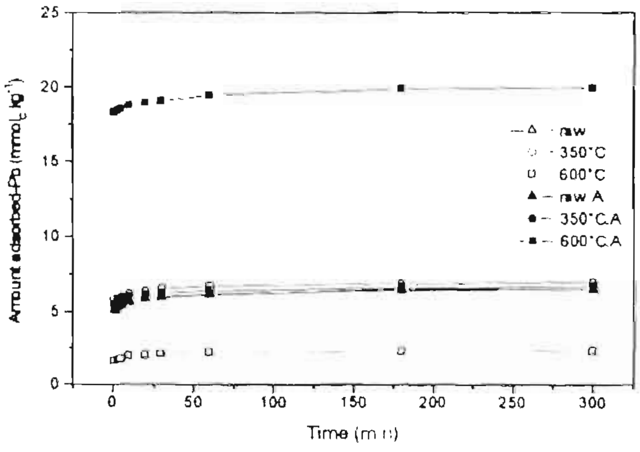


Fig. 3.7 Pb exchange kinetics for modified TK samples

The effect of ambient temperature on the exchangeability of metal ion was also evaluated (Figs. 3-9 to 3-13). The metals responded differently with equilibration

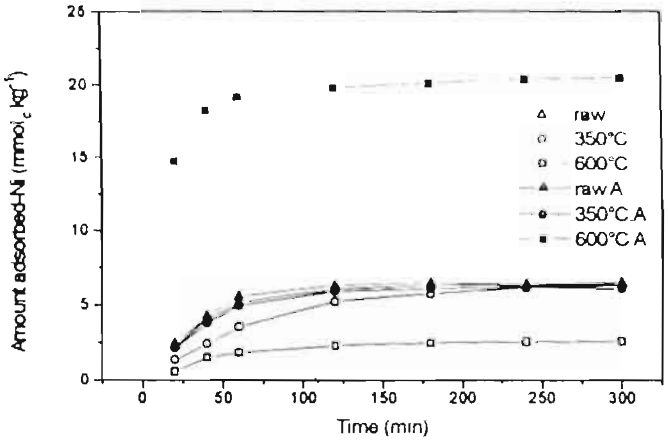


Fig. 3-8 Ni exchange kinetics for modified TK samples

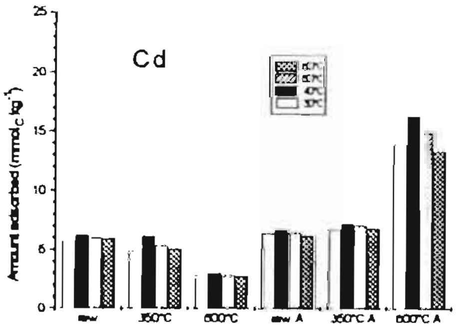


Fig.: 3-9 Effect of temperature on the adsorption of Cd on modified TK sample.

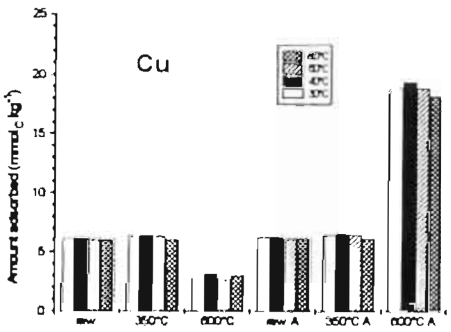


Fig: 3-10 Effect of temperature on the adsorption of Cu on modified TK sample.

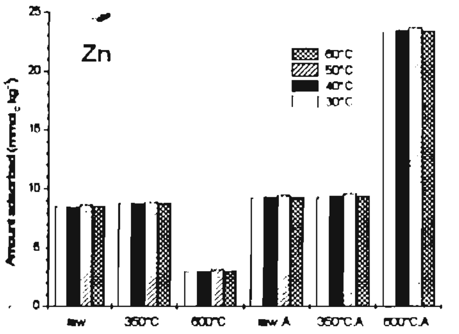


Fig: 3-11 Effect of temperature on the adsorption of Zn on modified TK sample.

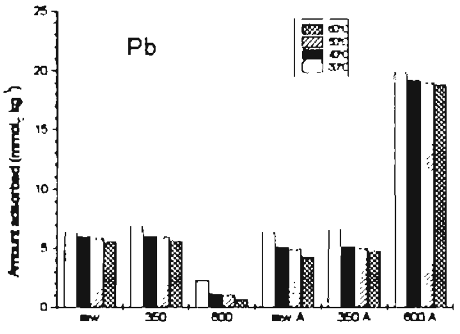


Fig: 3-12 Effect of temperature on the adsorption of Pb on modified TK sample.

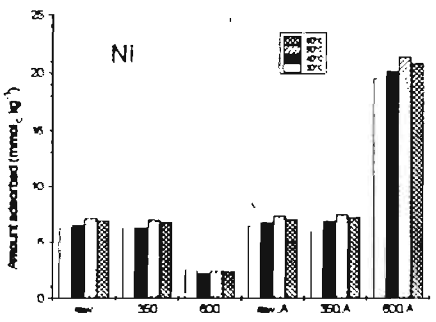


Fig. 3-13 Effect of temperature on the adsorption of Ni on modified TK sample.

mmol$_c$ kg^{-1} respectively. For Pb (Fig. 3-7), the values were 7.5, 3.3 and 29.93 mmol$_c$ kg^{-1} respectively and for Zn (Fig. 3-8), the values were 8.58, 3.07 and 23.35 mmol$_c$ kg^{-1} respectively. temperatures. For Cd, the metal uptake increased with temperature, with maximum exchangeability at 40°C (13.36 mmol$_c$ kg^{-1} ; Fig. 3-9). Further increasing the ambient temperature shows a reduction in the exchange capacity. Similarly Pb and Cu also preferred 40°C (19.27 and 25.16 for Pb and Cu respectively; Figs. 3-12 and 3-10). Ni and Zn (Figs. 3-13 and 3-11)showed a constant increase in the exchange capacity until 50°C and decreased thereafter (21.37 and 23.75 for Ni and Zn respectively).

3.6.2 Madai kaolinite:

MK also possessed similar exchange kinetics as that of TK (Figs. 3-14 to 3-18). Here also metal uptake of the raw sample decreased with metakaolinization, but upon acid activation, improved drastically. The metal uptake values for the raw MK sample, the metakaolinite sample and the acid activated metakaolinite sample (in $mmol_c$ kg^{-1}) are ~~as~~ follows: i.e. Cd - 6.55, 3.15 &13.64 (Fig. 3-14); Cu -6.21, 4.16 & 18.09(Fig. 3-15); Ni - 6.35, 2.25 & 2.21 (Fig. 3-18); Pb - 7.10, 3.20 and 24.12 (Fig. 3-17); Zn - 8.25, 2.75 & 22.81 (Fig. 3-16), respectively.

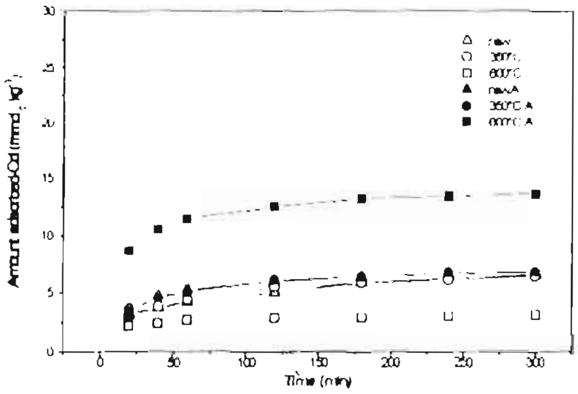


Fig. 3-14 Cd exchange kinetics for modified MK samples

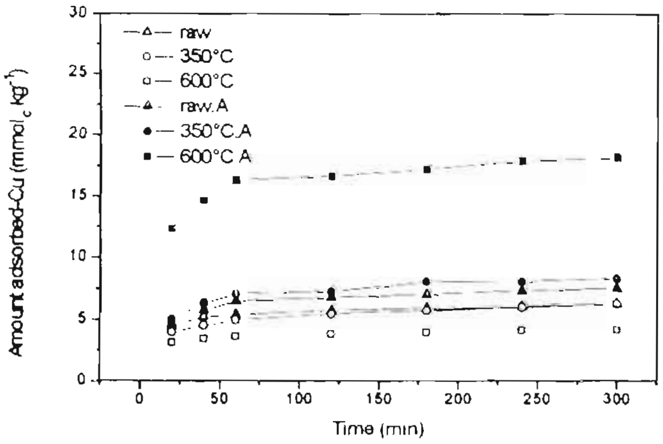


Fig. 3-15 Cu exchange kinetics for modified MK samples

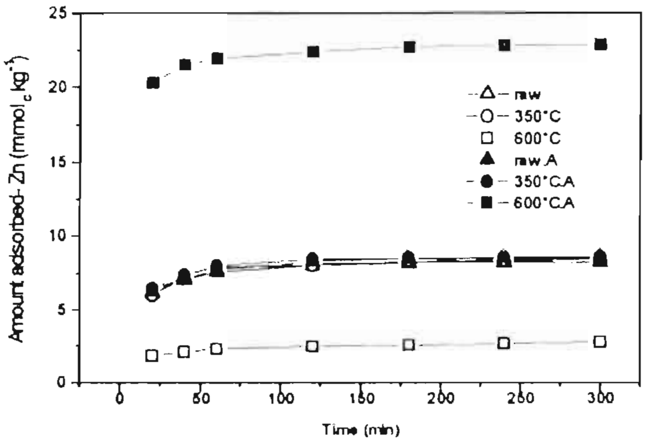


Fig. 3-16 Zn exchange kinetics for modified MK samples

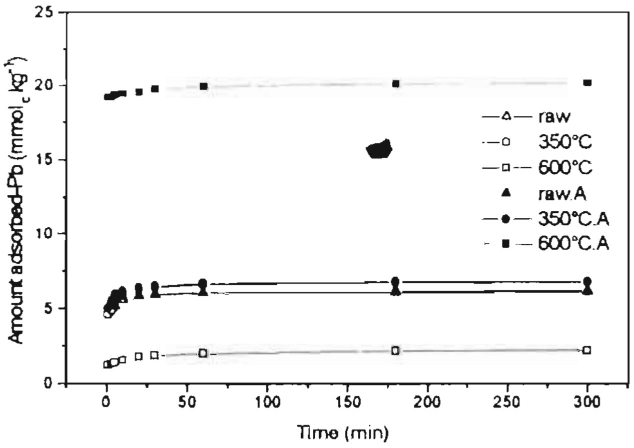


Fig. 3-17 Pb exchange kinetics for modified MK samples

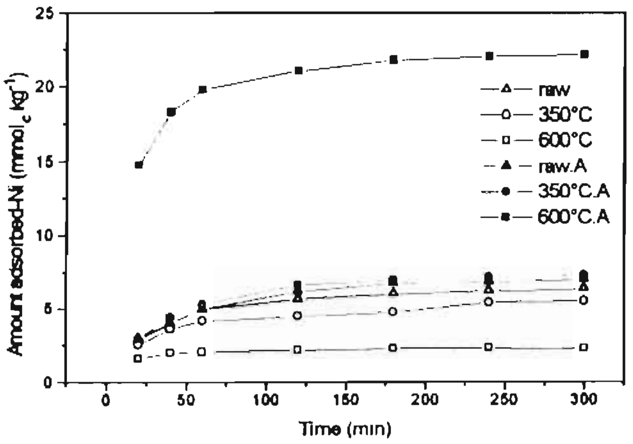


Fig. 3-18 Ni exchange kinetics for modified MK samples

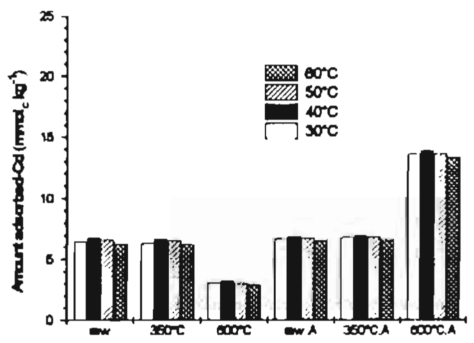


Fig. 3-19 Effect of temperature on the adsorption of Cd on modified MK sample.

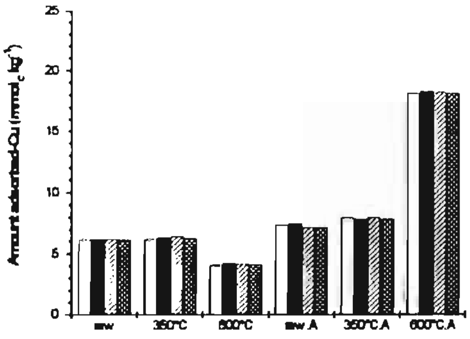
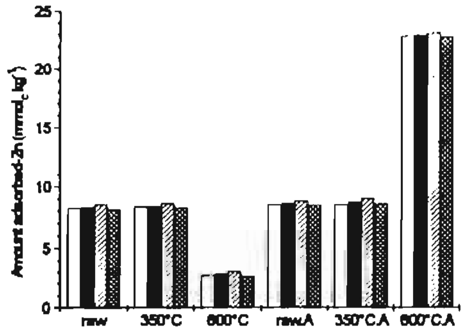


Fig. 3-20 Effect of temperature on the adsorption of Cu on modified MK sample.



Fig, 3-21 Effect of temperature on the adsorption of Zn on modified MK sample.

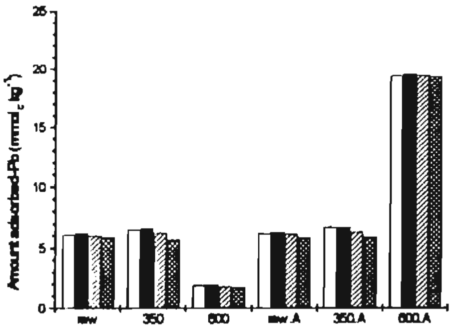


Fig. 3-22 Effect of temperature on the adsorption of Pb on modified MK sample.

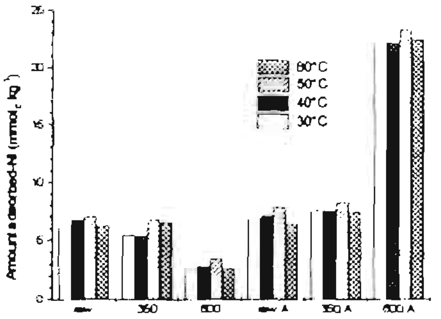


Fig. 3-23 Effect of temperature on the adsorption of Ni on modified MK sample

On varying the ambient temperature, similar behviour was displayed by MK as that of TK; i.e., Cd, Cu and Pb preferring 40°C while Ni and Zn preferring 50°C (Cd - 13.91 $\text{mmol}_c\ \text{kg}^{-1}$; Cu - 18.28 $\text{mmol}_c\ \text{kg}^{-1}$; Zn - 23.11 $\text{mmol}_c\ \text{kg}^{-1}$; Pb - 24.52 $\text{mmol}_c\ \text{kg}^{-1}$; Ni - 23.42 $\text{mmol}_c\ \text{kg}^{-1}$) (Figs. 3-19 to 3-23).

When the samples were heated to 350°C, the physically adsorbed water in the layer lattice together with a portion of the structural hydroxyl escapes (Theng, 1981), which in turn increases the surface area of the mineral. But at this temperature, only the loosely bound hydroxyl groups escapes whereas certain coordinated hydroxyls require still higher temperature for detachment from the structure. Thermogravimetric studies revealed that this weight loss is negligible and a noticeable increase in the exchangeability cannot be expected. On further calcining the sample to 600°C, dehydroxylation followed by collapse of layer structure and its accompanying transition to metakaolin takes place, obviously reducing the surface area available for ion exchange. Pore size distibution (Figs. 3-3a&b) also possess a lower distribution curve for the calcined sample (600°C) compared to the raw form, supporting the above statement. Here a shift in the coordination of aluminium from octahedral to tetrahedral through pentahedral takes place (MacKenzie, et al., 1985). Accordingly, in the tetrahedra structure, edges are shared rather than corners. Thus the edges become uncharged and therefore do not contribute to the adsorption or CEC (Table 3-2). But acid leaching improves the exchange capacity of these thermally modified samples. Wieland and Stumm (1992) describes this acid dissolution using coordinative chemical model of mineral weathering. The O^{2-} and OH^- ligands bridging adjacent metal centers at the surface will be replaced by OH^-, H_2O, or other ligands due to protonation / deprotonation of surface hydroxyl groups or by ligand exchange. Surface complexes polarize critical metal-oxygen bonds; reducing the activation energy of the critical metal center. This facilitates the detachment of the metal centers from the surface lattice structure. According to them, kaolinite dissolution is nonstoichiometric in the pH range 2.0 - 6.5, with a preferential release of silicon, and the detachment and readsorption of aluminium in the kaolinite structure describes the observed non-stoichiometry. But a contradictory statement was put forth by Xie and Walther (1992) as they observed Al dissolution rates greater than Si at $pH < 4$ and Si dissolution rates greater than Al at $4 < pH < 11$. Similar observation was made earlier by Carroll-Webb and Walther (1988), with preferential Al release at $pH < 6$. In our study, the Al_2O_3/SiO_2 ratio (Table 3-1) shows a slight increase for the raw sample and the one heated to 350°C after acid activation. This is due to the accumulation of aluminium as compared to silica which means that silica is being preferentially leached during the process. Here the variation in the ratio is very small and thus can explain the observed small variation in the cation exchange. But the Al_2O_3/SiO_2 ratio of the acid activated metakaolinite sample was reduced to almost half of their original value, which is indicative of the accumulation of Si rather than Al. Schulthess and Huang (1990) suggests stronger metal ion affinity for clay Si sites than the oxide Si sites; that is, the clay sites require a higher H^+ concentration for a hydronium ion exchange to take place. MacKenzie et al.(1985) reported that during metakaolinization, the conversion of octahedral Al to tetrahedral state makes the sample more susceptible to acid attack compared to the crystalline state. Rupert et al. (1987) attributes more weightage to this disorder compared [illegible] relative solubilities of Al^{IV} and Al^{VI}. Here, the accumulation of Si (or Si remaining) is much more as compared to the Al accumulation in the former two samples, and their contribution to ion exchange occurs at the negatively charged =XO sites (Wieland and Stumm, 1992). Furthermore, since the acid activated metakaolinite sample is having an amorphous structure, their existence in an aqueous medium resembles an aluminosilicate gel (Ferris and Jepson, 1975). This highly distorted crystal structure have increased availability of exchange sites thereby increasing their sorption capacity. This can be correlated with the observed increase in the surface area (Table 3-2). Figures 3-3a&b also show maximum pore size distribution for the acid activated metakaolin sample in the lower pore radius region.

An attempt to study the effect of temperature on the uptake of metal ions, at temperatures of 30, 40, 50 and 60°C showed preferences of certain temperatures. But the exact processes that determine the variation in metal uptake with temperature is unknown.

Metal ions adsorb on to soil particle surface via. three mechanisms with relative order of decreasing interaction strength inner-sphere complex > outer-sphere complex > diffuse-ion swarm (Sposito 1989). The relative affinity of a soil adsorbent for a free metal cation will increase with the tendency of the cation to form inner-sphere surface complexes, involving ionic as well as covalent bonding, resulting in a stable bond. But normally, metal ions in aqueous solutions are held electrostatically either as diffuse-ion complex on the surface forming diffuse double layer or as outer-sphere surface complex which undergoes ion-exchange with other cations in the system. Copper and cadmium are expected to form diffuse ion aqueous complexes on the surface of the clay minerals.

Copper shows better exchangeability compared to cadmium may be due to the formation of $Cu(OH)^+$ and $Cu(H_2O)_4^{2+}$ which can stabilize copper ions. It was also suggested that Cu^{2+} ions largely occupy the planar external surfaces rather than the edges of the platelets (McBride 1976). Farrah and Pickering (1976) attribute poly nuclear bridged copper(II) species to be the predominant adsorbed species on kaolinite. Cadmium however can form comparatively stable chloride complexes in solution which will not get readsorbed once it happened to desorbs into the solution due to the prevailing conditions (Doner 1978). From Fig. 3-5, it can be seen that even though there is an initial increase in the Cd-adsorption pattern, a definite desorption pattern is indicated with increased in equilibration time. This pattern remained similar for both the samples. It can be deduced that a disordered crystal structure (metakaolin) could not retain cadmium within it because of the weak bond formation, the chloride complex formed with the available chloride ions in solution being more stable.

3.7. *Adsorption isotherm*

Adsorption data for a range of adsorbate concentrations are most conveniently described by adsorption isotherms, such as Langmuir or Freundlich isotherm, which relate adsorption density q_e (metal uptake per unit weight of adsorbent) to equilibrium adsorbate concentration in the bulk fluid phase, C_e (Ref. Eq. 1-2). Since, similar plots were obtained for both clay samples, the plots of TK alone are given. The plots of C_e/q_e vs C_e of the acid modified metakaolinite sample were linear which shows that the adsorption of metal ions follows Langmuir isotherm model (Figs.3-24 to 3-28). Langmuir constants Q_0 and b are calculated from the slope and intercept of the plots and the values are given in Table 3-3. Their values varied with temperature and with the metal ions studied. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L which is defined by equation 1-4. The values at different temperatures and different concentrations, which are given in Table 3-4. The R_L values lies between 0 and 1 which indicate favorable adsorption of metal ions into the acid modified metakaolinite sample (Nassar, et al., 1995). The Freundlich isotherm was also applied to the uptake of metal ions by acid modified metakaolinite sample (Ref. Eq. 1-6). Logarithm of the equilibrium concentration, C_e (mg/l) was plotted against and the amount adsorbed at equilibrium time q_e which gave a linear plot, suggesting that the adsorption of metal ions onto the acid modified metakaolinite sample follows Freundlich isotherm model (Figs. 3-29 to 3-33). Values of n and k_f were calculated from the slope and intercept and are given in Table. 3-3. n gives an indication of the favorability and k_f the capacity of the adsorbent (Namasivayam and Ranganathan, 1995). Mckay, et al. (1980) suggests that a value of n between 2 and 10 represents good

		Thonnakkal kaolinite(TK)				Madai kaolinite(MK)			
Metal	Temp (°C)	Q_0 (mg/g)	b (l/mg)	n	k_f (mg/g)	Q_0 (mg/g)	b (l/mg)	n	k_f (mg/g)
	30	0.1458	0.0142	1.439	0.0040	0.1025	0.0239	1.739	0.0053
Cd	40	0.1866	0.0108	1.334	0.0035	0.1045	0.0240	1.740	0.0060
	50	0.1595	0.0127	1.382	0.0037	0.1038	0.0235	1.732	0.0059
	60	0.1335	0.0162	1.511	0.0045	0.1028	0.0230	1.709	0.0056
	30	0.0596	0.0632	2.169	0.0082	0.0548	0.0693	2.263	0.0083
Cu	40	0.0601	0.0649	2.214	0.0086	0.0568	0.0657	2.214	0.0081
	50	0.0593	0.0661	2.195	0.0083	0.0558	0.0674	2.238	0.0082
	60	0.0564	0.0663	2.184	0.0080	0.0554	0.0673	2.233	0.0081
	30	0.0476	0.0893	2.597	0.0090	0.0515	0.0983	2.767	0.0113
Ni	40	0.0467	0.0989	2.751	0.0102	0.0507	0.1010	2.810	0.0114
	50	0.0457	0.1151	3.101	0.0119	0.0500	0.1147	3.113	0.0130
	60	0.0458	0.1080	3.002	0.0113	0.0512	0.1030	2.814	0.0120
	30	0.2415	0.0205	2.370	0.0232	0.2359	0.0217	2.320	0.0223
Pb	40	0.2425	0.0209	2.375	0.0235	0.2408	0.0214	2.274	0.0218
	50	0.2384	0.0212	2.396	0.0236	0.2378	0.0217	2.298	0.0221
	60	0.2380	0.0208	2.384	0.0232	0.2341	0.0220	2.320	0.0223
	30	0.0691	0.0743	2.392	0.0115	0.0670	0.0756	2.405	0.0113
Zn	40	0.0710	0.0715	2.345	0.0114	0.0686	0.0737	2.374	0.0113
	50	0.0685	0.0775	2.471	0.0121	0.0643	0.0859	2.534	0.0122
	60	0.0671	0.0795	2.478	0.0120	0.0646	0.0818	2.484	0.0119

Table. 3-3 Langmuir constants Q_0 & b and Freundlich constants n & k_f of TK and MK

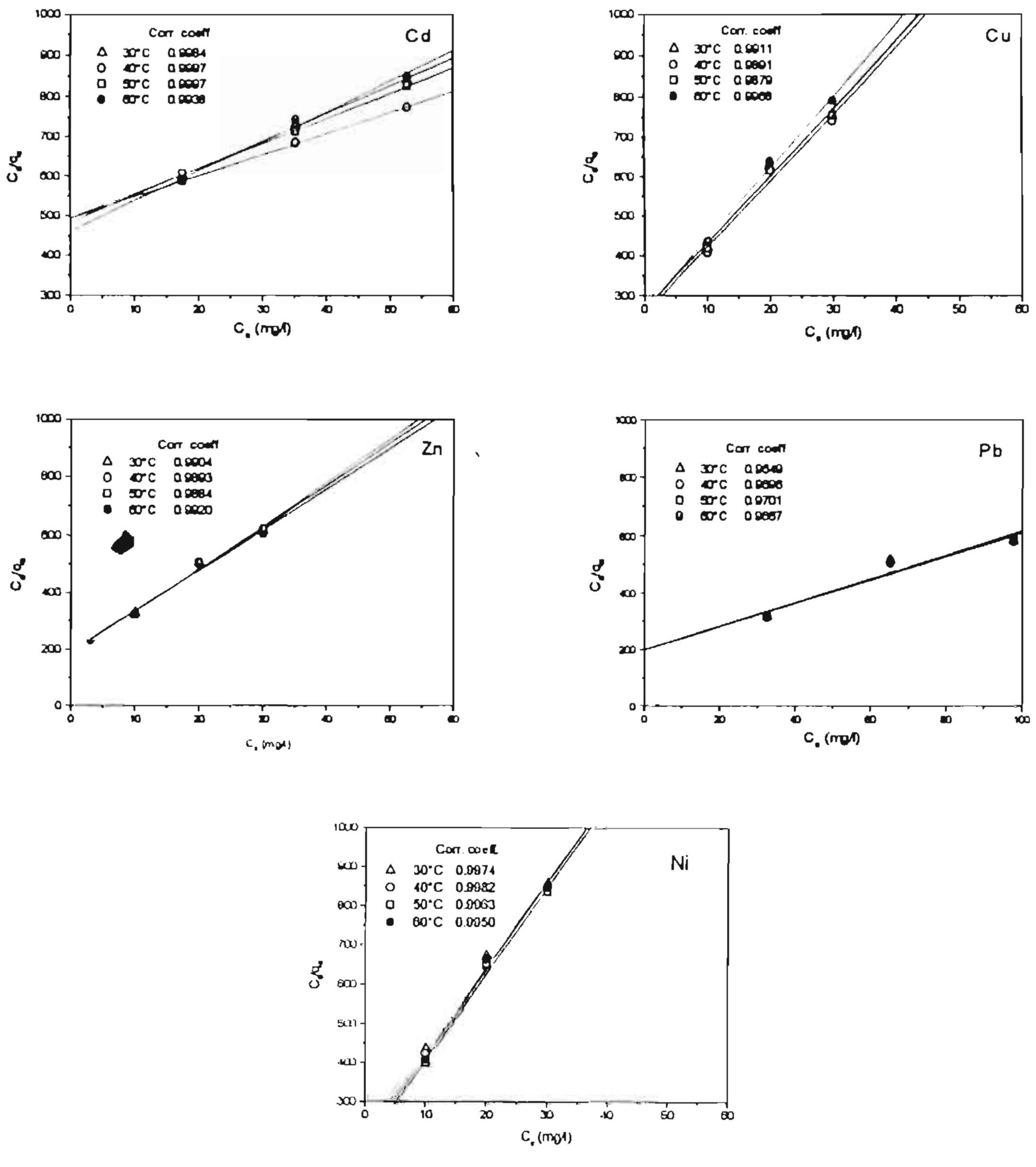
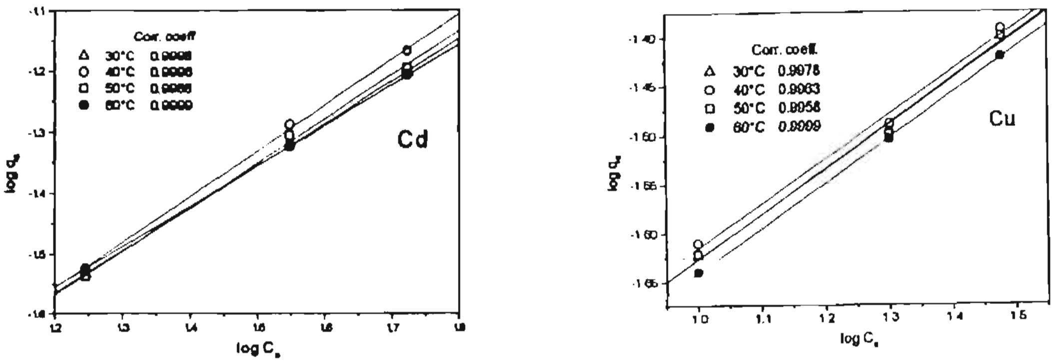


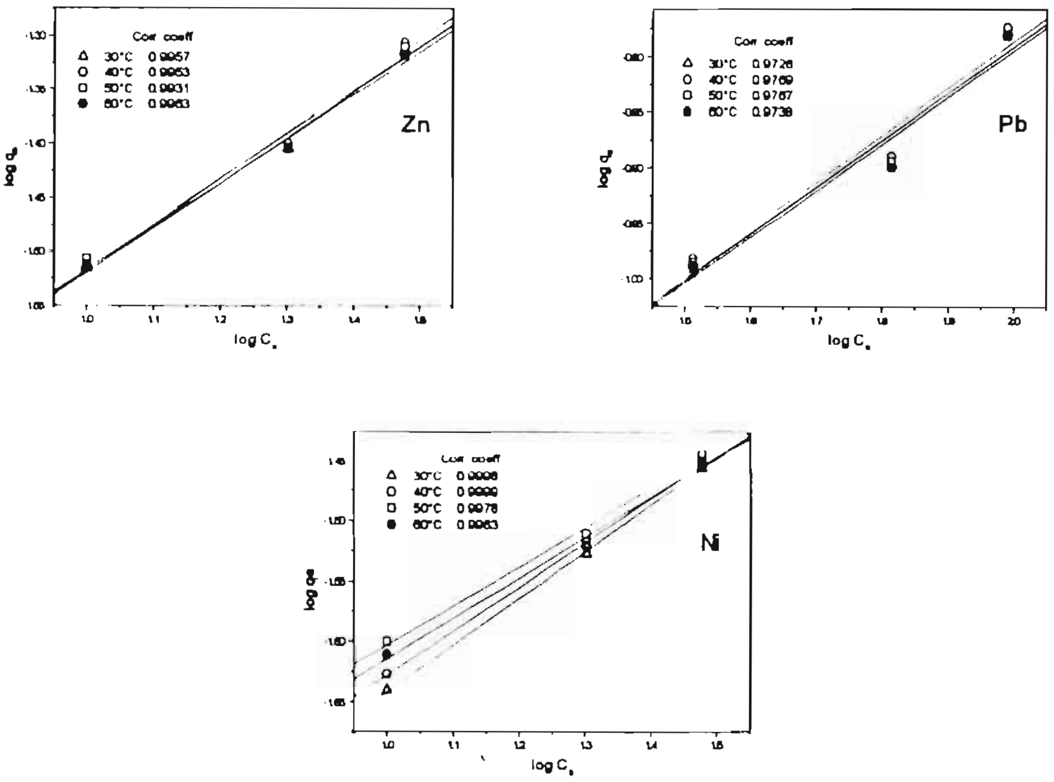
Fig:3-24 to 3-28 Langmuir plots for the adsorption of metal ions on modified TK sample.

Metal	Conc. (mg/l)	Thonnakkal clay(TK) 30°C	40°C	50°C	60°C	Madai clay(MK) 30°C	40°C	50°C	60°C
	17.6	0.8	0.840	0.817	0.778	0.704	0.703	0.707	0.712
Cd	35.3	0.666	0.724	0.690	0.636	0.547	0.541	0.547	0.552
	52.8	0.572	0.637	0.599	0.539	0.442	0.441	0.446	0.452
	10.0	0.613	0.606	0.602	0.601	0.591	0.604	0.597	0.598
Cu	20.0	0.442	0.435	0.431	0.430	0.419	0.432	0.426	0.426
	30.0	0.345	0.339	0.335	0.335	0.325	0.337	0.331	0.345
	10.0		0.503	0.465	0.481	0.504	0.496	0.466	0.493
Ni	20.0	0.339	0.336	0.305	0.316	0.337	0.331	0.304	0.327
	30.0	0.272	0.225	0.225	0.236	0.253	0.248	0.225	0.225
	32.6	0.599	0.595	0.591	0.496	0.586	0.589	0.586	0.582
Pb	65.2	0.428	0.423	0.420	0.424	0.414	0.417	0.414	0.411
	97.8	0.333	0.329	0.325	0.329	0.320	0.323	0.323	0.317
	10.0	0.574	0.583	0.563	0.557	0.569	0.576	0.538	0.550
Zn	20.0	0.402	0.416	0.392	0.386	0.398	0.404	0.368	0.379
	30.0	0.310	0.318	0.301	0.296	0.306	0.311	0.280	0.390

Table 3-4. Equilibrium parameter, R_L of different metal ions on TK and MK.



Figs. 3-29 & 3-30 Freundlich plots for the adsorption of metal ions on modified TK sample.



Figs. 3-31 to 3-33 Freundlich plots for the adsorption of metal ions on modified TK sample.

adsorption. Here, the values of *n* distributes towards the lower range (i.e. ~ 2) representing good adsorption for metal ions on to the modified kaolinite sample. Similar distributions were also reported by Christensen (1984) on Danish soil sandy loam for Cd(II) (k_f - 0.386 and *n* - 1.2). But a recent study by Namasivayam and Ranganathan (1995) reported a value of k_f - 16 to 21 mg/g and *n* - 5 to 6 for Cd(II) on Fe(III)/Cr(III) hydroxide.

4. CONCLUSION

The modified amorphous derivative of kaolinite shows better adsorption of metal ions studied. Thermal modification alone, eventhough showed a slight improvement at lower calcination temperatures (upto ~500°C), decreases the exchangeability of kaolinites at higher calcination temperatures (i.e. metakaolinite samples). But acid activating this porous amorphous metakaolinite created numerous vacant sites which improved drastically the cation exchange. Equilibrium was attained within the initial one hour of contact by these samples. Looking into the effect of pH on the metal uptake, the low fractional adsorption from solution at low pH, rises rapidly in a narrow pH range, on increasing the pH. This can be due to the charge reversal at the exchanging surface and the possible related composition between anions used for pH adjustments. An increase in the initial metal concentration showed a constant improvement in the amount of metal adsorbed. Finally, on varying the ambient temperature and equilibrating for three hours, it was found that preferential adsorption taking place for the metals under study, the exact reason was not clear.

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CHAPTER 4

PHYSICAL MODIFICATION

The development of modern ceramic and composite materials has led to the progress in the fine-grinding methods (Miloševic et al., 1992). The process of grinding is known to alter solid materials, not only by causing particles to fragment and by changing their surface area, but also by modifying their pore size distribution and inducing structural changes such as polymeric transformations, micro strains, complete or partial amorphization of the material, altered chemical reactivity, etc. (Gonzalez-Garcia et al. 1991). This chapter tries to examine the mechanochemical alteration behaviour of natural kaolin upon micronization on their metal ion exchange property.

Many works have been reported on the effect of grinding on montmorillonites (Cicel and Kranz 1981; Keller 1955), bentonite (Mingelrin et al., 1978; Perkins and Dragsdorf 1952), imogolite (Henmi and Yoshinaga 1981), chrysotile (Suquet 1989; Papirer and Roland 1981) and sepiolite (Cornejo and Hermosin 1988). Pérez-Rodríguez et al. (1988) and Wiewióra et al. (1993) studied pyrophyllite and suggested effects like delamination, gliding and folding of layer structure resulting in an increase in the surface area during the initial stages of grinding which tends to aggregate with continued grinding.

The significance of the uses of kaolin has fostered studies on the transformations it undergoes during wet and dry grinding. According to Cicel and Kranz (1981), wet grinding of kaolinite causes delamination of the clay crystals and thinning in the direction of c-axis. Rupture perpendicular to the 00*l* plane is of secondary importance. Dry grinding produces rapid degradation than wet grinding and causes a decrease in the degree of crystallinity of kaolinite crystals which also involves the rupture of tetrahedral and octahedral bonds. Another line of thought suggests the formation of a zeolitic substance having a structure similar to that of original kaolinite due to dry grinding (Laws and Page 1945). Earlier, Shaw (1942) studied the effect of grinding on kaolinite clay colloids using electron microscope and supported his view with similar theory.

Schrader et al. (1970) worked on mechanical activation of kaolin inorder to facilitate the acid dissolution of aluminium and observed that crystal structure has deformed mainly along the c-axis. Miller and Oulten (1970, 1972) tried the mechanochemical alteration of kaolinite on a percussion mill. The effect of grinding on a vibrating mill using infrared techniques were studied by Hlavay et al. (1977) where the surface area values reach maximum at varying grinding times. Hlavay et al. (1977). Aglietti et al. (1986a&b) and Juhasz and Opoczky (1990).

1. EXPERIMENTAL

Only one well crystallized kaolinite sample (Thonnakkal, Trivandrum Dt.) was chosen for this study. Sample details are given in chapter 3. Two different methods of micronization were employed; one a ball mill (Fritsch pulverissette, Germany) in which the samples are micronized in a zirconia pot using zirconia balls and the other an oscillatory mill (Siebtechnik, Germany) which works through the friction and impact caused by the oscillating rings and a cylinder (discs) inside the casing containing the samples. Grinding in an oscillatory mill proved to be extremely rapid. Both wet as well as dry grinding was carried out in the ball mill taking 5 g of the sample every time and ground for 30, 60, 120, 180, 240 and 300 min. (A slurry using 10 ml of distilled water was made for wet grinding). 30 g of the sample was ground in an oscillatory mill for 5, 10, 15, 20, 30 and 60 min., cooling the case for 30 min. between every 5 min. intervals. Wet grinding was not possible in this instrument as the oscillatory motion of the casing will spill water and damage the equipment.

The XRD patterns were obtained on a diffractometer (Philips PW 1710) using Cu Kα radiation operating at 40 KV and 20 mA on a diffraction range 10 to 30°C, 2θ. A thin slurry of the sample solution was pipetted out into glass slide, air dried at room temperature, oven dried at 60°C for one hour and used for XRD analysis. DTA and TG analysis was carried out (Seiko DTA/TG simultaneous analyzer) at a heating rate of 20°C/min. in air using alumina as the reference standard. IR absorption spectra was recorded (Perkin Elmer IR 882 spectrophotometer) in the 4000 cm^{-1} to 400 cm^{-1} region using KBr sample pellets. Surface area and pore volume measurements were carried out (Micromeritics Gemini 2360 Surface Area Analyzer) using ultra pure nitrogen gas as the adsorbate. Particle size measurements were made (Quantachrome Microscan

Particle Size Analyzer) after ultrasonically dispersing the sample using CALGON electrolyte. Scanning electron micrographs were obtained (Hitachi S-2400 SEM) using an air dried, finely dispersed slurry, taken on a fine polished brass-stud after giving an even gold coating. NMR spectra were recorded using Bruker (DSX-300) NMR spectrophotometer.

Since ball milling could not produce a significant micronization within the stipulated comparable time (e.g. 1 h in Figs. 4-1 & 4- 2), the products were not tried for their adsorption studies. The samples dry ground in an oscillatory mill were sodium saturated by shaking overnight in a 1 mg/ml solution (1:5 ratio), repeating the procedure 5 times inorder to attain maximum saturation. These micronized and sodium saturated samples (designated S0 to S60)were used for metal exchange studies. Heavy metals like Cd, Cu, Pb, Zn and Ni were chosen for equilibration studies considering their role as toxic metal pollutants in the environment. AnalaR grade of $CdCl_2.2\frac{1}{2}H_2O$ (Polskie Odczynniki Chem-Gliwice), $Pb(NO_3)_2$ (Merck), $CuSO_4.5H_2O$ (BDH), $ZnCl_2$ (BDH) and $NiSO_4$ (BDH) were used for the studies. 50 ml of 10 mg/l metal solution was equilibrated with 0.2 g of the clay sample for 30, 60, 120, 180, 240 and 300 min. of contact time. After centrifugation, the filtrate is analyzed for the remaining metal concentration, using AAS (ECIL model 4127) and the metal uptake was calculated. pH of 5.5-6.0 was maintained for the metal solutions, wherever possible, inorder to simulate natural conditions.

2. RESULTS AND DISCUSSIONS

2.1. X-ray diffraction studies

As stated, two methods of micronization were employed for this study. Fig. 4-1 shows the effect of grinding on kaolinites in a ball mill. From the XRD patterns, it is evident that dry grinding is more effective than wet grinding. The intensity of the 001 (7.14 Å) shows that after 5 h of dry grinding, there is a definite decrease in the peak intensity, however small the reduction is. Wet grinding the sample for an equal time does not show any appreciable reduction in the peak intensity. This clearly shows that while dry grinding the samples, the

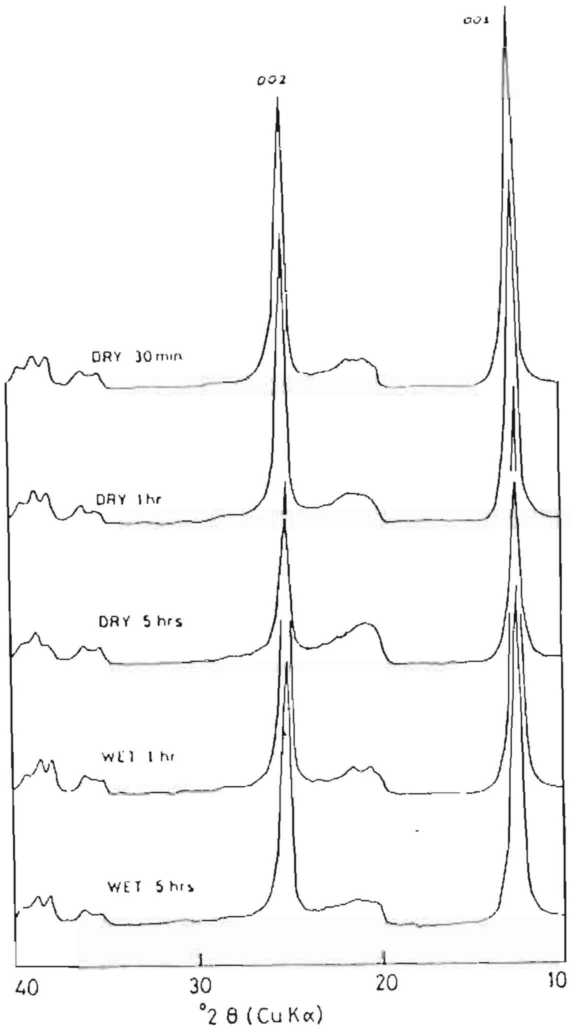

Fig. 4-1 X-ray diffraction patterns of kaolinite sample micronized using ball mill.

effect of zirconia balls on clay structure is more and is related to the direct impact on the lattice structure. During wet grinding, however, the effect of zirconia balls is dampened by the liquid medium, thereby retarding effective micronization. Papirer and Roland (1981) during their studies on chrysotile also observed that freshly produced surfaces could absorb water molecules and form a protective layer with thin film of water covering the entire surface. Hence wet grinding in a ball mill proves to be an extremely slow process when compared to dry grinding.

Grinding in an oscillatory mill was found to be much faster compared to that in a ball mill due to the friction and impact caused by the relative movement of rings and a cylinder placed within a casing containing the material, and can effectively delaminate the clay structure which results in size reduction. Fig.4-2 shows a decrease in the intensity of the characteristic basal reflections at 7.13 Å (001) and 3.57 Å (002) as a function of micronization time. Aglietti et al. (1986b) describes the reduction followed by the broadening of basal peak intensity as a consequence of the reduction in crystal size. Here, one hour of micronization produced almost complete collapse of the layer structure producing an X-ray

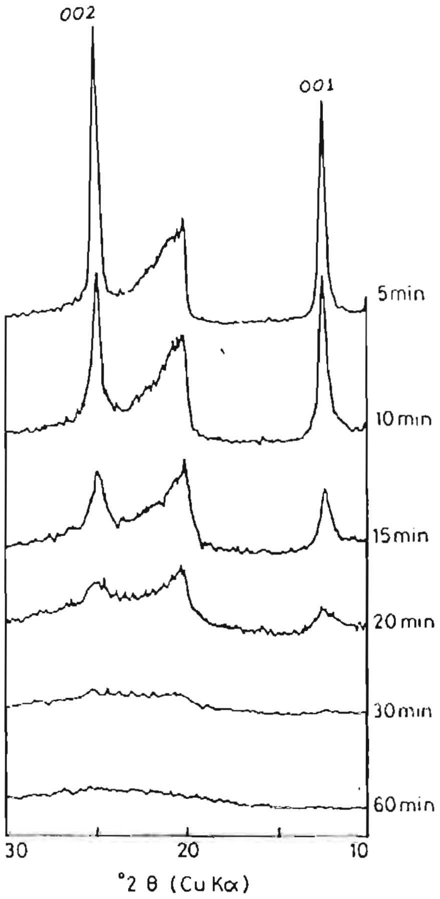

Fig.4-2 X-ray diffraction patterns of kaolinite samples micronized using an oscillatory disc mill.

amorphous material (Fig. 4-2), which resembled the XRD patterns of a metakaolinite sample obtained by thermal modification. Similar behaviour on milling kaolinite was observed by Takahashi (1957), Gonzalez Garcia et al. (1991 and Mackinnon et al. (1995) as well. Same phenomenon was also observed on other minerals like montmorillonite, pyrophyllite, bentonite, sepiolite and chrysotile (Cícel and Kranz 1981; Pérez-Rodríguez et al. 1988; Mingelrin et al. 1978; Cornejo and Hermosin 1988; Suquet 1989; Wiewióra et al. 1993).

Since ball milling is only a mild grinding process where the structural changes of a mineral is not appreciable, the results pertaining to oscillatory milling only are used for further investigations.

2.2. *Surface area measurements*

The surface area (Table 4-1) was found to increase with increasing time of grinding, attained a maximum value for S10 (from 15.11 to 32.43 m^2 g^{-1}) and decreased thereafter (11.11 m^2 g^{-1} for S60). Pore volume also showed complementary results; i.e. 0.0134 cm^3 g^{-1} for the raw sample (S0) which increased to 0.0287 cm^3 g^{-1} for the sample micronized for 10 min. (S10) but decreases to 0.0095 cm^3 g^{-1} (for S60)with further micronization. The initial increase in the surface area and pore volume is due to the cleaving and fracturing of the kaolinite flakes along the basal planes followed by splitting into fine crystals and flakes, accounting to the increase in the surface area and pore volume (Takahashi 1957; Gonzalez-Garcia et al. 1991). On continued micronization, primary particles tend to adhere each other due to the increased surface energy and the action of the amorphous surface layers formed during grinding (Cornejo and Hermosin 1988; Pérez-Rodríguez et al. 1988). Larger agglomerates thus formed behaves as single large particles thereby reducing the available surface

Sample	Grinding time (min.)	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
S0	0	15.11	0.013
S5	5	29.11	0.026
S10	10	32.43	0.029
S15	15	23.18	0.021
S20	20	17.72	0.016
S30	30	11.73	0.010
S60	60	11.11	0.009

Table 4-1. Surface area and pore volume distributions of the kaolinite sample micronized using oscillatory disc mill.

area. The observed reduction in the surface area and pore volume values (i.e. 11.11 m^2 g^{-1} and 0.0095 cm^3 g^{-1} for S60) suggests reaggregation of the disintegrated mass, which was later confirmed by the scanning electron micrographs (Fig. 4-4).

2.3. Particle size analysis

Particle size distribution analysis indicated conflicting results to that manifested in the surface area measurements. After ultrasonic dispersion of sample, the fineness of the particles micronized for 60 min. was definitely more

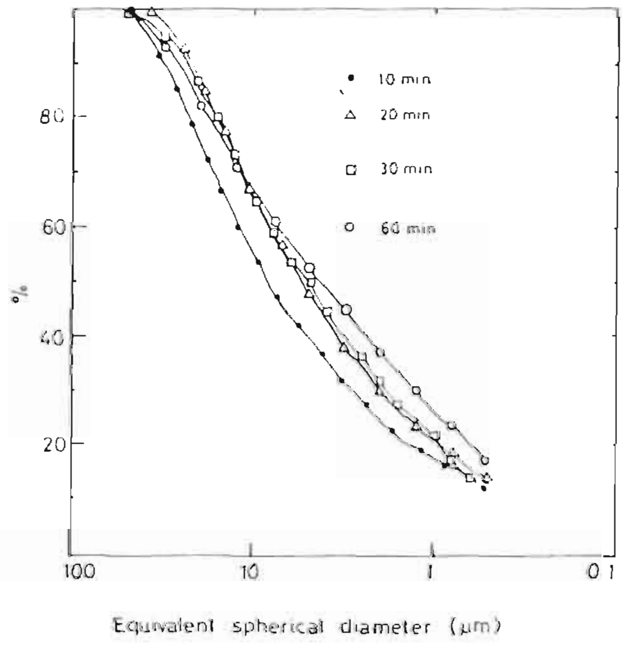

Fig.4-3. Particle size distribution curves for different time treatments.

than that micronized for 10 min. (Fig. 4-3) but surface area and pore volume measurements (Table 4-1) are suggestive of larger agglomerates in the 60 min. micronized sample. It is interesting to note that the samples micronized for 20, 30 and 60 min. have similar percentage fraction at 12 μm (about 68%). One has to consider the fact that an ultrasonic wave could impart several important physical consequences on a particulate dispersion (Einhorn et al., 1989). Moreover the presence of sodium hexametaphosphate (CALGON) in the solution will keep this finely dispersed mass in suspension, thus deriving a thoroughly dispersed slurry. This could be the reason for the observed nature of the particle size distribution pattern.

2.4. Scanning electron micrographs

A reduction in the particle size with increased time of micronization was clearly evident in the scanning electron micrographs (Fig. 4-4). Samples micronized for 10 min. (Fig. 4-4b) showed fine separated platelets having a size almost half that of the raw sample (Fig. 4-4a). This is accompanied by the agglomeration of these newly formed platelets into small balls (Fig. 4-4c, 2 μm average diameter), the size of which tends to increase with time (Fig. 4-4e, 5 μm average diameter). An initial splitting and reduction in the size of kaolinite flakes describes the observed increase in the surface area and pore volume of the sample. These individual platelets further reunite to form small agglomerates measuring ~ 2 μm in diameter (Fig. 4-4c) which further grow to form larger agglomerates (~ 5 μm) with increased time of micronization (Fig. 4-4e). These larger particles behave as individual large particles, thereby reducing the surface area of the sample. Gonzalez-Garcia et al. (1991) observed similar phenomenon using SEM on kaolinites and measured 15-20 μm for these tightly bound small particles whereas Hlavay et al. (1977) observed the same while studying the specific surface area changes by adsorbing water vapor. Studies made by Papirer and Roland (1981) on chrysotile also indicated a significant reduction in the specific surface area while dry grinding. While observing the defiberized and preheated (150°C) asbestos using SEM and TEM micrographs, indicate a rolling up of small chrysotile fibrils.

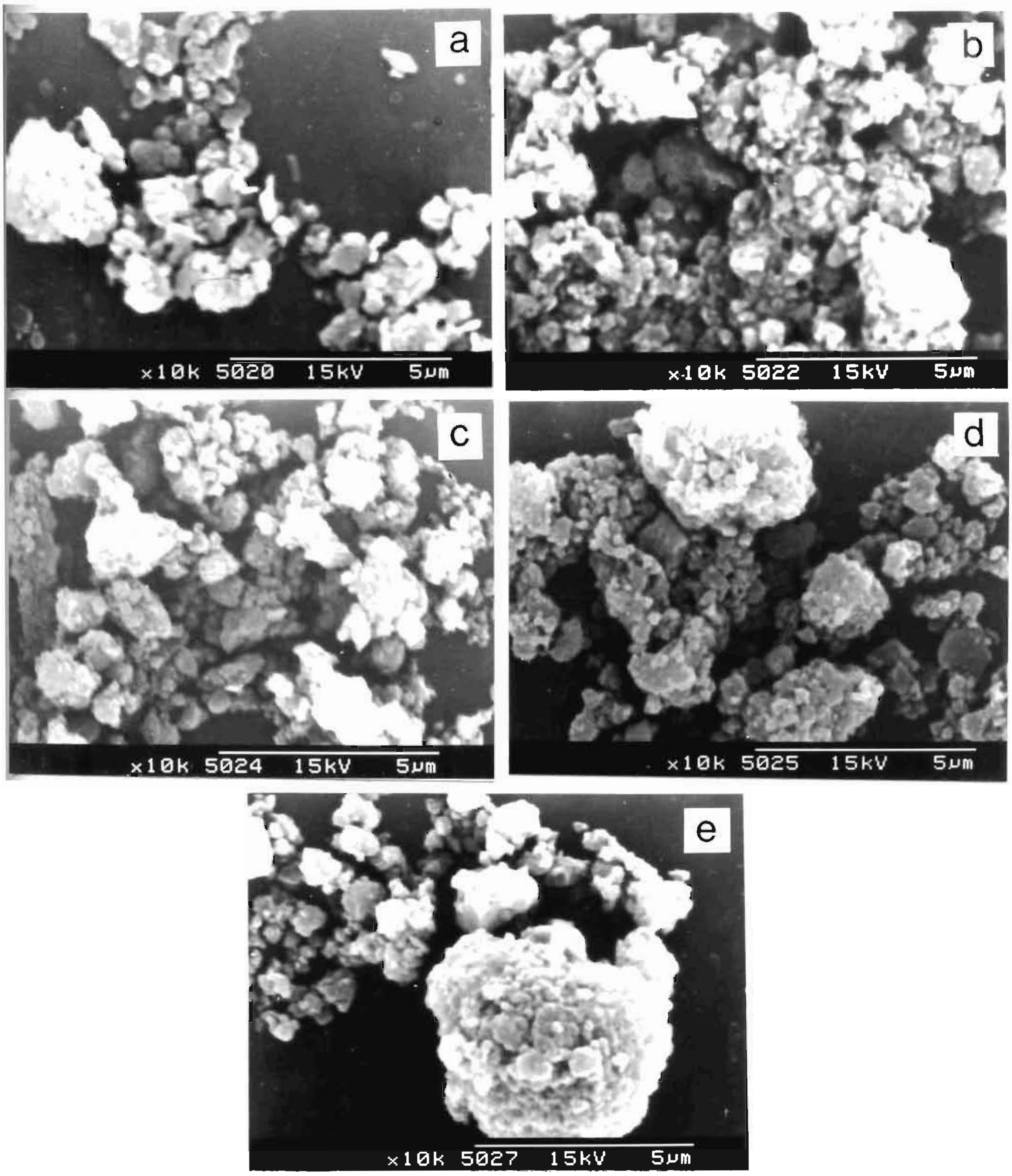

Fig. 4-4. Scanning electron micrographs of raw kaolinite sample (a) and those micronized in an oscillatory mill for 10 min. (b), 20 min. (c), 30 min. (d) and 60 min. (e).

2.5. Infra red absorption spectrometry

Infra red spectra of the raw sample (Fig. 4-5A) and that micronized for 30 min. (Fig. 4-5C) are given in Fig. 4-5. Complete band assignments were provided in Table 4-2. Raw sample exhibited all the characteristic kaolinite peaks. A spectra of metakaolin (i.e. sample A calcined to 600°C for 1 h) was also provided for comparison (Fig. 4-5B). The absorption band at 3708 cm^{-1} in the spectrum of the raw kaolinite was assigned to the stretching vibration of –OH groups located on one side of the sheet (inner surface hydroxyl) (ref. Fig. 1-2) while the sharp absorption band at 3620 cm^{-1} is due to the –OH groups located inside the sheet (inner hydroxyl) (Wilson 1987). Parker (1969) reported that the ratio of these absorption bands represents the nature of the kaolinite, the shape of the particles and also on the regularity of the crystal structure. A reduction in 3708 cm^{-1} and 3620 cm^{-1} peaks indicated the escape of hydroxyl groups on attainment of metakaolinite structure. The reflection bands at 918 cm^{-1} and 938 cm^{-1} represent the Al–OH bending vibration but the absence of the same in the metakaolin suggests the breakage of Al–OH linkage. But the persistence of 1010 cm^{-1} to 1114 cm^{-1} peak intensity explains the existence of Si–O bonds in this structure.

Wave length (cm^{-1})	Assignments
3700	Inner surface –OH stretching vibration
3620	Inner –OH stretching vibration
1114, 1035, 1010	Si–O bending vibration
938, 918	Al–OH bending vibration
692	Si–O stretching vibration
792, 754	Si–O–Al^{iv} compounded vibration
540	Si–O–Al^{vi} compounded vibration
471, 433	Si–O vibration

Table 4-2 Infra red band assignments of kaolinite sample

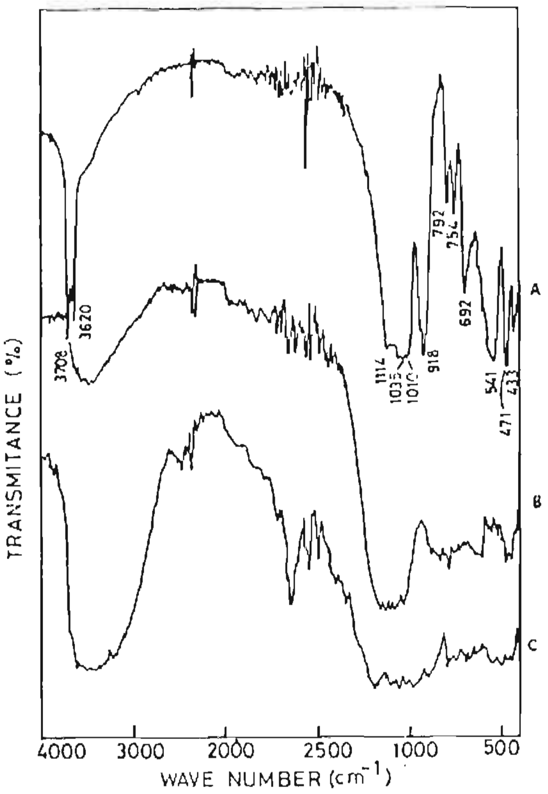

Fig. 4-5. Infra red spectra of raw kaolinite (A), metakaolinite (B) and the sample ground for 30 min. in a disc mill.

Dry grinding the kaolinite sample indicated a broadening of the 3708 cm^{-1} and 3620 cm^{-1} band and those vibrations due to surface –OH's (935 cm^{-1}) and internal –OH (918 cm^{-1}) were also broadened. Moreover the merging of Si–O and Si–O–Al vibration bands supports structural deterioration.

The presence of a broad band with very little change in the intensity (as compared to the raw sample) in the region together with broad Si–O and Si–O–Al bands (as observed in the metakaolin sample; Fig. 4-5B) in the infrared spectrum of the dry ground kaolinite sample (Fig. 4-5C) explains the extent of structural disorder brought in by the process. The broad band around 3500 cm^{-1} indicates adsorbed moisture which is confirmed by the reduced band in the spectrum of the metakaolinite sample. It has to be noted that the samples were oven dried at 90°C overnight and the pellet is prepared under infrared lamp so as to avoid atmospheric moisture. From a structural view point, destruction through dry grinding exposes directed –OH bonds located between the tetrahedral and octahedral layers (amorphization) and with prolonged grinding, –OH groups become less stable. The newly formed vacant sites during the grinding process accommodates extra structural water thereby broadening the -OH bands in the IR spectrum. The persistence of Al–OH vibrations in the 938 cm^{-1} and 918 cm^{-1} band regions indicates the availability of OH groups in the structure. The observed variation in the ratios of the inner surface -OH (3708 cm^{-1}) perpendicular to the kaolin planes and the inner -OH (3620 cm^{-1}) together with its capacity to accommodate external –OH groups confirms structural deterioration in the system (Aglietti et al. 1986b). The appearance of a new band in the 1620 cm^{-1} region also suggests adsorbed moisture (Suquet 1989).

2.6. *Thermal studies*

The raw kaolin exhibits two peaks in its DTA plot (Fig. 4-6); an endothermic peak at 538.1°C, associated with the loss of structural water and an exothermic peak at 999.6°C related to the formation of a spinel-type phase. A reduction in the endothermic peak area (538.1°C) together with a lowering of the peak temperature (to 470°C) was observed as the period of micronization increased. This peak completely disappeared when the sample was ground for 60 min. The reduction in the peak intensity and temperature with micronization can be due to the formation of broken bonds which exposes the directed OH groups and these hydroxyls require less thermal energy to get detached from the mineral structure (Aglietti et al. 1986a; Miloševic et al. 1992). A complementary reduction in the area of the peak at ~500°C was observed in the DTG pattern (Fig. 4-8). The formation of an endothermic hump at ~100°C with increased time of micronization represents adsorbed moisture (Hlavay et al. 1977). A sudden weight loss event observed in the TG pattern of the raw sample is seen to take a constant distribution pattern which starts at ambient temperature for well micronized samples (Fig. 4-7). The constant weight loss observed in the TG pattern supported by the DTG plots explains the structural changes occurred with increased time of micronization. Moreover, these newly created sites could

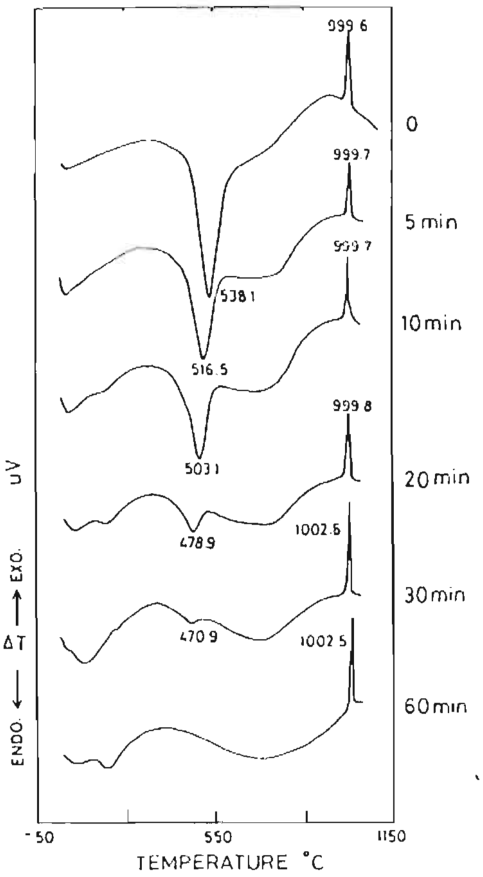

Fig. 4-6. DTA patterns of kaolinite ground in a disc mill

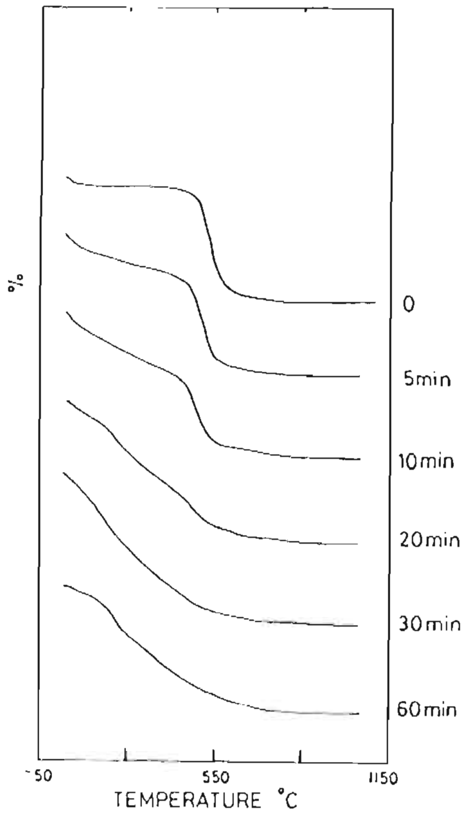

Fig. 4-7. TG patterns of kaolinite ground on a disc mill

possibly accommodate atmospheric moisture which explains the observed endothermic hump in the DTA patterns and the weight loss event in the DTG plots at ~ 100°C.

2.7. Nuclear magnetic resonance studies

The Si NMR spectra of the sample obtained at 60 MHz is given in Fig. 4-9. Raw kaolinite shows a single sharp peak at -92.213 ppm which is in good agreement with the previously reported values of kaolinite (MacKenzie et al. 1985; Massiot et al. 1995). But when the sample was ground for 30 min. (Fig. 4-9B), the silicon resonance was broadened and shifted to around -100 ppm, attributable to the presence of a number of silicon sites of differing bond lengths, bond angles or cation-oxygen bond strengths (Meinhold et al. 1985).

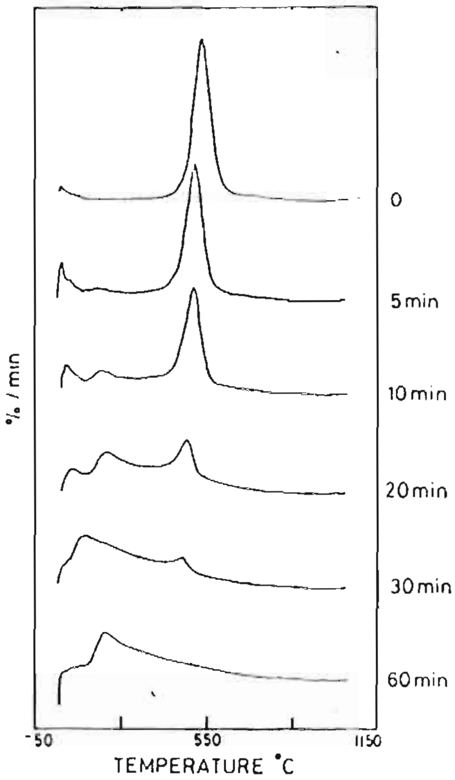

Fig. 4-8. DTG patterns of kaolinite samples under various micronization times.

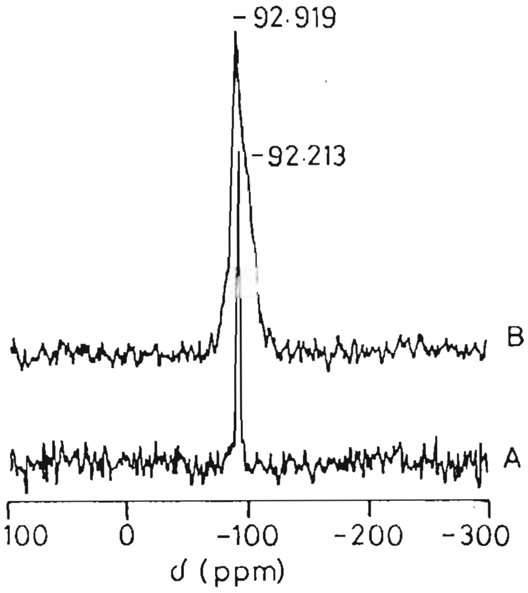

Fig. 4-9. High resolution solid-state 29Si NMR spectra of the raw kaolinite (A) and that ground for 30 min in a disc mill (B).

2.8. Adsorption studies

The adsorption kinetics of Cd, Cu, Pb, Zn and Ni were shown in Figs. 4-10 to 4-14. Almost similar exchange patterns were displayed by the metals studied except lead; an initial increase in the adsorption, which decreases upon prolonged grinding of the sample. This effect can be correlated to the surface area available for the uptake of metal ions (Table 4-1). In Fig. 4-10, Cd attains a slow equilibrium with moderately ground samples (S10) whereas well ground samples, eventhough adsorbs to the least, attains a quick equilibrium. Generally, Pb shows better adsorbability among the metals studied (Fig. 4-12). But, contrary to the other metals, lead quickly attains equilibrium with moderately micronized samples whereas highly micronized samples (S60) displayed delayed equilibrium.

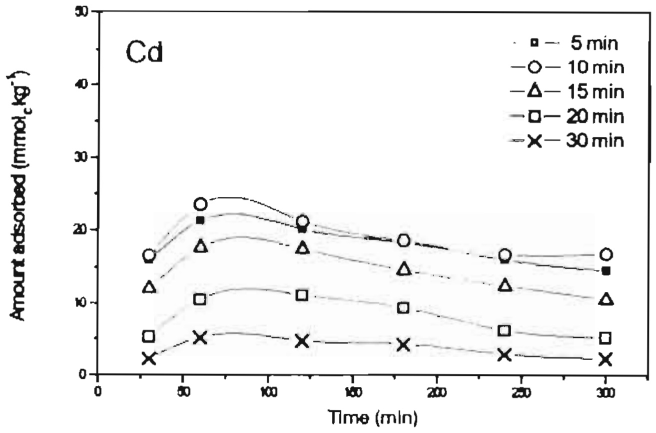

Fig. 4-10 Cd exchange kinetics on kaolinites micronized for various time intervals

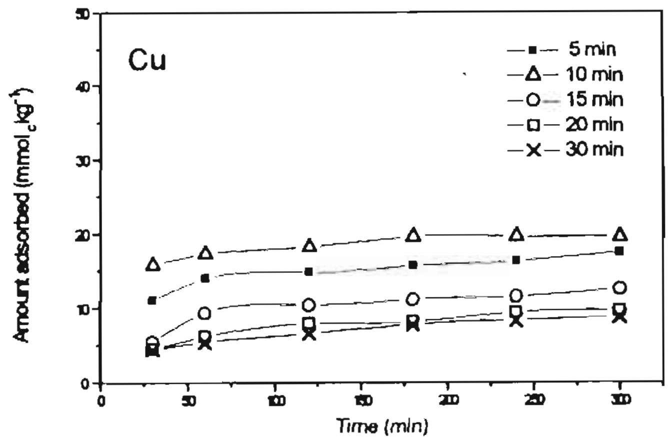

Fig. 4-11 Cu exchange kinetics on kaolinites micronized for various time intervals

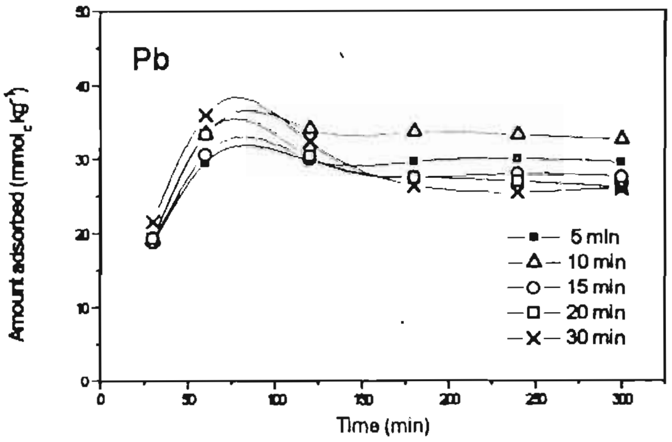

Fig. 4-12 Pb exchange kinetics on kaolinites micronized for various time intervals

Moreover, those highly micronized samples (S60) found to uptake more Pb ions during the initial hours (from 21.6 to 36.1 mmol$_c$ kg^{-1}) but with the advancement of equilibration shows desorption. Similar adsorption kinetics were displayed by Cd, Cu, Zn and Ni.

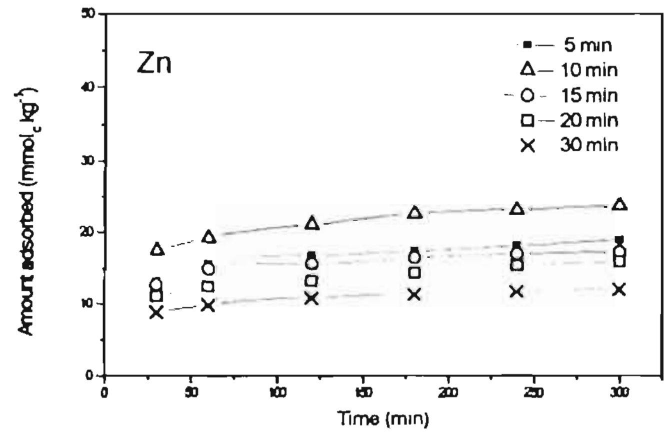

Fig. 4-13 Zn exchange kinetics on kaolinites micronized for various time intervals

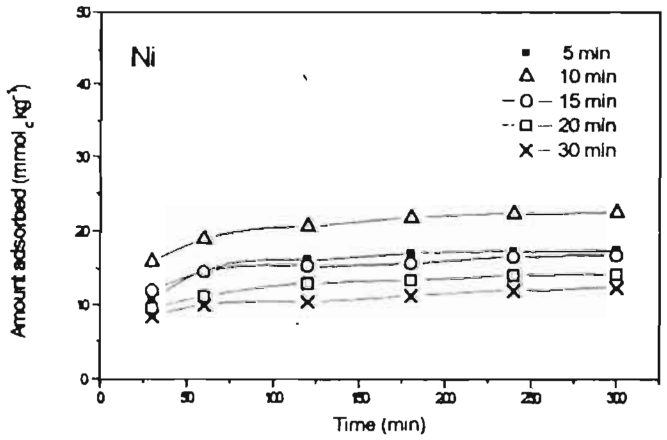

Fig. 4-14 Ni exchange kinetics on kaolinites micronized for various time intervals

As discussed earlier, during micronization, fracturing of kaolinite flakes will expose both inner and surface Al-OH and Si-O sites which accounts for the observed increase in the specific surface area as well as its exchangeability. But with prolonged dry grinding, the size of the kaolinite platelets will be reduced drastically which tends to neutralize itself by forming agglomerates thereby existing in a minimum surface energy conditions. These agglomerated platelets behave as a single large unit which explains the observed reduction in the surface area as well as its exchangeability. Laws and Page (1945) suggests the formation of a new permutite-like material (a combination of amorphous silica and alumina groups and free bases) which naturally accumulates on the flat surfaces of the plates, rather than edges, thus adding to the thickness of the plates thus reducing the exchange capacity of the mineral.

3. CONCLUSION

Two methods of micronization (ball milling and oscillatory milling) was tried on the crystalline structure of kaolinite to study their effect on the adsorption/ion-exchange properties of toxic heavy metals. Micronization using a ball mill was found to be a slow process where dry grinding proved to have some effect compared to wet grinding. But grinding in an oscillatory mill could produce almost complete destruction of the clay structure (amorphization) within one hour of grinding time. Adsorption kinetics for Cd, Cu, Zn and Ni show a slight improvement during the initial stages of grinding, brought in by the delamination after which the rate of adsorption decreases. For lead ions, there is an initial increased sorption with highly micronized samples which reverts to the pattern of kinetics displayed at a later stage. It was also observed that it takes a longer period for attaining equilibrium compared to cadmium and copper.

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CHAPTER 5

CHEMICAL ALTERATION

1. INTRODUCTION

An attempt to improve the metal ion exchange capacity of a kaolinite sample by subjecting to a highly alkaline environment is discussed in this chapter. At alkaline pH conditions (pH >11), kaolinite is known to possess stoichiometric dissolution (Xie and Walther 1992; Carroll-Webb and Walther 1988). This leaching out and reaggregation phenomenon is known to produce new crystal structures where the kaolinite will get ultimately converted to a totally different mineral. The transformation of layered kaolinite to three dimensionally ordered zeolite minerals were already reported (Roland, 1989).

The use of zeolites as cation exchangers in waste water treatments to remove ammonium and radioactive wastes are practiced widely (Davis et al. 1988; Wilson et al. 1982; Kasuo 1978; Hayhurst 1978; Hagiwara and Uchida 1978; Mercer 1978). Natural as well as synthetic zeolites have been shown to selectively extract trace quantities of heavy metals from waste water (Semmens and Seyfarth 1978) but such reports on the use of zeolites for the removal of heavy metal pollutants are scarce. The focus on the synthesis of new zeolites has resulted in the introduction of other minerals considered as precursors which are known equally good in taking up toxic metals. Suib (1993) provides an excellent review on the synthesis, characterization and application of these minerals. The ion exchange properties of the zeolites, both natural and artificial, are discussed in great detail (Coker and Rees 1992; Maliou et al. 1992; McAleer et al. 1991; Komerneni 1978; Komerneni and Roy 1981).

In our attempt to develop a better adsorbent from the low adsorbing kaolinite, a new material which is a mixture of zeolites was obtained. An appreciable improvement in the exchangeability was also observed.

2. EXPERIMENTAL

Kaolinite sample from Thonnakkal (Trivandrum district) was used for chemical alteration studies. A portion of the sample was metakaolinized as described in chapter 3 and used for this study. 10 g each of the raw kaolinite sample was weighed into several plastic bottles, mixed thoroughly with 100 ml of 2 M NaOH solution and aged upto 100 days, at room temperature, under stagnant conditions. After the stipulated time of aging, the contents of each bottle is transferred into a container and washed thoroughly with distilled water, until free of excess sodium ions. It is then dried overnight in an oven at 60°C, characterized and used for further adsorption studies (denoted ***raw60***, ***raw70***, ***raw100***, etc. for samples aged in NaOH for 60,70 and 100 days, respectively). Metakaolinite sample was also subjected to similar NaOH treatment (denoted ***meta60***, ***meta70***, ***meta100***, etc.). These samples were characterized as described in the previous chapters. The metal exchange capacity of these two types of samples was studied using Cd, Cu, Pb, Zn and Ni as the exchanging metal ion following the procedure described in chapter 3. Samples are equilibrated under different conditions of time, temperature and concentration of metal ion.

3. RESULTS AND DISCUSSIONS

3.1. X-ray diffraction studies

X-ray diffractograms of the raw sample subjected to 60 and 70 days of equilibration with NaOH are given in Fig. 5-1(B & C respectively). X-ray pattern of an untreated raw sample is also given for comparison (Fig. 5-1A). From the XRD patterns, it is clear that with time of aging, the intensity of the characteristic kaolinitic peaks decreases. The formation of new peaks is evident in Fig. 5-1B, which intensifies on Fig. 5-1C. The peaks at 7.14, and 3.56 together with the triplets at 4.33, 2.56 and 2.33 are characteristic of kaolinite. The formation of new peaks at 6.25, 3.61, 2.79 and 2.55 are all indicative of the formation of sodalite. The presence of kaolinitic basal reflection suggests its coexistence but the reduction in the intensity indicates the partial transformation of kaolinite to sodalite.

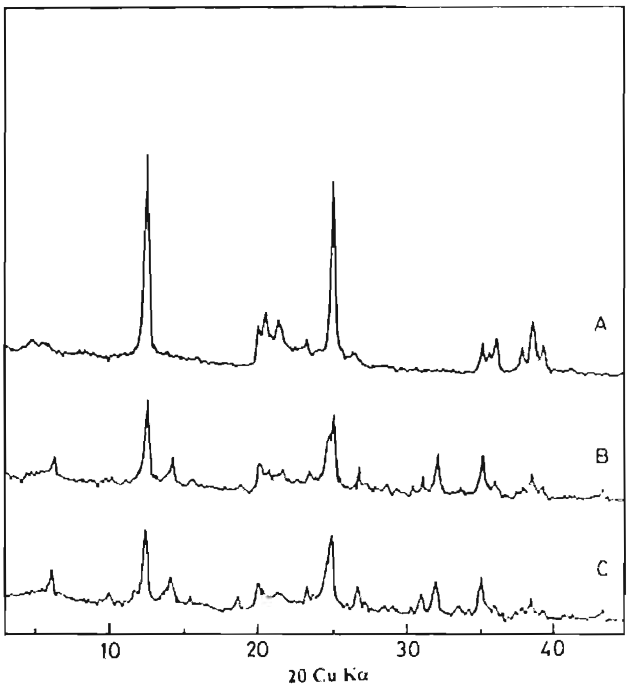

Fig. 5-1 XRD patterns of raw kaolinite sample (A) aged in 2M NaOH solution for 60 (B) and 70 (C) days.

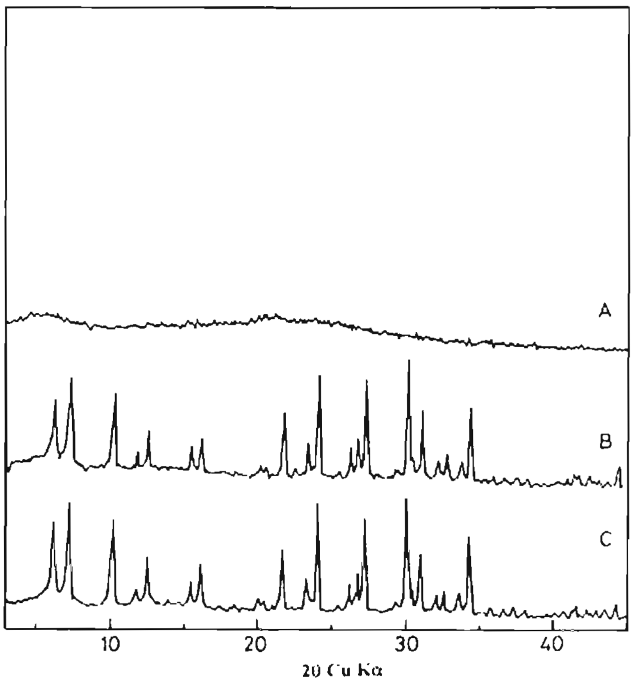

Fig. 5-2 XRD patterns of metakaolinite sample (A) aged in 2M NaOH solution for 60 (B) and 70 (C) days.

XRD pattern of the metakaolinite sample aged for 60 and 70 days are given in Fig. 5-2(B&C). XRD pattern of a metakaolinite sample without NaOH treatment is also given for comparison. Here also, with period of aging, the formation of new peaks is observed. The peaks at 7.27, 8.63, 7.06, 3.28, 2.97 and 2.61 resembles hydrated Linde type A (Zeolite 4A). The peaks at 5.72 and 3.40 resembles analcime and the peak at 14.27 represents NaX (Faujasite). Hence it can be concluded that this sample is a mixture of Zeolite 4A, analcime and traces of NaX. It has to be noted that the sample were kept idle with out any external energy disturbance. The formation of all these minerals is indicative of the extend of alteration taking place in the amorphous metakaolin sample as compared to that in the raw crystalline kaolinite sample. Another interesting feature is that, under similar conditions of alkalinity crystalline kaolinite produced sodalite whereas amorphous metakaolinite produced Zeolite 4A, analcime and NaX. Further increasing the aging time of the metakaolinite sample showed an increase in the intensity of the newly formed phases but no new additional phase was produced in the process.

3.2. Infrared spectroscopic studies

The infrared spectra of the raw kaolinite sample and metakaolinite aged for 60 days are given in Fig. 5-3. The presence of characteristic double peaks at 3704 and3632 cm^{-1} together with the 3675 cm^{-1} peak, is indicative of the crystallinity in kaolinite. The peaks at 3704 and 3632 cm^{-1} represents the internal surface –OH groups and internal –OH groups, respectively. The presence of a broad band at 3473 cm^{-1} together with a large peak at 1652 cm^{-1} represents adsorbed moisture. It has to be noted that, the sample is thoroughly dried at 100±2°C overnight and the sample was prepared under infrared lamp, thus preventing any moisture into the sample. The presence of a broad band with small indentations describes the rearrangement of the Si–O and Al–O bonds in the lattice. This also suggests the formation of new mineral phases. The presence of a broad band at ~3400 and ~1000 cm^{-1} in the infrared spectra of the modified kaolinite sample suggests the amorphous nature of the sample. The

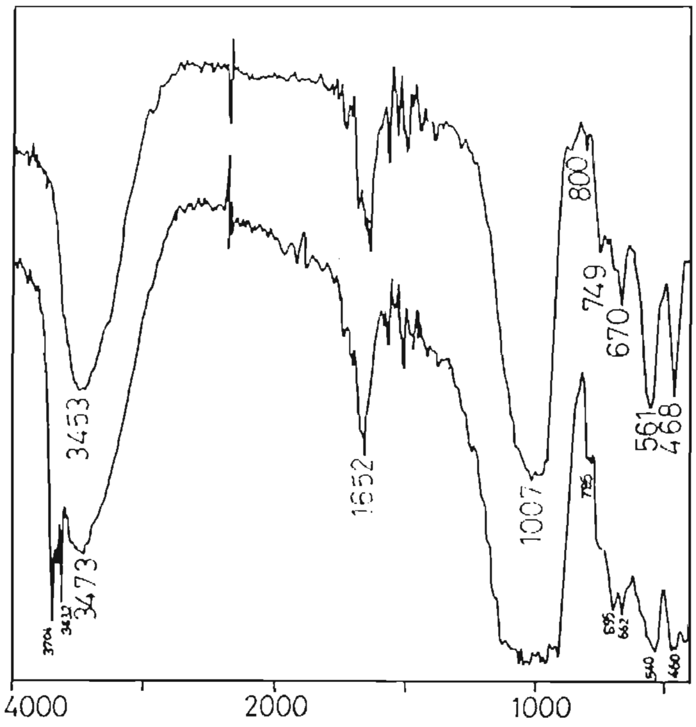

Fig. 5-3 Infrared spectra of the raw and metakaolinite sample aged for 60 days in 2 M NaOH solution

presence of another broad band at 1640 cm^{-1} is suggestive of adsorbed moisture which can get trapped inside the zeolitic structure of the newly formed material.

3.3. Scanning Electron Microsopic studies

Figs. 5-4a&b indicate the scanning electron micrographs of the phase transformations during alkali treatment of kaolinite and metakaolinite. The tubular crystals of Fig. 5-4a indicate sodalite and a mixture of mixture of zeolite 4A and analcime are clearly visible of the other (Fig. 5-4b)..

3.4. Adsorption studies

The metal exchange capacity of the material thus prepared with respect to concentration is given in Figs. 5-5 to 5-9. The effect of concentration on the uptake of Cd by raw kaolinite (Fig. 5-5a) and metakaolinite (Fig. 5-5b) aged for 100 days indicates similar exchange capacity. Here, metakaolinite is known to take up more Cd than raw kaolinite(i.e. 4444 $mmol_c$ kg^{-1} and 4311 $mmol_c$ kg^{-1} from 0.1M Cd solution).

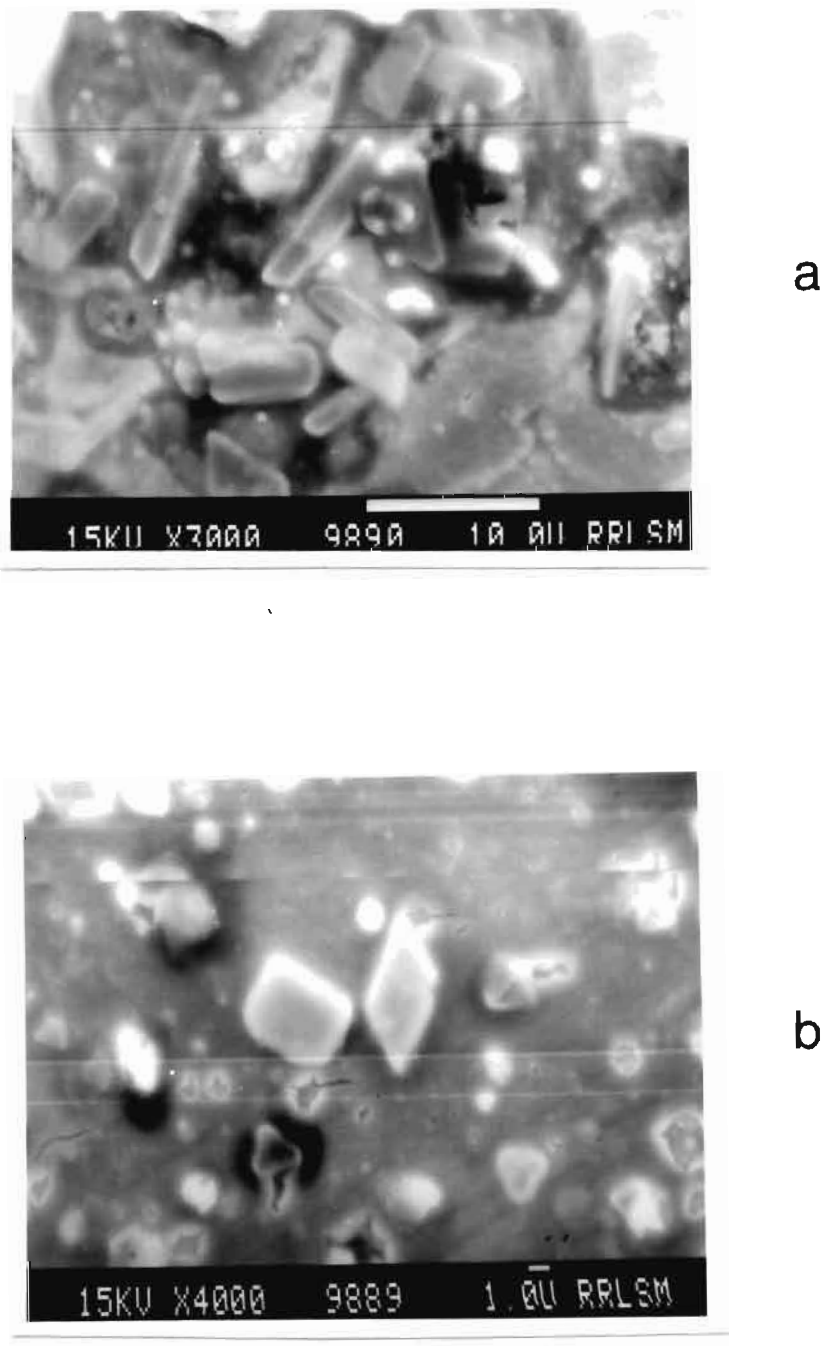

Fig. 5-4 Scanning electron micrographs of (a) Kaolinite and (b) Metakaolinite after alkali treatment of 70 days

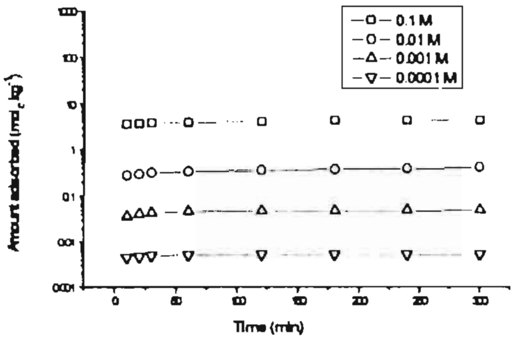

Fig. 5-5a Cd exchange kinetics for *raw100*

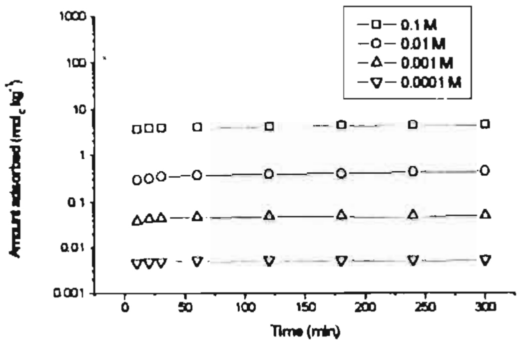

Fig. 5-5b Cd exchange kinetics for *metal00*

Moreover, with increasing concentration, the amount of Cd sorbed onto the material surface also increases. The amount of Cd sorbed by raw kaolinite and metakaolinite (in mmol$_c$ kg^{-1})are as follows: 4310 & 4440 from 0.1 M; 416 & 447 from 0.01 M; 49.9 & 50.0 from 0.001 M; 5.3 & 5.45 from 0.0001 M; respectively. Since metakolinite sample showed increased exchangeability, further studies on their metal exchange capacity with concentration are given in Figs. 5-6 to 5-9. The effect on sorption with concentration on all these metals are similar. But the amount of metal sorption varied with metal, giving a general trend Pb > Cu > Ni > Cd > Zn.

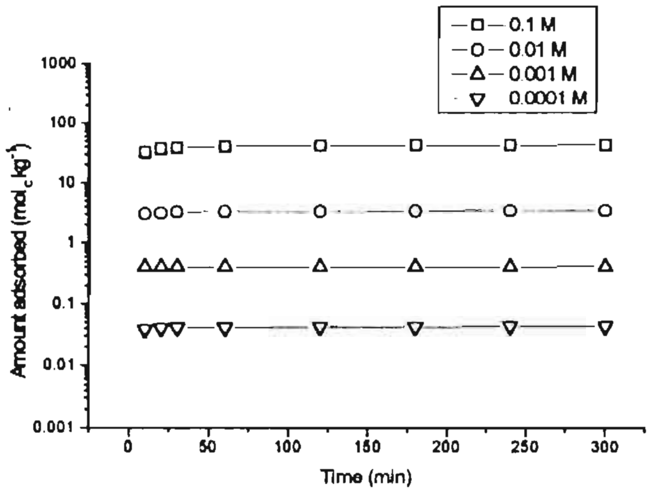

Fig. 5-6 Cu exchange kinetics for *metal00*

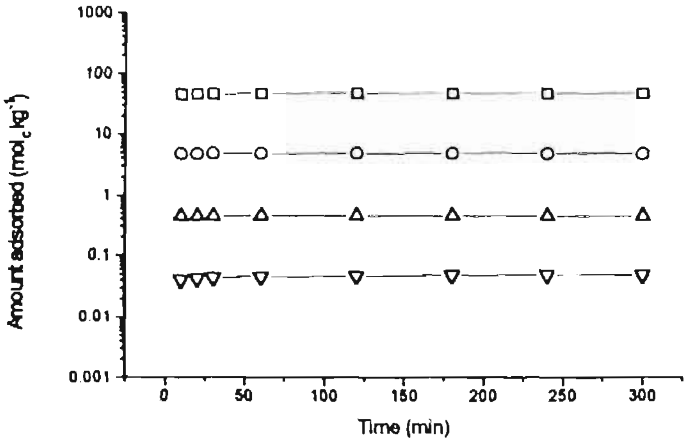

Fig. 5-7 Pb exchange kinetics for *metal00*

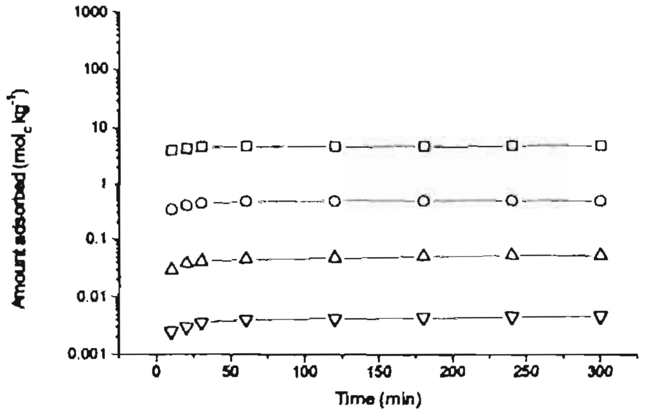

Fig. 5-8 Zn exchange kinetics for *metal00*

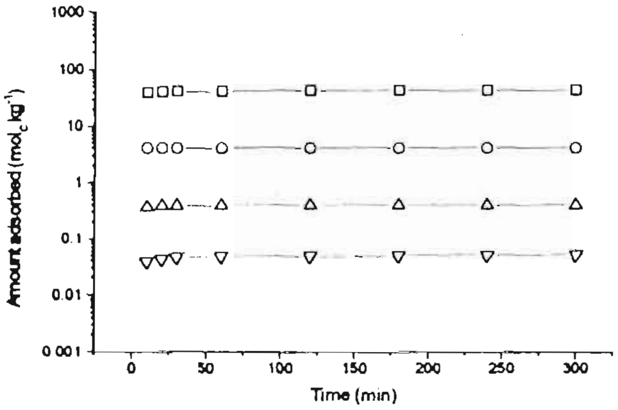

Fig. 5-9 Ni exchange kinetics for *metal00*

The effect of ambient temperature was also studied for the samples and the graphs are given in Fig. 5-10 to 5-13. Here Cd, Pb and Ni shows preference for 40°C (i.e., 42.46, 48.83 and 42.22 mmol$_c$ kg^{-1} for *raw100* and 40.87, 50.56 and 41.8 mmol$_c$ kg^{-1} for *metal00*, whereas Cu and Zn preferred 50°C (i.e.,41.77 and 37.1 mmol$_c$ kg^{-1} for *raw100* and 43.8 and 37.9 mmol$_c$ kg^{-1} for *metal00*, respectively). Similar preferences were also displayed by samples aged for 70 days.

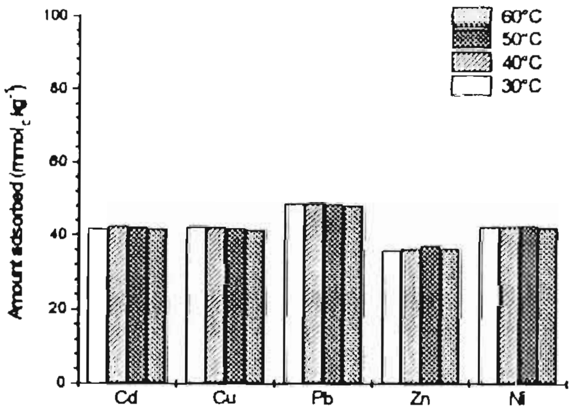

Fig. 5-10 Effect of temperature on the sorption of metal ions on *raw100*

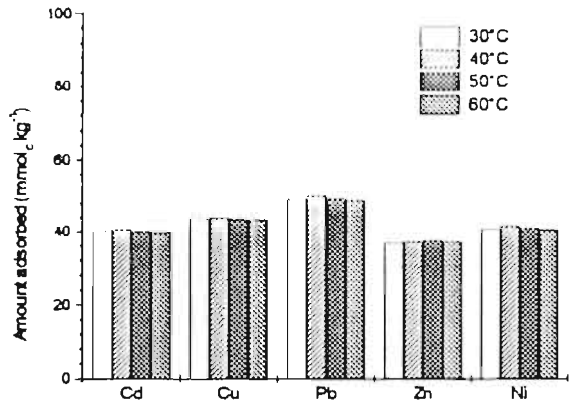

Fig. 5-11 Effect of temperature on the sorption of metal ions on *metal00*

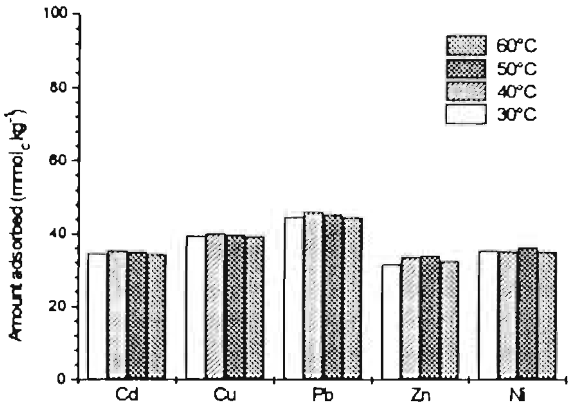

Fig. 5-12 Effect of temperature on the sorption of metal ions on *raw70*

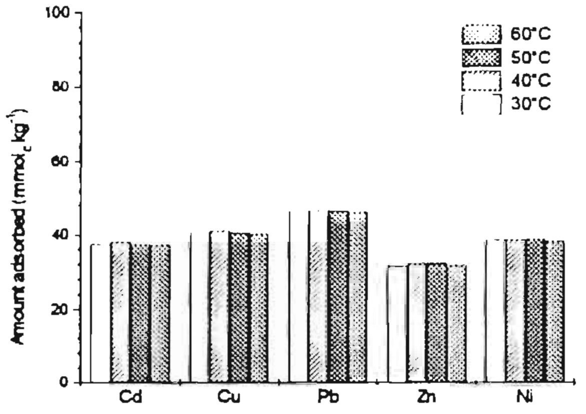

Fig. 5-13 Effect of temperature on the sorption of metal ions on *meta70*

3.4. *Adsorption isotherm*

Adsorption data for a wide range of adsorbate concentrations are most conveniently described by adsorption isotherms, such as Langmuir or Freundlich isotherm, which relate adsorption density q_e to equilibrium adsorbate concentration in the bulk fluid phase, C_e.. In Langmuir isotherm, the equilibrium concentration C_e and

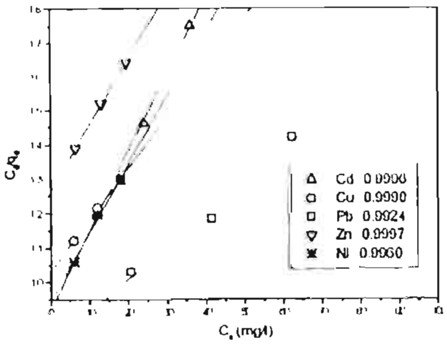

Fig. 5-14 Langmuir plots for the adsorption of metal ions on *raw100*.

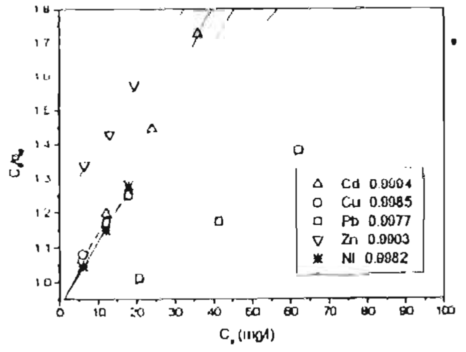

Fig. 5-15 Langmuir plots for the adsorption of metal ions on *meta 100*.

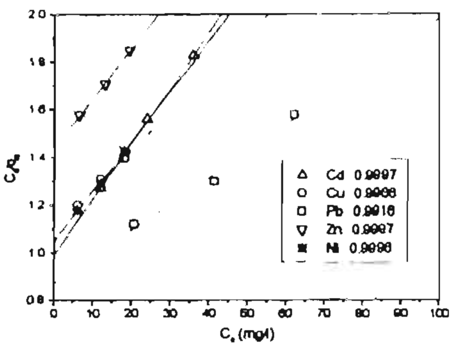

Fig. 5-16 Langmuir plots for the adsorption of metal ions on *raw70*.

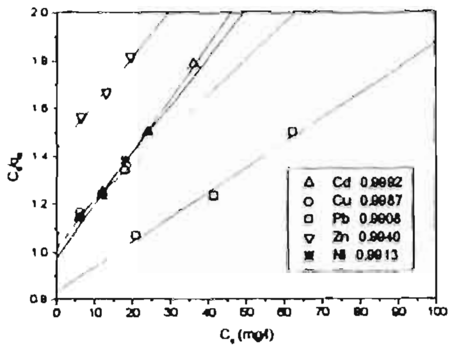

Fig. 5-17 Langmuir plots for the adsorption of metal ions on *meta70*.

the amount of metal adsorbed at equilibrium time was plotted as C_e/q_e vs C_e. (Figs. 5-14 to 5-17). These plots are linear and the Langmuir constants Q_0 and b were calculated from the slope and intercept of the plots. The values for raw kaolinite sample after 100 and 70 days of aging are given in Table 5-1 and the corresponding values for metakaolinite sample after 100 and 70 days of aging are given in Table 5-2. The Langmuir constants increased with period of aging.

Metal	Aged 100 days				Aged 70 days			
	Q_0 (mg/g)	b (l/mg)	n	k_f (mg/g)	Q_o (mg/g)	b (l/mg)	n	k_f (mg/g)
Cd	43.73	0.0248	1.378	1.567	42.86	0.0235	1.479	1.762
Cu	67.43	0.1435	1.153	1.135	61.84	0.0146	1.158	1.065
Pb	106.16	0.0115	1.394	2.324	90.01	0.0127	1.434	2.272
Zn	52.08	0.0152	1.175	0.955	48.15	0.0144	1.162	0.0825
Ni	50.63	0.0208	1.226	0.760	47.62	0.0200	1.206	1.158

Table: 5-1 Langmuir constants Q_0 and b and Freundlich constants n and K_f of raw kaolinite

The essential characteristics of a Langmuir plots are can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L (Hall, et al., 1966; Weber and Chakravorthy, 1974). The R_L values for different concentrations are listed in Table 5-3. The R_L values between 0 and 1 are considered favorable

Metal	Aged 100 days				Aged 70 days			
	Q_0 (mg/g)	b (l/mg)	n	k_f (mg/g)	Q_o (mg/g)	b (l/mg)	n	k_f (mg/g)
Cd	45.54	0.0236	1.483	1.895	44.86	0.228	1.466	1.782
Cu	70.57	0.0142	1.152	1.177	67.43	0.0139	1.145	1.083
Pb	111.98	0.0109	1.383	2.317	96.34	0.0124	1.423	2.340
Zn	55.31	0.0149	1.164	0.981	51.60	0.0135	1.152	0.8253
Ni	52.16	0.0206	1.213	1.318	50.20	0.0195	1.199	1.185

Table: 5-2 Langmuir constants Q_0 and b and Freundlich constants n and K_f of metakaolinite

adsorption whereas $R_L > 1$ is considered unfavorable. Table 5-3 indicates favorable adsorption of metal ions by modified kaolinite.

Metal	Conc. (mg/l)	Raw kaolinite aged		Metakaolinite aged	
		100 days	70 days	100 days	70 days
Cd	12.00	0.7707	0.7800	0.7793	0.7852
	20.00	0.6269	0.6394	0.6384	0.6463
	36.00	0.5283	0.5417	0.5407	0.5492
Cu	6.00	0.5373	0.9186	0.9215	0.9230
	12.00	0.3674	0.8511	0.8544	0.8510
	18.00	0.3790	0.7921	0.7964	0.7999
Pb	20.71	0.8076	0.7918	0.8158	0.7957
	41.42	0.6774	0.6553	0.6890	0.6607
	62.13	0.5833	0.5590	0.5962	0.5648
Zn	6.50	0.9101	0.9145	0.9117	0.9193
	13.00	0.8354	0.8470	0.8377	0.8507
	19.50	0.7714	0.7809	0.7749	0.7916
Ni	6.00	0.8890	0.8929	0.8900	0.8953
	12.00	0.8003	0.2941	0.8018	0.8104
	18.00	0.7276	0.2174	0.7295	0.7402

Table: 5-3 Equilibrium parameter R_L of the different metal ions on aged kaolinite and metakaolinite

The Freundlich adsorption isotherm was also applied for the adsorption of metal ions by modified kaolinite samples and are given in Figs. 5-18 to 5-21. Here, log C_e vs log q_e are plotted from which the Freundlich constants k_f and n are calculated from the slope and intercept. n gives an indication of the favourability and k_f, the capacity of the adsorbent (Pollards et al., 1991). The values of k_f and n are given in Tables 5-1 and 5-2. The plots obtained are linear which indicate that the adsorption of metal ions on modified kaolinites also follows Freundlich isotherm model. The values of n between 2 and 10 represent good adsorption (Mckay, et al., 1980).

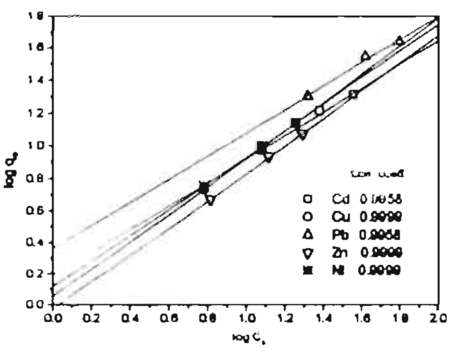

Fig: 5-18 Freundlich plots for the adsorption of metal ions on *raw100*.

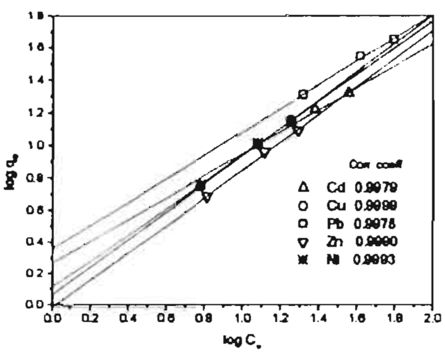

Fig: 5-19 Freundlich plots for the adsorption of metal ions on *meta100*.

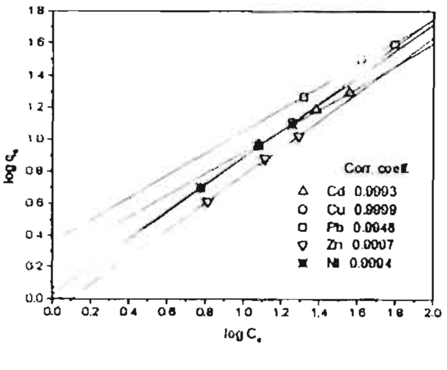

Fig: 5-20 Freundlich plots for the adsorption of metal ions on *raw70*.

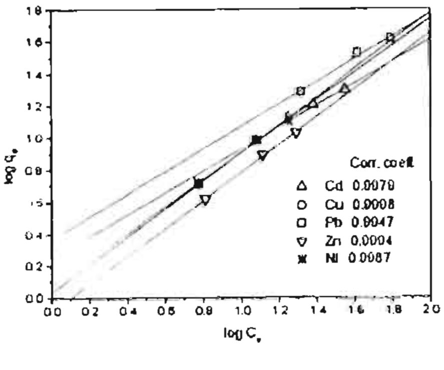

Fig: 5-21 Freundlich plots for the adsorption of metal ions on *meta70*.

4. CONCLUSION

Under the similar conditions of alkalinity (2 M NaOH at room temperature), crystalline kaolinite produced sodalite, whereas amorphous kaolinite produced Zeolite 4A, analcime and NaX. Adsorption studies shows that the modified kaolinite can be used as an adsorbent to effectively remove metal ions from waste water. Lead was preferred among the metal ions studied.

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