THE COMPOSITION OF INTERLAYERED CLAYS AFFECTS THE RETENTION AND TRANSFORMATIONS OF ORGANIC COMPOUNDS

BY

SRIMATHIE PRIYANTHIKA INDRARATNE

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

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THE UNIVERSITY OF MANITOBA

FACULTY OF GRADUATE STUDIES

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THE COMPOSITION OF INTERLAYERED CLAYS AFFECTS THE RETENTION AND TRANSFORMATIONS OF ORGANIC COMPOUNDS

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ABSTRACT

Indraratne, Srimathie Priyanthika. Ph.D., The University of Manitoba, June, 1998. The Composition of Interlayered Clays Affects the Retention and Transformations of Organic Compounds. Major Professor: Tee Boon Goh.

This study was conducted to compare the stability of Al-, Fe- and mixed Fe and Al- hydroxide interlayers in montmorillonite (Al-Mt, Fe-Mt and Fe,Al-Mt, respectively) and their ability to act as catalysts in the oxidative polymerization of hydroquinone and catechol. Hydroxy-Al polymers formed well-crystalline interlayers and showed the highest stability, whereas, hydroxy-Fe montmorillonite was found to be a poorly organized material with low stability to heat and chemical dissolution treatments. Mixed Fe- and Al- interlayered clay showed intermediate properties.

Soil minerals affect the abiotic transformation of diphenol to humic substances. In the absence of clay minerals, very little formation of humic substances occurred, in comparison to humification in the presence of montmorillonite alone and where interlayered clays were present. The amounts of humic acids extracted follows the order; Na-montmorillonite > Fe-Mt = Fe, Al-Mt > Al-Mt in clay-hydroquinone systems. The quantity and quality of the humic substances formed from two common diphenolic precursors were

compared. More humic substances were extracted from supernatants of clay-hydroquinone complexes than in clay-catechol systems. In contrast, higher amounts of humic substances were found in the solid phase of clay-catechol systems than in clay-hydroquinone, indicating the higher reactivity of catechols at the clay surfaces. The humic substances that were associated with the solid phase resemble natural humic and fulvic acids.

The associated changes in mineralogical properties of hydroxy-interlayered montmorillonite due to reaction with soluble, low-molecular-weight organic compounds was studied at an adjusted pH of 6, aging for 30 d. Hydroquinone and catechol did not cause any significant structural changes in hydroxy-interlayered or non-interlayered montmorillonites, whereas citric acid dissolved the interlayer hydroxy-polymers. Very high third-range buffer capacities were observed in hydroxy-interlayered-hydroquinone and -catechol complexes. The sorption of atrazine was dependent on the amounts of organic carbon, degree of humification and the chelating ability of organic compounds present in soil. These factors were in turn due to the unequal effects of the different types of interlayers in montmorillonite.

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to my advisor, Dr. Tee Boon Goh for his constant encouragement and guidance, and my committee members, Drs C. M. Cho, Frank Hawthorne and Dennis Oscarson, for their support and assistance given throughout this study.

I am indebted to Dr. H. Shindo for his invaluable suggestions.

I would like to thank Dr. G.J. Racz and the staff, all the graduate students, and also Helen and Pearl, for their help and friendliness. My special thank you goes to Brian Wiebe, who helped me in each and every phase of this study and to Roslyn Van De Velde for her friendship and help.

I would like to thank S. Mejia (SEM) and N. Ball (x-ray analysis) of Geological Sciences, and L. P. Sarna (GC), V. Huzel and G. Morden (AAS) of Soil Science, for their technical assistance.

I thank the Canadian Commonwealth Fellowship and Scholarship Plan for the financial support in the form of a scholarship. My gratitude is also extended to the University of Peradeniya for granting my study leave.

Finally I thank my mother, brothers, my husband Gamini and son Pasan, for their love and tolerance during this time period. I would like to dedicate this dissertation to my beloved parents, Mrs. and the late Mr. G. Jayawickrama.

FOREWARD

This thesis followed the format of manuscript style as outlined in the "Thesis Preparation for Graduate Students in the Department of Soil Science". Various parts of this thesis have been published, presented and submitted to journals as follows: Indraratne S.P., Goh Tee Boon, Hawthorne F.C., and Oscarson D.W. 1996. Characterization of interlayered clay minerals. Proc. of 39th Annual Meetings of the Manitoba Society of Soil Science. 39: 131-142; Indraratne S.P. and Goh Tee Boon, 1997a. Increasing reactivity in hydroxy-interlayered clays with citric acid. Proc. of 40th Annual Meetings of Manitoba Society of Soil Science. 40: 220-228; Indraratne S.P., Goh Tee Boon, Oscarson D.W., and Hawthorne F.C. 1997b. Hydroquinone-derived humic substances formed in the presence of hydroxy-interlayered clays. Proceedings of 11th International Clay Conference, June 15-21, 1997, Ottawa, Ont., Canada., (accepted); Indraratne S.P., Goh Tee Boon and Shindo H. 1997c. Chelation and oxidative polymerization of organic compounds in hydroxy-interlayered smectites. Paper presented at the Annual Meetings of Soil Sci. Soc. Am., Oct. 26-31, 1997, Anaheim, CA, USA., and submitted to the Soil Science Journal. Journals for the publication of other manuscripts in this thesis have yet to be decided.

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ABBREVIATIONS

Name	Abbreviation
Montmorillonite	Mt
Hydroxy-Fe interlayered-montmorillonite	Fe-Mt
Hydroxy-Fe,Al interlayered-montmorillonite	Fe,Al-Mt
Hydroxy-Al interlayered-montmorillonite	Al-Mt
Hydroquinone	HQ
Montmorillonite-hydroquinone	Mt-HQ
Hydroxy-Fe interlayered-montmorillonite-hydroquinone	Fe-Mt-HQ
Hydroxy-Fe,Al interlayered-montmorillonite-hydroquinone	Fe,Al-Mt-HQ
Hydroxy-Al interlayered-Montmorillonite-Hydroquinone	Al-Mt-HQ
Fe-hydrous oxide-hydroquinone	Fe-HQ
Fe,Al-hydrous oxide-hydroquinone	Fe,Al-HQ
Al-hydrous oxide-hydroquinone	Al-HQ

Catechol	CC
Montmorillonite-catechol	Mt-CC
Hydroxy-Fe interlayered-montmorillonite-catechol	Fe-Mt-CC
Hydroxy-Fe,Al interlayered-montmorillonite-catechol	Fe,Al-Mt-CC
Hydroxy-Al interlayered-montmorillonite-catechol	Al-Mt-CC
Montmorillonite-citrate	Mt-Ct
Hydroxy-Fe interlayered-montmorillonite-citrate	Fe-Mt-Ct
Hydroxy-Fe,Al interlayered-montmorillonite-citrate	Fe,Al-Mt-Ct
Hydroxy-Al interlayered-montmorillonite-citrate	Al-Mt-Ct

1. INTRODUCTION

It is generally known that pH, salt concentration, kinds of ions, layer charge and time are among the essential factors responsible for the genesis of Al-hydroxy interlayers in expansible-layer silicates (Barnhisel and Bertsch 1989). Furthermore, studies by Quigley and Martin (1963), Thomas and Coleman (1964), Singleton and Harward (1971), and Ghabru et al. (1990) have also provided some evidence that acid clays may contain considerable interlayer hydroxy-Fe. The hydroxy-Al polymers, which are fixed in the interlamellar spaces of montmorillonite, are the more widely investigated interlayer material. Studies of Krishnamurti et al. (1995) reported that the mixed hydroxy-Fe-Al components form stable interlayers in montmorillonites. Acidic environments are especially noted for the presence of hydroxy-interlayered clays and accumulation of organic acids, and therefore their interactions.

A wide variety of organic molecules are known to interact with clay minerals, with the formation of polymeric compounds in some cases. Such clay-organic systems are very important in agriculture, industrial processes, and environmental systems. Citric acid, which is produced by bacteria in the rhizosphere and during the decay of plant remains, has a significant effect on the formation of short-range-ordered aluminosilicates (Kwong and Huang 1979;

Goh and Huang 1986). Citric acid is thought to be effective in alleviating Al toxicities in soils (Hue et al. 1986). The perturbation of the formation of crystalline Al (Kwong and Huang 1977; 1979; Violante and Huang 1985) and Fe (Cornell and Schwertmann 1979) oxides has been widely investigated. These studies were carried out by introducing citric acid to the montmorillonite systems simultaneously with Al and OH ions. The low-molecular-weight phenolic compounds such as hydroquinone and catechol, are found in the chemical degradation products of humic substances (Schnitzer and Khan 1972), suggesting that they may be the precursors of soil organic matter.

Humic substances are natural organic polymers common in the environment. The oxidative reactions of phenolic substances, sometimes without any participation by microbial phenoloxidases, play an important role in the humification process. Hydroquinone and catechol are possible phenolic compounds which undergo oxidative polymerization in the formation of humic substances. The catalytic effects of clay minerals, oxides, natural and synthetic Fe, Al and Si in the formation of humic substances have been studied (Shindo and Huang 1985; McBride et al. 1988; Huang 1990). A further understanding of the formation of humic substances in Al- and Fe- interlayered clays at acidic pH levels would be helpful to predict the catalytic effects of tropical and sub-tropical soils. Most tropical soils are acidic, high in Al and Fe and low in organic matter. If conditions are favourable for humification, it could lead to enhanced soil-fertility by increasing humic substances in soils.

The fate and behaviour of pesticides in the environment depend the composite effects of the chemical properties of pesticides and of the media in which they are dispersed (Weber 1993). Pesticide adsorption on soil colloids is important in determining pesticide volatility, bioavailability, degradation rate and mobility in soil (Bouchard and Lavy 1985). Therefore the prediction and management of pesticide efficacy, fate and transport in soils require several types of physical and chemical information. Sorption studies are commonly used to compare the relative binding and potential mobility of pesticides in soils. Atrazine [2-chloro-4(ethylamino)-6-(isopropylamino)-s-triazine], is a widely used selective herbicide for the control of annual grasses and broad-leafed weeds. Soil organic-matter influences the fate of most pesticides in soils mainly through retention processes (Barriuso and Koskinen 1996). The adsorption and intercalation of organic molecules by smectites has attracted much attention, particularly the intercalation of different organic species and their interaction with the clay surface (Norris et al. 1992). The hypothesis of this study is that interlayer hydroxy-Al, -Fe and mixed -Fe,Al in montmorillonite catalyze the formation of humic substances. The rate and amount of humic substances produced by these interlayered clays differ according to the properties of the clays.

To test the hypothesis, this study has the following objectives;

(i) To prepare and characterize hydroxy-Fe, -Al and mixed -Fe,Al interlayers in Na-saturated montmorillonite

(ii) To conduct a comparative study of the interaction of common organic compounds in soil, namely, citric acid, hydroquinone, and catechol with hydroxy-interlayered-montmorillonites separately. These organic compounds can enter or adsorb strongly with hydroxy-interlayered clays, forming hydroxy-interlayered-organic complexes

(iii) To investigate the formation of humic substances in the hydroxy-interlayered-montmorillonite-hydroquinone and hydroxy-interlayered-catechol complexes

(iv) To study the influence of hydroxy-interlayered clay minerals and their organic complexes on the retention of atrazine

2. LITERATURE REVIEW

2.1 Hydroxy-interlayered montmorillonitic clays

Hydroxy-interlayered vermiculite and smectite can be considered as solid solutions, with vermiculite or smectite as one end-member and chlorite as the other (Schulze 1989). In crystalline $Al(OH)_3$, Al^{3+} are distributed in hexagonal rings, connected with OH bridges (Hsu 1989). Hydroxy-interlayered minerals, formed as Al^{3+} was released during weathering, hydrolyzed and polymerized to form large polycations with a postulated formula of $Al_6(OH)_{15}^{3+}$ (or similar) in the interlayers of vermiculite and smectite (Barnhisel and Bertsch 1989). Bertsch (1989) has also shown evidence for the proposed structure for hydrolytic Al species as a continuous series of polynuclear complexes with the basic unit $[Al_6(OH)_{12}(H_2O)_{12}]^{6+}$. The six-membered ring structure is perhaps the smallest polymer that may exist in clays that is not subject to exchange by other cations (Barnhisel and Bertsch 1989). Larger, more complex polymers of hydroxy-Al (as illustrated in Fig. 2.1) were proposed by Hsu and Bates (1964a; b). Assuming the parallel orientation of these polymers in the interlayer space as suggested by Turner and Brydon (1965), the structure would be consistent with the observed 1.4 to 1.47 nm peaks for interlayered minerals (Barnhisel and

Bertsch 1989). Observations of 1.8 to 1.9 nm d-spacings for interlayered minerals (Brindley and Kao 1980) suggested that the "Al_{13}" structure (Fig. 2.1) is likely the first stable interlayer polymer material (Vaughan and Lussier 1980).

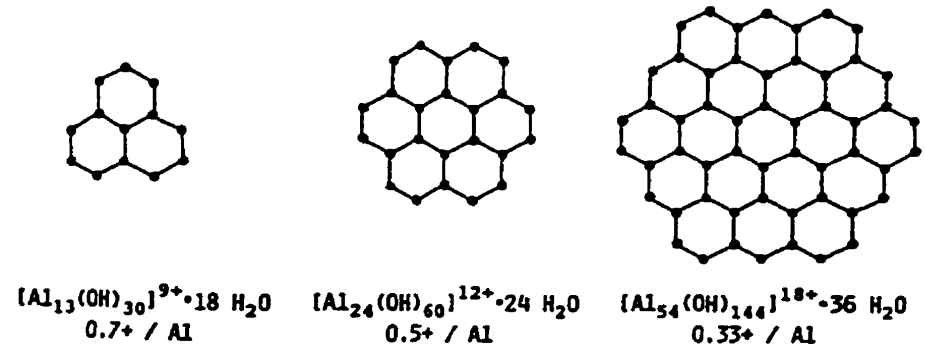


Fig. 2.1 Schematic representation of a series of positively charged OH-Al polymers (from Hsu 1989).

Two types of arrangements for the distribution of interlayer material have been suggested, as illustrated in Fig. 2.2. These are the marginal distribution of polymers forming an "atoll" structure and uniformly distributed polymers within the interlayer space (Dixon and Jackson 1962). In addition to the formation of hydroxy-interlayered minerals, positively charged hydroxy polymers can be adsorbed on the edges and external surfaces of phyllosilicates (Huang 1990). Polymers of hydroxy-iron and magnesium may be adsorbed by 2:1 expansible layer silicates by a similar mechanism, as in the case of hydroxy-Al polymers (Barnhisel and Bertsch 1989).

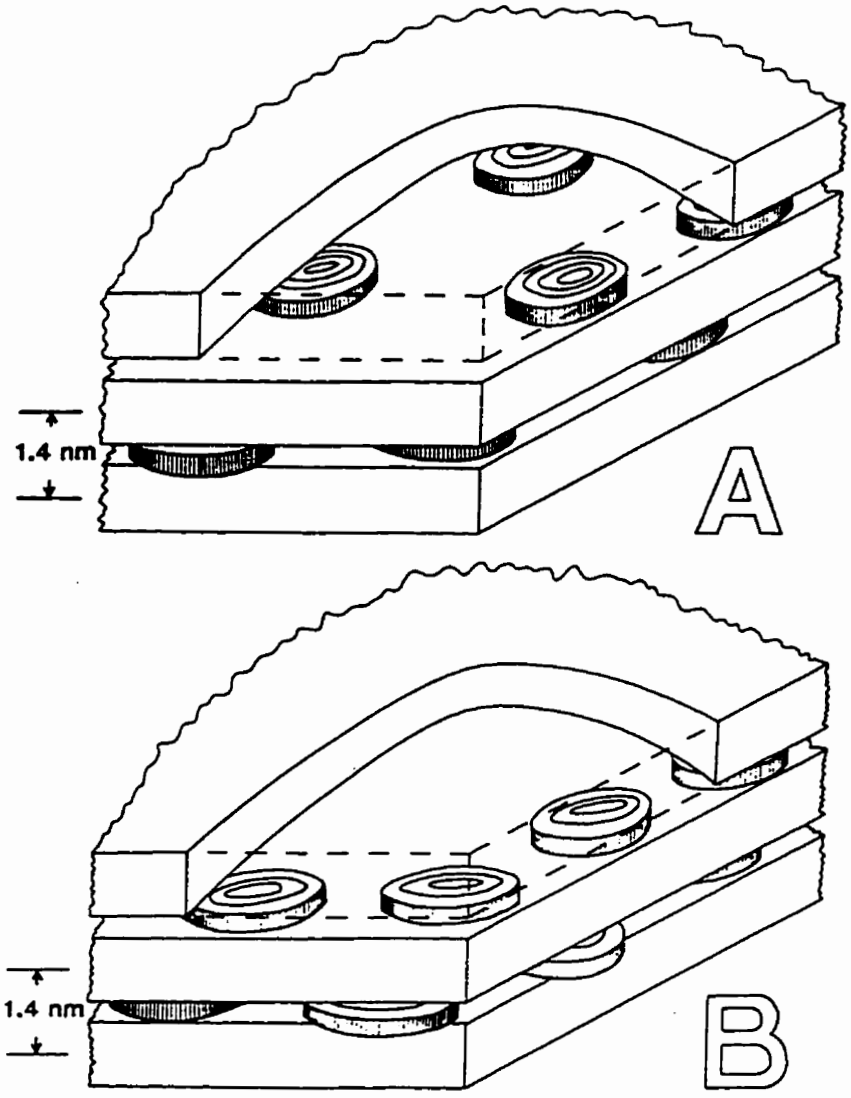


Fig. 2.2 Illustration of the distribution of hydroxy-Al polymers in the interlayer space of 2:1 clay minerals: (A) a uniform distribution; (B) an "atoll" arrangement (from Barnhisel and Bertsch 1989)

2.1.1 Formation and stability of hydroxy-interlayered clay minerals

Many natural occurrences suggest that interlayers form by precipitation and growth of hydroxy-Al polymers in the space between the layers of smectites or vermiculites. They also seem to form by replacement of interlayer K in micas and the brucite-like interlayer in trioctahedral chlorites by hydroxy-Al species in the interlayer space (Newman and Brown 1987). In acid soils, pH 4 to 6, hydroxy-Al is the principal interlayer material, whereas hydroxy-Mg is probably the dominant cation in alkaline and most marine environments (Newman and Brown 1987). Chlorite-like materials have also been synthesized with cations other than Al in the interlayer. Hydroxy-interlayers of Ni (Yamanaka and Brindley 1978), Zr (Yamanaka and Brindley 1979), Fe (Carstea et al. 1970a; Martin-Luengo et al. 1989), and Cr (Carr 1985; Dubbin et al. 1994) have been prepared in the laboratory.

Hydroxy-Fe interlayers in expandable clays show lower degrees of interlayering than Al systems (Carstea et al. 1970a; b). Mixed hydroxy-Al,Fe polymers in montmorillonite did not form a uniformly distributed material within the interlayer space and chemical, physicochemical and mineralogical properties vary according to their initial molar ratios (Colombo and Violante 1997). The stability of the hydroxy-Al interlayers in expansible layer silicates is a function of a number of factors such as i) OH/Al molar ratio and pH, ii) amount of hydroxy-Al species, iii) presence of organic or inorganic ligands, iv) particle size of clays, v) surface heterogeneity of clay minerals, and vi) temperature (Hsu

1968; Rich 1968; Violante and Jackson 1981; Barnhisel and Bertsch 1989).

2.2 Active sites on clay minerals for retention of organic compounds

Active sites can be described on the basis of their location (edge vs. basal surface), geometric arrangement of surface atoms, chemical composition, and accessibility (Johnston 1996). Clays and oxides often demonstrate the ability to catalyze electron-transfer reactions such as the oxidation of polyphenols (Larson and Hufnal 1980). According to Helsen (1982), the catalytic properties of clays are generally ascribed to the Bronsted and Lewis acidity of the surface. Bronsted acidity is the ability to donate protons, and Lewis acidity is the ability to share lone-electron pairs. Bronsted acidity of clay-mineral surfaces depends strongly on the nature of the exchangeable metal cation and on the amount of water present. The order of proton donation follows the order $Al^{3+} > Mg^{2+} > Ca^{2+} > Na^{+}$ and is strongly influenced by water content, and the basicity of the organic solute (Helsen 1982). Lewis acidity of clay minerals is due to the presence of threefold coordinated aluminum ions exposed at the edges of the platelets (Sposito 1989), and exchangeable or structural transition metals in their higher oxidation state (Johnston 1996). For example, exchangeable Cu^{2+} and Fe^{3+} or structural Fe^{3+} can function as surface Lewis acids by accepting electrons from adjacent unsaturated organic solutes (Voudrias and Reinhard 1986).

Isomorphic-substitution sites are characterized by a permanent negative charge. Organic cations and protonated organic bases can readily participate in cation-exchange reactions. In the presence of exchangeable metal cations, the organic solute coordinates directly with these metal cations (Johnston 1996). The degree of metal-organic interaction will depend on the ability of the organic solute to compete for coordination sites around the metal centre (Isaacson and Sawhney 1983; McBride 1987). The structural hydroxyl metal ion on broken edges, terraces, kinks or holes on surfaces of clay minerals are among the most abundant and reactive sites found on particles in soil and other subsurface environments (Sposito 1984). These sites, along with humic substances, are responsible for the development of the pH-dependent charge in soils and sediments (Thomas and Hargrove 1984). At low pH values, these sites develop a positive charge due to the adsorption of protons. Organic acids and oxyanions can interact strongly with these positively charged sites at low pH.

Metal cations and various inorganic and organic anions are capable of coordinating with surface groups, forming bonds that may have partial covalent character (McBride 1989c). When polyvalent cations occupy the exchange sites, the organic anions interact with these cations via an electrostatic bond (Mortland 1986). Unlike non-polar organic compounds, organic acids can interact with surface Bronsted- and Lewis- acid sites directly (Johnston 1996). In addition to clay minerals, Fe, Al, and Mg oxides can chemisorb organic

compounds, including catechol (McBride et al. 1988; McBride 1987), chlorophenols (Kung and McBride 1991) and substituted benzoates (Kung and McBride 1988). The ability of humic substances to form stable complexes with polyvalent cations is well established (Stevenson 1994). Their ability to form complexes with metal ions can be attributed to their high content of oxygen-containing functional groups, including carboxylic COOH, phenolic-OH, and enolic-OH, and C=O structures of various types. The preference of organic cations over alkali and alkaline-earth cations on 2:1 layer-silicate surfaces (Cowan 1961) is attributed to the combined action of electrostatic and non-Coulombic forces. In general, if the organic cation has a diameter of less than 6 Å as its smallest dimension, it can participate in most ion-exchange reactions (Johnston 1996). Size of the clay particles, type of exchangeable cations, total layer charge and the type of isomorphic substitution influence the interaction of organic cations with 2:1 layer silicates (Lagaly 1984).

2.2.1 Retention of non-polar organic compounds by clay minerals

The exposed siloxane surface of neutral 2:1 layer silicates that have been exchanged with alkyl-ammonium cations or other organic cations, are considered to have predominantly hydrophobic character (Lagaly 1982). These clays are referred to as organo-clays and have significantly different surface properties than the original clay (Boyd and Jaynes 1994). Because of the hydrophobic properties of the clay surface, organo-clays are efficient sorbents

for non-polar organic compounds (Jaynes and Boyd 1991). Aqueous-phase organic contaminants partition out into this derived organic phase on 2:1 layer silicates (Boyd and Jaynes 1994). In contrast to the low affinity of non-polar compounds for clay mineral surfaces, "organo-clays" are characterized by moderate to large sorption capacities for these organic solutes (Boyd and Jaynes 1994). The organic cation is anchored to the clay surface by electrostatic attraction between the positive charge on the cation and isomorphic-substitution sites on the clay surface. The organically modified clays then function as a partitioning medium for non-polar organic solutes. The distribution coefficient (K_d) of a solute in an aqueous phase in contact with a solid phase is given by the following expression:

$$K_d = C_s / C_w$$

where C_s is amount of material sorbed per unit mass of sorbent and C_w is the solution concentration at quilibrium. The uptake of non-polar organic solutes is generally controlled by the amount of organic C in the sorbent. Consequently, K_d is often normalized to the amount of organic C present by:

$$K_{om} = (C_s / C_w) / f_{om} = K_d / f_{om}$$

where f_{om} is the weight fraction of the solid which is organic matter.

2.3 Oxidative polymerization of polyphenols by clay minerals

Soil minerals play an important role in catalyzing the abiotic

polymerization of phenolic compounds and the subsequent formation of humic substances (Wang et al. 1986). Under natural conditions, inorganic catalysts may be less active than enzymes, but as a result of the longer persistence of inorganic catalysts, they seem to be equally important (Ruggiero et al. 1996). Furthermore, minerals are more abundant than enzymes in soil environments. Polymerization reactions are generally considered among the major chemically and biochemically mediated phenomena involved in the synthesis of humic substances (humification process) (Senesi and Steelink 1989). In laboratory experiments in particular, minerals with transition-metal ions (e.g., Fe,Mn) on the surface or within the structure (both clay minerals and oxides) have been shown to accelerate polymerization reactions of various phenols, leading to humic-like material (Shindo and Huang 1982). Oxidation and polymerization of phenolic compounds that is promoted by mineral surfaces has been reported by Kyuma and Kawaguchi (1964), Thompson and Moll (1973), Larson and Hufnal (1980) Shindo and Huang (1982; 1984), Isaacson and Sawhney (1983) Stone and Morgan (1984), and McBride (1987; 1989a; 1989b).

Polyphenols (quinones), synthesized by microorganisms and those liberated from lignin, polymerized alone or in the presence of amino compounds to form brown-coloured polymers (Stevenson, 1985). Recent literature on the synthesis or polycondensation pathways to humic macromolecules have supported the involvement of quinones derived from di- and poly-hydroxybenzene structures containing OH groups in the 1,2- or 1,4-ring

positions (Hayes et al. 1989). McBride (1989b) reported the reduction potentials of 1,2-dihydroxybenzoquinone as 0.78 V and 1,4-dihydoxybenzoquinone as 0.699 V, indicating that 1,2-dihydroxybenzene (catechol) is more difficult to oxidize than 1,4-dihydroxybenzene (hydroquinone). The chelating potential of catechol, that is conducive to electron transfer and subsequent radical formation (Shindo and Huang 1984; McBride 1989b), which is not an ability of hydroquinone also has to be considered when comparing these two diphenols.

2.3.1 Proposed mechanisms of abiotic formation of humic substances

Metal oxides and clay minerals that cause oxidation reactions may function as Lewis acids by accepting electrons from monomeric phenols, or as electron-transfer agents and complexation substances (Ruggierio et al. 1996). The Lewis-acid sites include structural aluminum and transition metal cations at edges of the mineral, and exchange cations, particularly transition-metal cations with unfilled d-orbitals (Boyd and Mortland 1990). Even when iron occupies sites within the octahedral sheet of 2:1 layer silicates, it may take part in redox reactions by accepting or donating electrons from/to external reactants (Solomon and Hawthorne 1983). Clay-mediated single electron-transfer reactions are characterized, in general, by (1) the formation of a darkly coloured complex (Pinnavaia and Mortland 1971), (2) loss of ESR signal from the paramagnetic metal cation (Rupert 1973), (3) a concomitant appearance of

a "new" ESR signal from the generation of an organic-radical cation (Eastman et al. 1984), and (4) strong perturbations in both the IR (Fenn et al. 1973) and Raman (Soma et al. 1984; 1985) spectra of the chemisorbed complex. The polymerization of radical cations to form dimers and trimers was revealed by mass spectroscopy (Boyd and Mortland 1985). By displacing protons from the phenolic groups, Al^{3+} seems to promote delocalization of electrons from phenolic oxygen atoms into the π-orbital system, which may then be more susceptible to oxidation (Huang 1990). Displacement of the highly electronegative proton allows electron density to be delocalized from the oxygen atom into the aromatic ring (Huang 1990). The formation of charge-transfer complexes facilitated by Al^{3+} can be stabilized by H-bonding and/or Coulombic attraction (Boyd 1982). The catalytic power of Mn(IV), Fe(III), Al, and Si oxides in the abiotic formation of humic polymers is greatly influenced by the nature of the oxides (Shindo and Huang 1985). Among the short-range-ordered oxides, Mn(IV) oxide has a notably high ability to promote the formation of humic polymers. O_2 as an oxidant is theoretically more powerful than $Fe(OH)_3$ and as powerful as MnO_2 (McBride 1994). Fukuzumi et al. (1975) proposed the following reactions for the formation of semiquinone radicals in the presence of Mn^{4+} (Illustration (1)). Their results strongly suggest that Mn(IV) in manganese dioxide is reduced to Mn(II) by reaction with hydroquinone.

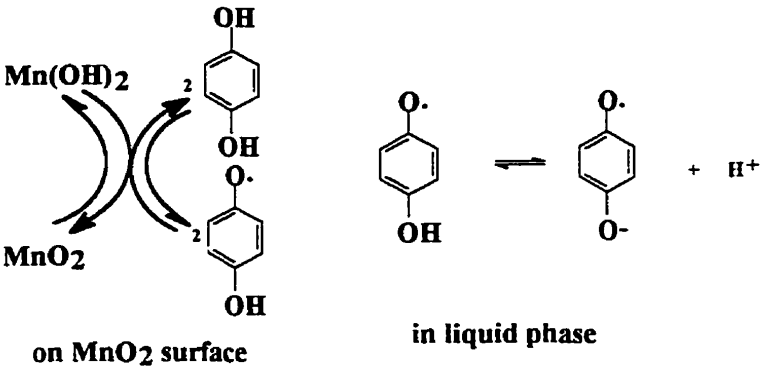
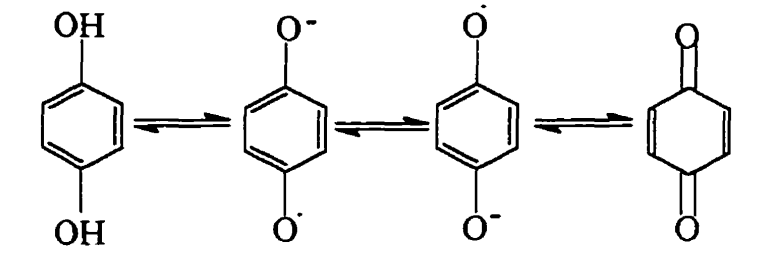


Illustration (1)

The extremely rapid simultaneous consumption of O_2 in a similar reaction system made McBride (1989a) suggest that these semiquinone radicals are rapidly oxidized to quinone by O_2. According to Schnitzer and Khan (1972), hydroquinone is oxidized via semiquinone-anion intermediates to quinone, consisting of a one-electron oxidation in each step, as illustrated below (Illustration (2)). Chambers (1974) pointed out that a number of factors, including the redox potential of the reagents, pH of the solutions, and the concentrations of quinones and hydroquinones, are critical factors in determining the redox behaviour of the system hydroquinone - semiquinone - quinone. In many cases in which structural or adsorbed Mn and Fe of minerals act as oxidizing agents, the mineral is only the catalyst, because O_2 ultimately reoxidizes the reduced Mn or Fe (McBride 1994) (Illustration (3)):



Hydroquinone Semiquinone radicals Quinone

Illustration (2)

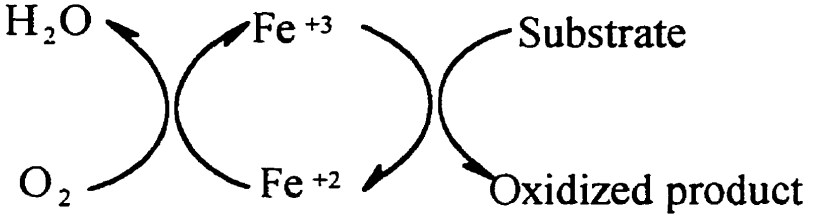


Illustration (3)

Every reaction pathway proposed for the catalytic polymerization of naturally occurring phenols proceeds through generation of phenolic radicals or reactive hydroxybenxoquinones and the nucleophilic additions of amino groups to free radicals (Ruggierio et al. 1996).

2.3.2 Optical properties of oxidative polymerized products

Absorption in the UV (200-400 nm) and visible (400-800 nm) regions is

caused by atomic and electromagnetic vibrations (Brown 1980). Constituents containing unbounded electrons on oxygen and sulfur atoms are capable of showing absorption, as well as systems containing conjugated C=C double bonds (Stevenson 1994). Many scientists are of the opinion that the dark colour of humic substances is due primarily to quinone-like structures and ketonic C=O in conjugation (Bloom and Leenheer 1989).

The relationship between absorption and concentration is given by the Beer-Lambert law :

$$\log (I_0/I) = kcd$$

where I_0 is the intensity of the incident light, I the intensity of the transmitted light, k the extinction coefficient, c the concentration, and d the path length of the cell. Essentially, the Beer-Lambert law states that the amount of light absorbed is proportional to the number of molecules of absorbing substances through which the light passes. The extinction coefficient, k, is equal to the optical density or absorbance ($\log I_0/I$) when the cell length is 1 cm and the concentration of the sample is 1 mol L^{-1} (Bloom and Leenheer 1989). For humic and fulvic acids, where molecular weight is variable or unknown, the extinction coefficient is expressed in terms of a given quantity of organic carbon (0.1 to 0.2 mg mL^{-1} is often used) (Kumada 1987). On the basis of equal concentrations, the extinction coefficient of humic compounds increases with: 1) increase in molecular weight, 2) C percentage, 3) degree of condensation, and 4) ratio of C in aromatic rings to C in aliphatic structures

(Bloom and Leenheer 1989).

Strong absorption in the UV region is expected for entities such as humic and fulvic acids which contain aromatic groups. In humic substances, heterogeneous substitution results in chromophores with overlapping bands (MacCarthy and Rice 1985). Also, slight differences in the environment of a macromolecular structure can result in spectral shifts (Brown 1980). The absorption spectra of humic substances in the visible region are generally featureless, with increasing absorbance at shorter wavelengths (Flaig et al. 1975; Stevenson 1994). The evidence of Tsutsuki and Kuwatsuka (1979) suggests that absorption in the visible region is associated with unsaturated structures that contain phenolic OH. Humic acids can have high molecular weights (Stevenson 1994) and scattering may contribute to the measured absorbance, in contrast to the fulvic acids which have relatively low molecular weights. Some investigators (Lindquist 1972; 1973) have suggested that charge-transfer bands or electron donor-acceptor complexes contribute to the absorption of visible radiation by humic substances. However, Hayes and Swift (1978) have pointed out that it is not possible to observe or measure one particular chromophore, or to derive definitive information with regard to chemical composition.

Despite the lack of discrete visible spectral bands, absorption in the visible region has been of great interest to many scientists, and the ratio of the absorbance at 464 nm to that at 665 nm by Kononova (1966) and 400 and

600 nm by Kumada (1987) (E_4/E_6 ratio) is commonly used to characterize humic substances. Ratios for humic acids are usually <5.0; those for fulvic acids range from 6.0 to 8.5 (Schnitzer, 1971). The ratio varies with sources of humic substances (Kononova 1966). The E_4/E_6 ratio decreases with increasing molecular weight and condensation, and is believed to serve as an humification index. Chen et al. (1977) concluded that the E_4/E_6 ratios of humic and fulvic acids is governed primarily by particle sizes and weights (due in part to scattering of light).

2.4 Humic substances in soils

The term humus, or humic substances, refers to organic materials that result from decomposition of plant and animal residues, but that do not fall into any of the discreet classes of compounds such as proteins, polysaccharides, polynucleotides, and so on (MacCarthy and Suffet 1989). Humic substances arise from the chemical and biological degradation of plant and animal residues and from synthesis activities of microorganisms (Schnitzer 1978). These products tend to associate into complex chemical structures that are more stable than the starting materials. The fact that no material that can be called a pure humic substance has yet been isolated (MacCarthy and Rice 1991), indicates the complicated, multicomponent nature of this material. Therefore, the humic substances are dark-coloured, acidic, predominantly aromatic,

polymeric complexes that are differentiated on the basis of solubility properties into humic acids, fulvic acids, and humins.

2.4.1 Extraction and properties of humic substances

Generally, humic substances are extracted from solid phases using alkali extraction of NaOH and Na_2CO_3 solutions of 0.1 to 0.5 M concentration in water and a soil : extractant ratio of 1:2 to 1:5 (g mL^{-1}). Humic substances are then classified into three useful categories on the basis of their solubility in aqueous systems (Aiken et al. 1985): (1) humic acid: the fraction of humic substances that is not soluble in water under acidic conditions (pH <2) but is soluble at alkaline pH values; (2) fulvic acid: the fraction of humic substances that is soluble under all pH conditions; (3) humin: the fraction of humic substances that is not soluble in an aqueous solution at any pH value. Data available suggest that the three humic fractions namely humic acid, fulvic acid, and humin, are structurally similar to each other, but differ in molecular weight, ultimate analysis and functional-group content (Schnitzer and Khan 1972).

Low-molecular-weight fulvic acids have higher O content but lower C contents than the high-molecular-weight humic acids (Stevenson 1994). The conformation of macromolecules of humic substances in solution is governed by the sample concentration, pH and ionic strength of the medium (Chen and Schnitzer 1989), as shown in Table 2.1. Both COOH and acidic OH groups contribute to the acidic nature of humic substances, COOH being the most

important (Stevenson 1994).

Table 2.1 Model macromolecular structures of humic and fulvic acids as influenced by pH and concentration of neutral salt (from Chen and Schnitzer 1989).

Acid	Sample concentration	Electrolyte concentration (M)				pH		
		0.001	0.005	0.010	0.050	2.0	3.5	6.5
Fulvic acid	Low							
	High							
Humic acid	Low							
	High							

3. MINERALOGICAL PROPERTIES OF MONTMORILLONITE CONTAINING HYDROXY-IRON, -IRON, ALUMINUM AND -ALUMINUM INTERLAYERS

3.1 Abstract

Interlayered montmorillonite, containing hydroxy-Fe (Fe-Mt), -Fe,Al (1:1 molar ratio) (Fe,Al-Mt) and -Al (Al-Mt) were prepared by adding pre-weighed amounts of $Fe(NO_3)_3$ and $AlCl_3$ at the rate of 600 cmol(+) kg^{-1} of sodium-montmorillonite (Mt), titrating with NaOH, and aging at an adjusted pH of 5.1. After 30 d, the clays were collected, washed, dialysed and freeze-dried before investigating their properties.

Significantly lower cation-exchange capacities and specific surface areas were observed in the interlayered clays. The highest reduction of surface area and CEC values from those of the Mt occurred in the Al-Mt clay, whereas the least reduction was observed in the Fe-Mt clay. Acidified NH_4OAc extracted higher Fe and Al amounts than could be accounted for by release from cation-exchange sites of the interlayers, indicating partial dissolution of separate solid phases of Fe and Al oxides. Neutral salts did not extract any Fe^{3+} from Fe-Mt and Fe,Al-Mt systems, but did extract exchangeable Al from Al-Mt clays.

X- ray diffraction patterns show hydroxy-Fe montmorillonite to be a

poorly organized material with low stability under heat or chemical-dissolution treatments. The presence of both Al and Fe in the interlayer complex of hydroxy-(Fe,Al) montmorillonite enhances its stability. Hydroxy-Al polymers form interlayers that are most stable. Slightly different morphologies were observed among the interlayered clays under the electron microscope. In the IR spectra of interlayers and Mt, the absorption maxima occur between 3620 to 3630 cm^{-1} due to the presence of Al-Al and Al-Fe^{3+} bonds in these clays. The presence of large permanent charge in hydroxy-interlayered clays made determination of variable charges, developed as a consequence of hydroxy polymers at edge and planar positions of montmorillonite, difficult.

3.2 Introduction

Hydroxy-interlayered clay minerals occur in soils as either weathering products derived from chlorite or by deposition of hydroxy-polymeric components within the interlayer spaces of 2:1 expanding-type clay minerals. They are chlorite-like minerals, but the interlayer-OH sheet of the chlorite structure is incomplete (Barnhisel and Bertsch 1989). The degree of interlayer filling with hydroxy-Al can vary from very low to nearly complete, and the properties of the clay vary accordingly (Schulze 1989). Hydroxy-interlayered vermiculite and smectite are most common in Alfisols and Ultisols. Within a given soil-profile they are often abundant near the surface, and their abundance

decreases with depth. The layer structure of hydroxy-interlayered minerals is variable depending upon three factors: (i) the structure of the basic 2:1 portion of the mineral, (ii) the degree of interlayer filling, and (iii) the chemical composition of the hydroxy materials that occur within the interlayer portion of these clay minerals (Barnhisel and Bertsch 1989).

The fixation of hydroxy-Al ions on montmorillonite can influence the levels of solution of Al species, and related ecological and toxicological problems in acid-vulnerable terrestrial and aquatic environments (Huang 1987; Lou and Huang 1988). For example, the interlayer-hydroxide sheet of chloritic minerals in acid tailings, when weathered by free acid, has been shown to cause the pH to rise from 1.8 to about 5.5 after aging several weeks at 70°C (Fordham 1993). Many investigators have demonstrated the restricted hydration of hydroxy-Al interlayered smectites. The swelling of Na-montmorillonite is reduced by the formation of hydroxy-Fe and -Al interlayers (El Rayah and Rowell 1973). The CEC of hydroxy-interlayered clays can be low with complete filling of the interlayer space, and near the CEC values of smectite at sparse interlayer occupancy. The major mechanisms proposed for charge reduction in hydroxy-interlayered clays are (i) precipitation of Al on surfaces and/or into interlayer spaces, sterically blocking exchange sites, and (ii) adsorption of positively charged hydroxy-Al polymers (Barnhisel and Bertsch 1989). Rich and Black (1964) suggested that K^+ fixation is nearly eliminated by Al interlayer formation as the hydroxy-Al interlayer groups act as "props",

inhibiting layer collapse. The presence of hydroxy-interlayers in 2:1 clay minerals significantly enhances the adsorption of anions because these minerals represent a very complex admixture of constant surface charge and constant surface potential surfaces (Barnhisel and Bertsch, 1989).

Dioctahedral expansible-layer silicates are those most frequently interlayered, and hydroxy-Al seems to be the principal component of the non-exchangeable interlayer material (Rich 1968). However, Quigley and Martin (1963) presented evidence for hydroxy-Fe interlayers in a soil clay. Laboratory synthesis of hydroxy-Fe clays was reported by Carstea et al. (1970a) and Martin-Luengo et al. (1989). Results suggested that hydroxy-Fe polymers are less organized, and less effective in filling the interlayers of 2:1 swelling clay minerals, than hydroxy-Al polymers (Frenkle and Shainberg 1980). Alperovitch et al. (1985) also found that hydroxy-Al polymers are more effective than Fe polymers at maintaining hydraulic conductivities during infiltration of a Na solution into clay-sand mixtures. The introduction of trinuclear acetato-hydroxy-iron (III) cations in the interlayer space of montmorillonite has proved to be a useful way of obtaining stable iron intercalates that persist even after heating to 773 K (Martin-Luengo et al. 1989). The formation and stability of mixed hydroxy-Fe,Al interlayers received attention recently (Krishnamurthi et al. 1995; Colombo and Violante 1997). Hydrolysis and polymerization of Al and Fe are believed to be involved in the formation of chloritic intergrade minerals in soils (Singleton and Harward 1971). There is little information on

naturally occurring interlayers composed largely of Fe-hydroxy compounds (Ghabru et al. 1990).

In acidic environments, Fe^{3+} and Al^{3+} are abundant cations. Mixed Fe-Al-oxide systems were studied by Goh et al. (1987), who reported the presence of two discreet oxide phases. In this study, Fe, Al and mixed Fe,Al were used to prepare hydroxy-polymers that to fix in the interlayer spaces of montmorillonite. The mineralogical and chemical characterization of hydroxy-Fe, -Al and mixed -Fe,Al interlayered montmorillonite is investigated to provide insight into how these minerals may influence the transformations of the other reactive-fraction organic compounds in soils. Investigation of the stability of these synthetic interlayered clay minerals may be useful in predicting the behaviour, influence and fate of these clays in relevant environments.

3.3 Materials and Methods

Montmorillonite (SWy-1, Crook County, Wyoming) was obtained from the Source Clays Repository of The Clay Minerals Society. The clay was Na-saturated by suspending in dilute Na_2CO_3 solution (pH 9.5) at 1:10 (W/V) ratio (Jackson 1979). The suspension was dispersed by ultrasonification at 50 W for 30 min and the <2-μm fraction was separated by sedimentation as described by Gee and Bauder (1986). This clay fraction was washed with distilled water eight times by decanting the supernatant after centrifugation.

Pre-weighed amounts of $Fe(NO_3)_3$, $AlCl_3$ and $Fe(NO_3)_3$ + $AlCl_3$ (1:1 molar ratio) were added to separate suspensions of 10 g of clay in 3 L of distilled water to give 600 cmol(+) kg^{-1} of clay. These suspensions were titrated with NaOH at 0.5 mL min^{-1} to 5.1. Another clay suspension containing the same amount of Na-saturated montmorillonite (10 g) of the $<2\mu m$ fraction, which did not have any Al, Fe or NaOH added, served as the control (Mt). All four suspensions were brought to a final volume of 4 L and then transferred to capped polypropylene bottles. The suspensions were aged at room temperature (about 25°C) with daily agitation for 30 d. After aging, each suspension was separated into its filtrate and solid phase by ultrafiltration through a Millipore filter of 0.025-μm pore size. The solid phase of each sample was washed and dialysed until free of Cl^- and/or NO_3^-, and also to remove soluble Al^{3+} and Fe^{3+} species that were not attached to clay surfaces. Finally, the samples were freeze dried before analysis. The initial and final pH of each suspension was recorded. The hydroxy-interlayered -Fe, -Fe,Al, and -Al montmorillonite and non-interlayered montmorillonite will be abbreviated as Fe-Mt, Fe,Al-Mt, Al-Mt, and Mt, respectively, throughout this dissertation.

Cation-exchange capacity was determined by saturating the samples with Ca, washing excess Ca with 99% methonol, and then replacing the Ca with Mg (0.5M $MgCl_2$) and measuring the amount of displaced Ca (Rich 1961). The specific surface of the solid fraction was determined by the ethylene-glycol-monoethyl-ether (EGME) method (Carter et al. 1986). Exchangeable Al

was obtained by using 0.1 g of hydroxy-interlayered clays and washing 5 times with 10 mL of 0.5 M $CaCl_2$ or 1 M KCl, separately. Neutral NH_4OAc, KCl, $CaCl_2$ and acid (pH 2.5) NH_4OAC (Page and Whittig 1961) procedures were used separately to extract exchangeable Fe. The amounts of extracted Fe and Al were determined by atomic absorption spectrometry (AAS). X-ray diffraction patterns of the clays before and after saturating with K and Mg and solvation with glycerol were obtained with a Philips PW1710 diffractometer using Cu$K\alpha$ radiation with Ni filter. The x-ray diffraction data of K-saturated samples after heating at 100, 300 and 550°C, were also collected. Scanning electron micrographs were recorded with a Cambridge Stereoscan 120 microscope operating at 20 kV after mounting the samples on aluminum stubs with C paint. Image enhancement and storage was done with an IBAS 20 image-analyser. A pellet 1 mm thick and 13 mm in diameter was prepared by mixing approximately 3 mg of finely ground sample with 300 mg of KBr. These pellets were scanned through the range of 1400 to 600 cm^{-1} in a Perkin Elmer 881 spectrometer to obtain infrared-absorption spectra.

Hydroxy-interlayered clays were subjected to either extraction by ammonium oxalate in the dark (AOD) (McKeague and Day 1966), or extraction by the sodium citrate-bicarbonate-dithionite method (CBD) of Mehra and Jackson (1960). Extracted amounts of Fe and Al were determined by AAS. The CEC of the resultant residue was measured and the XRD patterns after K-saturation and heating at 300°C for 4 h were obtained.

Potentiometric-titration curves were obtained to determine the point of zero charge (PZC) and the distribution of the net electric charge. Suspensions of hydroxy-interlayered clays were made by adding 50 mL KNO_3 of 1.0 M, 0.1 M, and 0.01 M to 0.5 g of clay. Titration curves were produced by titrating each suspension with 0.1 M KOH using a Metrohm 686 Titroprocessor. The PZC was considered to be the common intersection point of the titration curves carried out in the presence of three concentrations of KNO_3 (Van Raij and Peech 1972).

3.4 Results and Discussion

3.4.1 Physico-chemical Properties

Following the aging period, the filtrate obtained from each suspension contained no detectable Fe or Al (data not shown). This indicates that almost all the added Fe and Al was sorbed on the montmorillonite surfaces as Fe-OH, Al-OH or Fe,Al-OH species and/or had precipitated as separate solid hydroxides. Herrera and Peech (1970) reported that, to cover both planar surfaces of montmorillonite, eight Fe(III) atoms would be required per unit cell of montmorillonite, or 11.1 mmol g^{-1} of clay. Slaughter and Milne (1960) stated that 16 mmol of Al g^{-1} of clay are needed for full coverage of montmorillonite surfaces. This represents the amount of Al required to form a complete sheet in the interlayer of a 2:1 clay providing the hydroxy-polymeric material is evenly

distributed in the interlayer. The total concentration of charge in each suspension of this study was 600 cmol(+) kg^{-1} clay. Therefore, complete adsorption of all the cations to montmorillonite is a possibility in the clays synthesized for my study.

The interlayered clays displayed varying degrees of CEC reduction (Table 3.1). The three interlayered clays had significantly lower CEC values than the non-interlayered montmorillonite and were also significantly different from one another. The lowest CEC value was observed in Al-Mt, indicating the highest amount of interlayer filling. The Fe-interlayers were slightly less effective in reducing the CEC of montmorillonite than the Al interlayers. Herrera and Peech (1970) found that the reaction of Fe(III) with montmorillonite reduces the cation-exchange capacity to about one-half of the original value, coupled with a concomitant increase in positive charge. Shen and Rich (1962) and Inoue and Satoh (1993) showed that the CEC reduction was due to hydroxy-Al groups occupying exchange sites rather than $Al(OH)_3$ blocking pathways to these sites. Hydroxy-interlayered minerals form as Al^{3+} released during weathering hydrolyses and polymerizes to form large polycations (with a postulated formula of $Al_6(OH)_{15}^{3+}$ or similar) in the interlayers of vermiculite and smectite (Schulze 1989). Fixation of hydroxy-polymers in the interlayer space of montmorillonite is responsible for the reduction in CEC. The more completely the interlayer space is filled with hydroxy polymers, the greater the reduction in CEC. Therefore, the cation-exchange-capacity measurements

Table 3.1 Selected physicochemical properties of hydroxy-interlayered clays.

Clay mineral	Initial pH	Final pH	OH/cation	cations/clay		CEC	Specific surface area
				Fe	Al		
				cmol kg^{-1}		cmol(+) kg^{-1}	m^2 g^{-1}
Mt	9.2	9.2	-	0	0	78[a]	789[a]
Fe-Mt	5.1	4.8	2.00	600	0	54[b]	679[b]
Fe,Al-Mt	5.1	4.9	2.20	300	300	45[c]	596[c]
Al-Mt	5.1	4.9	2.20	0	600	33[d]	455[d]

Means followed by the same letter within a column are not significantly different (Duncan's multiple-range test, P = 0.05)

indicate the degree of hydroxy-interlayer formation. Variations in CEC are also due to the formation of external-phase hydroxy-polymers.

The pH values of all clay suspensions except the control decreased over the aging period (Table 3.1). The decrease in pH of the suspensions indicates that Al hydrolyzed and polymerized (Dubbin et al. 1994). A decrease in pH has been taken as an indication of the formation of hydroxy-Al interlayers (Shen and Rich 1962). However, Carstea et al. (1970a) showed that change in pH is not a good measure of interlayer formation in hydroxy-Fe and -Al interlayers. The formation of hydroxyl bridging from Al^{3+} or Fe^{3+} consumes hydroxyl ions and generates protons, H^{+}, thereby lowering the pH. This is an essential step under the conditions of this study, but it does not necessarily result in interlayers. Hydroxyl ions may condense to form hydroxide precipitates or charged polymers with or without attachment to the interlayer sites.

Fixation of hydroxy-polymers on montmorillonite causes a significant reduction in the specific surface area. All interlayered clays had lower specific surfaces than the non-interlayered clay (Table 3.1). Similar results have been reported by Inoue and Satoh (1993), and Dubbin et al. (1994). The highest reduction in surface area was obtained for Al-Mt and the lowest reduction was for Fe-Mt indicating the highest and lowest amounts of interlayer formation, respectively. Fe-OH species are less effective than Al-OH species in filling the interlayer spaces of swelling clays (Carstea et al. 1970a; Frenkel and Shainberg 1980). The measured decrease in specific-surface area is in accord with the

reduction in cation-exchange capacity. The external surface area of hydroxy interlayered-montmorillonite complexes might have increased due to the formation of irregular surfaces caused by fixation of hydroxy-cations on the planar surfaces of montmorillonite. Therefore, the net decrease in surface area could be less than that predicted by interlayer filling.

The amount of exchangeable Al extracted by KCl is higher than that extracted by $CaCl_2$, but the difference is not significant (Table 3.2). Higher amounts of Al were extracted by these salts from the Fe,Al-Mt than from the Al-Mt. The cation-exchange sites in montmorillonite were not homogeneous in their ability to retain hydroxy-Al polymers; this strength varied from very weak, with which the Al polymers were only loosely held, to very strong (Hsu 1968). Therefore, Al in the Fe,Al-Mt sample was less tightly bound than in the Al-Mt sample. Both experiment and theoretical calculations show that the solubility of hydroxy-Al is minimal in the pH range 5 - 7, and increases to both higher and lower values (Keren 1980). As neutral salts were used, the Al extracted from interlayered clays should have been released from cation-exchange sites, not from dissolution of hydroxy-Al polymers. No exchangeable Fe could be extracted by KCl, $CaCl_2$ or neutral ammonium acetate (Table 3.2). There is evidence that, when distilled water is used to remove excess ions, measurable amounts of Fe are precipitated in the system (Page and Whittig 1961). Hence, the Fe released from cation-exchange sites may be precipitated when neutral salts were used. Therefore, acidified (pH 2.5) NH_4OAC was used

Table 3.2 Amounts of Fe and Al extracted in cmol(+) kg^{-1} from hydroxy-interlayered clays by different treatments.

Clay mineral	Exchangeable Fe		Exchangeable Al		
	KCl / $CaCl_2$ / NH_4OAc-pH 7	NH_4OAc (pH 2.5)	KCl	$CaCl_2$	NH_4OAc (pH 2.5)
Mt	0	0	0	0	6.5
Fe-Mt	0	97	0	0	6.5
Fe,Al-Mt	0	93	37	31	155
Al-Mt	0	0	26	24	140

to extract exchangeable Fe. This process extracted more Fe and Al than expected, based on the cation-exchange capacities of the clays (Table 3.1). One reason for this could be the dissolution of precipitated $Fe(OH)_3$ at low pH, as can be predicted from its solubility product (Page and Whittig 1961). Another reason could be the presence of Fe in mono- or di-valent complex cation forms. Thomas and Coleman (1964) showed that exchangeable Fe^{3+} is not stable, but tends to hydrolyse in clay systems. In acid and neutral soil solutions, hydroxy-cations of Fe and Al: ($Fe(OH)^{2+}$, $Al(OH)^{2+}$ or others) are the most common ionic forms (Demumbrum and Jackson 1957). The neutral salts could not extract Fe from hydroxy-Fe interlayer systems, either due to precipitation of Fe during extraction, or because Fe was adsorbed very tightly to the clay system, or both.

The diffraction pattern of Fe-Mt is characterized by broad peaks and high background (Fig. 3.1), indicating a poorly organized, incompletely filled interlayered clay. Diffuse patterns and high backgrounds may also be caused by a poor orientation of the particles due to irregular masses of precipitate between and around the platelets (Carstea 1968). Coleman et al. (1964) pointed out that both Fe- and Al-hydrous oxides were deposited between montmorillonite plates in fairly thin layers, Al-hydrous oxides giving sharper x-ray patterns and larger CEC reductions due to uniform dispersion of these hydrous oxides. X-ray data shows that Fe-Mt and Fe,Al-Mt interlayers prevented collapse upon K-saturation, but could not resist expansion with

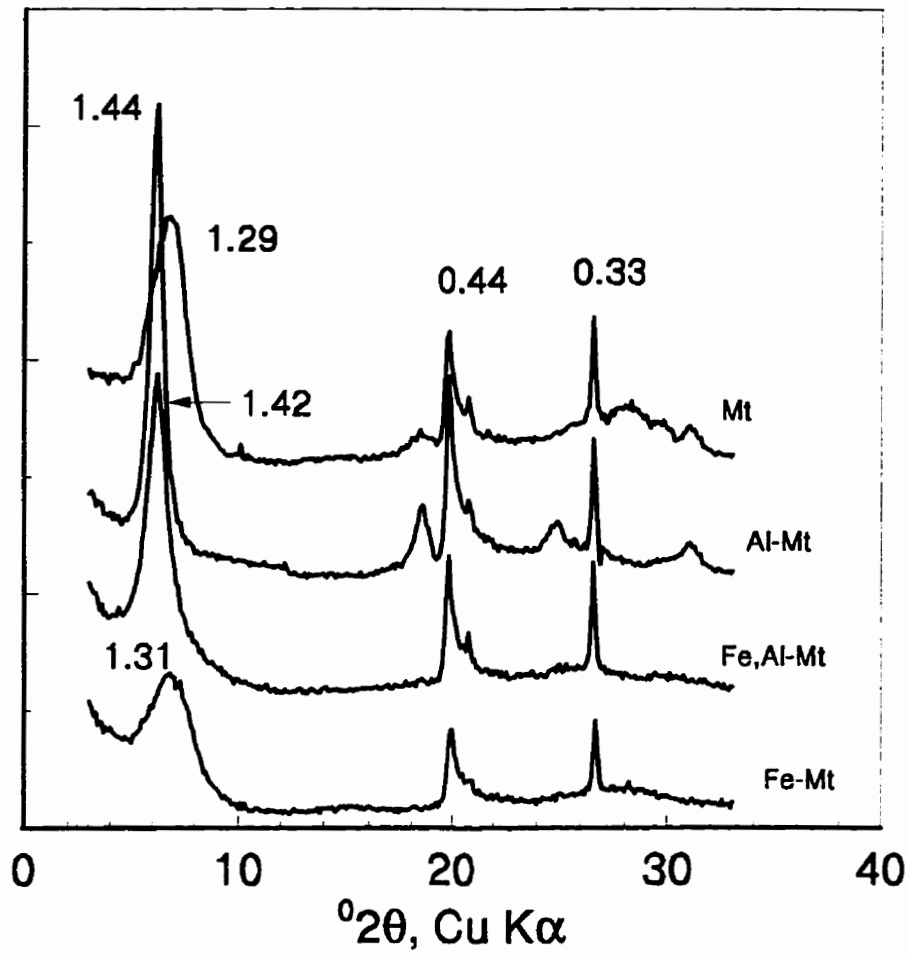


Fig. 3.1 X-ray diffractrograms of hydroxy-interlayered and non-interlayered montmorillonite (d-spacings are in nm).

glycerol solvation (Table 3.3), suggesting a structure of the smectite-chlorite type. Results are in accord with Carstea et al. (1970a). Their Fe- interlayers in montmorillonite prevented collapse upon K-saturation and heating, but did not prevent expansion upon solvation. The Fe,Al-Mt revealed a grater resistance to collapse upon K-saturation than Fe-Mt (Table 3.3) and also gave a sharper x-ray diffraction peak than Fe-Mt (Fig. 3.1). Iron could be substituted for Al in the mixed Fe, Al-hydroxy polymers. Krishnamurthi et al. (1995) and Violante et al. (1996) showed that mixed hydroxy-Fe,Al montmorillonite complexes with Fe/Al molar ratios of 0.1 to 1.0 show sharp and symmetrical x-ray diffraction peaks at room temperature. Colombo and Violante (1997) reported that the degree of interlayering of montmorillonite in mixed hydroxy-Fe,Al systems of Fe/Al molar ratios between 0.5 to 4, is very high, even after 120 d at 50°C. Rengasamy and Oades (1979) showed that polymerization of Al and Fe(III) in mixed solutions (OH/(Al+Fe) < 2.5) favours the formation of Al-Fe copoly-cations rather than a mixture of separate Al and Fe species. Colombo and Violante (1996) reported that mixed Fe-Al species form when Al and Fe are coprecipitated at different Fe/Al molar ratios. Therefore, the presence of Al in Fe,Al-Mt may cause uniform spreading of mixed Fe,Al-OH polymers in the interlayer space of montmorillonite. The 1.4 nm peak in Al-Mt (Fig. 3.1) is very sharp and prominent. This peak did not collapse to 1.2 nm on K saturation nor expand to 1.8 nm on glycerol solvation (Table 3.3). This behaviour is characteristic of a chlorite mineral. Unlike

chlorite hydroxy-Al showed stepwise collapsion upon progressive heating. Therefore, it is evident that this Al-interlayered montmorillonite sample closely resembles chlorite. Interlayer hydroxy-Al prevents smectite from shrinking and swelling (as it normally would).

3.4.2 Stability of interlayered clays to heat and chemical treatment

The temperature required to collapse (or partially collapse) the 1.4 nm spacing to 1.0 nm may be used to estimate the relative degree of filling of the interlayer space; the higher the temperature to shift the 1.4 nm peak, the larger the degree of interlayer filling. Therefore, the magnitude of the shift in d-spacing of the *001* reflection upon K-saturation and heating to 550°C is also a measure of the degree of the filling; small changes from 1.4 nm indicate large amounts of filling (Barnhisel and Bertsch 1989).

Iron-interlayered montmorillonite collapsed at 300°C (Table 3.3), indicating thermal instability. The Fe,Al-Mt showed restricted collapse at 300°C, indicating a moderate amount of interlayer filling and higher stability than Fe-Mt. Dubbin et al. (1994) found that, in a system containing both Al and Cr, Al determines the structure, serving as a template in the formation of gibbsite-like polymers. In the same manner, Fe may be substituted for Al in mixed Fe,Al hydroxy-polymers, Al giving higher stability. The 1.4 nm d-spacing of the Al-Mt reduces to 1.27 nm at 300°C and to 1.13 nm at 550°C (Table 3.3). Hydroxy-Al complexes formed the most stable of the three intergrade

Table 3.3 d-spacing (in nm) of the hydroxy-interlayered clays after subjected to different treatments.

Clay	----Saturating cation----			------Heat treatments------		
mineral	Mg	Glycerol	K	100°C	300°C	550°C
Mt	1.44	1.81	1.24	1.21	1.00	1.00
Fe-Mt	1.48	1.81	1.33	1.26	1.01	1.01
Fe,Al-Mt	1.48	1.81	1.40	1.39	1.11	1.05
Al-Mt	1.43	1.49	1.43	1.41	1.27	1.13

minerals. Non-interlayered montmorillonite showed total collapse upon heating to 300°C, as expected for a smectite with no interlayer material.

X-ray diffractrograms of K-saturated hydroxy-interlayered clays after treatment with citrate-bicarbonate-dithionite (CBD) or ammonium-oxalate in dark (AOD) are shown in Fig. 3.2. According to McKeague and Day (1966) and McKeague et al. (1971), AOD and CBD treatments can be used to extract amorphous and crystalline products of Fe and Al, respectively. Both treatments reduced the d-spacing of Fe-Mt to 1.24 nm after K saturation and to 1.0 nm after heating to 300°C (Fig. 3.2A). The results suggest that both oxalate and dithionite treatments attack the interlayer material of Fe-Mt, reducing the 1.33 nm K-saturated d-spacing (Table 3.3). Carstea et al. (1970b) also found that the dithionite-citrate treatment resulted in the greatest changes in Fe-interlayers as indicated by both X-ray and CEC data. Results for the hydroxy-(Fe,Al) montmorillonite again show the destruction of interlayer material by dithionite or oxalate treatment, even though the presence of Al, together with Fe, showed some degree of resistance to dissolution of interlayered material by oxalate treatment (Fig. 3.2B). The d-spacing obtained after oxalate treatment is indicative of the residual presence of interlayer material. The dithionite and oxalate treatments caused the least reduction in d-spacing in Al-Mt (Fig. 3.2C), indicating the highest stability for chemical treatments among the three interlayered minerals. The montmorillonite structure was not affected by either dithionite or oxalate treatments (Fig. 3.2D).

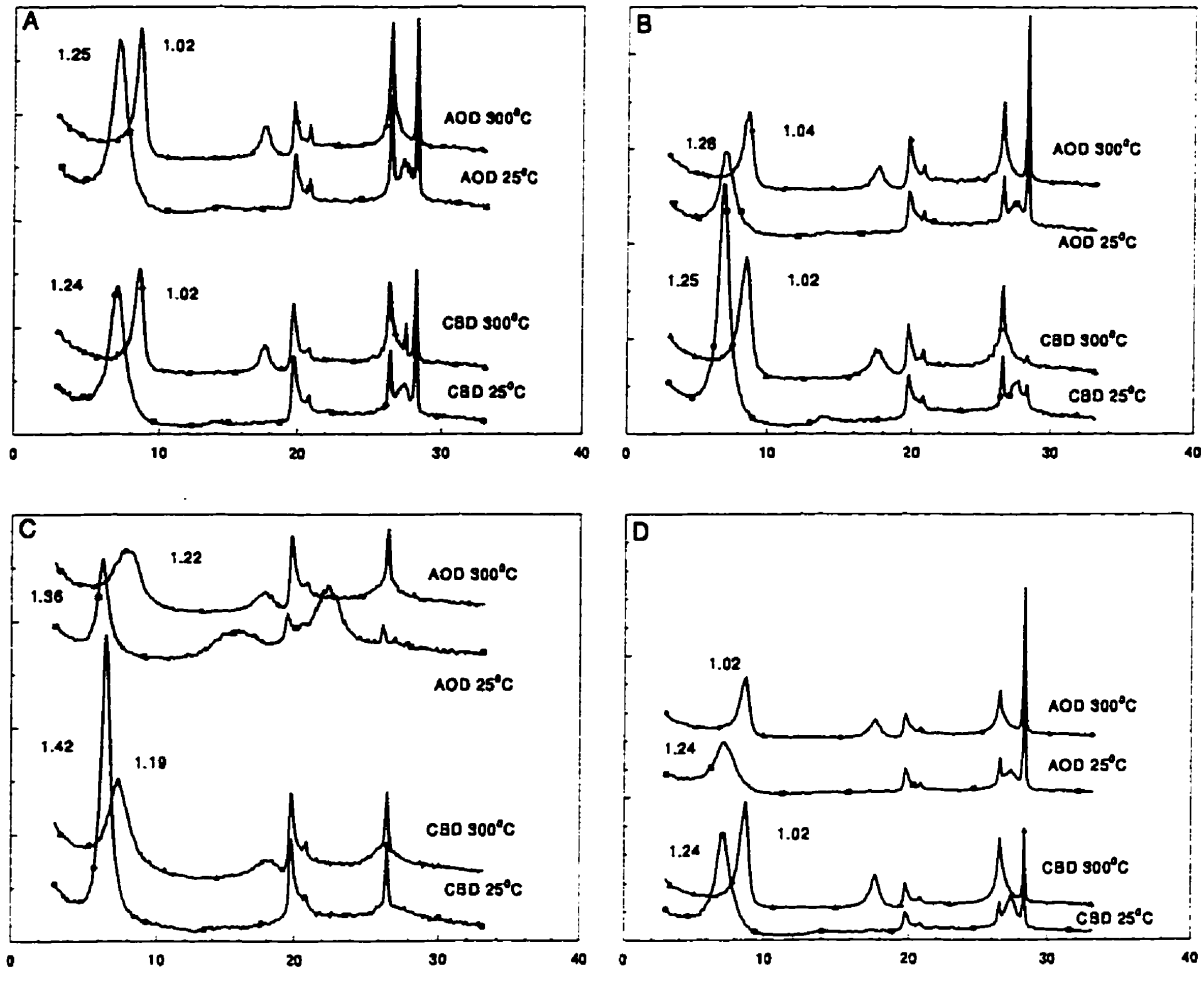


Fig. 3.2 X-ray diffractrograms of Fe-Mt (A), Fe,Al-Mt (B), Al-Mt (C) and Mt (D) after AOD and CBD treatments (spacings are in nm).

The amounts of Fe and Al extracted from the interlayered clay minerals by the CBD or AOD and the CEC values after the extraction are shown in Table 3.4. These treatments recovered almost all of the Fe initially used (600 cmol (+) kg^{-1}) to form the Fe-Mt, indicating that the interlayers were nearly completely destroyed. More Fe was extracted by AOD than CBD, suggesting that some of the hydroxy-Fe interlayers are noncrystalline (Iyengar et al. 1981). Larger amounts of Al or Fe extracted from AOD than CBD in Fe,Al-Mt (Table 3.4). In the hydroxy-Al interlayer, CBD dissolved more Al than the AOD treatment. AOD dissolved only 174 cmol (+) of Al out of the initially absorbed 600 cmol (+) Al per kg of clay. The Na-dithionite dissolves mainly crystalline Fe and Al (McKeague 1966), and the acid NH_4-oxalate (AOD) dissolves mainly amorphous Fe and Al (Iyengar et al. 1981). Much greater dissolution of layer silicates by AOD treatment may also be attributed to its low pH, where Fe, Al, and Mg are more soluble (Arshad et al. 1972). Therefore, the chemical dissolution treatments further confirm the higher stability and organized nature in hydroxy-Al polymers compared with poorly ordered interlayer materials of Fe-Mt and Fe,Al-Mt

The CEC values of Fe-Mt and Fe,Al-Mt determined after CBD and AOD treatments show that these samples have regained much of their original CEC values except for the AOD-treated Fe,Al-Mt (Table 3.4). Singleton and Harward (1971) reported that dissolution treatment of CBD caused increase in CEC from 94 to 131 cmol/kg in intergrade minerals separated from natural

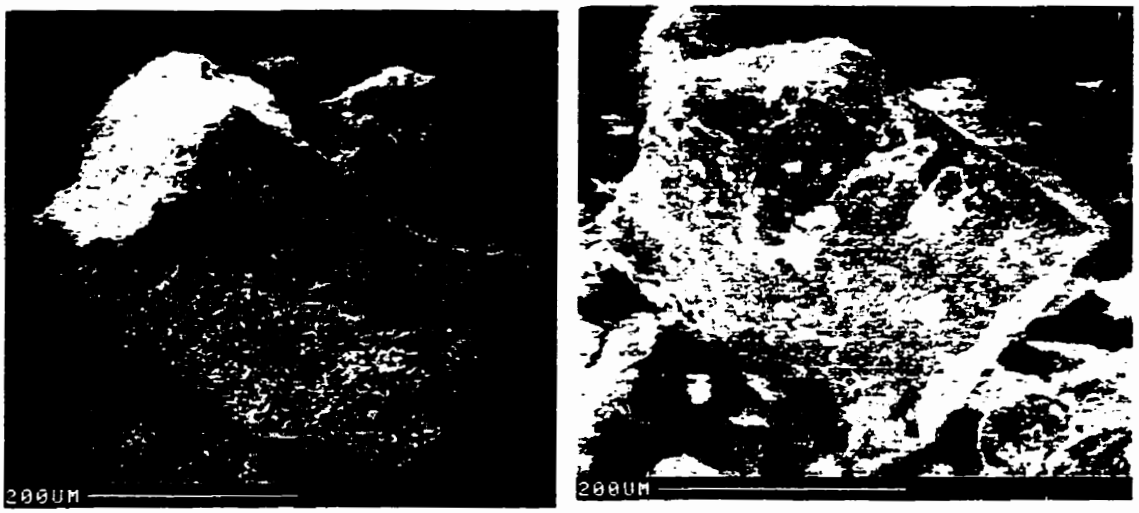
Table 3.4 Amounts of Fe and Al extracted from hydroxy-interlayered clays by CBD and AOD treatments

	CBD			AOD		
Clay mineral	Fe	Al	CEC	Fe	Al	CEC
	cmol kg^{-1}					
Mt	7	7	144	3	7	120
Fe-Mt	432	8	105	578	15	108
Fe,Al-Mt	255	259	116	299	256	48
Al-Mt	4	312	67	4	174	46

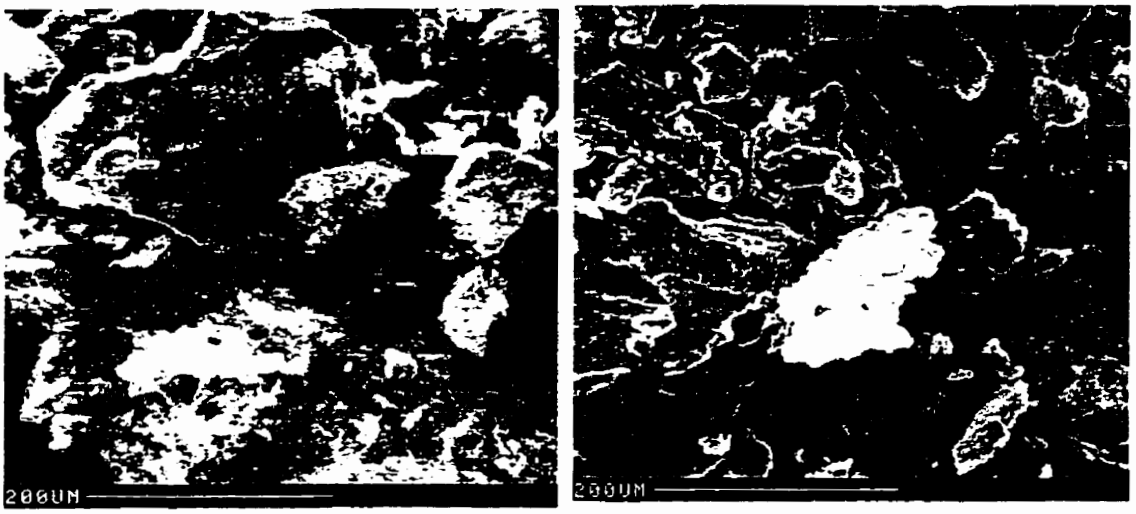
soils. The (Fe,Al) polymers remaining in Fe,Al-Mt after dissolution with AOD blocked entry of the indicator Ca^{+2} cation from internal spaces. Results for Al-Mt show the stability of interlayer material, even after CBD and AOD treatments.

3.4.3 Scanning electron microscopy

Scanning electron microscopy of the clays (Fig. 3.3A and 3.3B) revealed that discreet flakes of clay particles are not present in the hydroxy-Fe interlayered sample. In fact, the clay appears as single grains that are compact and massive with significant variation in particle size. Hydroxy-Al montmorillonite has uniform crystal shape; elongated plates that consist of stacks of platelets were observed. Non-interlayered montmorillonite show the irregular cloud-like appearance of flakes of clay. More dispersed surface morphology is observed in Fe-Mt compared to the other two hydroxy-interlayers in higher magnification SEM images (Fig. 3.3B). It has been reported that hydroxy-Fe polymers are not as effective in preventing dispersion of particles by adsorbed Na as hydroxy-Al polymers (Frenkel and Shainberg 1980). Hydroxy-Al polymers formed during the neutralization reaction apparently acted as cementing agents and prevented the dispersion of particles. However, under the SEM observation, differences in this capacity to prevent dispersion among interlayered clays, is very difficult to observe in this study.

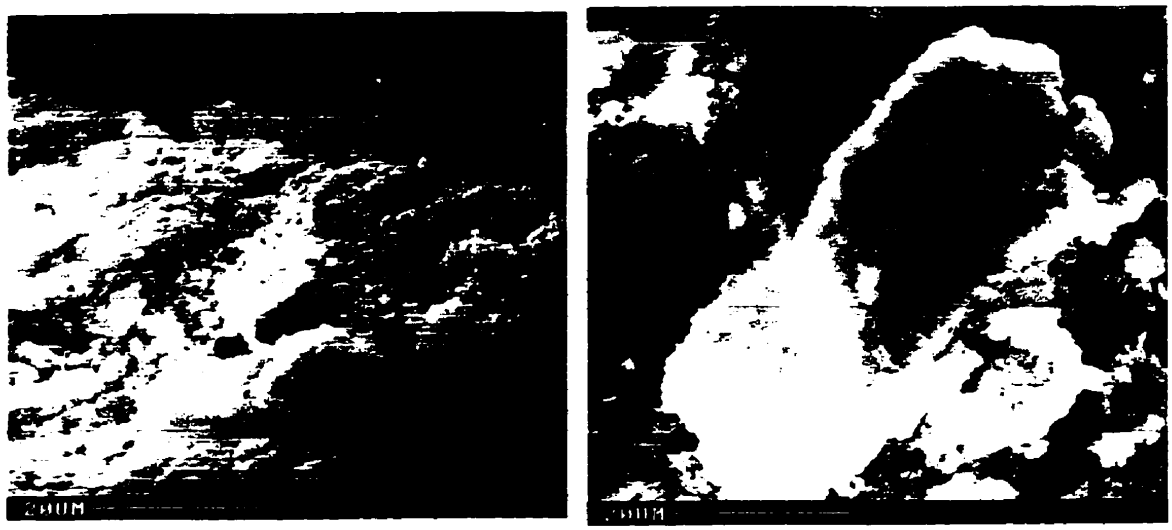


A. Fe-Mt B. Fe,Al-Mt



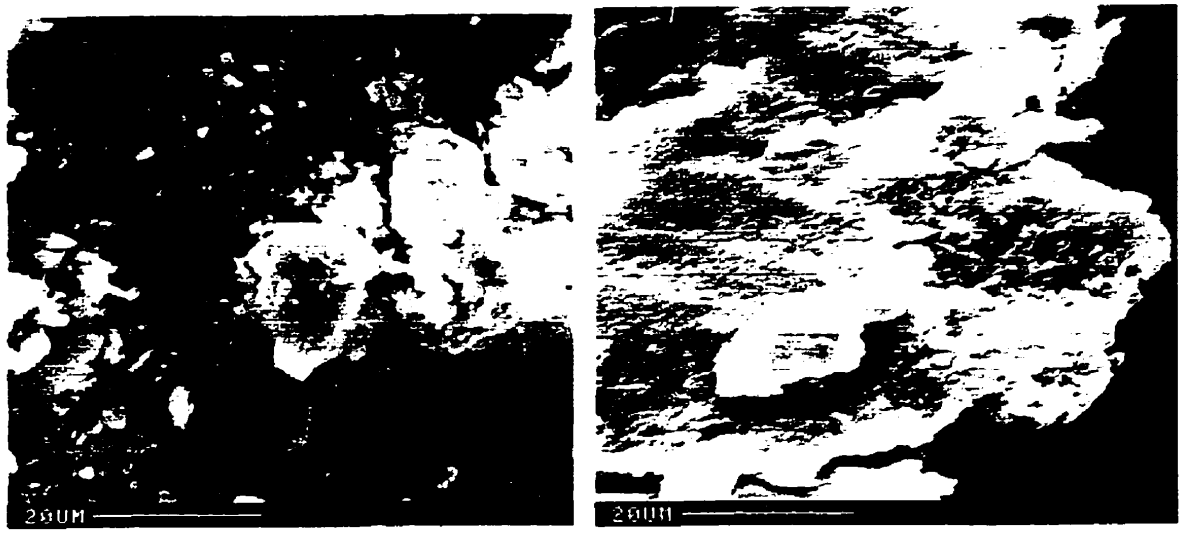
C. Al-Mt D. Mt

Fig. 3.3A Scanning electron microscope images of hydroxy-interlayered clay minerals at lower magnification (approximately 170 times).



A. Fe-Mt

B. Fe,Al-Mt



C. Al-Mt

D. Mt

Fig. 3.3B Scanning electron microscope images of hydroxy-interlayered clays at higher magnification (approximately 1150 times).

3.4.4 Infrared spectroscopy

The major absorption peaks observed in the spectra of all samples are between 3300 and 3700 cm^{-1} (Fig. 3.4). This is the OH-stretching region and these peaks probably indicate stretching of the H_2O and/or OH molecules. The main stretching band for H_2O is at a distinctly lower wave-number than that for OH, and is also much broader. Therefore, sharp peaks are due to OH than the H_2O. White (1971) observed that Crook County montmorillonite has an OH-stretching band at 3631 cm^{-1} for coordination of OH by Al-Al. The Al-Al and Al-Fe^{3+} dioctahedral OH-stretching vibrations occur at 3620 to 3630 cm^{-1} (Jackson, 1979). Accordingly, the absorption maxima at 3633, 3636, and 3631 cm^{-1} for Mt, Fe,Al-Mt and Al-Mt, respectively, indicate the presence of local clusters of Al-Al, and/or Al-Fe^{3+}. Hydroxy-Fe interlayered clay has an absorption band at 3622 cm^{-1}, due to the Al-Al cluster in the octahedral sheet in montmorillonite. The broad absorption maxima in the region 3426 to 3478 cm^{-1} in all clays indicated stretching of the H_2O molecules.

Silicate minerals have many strong Si-O absorption bands near 600 and 1000 cm^{-1}, and these are further complicated by considerable variation due to Al substitution for Si (White 1971). The absorption band at 799 cm^{-1} is probably due to the presence of quartz (Drees et al. 1989). Major absorption peaks were observed in the 1100 to 1000 cm^{-1} region for all samples (Fig. 3.4). Montmorillonite shows a single peak at 1038 cm^{-1}, whereas the Fe-Mt shows a doublet at 1055 and 1034 cm^{-1}, and Fe,Al-Mt at 1040 and 1030 cm^{-1}. A

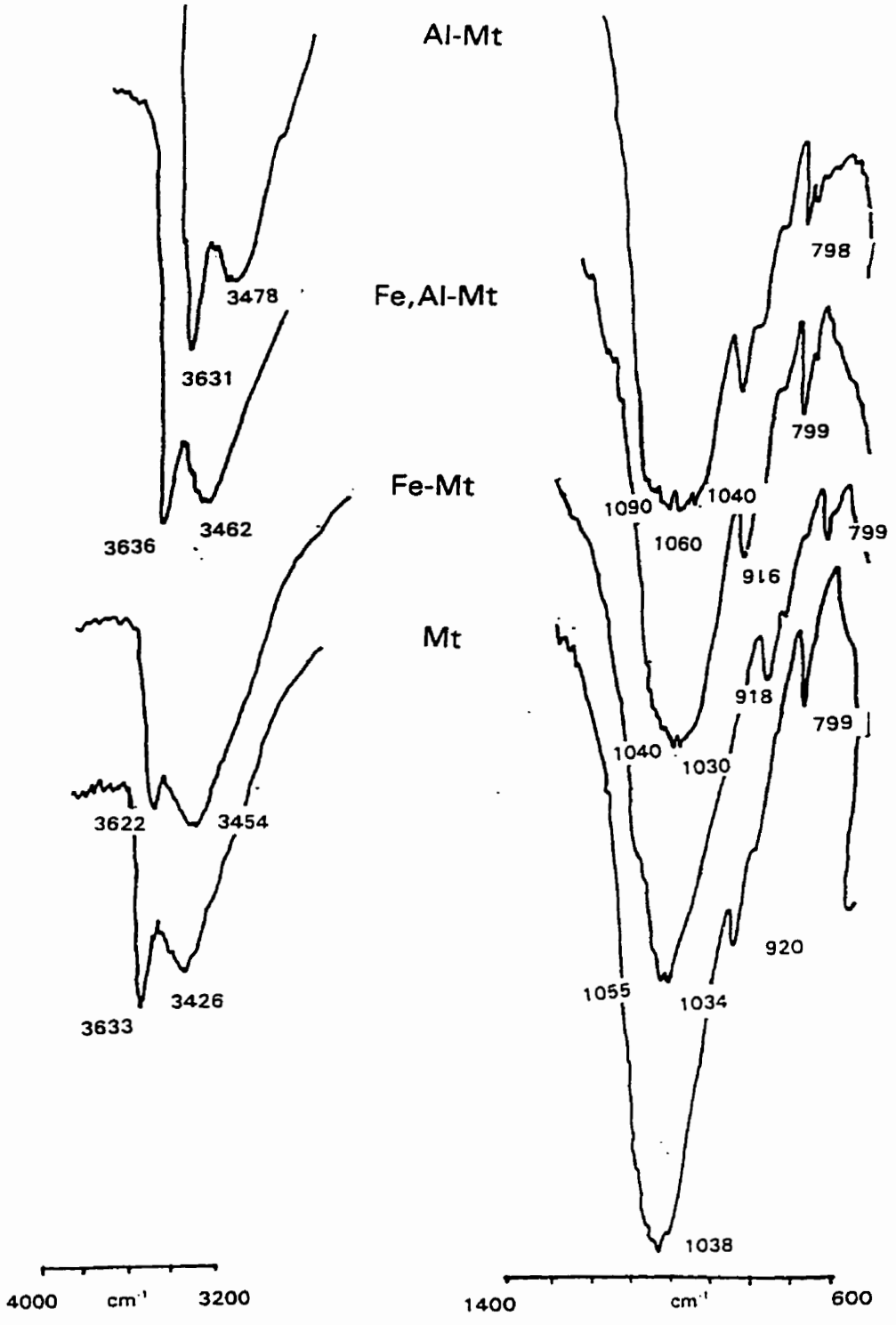


Fig. 3.4 Infrared spectra of the hydroxy-interlayered clays and non-interlayered montmorillonite.

broader peak that includes three absorption maxima at 1090, 1060 and 1040 cm^{-1} is observed in the Al-Mt. The absorption bands due to Si-O stretching vibrations occur near 1100 cm^{-1}. The slight differences among the samples may be due to substitution of Al and Fe in the octahedral sheet.

3.4.5 Charge characteristics

For single-component amphoteric solids, the PZC can be determined from the cross-over point of titration curves obtained at different electrolyte concentrations (Van Raij and Peech 1972). Figure 3.5 shows that there is no common cross-over point in Fe,Al-Mt and Al-Mt. Permanent-charge minerals, such as montmorillonite, are not expected to have a PZC, as the negative charge is too great to be balanced by the small amount of positive charge that may develop on edges of layer-silicate plates (McBride 1989c). Therefore, the absence of a common cross-over point in Fe,Al-Mt and Al-Mt is probably due to the presence of a large amount of negative charges. After treating montmorillonite with hydroxy-Al, the CEC of the hydroxy-Al-montmorillonite complexes decreased, whereas their variable charge increased (Inoue et al. 1990). The isoelectric point of amorphous $Al(OH)_3$ is in the range 7.3 - 7.5 (Parks 1965). The oxides and hydroxides of Al and Fe possess variable-charge-generating cation- and anion-exchange capacity as a result of the adsorption of potential-determining ions (usually H^+ and OH^-). The Fe,Al-Mt and Al-Mt complexes may still have many exposed $Fe\text{-}OH_2^{0.5+}$ and/or $Al\text{-}OH_2^{0.5+}$ groups

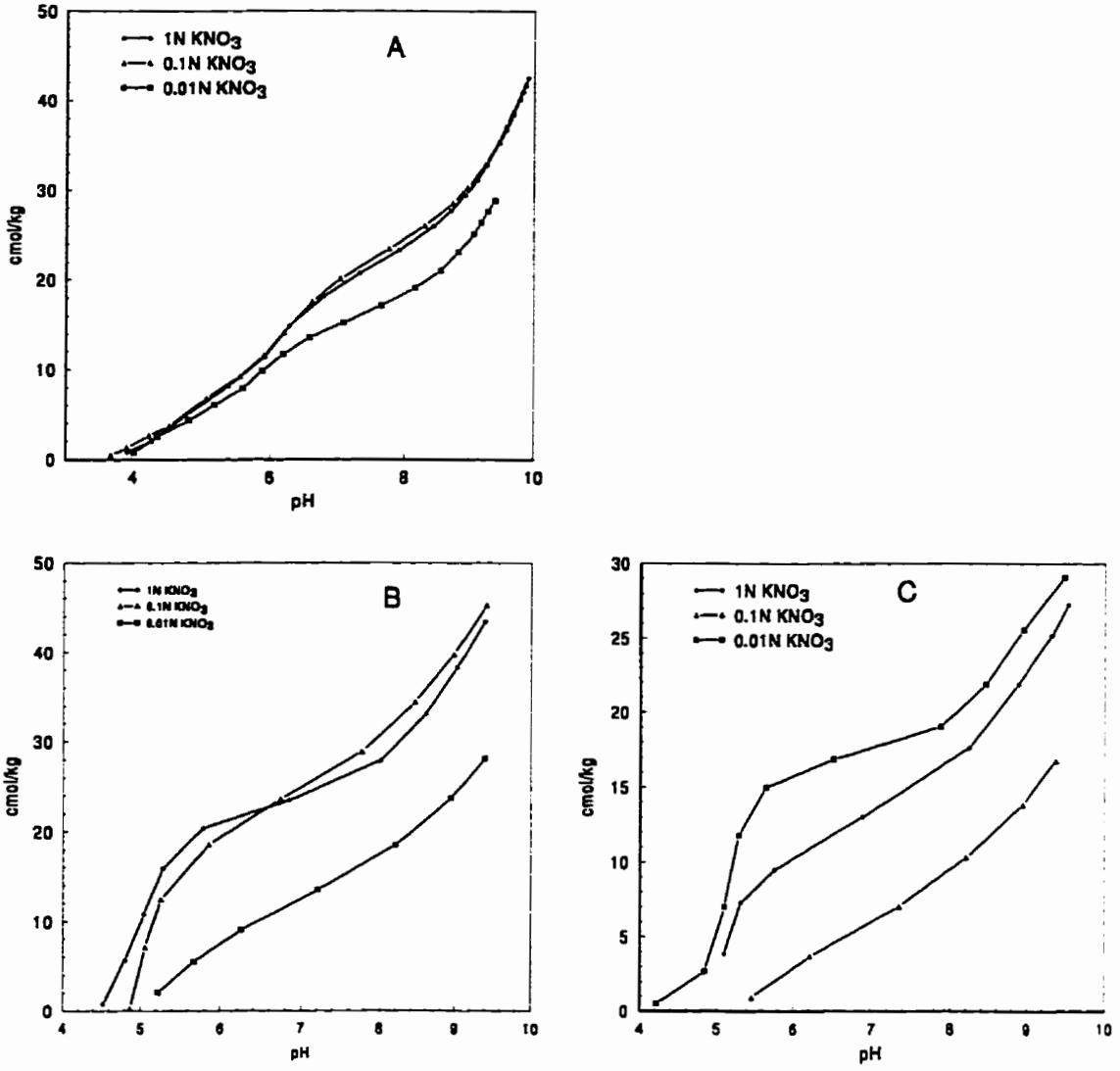


Fig. 3.5 Titration of Fe-Mt (A), Fe,Al-Mt (B), and Al-Mt (C) with OH^- in electrolyte of varying concentrations.

available for anion exchange and adsorption reactions, even though it did not show a PZC. The Fe-Mt clay mineral shows a common cross-over point at pH 4.6 (Fig. 3.5). The reaction of Fe(III) with montmorillonite brings about a reduction of the cation-exchange capacity to about one-half of the original value, and a concomitant increase in positive charge (Herrera and Peech 1970). The PZC for Fe_2O_3 is between pH 6.5 and 8.0 (Parks 1965). In soil clays that are mixtures of variable-charge and permanent-charge minerals, the latter are expected to shift the PZC estimated from titration curves to a lower value than the PZC of the variable-charge component (Laverdiere and Weaver 1977). Therefore, Fe-Mt has the highest amount of variable charge of the three interlayered clays.

3.5 Conclusions

Laboratory-synthesized hydroxy-Fe, hydroxy-Al and hydroxy-(Fe,Al) interlayered montmorillonite can be characterized by physicochemical, mineralogical and spectroscopic techniques. Hydroxy-polymers were fixed in the interlayer spaces and adsorbed on the external planar- and edge- surfaces of montmorillonite, reducing its cation-exchange capacity and specific surface area. Deposition of hydroxy-Al in the interlayer space was more uniform, and deposited in larger amounts than hydroxy-Fe polymers. Hydroxy-Al interlayered material showed the highest stability among the three interlayered materials,

whereas hydroxy-Fe was the least stable. The presence of Al together with Fe in hydroxy-(Fe,Al) imparted a higher stability than in purely hydroxy-Fe interlayered clay minerals, by substituting Al for Fe in the hydroxy-polymers.

The CBD and AOD treatments were used to determine the stability and crystallinity of the three hydroxy-interlayers by extracting crystalline and amorphous materials, respectively. Both treatments reduced the d-spacings of Fe-Mt, and Fe,Al-Mt to 1.2 nm after K saturation. This suggests that both treatments attack interlayer material in hydroxy-Fe interlayered clays. Hydroxy-Al interlayer was only slightly affected by AOD and CBD treatment and was deemed more stable. The stability of hydroxy-interlayers depended on the amount of interlayering and the crystallinity of the interlayer material.

4. HYDROQUINONE-DERIVED HUMIC POLYMERS FORMED IN THE PRESENCE OF HYDROXY-INTERLAYERED CLAYS

4.1 Abstract

The formation of humic substances was studied in montmorillonite and montmorillonite with interlayered hydroxy-Fe, mixed hydroxy-Fe,Al and hydroxy-Al. Clay-hydroquinone mixtures were prepared by adding pre-weighed amounts of hydroquinone to the clay suspensions at pH of 5 or 6. These suspensions were aged for 30 d in the dark and then filtered. The supernatant and clay-hydroquinone complexes were analyzed for organic C fractions. Infrared and XRD analysis of the solid-phase complexes was also done.

Humic acids separated from supernatant solutions were correlated to the darkening of hydroquinone as measured by the absorbance at 400 nm. The rate and degree of darkening varied with clay-mineral type, the stability of the hydroxy-interlayered material, and pH. Non-interlayered montmorillonite, with Na as the exchangeable cation, contained the highest amount of humic-acid C in the supernatant, whereas Fe-Mt-HQ, and Fe,Al-Mt-HQ yielded modest amounts. The most stable hydroxy-Al interlayered clay gave the lowest amount of humic-acid C in the supernatant. These results are supported by

K_{400}, Δ log K and RF values.

Less than 2% of the added organic C was retained by the clay minerals. Variations in the amount of C retained as clay-hydroquinone complexes are explained on the basis of specific surface area and positively charged functional groups of the clays. Less than half of the adsorbed C was extracted by alkaline solutions, suggesting its incorporation into stable organo-mineral complexes.

4.2 Introduction

The oxidative polymerization of polyphenols in soils is regarded as one of the major pathways in the formation of humic substances (Flaig et al. 1975), and both microbial and abiotic processes contribute to this. Among microbial influences, humic substances may be derived from lignin that is incompletely utilized by microorganisms, with the result that the residuum becomes part of the soil humus (Riffaldi and Schnitzer 1973). In addition, phenolic aldehydes and acids released from lignin during microbial attack may undergo enzymatic conversion and polymerize to form humic-like macromolecules, and polyphenols that are synthesized by microorganisms from non-lignin C sources could undergo enzymatic conversion and polymerize to form humic-like macromolecules (Stevenson 1994). The participation of microbial phenoloxidases is important in the above-mentioned biotic pathways of humus

formation through reactions involving polyphenols and quinones.

The abiotic formation of humic polymers also proceeds via oxidative polymerization of polyphenols (Huang 1990; Shindo and Huang 1982). The catalytic effects of clay minerals, oxides, natural and synthetic Fe, Al and Si in the formation of humic substances have been studied (Huang 1990; Shindo and Huang 1984; 1982). Shindo et al. (1996) further demonstrated that manganese oxide suspended in combined hydroquinone and lysozyme solutions resulted in the copolymerization of enzymes during the synthesis of humic substances, producing humic-enzyme complexes.

Abiotic catalysts are heterogeneous catalysts, whereas enzymes function as homogeneous catalysts (Pal et al. 1994). Catalysis by clays is usually detected through an increase in the rate of oxygen consumption or an accelerated appearance in solution of coloured oxidation products relative to the rate observed in solutions of the phenols without clays (McBride 1987). Oxidative polymerization of polyphenols in soils is regarded as one of the main processes in the formation of humic substances (Shindo and Huang 1982). Schnitzer (1982) implied that the synthesis of humic acid from simple phenols and phenolic acids is a one-electron transfer process, and that the rate-determining step is the formation of semiquinone radicals. Some semiquinones, which are normally relatively unstable, will couple with each other to form a stable humic-acid polymer. In contrast to electron-transfer reactions, coupling of radicals requires no activation energy (Chang and Allan 1971), and hence the

coupling of semiquinones rather than the formation of quinones should be the kinetically preferred reaction path (Shindo and Huang 1984).

Many investigators have observed the heterogeneous catalytic effects of inorganic soil components on the oxidative polymerization of phenols (Filip et al. 1977; Shindo and Huang 1982; McBride 1987). Non-crystalline forms of Fe and Al oxides/hydroxides have been widely investigated in this context (Shindo and Huang 1984). Aluminum and Fe^{3+} minerals have often been suggested as active oxidizing sites for organic molecules, and this catalytic oxidation effect of Fe and Al oxides/hydroxides has been demonstrated indirectly (Wang et al. 1983a). Studies have also been done where exchangeable Fe(III) and other cations occupy the exchange complex of clays (Thompson and Moll 1973). Experimental results have often been inconsistent, but all studies show that the catalytic effect exerted by Fe and Al oxides/hydroxides is less than that of Mn(IV) minerals.

Characteristics of the Mt, Fe-Mt, Fe,Al-Mt and Al-Mt were discussed in Chapter 3. The objective of this study is to examine the catalytic effects of laboratory-synthesized hydroxy-interlayered clays in comparison with non-interlayered montmorillonite on the polymerization of hydroquinone. Mineralogical and physicochemical differences among these clays (Chapter 3) may affect their catalytic ability. This study will facilitate further understanding of humus-forming processes and the abiotic polyphenol pathway in soils containing hydroxy-Fe and -Al interlayered clays.

4.3 Materials and Methods

4.3.1 Synthesis of humic materials

Three hydroxy-interlayered montmorillonites, hydroxy-Fe, mixed hydroxy-Fe,Al and hydroxy-Al, and a non-interlayered Na-montmorillonite were used in this study. The preparation of these clays is described in Chapter 3. Iron and Al salts were added separately to Na-saturated montmorillonite suspensions to give 600 cmol(+) kg^{-1} of clay. These suspensions were titrated with 0.1 M NaOH to pH 5.1. Blank experiments were done using synthetic hydrous oxides of Fe, Fe-Al, and Al without montmorillonite. These hydrous oxides were prepared using the same number of moles of (+) charges and titrating to the same pH as for the hydroxy-interlayer-clay preparations. Certified reagent-grade hydroquinone (1,4 dihydroxybenzene) was the diphenol used. Hydroxy-interlayered-hydroquinone mixtures were prepared by adding measured amounts of hydroquinone (HQ) to clay suspensions of 10 g clay in 2 L distilled water, to give 300 cmol HQ kg^{-1} of clay under constant stirring. The study was done at two pH levels, 5.0 and 6.0, for each clay. The pH of the suspension was adjusted with 0.1 M NaOH or 0.05 M H_2SO_4. Suspensions were aged in polypropylene bottles after bringing the final volume to 3 L, covered with black plastic bags for 30 d, and were agitated daily. After aging, each suspension was separated into its filtrate (supernatant) and solid phase by passing through a 0.025 μm Millipore filter. The solid phase of each sample was washed,

dialysed and freeze dried. Hydrous-oxide-hydroquinone complexes were also prepared by giving similar conditions as clay suspensions, without clay and using the same amount of cations as used for interlayered-clays. A control of hydroquinone, without clay and oxides, was also run at the same conditions. The hydroquinone complexes of Fe-Mt, Fe,Al-Mt, Al-Mt and Mt will be abbreviated as Fe-Mt-HQ, Fe,Al-Mt-HQ, Al-Mt-HQ, and Mt-HQ, respectively. The hydrous-oxides of Fe, Fe,Al and Al-hydroquinone complexes and the hydroquinone-only sample (without clay controls) will be known as Fe-HQ, Fe,Al-HQ, Al-HQ and HQ.

4.3.2 Analysis of supernatant and solid phase hydroquinone complexes

The pH, total C, absorbance at 400 and 600 nm (HP 8452A Diode array spectrophotometer), and amounts of Fe and Al in the supernatants were measured. The cation-exchange capacity of clay-hydroquinone complexes was determined according to the procedure of Rich (1961). The specific surface area was determined using ethylene glycol monoethyl ether (EGME) (Carter et al. 1986). The modified Mebius procedure (Yeomans and Bremner 1988) was used to determine organic C. Exchangeable Al and Fe were obtained by washing 100 mg of the complexes five times (10 mL each) with 0.5 M $CaCl_2$. Aluminum and Fe in the extract were determined by atomic absorption spectroscopy. X-ray diffraction patterns were obtained after K-saturation using Cu$K\alpha$ radiation with a Philips PW1710 diffractometer. The IR spectra of the

clay-hydroquinone complexes were obtained from 400 to 4000 cm^{-1} on 3% KBr discs.

Humic substances associated with soil often extracted using a strong base like NaOH (Stevenson 1994). The alkaline-soluble C of the solid-phase hydroquinone complexes was extracted as follows: To 1 g of solid fraction, 50 mL of 0.1 M NaOH was added and left to stand for 24 h. A 40% Na_2SO_4 solution was added until the final concentration of the solution was 3% with respect to Na_2SO_4 before centrifugation. The extract was collected after centrifugation at 10,000 *g*. The residue was washed twice (or until the extract was colourless) with 50 mL of 0.1 M NaOH containing 3% Na_2SO_4. The extracts were combined and 0.1 M NaOH was added to bring the volume to 200 ml. Total alkaline-soluble C was determined using an aliquot of the extract, and the remainder was used for humic-acid fractionation.

4.3.3 Determination of humic acids

The nature and quantity of the humic acids in the supernatant and their corresponding NaOH extracts of the solid complexes were determined as described by Kumada (1987). A known amount of the supernatant or alkaline-extract of the solid phases was acidified with H_2SO_4 to pH 1.5 and allowed to stand overnight. The precipitate (humic acid) was washed with H_2SO_4 (1:100), repeatedly. The humic acid was dissolved again in 50 mL of 0.1 M NaOH, and its absorbance at 400 and 600 nm was measured within 2 h. The

degree of humification of the humic acid was estimated using K_{400}, Δ log K and RF parameters. The Δ log K value is the logarithm of the ratio of the absorbance of humic acid at 400 nm to that at 600 nm; K_{400} is the absorbance value of humic acid at 400 nm; the RF value is the absorbance of humic acid at 600 nm divided by mg C mL^{-1} of humic-acid solution, which is used to determine the uv-visible spectra, multiplied by 15 (Kumada 1987). The E_4/E_6 ratio was also determined by the absorbance of humic acid at 400 and 600 nm (K_{400}/K_{600}) (Kumada 1987).

4.4 Results and Discussion

4.4.1 Formation of humic substances in the presence of hydrous oxides

The results of the control experiments (Fe-HQ, Fe,Al-HQ, Al-HQ, and HQ without clay) are shown in Table 4.1. Reduction of pH due to oxidative polymerization and minute amounts of Al (1-4 cmol (+) kg^{-1}) and Fe (1-3 cmol (+) kg^{-1}) were measured in the supernatants of control experiments. The degree of darkening of these supernatants, as measured by the absorbance at 400 nm, was in the range 0.03 to 0.15 absorbance units. The amounts of humic acids extracted from the supernatants of these samples were low. The absorbance values at 400 nm of these humic acids range from 0.04 to 0.08. Because the absorbance values at 600 nm were <0.01 in all samples (data not shown), the humic acids could not be characterized using E_4/E_6, Δ log K, or RF

Table 4.1 Characteristics of the supernatants of hydrous oxide-hydroquinone systems in the absence of clay after 30 d.

Hydrous-oxide -hydroquinone	Initial pH	Final pH	supernatant K_{400}	Fe	Al	---Humic acid-- Amount	K_{400}
				cmol(+) kg^{-1}		mg kg^{-1}	
HQ	5.0	5.0	0.03	0	0	313	0.05
HQ	6.0	5.1	0.05	0	0	573	0.08
Fe-HQ	5.0	4.4	0.14	3.1	0	522	0.06
Fe-HQ	6.0	4.8	0.15	2.5	0	468	0.06
Fe,Al-HQ	5.0	4.3	0.09	1.1	1.0	642	0.07
Fe,Al-HQ	6.0	4.8	0.09	0.7	0.8	562	0.04
Al-HQ	5.0	4.3	0.04	0	4.4	604	0.06
Al-HQ	6.0	4.5	0.06	0	3.5	540	0.06

parameters. Abiotic formation of humic substances through the polymerization of phenolic compounds is the major humification process in the present study. The products of oxidized hydroquinone may be dimers or polymers of ill-defined composition. Therefore, humification processes yielded intermediate products of humic substances. It seems that the darkening in these control systems was due mainly to the formation of lower-molecular-weight phenolic polymers rather than humic acids. According to Shindo and Huang (1984), the catalytic effect of Fe-oxide in the formation of humic acid is relatively minor, and a catalytic effect was not observed at all in the Al-oxide systems. Aging of Fe-HQ, Fe,Al-HQ, Al-HQ and HQ for 30 d at pH 5 or 6, yielded low amounts of humic acids in supernatants (Table 4.1). The effects of Fe and Al oxides on the amount of humic acid formed at pH 5.0 were pronounced (Table 4.1). Solid phases of Fe-HQ, Fe,Al-HQ and Al-HQ were not used for the extraction of the humic substances due to the small amounts produced. Therefore, supernatant characterization for the formation of humic substances in hydrous oxide showed that the participation of these hydrous oxides in humification process is minimal.

4.4.2 Formation of humic substances in the presence of interlayered and non-interlayered montmorillonitic clays

4.4.2.1 Properties of clay-hydroquinone complexes. The properties of hydroquinone complexes of Fe-Mt, Fe,Al-Mt, Al-Mt and Mt are shown in Table

4.2. Slight pH reduction was observed in supernatants of most samples as compared to the larger decreases observed in the corresponding controls (Table 4.1). The process of hydroquinone oxidation releases protons (H^+) (Kung and McBride 1988). Accordingly, the pH of the clay suspension after oxidation should be lower than the starting pH. The slight pH reduction (compared to the controls) is expected as the hydroxy-interlayered-clays in suspension would adsorb more protons than the suspensions of hydrous oxide only.

There was no detectable Al and only trace amounts of Fe in the corresponding supernatants of the hydroquinone complexes (data not shown). Therefore, no relationship could be obtained between the yields of humic acids and Al and Fe contents in the supernatant. There was no significant difference between the amounts of Al extracted by 0.05 M $CaCl_2$ from Al-containing interlayered-hydroquinone (Table 4.2) and Al-containing interlayers (Table 3.2). The Fe was not extractable in Fe-containing hydroxy-interlayers (Table 3.2), whereas in respective hydroquinone complexes, minute amounts of Fe (3.6-1.3 cmol (+) kg^{-1}) were extracted by $CaCl_2$ (Table 4.2).

The CEC and specific surface-area values of the hydroxy-interlayered-hydroquinones (Table 4.2) are not significantly different from the valuesobtained for the same hydroxy-interlayered clays before hydroquinone complexation (Table 3.1). Furthermore, the complexation of hydroquinone with Fe-Mt and Mt did not change the d-spacing of the clay (Table 3.3 and Table 4.2). The d-spacings of Fe-Mt-HQ and Fe,Al-Mt-HQ were reduced slightly

Table 4.2 Properties of the montmorillonite and hydroxy-interlayered - hydroquinone complexes.

Clay-hydroquinone	Initial pH	Final pH	Surface area	$CaCl_2$ extractable			d-spacing
				CEC	Fe	Al	
			$m^2\ g^{-1}$	---------cmol(+) kg^{-1}-------			nm
Mt-HQ	5.0	5.2	778	81	0	0	1.23
Mt-HQ	6.0	5.6	782	84	0	0	1.24
Fe-Mt-HQ	5.0	4.8	665	55	3.6	0	1.30
Fe-Mt-HQ	6.0	5.9	672	60	1.8	0	1.29
Fe,Al-Mt-HQ	5.0	4.7	569	41	1.3	26	1.36
Fe,Al-Mt-HQ	6.0	5.8	598	44	1.4	28	1.35
Al-Mt-HQ	5.0	4.9	460	30	0	24	1.42
Al-Mt-HQ	6.0	6.1	478	30	0	19	1.42

(Table 4.2) from their original values of 1.33 nm and 1.40 nm, respectively. Shindo et al. (1995) stated that, after penetration of hydroxy-Al polymers into the interlayer spaces of expansible 2:1 clays, the interference of humic acids with the interlayering is much less pronounced. Therefore, the structural and physicochemical changes in hydroxy-interlayers are minimal upon hydroquinone complexation. Minerals rich in Fe are more susceptible to attack by fulvic acid than those containing little or no Fe (Schnitzer 1986). Fulvic acid was estimated by the difference between the amounts of C that were alkali soluble and acid insoluble (humic-acid). The amounts of fulvic acid extracted from Fe-containing-hydroquinones are higher than that from other clays (Table 4.4). Dissolution of hydroxy-Fe interlayers by fulvic acid explains the slight reduction of d-spacing in these clays. No significant differences were observed in the IR spectra of hydroxy-interlayered clays before and after mixing with hydroquinone (data not shown). The total amounts of organic C retained by the clays were between 2990 to 4060 mg kg^{-1} of clay (Table 4.4). The retention of small amounts of hydroquinone and its oxidation products onto clay surfaces (Kung and McBride 1988) may be the reason for the similarity in the IR spectra before and after hydroquinone complexation.

4.4.2.2 Formation of humic substances in supernatants of clay-hydroquinone complexes. The degree of humification of humic acid is commonly determined using the absorbance of light at 400 and 600 nm (Shindo and Huang 1984).

Table 4.3 shows the characteristics of humic acids separated from supernatants of hydroquinone complexes and supernatant K_{400} values. Darkening of supernatant solutions (as measured by the absorbance at 400 nm) ranged from 0.05 to 0.3 absorbance units (Table 4.3). There was a positive linear correlation ($r^2 = 0.81$) between the darkening of the supernatant solutions and the amount of humic-acid C extracted from the supernatants. There was a strong relation ($r^2 = 0.91$) between K_{400} of dissolved humic-acid, extracted from supernatants, and amounts of humic-acid C. According to the degree of darkening of humic acids extracted from the supernatant, the clays examined here can be grouped as follows: Mt-HQ > Fe-Mt-HQ > Fe,Al-Mt-HQ > Al-Mt-HQ (Table 4.3). Based on the amounts of humic acids extracted from the clay-hydroquinone complexes (Table 4.3) and the controls (Table 4.1), it is concluded that clay minerals accelerate the polymerization of hydroquinone to varying degrees. The values of Δ log K and RF are negatively correlated ($r^2 = 0.85$). The degree of humification of humic acid increases as Δ log K decreases and RF increases (Kumada 1987). The Δ log K and RF values of the supernatants follow the same pattern as that of K_{400} (Table 4.3). The ratio of optical densities at 400 and 600 nm of dilute aqueous humic-acid and fulvic-acid solutions are widely used by soil scientists for the characterization of these materials. This ratio, usually referred to as E_4/E_6, is independent of the concentration of humic materials, but varies for humic materials extracted from different soil types (Schnitzer and Khan 1972). The magnitude of E_4/E_6 ratios

Table 4.3 Humic acid characteristics in the supernatant of clay- hydroquinone complexes.

				----------Humic acid----------			
Clay-hydroquinone	Initial pH	supernatant K_{400}	Amount mg kg^{-1}	K_{400}	E_4/E_6	ΔlogK	RF
Mt-HQ	5.0	0.24	5890	0.28	4.1	0.61	0.32
Mt-HQ	6.0	0.30	6770	0.35	4.5	0.65	0.31
Fe-Mt-HQ	5.0	0.14	3280	0.15	4.9	0.69	0.26
Fe-Mt-HQ	6.0	0.24	3825	0.23	3.9	0.59	0.42
Fe,Al-Mt-HQ	5.0	0.20	3660	0.14	9.4	0.97	0.11
Fe,Al-Mt-HQ	6.0	0.15	3088	0.12	6.9	0.84	0.14
Al-Mt-HQ	5.0	0.14	2330	0.08	10.8	1.03	0.09
Al-Mt-HQ	6.0	0.05	1459	0.08	9.8	0.99	0.16

of fulvic acids and humic acids is governed primarily by particle size and mass (Chen et al. 1977); a low ratio is indicative of a relatively high-molecular-weight material. Accordingly, the results obtained from this study suggest that Al-Mt-HQ has the lowest, mixed Fe,Al-Mt-HQ has moderate, and Mt-HQ and Fe-Mt-HQ have the highest molecular-weight humic materials. The results of K_{400}, Δ log K and RF values are in agreement with this sequence. Therefore, I conclude that the different clay minerals catalyzed the formation of different organic polymers, different in structure and molecular size, and forming at different rates. There was no significant difference in the formation of humic substances between the two pH levels for each clay mineral (Table 4.3). The oxidation of hydroquinone is pH dependent, showing higher oxidation at higher pH values (Wang et al. 1977). The lower pH levels could also facilitate the oxidation reaction by dissolving structural Fe and Al. The resultant effect of oxidation of hydroquinone at higher pH and then dissolution of Fe and Al at lower pH (and the narrowness of the selected pH values, 1 pH unit apart) may be the reasons for the insensitivity in yield of humic acid with pH in this study.

How did the clays in suspension catalyze the oxidation of hydroquinone in solution? Several possibilities exist: The oxidation of diphenols, $C_6H_4(OH)_2$, by Fe(III) is thermodynamically favourable, as indicated by the E^0 values of eq. (1) and (2) (Weast 1978).

$$C_6H_4(OH)_2 \rightharpoonup C_6H_4O_2 + 2H^+ + 2e^- \quad E^0 = -0.6992V \qquad (1)$$

$$Fe^{3+}+e^- \rightleftharpoons Fe^{2+} \quad E^0=0.770V \qquad (2)$$

Nevertheless, the accelerating effect of Fe oxide on the darkening of hydroquinone is relatively limited (Shindo and Huang 1984). Whereas Fe^{3+} present as an exchangeable cation on smectites oxidizes hydroquinone, once it hydrolyses to hydroxy-Fe, it is less effective as an oxidizing agent (Filip et al. 1977). Only trace levels of Fe^{2+} were detected in solution for similar experiments involving Fe oxides (McBride 1987). Oxidation of Fe^{2+} by O_2 in solution is relatively rapid at moderate pH. As Fe^{2+} is easily reoxidized to Fe^{3+}, Fe^{2+} was not detected in the reaction mixture upon oxidative coupling of phenolic compounds. McBride (1987) concluded that O_2 is the ultimate oxidizing agent in Fe-oxide systems, accounting for the loss of O_2 from solution without a concomitant rise in Fe^{2+} concentration. Therefore, the increased probability of interaction between O_2 and the phenol due to the presence of a surface might be the most likely reason for the highest degree of humification in montmorillonitic clay. Huang et al. (1977) observed that the internal surface of vermiculitic minerals are generally not of great significance in the retention of phenolic acids. This was interpreted as due to steric hindrance and negative repulsion by the interlayers toward the phenolic acids. Consequently, the external surface of the 2:1 clays might serve as the catalytic surface for oxidation. Thompson and Moll (1973) showed that oxidation of hydroquinone

in the presence of smectites increases with increasing CEC and specific surface area.

Clay suspensions that maintain the highest pH provide the most favourable conditions for phenol oxidation (McBride 1987). Therefore, adsorption of protons generated by oxidation of hydroquinone may also play a part in this reaction. The sorption by layer silicates of protons generated in the oxidation reaction can be expected to catalyze the oxidation by buffering against decreasing pH. The exchangeable cations on the clay very likely enter into the reaction as well.

4.4.2.3 Characterization of humic substances separated from solid clay-hydroquinone complexes. Less than 2% of the 2.16 g of C added as hydroquinone was retained by the clay-hydroquinone complexes (calculated from Table 4.4). Al-Mt-HQ had the least amount of total C, whereas montmorillonite and hydroxy-Fe systems retain the highest amounts (Table 4.4). The noncrystalline nature of the Fe-interlayered clays (Chapter 3) that produced $Fe\text{-}OH_2^{0.5+}$ groups in acidic pH, likely plays a significant role in this retention. The high CEC and SSA values of montmorillonite (Table 4.2) favour its retention of organic C. The drastic decrease in specific surface in Al-Mt (chapter 3) largely accounts for the relatively small amount of C retained. Of the total amounts of C associated with the complexes, $<50\%$ was extracted as alkaline-soluble C, which represented the total humic and fulvic acids

Table 4.4 Amounts of C and optical properties of the humic substances occurring in solid clay-hydroquinone complexes.

Clay-hydroquinone	Initial pH	Total C	Alkaline soluble C	Residual C	Humic acid				
		mg kg^{-1}			amount mg kg^{-1}	K_{400}	E_4/E_6	ΔlogK	RF
Mt-HQ	5.0	3650	736	2914	230	0.10	2.90	0.46	0.15
Mt-HQ	6.0	3560	604	2950	290	0.10	2.88	0.46	0.12
Fe-Mt-HQ	5.0	4010	1580	2430	360	0.11	2.82	0.45	0.11
Fe-Mt-HQ	6.0	3960	1480	2280	320	0.11	3.23	0.50	0.10
Fe,Al-Mt-HQ	5.0	3850	1540	2210	370	0.16	3.04	0.48	0.14
Fe,Al-Mt-HQ	6.0	4060	1640	2420	430	0.20	2.73	0.42	0.17
Al-Mt-HQ	5.0	2990	730	2260	270	0.05	2.97	0.47	0.07
Al-Mt-HQ	6.0	3110	798	2312	290	0.10	2.90	0.46	0.12

separats from the solid phases (Table 4.4). The rest remained with the complexes, indicative of stable organo-mineral complexes (Goh and Huang 1986). Humic substances are the principal organic components of soils, where they interact with clay minerals to form organo-mineral complexes with a wide range of chemical and biological stabilities.

Only a small amount of alkaline-soluble C was separated as humic acid by precipitation in acid (Table 4.4). The amounts of humic acid extracted from the Fe-Mt-HQ and Fe,Al-Mt-HQ complexes was substantially higher than that from Mt-HQ (Table 4.4). The low E_4/E_6 ratio indicates that the humic acids have high molecular weight. Also, the small differences in K_{400}, RF and Δ log K values between these samples indicate that there are no differences in degree of humification of the humic acids extracted from the solid-hydroquinone complexes. Overall, the amounts of humic acids extracted from supernatants were higher than those extracted from solids (Table 4.3 and 4.4). Fukuzumi et al. (1975) observed that the free radicals formed on surfaces are not stabilized on the surface, but desorbed into the homogeneous liquid phase. During liquid-phase oxidation in the presence of heterogeneous catalysts, the chain initiation occurs on the solid phase, but the propagation of chains proceeds in the liquid phase. Therefore, the higher yield of humic acids in supernatant rather than in the solid-hydroquinone complexes is to be expected for a diphenol that are bonded rather weakly onto clay surfaces.

4.5 Conclusions

Hydroxy-interlayered clay minerals and non-interlayered montmorillonite catalyze the formation of humic substances. Darkening of supernatant solution is correlated with the amounts of humic acid produced in clays, but absorbance values of dissolved humic acid extracted from supernatants show better correlation with amounts of humic acids. The results obtained in the present study show that hydroxy-interlayered clays accelerate the polymerization of hydroquinone to various degrees, depending on the stability of the interlayer and interlayer cation. The amounts of humic acid present in the supernatant was higher than that extracted from the corresponding solid phase. Quality of the humic acids extracted from solid phase show no differences among the clay minerals. More than half of the organic C associated with the solid phase contributed to the formation of stable organo-mineral complexes. Catalytic effects exerted by hydroxy-interlayered clays may have great significance in humus formation and accumulation in Ultisols and Alfisols, which are rich in hydroxy-interlayered clays.

5. RETENTION OF ORGANIC COMPOUNDS BY HYDROXY-INTERLAYERED CLAYS THROUGH CHELATION AND HUMIFICATION PROCESSES

5.1 Abstract

Laboratory synthesized hydroxy-Fe-, mixed hydroxy-Fe,Al-, and hydroxy-Al-interlayered montmorillonite and non-interlayered montmorillonite were used for the study. Citric acid is an organic acid with a high chelating ability for Fe and Al. Hydroquinone and catechol are reducing agents that can be converted into oxidized polymers by layer silicates. Citrate, hydroquinone and catechol complexes of hydroxy-interlayered and non-interlayered montmorillonites were prepared by aging suspensions at an adjusted pH of 6 for 30 d.

The increase in pH, CEC and specific surface area indicate that citrate dissolved the interlayer hydroxy-polymers. The amounts of Fe and Al released to solution, as well as d-spacing reduction upon K-saturation, confirm the interlayer dissolution by citric acid. Hydroquinone and catechol did not cause any significant structural changes in hydroxy-interlayered or non-interlayered montmorillonites (as measured by XRD analysis) and the amounts of structural cations dissolved. Instead, these clays catalyzed the formation of hydroquinone- and catechol- derived humic substances. Slight reductions of

pH indicate the oxidation of polyphenols, whereas the increase in CEC in catechol complexes suggest the presence of humified materials, despite charge blocking by hydroxy-interlayers. The amount of organic C retained by the clay minerals is related to the kind of organics added and their effects on the clay mineral, the type of clay mineral, and the stability of the hydroxy-interlayered material. Very high third-range buffer capacities were observed in hydroxy-interlayered-catechol and -hydroquinone complexes.

5.2 Introduction

The interaction of organic substances with clay has amany consequences that are reflected in the physical, chemical and biological properties of the soil (Stevenson 1994). The surface chemistry of clay minerals plays an important role in governing the overall behaviour of organic solutes in soil and subsurface environments. A broad range of interactions between organic solutes and clay surfaces is possible, depending on the nature of active sites present on the clay surface, the properties of the active clay surface, the pH of the soil solution, the temperature and water content (Johnston 1996). Organic substances can be retained by clay-minerals in two ways: 1) by attachment to clay mineral surfaces, 2) by penetration into the interlayer spaces of expanding-type clay minerals (Stevenson 1994). A third possibility is the humification and subsequent residence of the resultant "humus". Properties such as buffering

capacity, metal-binding capacity, sorption of hydrophobic compounds, stability of aggregates of soil particles, and water-holding capacity, depend on the amount of humus in a soil (Wershaw 1993).

Among the naturally occurring low-molecular-weight organic acids, citric acid has been credited with alleviating Al toxicities in soils (Hue et al. 1986). Citric acid has strong chelating properties and could destroy the hydroxyl-bridging mechanism indispensable for the formation of crystalline Fe and Al hydroxides (Kwong and Huang 1977). The stability of chlorite-like complexes in montmorillonite is known to be influenced by the citrate/Al ratio and the concentration of Al (Violante and Jackson 1981; Goh and Huang 1986). These studies were done by simultaneously introducing citric acid, Al^{3+} and OH^- ions into the montmorillonite system. They observed that citrate acting as a complexing ligand, and the negatively charged surfaces of montmorillonite competed for Al. On the other hand, aggregate formation and stability by binding humic substances through Al and Fe in acid soils enhances the physical properties of soils.

Oxidative polymerization of polyphenols in soils is regarded as one of the main processes in the formation of humic substances (Shindo and Huang 1982). Layer silicates catalyze the humification process, and the presence of free Fe and Al seem to darken the colour of the final product (Lehman et al. 1987). Although the reaction mechanism itself was not determined, participation of phenolic acids in the formation of humus-like materials was

clearly demonstrated. Phenols are common in decomposition products of plant and animal materials. They exist in the microbial metabolites and are regarded as important precursors of humic substances in soils (Hayes and Swift 1978).

Acidic environments are especially noted for the presence of hydroxy-interlayered clays and the accumulation of organic acids, and therefore their interactions. Mineral weathering occurs in two distinctive ways: (1) lowering of pH due to the ionization of acidic functional groups; (2) formation of chelate complexes (Stevenson and Vance 1989). Both low-molecular-weight biochemical compounds and higher-molecular-weight humic and fulvic acids have been implicated in the degradation of mineral matter in nature (Stevenson 1985). Baker (1973) reported that humic acids exhibit an activity of the same order as that of several simple organic chelating agents. The ability of humic substances to decompose common soil minerals has been shown by Huang and Keller (1971) and Schnitzer and Kodama (1966).

The catalytic ability of hydroxy-interlayered clays in oxidative-polymerization of hydroquinone was reported in the Chapter 4. Interlayered clays may form complexes with catechol, hydroquinone and citrate by entering into interlayer spaces or by adsorbing strongly on external surfaces. Thus the comparison of physicochemical and mineralogical changes in interlayered clays due to complexation with hydroquinone, catechol and citrate, that are either chelating and/or reducing organic compounds, is a matter of considerable interest to soil chemists and clay mineralogists.

5.3 Materials and Methods

5.3.1 Synthesis of hydroxy-interlayered-organic complexes

Three hydroxy-interlayered montmorillonites, viz., hydroxy-Fe, mixed hydroxy-Fe,Al and hydroxy-Al, and a non-interlayered Na-montmorillonite, were used for the study. The preparation of these clays is described in Chapter 3. Hydroxy-interlayered-hydroquinoneandhydroxy-interlayered-catecholmixtures were prepared by adding measured amounts of hydroquinone and catechol to these separate clay suspensions to give 300 cmol of diphenol kg^{-1} of clay. The pH of the suspension was adjusted to 6.0 by titrating either with 0.1 M NaOH or 0.05 M H_2SO_4. Suspensions of 10 g of clay and 0.03 mol of diphenol in a final volume of 3 L of distilled water, were aged in polypropylene bottles covered with black plastic bags for 30 d, and were agitated daily. Citrate complexes of hydroxy-interlayered clays were prepared by aging them with citric acid at the same organic/clay ratio, and at an adjusted pH of 6.0 for 30 d in suspension with 3 L of distilled water. After aging, each suspension was separated into its filtrate and solid phase by ultrafiltration through a Millipore filter of 0.025 μm pore size. The solid phase of each sample was washed, dialysed and freeze dried. Catechol (CC), hydroquinone (HQ) and citrate (Ct) complexes of Fe-Mt, Fe,Al-Mt, Al-Mt and Mt will be referred to as Fe-Mt-CC, Fe,Al-Mt-CC, Al-Mt-CC, Mt-CC, Fe-Mt-HQ, Fe,Al-Mt-HQ, Al-Mt-HQ, Mt-HQ, Fe-Mt-Ct, Fe,Al-Mt-Ct, Al-Mt-Ct and Mt-Ct, respectively.

5.3.2 Properties of hydroxy-interlayered-organic complexes

The pH and amounts of Fe and Al were measured in the filtrate. The absorbance at 400 and 600 nm (HP 8452A Diode array spectrophotometer) of the filtrates of hydroquinone and catechol complexes were measured to compare the oxidative polymerization. The solid fractions of the complexes were characterized according to their cation-exchange capacity (Rich 1961). Furthermore, the specific surface area (SSA) was determined using the EGME method (Carter et al. 1986). The modified Mebius procedure (Yeomans and Bremner 1988) was used to determine organic C. Exchangeable Al, Fe and C were obtained by washing 100 mg of the complexes five times (10 mL each) with 0.5 M $CaCl_2$. Aluminum and Fe in the combined extracts were determined by atomic absorption spectroscopy (AAS). X-ray diffraction patterns were obtained after K-saturation using Cu$K\alpha$ radiation with a Philips PW1710 diffractometer. The potentiometric titration of the clays and clay-organic complexes and the calculated base consumption over a specified pH range were used to determine the buffering capacity. A sample of 0.5 g, suspended in 50 mL of 1M KNO_3, was titrated under constant stirring against 0.1 M KOH using Metrohm Brinkmann 666 Titroprocessor.

5.4 Results and Discussion

The pH of the suspensions of the hydroxy-interlayered-citrate complexes

increased over the aging period as the bridging hydroxyls were released from hydroxy-Fe and/or hydroxy-Al polymers (Table 5.1). Increase in pH due to perturbation of hydroxy-Al interlayers by citric acid after one month of aging was also reported by Goh and Huang (1984). The increase in CEC and specific surface area (SSA) values over the hydroxy-interlayered clays without organics (Table 5.1) may be due to the destruction of hydroxy-interlayered polymers by citric acid. The H^+ ions released from the citric acid can be incorporated into the clay structures through Al-OH_2, Fe-OH_2 and silanol groups (Jackson 1979). Slight pH reduction was observed in clay-hydroquinone samples (Table 5.1). Oxidation of diphenols into quinone releases H^+ into solution (Kung and McBride 1988). Therefore, the pH of the clay suspension after oxidation should be lower than the starting pH. A very slight pH reduction compared to the initial pH in hydroquinone systems (Table 5.1) indicates a buffering capacity against the H^+ produced. The CEC and specific surface values of the clay-hydroquinones are not significantly different from the values obtained for the same interlayered clays before hydroquinone complexation, i.e., with no organic added (Table 5.1). The pH-reduction in clay-catechol complexes is greater than that of clay-hydroquinone (Table 5.1). This might be due to the greater degree of oxidation of catechol, thereby releasing more H^+ into solution. The degree of darkening of the supernatant solutions (Fig. 5.2) are in agreement. The slight increase in CEC of clay-catechol complexes, compared to their original interlayers, are due to the presence of humified

Table 5.1 Some physicochemical properties of hydroxy-interlayered-organic complexes.

Property	Clay type			
	Fe-Mt	Fe,Al-Mt	Al-Mt	Mt
	No organics added			
CEC (cmol(+) kg^{-1})	54	45	33	78
Specific surface (m^2 g^{-1})	679	596	455	789
	Clay-citrate complexes			
Final pH	6.8	7.1	7.4	6.1
CEC (cmol(+) kg^{-1})	68	75	71	77
Specific surface (m^2 g^{-1})	627	635	553	809
	Clay-hydroquinone complexes			
Final pH	5.9	5.8	6.1	5.6
CEC (cmol(+) kg^{-1})	60	44	30	84
Specific surface (m^2 g^{-1})	678	598	478	782
	Clay-catechol complexes			
Final pH	4.3	4.8	5.0	4.8
CEC (cmol(+) kg^{-1})	76	68	41	86
Specific surface (m^2 g^{-1})	670	588	488	768

materials.

The amounts of Fe and Al released during aging with organics are shown in Table 5.2. The results for the citrate complexes show that citrate dissolved the interlayer hydroxy-polymers and released the interlayer cations to the supernatant. The remaining polymers probably formed inner-sphere complexes with the citrate, and were re-adsorbed to the external and internal surfaces of the clay (Goh and Huang 1985). The chelate structures of Al with citrate was illustrated by Stevenson and Vance (1989). Goh and Huang (1984) have also observed a structural perturbation of the interlayer Al-hydroxide sheet in montmorillonite, resulting from the presence of citrate in the system. Smith et al. (1997) also found that the concentration of Al in solution was reduced as the citrate : Al ratio increased. They also observed pH that increases with increasing concentration of citric acid, whereas catechol did not cause any change in pH. This was explained by the greater effectiveness of citric acid as a complexing agent of Al species in solution. Destruction of hydroxy-Fe and -Al polymers released Al, Fe^{3+} and OH ions into solution. The ability of citric acid to form complexes with Fe and Al accounts for the pH increase in clay-citrate complexes (Table 5.1). Wang et al. (1983b) stated that the citrate anion complexed with Al strongly, so that the hydroxyl cannot replace citrate at a molar ratio of citrate : Al above 0.475. Therefore, Al and Fe^{3+} complexed with citrate during the aging left OH^- ions in the solution, causing the increase in pH. The amounts of Fe and /or Al released to the supernatants during aging

Table 5.2 Amounts of Fe and/ or Al in supernatants from clay-organic complexes after 30 d aging period.

Clay	Clay-citrate		Clay-hydroquinone		Clay-catechol	
mineral	Fe	Al	Fe	Al	Fe	Al
	----------cmol kg^{-1}----------					
Mt	3	8	0	0	0	0
Fe-Mt	229	8	1.8	0	8.8	0
Fe,Al-Mt	170	227	1.4	0	2.3	18
Al-Mt	0	347	0	0	0	15

with hydroquinone and catechol were minute compared to the amounts released during aging with citrate (Table 5.2). There was no detectable Al, and only trace amounts of Fe in the supernatants of the hydroxy-interlayered-hydroquinones, whereas Al and Fe were found in supernatants of clays aged with catechols (Table 5.2). Higher oxidation in catechol compared to hydroquinone (Fig. 5.2) is a possible reason. It has been established that these reactions proceed through a single electron transfer from the unsaturated organic solute to the transition-metal cation (Soma et al. 1984).

Aging with citric acid for 30 d caused a reduction in d-spacing in all the interlayered clays to about 1.25 nm (Fig. 5.1). The complexation of hydroquinone and catechol with Al-Mt and Mt did not change the d-spacing of the clay. The d-spacings of Fe-Mt and Fe,Al-Mt were reduced slightly upon complexation with hydroquinone and catechol (Fig. 5.1). After penetration of the Al polymers into the interlayer spaces, the interference of humic acid with the interlayering is much less pronounced (Singer and Huang 1993). Therefore, the structural and physicochemical changes in interlayered clays are minimal upon hydroquinone complexation. Minerals rich in Fe are most susceptible to attack by humic materials (Schnitzer and Kodama 1976). This explains the slight reduction of d-spacing in hydroxy-Fe interlayered clays. The high affinity of humic acid or fulvic acid for Fe and the low crystal-field stabilization energies of Fe^{3+} provide possible explanations (Schnitzer 1978).

The amounts of Fe, Al, and organic C extracted from hydroxy-

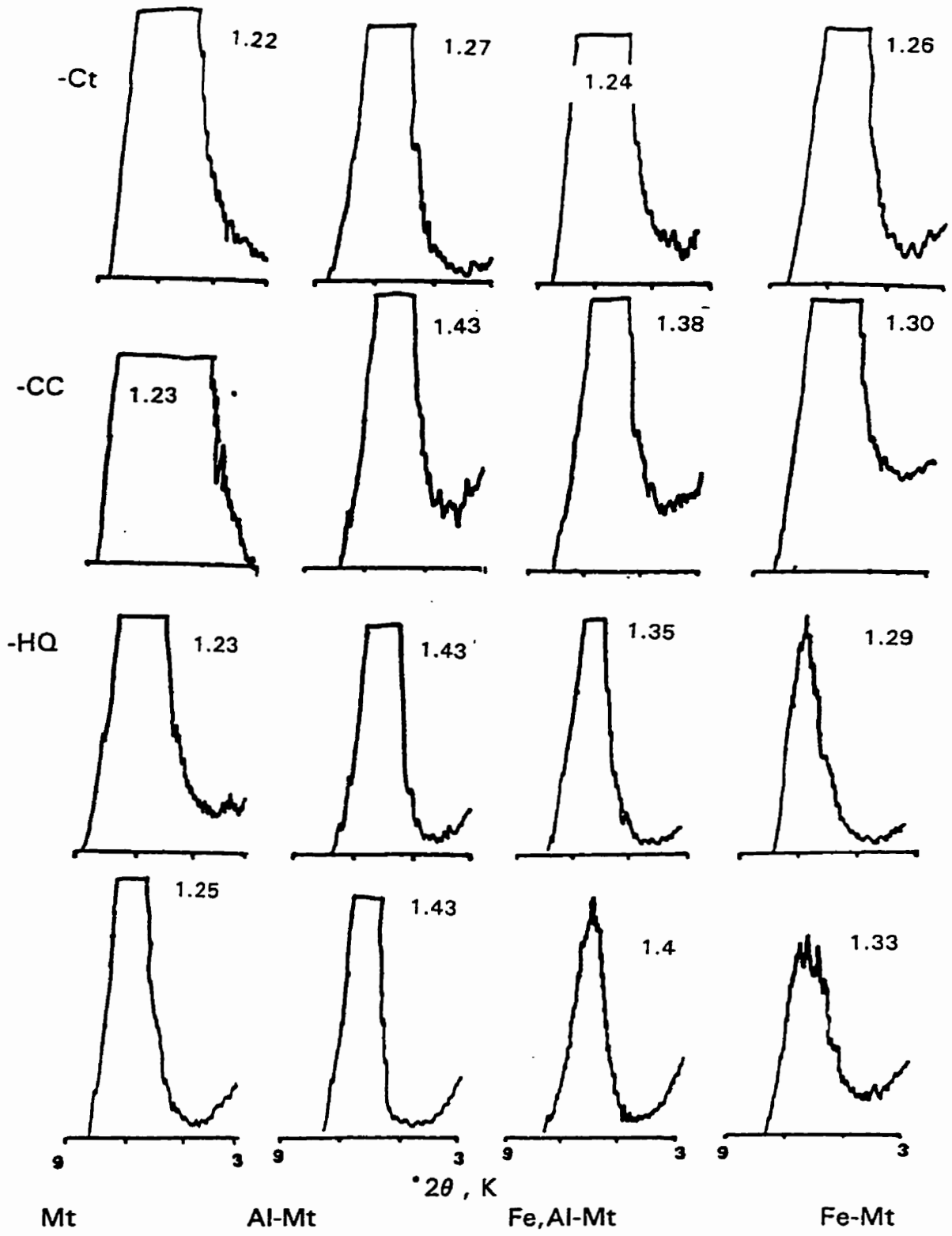


Fig. 5.1 X-ray diffractograms of hydroxy-interlayered clays and their organic complexes (spacings are in nm)

interlayered-organic complexes by $CaCl_2$ are presented in Table 5.3. The amounts of Al extracted from clay-hydroquinone and clay-catechol complexes were not much different from the amounts extracted from original hydroxy-Al interlayers that were aged in the absence of organics (Table 3.2). The amounts of Al extracted from clay-citrate complexes by $CaCl_2$ were less than those from the catechol or hydroquinone complexes. Small amounts of Fe were extracted by $CaCl_2$ in hydroxy-Fe interlayer-organic systems (Table 5.3), but no detectable amount was extracted from the organic-free interlayered clays (Table 3.2). The structural distortion in the interlayer sheet due to complexation with organic compounds reduced the tenacity with which the cations were held in hydroxy-polymers. Therefore, more cations were exchanged in interlayered clay-organic complexes with neutral salts than in interlayered clays without organics.

Regardless of whether the clay mineral is interlayered, the amounts of organic C extracted during washing with 0.5 M $CaCl_2$ were neally equal for all clay-citrate and clay-hydroquinone complexes (Table 5.3). This observation leads to the conclusion that the amounts extracted by $CaCl_2$ were from external surface complexes. Extensive washing and dialysis of the clay-organic complexes before freeze-drying removes weakly adhering organics from the complexes. Goh and Huang (1984) postulated that the organic C remaining in thesamples after Al is extracted by KCl is the nonexchangeable fraction and is fixed in the interlayerr spaces. The data obtained from the present study lend

Table 5.3 Amounts of Fe, Al and organic C extracted by $CaCl_2$ from clay-organic complexes.

Interlayer	Clay-citrate			Clay-hydroquinone			Clay-catechol		
Type	Fe	Al	C	Fe	Al	C	Fe	Al	C
	cmol kg^{-1}		mg kg^{-1}	cmol kg^{-1}		mg kg^{-1}	cmol kg^{-1}		mg kg^{-1}
Mt	0	0	1770	0	0	1700	0	0	4100
Fe-Mt	0.3	0	1660	0.3	0	1900	1.1	0	3900
Fe,Al-Mt	2.6	6.7	1710	0.8	24	2000	2.1	28.	3800
Al-Mt	0	11.5	1730	0	21	1800	0	21.	3500

further support to this idea. Hydroxy-Al polymeric interlayers of smectites are considered nonexchangeable forms of Al as they are not readily replaced with an unbuffered salt like 1 M KCl. However, it has been shown that KCl can cause hydrolysis of nonexchangeable Al, which is then measured as exchangeable Al^{3+} (Sparks 1995). Extraction of Al from hydroxy-metal-organic complexes is difficult (Schnitzer and Skinner 1963; White and Thomas 1981). More organic C was extracted from clay-catechol complexes than from citrate and hydroquinone complexes by the neutral salt (Table 5.3); this is likely a consequence of the larger quantities of organic C associated with clay-catechol complexes (Fig. 5.3).

The degree of humification of soil humic acid is commonly determined by optical absorbance of the supernatant solution at 400 and 600 nm (Shindo and Huang 1984). Soil minerals play an important role in catalyzing the abiotic polymerization of phenolic compounds and the subsequent formation of humic substances (Huang 1990). A higher degree of humification was observed in the clay-catechol than in the clay-hydroquinone complexes (Fig. 5.2). The darkening of supernatant solutions resulted in absorbance units ranging from 0.94 to 0.05 (Fig. 5.2). The degree of humification among the hydroxy-interlayered clay minerals can be ordered as follows: Fe-Mt > Fe,Al-Mt > Al-Mt. This sequence is observed in both catechol and hydroquinone complexes of hydroxy-interlayered clays. The non-interlayered Na-montmorillonite exhibited the highest degree of darkening in clay-hydroquinone systems

(Chapter 4). In contrast, montmorillonite with hydroxy-Fe and -Fe,Al-interlayers promoted further darkening in the clay-catechol-reacting systems. The lowest specific surface of Al-Mt (Chapter 3) seems to be critical in reduced oxidative polymerization. The oxidation of diphenols, $C_6H_4(OH)_2$, by Fe (III) is thermodynamically favourable (Weast 1978). Hydroxy-Fe interlayers showed the lowest stability and crystallinity among the clay minerals studied (Chapter 3). Participation of Fe^{3+} in the single electron-transfer reaction that is essential for oxidative polymerization causes humification in hydroxy-Fe interlayers. Oxidation of diphenols in the presence of smectites increases with increasing CEC and specific surface (Thompson and Moll 1973). Accordingly, reasonable amounts of humification were observed in the non-interlayered montmorillonite where neither the CEC nor the surface seem to have been blocked. Clays have various Lewis-acid sites in their structures, and these act as electron acceptors (Boyd and Mortland 1990); these include structural Al and transition-metal cations at the edges of the mineral, and exchange cations (Boyd and Mortland 1990). Electron transfer between organics and oxides of Fe is facilitated by complexation of the organics to the oxide surface (Stone and Morgan 1984). Clay-mediated single-electron-transfer reactions are characterized, in general, by the formation of darkly coloured complexes (Pinnavaia and Mortland 1971). Due to the chelating ability of catechol, very high stability was observed in Al- and Fe^{3+}- catechol complexes (McBride 1987). This explains the higher degree of humification in catechol complexes than hydroquinone complexes. The

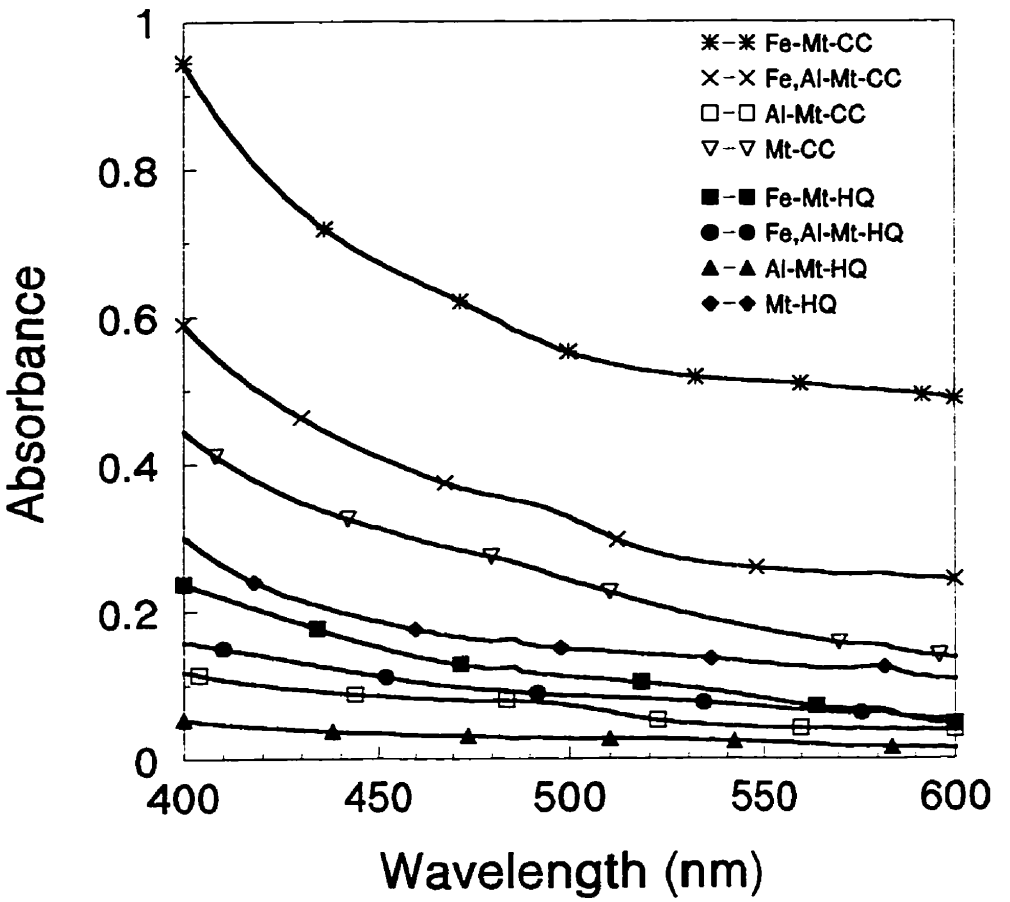
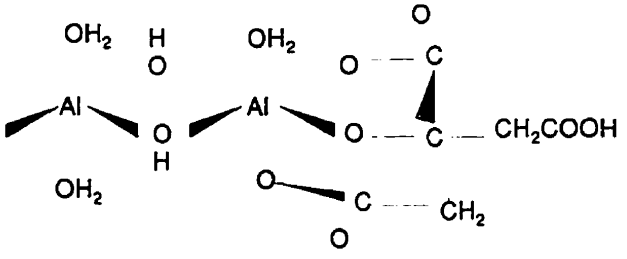


Fig. 5.2 Darkening of supernatant solutions of clay-hydroquinone and -catechol complexes

negatively charged clay surface promotes the single-electron-transfer reaction by increasing the surface Lewis acidity of the metal cation, and further stabilizes the radical organic cation (Mortland and Raman 1968).

The clay-hydroquinone complexes retained the least amount of organic C among the three clay-organic complexes (Fig. 5.3). Clay-citrate complexes retained larger amounts of organic C than clay-hydroquinones (Fig. 5.3). Hydroxy-interlayered clays retained larger amounts of citrate than did montmorillonite. The possible mechanism would be the inner-sphere adsorption of citric acid (Goh and Huang 1985) through the following structure (Stevenson and Vance 1989).



Hydroxy-Al-citrate

Montmorillonite, which exposes only silanol and no Al-OH and Fe-OH groups (except a small amount at the edges) compared to the hydroxy-interlayered clays, retained the lowest amount of C. Although the clay particles always exhibit a negative total charge, there are positive sites in the acidic medium on the edge surface of the alumina sheet. The adsorption of organic-acid molecules takes place at these sites (Siffert and Espinasse 1980). The

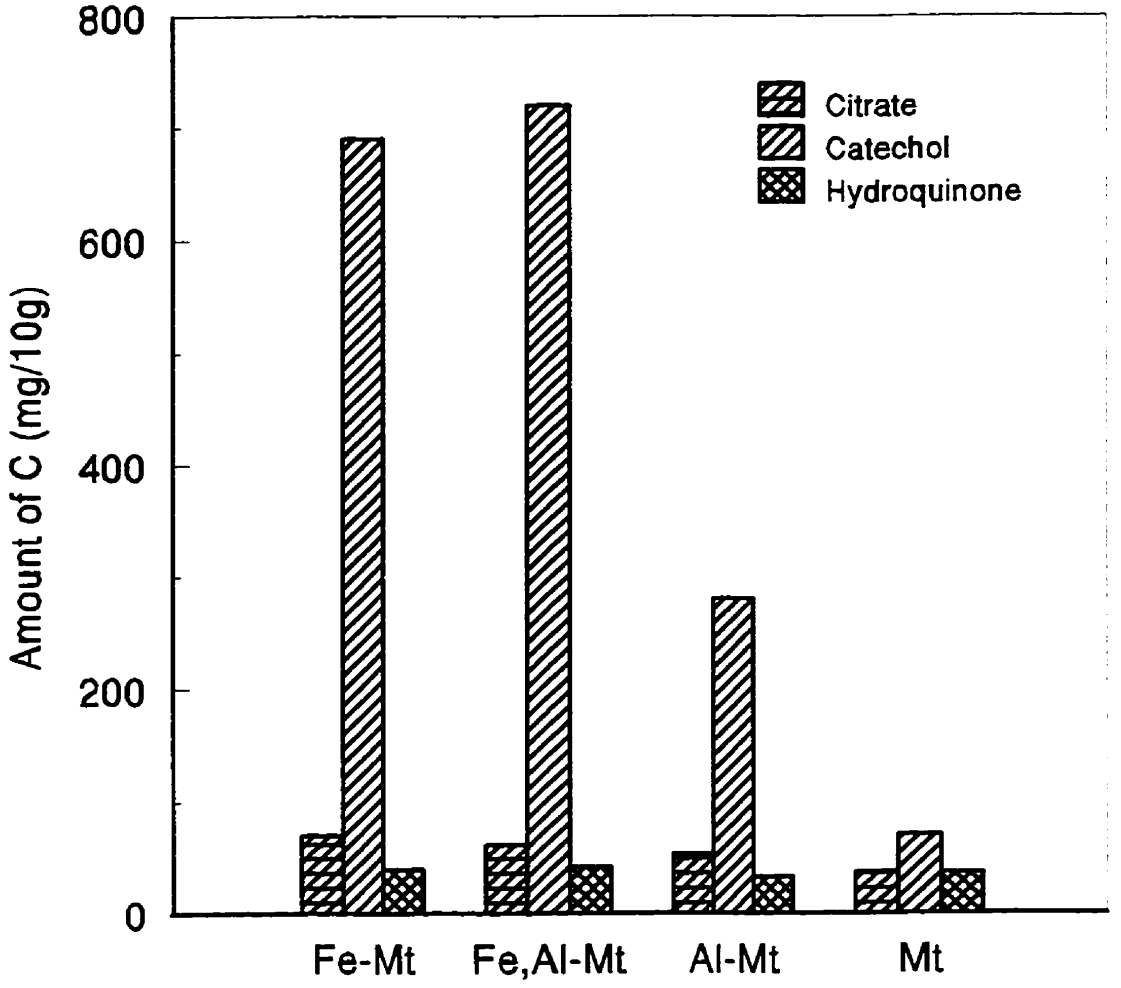
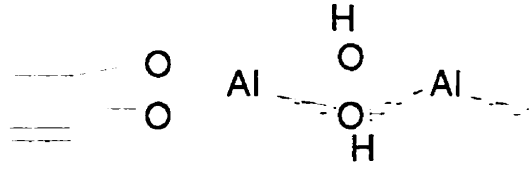


Fig. 5.3 Organic C retained in hydroxy-interlayered clays after aging with organic compounds.

catecholcomplexes showed the highest amount of organic C in all hydroxy-interlayered and noninterlayered montmorillonites (Fig. 5.3). As organic anions are normally repelled from negatively charged clay surfaces, adsorption of humic and fulvic acids by clay minerals such as montmorillonite occurs when polyvalent cations are present on the exchange complex (Stevenson 1985). According to McBride et al. (1977), it is unlikely that the phenols adsorb to a significant degree on unmodified layer silicates in aqueous suspension. Catechol, which is a ortho-diphenol, readily adsorbs on oxides by bidentate bonding and may similarly bond at layer-silicate edges as indicated:



Hydroxy-Al-catecholate

Hydroquinone also has a measurable tendency to adsorb on oxides, despite its inability to form chelate compounds (McBride 1987). Following adsorption, hydroxy-Fe and hydroxy-Al compounds can subsequently protect against biotic degradation of phenolic compounds. In addition, the catalytic effect in an oxidative polycondensation of phenolic units result in the formation of stable skeletons in soil-humic materials.

The titration curves of hydroxy-interlayered clays prepared in the absence

of organic ligands and those of the citrate are shown in Fig. 5.4A and those of hydroquinone and catechol complexes are shown in Fig. 5.4B. The exchangeable Al and hydroxy-Fe and -Al (Schwertmann and Jackson 1964) contribute to buffering capacity of many soils. Exchangeable acidity is that portion of the soil acidity that can be replaced with a neutral, unbuffered salt such as KCl, $CaCl_2$ or NaCl. The non-exchangeable polymers fixed in interlayer spaces of clay minerals show third-buffer-range buffering capacity that is characterized by base consumption in the pH range 5.5 to 7.6 (Schwertmann and Jackson 1964). Hydroxy-interlayered clays used in this study show substantial amounts of buffering capacity (Fig. 5.4A). After aging with citric acid, the buffering capacity of interlayered clays was greatly reduced. This is because of the dissolution of much of the hydroxy-Fe and -Al polymers from these clays. Despite this, the Mt-Ct complex gained total acidity after the aging (Fig. 5.5). On the whole, the third-range buffer-capacities of citrate complexes were still higher than the non-interlayered montmorillonite (Fig. 5.5). The contribution of citric acid to the third-buffer-range through the chelation with hydroxy-Al adsorbed in montmorillonite interlayers was reported by Goh and Huang (1985). Soil organic matter is a major contributor to the buffering capacity of soils. Three types of weak acids, viz., a very weak acid phenolic proton and two carboxyl protons with similar acidities, are believed to be involved (Bloom 1981). The hydroquinone and catechol complexes show higher buffer capacities (Fig. 5.4B) than pure hydroxy-interlayers due to the

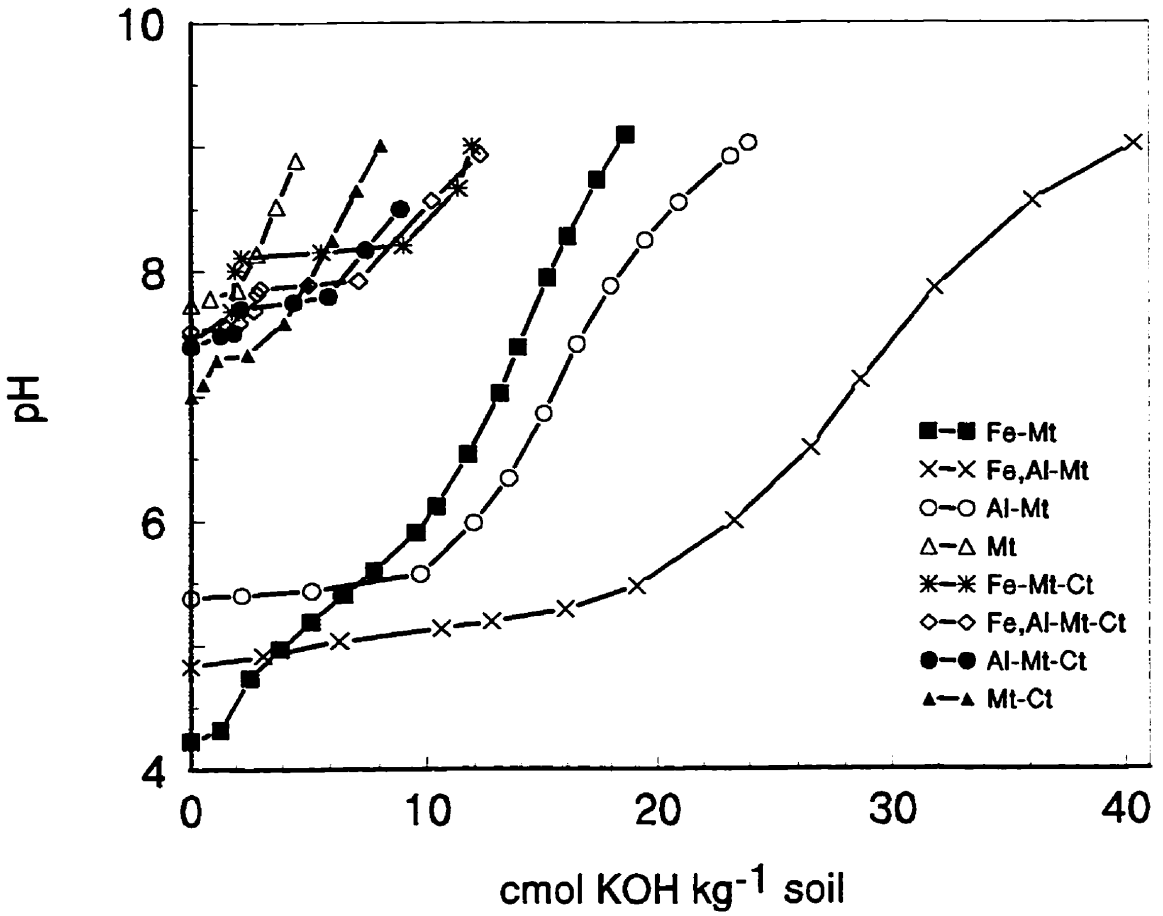


Fig. 5.4A Buffer curves of hydroxy-interlayered clays before and after aging with citric acid

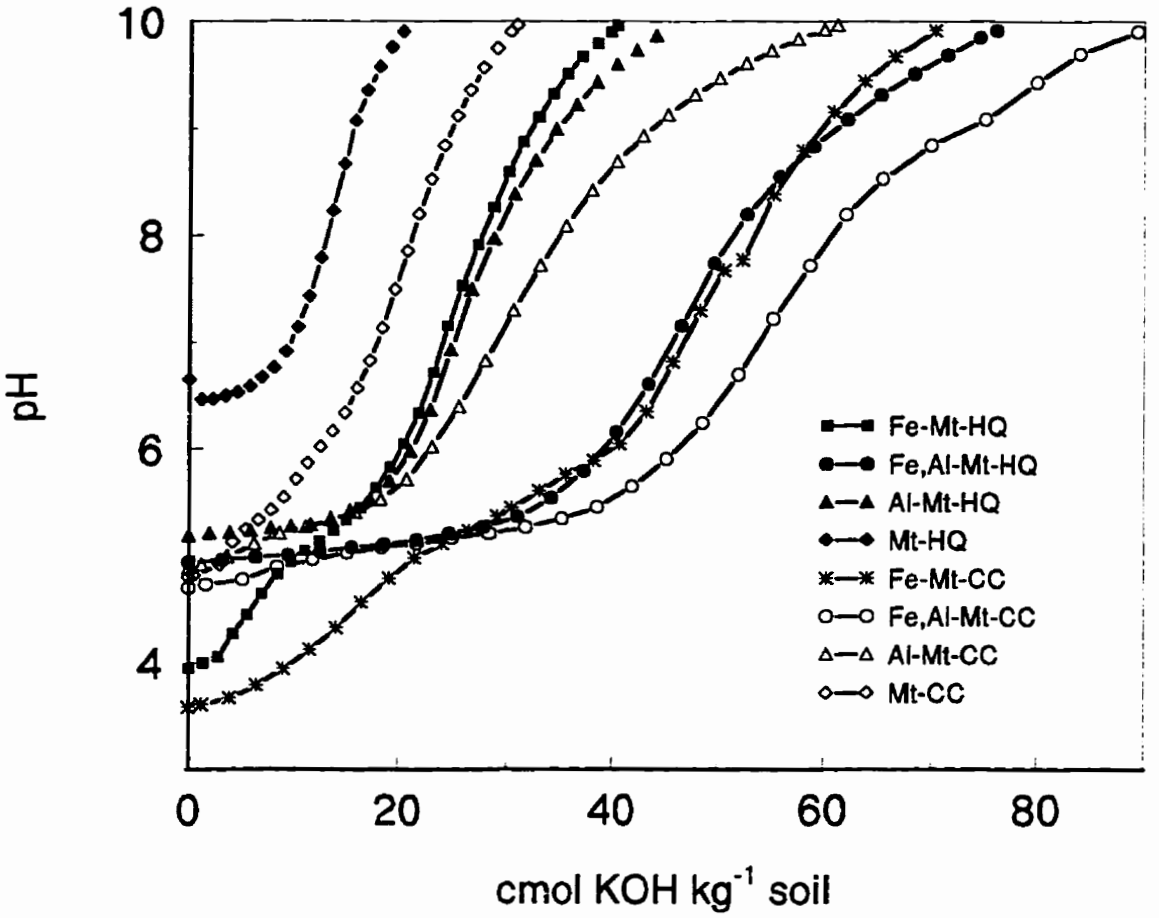


Fig. 5.4B Buffer curves of hydroxy-interlayered clays after aging with hydroquinone and catechol

presence of humified materials.

The changes in total acidity of hydroxy-interlayers after complexation with citrate, hydroquinone and catechol are shown in Fig. 5.5. The total titratable acidity of the complexes is usually in the order citrate < hydroxy-interlayers only (no organic) < hydroquinone < catechol. The third-buffer-range acidity (base consumption between pH 5.5 to 7.6) follows the same order (Fig. 5.4A and 5.4B). Within hydroxy-interlayers of hydroquinone and catechol systems, total acidities are in the order of Fe,Al-Mt > Fe-Mt > Al-Mt > Mt (Fig. 5.5). This clearly shows that the destruction of hydroxy-polymers in interlayers by citric acid results in the least total acidities in the clay minerals studied. In contrast, the formation of hydroquinone-derived and catechol-derived humic substances led to higher total acidities in these clay minerals.

5.5 Conclusions

Citrate, hydroquinone and catechol adsorb readily on the layer silicates because of the involvement of hydroxycarboxylic and ortho-diphenolic groups and weak bonds. Adsorbed catechol and hydroquinone undergo oxidative polymerization, whereas citric acid was not humified. Hydroxy-interlayered clays accelerate the polymerization of hydroquinone and catechol to various degrees, depending on the stability of the interlayer and the interlayer cation.

Titration curves can be used to measure both the type and quantity of

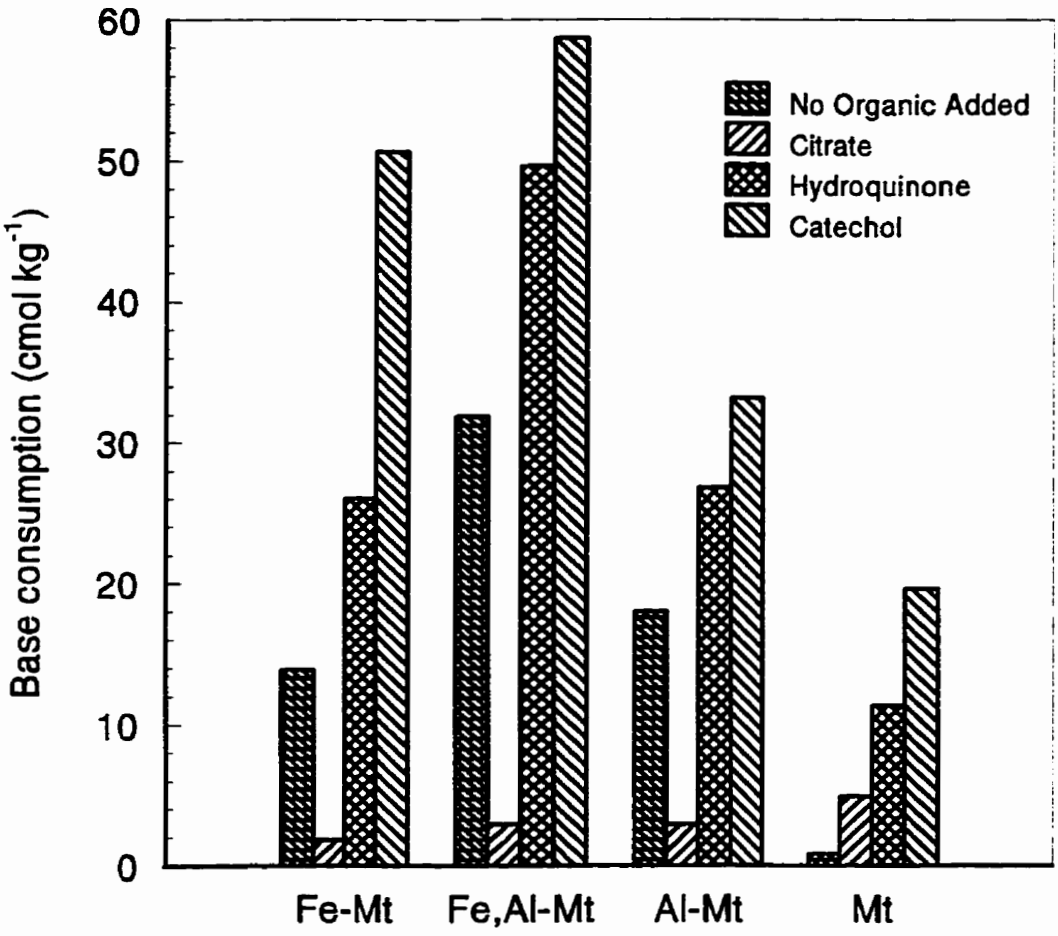


Fig. 5.5 Total acidity to pH 7.6 of hydroxy-interlayers and their organic complexes

acidity. The base-consumption values obtained from this study reflect the buffer capacity of hydroxy-Fe, and/or -Al and their organic complexes. Dissolution of hydroxy-polymers decreases the buffer capacity, whereas humification and complexation of humic materials with these interlayers has the opposite effect. The presence of humic materials with the hydroxy-interlayers increases their reactivity without any structural change to the layer silicate.

6. COMPARISON OF OXIDATIVE POLYMERIZATION OF HYDROQUINONE AND CATECHOL IN SUSPENSIONS OF INTERLAYERED CLAY

6.1 Abstract

The abiotic formation of humic substances via the oxidation of diphenols is accompanied by darkening of the organic aqueous phase. This oxidative polymerization pathway is catalyzed by soil-active sites that facilitate electron transfer. The optical properties of humic and fulvic acids formed depend, therefore, on precursor organic compounds as well as the nature of the mineral catalysts.

Hydroxy-interlayers of -Fe (Fe-Mt), -Al (Al-Mt), and mixed -Fe,Al (Fe,Al-Mt) -montmorillonite having varying degrees of stability and crystallinity, and non-interlayered Na-montmorillonite (Mt) were used as catalyzing agents. Two diphenols, hydroquinone, which has very low oxidation potential, and catechol, having slightly higher oxidation potential than hydroquinone, but with chelating ability as well, were compared. The nature of the humic substances formed in hydroxy-interlayered-diphenol (solid) complexes and in respective supernatants (SU) were determined using K_{400}, K_{600}, E_4/E_6, $\Delta \log K$, RF and UV-visible spectra.

Interlayered clays catalyzed the oxidative polymerization of diphenols in

the following order; Fe-Mt > Fe,Al-Mt > Al-Mt. Oxidation of hydroquinones yielded more humic acids in the supernatants than did oxidation of catechols. Larger quantities of humic acids and other organic C fractions were extracted from the solid clay-catechol complexes compared to the clay-hydroquinone, indicating higher reactivity of catechols at the clay surface. Humic substances extracted from solid-phase-diphenol complexes resembled natural humic and fulvic acids as indicated by E_4/E_6, Δlog K, and RF values. Results suggest that montmorillonite and montmorillonites with interlayers of -Fe, -Fe,Al and -Al in soils may, by a similar mechanism, catalyze the oxidation of phenolic compounds by O_2.

6.2 Introduction

The mechanisms of formation of humic substances are very complicated processes in which a variety of organic components, such as phenolic substances, carbohydrates, and nitrogenous substances, can participate as starting materials (Huang 1990). Many different types of reactions can lead to the production of dark-coloured pigments (e.g., humic and fulvic acids) in soil. The major pathway in most soils seems to be through condensation reactions involving polyphenols and quinones (Stevenson 1994). Approximately 50-60% carbohydrates, 1-3% proteins, 10-30% lignins and some phenolic compounds participate in humification processes (Choudhry 1983).

Clays have intrinsic catalytic properties that, as in homogeneous catalysis, may proceed via Bronsted or Lewis acidity, as they may have various sites in their structures that act as electron acceptors (Boyd and Mortland 1990). These include structural aluminum and transition-metal cations at edges of the mineral and exchange cations, particularly transition-metal cations with unfilled d-orbitals (Boyd and Mortland 1990). The Bronsted acidity sites at the mineral surface can donate protons to adjacent organic solutes more readily than bulk water, and can promote a variety of chemical reactions (Voudrias and Reinhard 1986). Exchangeable or structural transition metals in their upper oxidation state can interact directly with certain organic solutes (Johnston 1996). For example, exchangeable Cu^{2+} and Fe^{3+} or structural Fe^{3+} can function as surface Lewis acids by accepting electrons from adjacent unsaturated organic solutes (Voudrias and Reinhard 1986). Single-electron-transfer reactions proceed through single-electron-transfer from the unsaturated organic solute to the transition-metal cation (Pinnavaia et al. 1974; Soma et al. 1984). If the ionization potential of the organic solute is below 10 eV and the reduction potential of the metal cation is favourable, single-electron-transfer can occur (Johnston 1996).

The frequency of occurrence of hydroxy-interlayers is greatest in the Ultisols and Alfisols (Barnhisel and Bertsch 1989)). As hydroxy-interlayered clays are present in acidic environments, especially in sub-tropical climates, its role in abiotic formation of humic substances should not be overlooked. The

existing evidence indicates that abiotic formation of humic substances through polymerization of phenolic compounds and polycondensation of phenolics and their derivatives, as catalyzed by soil-mineral components, merits close attention. Abiotic humus synthesis would not be the main pathway for naturally occurring humic polymers. However, chemical synthesis could contribute to humus formation where a variety of phenols are present in the appropriate chemical environments in the soil (Hayes and Swift 1978). In this way, chemical processes might supplement enzyme catalyzed reactions. The purpose of this study is to evaluate the effectiveness of hydroxy-interlayered clays of -Fe, -Al and mixed -Fe,Al, and Na-montmorillonite in catalyzing oxidation of hydroquinone and catechol.

6.3 Materials and Methods

6.3.1 Synthesis of humic materials

Three hydroxy-interlayered montmorillonites, viz., hydroxy-Fe (Fe-Mt), mixed hydroxy-Fe,Al (Fe,Al-Mt) and hydroxy-Al (Al-Mt); and a non-interlayered Na-montmorillonite (Mt), were used for the study. Preparation of these interlayered clays is discussed in Chapter 3. Freeze-dried samples of these clays were crushed and 10 g of each were suspended in 2 L of water. Clay-hydroquinone and clay-catechol mixtures were prepared by adding measured amounts of hydroquinone or catechol to separate clay suspensions to give

0.03 mol of diphenols per 10 g of clay (Chapter 5). The pH of the suspension was adjusted to 6.00 by titrating with 0.1M NaOH or 0.05 M H_2SO_4. Suspensions were aged, after bringing the final volume to 3 L, in polypropylene bottles covered with black plastic bags for 30 d, and were agitated daily. After aging, each suspension was separated into its filtrate and solid phase by ultrafiltration through a Millipore filter of 0.025 μm pore size. The solid phase of each sample was washed, dialysed and freeze dried. These solid phases (the same as in Chapter 4 and 5) are referred to Fe-Mt-HQ, Fe,Al-Mt-HQ, Al-Mt-HQ, Mt-HQ, Fe-Mt-CC, Fe,Al-Mt-CC, Al-Mt-CC and Mt-CC, respectively, for the hydroquinone and catechol complexes. The filtrates of each individual clay-diphenol complex will be called the supernatant of that complex. Control experiments were done under the same conditions using solutions of hydroquinone (HQ) and catechol (CC) but without any clay. The degree of darkening of supernatants was measured using the absorbance values at 400 and 600 nm.

6.3.2 Separation of humic substances from solid-diphenol complexes

Alkaline-soluble C representing the humic and fulvic acids from solids was collected as follows. One gram of the solid fraction was dissolved in 50 mL of 0.1 M NaOH and left to stand for 24 h. A 40% Na_2SO_4 solution was added until the final concentration of the solution was 3% with respect to Na_2SO_4. The extract was collected after centrifugation at 10,000 *g*. The

residue was washed twice (or until the extract was colourless) with 0.1 M NaOH containing 3% Na_2SO_4. The extracts were combined and 0.1M NaOH was added to bring the volume to 200 ml. Alkaline soluble C was determined using an aliquot of the extract, and the remainder was used for humic-acid fractionation, as discussed in 6.3.3. This is the procedure described by Kumada (1987) as the Nagoya method, with slight modification. The modified Mebius procedure (Yeomans and Bremner 1988) was used to determine total organic C, alkaline soluble C and humic-acid C.

6.3.3 Separation and determination of humic acids from supernatants and solid phases of clay-diphenol complexes

The fraction that was precipitated upon acidification of supernatants was considered to be humic acid (HA), whereas what remained in solution was considered as fulvic acid (FA). Alkaline extracts of the solid phase consisting of both humic and fulvic acids, was fractionated again using solubility and non-solubility upon acidification. The nature and quantity of the humic acids, fractionated from alkaline extracts of the solid clay-diphenol complexes and from the supernatants were determined using methods described by Kumada (1987). A known amount of the supernatant or extracts from the solid phase was acidified with H_2SO_4 to pH 1.5 and allowed to stand overnight. The precipitate was considered to be humic acid, whereas the filtrate is fulvic acid. Further, the precipitate was washed with (1:100) H_2SO_4 and water,

successively. The humic acid was then re-dissolved in 50 ml of 0.1M NaOH, and its degree of darkening was determined by measuring absorbance at 400 and 600 nm within 2 h. Absorbance values at 400 and 600 nm in the filtrate measured the degree of darkening of fulvic acid. The degree of humification of the humic acid was calculated using K_{400}, Δ log K and RF parameters. The Δ log K value is the logarithm of the ratio of the absorbance of humic acid at 400 nm to that at 600 nm; K_{400} is the absorbance value of humic acid at 400 nm; the RF value is the absorbance of humic acid at 600 nm divided by C mg per ml of humic-acid solution which is used to determine the uv-visible spectra, multiplied by 15 (Kumada 1987). The E_4/E_6 ratio of humic and fulvic acids was also determined using the absorbance of respective solutions at 400 and 600 nm (Kumada 1987). The humic acid (HA), fulvic acid (FA) and supernatant (SU) are abbreviated as shown.

6.4 Results and discussion

6.4.1 Characterization of humic substances separated from supernatants

Clay-diphenol complexes had more humification than the corresponding controls of hydroquinone or catechol, as indicated by the K_{400} or K_{600} values of the supernatants (Table 6.1). Clay-catechol complexes also showed higher degrees of darkening than clay-hydroquinones in supernatants, as measured by K_{400} (Table 6.1). In supernatants of clay-catechol systems, the correlation

between amounts of HA and degree of darkening (K_{400}) is very low ($r^2 = 0.52$). In contrast, in clay-hydroquinone systems, the degree of darkening (K_{400}) is closely correlated with the yields of humic acid (Chapter 4). Consequently, lower amounts of humic acids were separated from supernatants of clay-catechol complexes than from clay-hydroquinones (Table 6.2), despite the larger K_{400} values in clay-catechol than in clay-hydroquinones (Table 6.1). Reduction potentials of 1,2-benzoquinone and 1,4-benzoquinone were reported as 0.78 and 0.699 V, respectively, indicating that catechol is more difficult to oxidize than hydroquinone (Shindo and Huang 1984). The humic acids in clay-catechol systems exhibited a higher degree of humification than clay-hydroquinones, as indicated by their lower Δlog K values (Table 6.2). The E_4/E_6 values of catechol-derived humic acids also had lower values than hydroquinone-derived humic acids, indicating the presence of higher amounts of aromatic compounds in the former. Therefore, it can be concluded that clay-catechol systems produced lesser amounts of HA in the supernatant than in clay-hydroquinone systems, but the catechol-derivatives were of higher degrees of humification and aromaticity than those of clay-hydroquinone systems.

Even though the amounts of fulvic acids separated from supernatants were not determined, their properties can be measured using optical parameters (i.e., absorbance at 400 and 600 nm, and E_4/E_6, Table 6.1 and 6.2). Fulvic acids separated from supernatants of all the diphenol complexes show < 0.01 absorbance value at 600 nm (Table 6.1). The E_4/E_6 of the fulvic acids were

Table 6.1 Absorbance values of humic and fulvic acids separated from supernatants of clay-diphenol complexes.

Clay-diphenol	Final pH	Supernatant		Humic acid		Fulvic acid	
		K_{400}	K_{600}	K_{400}	K_{600}	K_{400}	K_{600}
CC (control)	4.2	0.16	0.03	0.28	0.08	0.12	.004
Mt-CC	4.8	0.45	0.14	0.51	0.23	0.17	.01
Fe-Mt-CC	4.3	0.94	0.49	0.52	0.24	0.32	.009
Fe,Al-Mt-CC	4.8	0.59	0.24	0.33	0.17	0.21	.006
Al-Mt-CC	5.0	0.12	0.04	0.39	0.30	0.05	.008
HQ (control)	5.1	0.05	0.01	0.08	0.01	0.03	.009
Mt-HQ	5.6	0.30	0.11	0.35	0.07	0.06	.004
Fe-Mt-HQ	5.9	0.24	0.05	0.23	0.06	0.13	.006
Fe,Al-Mt-HQ	5.8	0.15	0.05	0.11	0.02	0.08	.002
Al-Mt-HQ	6.1	0.05	0.01	0.08	0.008	0.03	.001

higher (Table 6.2) than the predicted true fulvic acid values of 6 to 8 (Kononova 1966). This indicates that supernatants of diphenol complexes have very low amounts of fulvic acids and they hardly resemble the fulvic acids. In the abiotic formation of hydroquinone-derived polymers, the polymers with MW > 1000 resembled natural humic substances, whereas those with MW < 1000 were quite different (Wang and Huang 1987). Therefore, it is possible to form hydroquinone- and catechol-derived polymers that do not resemble natural humic substances. The possibility also exists that some phenol molecules are broken into smaller fragments which these recombine with themselves and unaltered phenol to produce a variety of masses (Mortland and Halloran 1976). This explains the low aromaticity in humic substances (as indicated by higher E_4/E_6, Kononova 1966) separated from supernatants of diphenol complexes (Table 6.2).

The nature of humic acid formed in the hydroquinone- and catechol-only systems (controls) was not examined because it was present in only trace amounts. Within the clay- catechol systems, the clays can be grouped as follows, according to the amount of HA formed in the supernatant; Mt-CC < Al-Mt-CC < Fe,Al-Mt-CC < Fe-Mt-CC (Table 6.2). The degree of darkening in the supernatant (Table 6.1) is in accord with this except that the supernatant of Al-Mt-CC sytem showed the least degree of darkening. The colour (white) of the Al-Mt was only slightly changed after the reaction. This is probably because the catalytic effect of this interlayer is minimum (Table 6.1) among the

Table 6.2 Characterization of humic and fulvic acids separated from supernatants of catechol and hydroquinone systems.

	---------Humic acid---------			---Fulvic acid---	
Clay-diphenol	Amount mg kg^{-1}	E_4/E_6	Δlog K	Amount mg kg^{-1}	E_4/E_6
Mt-CC	2116	2.2	0.35	*ND	15
Fe-Mt-CC	3508	2.1	0.33	ND	34
Fe,Al-Mt-CC	3311	2.0	0.29	ND	32
Al-Mt-CC	3108	1.3	0.10	ND	6.8
Mt-HQ	6770	4.5	0.65	ND	14
Fe-Mt-HQ	3825	3.9	0.59	ND	20
Fe,Al-Mt-HQ	3088	6.9	0.84	ND	46
Al-Mt-HQ	1459	9.8	0.99	ND	18

*ND - not detected

hydroxy-interlayered clays in this study, and those darkening substances which formed by oxidation of phenolic compounds may be readily adsorbed by these interlayers. The Fe-Mt-CC and Fe,Al-Mt-CC resulted in colours darker than expected from the amounts of HA, due to the colour of Fe^{3+} ions (Table 6.1). McBride et al. (1988) showed that aqueous Al increased the rate of oxidation of catechol by O_2, favouring the formation of highly coloured polymeric products which may posses charge-transfer properties. A proposed mechanism for the role of Al in promoting oxidative polymerization is based on the concept that Al cations tend to stabilize ortho-semiquinone radicals at low pH that direct the manner in which these radicals polymerize. Aluminum may also stabilize charge-transfer complexes by bridging oxidized and reduced molecules (McBride et al. 1988). McBride (1987) observed evidence for direct coordination of catechol to surface Fe^{3+} on iron oxides. Such a coordination process would be conducive to subsequent electron transfer. These results explain the higher humification in hydroxy-interlayered clays of catechol complexes than in Mt-CC. Sawhney (1985) and Isaacson and Sawhney (1983) observed that, upon sorption of phenolic compounds, varying degrees of polymerization occurred in the order Fe > Al > Ca > Na, depending on the type of exchangeable cation present. The absence of such metal cations in Na-montmorillonite explains the small degree of humification in Mt-CC among the clay-catechol minerals studied. Clay-hydroquinone complexes can be grouped according to the amount of HA produced: Al-Mt-HQ < Fe,Al-Mt-HQ < Fe-Mt-

HQ < Mt-HQ (Table 6.2). Hydroquinone and its semiquinone radicals are not likely to form strong bonds with layer-silicate surfaces (McBride and Wesslink 1987), but ortho-diphenols such as catechols readily adsorb on oxides by bidentate bonding, and similarly bond at layer-silicate edges (McBride 1987). Thompson and Moll (1973) reported that the oxidation of hydroquinone by smectites proceeds mainly on the surface of smectite by adsorbed O_2 molecules or radicals. The larger the specific surface and lattice imperfection of the clay minerals, the easier is the adsorption of O_2 molecules or radicals (Huang 1990). Therefore, the lack of chelating ability in hydroquinone and the presence of larger surface area in Na-montmorillonite explains the lower degree of humification in hydroxy-interlayered clays than in Mt-HQ.

6.4.1.1 Characteristics of UV-visible spectra of supernatant solutions

Absorption of radiation in the ultraviolet (UV) (200-400 nm) and visible (400 - 800 nm) regions of the electromagnetic spectrum results from electronic transitions involving bonding electrons (Brown 1980). The absorption of UV-visible radiation by organic compounds is due to the presence of one or more chromophores. Chromophores are groups of atoms which contain unsaturated bonds (π-bonding electrons) (Bloom and Leenheer 1989). Many scientists are of the opinion that the dark colour of humic substances is due primarily to quinone-like structures (ortho-quinone and para-quinone) and ketonic C = O in conjugation (Stevenson 1994).

The ultra-violet (UV)-absorbance spectra for supernatants (SU) as a whole, and HA and FA formed in SU of Al-Mt-HQ and Al-Mt-CC, are shown in Fig. 6.1. The spectral patterns of SU, HA, and FA are representative for all the other clay-diphenol complexes. Two prominent peaks were observed in SU and FA spectra of Al-Mt-CC at 225 nm and 270 nm, whereas, in Al-Mt-HQ, a slight shift of these peaks to 280 nm was observed. The complexation of catechol with Al^{3+} is shown by shifts in the UV spectrum from 275 to 282, with appearance of shoulders at 235 and 294 nm (McBride et al. 1988). The intense peaks centered around 255 nm in the UV spectrum was also observed by Mortland and Halloran (1976), who ascribed them to polymeric materials with some aromatic character. Humic acids separated from SU of Al-Mt-HQ and Al-Mt-CC had three peaks at 220, 270, and 325 nm (Fig. 6.1). This is the unique feature in the HA spectra of all the clay-diphenol complexes. The spectra of HA separated from supernatants of controls (i.e., HQ and CC) shows the peaks at the same positions as their corresponding clay-diphenol complexes, and the difference in sharpness of the peaks between two diphenols (i.e., sharp in CC and broad in HQ) was also clearly visible (spectra not shown). Therefore, the difference between HA spectra of clay-hydroquinone and clay-catechol is due to the difference between diphenols itself.

The visible spectra of HA separated from controls(i.e., HQ and CC) did not show any characteristics other than dropping very steadily from 400 to

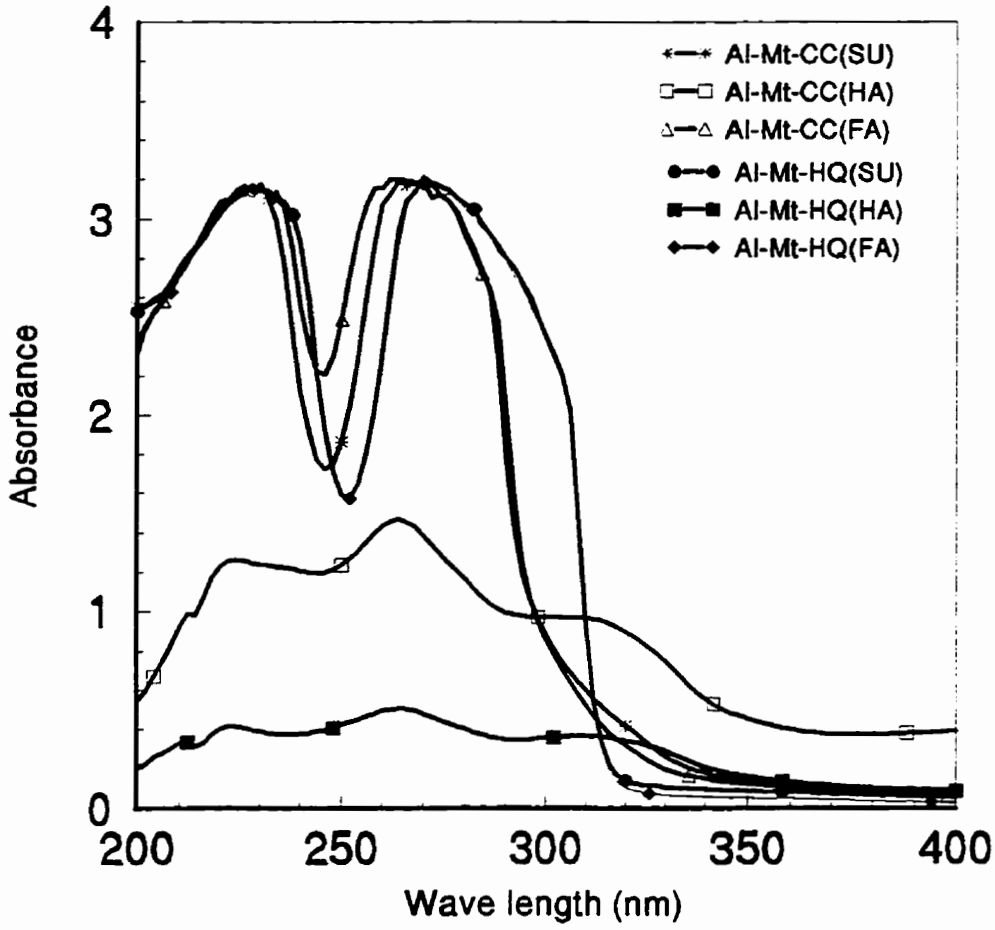


Fig. 6.1 UV spectra of the supernatant (SU) and, humic (HA) and fulvic acid (FA) separated from supernatants of Al-Mt-HQ and Al-Mt-CC complexes

600nm (spectra not shown). Only some of the visible spectra of the humic acids separated from supernatants of clay-hydroquinone and clay-catechol complexes exhibited absorbance peaks (i.e., Mt-HQ and Al-Mt-CC at 420-430 nm, and Al-Mt-CC again with a peak at around 600 nm, Fig. 6.2). The coloured products of adsorbed catechol on Al hydroxide have absorption peaks at 380, 412 and 615 nm (McBride et al. 1988). Visible spectra of the fulvic acids separated from SU solutions of clay-diphenols do not show any prominent peaks, but sharply drop from 400 to 600 nm. Very low absorbance values at 600 nm for all the samples indicates that little or no FA formed in the supernatants of clay-diphenol complexes.

6.4.2 Characterization of humic substances formed in solid clay-diphenols

Different fractions of organic C (total, alkaline soluble, humic acid and fulvic acid, separated from clay-diphenol complexes are presented in Table 6.3. Larger amounts of C in all the fractions mentioned above were extracted from clay-catechol complexes than clay-hydroquinones. The amounts of C in the various fractions separated from clay-diphenol complexes can be ordered as follows: Total C > alkaline soluble C > fulvic acid > humic acid (Table 6.3). Amounts of humic acid associated with solid-diphenol complexes can be ordered as follows; Fe,Al-Mt-CC > Fe-Mt-CC > Al-Mt-CC > > clay-HQ > Mt-CC. The layer-silicate surfaces act as Lewis acids which accept electron pairs from hydroquinone/catechol, leading to the formation of semiquinones and

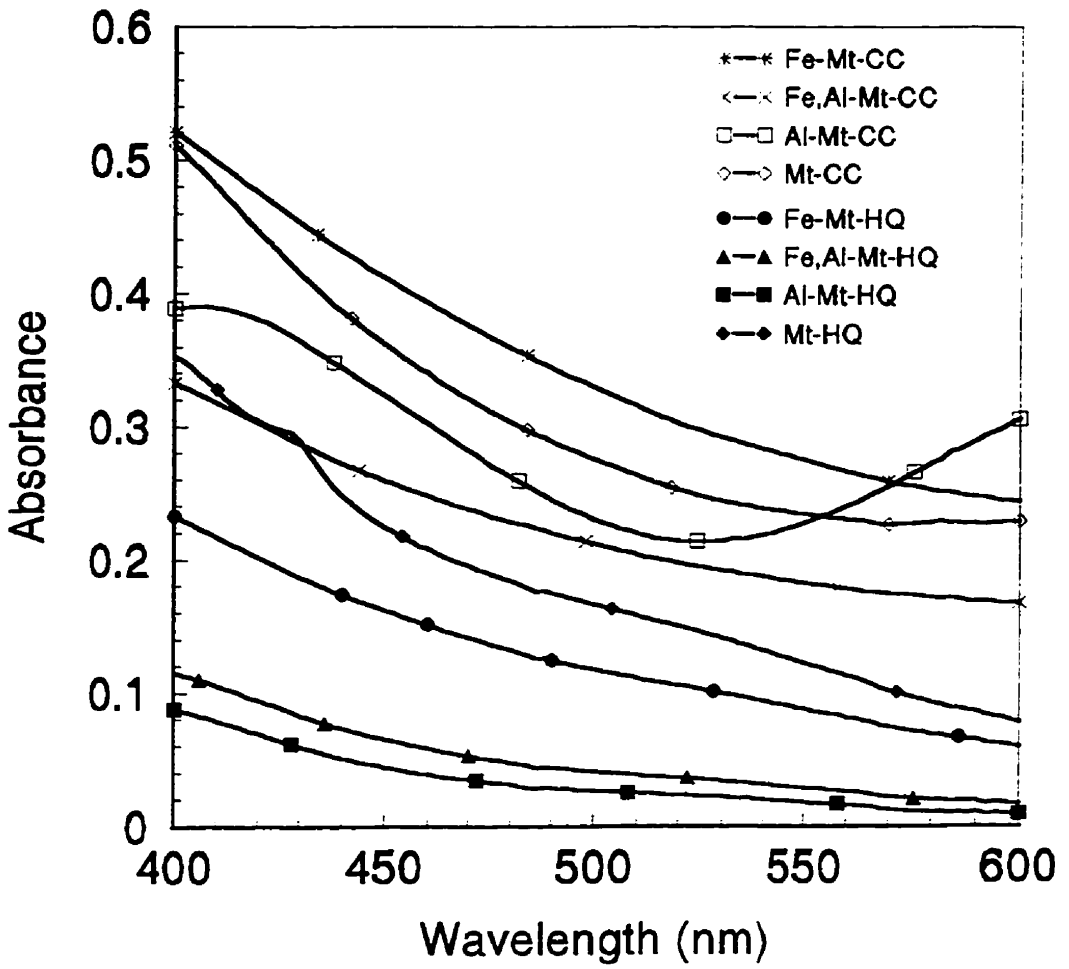


Fig. 6.2 Visible spectra of humic acids from supernatants of clay-hydroquinone and clay-catechol complexes.

Table 6.3 Amounts of C retained and characterization of humic and fulvic acids separated from the solid clay-diphenol complexes.

Sample	Total C	Alk. Sol. C	Humic acid C	*Fulvic acid C
		----------mg kg^{-1}----------		
Mt-CC	6890	1506	280	1226
Fe-Mt-CC	69080	9508	1539	7969
Fe,Al-Mt-CC	72042	11913	2038	9875
Al-Mt-CC	28035	9808	2144	7664
Mt-HQ	3560	604	290	314
Fe-Mt-HQ	3960	1480	320	1160
Fe,Al-Mt-HQ	4060	1640	430	1210
Al-Mt-HQ	3110	798	290	508

*Calculated by the difference between alkaline soluble C and humic acid C amounts

theirsubsequent polymerization. The strong complexing ability of catechol to metal-oxides/hydroxides facilitated retention of catechol and ortho-semiquinone radicals to surfaces of hydroxy-interlayered clays for longer times. Higher amounts of organic-C fractions extracted from catechol complexes suggest that surface-complexed catechol derivatives have oxidized and polymerized to form humic substances. Therefore, the solid fractions of clay-catechols have remarkably higher amounts of alkaline soluble, humic-acid, and fulvic-acid C-fractions than those of hydroquinone complexes (Table 6.3).

In order to further understand the catalytic effects of interlayers and Mt on the formation of humic substances, the nature and quantity of humic acids separated from clay-diphenol complexes were determined (Table 6.4). The degree of humification of humic acids is deemed greater as Δlog K values decrease (Kumada 1987). The yields of humic acids formed in the clay-diphenol complexes were highly correlated ($r^2=0.97$) with the degree of darkening of separated humic-acid solutions measured at 400 nm. Therefore, higher K_{400} in HA formed in solid-phase represent higher HA yields. There was no difference among the humic acids separated from clay-diphenols in the degree of humification, as indicated by their Δlog K values. The E_4/E_6 values of these humic acids lie between 2.4 and 3.2, within the range, (i.e., <5) reported for humic acids (Kononova 1966). The fulvic acids separated from clay-diphenol complexes resemble the true fulvic acids, i.e., E_4/E_6 between 5 and 8, except for Mt-CC which has very low degree of darkening even at 400

Table 6.4 Characterization of humic and fulvic acids separated clay-diphenol complexes.

	Humic acid				Fulvic acid	
Sample	K_{400}	K_{600}	E_4/E_6	Δlog K	K_{400}	E_4/E_6
Mt-CC	0.03	0.01	2.7	0.44	0.01	22
Fe-Mt-CC	0.74	0.27	2.7	0.43	0.41	6.1
Fe,Al-Mt-CC	0.83	0.34	2.4	0.38	0.41	6.9
Al-Mt-CC	0.79	0.34	2.3	0.35	0.35	8.0
Mt-HQ	0.10	0.03	2.8	0.46	0.02	8.7
Fe-Mt-HQ	0.11	0.03	3.2	0.50	0.05	6.6
Fe,Al-Mt-HQ	0.20	0.07	2.7	0.42	0.05	10
Al-Mt-HQ	0.10	0.03	2.9	0.46	0.03	11

nm (Table 6.4). Therefore, the properties of humic substances formed in all the solid-phases show that they resemble natural humic substances.

6.4.2.1 Characteristics of UV- visible spectra of humic substances formed in the solid-phase. The UV spectra of the humic acids (HA) separated from solid-phase clay-diphenol complexes are shown in Fig. 6.3. All the interlayered-clay-catechol complexes show very high-intensity broad peaks at wave lengths between 220 to 260 nm. All the clay-hydroquinone and Mt-CC complexes follow the same pattern but have a lower-intensity absorbance peak in the 220-230 nm range. Absorption spectra do not provide much detailed information on chemical structure, but the similarity of the spectra suggests compounds with similar basic structures (Schnitzer 1971). Fulvic acids separated from solid complexes show the same uncharacteristic pattern in their UV spectra (not shown). Strong absorption in the UV region is expected for humic and fulvic acids, which contain aromatic groups (Stevenson 1994). Lindquist (1972) showed that catechol and hydroquinone can form complexes with humic acid, and that the formation of such complexes caused an increase in the absorptivity of humic acid in the range 320-680 nm.

Visible spectra of fulvic and humic acids separated from diphenol complexes show higher absorbance at lower wavelength and gradually dropp as the wavelength increases (spectra not shown). The absorption spectra of humic substances in the visible region are generally featureless, with increasing

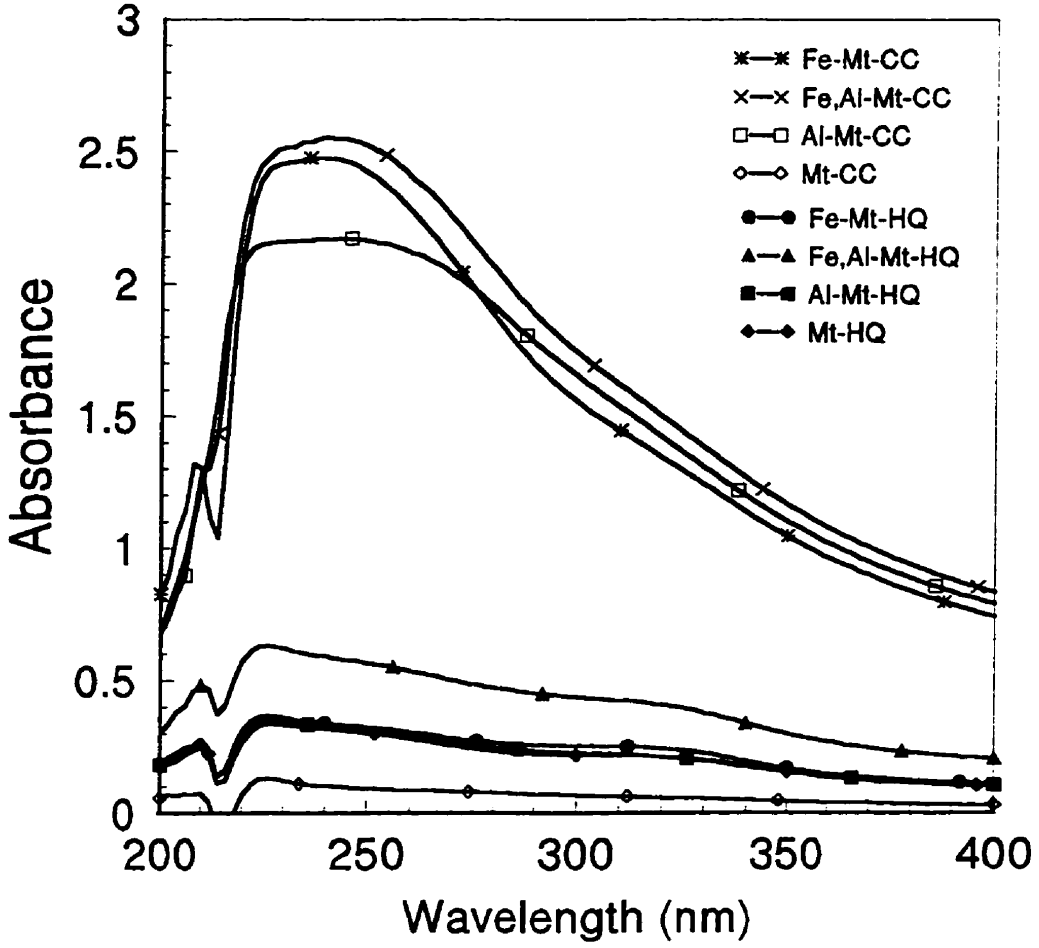


Fig. 6.3 UV-spectra of humic acids separated from solid clay-hydroquinone and clay-catechol complexes

absorbance at shorter wavelengths (Kumada 1987). Tsutsuki and Kuwatsuka (1979) suggest that absorption in the visible region is associated with unsaturated structures containing phenolic OH. Chen et al. (1977) concluded that much of the observed visible absorption is due to scattering of light. Humic acids can have high molecular weights (Stevenson 1994), and scattering may contribute to the measured absorbance (Chen et al. 1977). Fulvic acids have relatively low molecular weights (Stevenson 1994) and the contribution of scattering is not likely to be significant for fulvic acids (Chen et al. 1977).

6.5 Conclusions

The results presented here support the hypothesis that interlayered clays (Fe-Mt, Fe,Al-Mt, and Al-Mt) aid polymerization of polyhydroxybenzenes by increasing the Lewis-acid sites at the clay surfaces. The rate and degree of polymerization and polycondensation of phenolic compounds vary with the chemistry of the phenolic compound, type of the hydroxy-interlayer, and the stability of hydroxy-interlayer.

Interlayers of Fe-Mt Al-Mt and Fe,Al-Mt, tend to stabilize ortho-semiquinone radicals in catechol complexes and direct the manner in which these radicals polymerize and adsorb to these clays, releasing smaller amounts to the supernatants. Hydroquinone (which is unable to form chelate complexes with clays) oxidizes using layer-silicate surfaces for interaction between

molecular O_2 and phenol, releasing polymerized materials into supernatants. This phenomenon is supported by the observation that non-interlayered montmorillonite catalyzes the formation of the largest amounts of humified materials from hydroquinones. By contrast, interlayered clays yield the largest amounts of humified materials from catechol complexes. The humic substances formed in supernatants do not represent natural products, whereas solid clay-catechol and clay-hydroquinone form humic and fulvic acids that resemble humic substances found in nature.

7. ADSORPTION OF ATRAZINE BY INTERLAYERED CLAYS AND THEIR ORGANIC COMPLEXES

7.1 Abstract

Sorption of atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine] on Al- and Fe-hydroxy-interlayered montmorillonite and their organic complexes with various organic C contents were determined using the batch-equilibration procedure. Atrazine at concentrations of 5.9×10^{-2}, 7.5×10^{-2}, 8.9×10^{-2} and 10.5×10^{-2} $\mu g\ mL^{-1}$, was equilibrated with hydroxy-Fe interlayered montmorillonite (Fe-Mt) and its citrate (Fe-Mt-Ct), hydroquinone (Fe-Mt-HQ) and catechol (Fe-Mt-CC) complexes, and hydroxy-Al-interlayered montmorillonite (Al-Mt) and its citrate (Al-Mt-Ct) and hydroquinone (Al-Mt-HQ) complexes, under constant shaking.

Conformity to the Langmuir adsorption equation was found for all clays studied, except for interlayered clay-citrate complexes (Fe-Mt-Ct and Al-Mt-Ct). Varying adsorption maxima (M) were observed among sorbents. The relative sorption of atrazine, by each sorbent as indicated by the mean percentages sorbed, was as follows; Fe-Mt-CC > Fe-Mt-HQ > Al-Mt-HQ > Al-Mt > Fe-Mt > Al-Mt-Ct ≥ Fe-Mt-Ct. Atrazine retention in soils depends on the amount

and chemical composition of organic substances associated with the hydroxy-interlayered clays. Interlayered clays associated with humified material sorbed more atrazine than clays with non-humified organic compounds. The pH of the clay surface plays a major role in atrazine sorption by hydroxy-interlayered clays and their organic complexes. Adsorption of atrazine occurred through hydrophobic interactions with organic-matter surfaces and through weak van der Waal's forces and H-bonding with clay-mineral surfaces.

7.2 Introduction

Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine] is a selective herbicide for the control of annual grasses and broad-leaved weeds. Because adsorption can influence the translocation, volatility, persistence, and bioactivity of a herbicide, probably it is the major process that affects the behaviour of a soil herbicide (Bailey and White 1970). More recently, Barriuso et al. (1994) suggested that atrazine is primarily retained on surfaces of smectites through relatively weak van der Waal's forces or H bonds. Surface acidity leads to protonation and hydrolysis of herbicide sorbed on smectite (Laird 1996). The sorption of s-triazine herbicides on montmorillonite as protonated species is preceded by sorption as molecular species on hydrophobic microsites of the clay, unless the pH of the bulk solution is close to the pK_a (Celis et al. 1997).

Sorption of nonionic compounds in soils can be via hydrophobic partitioning between soil solution and a hydrophobic phase found in soil organic matter (Senesi and Testini 1980). Organic-matter content has been cited as a major soil property affecting pesticide behaviour (Felsot and Dahm 1979). Although organic matter interacts strongly with pesticides, measurement of organic-C content can rarely be used alone for predictive purposes (Meggit 1970) because of the intimate association of organic matter with inorganic-colloid constituents. Therefore, it is the combined inorganic-organic colloid interaction that needs to be evaluated in determining the full magnitude of pesticide-adsorption capacity by colloids (Saltzman 1972).

Hydroquinone and catechol that are precursors of humic substances and citric acid that is produced in rhizosphere by bacteria could be present in soils as clay-organic complexes. Surprisingly, adsorption studies of atrazine in the presence of such organic compounds associated with clays are lacking. In the present study, the effect of hydroxy-interlayered montmorillonite and its organic complexes on sorption of atrazine, are determined and discussed in terms of the chemistry of the organic adsorbate and surface characteristics of the clays. The presence of hydroquinone, catechol and their polymerized products, citric acids, hydroxy-interlayered clays, and hence the clay-organic interactions are possible in tropical and sub-tropical environments, where atrazine could be applied as a herbicide. Therefore, the sorption results obtained in this work should lead to a better understanding of the retention processes of atrazine by

colloidal-particle constituents.

7.3 Materials and Methods

Preparation of hydroxy-interlayered clays (chapter 3) and their citrate, hydroquinone and catechol complexes (Chapter 5) were discussed earlier. Hydroxy-interlayered Fe (Fe-Mt) and Al (Al-Mt), prepared by using 600 cmol (+) cations kg^{-1} of montmorillonite, were the hydroxy-interlayered clays used in this study. Their citrate (Fe-Mt-Ct, Al-Mt-Ct), hydroquinone (Fe-Mt-HQ, Al-Mt-HQ) and catechol (Fe-Mt-CC) complexes were prepared by adding 300 cmol organic compounds per kg of hydroxy-interlayered clay. The physico-chemical properties of these clays are listed in Table 7.3.

7.3.1 Sorption of atrazine by clays and clay-organic complexes

Freeze-dried clay (0.1 g) was suspended in approximately 15 mL deionized water for about 2 d, with constant shaking. This wetted all the surfaces of the soil particles. The equilibration reaction was started by addition of a calculated aliquot of atrazine standard-stock solution, with the total slurry volume being adjusted to 25 mL. The initial atrazine concentrations used in this study were 5.9 $x10^{-2}$, 7.5 $x10^{-2}$, 8.9 $x10^{-2}$ and 10.5 $x10^{-2}$ μg mL^{-1}. Two replicates were used for each concentration of each clay, and blanks without any atrazine were run at the same time. These suspensions were shaken for

another 48 h in 50 mL Teflon centrifuge tubes, standing vertically. At the end of the reaction period, suspensions were centrifuged at 10,000 *g* for 10 minutes and the clear supernatants were separated using 0.45 μm Millipore filters. A 20 mL aliquot of the supernatant was used to extract the atrazine by 10 mL Dichloromethane (DCM) twice using a 250 mL glass separator. The DCM-extracted atrazine was evaporated under N_2 gas and the atrazine was dissolved in 2 mL of toluene. A 2 μL aliquot was injected into a DB-5 capillary column (30 m long, 0.25 mm (id), 0.1 μm film thickness, J&W Scientific Inc., Folsom, CA, USA) of a Gas Chromatograph (Hewlett-Packard 5890 GC). The difference between atrazine added and extracted from the supernatants was considered to be the amount adsorbed. Relative sorption of atrazine by each sorbent was calculated as

$$\% \text{ sorbed} = [\text{amount sorbed } (\mu g) / \text{ weight of soil (g)}] \times 100.$$

The equilibrium pH values of clay-atrazine systems were measured at the end of the equilibrium time. Atrazine standards were prepared using the calculated aliquot from stock solution of 19.8 μg mL^{-1}. A calibration-curve was calculated for atrazine standards at concentrations of 0.1, 0.2, 0.4, 0.6 and 0.8 μg mL^{-1}.

7.3.2 Sorption isotherms

To compare in sorption among the clays, the data were fitted to the nonlinear Freundlich adsorption equation:

$$S = k_f C^N$$

where S = μg of atrazine adsorbed per g of clay, C = equilibrium concentration of the solution (μg mL^{-1}) and K_f (mL g^{-1}) and N (dimensionless) are empirical constants.

Conformity to the Langmuir-type adsorption isotherm was tested using the Langmuir equation:

$$C/S = 1/KM + C/M$$

where S= amount of atrazine adsorbed in μg/g, C = equilibrium solution concentration, in μg mL^{-1}, M= maximum amount of atrazine that can be adsorbed in a monolayer (μg g^{-1}) and K (dimensionless) = equilibrium constant.

7.4 Results and discussion

There was no difference in equilibrium concentrations in sorbents at 48 and 72 h (data not shown), indicats that equilibrium was reached within 48 h. Results of statistical analysis of the adsorption isotherms are presented in Table 7.1. All sorbents gave high conformity to the Freundlich isotherm as shown by their r^2 values. All sorbents, except clay-citrate complexes (Fe-Mt-Ct and Al-Mt-Ct), gave very low N values (Table 7.1). The N values range from 0.27 to 0.95, and K_f values vary from 18.9 to 69.8 mL g^{-1} (Table 7.1). According to the Freundlich equation, K_f values change with concentration when N values are not close to 1.0. Therefore, the K_f values cannot be used as a constant for these clays. Conformity to the Langmuir equation was observed for all

sorbents studied, except the clay-citrate complexes (Table 7.1, Fig. 7.1). According to the adsorption maxima (M), these clays can be ordered as follows: Fe-Mt-CC > Fe-Mt-HQ > Al-Mt-HQ > Al-Mt > Fe-Mt. Hence, sorption of atrazine was much greater by catechol- and hydroquinone-interlayered complexes than by hydroxy-interlayered clays without humified matter. As Fe-Mt-Ct and Al-Mt-Ct show poor conformity to the Langmuir equation, maximum adsorption values could not be used to order them. The relative sorption of atrazine by each sorbent (as indicated by the mean percentage sorbed) is presented in Table 7.2. Significantly different amounts of atrazine was retained in the sorbents, as follows: Fe-Mt-CC > Fe-Mt-HQ > Al-Mt-HQ > Al-Mt > Fe-Mt > Al-Mt-Ct ≥ Fe-Mt-Ct. Results are in agreement with the adsorption-maxima (M) of the sorbents. Weber (1993) observed that ranking of sorbents according to the mean percentages sorbed follows the K_f values. The results indicate that the type of organic compound present and the type of the interlayer determined the adsorption of atrazine. The presence of humified materials in clay-hydroquinone and -catechol complexes resulted in the highest amount of atrazine retained among sorbents, as indicated by higher sorbed percentages (Table 7.2). In contrast, the presence of citrate with interlayered clays reduced the sorption of atrazine, giving lowest atrazine sorption in citrate complexes among the sorbents. The degree of organic-metal complexation probably affects the Lewis-acid strength of the metal and its ability to further interact with the surface sites (Schulthess and Huang 1991). Inner-sphere

Table 7.1 Adsorption isotherm constants for the sorption of atrazine on sorbents

Sorbents	Nonlinear Fruendlich $S = K_f C^N$			Langmuir $C/S = 1/KM + C/M$		
	K_f(mL g^{-1})	N	r^2	K	M(μg g^{-1})	r^2
Fe-Mt-CC	69.8	0.44	0.97	48.7	25.7	0.89
Fe-Mt-HQ	45.2	0.44	0.98	34.7	19.2	0.86
Al-Mt-HQ	21.2	0.27	0.99	67.5	12.3	0.99
Al-Mt	19.4	0.32	0.98	43.7	10.9	0.93
Fe-Mt	18.9	0.34	0.98	38.1	10.5	0.91
Al-Mt-Ct	20.6	0.92	0.97	-	-	*
Fe-Mt-Ct	20.4	0.95	0.97	-	-	*

*r^2 values are very low

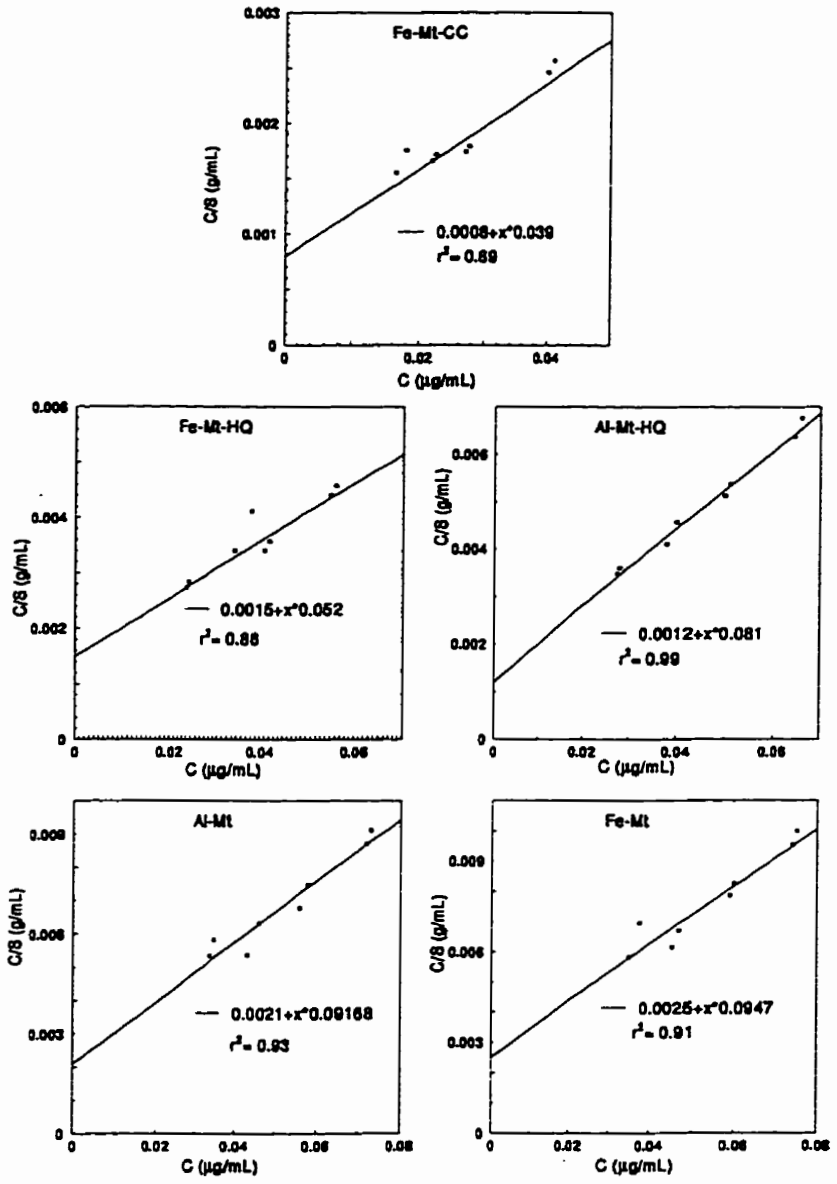


Fig. 7.1 Langmuir-sorption isotherms for atrazine sorption on interlayered clays and their organic complexes

complexation of citrate with Fe and Al in hydroxy-interlayered clays (Chapter 5) may have reduced the surface $[Fe\text{-}(OH)_2]^+$ and $[Al(OH)_2]^+$ sites on Fe-Mt-Ct and Al-Mt-Ct, making them more difficult to produce weak van der Waals forces and H-bonds with atrazine. In low-organic-matter soils and sediments, clay minerals likely control sorption/desorption interactions (Mingelgrin and Gerstl 1983, Hayes and Mingelgrin 1991).

The pH values of clay suspensions were in the range 4.7- 6.4 (Table 7.3), substantially above the pK_a (1.68) of atrazine. The equilibrium pH values are negatively correlated ($r^2 = 0.66$) with the amount of atrazine sorbed. The surface acidity of montmorillonite is usually 3-4 pH units lower than the suspension pH (Bailey et al. 1968). Atrazine can act as a weak base that become protonated at low pH (Bouchard and Lavy 1985). Sorption of atrazine may also occur via H-bonding between the herbicide molecules and the colloid surfaces due to the basic nature of atrazine. The possible mechanisms for the adsorption of atrazine by clays and their organic complexes are (1) physical adsorption due to van der Waal's forces and H-bonding, and (2) chemical adsorption as protonated species. The presence of hydroxy-polymers, citrate, and polymerized products of hydroquinone and catechol might have changed the surface characteristics of montmorillonite, enabling the adsorption of atrazine as a protonated species. The relation between sorption and soil properties was determined through linear regression analysis. Poor relations were observed with CEC and total-surface-area values. Laird et al. (1992) and

Table 7.2 Amounts of atrazine sorbed in the interlayered clays and interlayered clay-organic complexes.

Sorbent	Initial Conc. $\mu g\ mL^{-1}$	Equili. Conc. $\mu g\ mL^{-1}$	Amount Sorbed x/m $\mu g\ g^{-1}$	Sorbed fraction in % (% sorbed)	Sorbed fraction average (%)
Fe-Mt-CC	0.059	0.017	10.44	70.76	67.97[a]
	0.075	0.022	13.19	70.33	
	0.089	0.027	15.44	69.38	
	0.105	0.04	16.13	61.42	
Fe-Mt-HQ	0.059	0.024	8.69	58.89	52.74[b]
	0.075	0.036	9.69	51.66	
	0.089	0.042	11.88	53.37	
	0.105	0.055	12.37	47.14	
Al-Mt-HQ	0.059	0.028	7.82	52.96	45.49[c]
	0.075	0.039	9.00	48.00	
	0.089	0.051	9.63	43.26	
	0.105	0.065	9.93	37.86	
Al-Mt	0.059	0.034	6.15	41.69	37.31[d]
	0.075	0.045	7.63	40.66	
	0.089	0.057	8.00	35.95	
	0.105	0.072	8.12	30.95	
Fe-Mt	0.059	0.036	5.69	38.55	34.76[e]
	0.075	0.046	7.18	38.33	
	0.089	0.060	7.37	33.14	
	0.105	0.074	7.62	29.04	
Al-Mt-Ct	0.059	0.053	1.44	9.74	9.24[f]
	0.075	0.068	1.63	8.66	
	0.089	0.081	2.13	9.55	
	0.105	0.095	2.38	9.04	
Fe-Mt-Ct	0.059	0.054	1.19	8.05	8.41[f]
	0.075	0.068	1.63	8.67	
	0.089	0.081	1.97	8.82	
	0.105	0.096	2.12	8.09	

*Means in the same column followed by the same letter are not significantly diffrent (Duncan's multiple range test, $p = 0.05$)

Table 7.3 Selected physical and chemical properties of the sorbents studied

Sorbent	pH	Organic C	CEC	Specific surface	Exchangeable Fe or Al	d-spacing
		mg kg^{-1}	cmol(+) kg^{-1}	m^2 g^{-1}	cmol(+) kg^{-1}	nm
Fe-Mt-CC	4.7	69080	76	670	1.1	1.30
Fe-Mt-HQ	5.5	3960	60	678	0.3	1.29
Al-Mt-HQ	6.1	3110	30	670	21	1.42
Al-Mt	5.9	-	33	455	24	1.42
Fe-Mt	6.4	-	54	679	0	1.33
Al-Mt-Ct	6.5	5300	71	553	11.5	1.27
Fe-Mt-Ct	6.0	6900	68	627	0.3	1.26

Sawhney and Singh (1997) found that sorption of atrazine increased with decreasing layer charge in smectites. Changes in CEC of the sorbents are due to a number of factors: blocking of the internal surfaces, dissolution of interlayer material, complexation with organics, presence of humified materials, etc., as discussed in Chapter 5. Those CEC governing factors change in surface properties of clay minerals result in varying amounts of atrazine retention. Therefore, it is evident that a knowledge of the surface properties of clay minerals is very important in predicting the fate of atrazine in agricultural soils. The presence of Fe^{3+} as an interlayer cation greatly enhances the sorption of atrazine by montmorillonite, but ferrihydrite does not sorb triazine herbicides (Celis et al. 1997). The greater sorption of atrazine by Al- than by Ca-saturated smectite reported by Sawhney and Singh (1997). Therefore, the higher amounts of atrazine sorbed by Fe-Mt and Al-Mt than their corresponding -citrate complexes (Fe-Mt-Ct, Al-Mt-Ct) (Table 7.2) was to be expected.

Out of the 7 sorbents used, 5 are organic complexes and organic C was $<1\%$ in all of them except Fe-Mt-CC (Table 7.3). Hydroquinone and catechol undergo oxidative polymerization during aging, and produced polymerized humic-like substances (Chapter 6). The difference in retention of atrazine between citrate and hydroquinone complexes suggests that atrazine retention in these complexes depend not on the amount but on the type of organic compound. Higher retention of atrazine in hydroquinone complexes than in citrate complexes (the later has higher organic-C contents than the former,

Table 7.3) shows that the latter does not have enough polymerized substances to retain atrazine. Moreover, the sorbed atrazine in the samples are not highly correlated with organic-C content ($r^2 = 0.38$). Therefore, H-bonding between atrazine and the hydrated exchangeable cation on montmorillonite (Sawhney and Singh 1997) might be playing a major role in these montmorillonitic derivatives with low-organic C, no humified organic C, and no organic C. Studies on surface behaviour and adsorption should weigh heavily on the chemical composition of the outermost layer of the solid phase (Schulthess and Sparks 1991). Laird (1996) proposed physical sorption on hydrophobic microsites as the initial mechanism for retention of atrazine on smectite surfaces under neutral pH conditions.

7.5 Conclusions

Only a narrow pH range (4.7 to 6.2) was evaluated in this study and all the pH values were above the pK_a of atrazine. Atrazine was sorbed by physical forces at near-neutral pH and by ionic bonds at low pH. The presence of hydroxy-polymers and polymerized products of hydroquinone and catechol with montmorillonite reduced the surface acidity and increased the functional groups enabling these complexes to sorb atrazine through H- and ionic bonds. The amounts of polymerized humic-like substances (rather than the amount of organic C) was the determining factor in the retention of atrazine in this study.

Chelation of surface Fe and Al functional groups with citrate was the probable reason for the least atrazine sorption in interlayer-citrate complexes among the sorbents.

8. SUMMARY AND CONCLUSIONS

Reduction of specific surface area and CEC in hydroxy-interlayered clays compared to that of the non-interlayered montmorillonite indicates the presence of hydroxy polymers in interlayer spaces. In natural systems, Fe^{3+} and Al are ubiquitous in soils and sediments, and may play a role in polymerization reactions similar to that shown here. Differences in degree of interlayering among the hydroxy-interlayers was as follows: Al-Mt > Fe,Al-Mt > Fe-Mt. According to the AOD and CBD results, hydroxy-Fe interlayer was the least stable out of the three interlayered materials studied, and hydroxy-Al showed the highest stability and crystallinity.

Soil minerals have an important role in catalyzing abiotic oxidative polymerization reactions of diphenols. Hydroxy-interlayered clays showed three to ten fold higher degree of humification than the corresponding hydrous-oxides (without clay) with hydroquinone. The interlayered clays of Fe-Mt, Al-Mt and mixed Fe,Al-Mt promoted polymerization of polyhydroxybenzenes by increasing the Lewis-acid sites at the clay surface. The results obtained in the present study show that hydroxy-interlayered clays accelerate the polymerization of hydroquinone and catechol to various degrees, depending on the interlayer cation and stability of the interlayer. Degree of oxidative polymerization of

hydroquinone and catechol in solid- and solution-phases of hydroxy-interlayered clays behave differently, showing higher amounts of humic acids in solution for hydroquinone and higher amounts of humic acids in the solid phase for catechol. These interlayered clays tend to stabilize ortho-semiquinone radicals (derived from catechol), facilitating polymerization and adsorption to the clays and releasing smaller amounts to the supernatants. Hydroquinone is unable to form chelate complexes with clays, and oxidizes using layer silicate surfaces to promote interaction between molecular O_2 and the diphenol, releasing polymerized materials into supernatants. Therefore, the rate and degree of polymerization and polycondenzation of phenolic compounds vary also with the chemical detail of the phenolic compound. The humic substances separated from solids (but not that of supernatants) resembles true fulvic and humic acids. The polymerized products formed in relatively mild conditions of the present study revealed the effects of the negatively charged silicate surface in promoting the formation of free radicals and their subsequent polymerization. Therefore, chemical synthesis of polyphenols and polyquinone structures could contribute to humus formation where polyphenols are present in appropriate chemical environment in the soil.

To summarize the behaviour of hydroquinone and catechol, the following reaction sequences are supposed to occur on clay-mineral surfaces in clay suspensions. Aluminum and Fe in hydroxy-interlayered clay minerals act as electron-acceptor sites, catechol through chelation with Fe and Al, and

hydroquinone through H-bonds coordinated with the cations by assuming a direct ligand position. Therefore, in hydroxy-interlayered clay minerals, the radical ions are formed by electron transfer from organic compound to Fe^{3+} and also due to the promotive ability of Al in oxidation and in the formation of charge-transfer complexes. The radical ions formed may then undergo polymerization. The bonds may be either C-H bridge, C-C bridge, or coupling of rings. When polymerized quinones and semiquinones are present, they also participate in the reaction. As the possible reactions are myriad, they are complicated. Therefore, the resulting products of hydroxy-interlayered and non-interlayered diphenol complexes may include dimers, trimers, and tetramers of the parent diphenol and of the corresponding quinones. The more detailed chemistry of the isolated humic acids and other organic polymers derived from hydroquinone and catechol is beyond the objectives of this thesis. Nevertheless, these analyses, which could be done using techniques like ^{13}C NMR and Pyrolysis-soft Ionization Mass Spectrometry, would be beneficial in the examination of natural humification processes and humified materials.

Citrate, hydroquinone and catechol adsorb readily on layer silicates because of the involvement of hydroxycarboxylic, ortho-diphenolic groups and weak bonds. Adsorbed catechol and hydroquinone undergo oxidative polymerization, whereas citric acid was not humified. The base consumption values obtained from this study reflect the buffer capacity of hydroxy-Fe, and/or -Al and their organic complexes. Hydroxy-interlayered clays aging with

citric acid caused the destruction of hydroxy-polymers, subsequently reducing the third-buffer-range buffer-capacity and increasing the pH in the suspension. As a result of oxidation and subsequent polymerization of catechol and hydroquinone, the presence of humic materials with the hydroxy-interlayered clays increases their reactivity and buffer capacity without any structural changes to the layer silicates. Hydroxy-interlayered clays adsorbed higher amounts of citrate through Al-OH_2, Fe-OH_2 and silanol groups than that of non-interlayered montmorillonite.

Atrazine sorption is correlated with the pH of the equilibrium suspensions of the sorbents. Therefore, atrazine was sorbed by physical forces and ionic bonds in Fe-Mt, Al-Mt and their citrate, hydroquinone and catechol complexes at near-neutral and acidic pH. The presence of hydroxy-polymers and polymerized products of hydroquinone and catechol with montmorillonite reduced the surface acidity and increased the functional groups, enabling these complexes to sorb atrazine through H- and ionic bonds. Varying amounts of atrazine was sorbed, as follows; Fe-Mt-CC > Fe-Mt-HQ > Al-Mt-HQ > Al-Mt > Fe-Mt > Al-Mt-Ct ≥ Fe-Mt-Ct. Therefore, the amount of the polymerized humic-like substances rather than the amount of organic C is the determining factor in retention of atrazine in this study.

9. CONTRIBUTION TO KNOWLEDGE

Interlayer spaces of montmorillonitic clays are accessible for hydroxy polymers of -Fe, -Al and mixed -Fe,Al. The degree of interlayering and stability of these interlayers follows the order: Al-Mt > Fe,Al-Mt > Fe-Mt, when these were prepared using 600 cmol(+) kg^{-1}, at initial pH of 5.1 and aging for 30 d.

Non-interlayered Na-montmorillonite and its Fe-Mt, Al-Mt, and mixed Fe,Al-Mt interlayered montmorillonite enhances the oxidative polymerization of catechol and hydroquinone. Hydroxy-interlayered clays catalyze the humification process to varying degrees, depending on interlayer material, its stability and its ability to retain diphenol.

A higher degree of humification in hydroquinones in comparison with catechols has been observed by other scientists by determining the nature and amount of humic acids separated from supernatants. In my study, it is shown that the analysis of the nature and amounts of humic acids should be made in both supernatant and solid complexes when comparing these two diphenols.

Perturbation in hydroxyl bridging by citric acid in hydroxy polymers has been shown, when citric acid was introduced at the same time as the cation and OH^- ions. This present study showed that citric acid dissolves hydroxy-polymers even when citric acid was added to preformed hydroxy-interlayered

materials. Addition of citric acid to hydroxy-interlayered suspensions caused the dissolution of these interlayers, resulting in an increase in pH.

The importance of organic matter in soils or the retention of atrazine through partitioning to the organic phase has been emphasized by many scientists. My study showed that the humified materials in the system determines the sorption. Clay minerals with no humified materials retained atrazine through physical adsorption. When surface functional groups are complexed with a strong chelator, sorption of the herbicide was reduced, even when the chelator was an organic compound.

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IMAGE EVALUATION
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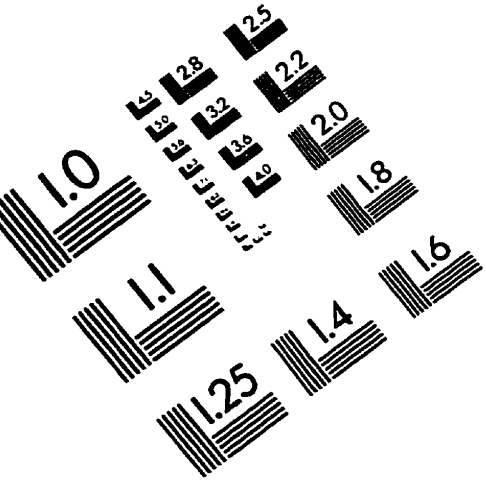

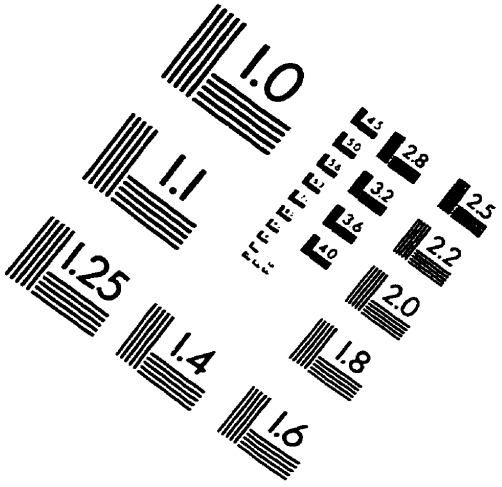

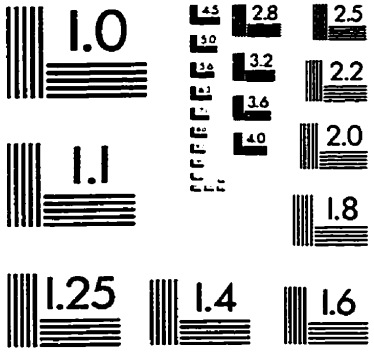

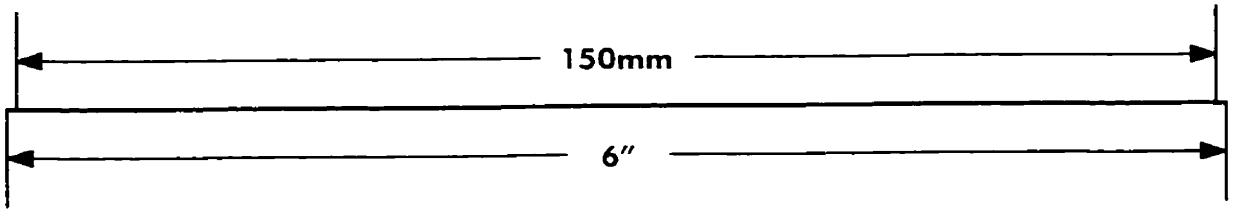

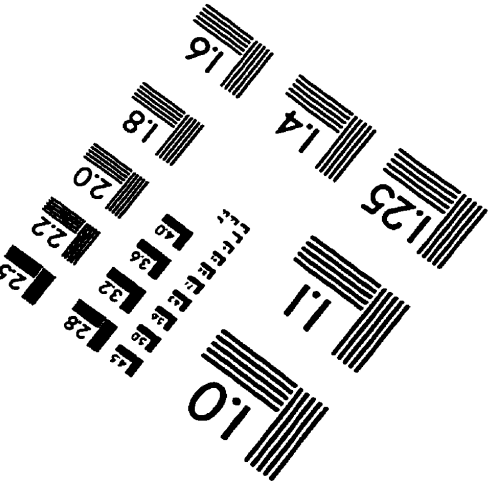

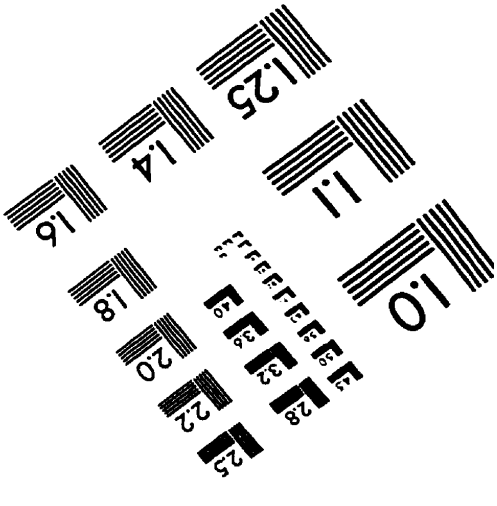

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