



CHAPTER II

Literature Review

2.1 Over View

Most active portions of the soil are the components in colloidal state. The two distinct types of colloidal matter, i.e., minerals or inorganic constituents and organic matter, exist in intimate intermixture. The representative of the latter one is humus. Nature and characteristic of humus will be emphasized latter on. Clay minerals consist of two general groups. One is silicate clays and the other is iron-aluminium oxide and hydrous oxide group. The effects of types, structures and properties of clays, especially silicate clays, on soil reaction will be discussed in the next part of this chapter.

2.2 Clay Minerals

2.2.1 Silicate Clays.

2.2.1.1 Montmorillonite, $[\text{Na}_x(\text{Al}_{2-x}\text{Mg}_x, \text{Si}_4\text{O}_{10}(\text{OH})_2]$

Montmorillonite is 2:1-layer silicate type. The unit layer is one octahedral sheet sandwiched between, and sharing oxygen atom with, two tetrahedral sheets. It is high colloidal activity, including high plasticity and cohesion, high swelling and shrinkage. Normally, it occurs as a fine clay and slightly pH-dependent cation exchange capacity (Fig 2.1 a).

2.2.1.2 Kaolinite, $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$

The structural unit is formed by the superposition of a tetrahedral sheet upon an octahedral sheet. It is called 1 : 1-layer silicate type. Kaolinite occurs commonly in soils, often as hexagonal crystals with an effective diameter of 0.2 to 2 μm . Generally, it is a coarse clay with

low colloidal activity, including low plasticity and cohesion and low swelling and shrinkage. Its cation exchange capacity is highly pH-dependent suggesting that isomorphic substitution is not the predominant source of charge. (Fig. 2.1.b).

2.2.1.3 Illite $[K_{1.33} (Si_{6.66} Al_{1.33}) Al_4 O_{20} (OH)_4]$

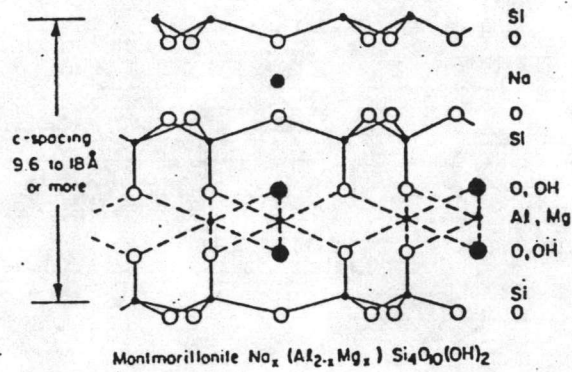
Similar to montmorillonite, illite is 2 : 1-type lattice, one octahedral sheet sandwiched between two tetrahedral sheets. The result of partial silicon atoms in silica sheet are occupied by aluminium atoms cause a high net negative charge in the tetrahedral layer. Potassium ions are satisfied this charge between the crystal units and act as a binding agent. Hence, its particles are much larger than those of montmorillonite and unexpandable like (Fig. 2.1.c).

2.2.2 Iron-Aluminium Oxide and Hydrous Oxide

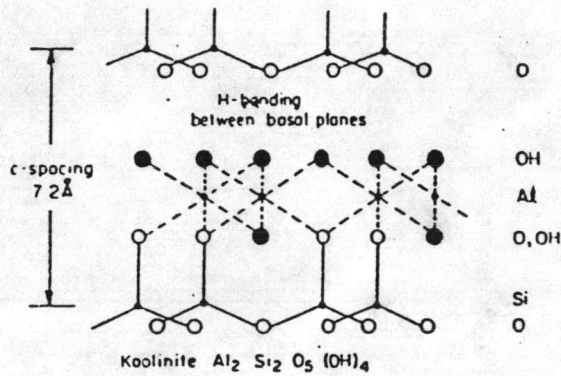
The oxides of iron and aluminium are almost universal constituents of soil clays occurred in several mineralogical forms as discrete particles or associated with surfaces of other minerals. Eventhough, they are usually present in lesser amounts than the silicate clay minerals they may be important in their effect on soil properties. Iron oxides are found in most soils and are responsible for the red, orange, yellow and brown colors that are so widely used to distinguish soils and soil horizons. Goethite (α -FeOOH) is the commonest iron oxide in soils and is found in temperate, sub-tropical and tropical regions. Boehmite (γ -AlOOH) and Gibbsite (γ -Al(OH)₃) are the only aluminium oxide and hydroxide found in many strongly weathered soils of tropical regions.

2.3 Organic Colloid or Humus

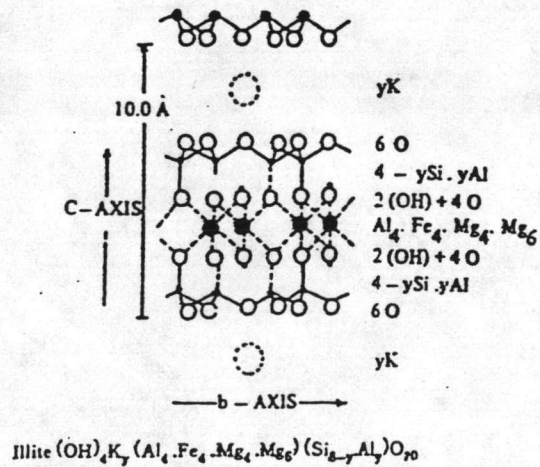
As mentioned above, humus acts as soil organic colloids, and it may take part in soil sorption as well as clay minerals. This part of the paper deals with nature and



(a) montmorillonite



(b) kaolinite



(c) illite

FIGURE 2.1 Schematic diagram of the crystal structural of silicate clays
Source : Bohn, McNeal, and O'connor (1979).

characteristics of humus.

2.3.1 Definition of Humus

Humus is a complex and rather resistant mixture of brown or dark amorphous and colloidal substances modified from the original tissues or synthesized by the various soil organisms (Brady, 1974).

2.3.2 Nature and Characteristics of Humus

Humus is highly colloidal, amorphous and not crystalline, low plasticity and cohesion, and black or brown color of soil, and shows adsorptive capacity on its surface area. Humus is similar to inorganic colloid by a highly charged anion or micelle. Carbon, hydrogen and oxygen are major composition of the humic micells with minor quantities of nitrogen, sulfur, phosphorus and other elements. It is thought that the major source of negative charged are partially neutralized carboxylic ($-\text{COOH}$) and phenolic ($\text{C}_6\text{H}_5-\text{OH}$) groups associated with central units of varying size and complexity (Fig. 2.2).

Similar to silicate clays, the charge on humus colloids is pH dependent. Under strongly acid conditions hydrogen is tightly bound and not be easily replaced by other cations. Therefore, the colloid exhibits a low negative charge. In contrast, after addition of bases resulted in consequently rising in alkalinity, the hydrogen from the carboxyl groups firstly ionized and then from the phenolic groups, and it is replaced by other cations. Humus consists of at least three classes :

(a) fulvic acid, lowest in molecular weight and lightest in color, soluble in both acid and alkaline,

(b) humic acid, medium in molecular weight and color, soluble in alkaline but insoluble in acid ; and

(c) humin, highest in molecular weight, darkest in color, and insoluble in both acid and alkaline.

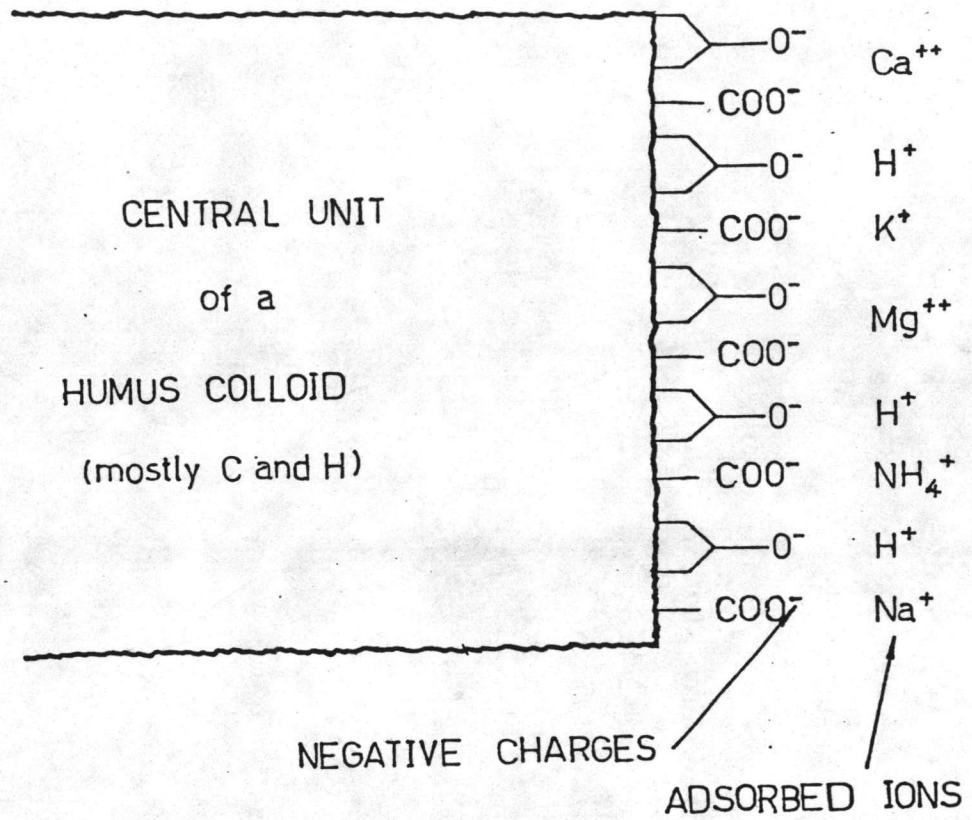


FIGURE 2.2 Adsorption of cations by humus colloids

Source : Brady (1974).

2.4 Adsorption and Desorption

This part is dealt with the interactions which retain mobile chemical species in the soil environment. Emphasis is centered on the binding of cations to soil colloidal particles, i.e, humus and clay minerals. It will be primarily concerned here with uptake from the liquid phase by solid soil components and then release from solid soil components to the liquid phase.

2.4.1 Definition of Adsorption and Desorption

Adsorption is the process of a chemical species passes from one bulk phase to the surface of another where it accumulates without penetrating the structure of this second phase. Desorption refers to the reverse of the process of adsorption (Burchill, Hayes and Greenland, 1981). When adsorption takes place, the soil solid phase is regarded as the adsorbent. The reaction will continue until the concentration of adsorptive in the bulk phase has not been changed at an appropriate time. Hence, the system reached an equilibrium state. The relationships between the concentration of adsorbate and its bulk phase at a given temperature termed the adsorption isotherm.

2.4.2 Classes of Adsorption Isotherm

On the basis of initial slope, Giles, Smith and Huitson (1974, cited by Burchill, et.al.,1981) stated that adsorption isotherms are classified as Langmuir isotherm (L-type), High affinity (H-type), Sharp isotherm (S-type), and Constant partition (C-type) as shown in Fig.2.3.

2.4.2.1 L-curve Isotherm

For the L-type, initial slope does not increase with the concentration of adsorbate in the bulk solution. This property is result of a high relative affinity of the adsorbent for substance at low concentration coupled with a decreasing amount of adsorbing surface as the surface excess of

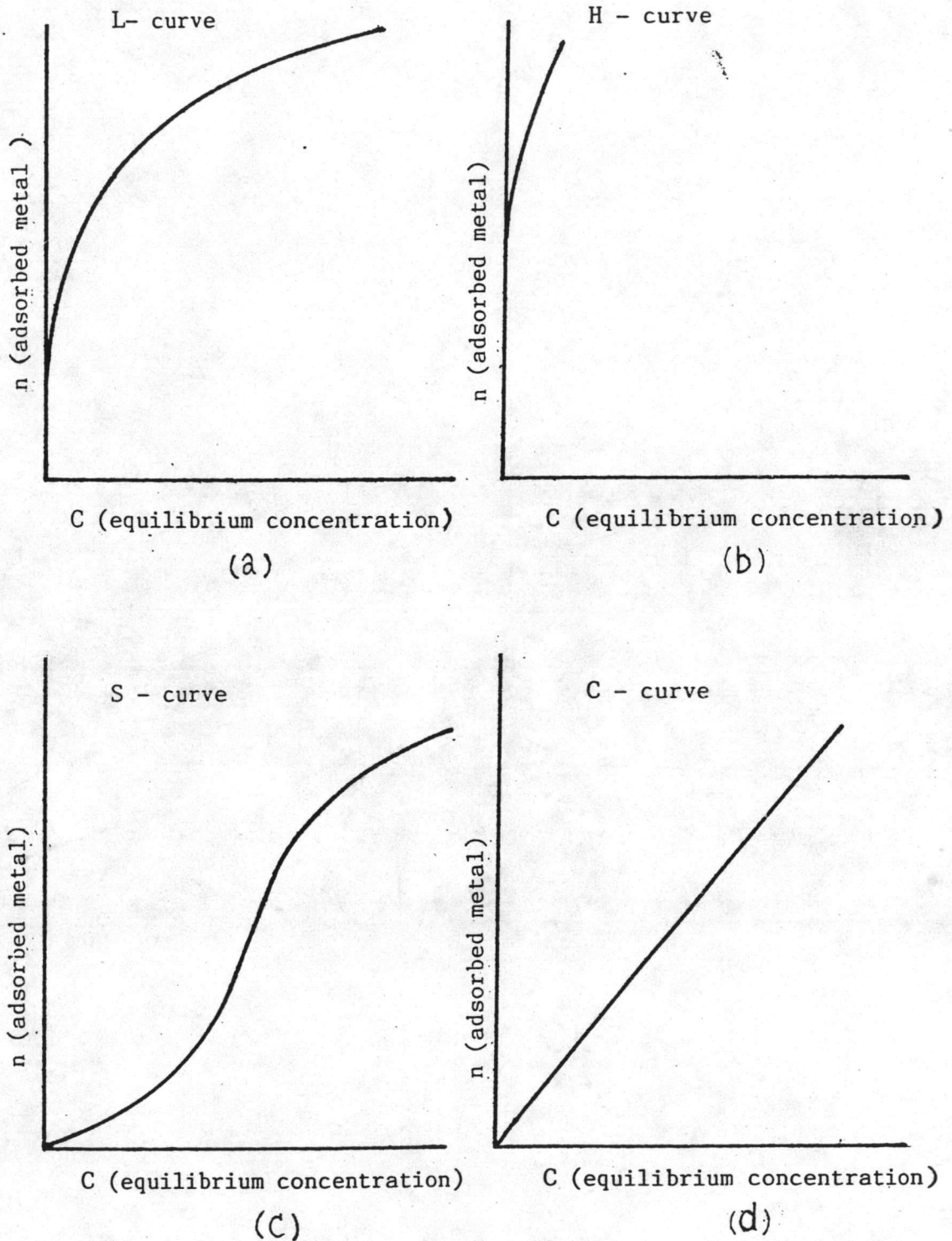


FIGURE 2.3 Classes of adsorption isotherm

Source : Sposito (1984).

the adsorbate increases. Fig 2.3 (a) shows the first stage of L-curve is rather sharp because of high affinity of solid phases. Furthermore, the curve is gradually increased resulted from the combination of lower in affinity and higher in steric effects.

2.4.2.2 H-curve isotherm

H-type is an extreme version of the L-isotherm. Its characteristic of large initial slope suggests a very high relative affinity of the solid phases for adsorbate. This condition is usually produced either by highly specific significant van der Waals interactions contributing to the adsorption process [Fig.2.3 (b)].

2.4.2.3 S-curve Isotherm

S-type, initial slope increases with the concentration of adsorbate in soil solution. Suggested that the relative affinity of the solid phase at low concentration is less than the affinity of soil solution [Fig.2.3 (c)].

2.4.2.4 C-curve Isotherm

C-type, initial slope remains independent of the concentration of adsorbate in the solution until the maximum possible adsorption [Fig.2.3 (d)]. Either by a constant partitioning of adsorbate between surface and bulk phase or by a proportional increase in the amount of adsorbing surface excess of an adsorbate increase characterizes the isotherm (Sposito, 1984).

2.5 Factors Affecting Heavy Metal Adsorption and Desorption

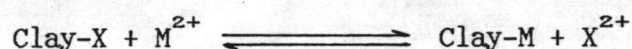
Several factors influence adsorbability of ions on clays, including type of soil colloids, heavy metal cations, pH, and competitive and complexing ions.

2.5.1 Soil Colloids

Soil colloids are made up of the complex negative radical micelles of clay minerals and humus. Generally, heavy

metal ions are adsorbed on the surface of the micelles by two means, i.e., an exchange process and specific bonding (Farrah and Pickering, 1977). The exchange processes are found on the surfaces of clay minerals and organic matters, but the specific bonding is due to ligands or groups that are able to form chelates and/or complexes with the metals. A formal discussion of the exchange reactions are given as follows.

Heavy metal cations take part in reaction with negatively charge surfaces of clay minerals as set out below whereas X is any adsorbed cations on clay minerals (Burchill, et.al., 1984).



From 1959 to 1976, several investigators focused on clay minerals, especially on clay fractions, that adsorb heavy metal ions (Heydermann, 1959; El-Sayed et.al, 1970; Farrah and Pickering, 1976, cited by Farrah et.al., 1977). The total capacity varies with the nature of the clay minerals, with pH and the presence of ligands in aqueous phase. However, clay fractions in natural soil are rarely monomineralic or homoionic. Farrah et.al. (1977) tried to show that the extent to which heavy metals (Cu, Pb, Cd) are removed from the bulk solution by highly pure clay suspensions (kaolinite, illite and montmorillonite) varied with the nature of clay, solution, pH, concentration of competitive cations and the nature (also concentration) of any ligand present. The affinity order for divalent cations also appear to vary with clay type. As the pH increases beyond 5, increasing proportions of all heavy metal ions can be bound as hydroxy complexes, unless there are present, in solution, as excess of ligand capable of forming stable, uncharged or anionic metal complexes. They also reported that only a slight pH dependence for the adsorption of Cd on montmorillonite in water

to which no other electrolyte has been added.

Another group of investigator was interested in the adsorption by different major cation-exchange materials. The adsorption of metals (Pb, Cu, Zn, Co, and Cd) using calcium as reference ion was studied (Wada and Abd-Elfattah, 1979). On the basis of exchange reaction and selectivity coefficient, K^{Zn} . All natural samples, except those containing halloysite, exhibited no or very small selective Zn adsorption but all Ca-saturated sample exhibited selective Zn adsorption. It indicated that it may depend on cation exchange materials. The moderate to low selective size for Zn predomination in soil containing montmorillonite, vermiculite and humus, whereas those with high selectivity for Zn dominate in soils containing allophane, imogolite and halloysite. Wada and Kakuto (1980) investigated that montmorillonite is a weak adsorbent for Zn.

Abd-Elfattah and Wada (1981) studied the adsorption of heavy metals by soils that differ in clay minerals. They concluded that the proportion of selective adsorption site with specified values of the selectivity coefficient calculated using Ca as reference ion increased in the order of montmorillonite (Mt) < humus, kaolinite (Kt) < allophane (A), imogolite (Im) < halloysite (Ht), iron oxides (Fe-ox).

The following sequence of cation-exchange materials are derived for the selective adsorption of the respective cations :

Pb ; Fe - ox, Ht, A-Im, A > Humus, Kt > Mt
 Cu ; Fe - ox, Ht, A-Im, > Humus, A, Kt > Mt
 Zn ; Fe - ox, Ht, A-Im, > Kt > A, Humus > Mt
 Co ; Fe - ox > Ht > Humus, A-Im, Kt > Mt, A
 Cd ; Fe - ox, A-Im > Humus > A, Kt > Ht, Mt,

Gadde and Laitinen (1974) studied individual adsorption of heavy metal ions of Cd, Zn, Pb and thalium (Tl) on hydrous iron and manganese oxides. They found that the

adsorption processes are reversible with respect to hydrogen ions and other adsorbing ions. The adsorption on hydrous iron oxide and hydrous manganese oxide followed the order $Pb^{2+} > Zn^{2+} > Cd^{2+} > Tl^{2+}$. They concluded that hydrous oxides in aqueous solution carry a surface charge which is very pH dependent.

The strong affinity for heavy metal cations retention may be correlated with the content of organic matter. Although it may provide sites for cation exchange reaction but its strong affinity is due to chelation and/or complexation. Unfortunately, the complexes formed between the solid phase in soil and native organic matters in soil solution are not yet well defined because the structure of the latter one has not been established completely (Harter, 1983).

Cadmium was found to be strongly bounded to clays coated with Al or Fe hydroxides. Its adsorption to density clay fractions showed that the greatest adsorption was to the fractions containing high quantities of organic matter and sesquioxide. Desorption with 0.01 M $Ca(NO_3)_2$ showed that Cd was adsorbed more tenaciously to sesquioxides than organo-clay complexes (Levy and Francis, 1976).

From the above data, it is said that silicate clays, hydrous oxides, humus and organo-clay complexes may influence the adsorbability and desorbability of cations, especially of heavy metals.

2.5.2 Metal Cations

In the case of cations, selective adsorption are depended on the exact matching between cation size and the structure holes on the surfaces or inter-layers. The greater attraction of the clay surface for the lesser hydrated cations is more preferable because of their coulombic attractions (shorter distance). The second reason for differences in cation selectivity in the layer minerals is the siting of isomorphous substitution which is relative to the surface where exchanges

occur. The source of negative charge nearer the interlayer space where compensating cations reside are important. The closer proximity of opposite charges leads to stronger coulombic attraction, and therefore, the increased selectivity of cations by tetrahedrally substituted minerals relative to octahedrally substituted minerals (Talibudeen, 1981).

For common cations, i.e., Na and K, in most of clays, it is found that K is more preferred than sodium with selectivity coefficient of about five times. Differences in selectivity of divalent cations seem to be smaller magnitude, e.g., Ca trends to be preferred over magnesium (Mg) with a factor 1.2 where as its selectivity with respect to other divalent cations, i.e., barium (Ba), strontium (Sr), Zn and Ni is closed to unity (Talibudeen, 1981). Conversely, for organic adsorbents the situation with respect to divalent ions may be quite different due to chelate formation. The adsorption by peat, the selective order was $Pb > Cu > Cd > Zn > Ca$ (Bunzl, Schmidt and Sansoni, 1976). But the sequence was opposite the adsorption by pure clay minerals, montmorillonite; $Ca > Pb > Cu > Mg > Cd > Zn$, kaolinite; $Pb > Ca > Cu > Mg > Zn > Cd$ and illite ; $Pb > Cu > Zn > Ca > Cd > Mg$ (Farrah and Pickering, 1977). For soil clays, the greater affinity of Zn compared to Cd and Ni but organic-rich sample exhibited little difference in affinity between the 3 cations (Tiller, Gerth and Brummer, 1984). It indicated that the affinity orders depend on crystallinity and mineral forms of heavy metal.

2.5.3 Effect of pH

Raising in soil pH value increases both the amount and affinity of metal adsorption. Harter (1983) recommended that the quantity of metals that can be retained by any soil is strongly influenced by the soil pH and confirmed by Sanders and El Kherbawy (1987). For the transition and heavy metal cations, the adsorption is also strongly pH dependent and becomes

significant when the pH range is between 4.0 to 6.0 and between 6.0 to 8.0 for the alkaline earth cations (Kinniburgh and Jackson, 1982). McKenzie (1980) has studied the adsorption of lead and other heavy metals on synthetic oxides of manganese and iron. He concluded that increasing in pH resulted in increasing of metal adsorbability, i.e., Pb, Cu, Mn, Co, Zn and Ni. And it was also found that Ni adsorption showed less pH dependent between pH range of 3-6 on manganese oxides.

2.6 The Approach Based on the Exchange Reaction Equation

The negative charges in soil constituents are derived from isomorphous substitution within the structures of layer silicate minerals, broken bonds at mineral edges and external surfaces, dissociation of acidic functional groups in organic compounds. (Tisdale, 1975). The preferential cation exchange reaction in soils is a reversible chemical reactions on the particle surfaces. Based on those reactions, Abd-Elfattah and Wada (1979) defined the selectivity coefficient, K_{Ca}^M by the equation,

$$K_{Ca}^M = \frac{[M]_{soil} [Ca]_{sol}^2}{[Ca]_{soil} [M]_{sol}^2} = 1$$

whereas $[M]_{soil}$ and $[Ca]_{soil}$ are the amount of heavy metal and calcium adsorbed by soils. $[M]_{sol}^2$ and $[Ca]_{sol}^2$ are the concentrations of metal and calcium in the bulk solution at equilibration. Calcium was used as reference ion and assumed that only one kind of heavy metal and calcium act as exchangeable cation

2.7 The Approach Based on the Langmuir Adsorption Equation.

The Langmuir isotherm was the most commonly used in the adsorption studies. Not only its ability to fit a wide variety of adsorption data quite well, but it may also partly reflect the appealing simplicity of the isotherm equations and the ease with which its adjustable parameters can be estimated. The simple Langmuir is given by equation (Sposito, 1984; Kinniburgh, 1986).

$$n = \frac{KcM}{1+Kc} \quad \text{--- 2}$$

where n is the amount adsorbed, c is the equilibrium concentration, M is the adsorption maximum, K is an affinity parameter. The isotherm equation can be transformed to a linear form and so the two adjustable parameter, M and K are easily estimated either by graphical means or by linear regression. The transformed equation is given :

$$\frac{c}{n} = \frac{1}{KM} + \left[\frac{1}{M} \right] c \quad \text{--- 3}$$

when plots c/n ratio versus c , slope/intercept is estimated as affinity parameter and $1/\text{slope}$ was the adsorption maximum. In the other hand the simple linear regression will result in different parameter estimates (c/n , c) from the transformed equation (3). By easy-to-use computer programs, the least squares methods, the fitting of linear Langmuir isotherm is noticed by regression squared.

2.8 Relationship Among Heavy Metals, Soils and Plants

Heavy metals are widely added to soil by several means, e.g, natural and mostly by human activities. Normally, they present in small quantities in soil as the result of parent material weathering. Anyway, the concentration trend of those may be significantly increasing by using of pesticides, fertilizers, aerial emission, sewage sludge and so on (Jones and Jarvis, 1981) Heavy metal soil pollutants are able to restrict the growth of plant which intended for direct or indirect human consumption. To study on plant effect dues to soil heavy metal concentration, the background levels are need.

During 1978 to 1982, metal determinations in soil-feed livestock were conducted in Ontario, Canada. Grass-legume hays, grain corn, corn silage and soil those crops were raised, were collected from farms across the Province. The results of the metal analyses spanned five orders of magnitude with the highest being Zn (10,000 ug/kg of soil) while Cr, Cu and Ni into the 1,000 to 10,000 $\mu\text{g}/\text{kg}$ level (Frank, Stonefield and Suda, 1985). By quotations of Goldschmidt, 1958, Bowen, 1966, and Allaway, 1968 (cited by Jones and Jarvis, 1981) the concentrations of metals in lithosphere, soils and plants are shown in Table 2.1

From Mortvedt's report (1985), the plant uptake of Cd contaminants in several Zn fertilizers made from industrial by products was not significantly affected by corn forage eventhough those fertilizers contained up to 2,165 mg of Cd/kg. In addition, Ni and Pb uptake by corn should be significantly affected although soil pH level as low as 5.5. In contrast, Cd uptake by Swiss chard was significantly increased by application of the same fertilizer at the confidence level of 95%, particularly on acid soil, but uptake of Ni and Pb shown no affected.

Table 2.1 Concentrations of Heavy Metals in the Lithosphere (Goldschmidt, 1958), soils (Bowen, 1966) and Plants (Allaway, 1968) cited from Jones and Jarvis, 1981.

Metal	Lithosphere	Soil		Plants
		Typical	Range	
Cd	0.2	0.06	0.01-0.7	0.2-0.8
Cr	200	100	5-3,000	0.2-1.0
Ni	100	40	10-1,000	1
Zn	80	50	10-3,000	8-100

Remark : concentration in $\mu\text{g/g}$ dry matter.

Heavy metal concentration in soil may lead to plants by mass action and diffusion through soil solution, but there is no closed relationship between concentrations in soil and in plant. Their mobility and uptake is related to their chemical forms, especially, exchangeable and carbonate forms (Xian, 1989). Furthermore, the correlations between concentrations in plants and soil extracts showed the distinguished data. Soil treated with metal loaded sewage sludges were used for plant raising. The correlation coefficient between metal concentrations in plants and in soil extracted by CaCl_2 were more than 0.85 for Zn and Ni at $p < 0.001$ (Sanders, McGrath and Adams, 1987).