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Sorption of Lead and Arsenic on Soil Components and Effectiveness of Phosphates for Remediating Lead and Arsenic Contaminated Soils

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Dissertation submitted to the
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ABSTRACT

Sorption of Lead and Arsenic on Soil Components and Effectiveness of Phosphates for Remediating Lead and Arsenic Contaminated Soils

Harjinder Sandhu

High concentration of trace elements such as arsenic (As) and lead (Pb) represents one of the potentially costly threats to water and soil resources as well as serious threats to humans. Clay minerals are potential binding agents for pollutants due to their high cation exchange capacity and large surface area. Laboratory investigations were undertaken to evaluate the effect of Fe and Al hydrous oxide coatings on the sorption of Pb and As. Four clay minerals attapulgite, illite, kaolinite and montmorillonite with a range of surface characteristics were selected to investigate the Pb and As sorption. The minerals were coated with three different levels of each of Fe and Al hydrous oxides. Adsorption and desorption studies were performed for each of these heavy metals at seven different pH levels. Coating with both Fe and Al hydrous oxide increased the retention of Pb and As. Lead desorption was decreased when minerals were coated with highest levels of Fe and Al. In order to fully understand the fate and transport of metal in the environment, there is a need to accurately describe and model the complex natural system. The ability of surface complexation models (SCMs) to fit sets of titration data as a function of changes in model parameters was evaluated using FITEQL and acid base titration of clays coated with Fe and Al hydrous oxide. Three SCMs were evaluated: the constant capacitance model, the diffuse-double layer and triple layer model. For all the models evaluated, increasing the value of total number of sites resulted in a decrease in the FITEQL best fit equilibrium log K value. Generally better F value fits were obtained when the site density (N_s) value was between 1 to 10 sites/nm^2.

Sequestering heavy metals in insoluble phosphate minerals has been suggested as an *in situ* remediation technique for Pb contaminated soils. Lead sequestered in apatite minerals has great durability and leaching resistance, significantly exceeding other chemically stabilized forms. Sequential extractions of Pb have been used to determine the suitability of phosphates to immobilize Pb . Laboratory studies were conducted to investigate whether the lead pyromorphite formation is the artifact of the sequential extraction or it is actually formed. It was found that formation of pyromorphite might be due to the artifact of extraction process. There are concerns about the use of phosphate in soils contaminated with both Pb and As because As and phosphate compete for the same sorption sites. Greenhouse experiments were conducted on soils contaminated with both Pb and As. These soils were treated with four rates of phosphates and seeded with Japanese millet (*Echinochloa crusgalli*) and red clover (*Trifolium pratense*). Results showed that when soils were contaminated with arsenic (As) only, application of phosphates resulted in increased concentrations of As in soil solution, however when soils were contaminated with both Pb and As, application of phosphorus did not increase As concentration in soil solution. Laboratory investigations were conducted to determine the mechanism responsible for reduced As mobility in soils that are co-contaminating with Pb. The results suggested that As in Pb contaminated soils coprecipitates with lead phosphates.

TO MY PARENTS

WHOSE BLESSINGS AND INSPIRATIONS

BROUGHT ME THIS FAR

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Chapter 1

Introduction

Rationale and Scope of Research

Pollution of the biosphere with toxic elements has accelerated dramatically since the beginning of the industrial revolution. As a result of accumulation in the biosphere, lead(Pb) and arsenic(As) pose more serious worldwide environmental and health hazards than any other elements (Jaworski, 1987; Huang Yan-Chu, 1997).

Lead concentration in agricultural soils of the US ranges from <1 to 135 mg/kg with an average of 12.3 mg/kg (Holmgren et al., 1993). However, the number of soils containing elevated Pb concentration has increased during the past half century due to anthropogenic contamination resulting from leaded paints, leaded gasoline, and Pb emission and waste from industries (Mielke, 1994). Lead contamination can cause a variety of environmental problems including Pb toxicity to plants, animals, and humans (Buchauer, 1973; Johnson and Eaten, 1980). Ingestion of contaminated soil is the most common pathway for lead poisoning in children (Chaney, 1989; EPA, 1993) . Lead can enter the food chain through contaminated vegetation; however, Pb concentration of plants is generally less than 1 mg/kg in fruits and seeds, and 1 to 3 mg/kg in leaves.

Arsenic is a commonly occurring toxic element in natural ecosystems. The natural concentration of As in soil is 5-6 mg/kg (Vinogrador, 1959; Backer and Chesnin, 1975; Bowen, 1979). The total amount of As in soil and its chemical form have an important influence on plant growth, and animal and human health. The sources of As in soils are the parent rock and human activities. Human activities may result in an accumulation of As in soil through use of arsenical pesticides, application of P fertilizer, irrigation, dust from burning of fossil fuels, and disposal of industrial and animal wastes (Sandberg and Allen, 1975). The anthropogenic influence on the level of As in soils depends on the intensity of human activity, the distance from the pollution sources, and the pollutant dispersion pattern.

Soil serves as an important medium for accumulation, transformation, and migration of the toxic chemicals. Sources of Pb and As contamination can be agricultural activities such as application of insecticides ($PbHAsO_4$) and industrial activities such as mining and smelting. Existing and abandoned disposal sites of As and Pb are potential sources of soil, and ground and surface water pollution. There is a need for remediation methods that do not destroy soil structure or fertility and are cheap and suitable for application on arable land (David et al., 1995).

Amorphous oxides of Fe and Al are known to adsorb Pb and As (Mckenzie, 1980; Bhumbla and Keefer, 1997). These oxides may occur as discrete particles, having little contact with clay surfaces or coating on clays, or as interlayers between clay mineral surfaces. Heavy metal adsorption characteristics of hydrous oxide coated clay may differ from either the hydrous oxides alone or clay minerals occurring as individual phases. Heavy metal adsorption on hydroxy-coated mineral surfaces may be affected by such factors as type of clay mineral and extent of surface coating with oxides/hydroxides. The type of clay mineral should influence the heavy metal adsorption because of variable particle sizes and different surface areas available for adsorption. The extent of surface coating should determine the extent of heavy metal adsorption because the cation adsorption characteristics of hydrous oxides and silicate clays differ markedly. Most soils are heterogeneous media that contain a host of different minerals, solids and oxides. As a result exploring the effect of coatings on adsorption/desorption of Pb and As is worthy of investigation.

Soil may act as a reservoir and can become an environmental pathway or carrier of Pb and As to biota. Thus, it is important to develop methods to minimize Pb and As bio-availability. Phosphate minerals have been used to immobilize Pb *in situ* from aqueous solutions and in Pb-contaminated soils (Chowdhury et al., 1994; Ma et al., 1995,1993, Mench, 1994). The primary mechanism of Pb immobilization appears to be phosphate mineral dissolution and subsequent precipitation of pyromorphite like

$(Pb_{10}(PO_4)_6(OH)_2)$ minerals through such mechanisms as cation substitution. Adsorption and precipitation as other minerals are also possible (Ma et al., 1993). Phosphate minerals with moderate solubility supply sufficient P to precipitate Pb, while causing minimum P contamination to the environment (Ma, 1996).

The effect of P on As phytotoxicity is unpredictable. Tsutsumi (1983) found that phosphate fertilizer additions to soils having lead arsenate pesticide residue can increase As availability. This increase of As availability may be due to: 1) competition between As and P fixation sites on soil (Woolson et al., 1973); 2) displacement of As ions by P ions from adsorption sites, rendering more As available; and 3) antagonism between P and As on plant roots and within the plant system.

The toxicity from Pb and As and their presence in the environment at dangerous levels are well established facts; however, the questions remain: what will be the impacts of using phosphate to remediate Pb and As contaminated soils, and how can significant risks be accurately evaluated? Finding effective answers to these questions hinges on a clear understanding of the mechanisms of Pb/As- phosphate interactions. This will provide scientists and engineers information to implement better strategies for dealing with Pb and As contaminated soils, and will allow for better decisions on Pb and As disposal that will not cause further threats to society and the environment.

Chapter 2

Overview

2.1 Lead

The contamination of soil by Pb from anthropogenic activities such as mining, use of leaded gasoline and the manufacture and testing of Pb based explosives is a worldwide environmental concern. Soils polluted with Pb pose health threats to humans as well as plants and animals, often necessitating extensive remediation practices. Various biological and chemical processes are already being used to remediate contaminated soil and water. These processes include the following

1) Phytoremediation

2) Application of soil amendments, and

3) Fixation

2.1.1 Phytoremediation

Remediation of metal contaminated soils using plants that accumulate heavy metal is currently being studied throughout the world (Wu et al., 1999; Cunningham et al., 1995; Schnoor et al., 1995). This remediation strategy, termed phytoremediation and defined as the use of plants for environmental clean up, may provide a more economical and aesthetically pleasing alternative to conventional remediation options.

Most plants are highly sensitive to heavy metals and cannot endure even low concentrations in soils (Larcher,1980), but there exists some plants that are metal resistant (Shaw,1990). Metal resistance can be achieved through a variety of mechanisms that can be defined as either a mechanism of avoidance or mechanism of tolerance. Levitt (1980) defines avoidance as the ability to prevent excessive metal uptake, and tolerance as the ability to cope with metals that are excessively accumulated in some part of the plant. Plants that use mechanisms of avoidance are often called as metal excluders and metal tolerant plants are called metal accumulators.

The initial emphasis in phytoremediation research has been on a small number of wild plants termed hyper-accumulators that are able to accumulate high concentrations of specific metals in aboveground tissues (Baker et al., 1988; 1994; Chaney et al,. 1995).Therefore, current efforts have emphasized use of agricultural species such as *Brassica spp., Zea mays* L., and *Nicotiana spp.,* that could be grown efficently following established agricultural practices (Wu et al., 1999; Huang and Cunningham, 1996; Kumar et al., 1995; Mench and Martin, 1991). Advantages of using metal accumulator plants are low costs, generation of recyclable metal-rich plant residues containing a range of toxic metals, minimal environmental disturbance, elimination of secondary air or water borne wastes, and public acceptance.

This research is promising since a variety of species have been identified that can accumulate high concentrations of certain metals. Such species generally require significant maintenance in the form of irrigation, fertilization, and use of herbicides, insecticides and other soil amendments. Thus the use of these species is restricted to arable lands and would not be applicable to more highly disturbed and remote areas such as abandoned mine sites (Klassen et al., 2000).

Approaches to enhance the effectiveness of phytoremediation will likely include manipulating agronomic practices (e.g. cropping, fertilizing) to optimize plant growth and biomass using plant breeding and genetic engineering to develop high biomass metal accumulation and using chemical amendments to increase soil Pb availability.

Recent research has shown that chemical amendments such as synthetic organic chelates may enhance phytoextraction by increasing Pb availability, plant uptake and translocation of Pb. Huang et al. (1997) conducted greenhouse studies on the effect of EDTA, HEDTA, CDTA, DTPA and EDDHA on soil solution and Pb uptake by corn (*Zea mays),* pea (*Pisum aestivum*), ragweed (*Ambrosia artemissifolia),* sunflower (*Helianthus annus).* They found EDTA to be the most effective chelate for enhancing Pb uptake and Pb solubility in soil. Research by Blaylock et al. (1997) evaluated the potential of CDTA, DTPA, EDTA and EGTA to enhance Pb uptake by Indian mustard (*Brassica juncea).* They also found EDTA to be the most effective chelate in increasing the availability of Pb to the plants. Despite the impact of chelates on Pb availability and solubility, Copper et al.(1999) reported that research is still needed to determine the most successful combination of plants, soil management practices, and type, rates and method of application of chelates for successful remediation of Pb-contaminated soils. The other issue that needs to be considered in chelate-assisted phytoextraction is that the potential environmental impact associated with increased Pb solubility (i.e. leaching and runoff of Pb).

2.1.2 Application of Soil Amendments

Soil amendments can be used to alter soil chemistry and sequester the metal contaminants, thus having a dramatic effect on presumed environmental hazards (Mench et al., 1984). Cox and Rains (1972) reported that raising the pH of acid soils by liming, combined with a suitable choice of plant species and proper grazing management, could substantially reduce the entry of Pb into the food chain. Maclean et al. (1969) suggested that lime repressed the solubility of Pb because of the greater capacity of organic matter to complex lead at increased pH. Berti and Cunningham (1997) used various types of organic materials such as ground alfalfa (*Medicago sativa*), sphagnum peat moss and composted leaves. They concluded that these organic materials reduced the bioavailability of Pb as measured with PBET (physiologically based extraction test). Pearson et al. (2000) investigated the effectiveness of organic matter as possible *in situ* remediation technique for metal contaminated soils. Their study was designed to determine the bioavaliability of Pb to the earthworm (*Eisenia fetida)* in an artifical soil amended with varying levels of organic matter. They reported that organic soil amendments increased the bioavailabitity of Pb to the earthworm. Zimdahl and Foster (1976) reported that organic matter addition offers some promise for reduction of Pb uptake by plants. The mechanism involved has not been described, but it is probably related to sorptive capacity of organic matter. They further reported that there is more Pb immobilization at higher pH.

2.1.3 Fixation

2.1.3.1 Effect of metallic oxides and hydroxide

Lead has been shown to accumulate in MnO_2 in soils (Taylor and Mckenzie, 1966; Norrish, 1975) and the addition of MnO_2 to soils contaminated with Pb reduces the uptake of Pb by plants (Mckenzie 1978). Mckenzie (1980) reported that possible mechanisms to account for the binding of Pb by oxides of Mn are: strong specific adsorption of Pb, a strong affinity of Pb for oxides of Mn, oxidation of Pb on Mn oxide surfaces, and formation of some specific Pb-Mn mineral such as coronadite ($Pb_2Mn_8O_{16}$). Mckenzie (1980) further reported that a significant amount of Pb entered the interlayer spaces of fine grained birnessites ($(Na_{0.7}Ca_{0.3})Mn_7O_{14}.2.8H_2O$) resulting in an uptake of Pb in excess of the amount required for a monolayer on the surface. Stumm and Morgan (1996) also reported that iron (hydr)oxides are known to bind heavy metals through adsorption or co-precipitation. Due to these mechanisms, iron oxides can control the distribution and concentration of heavy metals in aqueous systems and have been utilized in environmental technologies to remove metals from waste water and liquid hazardous waste (Benjamin et al., 1996). Postma and Jakobsen (1996) reported that freshly precipitated iron oxides are amorphous or poorly crystallized, and although their large surface area is advantageous for metal retention, but they are metastable and can , over time, undergo transformation into crystalline compounds such as hematite or goethite. The solubility of the latter crystalline phases is orders of magnitude lower than that of the amorphous solids, and the vulnerability of these compounds to microbial iron reduction is also considerably reduced.

Sorensen et al. (2000) heated iron oxides containing heavy metals (e.g. Pb, Hg, Cr and Cd) and 50, 600 and 900^0 C to simulate their transformations caused by heat treatment prior to disposal or aging at a proper disposal site. They found that heat treatment at 600 and 900^0 C and aging resulted the in transformation of amorphous iron oxide to hematite, which has less surface area, and less retaining power for the Pb. At low concentration, the affinity of Pb for hematite (Fe_2O_3) surfaces was greater than that for goethite (FeOOH) surfaces, although the surface area of the hematite was much smaller than that of goethite. Coupled with greater difficulty in extracting adsorbed Pb from hematite, this suggests that hematite is likely to be an important sink for Pb in soils. Sposito (1984) reported that Fe oxide and hydroxide could specifically adsorb Pb and, the adsorption increased at high pH (7-9). McBride (1994) reported that Fe and Al oxides as well as silica adsorb Pb and Cu more strongly than any other divalent metals.

Ponder et al. (2000) reported the use of nanoscale zero valent iron for remediation of Pb. They reported that the zero valent iron removes aqueous contaminants by reductive dechlorination, in the case of chlorinated solvents or by reduction to an insoluble form in the case of aqueous metal ions. One important parameter in the rate at which remediation occurs is the surface area of the zero valent iron particles. They also reported that rates of remediation of Pb are up to 30 times higher for zero valent iron nanoparticles than for iron powder on a (Fe) molar basis.

2.1.3.2 Inorganic Material

Cost effectiveness and environmental friendliness have made the addition of phosphate minerals a promising technology to remediate Pb contaminated soil (Zhang and Ryan, 1999). Nriagu (1984) suggested that phosphate minerals should have potential to immobilize Pb in lead contaminated sites and wastes due to low solubility of Pb orthophosphates. Recent research results have demonstrated the reduction in soluble Pb levels of soil solutions by mixing phosphate minerals with Pb- contaminated soils and the formation of pyromorphite (Ma, 1996). Experiments have been carried out using highly soluble forms of phosphate, e.g. K_2HPO_4 , but due to the soluble nature of the P source there would be eutrophication risk associated with such kind of treatment.

Ma et al. (1994) successfully used hydroxyapatite as a Pb-immobilization material. They reported : 1) hydroxyapatite had the ability to immobilize Pb^{2+}in the presence of interfering cations, anions and dissolved organic matter; 2) the reaction product was stable in the contaminated environment, and 3) the reaction was very rapid. The primary mechanism of Pb immobilization appears to be through phosphate mineral dissolution, and subsequent precipitation of a pyromorphite ($Pb_{10}(PO_4)_6(OH)_2$). Mechanisms such as cation substitution, adsorption and precipitation as other Pb minerals are also possible (Ma et al., 1996). The formation of pyromorphite from soluble phosphate and Pb has been found to be a rapid process; soluble Pb can be depleted from solution within a few seconds if a stoichiometric amount of phosphate is provided and the system is well mixed. Thus the soluble Pb concentration in the aqueous system containing apatite and Pb-bearing solids will be determined by the dissolution rate of apatite and overall Pb release rate (desorption, dissociation and dissolution) of the Pb species (Zhang and Ryan, 1999). Ma et al. (1995) reported that rock phosphate is also effective in immobilizing Pb in contaminated soils. Preliminary experiments (Hodsen et al., 2000) using a moderately contaminated soil indicated that bonemeal treatment could be a useful remediation method. Hodson et al. (2000) reported that poorly crystallized apatite e.g. bone apatite (in the form of bonemeal-finely crushed bone), might represent a low cost, readily available phosphate source that could be used to remediate metal contaminated land without causing excessive runoff. Phosphate is effective only when Pb is the sole contaminant, i.e. without As at the same soil/site.

2.2 Arsenic

Arsenic is of environmental concern due to its toxicity to plants, animals and human beings. It occurs naturally in about 245 minerals, which when subjected to weathering can release soluble As into natural waters. Arsenic can also be found in waste streams from a variety of industrial processes. For example, As waste can be generated from petroleum refining, glass, melting and smelting of ores that are mined for their Pb, Cu, Zn, Au and Ag. Arsenic is also released into the environment by the dispersion of arsenic containing fertilizers, pesticides, and wood preservatives (Smith et al.,1998). The availability, physiological and toxicological effects of arsenic depend on its chemical form. Arsenate(+5) and arsenite(+3) are the primary forms of inorganic As in soils and natural waters. Of these forms, As(+3) is the most toxic, soluble, and mobile (Duele and Swoboda, 1972) species found in the environment. The concentrations of these species in soil solution depend on a number of soil parameters, including redox potential (Eh) (Masschelyn et al., 1991), pH (Pierce and Moore, 1980), Fe and Al hydroxides (Livesely and Huang, 1981), and clay content (Frost and Griffin, 1977).

Lime additions to As containing wastes have been proven to be beneficial in reducing the mobility of dissolved As, presumably through the formation of low solubility calcium arsenates (Bothe and Brown,1999). Arsenic from the aqueous waste streams also can be removed by precipitation as arsenic sulfides and iron arsenates. These precipitates reactions have limited pH ranges within which they exhibit solubility maxima (Bothe and Brown, 1999). Robins (1992) reported that calcium arsenate exhibits the lowest equilibrium concentrations of arsenate ion and are stable at high pH, whereas ferric arsenates (i.e. scorodite) are stable only at low pH.

The adsorption and retention of As by soils control its persistence, activity, movement, transformation, and ecological effects (Luo et al., 1991). Arsenic adsorption on a wide variety of adsorbents, including phyllosilicates (Manning and Goldberg, 1997), aluminum oxides (Gupta and Chen, 1978), and iron oxides (Raven et al., 1998) has been studied.

2.2.1 Role of Oxides of Aluminum and Iron In Arsenic Adsorption

Arsenic availability to plants is controlled by adsorption- desorption reactions (Bhumbla and Keefer, 1997). The clay fraction and Fe oxides have frequently been implicated in the sorption of As by soils. Arsenic toxicity to plants decreases as the clay and Fe oxide concentrations increase (Crafts and Rosenfels, 1939), presumably due to lower level of As maintained in the soil solution. Several investigators (Keaton and Kardos, 1940; Misra and Tiwari, 1963) have shown that similar textured soils are high in reactive Fe compounds (either native or added) sorb larger amounts of As than soils low in Fe. Mica minerals strongly sorb arsenate as they weather (Stewart et al., 1975) and this seems to be a function of the spacing in the clay lattice and the amount of hydroxyaluminum present on the clay surface.

Retention of As has been shown to be proportional to sesquioxide concentration of soils and this retention decreased as the amorphous Al and Fe compounds were removed (Holm et al., 1979; Gulens et al., 1979). The adsorption of As depended on the oxidation state; generally As(+5) was adsorbed more strongly than As (+3) . Raven et al.(1998) reported that iron oxides, including the poorly crystalline iron oxides, e.g. ferrihydrite, have a strong affinity for both arsenite and arsenate. The retention of arsenite and arsenate is predominantly by ligand exchange with surface structural OH_2 and /or OH^- at surface adsorption sites. The retention of arsenite and arsenate is strongly pH-dependent, but with the opposite trends. At low to moderate As adsorption levels, the adsorption envelopes of arsenite and arsenate usually cross within the pH range of 6-7.5 i.e. ferrihydrite exhibits a relatively greater retention of arsenate at lower pH values, whereas arsenite is more strongly retained at higher pH values (Ravin et al., 1998) Arsenite adsorption maximized between pH 7 and 9 (Pierce and Moore, 1980; Gupta and Chen, 1978). Wanen and Jones (1984) found that As was effectively removed from acidic solutions by adsorption onto soil minerals, indicating that As oxyanions were naturally retained in the presence of oxides and clay minerals (Holm et al., 1979; Frost and Griffin, 1977), and strongly adsorbed by Fe (Leckie et al., 1980), Al (Gupta and Chen, 1978; Anderson et al., 1976) and Mn oxides (Oscarson et al., 1983). Only a few studies have investigated the adsorption of As(+3) on aluminum oxides or aluminosilicate minerals despite the abundance of these materials in the terrestrial environment. One reason is the relatively weak affinity of aluminum oxides for As(+3) when compared with iron oxides. Activated alumina has a 2-fold higher affinity for arsenate than arsenite at pH 7. Kaolinite and montmorilloinite were investigated as sorbents of As(+3) and As(+5) from landfill leachate and exhibited higher affinites for As(+5) than As(+3). Though phyllosilicates exhibit a lower affinity for anions than iron and aluminum oxides, they can be abundant mineral components in soil and sediments.

2.2.2 Effects of P on As availability and uptake

Arsenic is toxic to biota, and P has been found to enhance its mobility in well-aerated soils by competing for sorption sites (Woolsen et al.,1973). Arsenic, like P is strongly adsorbed by amorphous Fe oxide (Jacob et al., 1970) and is released under anaerobic conditions (Fordham and Norrish, 1979). Phosphate is adsorbed by both soil colloidal Fe and Al oxides, whereas As is adsorbed by soil colloidal Fe oxide. Arsenic and phosphate in soil exhibit similar behavior (Fassbender, 1975; Johnston and Barard, 1979), but the amount of phosphate sorbed is greater than that of As (Dean and Rubins, 1947).

The adsorption of phosphates and arsenates indicates an analogous sorption behavior. Under comparable conditions, a larger quantity of phosphates is sorbed presumably due to different ionic radii of anions in question (Holobrady et al., 1969). Phosphate substantially suppresses As adsorption by soils and the extent of suppression varies from soil to soil (Livesey and Huang, 1981). Johnson and Hiltbold (1969) showed that the arsenates in soils were more soluble than phosphates.

There are conflicting reports in the literature as to the effect of phosphate on availability and uptake of As. Toxicity of As in nutrient solution was reduced by increasing phosphate concentration (Hurd-karrer, 1939). Benson (1953) reported that As toxicity to barley was overcome by phosphate in pot culture, but there was little or no response to phosphate application to the field. Jacobs et al. (1970) reported that increasing the level of P in the spoil increased As in the plant at 80 mg of As kg^{-1}, but the increase was greater in sandy soil than in silty soil. The sandy soil was relatively low in As or P retention capacity. Addition of P to the soil resulted in enhanced As toxicity from displacement of As by P. The inconsistency in the literature can be reconciled if the effect of P on As uptake is considered as two separate factors: plant and soil. The plant factor considers an antagonism between P and As at the root surface. When phosphatic fertilizers were applied to As contaminated soils, As toxicity was increased by As being displaced from the soil surfaces to the soil solution. Bhumbla (1991) reported that application of rock phosphate had no effect on amounts of available As in soils as rock phosphate did not supply sufficient P to mobilize As from sorption sites in soil. Benson (1953) suggested that As may substitute for P in calcium phosphate minerals. This substitution can potentially reduce the availability of As to plants.

Schwiezer (1967) noted that addition of P may enhance As phytotoxicity. This is because P and As have similar chemical and physical properties. Phosphorus competes for As fixation sites in soil and thus may affect As availability. Several investigators noted reduction in phytotoxicity of As as P level increased in a wide variety of crops (Rumburg et al.,1980). Peryea (1991) and Creger and Peryea (1994) reported that phosphate fertilizer addition to soils containing Pb-As pesticide residues increase As solubility because of PO_4^{3-}- AsO_4^{3-} exchange. Woolsen and Kearney (1973) further reported that As release was positively related to added phosphate source. Arsenic solubility was consistent with a mechanism of specific PO_4^{3-}- AsO_4^{3-} exchange while PO_4^{3-} solubility was consistent with control by metastable PO_4^{3-} Minerals. As a result, the effects of P on As phytotoxicity are unpredictable.

In nature, Pb and As are often present together. The most important commercial compound of As, arsenic oxide, is produced as a by-product in smelting of Pb ores. It has been also introduced into the biosphere via the use of Pb-As pesticides in agriculture and forestry. Before the wide spread use of organic pesticides lead arsenate was the most common pesticide used in orchards.

Unlike the layer silicates, oxides and hydroxides of Fe and Al retain Pb and As by direct co-ordination to the surface oxygen anions by the process of chemisorption (Mckenzie 1980;Sposito 1990;Manning and Goldberg, 1997). Jenne (1968) suggested that the reactivity of hydroxide coating on clay would be considerably higher than reactivity of free hydroxides especially with respect to heavy metal adsorption. Cavalloro and McBride (1984) observed a pronounced decrease in the adsorption of heavy metal ions after removing the Fe hydroxide and Al hydroxide from a soil clay. The chemical, physical, and mineralogical characteristics of natural and laboratory synthesized clay-Al hydroxide and clay-Fe hydroxide complexes are well documented (Rich, 1968; Barnhisel, 1977), whereas information about the adsorption of Pb and As by synthesized clay-hydroxide mixture is scarce.

Therefore, adsorption of Pb and As on hydrous oxide coated clay surface is important in governing Pb and As related pollution. Information available in the literature is too limited to draw a meaningful conclusion about the adsorption chemistry of Pb and As in hydrous oxide coated clay and the fate of applied P fertilizer in Pb and As contaminated sites. In order to fully understand the fate and transport of metal in the environment, we need to be able to accurately describe and model complex natural systems. Surface complexation models (SCMs) are capable of simulating the experimentally observed acid-base titration properties of metal oxide and pure clay minerals (Schindler and Stumn, 1987). However, no study has been conducted to simulate acid-base titration on Fe and Al coated clays. Data from experimental studies of Pb and As co-precipitation with Fe and Al coated clay, insight gained from modeling complex natural systems by using SCMs and the effect of P fertilizer on As solubility or Pb immobilization could be vital in remediating Pb and As contaminated sites.

The objectives of the present investigation are:

1) To determine the effect of hydrous oxide coating on adsorption of Pb and As by clays.

2) To describe a methodology for determining a unique set of model parameters for SCMs from titration data for iron and aluminum coated clay minerals.

3) To explore the effectiveness of the P fertilizer on Pb immobilization and/or As immobilization/ release in Pb and As contaminated sites.

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Chapter 3

Sorption of Lead and Arsenic by Iron and Aluminum Coated Clays

3.1 Introduction

Pollution of the biosphere with toxic elements has accelerated dramatically since the beginning of industrial revolution. Soils serve as an important medium for accumulation, transformation and migration of the toxic chemicals. As a result of their accumulation in the biosphere, Lead and As pose more serious worldwide environment and health hazards than any other elements (Jaworski, 1987; Huang Yan-Chu, 1997). Sources of Pb and As contamination can be agricultural activities such as application of lead arsenate ($PbHAsO_4$) insecticides and industrial activities such as mining and smelting. Existing and abandoned disposal sites of Pb and As are potential sources of soil, and ground and surface water pollution.

Clay minerals are potential harborers of pollutants as they have a large specific area and high cation exchange capacity. Clays exhibit two kinds of charge : permanent negative surface charge and pH-dependent charge. Permanent charge, which is caused by isomorphic substitution, for the most part is compensated by cation intercalated in the interstitial space (McBride, 1994). The binding mechanism of cation on permanent charged sites is mainly characterized by electrostatic interactions, which are reversible in nature. The pH dependent charge is located at edge sites, where the surface hydroxyl can be protonated or deprotonated depending on the solution pH. The adsorption of heavy metal cation by hydroxyl groups is governed by covalent binding and therefore is chemically specific.

In addition to the clay minerals, the finer inorganic soil fractions contains poorly crystallized phases which usually are very intimately associated with the clay surface (Sposito, 1989). The crystalline form of these solids, the most common being goethite (FeOOH) and gibbsite ($Al(OH)_3$) (Hsu, 1977; Schwetman and Taylor, 1977) exhibit variable (pH dependent) charge surfaces when suspended in aqueous system (Barrow, 1985). The occurrence of hydrous oxides as discrete crystalline phases, although found in some natural soils, is not a common phenomenon (Hsu, 1977; Schwertmann and Taylor, 1977; Sposito, 1989). The most common mode of their natural occurrence in natural soil is either as poorly crystallized phases or two dimensional amorphous phases both of which are intimately associated with clay surfaces (Hendershot and Lavkulich, 1983). Heavy metal retention by pure oxides of Fe and Al (Mckenize, 1980; Bhumbla and Keefer, 1997) and pure clay minerals (Frost and Griffins, 1976) has been experimentally demonstrated. The pure form of clay minerals and hydrous oxides have fundamentally different surface charge characteristics (Barrow, 1985). The solid phases resulting from intimate association between the two should have surface charge characteristics that are different from either of them which, eventually affect the heavy metal adsorption characteristics on them. Heavy metal adsorption on hydroxy coated mineral surfaces may be affected by such factors as type of clay minerals, type of hydrous oxide and extent of surface coating with oxides/hydroxides. The type of clay mineral should influence the heavy metal adsorption because of variable particle sizes and different surface area available for adsorption. The extent of surface coating should determine the extent of heavy metal adsorption because the cation adsorption characteristics of hydrous oxides and silicate clays differ markedly.

Therefore, adsorption of As and As on hydrous-coated clay surface is important in governing Pb and As related pollution. Information available in the literature is too limited to draw a meaningful conclusion about the adsorption chemistry of Pb and As in hydrous oxide coated clay in Pb and As contaminated sites. The information gained from the experimental studies of Pb and As adsorption with Fe and Al coated clay could be vital in remediating Pb and As contaminated sites. So the objective of this paper is to determine the effect of hydrous oxide coating on the adsorption of Pb and As by clays.

3.2 Materials and Methods

Clay mineral samples of pure attapulgite, illite, kaolinite and montmorillonite obtained from the Source Clay Mineral Repository of the Clay Mineral Society were used for this investigation. Important physico chemical characteristics are given in Table 3.1.

Table 3.1: Important physico-chemical characteristics of clay minerals

Characteristics	Minerals			
	Attapulgite	**Illite**	**Kaolinite**	**Montmorillonite**
N_2 Surface Area(m^2g^{-1})	136.35±0.31	-	23.50±0.06	83.79±0.22
Cation Exchange Capacity(c mol_c kg^{-1}	19.5	15.0	3.3	84.4
SiO_2(%)	60.9	55.1	43.9	70.1
Al_2O_3(%)	10.4	22.0	38.5	16.0
Fe_2O_3(%)	2.98	5.28	0.98	0.65
MgO(%)	10.2	2.80	0.03	3.69

Source: Hower and Mowatt(1965) and van Olpen and Fridiat(1979)

All the clay samples were separated into <2 m (Stokes' diameter) fraction by sedimentation technique. The <2 m fraction of clay samples obtained after separation was coated with Fe and Al coatings by the following procedure. The obtained samples (<2 m) of clay were washed three times with 0.1 M HCl. The solution obtained after washing was analyzed for Fe and Al concentration which was found to be very low (<100 ppb). The sample was redried at 40 ^{0} C and 20 grams of clay samples were weighed into each of a series of four 250ml centrifuge bottles containing 60 ml of 0.1M HCl. Concentrated solution of Fe and Al were prepared by dissolving ferric chloride ($FeCl_3.6H_2O$) and aluminum chloride ($AlCl_3$) in reagent grade water. Appropriate volumes of these Fe^{3+} and Al^{3+}solution were added to centrifuge bottles containing clay to give 0, 0.5, 2.00 and 4.00 per cent by weight of $Fe(OH)_3$ and $Al(OH)_3$. After shaking the samples for 2 hours, the pH of each sample was adjusted to 7.00 with NaOH. The samples were again put on a shaker for overnight shaking and pH was adjusted to 7.00, if necessary. This process continued until the pH of samples remained constant. Then, samples were centrifuged and the supernatant was collected to analyze for Fe^{3+} and Al^{3+} by Perkin-Elmer Inductively Coupled Plasma (ICP) spectrophotometer. The solid obtained after centrifuging was put in to a dialysis tube and suspended in reagent grade water until the samples were free of chloride. $AgNO_3$ test was used to check that samples were free of chloride. The salt free samples were transferred to a plastic beaker and dried at 40^0C. Aging of samples was done by six wetting and drying cycles. After the last dry cycle, samples were crushed and stored in tightly capped plastic bottles.

3.2.1 Adsorption and desorption experiment: Lead and As adsorption on iron oxide/hydrous oxide clays was studied in batch experiments. An array of pH values with fixed metal concentration was used to obtain adsorption edges. Volume of acid and base required to achieve a particular pH was determined by using a kinetic program in the autotitrator. To obtain adsorption edges, 50-mg solid samples were shaken with 0.1M $NaClO_4$ solution containing (100 μM Pb and 100 μM As) at room temperature in 50-ml centrifuge tubes. The centrifuge tubes were purged with Argon to reduce CO_2 partial pressure. The reaction bottles were shaken for 24 hours. After this, tubes were centrifuged at 3000 rpm for 15 minutes and supernatants were filtered through Whatman No. 42 filter paper. Filtrates were analyzed for Pb and As using either an ICP spectrophotometer (for samples having Pb and As (> 100 μg/g) and graphite furnace atomizer (for samples having Pb and As ≤ 100 μg/g).

To quantify the exchangeable fraction of adsorbed Pb, 9 ml of 37 mM $Mg(NO_3)_2$ solution were added to the remaining 1 ml of wet sediment. The samples were shaken for 2 hrs and analyzed for dissolved Pb concentration. Statistical analysis was done on all the samples and standard error values are shown in the all the figures.

3.3 Results

3.3.1 Adsorption of Pb and As by clay minerals: Compared to pure montmorillonite, the presence of 0.5% and 4% coatings of Fe and Al led to a decrease in the dissolved Pb and As concentration (Figures 3.1-3.4). The effect was more pronounced for As as compared to Pb (Figures 3.3-3.4). Moreover, in the case of As, the effect was more pronounced at 4% Fe coatings (Figure 3.3). For Illite, there was not much difference in the dissolved concentration of Pb on Fe and Al-coated as compared to pure illite (Figures 3.5-3.6). But there was drastic reduction in the dissolved concentration of As by both 4% Fe

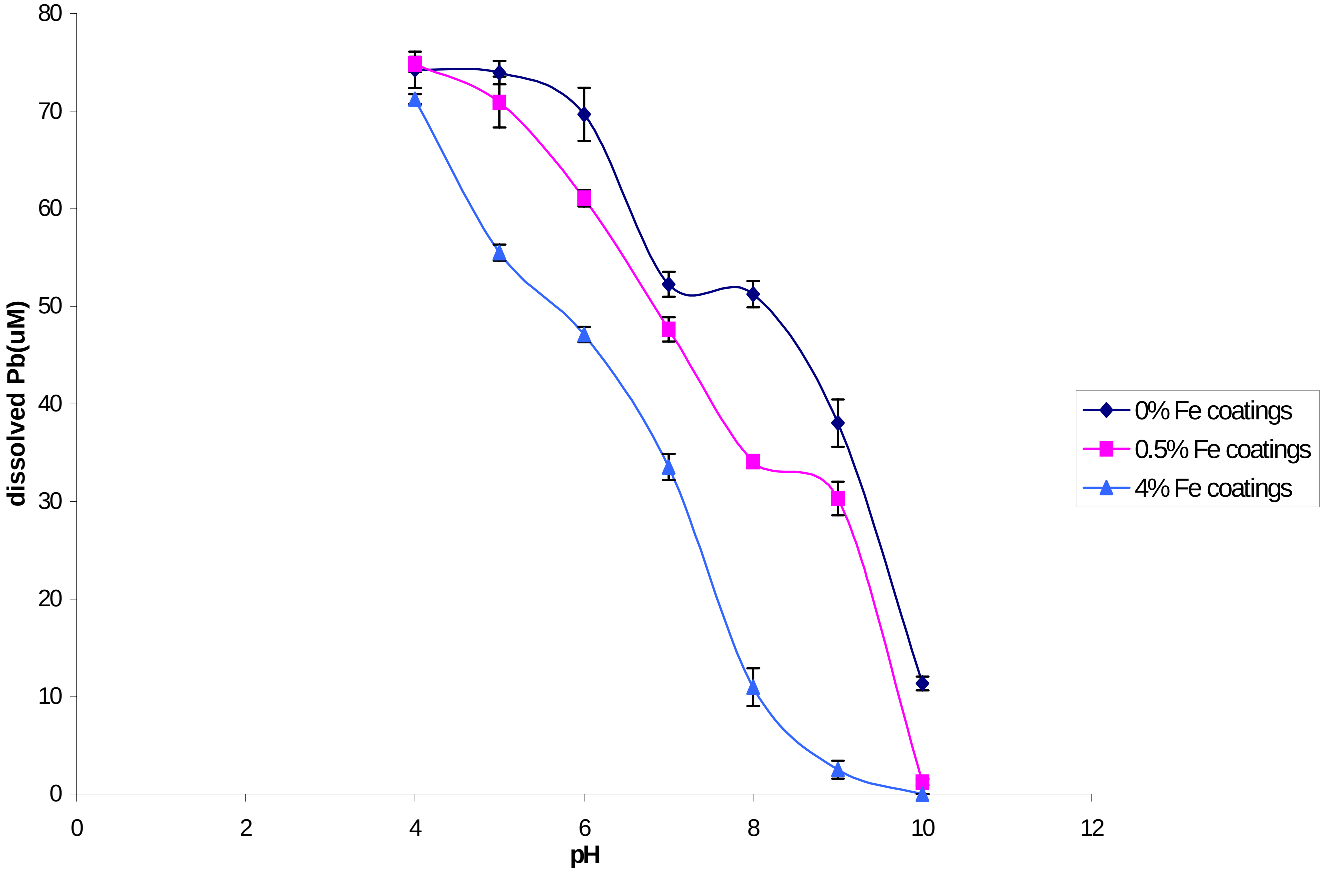


Figure 3.1: Effect of different levels of iron coatings on the adsorption of lead by montmorillonite

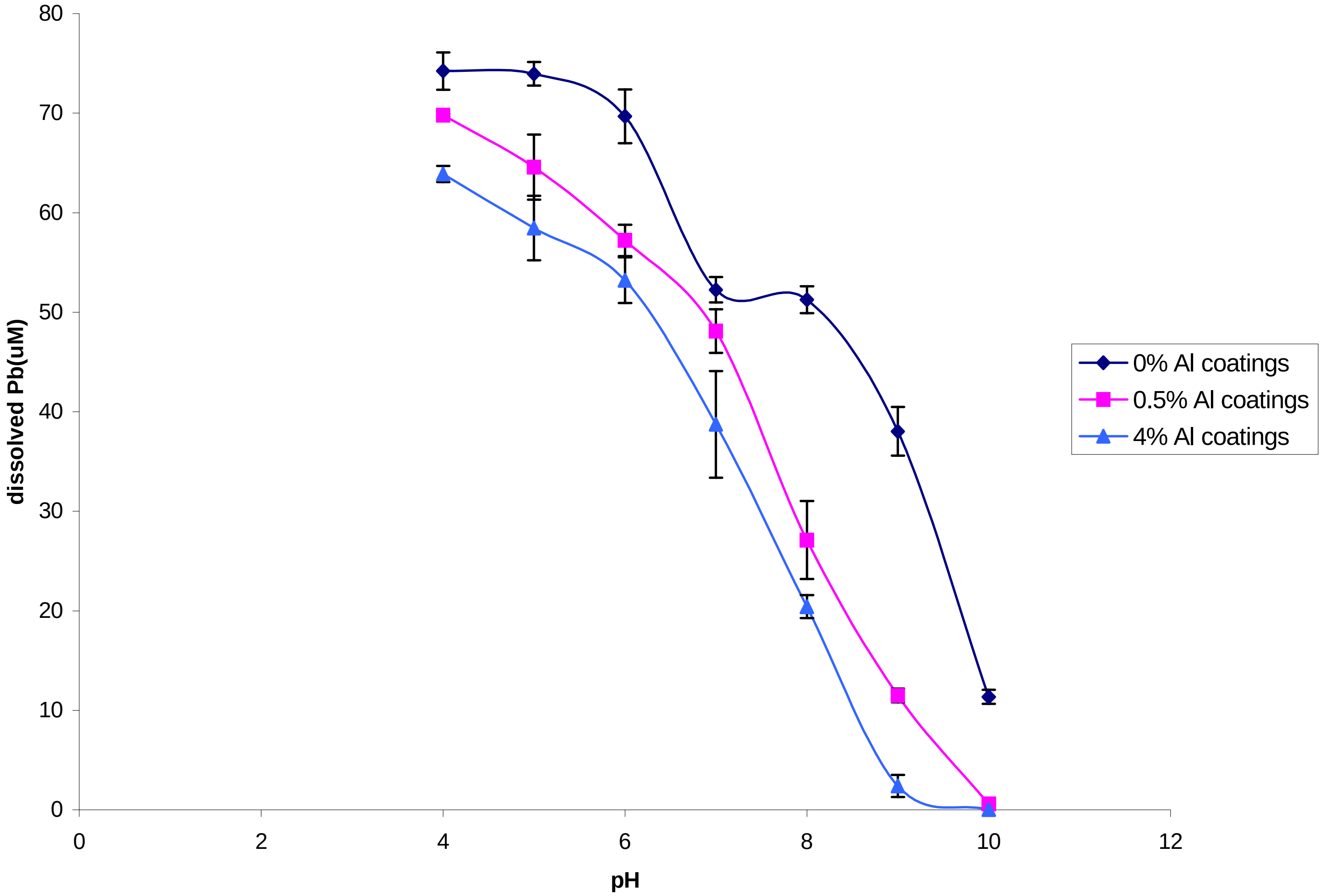


Figure 3.2: Effect of different levels of aluminum coatings on the adsorption of lead by montmorillonite

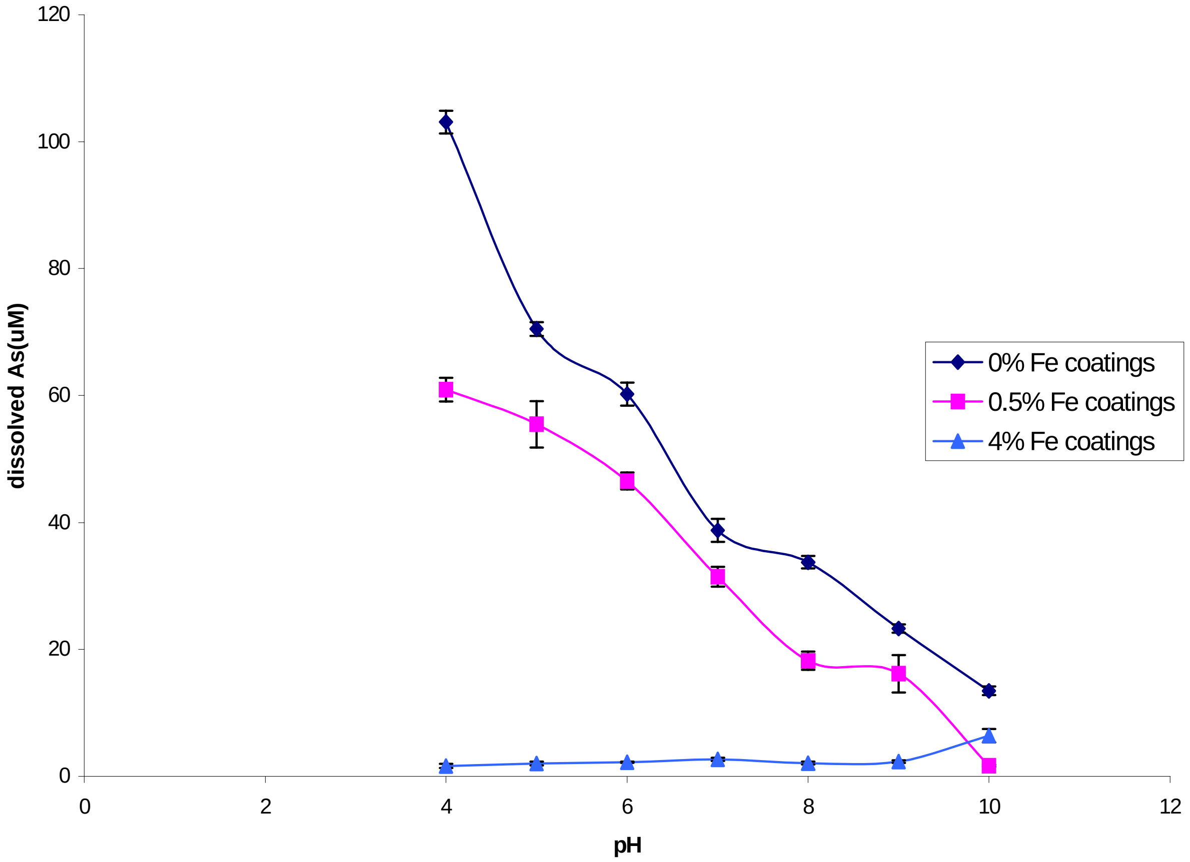


Figure 3.3: Effect of different levels of iron coatings on the adsorption of arsenic by montmorillonite

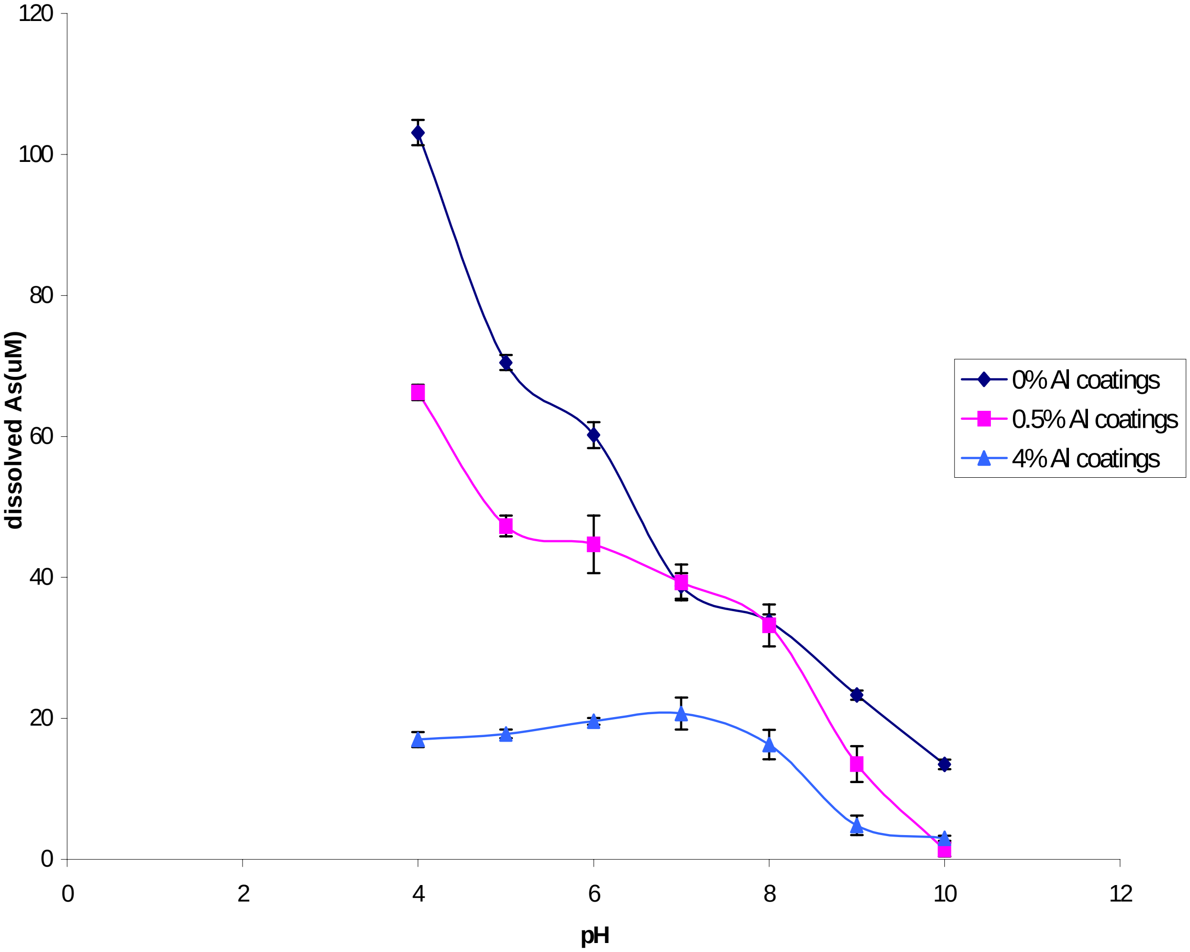


Figure 3.4: Effect of different levels of aluminum coatings on the adsorption of arsenic by montmorillonite

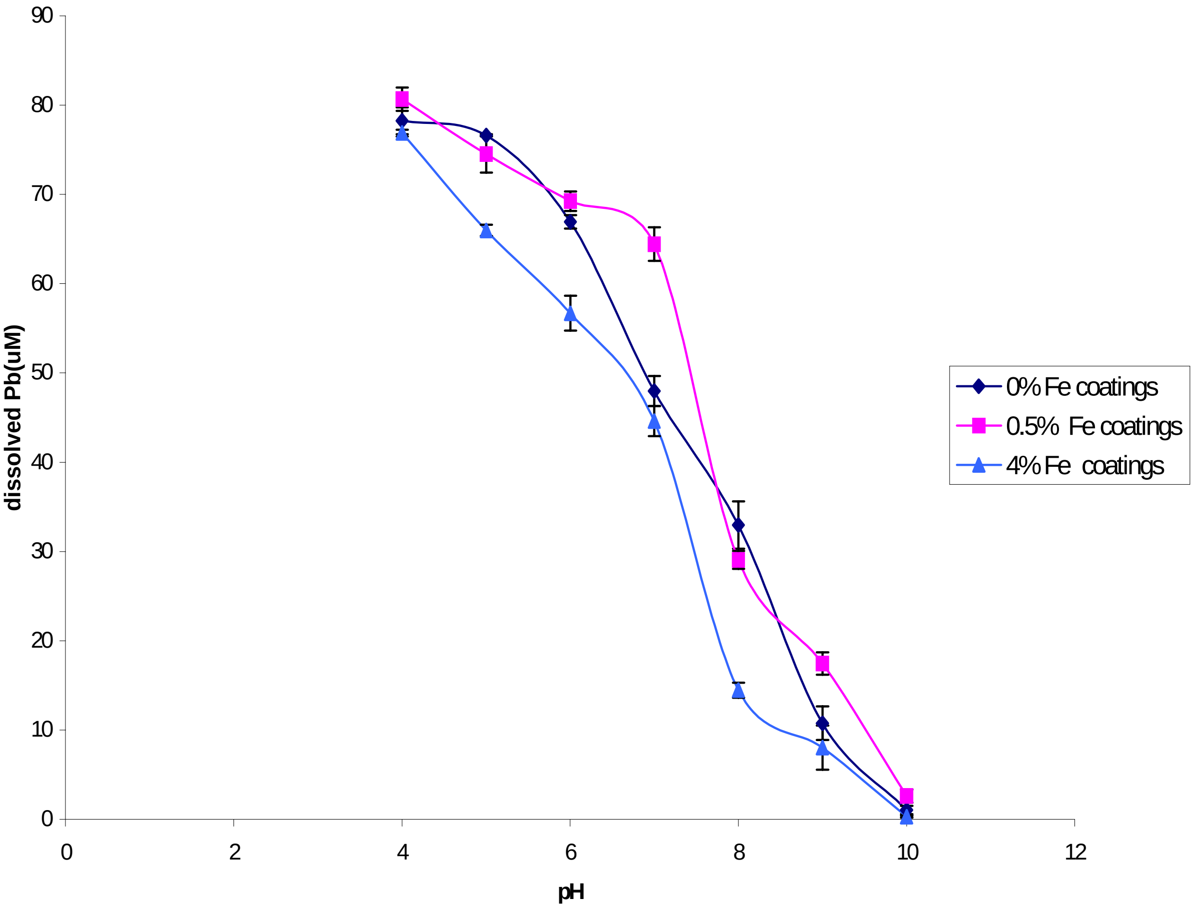


Figure 3.5: Effect of different levels of iron coatings on the adsorption of lead by Illite

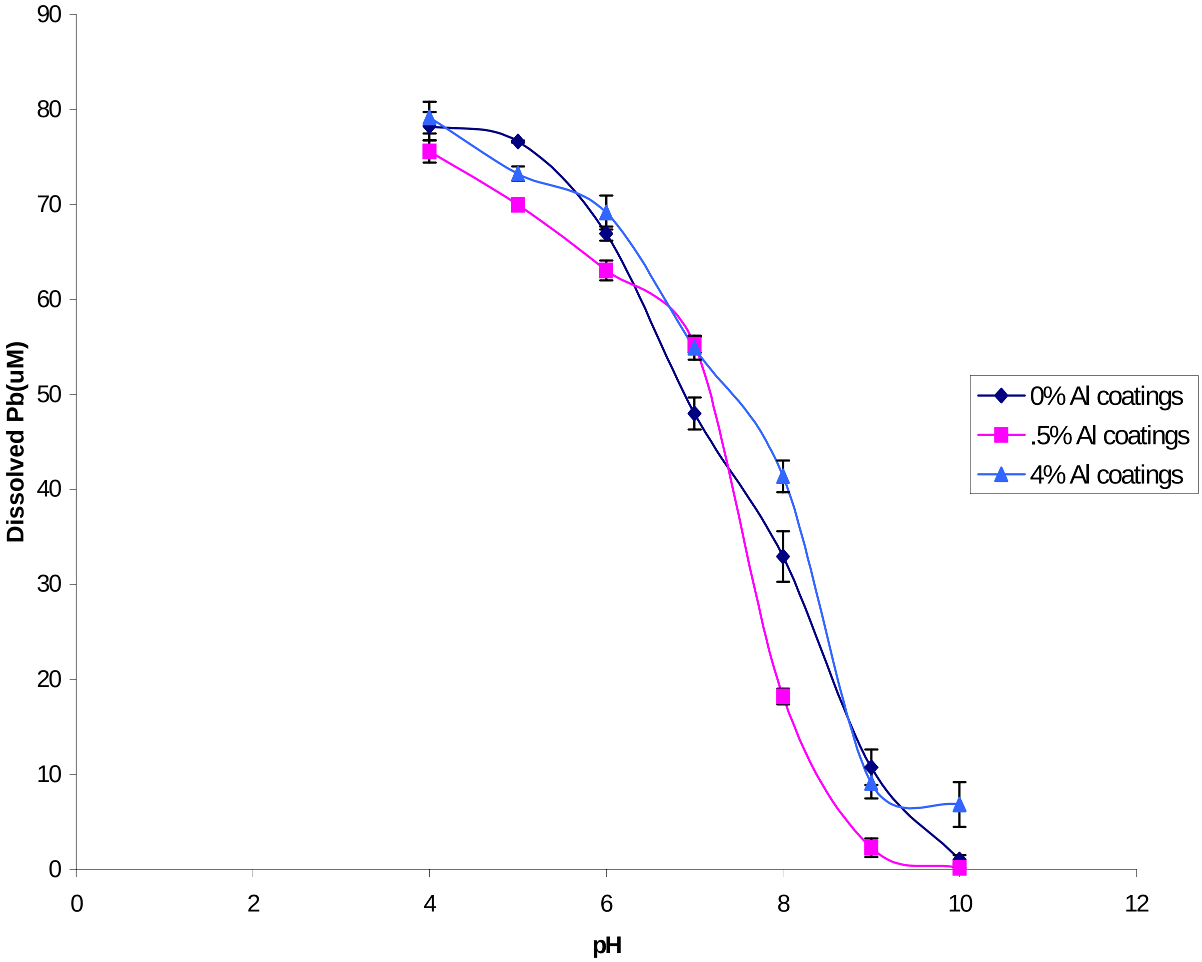


Figure 3.6: Effect of different levels of aluminum coatings on the adsorption of lead by Illite

and 4% Al coated illite as compared to pure illite (Figures 3.7-3.8). Dissolved As concentration was less at all the pH values for 4% Fe coatings on illite as compared to 4% Al coatings. Pure kaolinite showed more dissolved concentration of Pb and As as compared to Fe and Al coated kaolinite at all the pH values (Figures 3.9-3.12). The dissolved concentration of As was much less at all pH's (4-10) for 4% Fe coated illite as compared to 0.5% Fe coated and pure kaolinite (Figure 3.11). Dissolved Pb and As concentration at different levels of Al and Fe hydrous oxide coated attapulgite exhibited similar trends to those of kaolinite and illite (Figures 3.13-3.16). There was a decrease in the dissolved concentration of As and Pb with the increase in Fe as well as the Al hydrous oxide coatings. Amount of As and Pb present in the solution was lower in the case of Fe hydrous-coated samples than Al hydrous coated samples.

3.3.2 Exchange of Pb by Magnesium: Pb adsorbed on all the pure clay minerals in this study was considerably remobilized after the addition of 37 mM $Mg(NO_3)_2$. This indicates that the Pb was nonspecifically adsorbed on pure clays. This is shown by significant desorption of Pb generally by all the clay minerals. Coatings with both Al as well as Fe hydrous oxides on all the clay minerals results in lower desorption of Pb in the soil solution (Figures 3.17-3.24).

3.4 Discussion

3.4.1 Adsorption of Pb and As on pure and coated clay minerals: Significant immobilization of Pb was observed on pure and coated montmorillonite. About 25 M Pb was adsorbed without pH limitation down to 4 (Figure 3.1). On the other hand, Pb adsorption on all the clay minerals gradually increased with increasing amount of both Fe and Al coatings. This is due to the fact that low affinity sites on permanently charged clay surfaces were replaced by high affinity aluminum and iron hydroxyl functional groups with variable charge (Lothenbach et al., 1997).

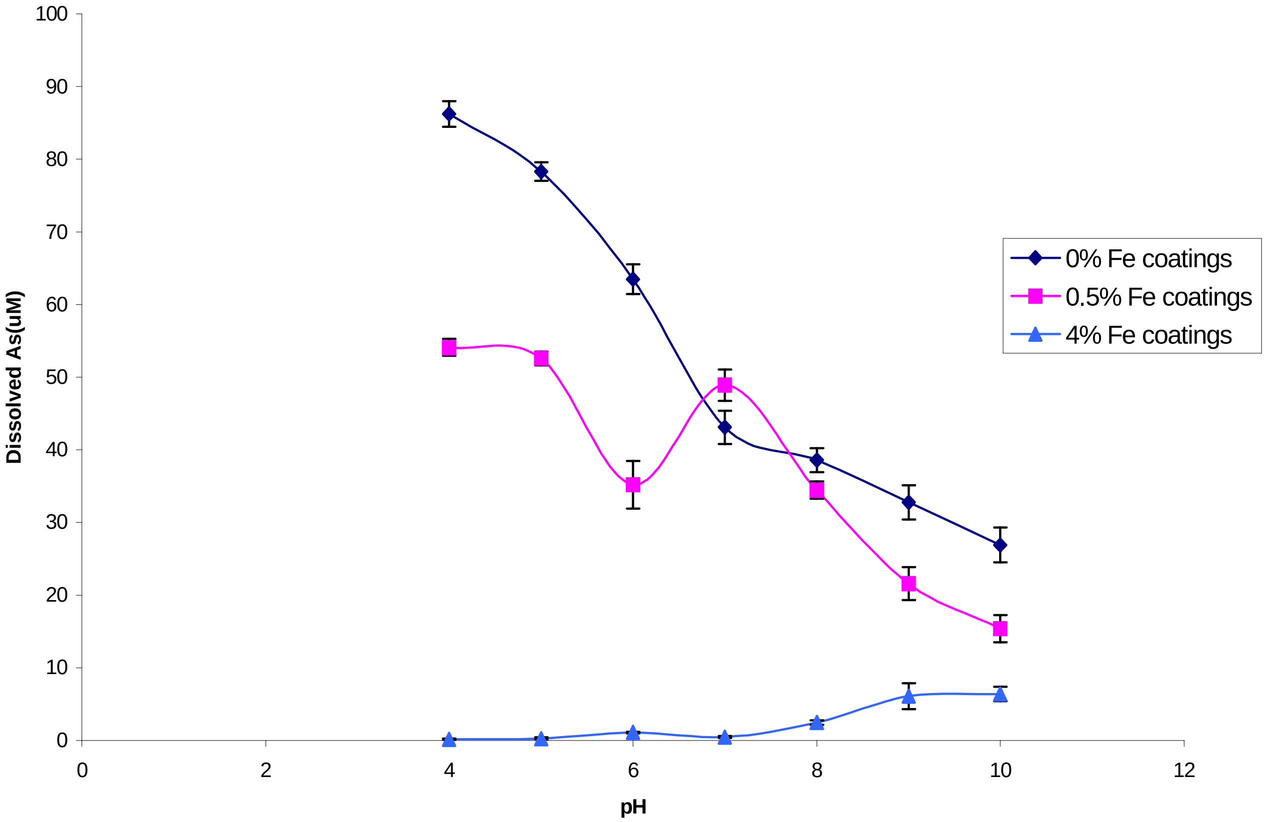


Figure 3.7: Effect of different levels of iron coatings on the adsorption of arsenic by Illite

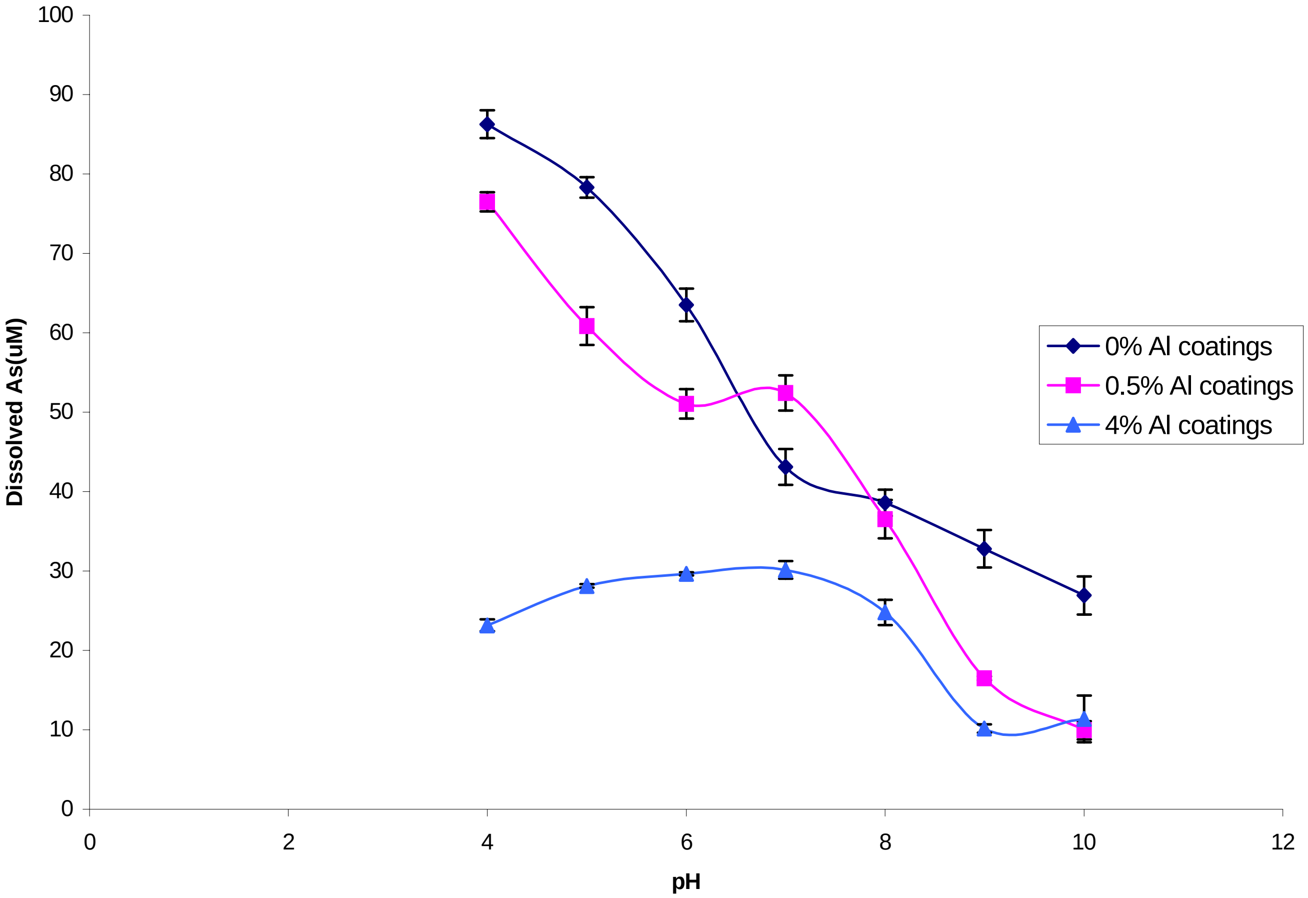


Figure 3.8: Effect of different levels of aluminum coatings on the adsorption of arsenic by illite

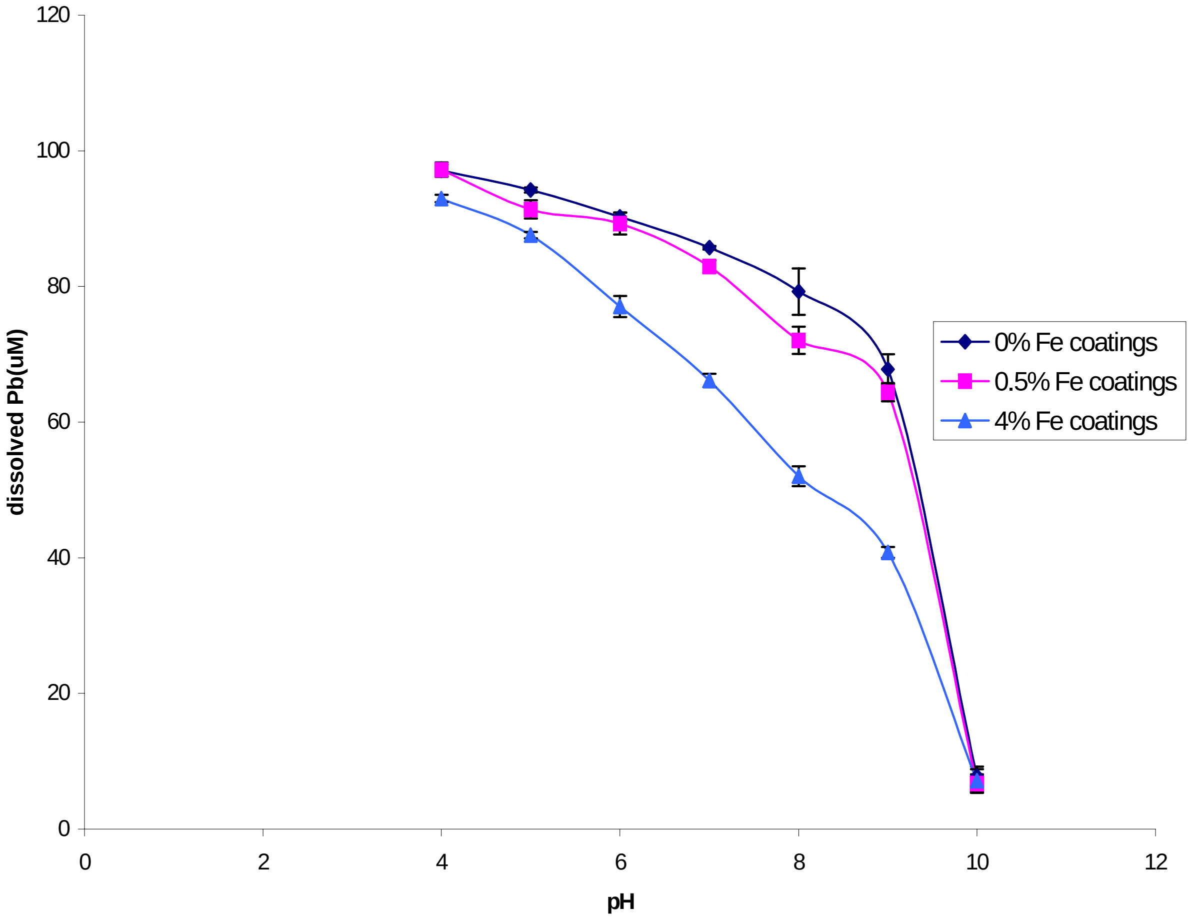


Figure 3.9: Effect of different levels of iron coatings on the adsorption of lead by kaolinite

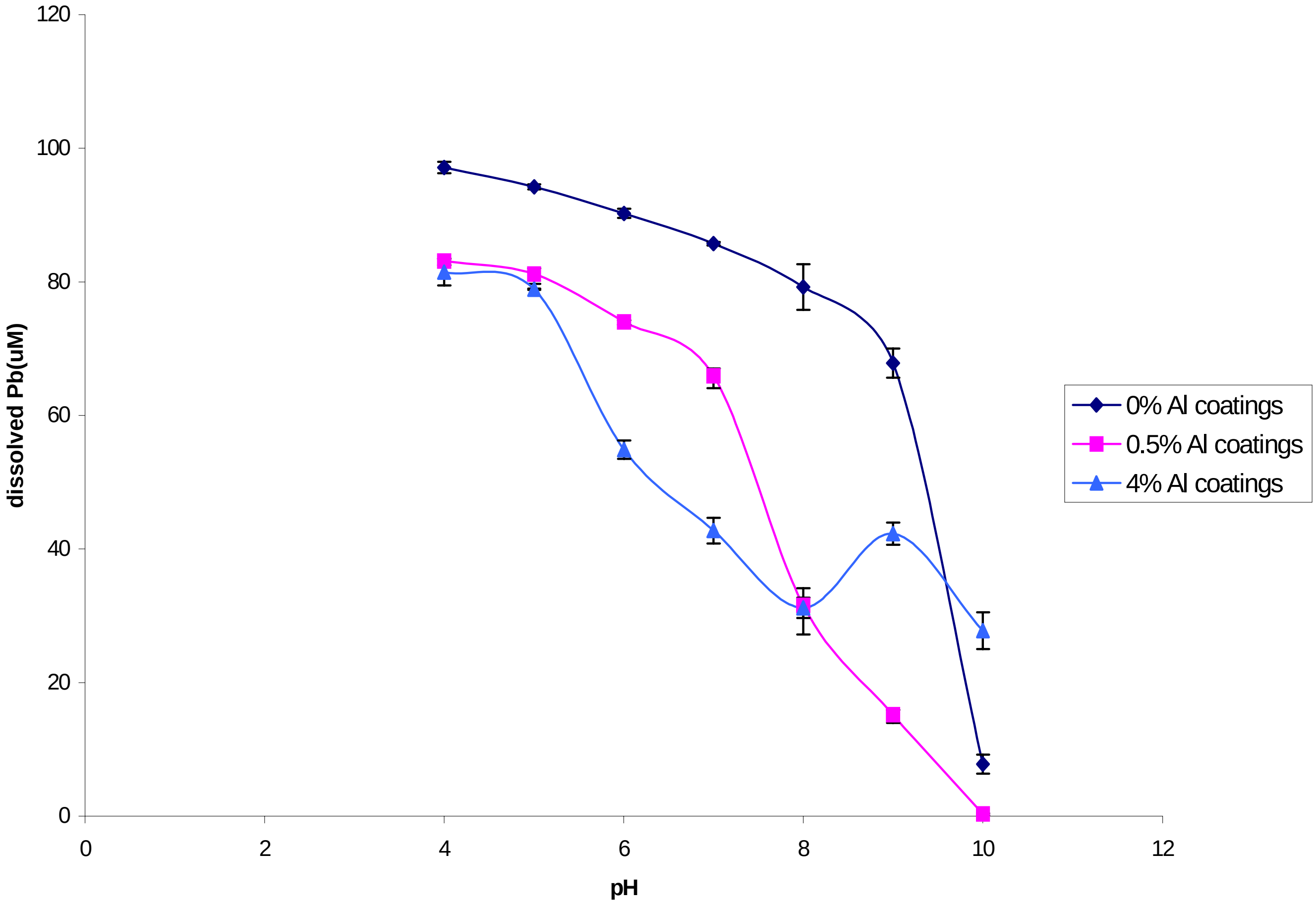


Figure 3.10: Effect of different levels of aluminum coatings on the adsorption of lead by kaolinite

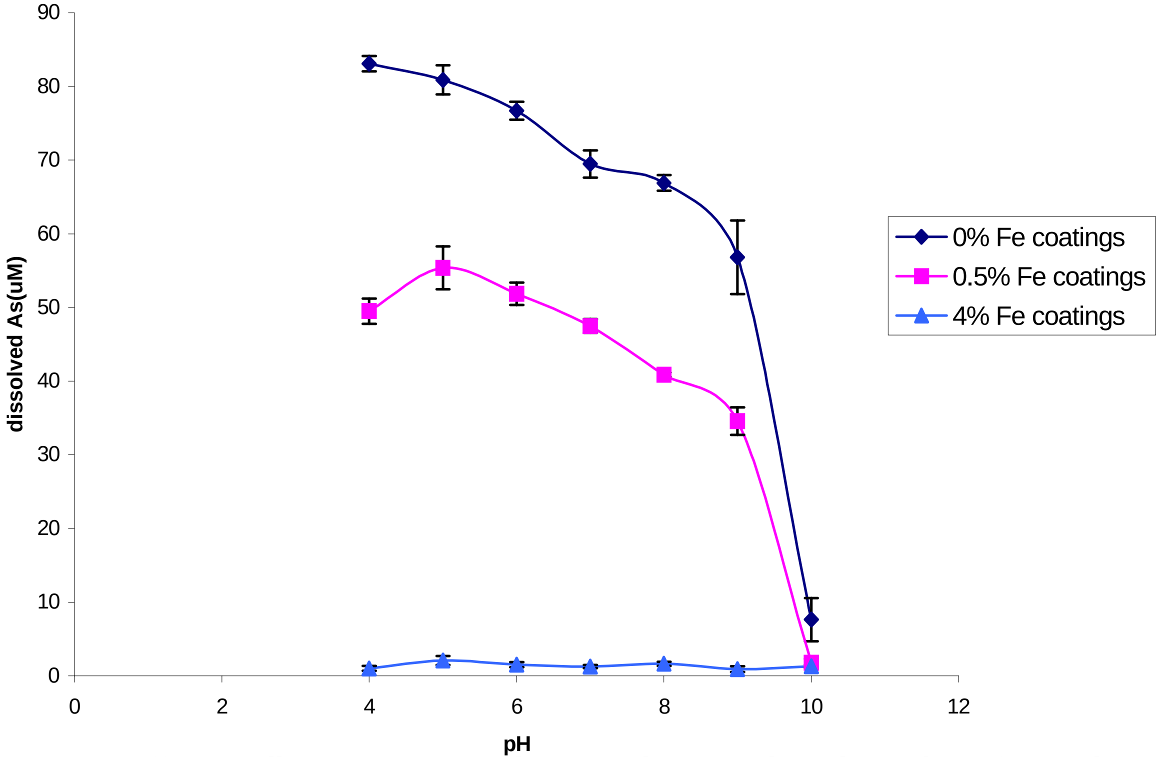


Figure 3.11: Effect of different levels of iron coatings on the adsorption of arsenic by kaolinite

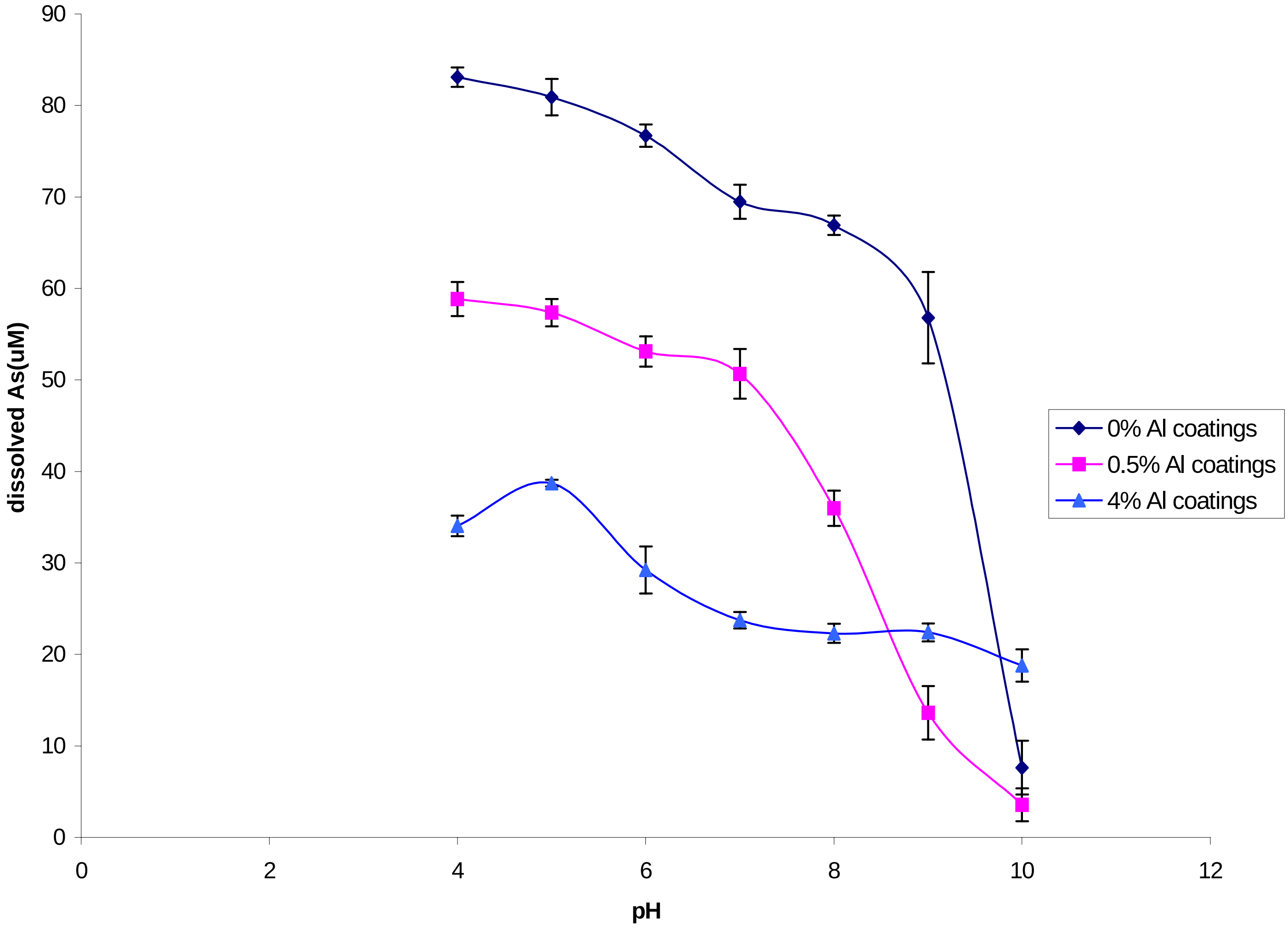


Figure 3.12: Effect of different levels of aluminum coatings on the adsorption of arsenic by kaolinite

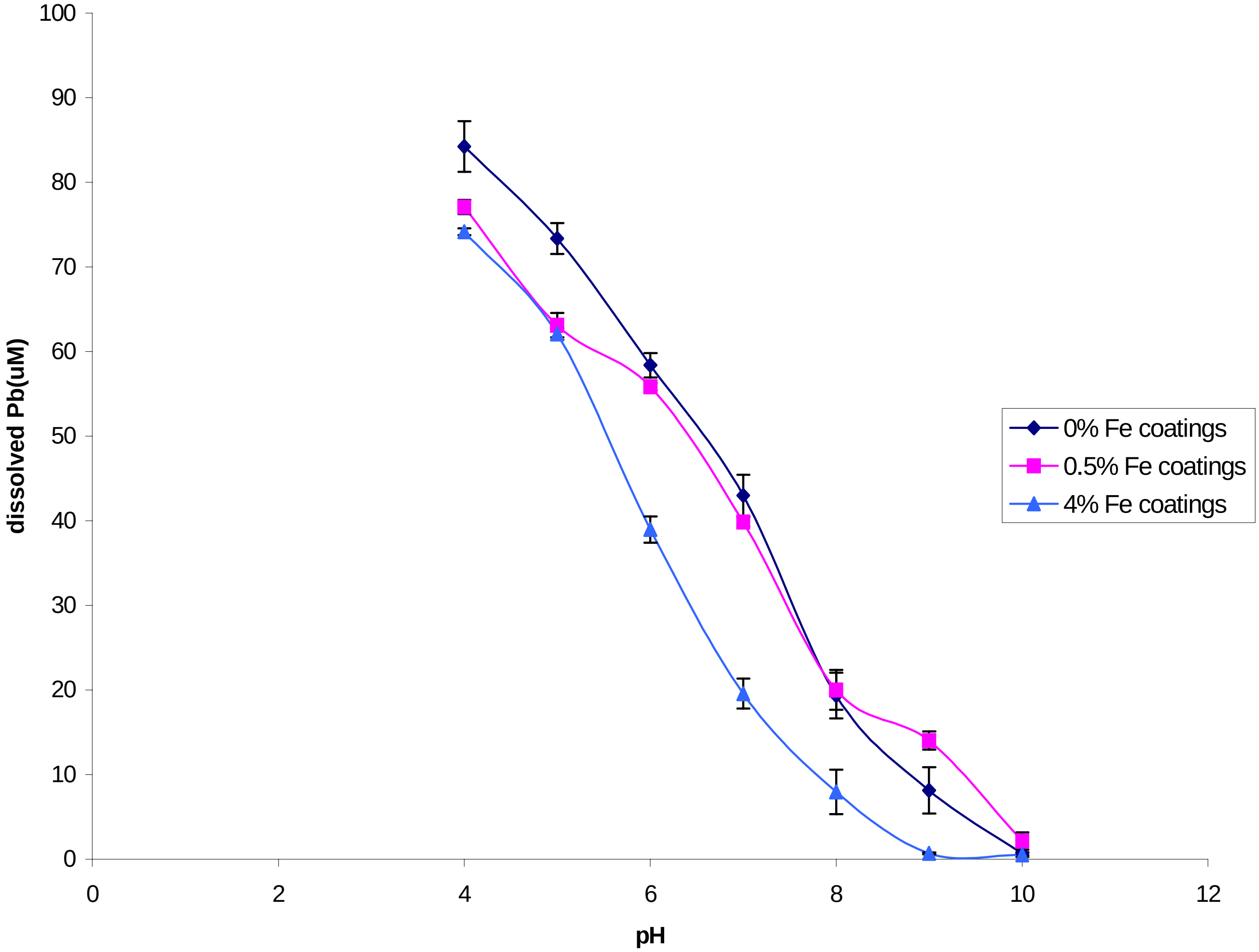


Figure 3.13: Effect of different levels of iron coatings on the adsorption of lead by attapulgite

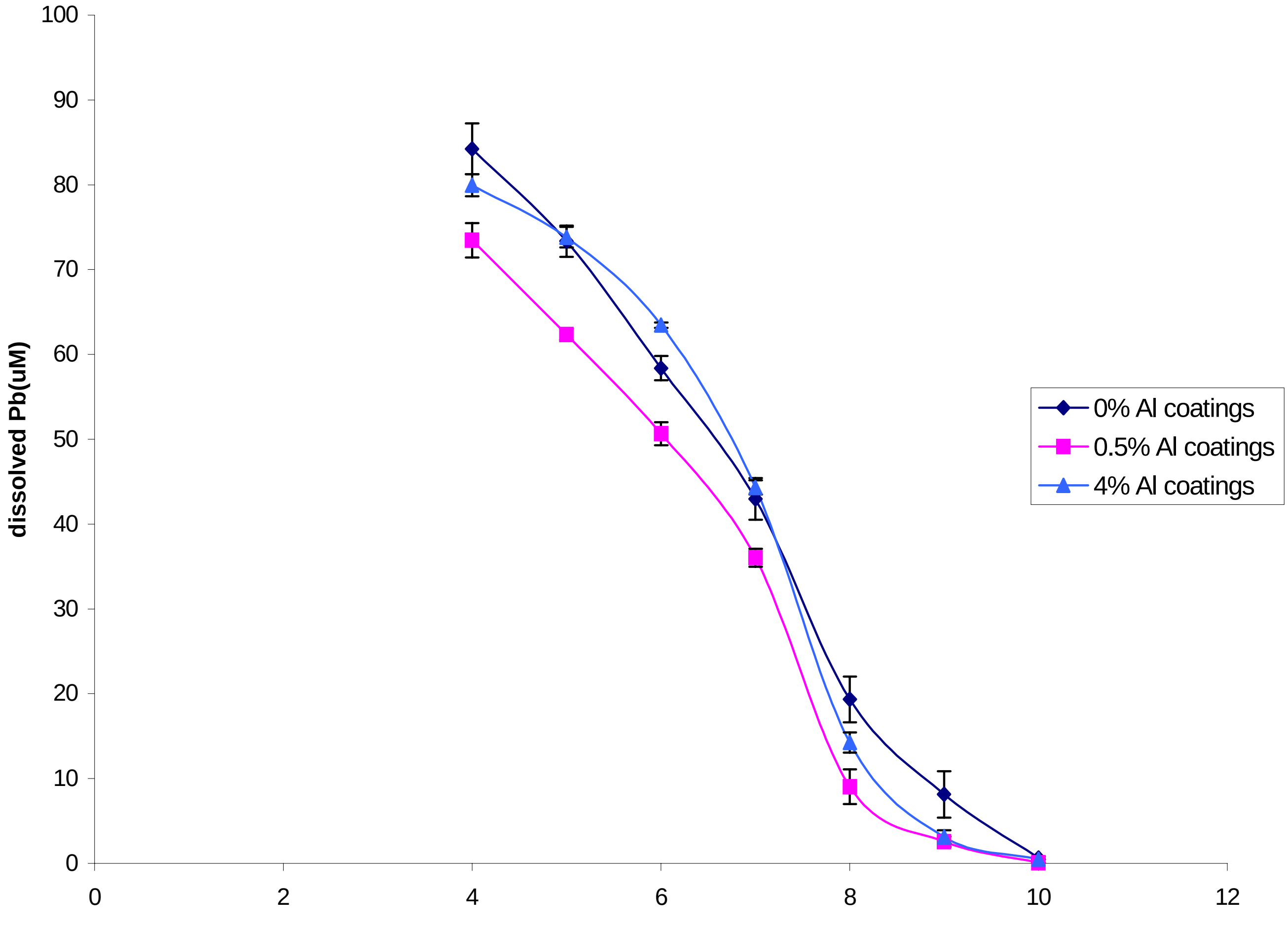


Figure 3.14: Effect of different levels of aluminum coatings on the adsorption of lead by attapulgite

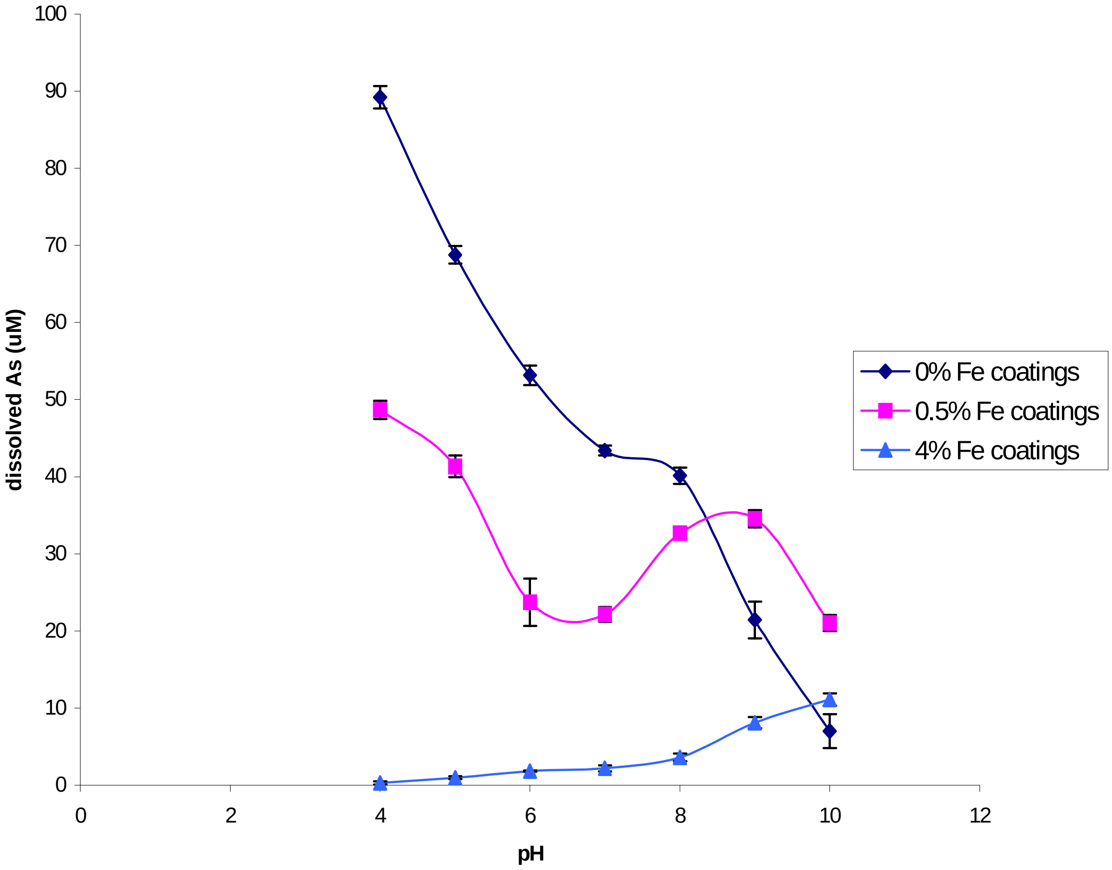


Figure 3.15: Effect of different levels of iron coatings on the adsorption of arsenic by attapulgite

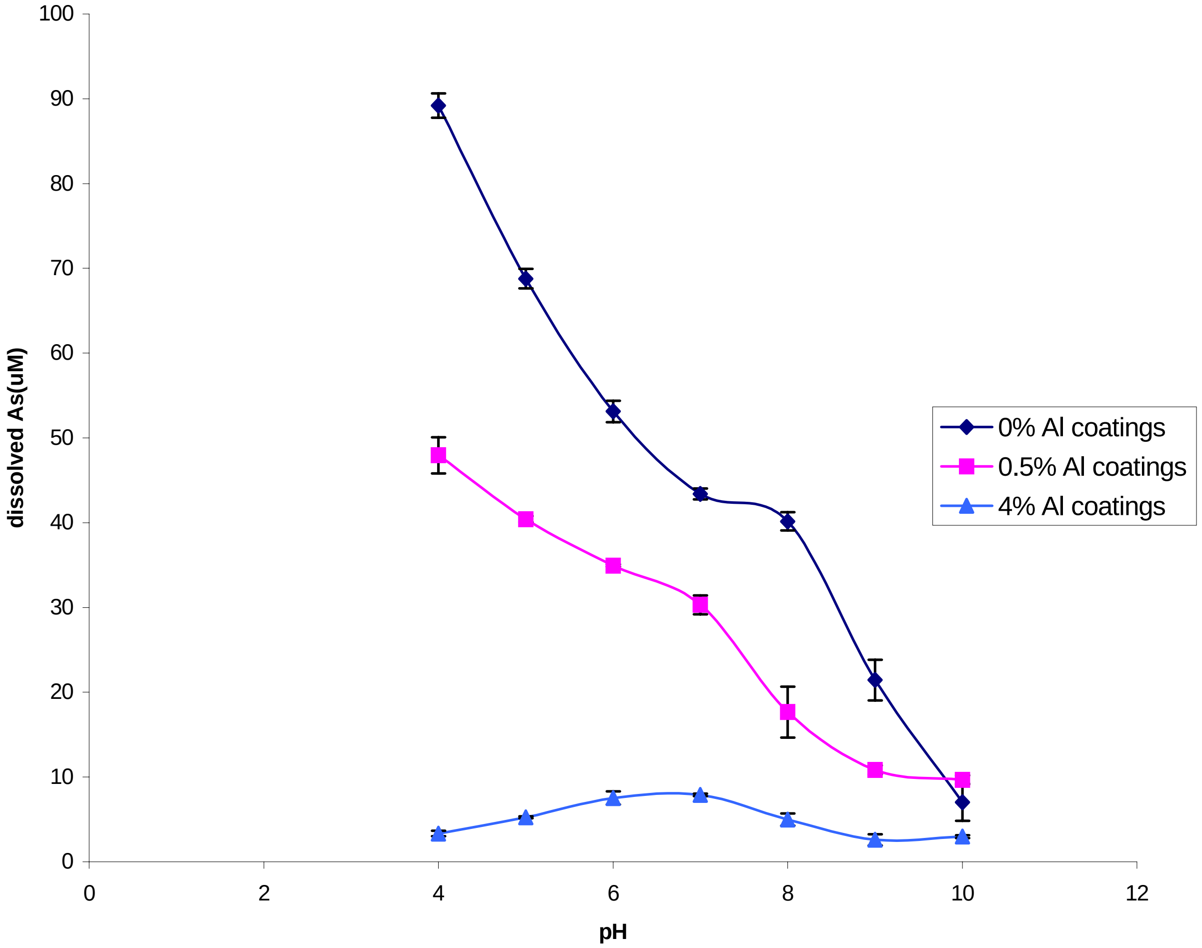


Figure 3.16: Effect of different levels of aluminum coatings on the adsorption of arsenic by attapulgite

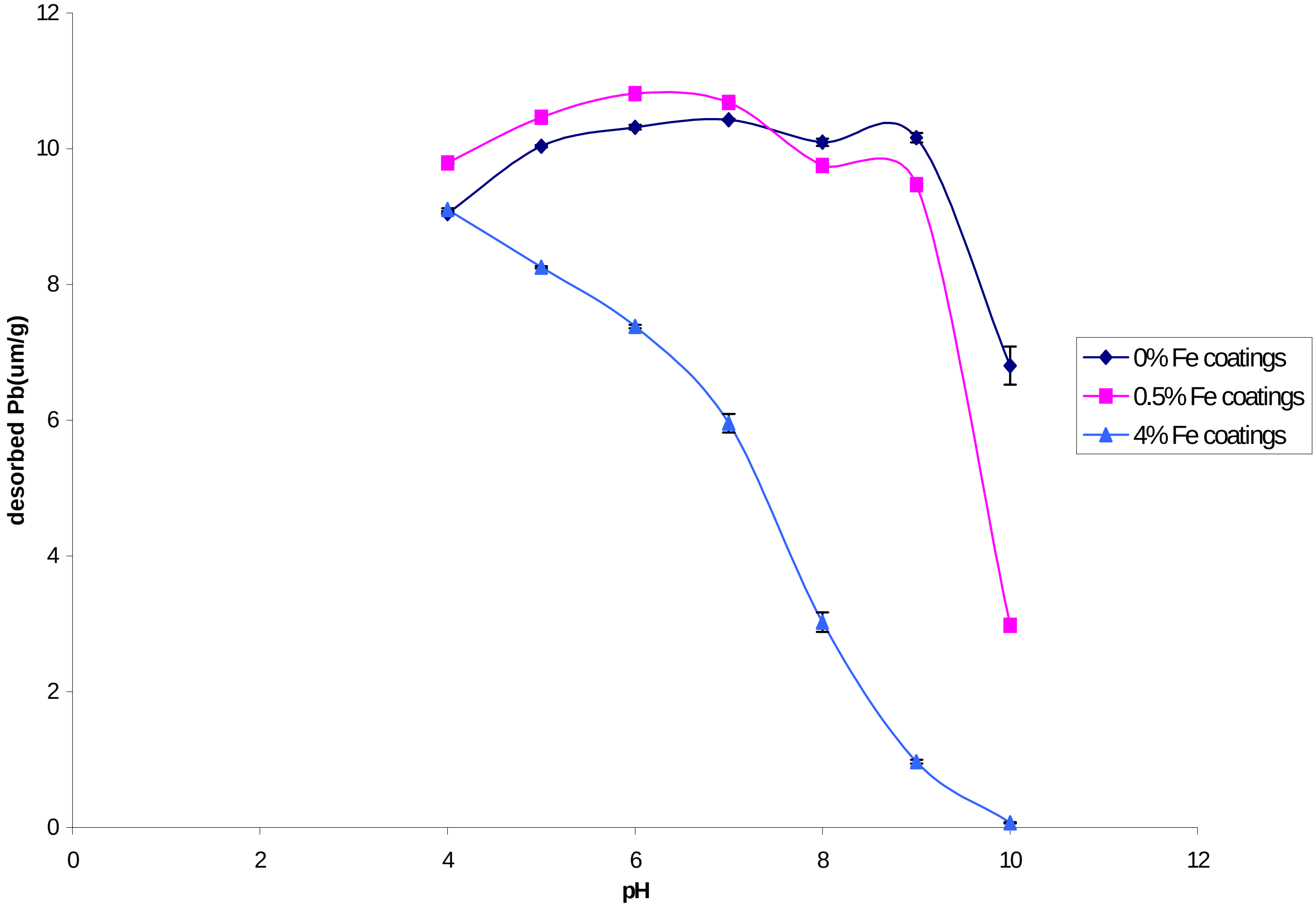


Figure 3.17: Effect of different levels iron coatings on the desorption of lead by montmorillonite

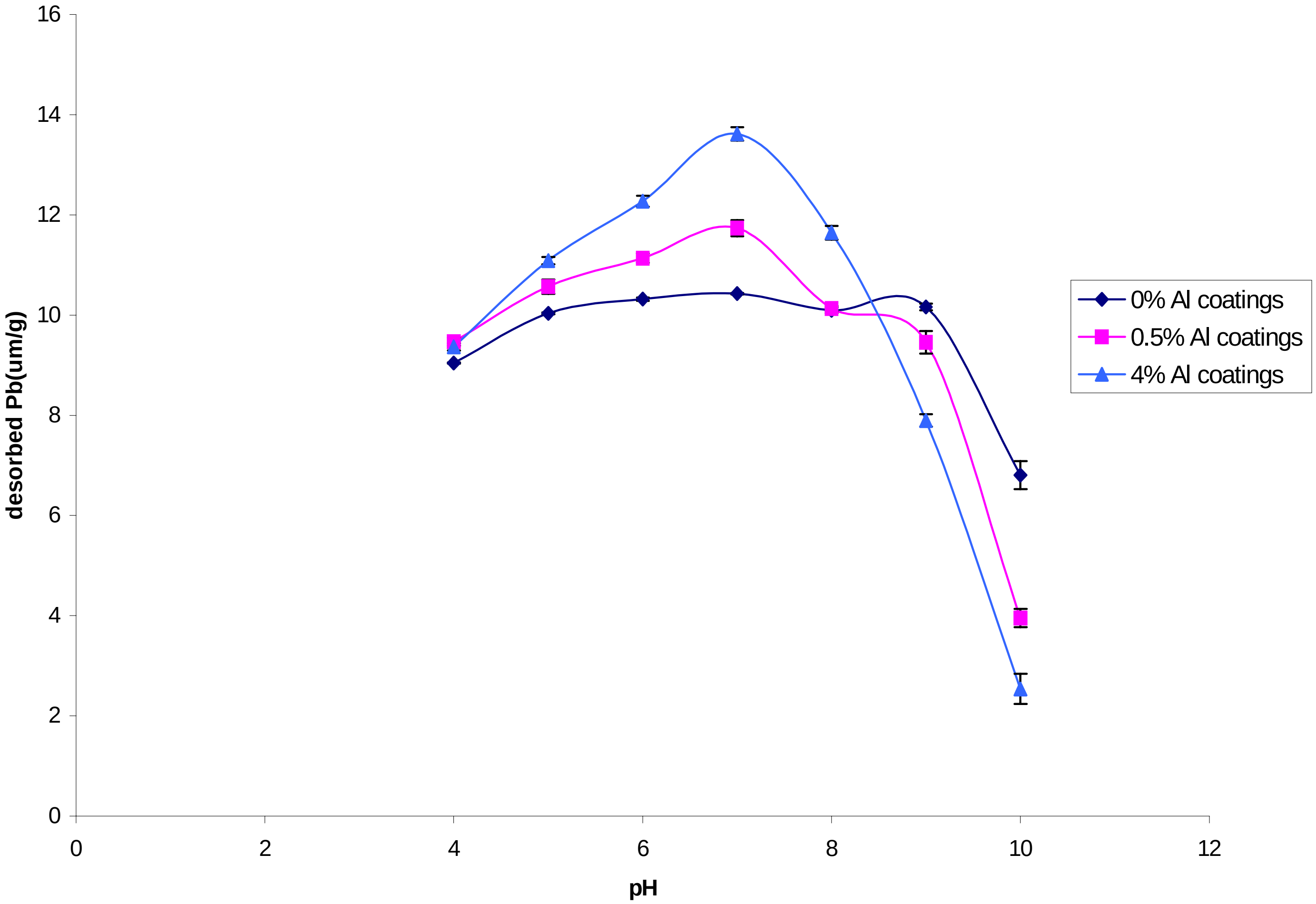


Figure 3.18: Effect of different levels of aluminum coatings on the desorption of lead by montmorillonite

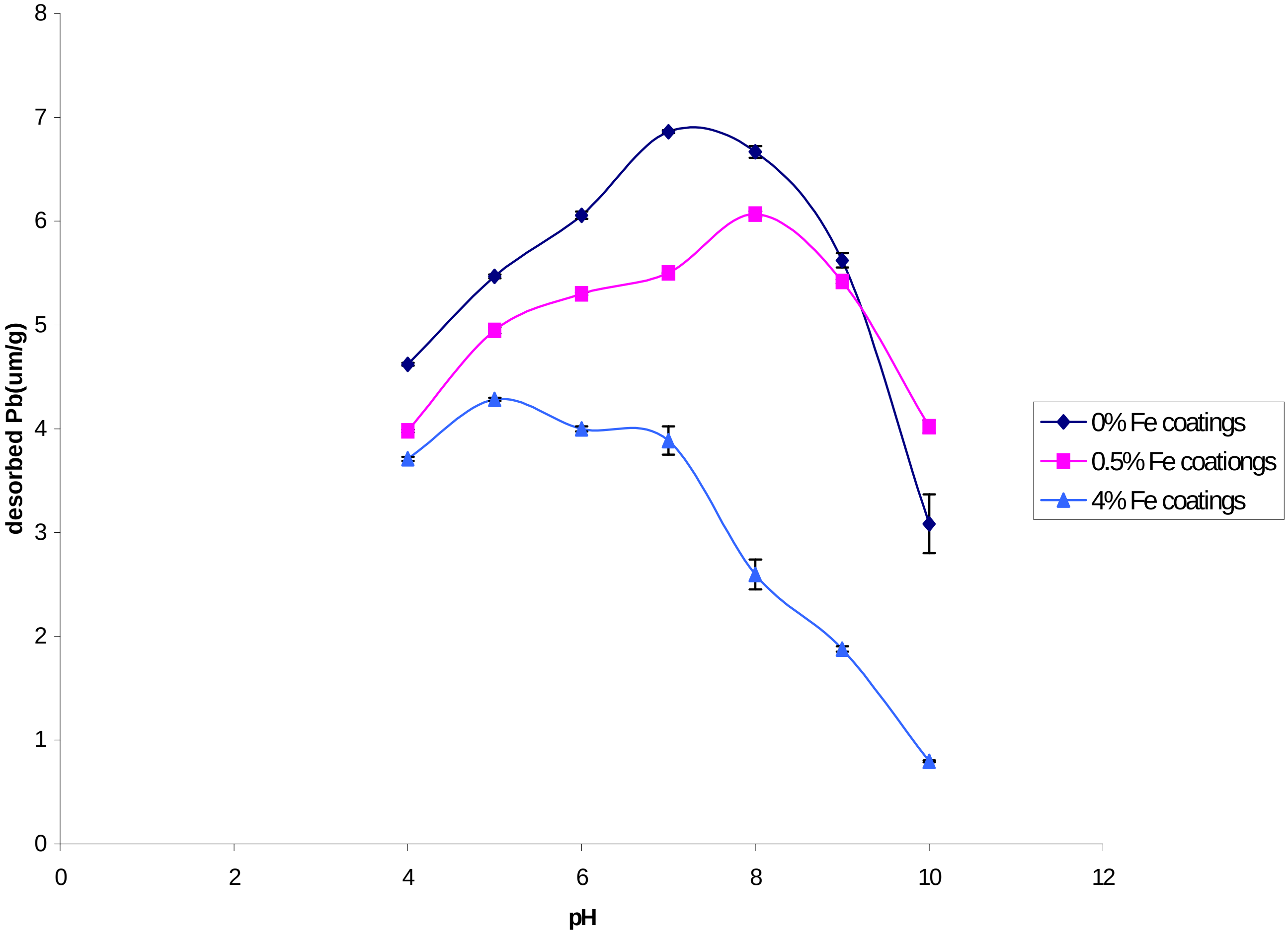


Figure 3.19: Effect of different levels of iron coatings on the desorption of lead by illite

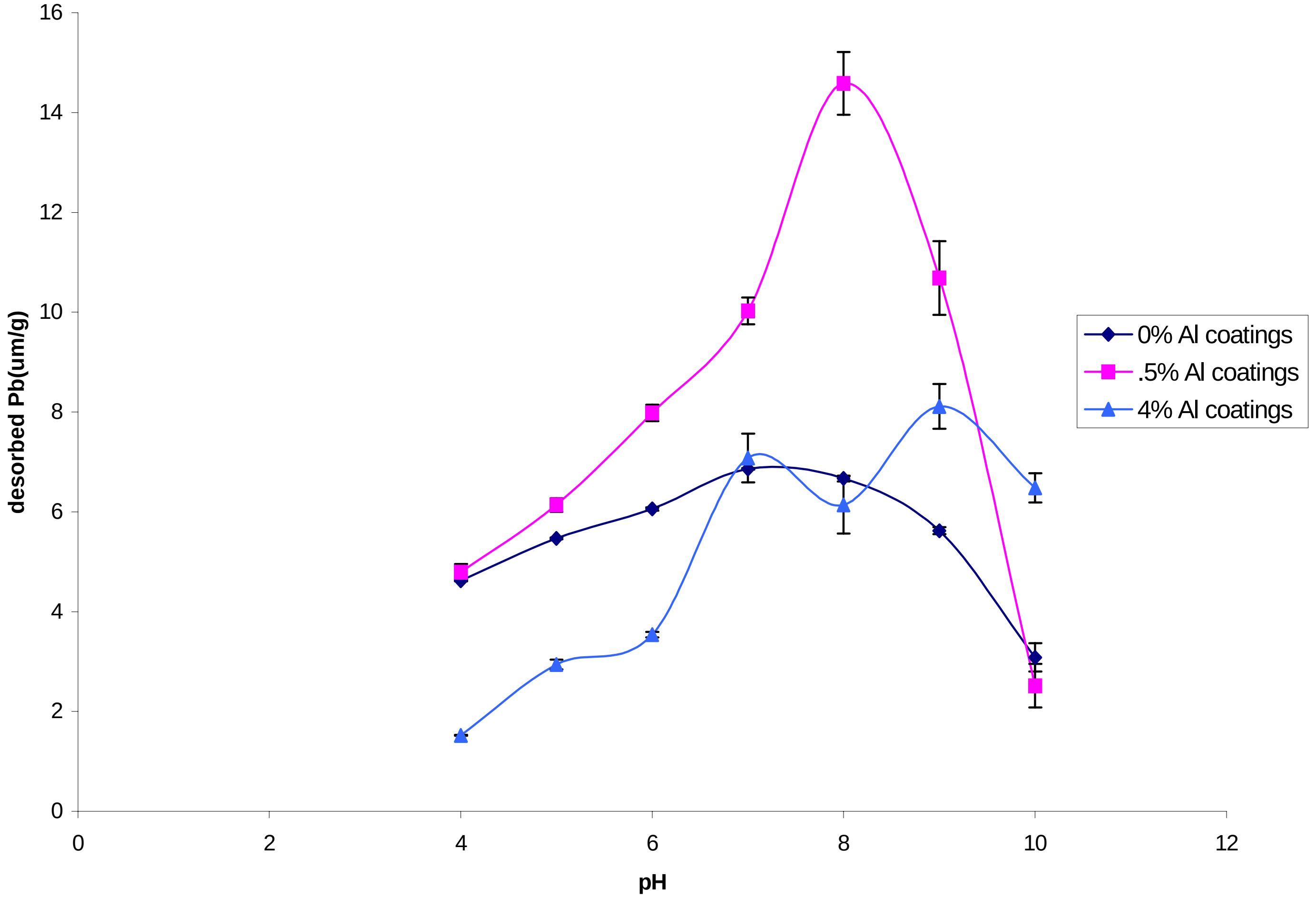


Figure 3.20: Effect of different levels of aluminum coatings on the desorption of lead by Illite

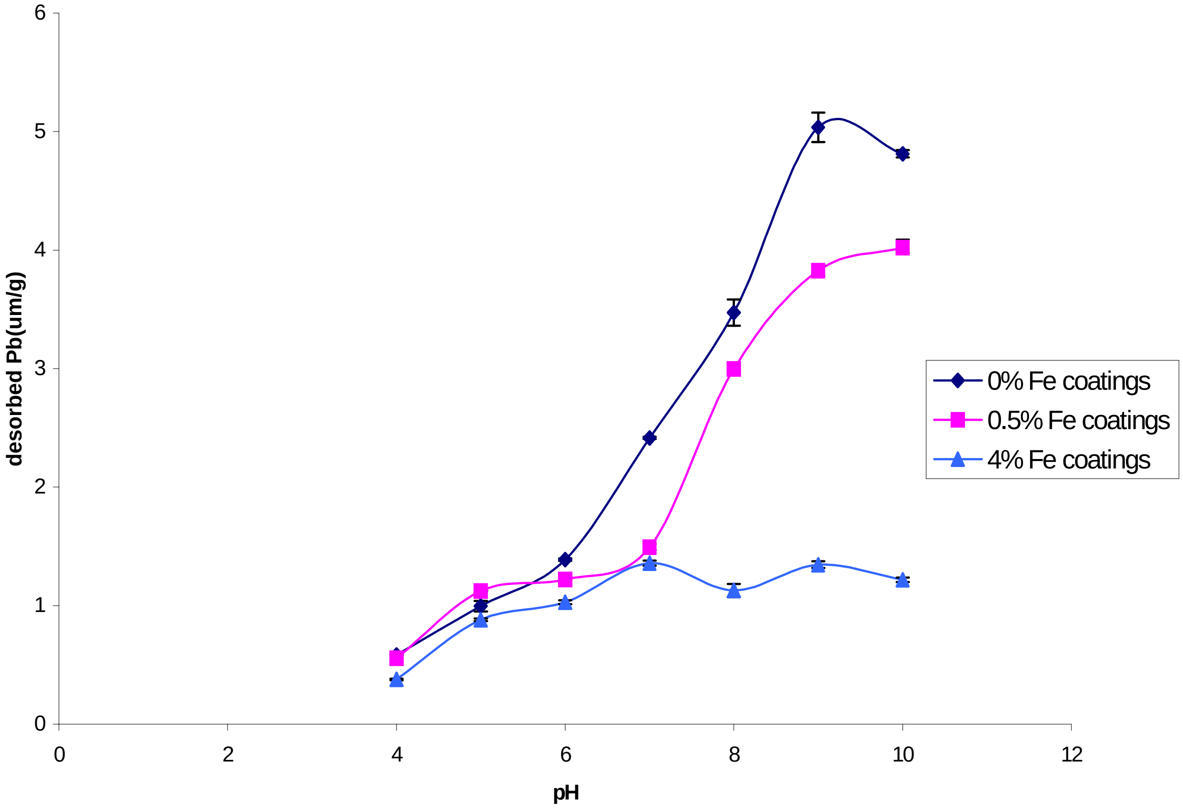


Figure 3.21: Effect of different levels of iron coatings on the desorption of lead by kaolinite

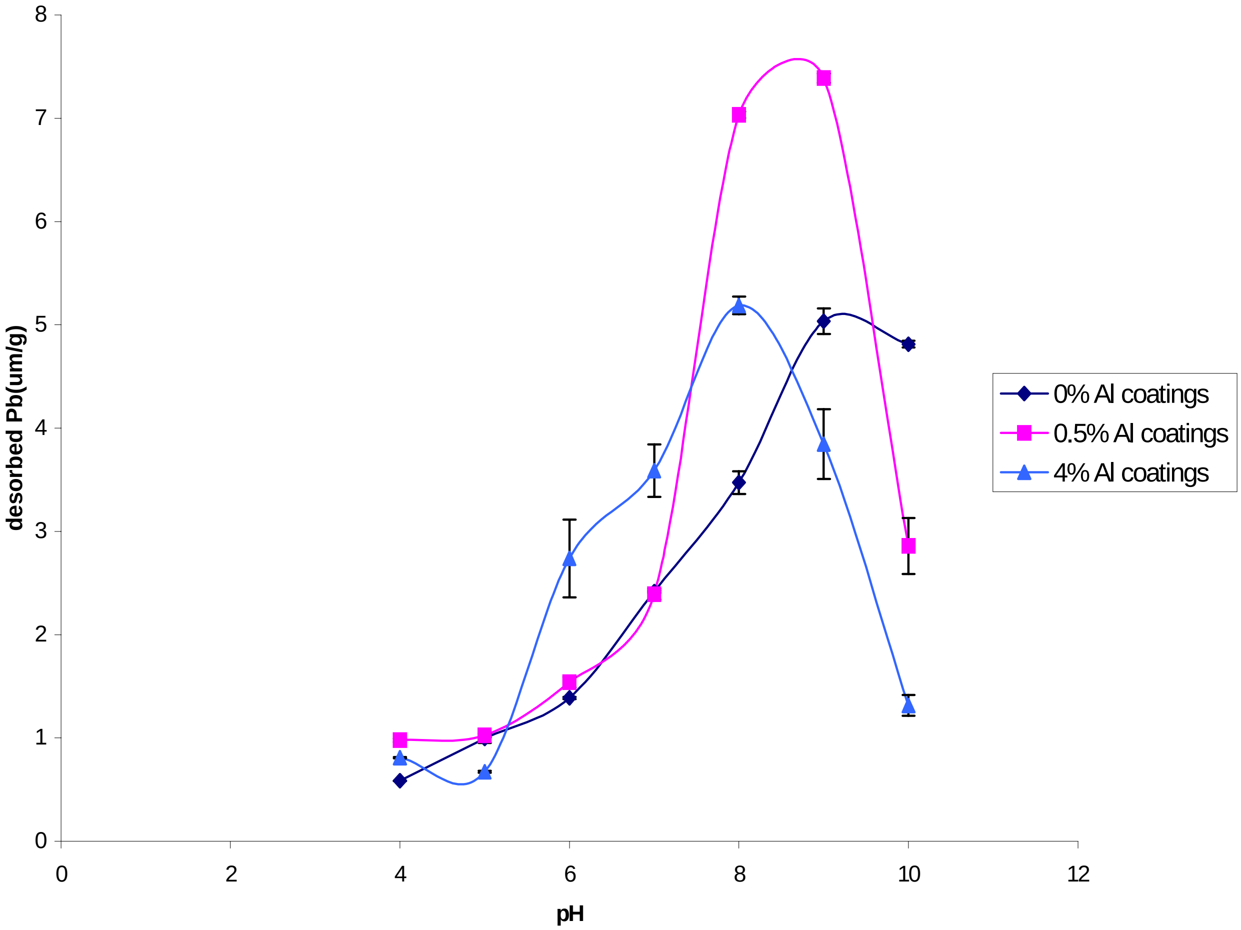


Figure 3.22: Effect of different levels of aluminum coatings on the desorption of lead by kaolinite

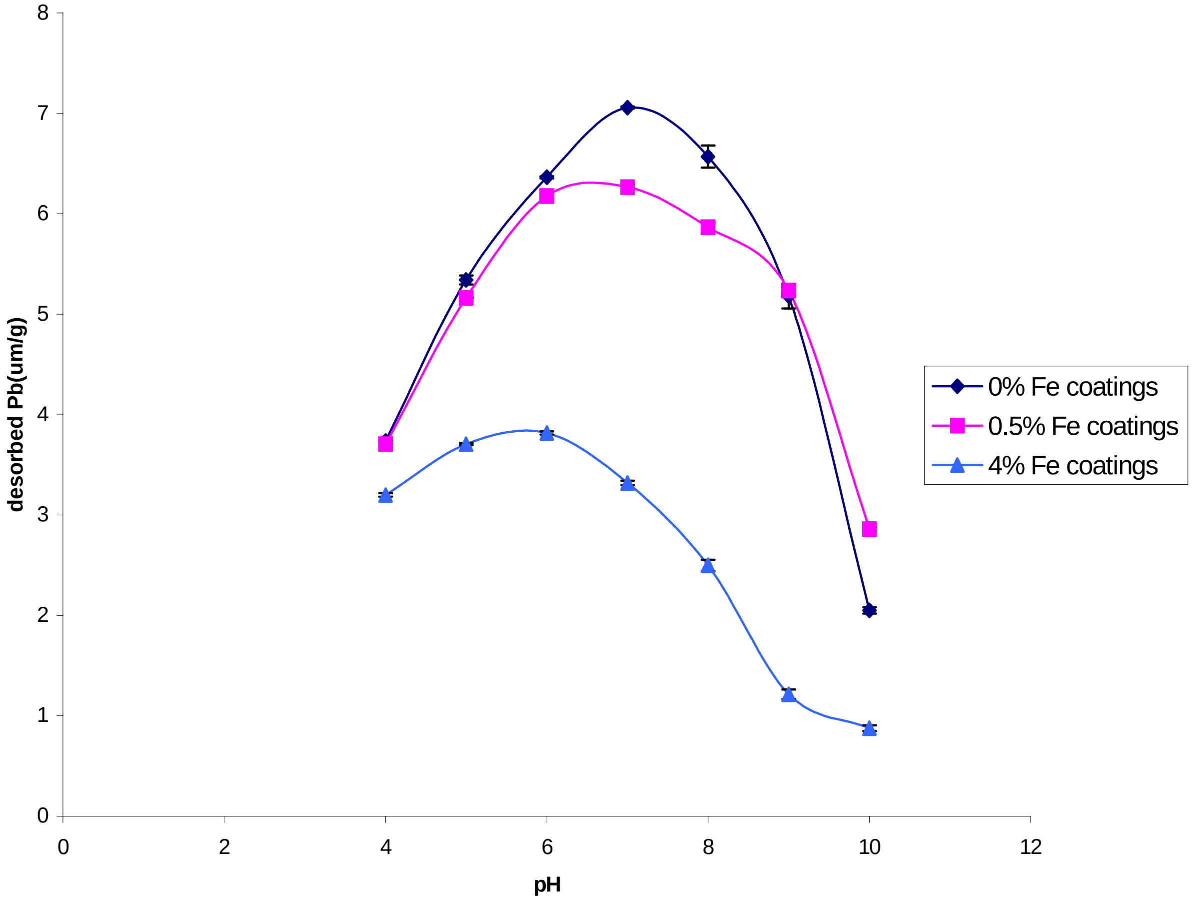


Figure 3.23: Effect of different levels of iron coatings on the desorption of lead by attapulgite

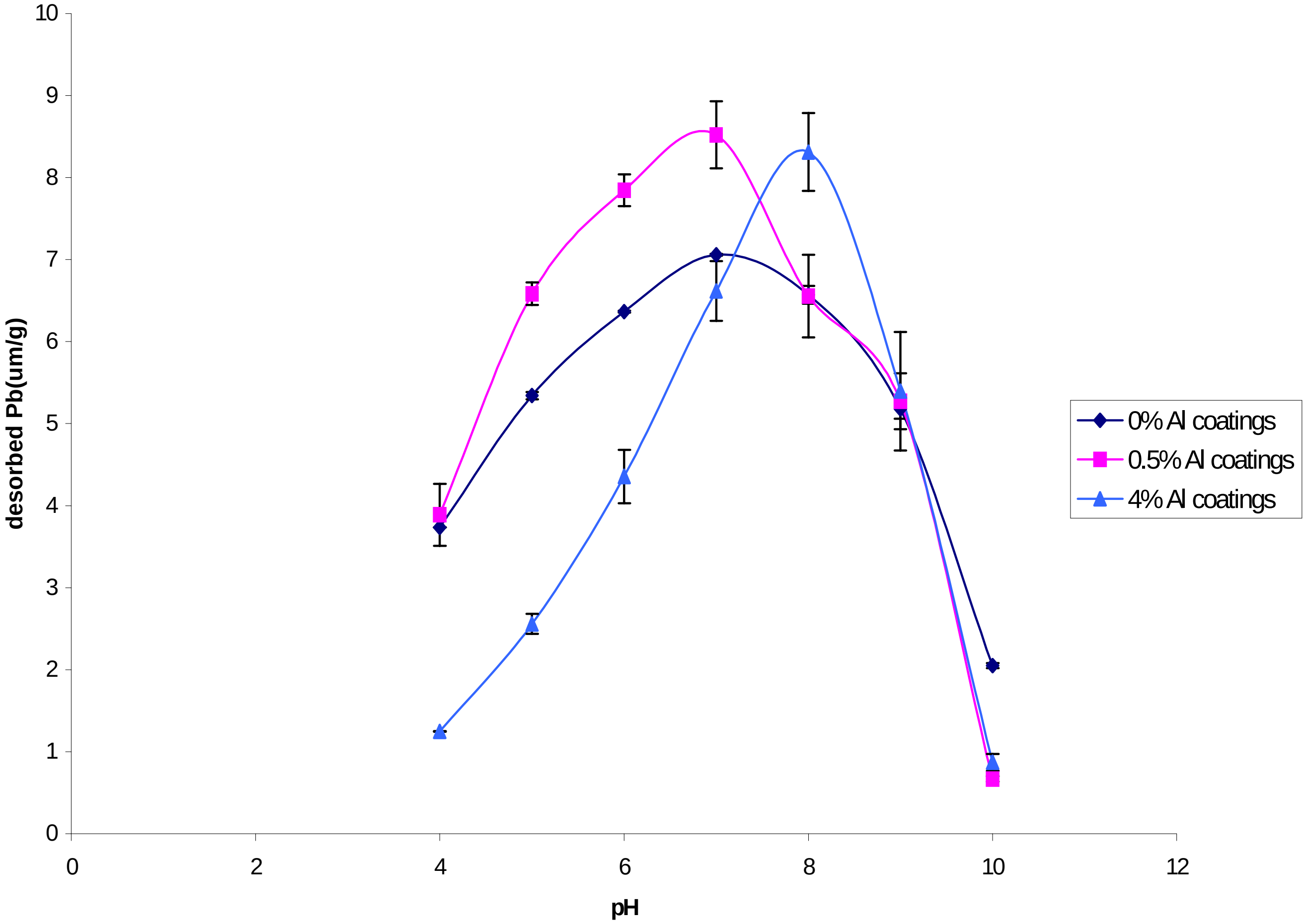


Figure 3.24: Effect of different levels of aluminum coatings on the desorption of lead by attapulgite

After the addition of Mg there was relatively more desorption of Pb into solution from the pure minerals. More desorption of Pb into the soil is mainly due to non-specific adsorption of Pb on pure minerals. But in the case of Al and Fe coated clay minerals, the desorption was relatively low. This effect was observed by Schulthess and Huang (1990) , Zachara et al. (1992), and Bradbury and Baeyens (1995), who postulated that the metal cations are specifically adsorbed on hydroxyl sites located on the mineral edge surfaces($S^{w}OH$). Specific adsorption of Pb on ϒ-Al_2O_3 as already proposed by Hohl and Stumn (1976) and Chisholm-Brause et al. (1989) observed the specific binding of Pb on ϒ- Al_2O_3 by X-ray absorption spectroscopy .

Dissolved As concentrations at various pH values and various levels of Fe and Al hydrous oxide coatings for all the minerals are given in Figures 3.3, 3.4, 3.7, 3.8, 3.11, 3.12, 3.15, and 3.16. The concentration of dissolved As in the presence of uncoated clay minerals was relatively high as compared to that in the presence of Al and Fe coated clay minerals. The results indicate that uncoated minerals have a limited number of anion adsorption sites. For example, the variable charge sites responsible for chemical interactions with anions dominantly consist of Si-O groups located on edge surface of montmorillonite. Montmorillonite does have Al-O sites but the percentage compared with Si-O sites is low. By coating the montmorillonite and other clay minerals, there is increase in the Al-O and Fe-O sites, which should definitely chemisorb anions involved in inner sphere complex formation with hydroxylated surface.

Results of this investigation also indicate that in all four clay minerals, Al hydrous oxide created a lower number of adsorption sites than those created by equivalent amounts of Fe hydrous oxide coatings. The number of sites eventually affect the Pb and As adsorption. The effect was more pronounced in case of As adsorption. The disparity between Al and Fe hydrous coatings can be ascribed to many factors. First, Al is known to polymerize in solution before complete precipitation (Hsu, 1977), and precipitation of polymeric species of Al produces a three dimensional order on the surface of clay minerals reducing the number of Al atoms exposed on the surface. This would in turn reduce the number of single co-ordinated OH groups involved (Prafitt and Russel, 1977). Second, there could be greater chemical affinity between arsenate and Fe-O sites than between arsenate and Al-O sites. Third, Fe hydrous oxide coated clay samples have been shown to have higher surface area compared to Al hydrous oxide coated clay samples (Hendeshot and Lavkulich, 1983). Therefore, Fe hydrous oxide coated samples may have higher number of adsorption sites as well.

3.4.2 Amount of adsorption- Comparisons of different minerals : Adsorption of Pb was the highest for pure montmorillonite and lowest for pure kaolinite. The reason for this is the high surface area and cation exchange capacity of montmorillonite compared to all other minerals. With the increase in Fe and Al coatings, montmorillonite consistently adsorbed higher amounts of Pb than all the other clay minerals (Figures 3.25-3.26).

Among the pure minerals, higher As adsorption was observed for montmorillonite and attapulgite and lower was observed for kaolinite (Figure 3.27). This may be due to higher external surface area of montmorillonite and attapulgite that in turn results in higher edge area and higher adsorption of As (Frost and Griffin,1977). Moreover, attapulgite contains higher proportion of octahedrally co-ordinated cations (Al, Fe, and Mg) that give rise to anion adsorption sites. With the increase in Fe and Al coatings to 4% , adsorption of As was greater for illite compared to that for attapulgite (Figure 3.28). Coating material probably covers the sites arising from both octahedrally (Al, Fe and Mg) and tetrahedrally (Si) co-ordinated cations. Since uncoated attapulgite has a higher proportion of octahedrally coordinated sites (Table 3.1) a higher proportion of those sites could be covered by the coating material compared with that in illite (Dhaliwal, 1996). This is reflected by adsorption of lower amount of As by coated samples of attapulgite than coated samples of illite (Figures 3.27-3.28).

3.5 Relevance to Soils: Adsorption/desorption reactions may be important in controlling the aqueous concentration of As and Pb which eventually determine their bioavailability and toxicity. In this adsorption study, Fe and Al coatings on the different minerals were able to immobilize As and Pb specifically. This property of Fe and Al coatings can be potentially used for the gentle immobilization of heavy metals in polluted agricultural soils.

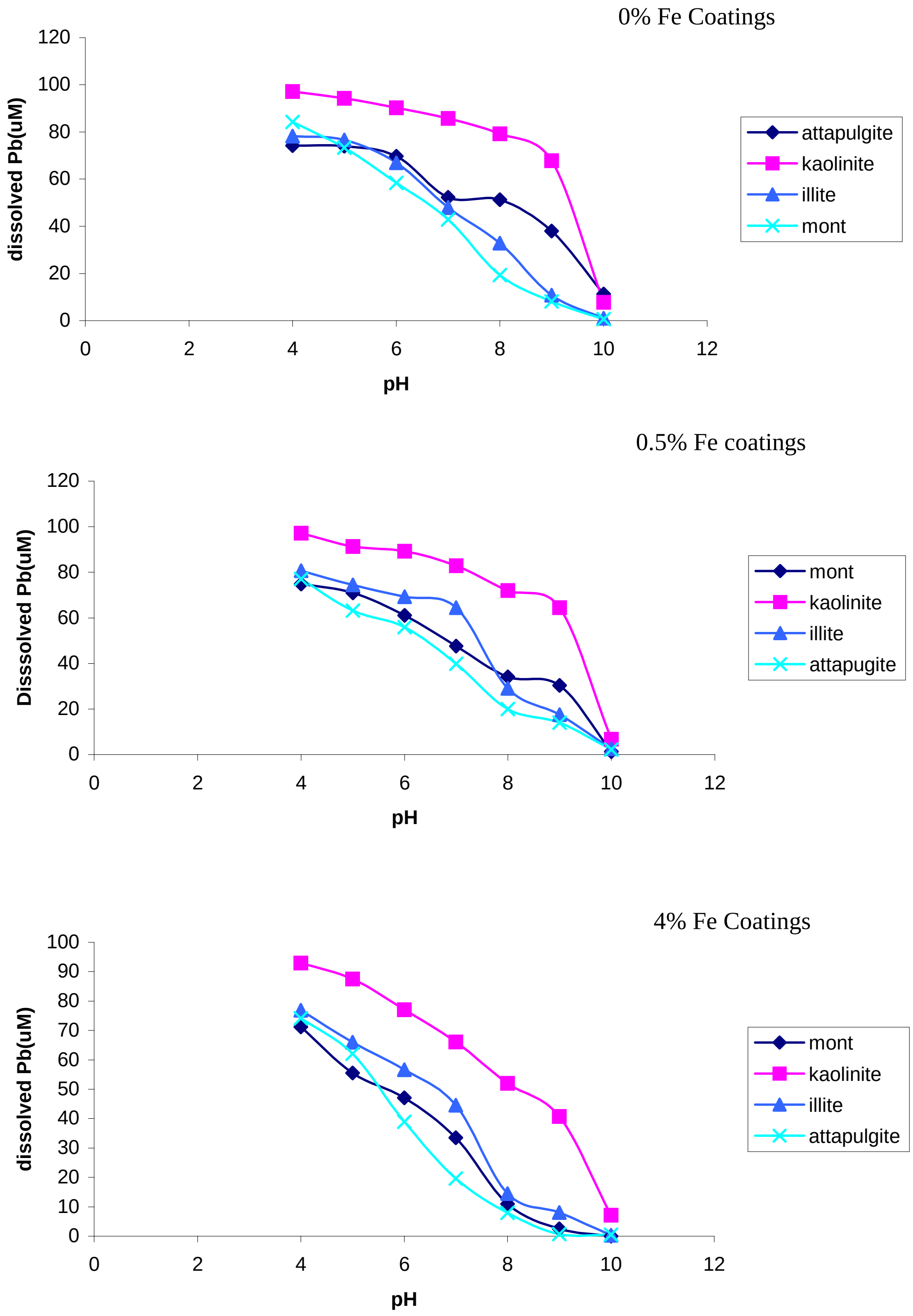
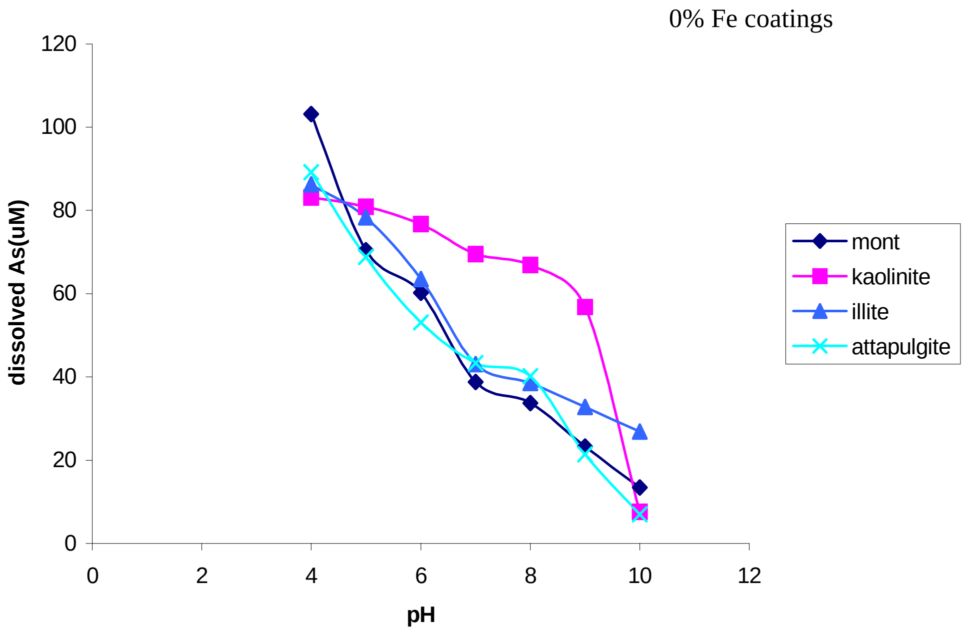
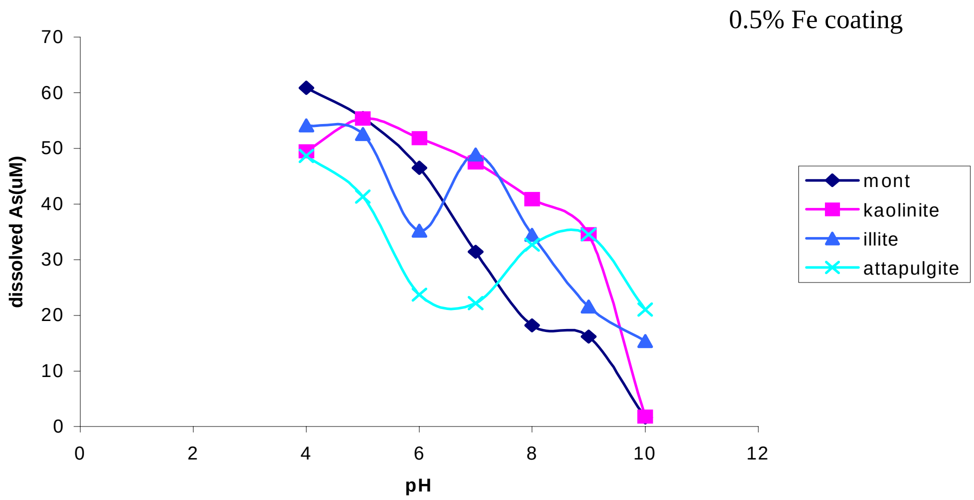
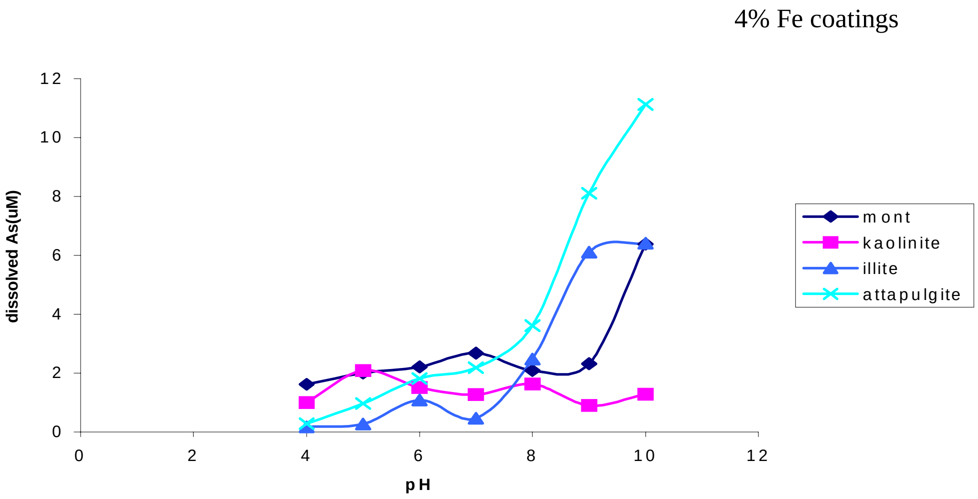


Figure 3.25: Lead adsorption on pure and Fe coated clay minerals


0% Fe coatings
120
100
80
60
40
20
0
dissolved As(uM)
0
2
4
6
8
10
12
pH
mont
kaolinite
illite
attapulgite


0.5% Fe coating
70
60
50
40
30
20
10
0
dissolved As(uM)
0
2
4
6
8
10
12
pH
mont
kaolinite
illite
attapulgite


4% Fe coatings
12
10
8
6
4
2
0
dissolved As(uM)
0
2
4
6
8
10
12
pH
mont
kaolinite
illite
attapulgite

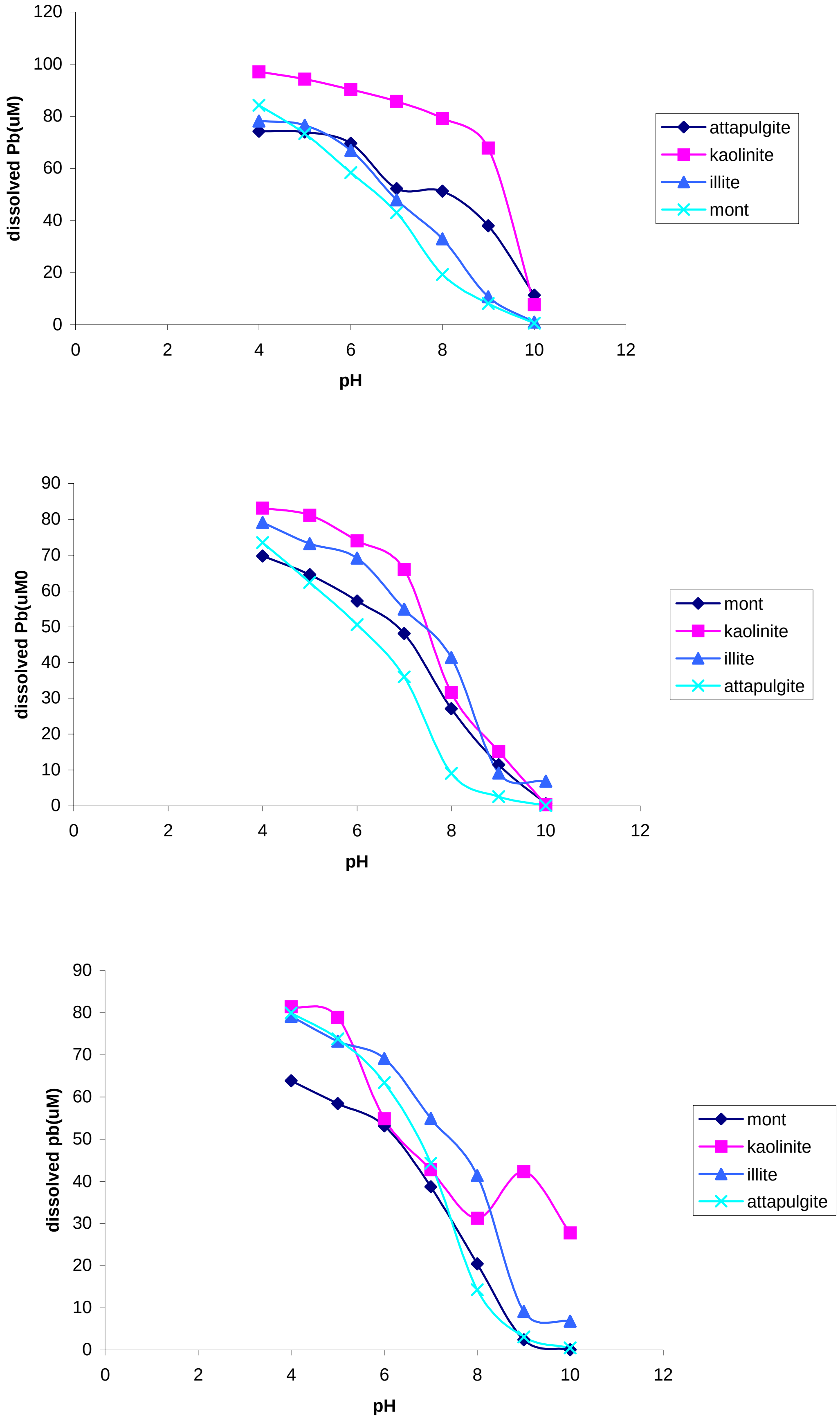


Figure 27: Pb adsorption on pure and Al coated clay minerals

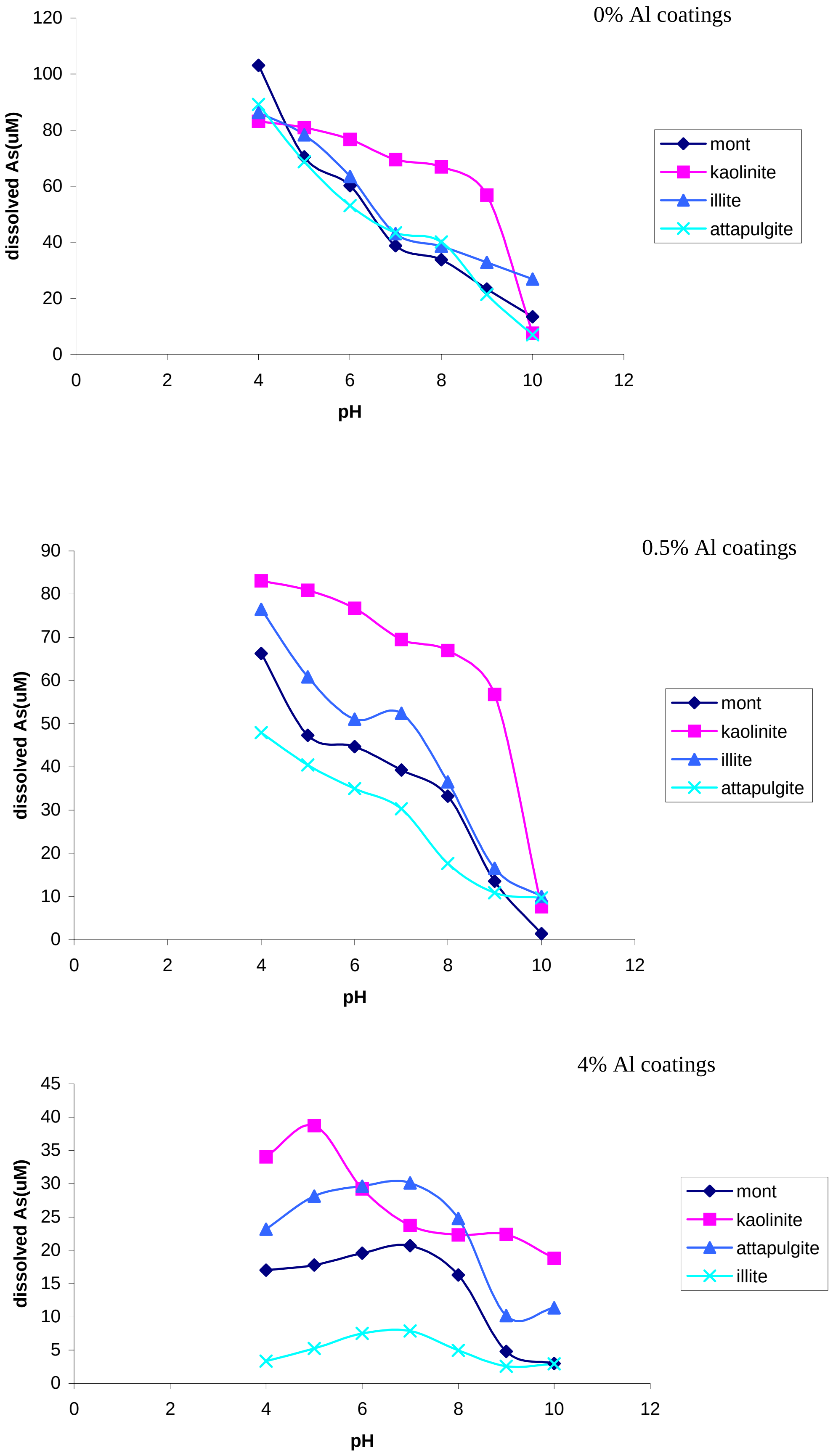


Figure 3.28: As adsorption on pure and Al coated clay

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Chapter 4

Surface Complexation Modeling

4.1 Introduction

Iron and Al(hydr)oxides are common in the clay fraction of soils. They may occur as discrete particles having hardly any contact with clay or coatings on clays or as interlayer between clay mineral surfaces. Surface complexation models (SCMs) have the capability to simulate the adsorption of cations and anions as a function of pH, solute concentration and ionic strength (Hayes & Leckie, 1987; Hayes et al., 1988). Unlike empirical models, surface complexation models are chemical models that provide a description of a chemical system consistent with its chemical properties, and they give a general molecular description of adsorption phenomena using an equilibrium approach .

Parameters which adequately account for acid-base protolysis reactions of the surface must be determined in order to use surface complexation models to model the sorption processes. All models contain equilibrium constants (K_i), the capacitance density for i^{th} surface plan (C_i) and the total number of reactive surfaces with the hydroxyl group as the adjustable parameter ($[\;SOH_T]$). Different methods have been used for the parameter estimation. However depending on the method chosen, different values of model parameters for a given SCM and titration data may be obtained.

In order to fully understand the fate and transport of metal in the environment, we need to be able to accurately describe and model complex natural systems. Surface complexation models are capable of simulating the experimentally observed acid-base titration properties of metal oxide and pure clay minerals (Schindler and Stumn, 1987). However, no study has been done to simulate acid-base titration on iron and aluminum coated clays. The objective of this paper is to describe a methodology for determining a unique set of model parameters from titration data for iron and aluminum coated clay minerals.

4.1.1 Surface Complexation Models

The SCMs chosen for evaluating the sensitivity of model simulation to changes in parameter values were diffuse layer model (DLM) (Hayes & Leckie, 1987; Hayes, 1987; Westall & Hohl, 1980; Huang and Stumn, 1973), the constant-capacitance model (CCM) (Dzombak and Morel, 1990; Hohl & Stumn, 1976) and the triple layer model (TLM) (Hayes & Leckie, 1987; Hayes et al., 1988; Davis et al., 1978 and James & Parks, 1982). Each model treats surface as if it were composed of amphoteric hydroxide functional groups which are capable of reacting with sorbing cationic or anionic species to form surface complexes. These models differ in their description of the diffuse double layer and the manner in which changes in the background electrolyte concentration are incorporated in model computations. These models require a different numbers of adjustable parameters. The most simple, DLM, requires three adjustable parameters and the most complex, TLM, requires seven adjustable parameters.

In the DLM, the three adjustable parameters required for simulating titration behavior are two surface protolysis constants, K^+ and K^- and the total number of sites, N_T. The four adjustable parameters in the CCM are two surface protolysis constants, K^+, and K^-, the total number of surface sites, N_T and an inner layer capacitance term, C_i. The more complex TLM has seven adjustable parameters including two surface protolysis constants, K^+ and K^-, two capacitance, C_1 and C_2 , total site concentration, $N_{T,}$ and two electrolyte surface-binding constants, K_{an} and K_{cat}. Table 4.1 summaries the three SCM’ s in terms of protolysis reactions, surface complexation reactions, ion pair complexes, charge-potential relationships, and adjustable model parameter. Table 4.2 shows the placement of ions, potential, charge, and capacitance for CCM, DDM, & TLM.

<u>Modeling Titration Behavior</u>: Surface change characteristics were determined from acid-base titration data. For the DLM & CCM:

$$[H^+] - [OH^-] + [SOH_2^+] - [SO^-] = C_A - C_B \qquad (1)$$

The protolysis reactions are given by

$SOH + H^+ \leftrightarrow SOH_2^+ \quad K^{app}_{a1} \qquad (2)$

$SOH \leftrightarrow SO^- + H^+ \quad K^{app}_{a2} \qquad (3)$

$H_2O \leftrightarrow H^+ + OH^- \quad K_w \qquad (4)$

With thermodynamic equilibrium constants

$$K^+_{int} = \frac{[SOH_2^+]}{[SOH]\,[H^+]} e^{F\Psi o/RT} \qquad (6)$$

$$K^-_{int} = \frac{[SO^-]\,[H^+]}{[SOH]} e^{F\Psi o/RT} \qquad (7)$$

$$K_w = [H^+](\gamma_{H+})[OH^-](\gamma_{OH-})$$

Where $e^{-F\Psi i/RT}$ is a electrostatic potential term. The electrostatic potential term should simply be considered as a solid phase activity coefficient correcting for the charge on surface complexes.

Table 4.1: Surface Chemical Reaction and Model Parameters

DLM	**CCM**	**TLM**
	Protolysis Reaction	
$SOH + H^+ \leftrightarrow SOH_2^+$ K^+ $SOH \leftrightarrow SO^- + H^+$ K^-	$SOH + H^+ \leftrightarrow SOH_2^+$ K^+ $SOH \leftrightarrow SO^- + H^+$ K^-	$SOH + H^+ \leftrightarrow SOH_2^+$ K^+ $SOH \leftrightarrow SO^- + H^+$ K^-
	Surface Complexation Reactions	
$SOH + M_e^{2+} \leftrightarrow SOH^{(m-1)\ +} + H^+$ K_m $\mathbf{SOH + L^l \leftrightarrow SL^{(l-1)-} + OH^-}$ $\mathbf{K_m}$	Same as DLM	Same as DLM
	Ion Pairs	
Not allowed	Not allowed	$SOH + M^{m+} \leftrightarrow SO^- - M^{m+} + H^+$ $\mathbf{SOH + L^{l-} \leftrightarrow SOH_2 - L^{l-}}$
	Charge Potential Relation	
$\sigma_d + \sigma_o = 0$ $\sigma = 2.51^{1/2}\psi$	$\sigma_o = C_1\psi_o$	$\psi_o - \psi_b = \sigma_o/C_1$ $\psi_b - \psi_d = -\sigma_d/C_2$ $\sigma_d = -(8RTCEoD)^{1/2} \sinh(F\psi_d/2RT)$
	Adjustable Model Parameters	
K^+, K^-, N_S	K^+, K^-, N_S, C_1	$K^+, K^-, K_{Ca}, K_{An}, C_1, C_2, N_S$

Table 4.2: Mass Law and Mole Balance Equation

Model	Surface mole balance equations	Surface Mass Balance equation
DLM	$\sigma = [SOH_2^+] - [SO^-]$ $+(m-1)\ SOH^{(m-1)} - (l-1)[SL^{(l-1)}]$	$[SOH]_T = [SOH] + [SOH_2^+] + [SO^-]$ $+[SOM^{(m-1)}] + [SL^{(l-1)}]$
CCM	Same as for DLM	Same as for DLM
TLM	$\sigma_o = F/S_a\{[SOH_2^+] + [SOH_2^+ - An^{l-}] - [SOM]$ $-[SO^-] - [SO^- - Ca^+]$ $\sigma_d = F/Sa[SO^- - Ca^+] - [SOH_2^+ - An^{l-}]$	$S_T = [SOH] + [SOH_2^+] + [SO^-]$ $+[SOH_2^+ - A^- n^{(l-1)}] +$ $[SO^- - C] + [SL] +$ $[SOM^{(m-1)}]$

For TLM surface charge characteristics were determined from the following relation:

$$[H^+] - [OH^-] + [SOH_2^+] - [SO^-] + [SOH_2^+\text{-}An^-] - [SO^-\text{-}Cat^+] = (C_A - C_B) \qquad (8)$$

The protonation and dissociation constants remain as written in eq. (2)-(4) for TLM. The other intrinsic conditional equilibrium constants are (Davis et al., 1978; Davis and Leckie, 1978,1980):

$$SOH + C^+ \leftrightarrow SO^- \text{-}C^+ + H^+ \qquad (9)$$

$$SOH + H^+ + A^- \leftrightarrow SOH_2^+\text{-}A^- \qquad (10)$$

$$K_{C+}(int) = \frac{[SO\text{-}C^+][H^+]}{[SOH][C^+]} \exp[(\psi_B - \psi_O)F/RT] \qquad (11)$$

$$K_{A-}(int) = \frac{[SOH_2^+\text{-}A^-]}{[SOH][H^+][A^-]} \exp[(\psi_O - \psi_B)F/RT] \qquad (12)$$

4.1.1 Ionic strength effects:

CCM: In this model the constant ionic medium reference state determines the activity coefficients of the aqueous species in the conditional equilibrium constants and therefore no complexes are formed with ions in the background electrolyte. The relationship between surface charge and surface potential is given by

$$\sigma = (Csa/F)\Psi \qquad (13)$$

According to this equation, interfacial potential is independent of ionic strength. Therefore, a different set of CCM surface constants is required for each set of ionic strength conditions to be modeled.

DDL: Because a diffuse layer of counter ion charges is assumed for the solution side of the interface, the relationship between surface charge and potential is fixed by electrical double-layer theory. In the DLM, ionic strength effects on protolysis equilibrium are accounted explicitly through the Gouy-Chapman-Stern Grahame (GCSG) charge-potential for a symmetrical electrolyte and is given by :

$$\sigma = 0.1174\sqrt{I}\,\sinh(Z\psi \text{ x } 19.46) \qquad (14)$$

According to the above equation, the effects of ionic strength on interfacial potential can be taken into account and only one set of DLM surface constants should be necessary to model sorption over a range of ionic strength conditions.

TLM: Like DLM, TLM can be used to model surface reaction over a range of ionic strength conditions with one set of surface equilibrium constants. It accounts for ionic strength by considering equation (14) and by considering the formation of ion-pair complexes with the background electrolytes.

4.1.2 Model Parameter Estimations

Studies have used surface complexation models to describe ion sorption onto natural particles (Goldberg and Glaubig, 1988; Sposito et al., 1988; Davis, 1998). To use SCM' s for model sorption processes, experimental or theoretical methods are required to determine the values for various model parameters. All models contain K_i, equilibrium constants; C_1, the capacitance density for ith surface plane and $[\ SOH]_T$, the total number of reactive surface hydroxyl groups. For any of these, the preferred method of obtaining the parameter value is to measure it directly. But in some cases it is not possible to calculate the value of the parameter. In those cases, the best set of values is typically based on a goodness of fit criterion.

For minerals, the total site concentration N_T (moles/liter) can be calculated from measured values for surface area, S_A, site density, N_S and solid concentration C_S (with units of m^2/g, sites/m^2, g/liter, respectively) measurements (Hayes et al., 1991).

$$\mathbf{N_T = N_S * S_A * C_S * 1.66 \times 10^{-6}} \quad \textbf{(15)}$$

The most popular method of measuring specific surface area is the gas sorption and data analysis method proposed by Brunauer, Emmett and Teller(1938). Their technique is known as BET method. While the BET method of measuring surface area is reproducible and easy to perform, it does have some limitations, particularly when results are to be applied to a solid suspended in water. The structure and surface characteristics of solids that interact strongly with water, such as metal oxides, can significantly change during the drying step required in BET method. Another method of determining surface area is by the retention of a polar liquid. Carter et al.(1965) introduced the use of ethylene glycol monethyl ether (EGME) as a polar molecule for determining the surface area of layer silicate minerals and soils. The convenient and rapid EGME method for estimation of surface area of soils and clays also involves assumptions and has limitations. One assumption is that EGME covered all interlayer and external surfaces. This assumption is difficult to prove. Because the experimental techniques employed to measure the specific surface area of finely divided solids vary so widely, the results vary significantly as well. For metal oxides, surface area measurements made with various methods typically differ by factor of 2 to 4 (Dzombak and Morel, 1990).

The value of site density has been determined either experimentally by tritium exchange (Davis and Leekie, 1978,1980), potentiometric titration (Balisterieri and Murray, 1981; Hohl and Stumn, 1976) fluoride adsorption (Sigg, 1979), maximum adsorption (Goldberg and Sposito, 1984a; Goldberg, 1985,1986a), calculated from crystal dimensions, or optimized to fit experimental adsorption data (Hayes et al., 1988). Site density estimates obtained for different methods typically differ by factor of 2 to 3 and sometimes more. Hayes et al. (1991) after doing sensitivity analysis for acid-base titration data on goethite, aluminum oxide and titanium oxide showed the models to be relatively insensitive to surface site density in the range 2-20 sites/nm^2.

To date, no method exists for independently measuring electrical double-layer capacitance parameters for oxide water systems (Hayes et al., 1991). CCM model required the value of C_1 and TLM required the value of inner capacitance (C_1) and outer capacitance (C_2). Goldberg (1992), pointed out that value of C_1 can be obtained from titration data. Based on direct measurements of the capacitance of AgI-electrolyte interface assumed the value of C_1 as 0.2 F/m^2 for TLM. However the applicability of these direct measurement to oxide surface is uncertain. Bousse and Bergveld (1983), made impedance measurements on SiO_2 coated, ion-sensitive field effect transistors and supported the C_2 value of 0.2 F/m^2 for oxides. Israelachvilli (1985) pointed out that theoretically range of capacitance value for various models can be calculated from the definition of integral capacitance.

$$C_1 = \frac{\in_T \in_D}{B} \qquad (16)$$

Given that range of reasonable values for $\in_T$ in the double -layer region is form 6 to 50 and that the distance of closest approach of a hydrated radius of a univalent ion is the range of 2.3 to 4.9 A^o , if the capacitance values are required to fit the titration data, the value of C_1 should be in the range of 0.1 to 2.0 F/m^2.

In general, values of intrinsic protonation and dissociation constants can be obtained for alkimetric or acidimetric titration curves carried out in the absence of specially adsorbing metal or ligand ions (Stumm et al., 1980). The two most common methods for determining surface equilibrium constants from titration data are by using objective curve fitting routines (Westall, 1982) or by graphical extrapolation methods(Davis and Hayes, 1986; James et al., 1978 and Kent et al., 1986). Graphical extrapolation technique involve plotting an approximation for conditional protolysis equilibrium constants given by

$$PO^* = -\log [H^+] \pm \log \left(\frac{\alpha}{1-\alpha} \right) \qquad (17)$$

versus the fractional ionization (Hayes et al., 1991).

where

$$\alpha = \frac{\alpha_O}{N_S} \text{ x } \left(\frac{N_A}{F} \right) \qquad (18)$$

Where (N_A/F) converts σ_O to net number of charged sites/m^2 to give the dimensionless fractional ionization. By plotting this graph according to these equations, the value of K^+ K^- are obtained by y-intercept. Graphical methods are tedious, less precise, difficult to apply to complex systems and often applicable only to limited experimental ranges. Also graphical methods may yield biased results due to approximations required to implement them (Dzombak and Morel, 1987; Westall, 1986) In contrast, non-linear optimization programs are fast, reproducible, bias-free and applicable to complex systems over extended ranges. Other advantages of non-linear optimization are that the same best fit criterion can be applied to all data set and error bars associated with parameter can readily be obtained. (Dzombak & Morel, 1990);

For this study, we have used FITEQL(Westall and Morel,1977;Westall, 1982). FITEQL is an iterative, gradient-directed non-linear least square optimization program based on the Gauss method (Bard, 1974; Gans, 1976) for unconstrained problems. The program is designed to determine the optimal valued of equilibrium constants or total component concentrations in a chemical adjustable parameters by changing their values until the sum of the squares of the residuals between the measured titration data and FITEQL calculated value is minimized. In general FITEQL convergence is most likely to occur when fitting data using only two adjustable parameters.

4.2 Materials and Methods

Clay mineral (attapulgite, illite, kaolinite & montmorillonite) samples used in this investigation were obtained from the Source Clay Mineral Repository of the Clay Minerals Society. Then these clay mineral were separated for the particle size <2μm fraction. Characterized samples of pure attapulgite, illite, kaolinite & montmorillonite were coated with hydrous oxides of Fe using the method of Chao et al. (1964). The coated material was characterized with respect to surface characteristics. Surface area was determined by ethylene glycol monoethyl ether (EGME) method (Carter et al., 1986). Values for surface area are given in the Table 4.3. The surface areas reported here along with assumed value of site density were used to calculate total number of sites.

4.2.1 Titration data: For obtaining potentiometric titration curves, 0.200 g of sample were weighed into each of a series of 60 ml plastic bottles. Each bottle contained 25ml of solution consisting of 0.001M $NaClO_4$ solution and a known concentration of acid and base. Samples were analyzed for pH and more $NaClO_4$ was added in each sample to increase the ionic strength to 0.01M. The samples were shaken for 30 minutes and pH values determined again. This process was repeated again so that there was a total of three pH values for each sample representing ionic strengths of 0.001, 0.01, and 0.1 M $NaClO_4$. At all times samples were stirred to prevent settling and maintained under argon atmosphere. Whenever a bottle was opened, it was refilled with argon. Acid/alkali was added using 100 & 1000μl Eppendorf pipettes. After pH measurements, the samples were individually centrifuged and filtered. Each of the supernatants was weighed and back titrated to original pH to determine amount of H^+/OH^- adsorbed by the mineral species. The back titrations were done with an auto titrating system. The same procedure was used for obtaining potentiometric titration data for all the samples.

Table 4.3: Surface area (m2/g) of clay minerals

Solid	**Amount of coatings**		
	0%	4% Fe	4% Al
Attapulgite	306.7	171.1	249.6
Illite	113.2	74.5	65.5
Kaolinite	40.2	29.7	25.2
Montmorillonite	589.5	533	536.2

4.2.2 Sensitivity Analysis

Each Surface Complexation has a different number of adjustable parameter, so different sensitivity analysis strategies were implemented.

DLM Sensitivity Analysis: DLM has three adjustable parameters log K^+, log K^-, and N_T. So sensitivity analysis was done varying the value of N_T in the FITEQL input file and observing the effect on the optimized values of log K^+ and logK^{-1}.

CCM Sensitivity Analysis: CCM has four adjustable parameters log K^+, log K^-, C_1, and N_T. log K^+, log K^- are optimized by varying the value of C_1 and N_T.

TLM Sensitivity Analysis: In the case of TLM, there are six adjustable parameter log K^+, log K^-, C_1, N_T, log K_{an} and log K_{ca}. C_1 value of 0.2 F/m^2 has been used as reported by Westall and Hohl (1980) and Davis et al. (1978). Another constraint which was used is the relationship

$$\left(\frac{\log K^+ + \log K^-}{2}\right) = pH_{PZSE} \qquad (19)$$

This was used to reduce the degree of freedom by one. The value of pH_{PZSE} for all the clay minerals is given in Table 4.4. This relationship was used to estimate the value of log K^+ and log K^- for TLM sensitivity analysis,. FITEQL will never converge if the protolysis constants and electrolyte binding constants are simultaneously declared as adjustable parameters, a consequence of interdependence of surface reactions. The values of N_T and C_1 were systematically varied, one variable at a time in the input file and best fit values of equation were obtained by FITEQL.

Tabel 4.4: Point of zero salt effect (PZSE) of different clay minerals

Solid	**Amount of coatings**		
	0%	4% Fe	4% Al
Attapulgite	4.05	4.3	4.72
Illite	3.1	4.15	4.65
Kaolinite	4.35	6.02	5.41
Montmorillonite	<2.47	<3.81	<3.46

4.2.3 Estimation of Goodness of fit: This was done by overall variance, Vy, which is the weighted sum of squares of residuals divided by the degrees of freedom (SOS/DF)

$$Vy = \frac{SOS}{\mathbf{DF}} = \frac{\Sigma[\ Y_R(m)/S_R(m)]^2}{\mathbf{N_P N_R - N_u}} \qquad (20)$$

where

Y_R= TOTR(calc)-TOTR(expt) for all component (i.e. those for which both the total concentration and free concentration are known)

S_R= is error calculated from the experimental error estimates. The value of experimental error S_R is calculated form propagation of experimental error

$$S^2_{R(m)} = \left(\frac{\delta y}{\delta T_{I,II}}\right)\Bigg|_m^2 S^2_{T\ I,II(m)} + \frac{\delta y}{\delta x_{II,III}}\Bigg|_m^2 S^2 x_{II<III(m)} \qquad (21)$$

Where S_T & S_X are estimated errors in the experimentally measured $T_{I,II}$ and $X_{II,III}$. It is assumed that errors in T' s and X' s are independent such that cross terms can be neglected.

$$\sum_m \left(\frac{\delta y}{\delta_T}\right)\left(\frac{\delta y}{\delta_X}\right) \delta_T\delta_X = 0 \qquad (22)$$

The derivatives that appear in the error propagation equation are calculated from the chemical equilibrium equations. The value of $S_T(m)$ and $S_X(m)$ that are necessary to complete the error propagation should be supplied as input for all m titration points. It is more practical to calculate $S_T(m)$ and $S_x(m)$ from the following formulae:

$$S_T(m)= S_T(abs)+S_T(rel)* T(m) \qquad (23)$$

$$S_X(m)= S_X(abs)+S_X(rel)* X(m) \qquad (24)$$

Where S(abs) and S(rel) are estimates for the absolute and relative errors in experimental measurements. In all FITEQL runs reported, unless otherwise noted, the assumed absolute and relative errors of the titration data points were chosen to be representative of those errors expected in titration experiments. Typical values were 0.01 for relative error and $2.0x10^{-6}$ M absolute error (Hayes et al., 1990).

$\mathbf{N_P}$ = number of data point

$\mathbf{N_R}$= the number of components for which both the total and the free concentrations are known.

$\mathbf{N_U}$ = the number of adjustable parameters. The goodness of fit of the proposed model to the data is indicated by the proximity of Vy to 1. The value of Vy depends on the experimental error estimates and Westall(1982) noted that values of Vy between 0.1 to 20 indicate a reasonable good fit values of Vy greatly in excess of 20 indicate that the model is inappropriate, while values significantly less than 0.1 generally indicate that the model has too many adjustable parameters.

4.3 Results and Discussions

As the purpose of this work was to evaluate the merits of each model so the sensitivity analysis results for each model are discussed separately.

4.3.1 Diffuse double layer: The effects of different ionic strength (0.001, 0.01, and 0.1 M) and N_S (1 to 100 sites/nm2) on the best fit value of protolysis constants for all the clay minerals were evaluated .

Sensitivity analysis for pure clay minerals: For all pure clay minerals titration data set , FITEQL best fit values for log K^+ and log K^- decreased with increasing value of N_S (Table 4.5, Figures 4.1-4.3) .The explanation for this trend is that in order for the computed number of protons released or consumed at a given pH to fit the titration data for different values of $N_{S,}$ it is necessary that the surface constants decrease as N_S increases (Hayes et al., 1990) . For attapulgite, illite, kaolinte, and montmorillonite data set, based on F values, slightly better fits were obtained at all the three ionic strengths for N_S less than 10 site/nm^2 compared to fit obtained for N_S between 10 and 100 sites/nm^2. Generally better FITEQL fits were obtained at lower ionic strength as compared to higher ionic strength which is consistent with the findings of Hayes et al. (1990), who reported that based on the theoretical consideration, the DDL, are often limited to lower ionic strength conditions. Moreover, Dzombak and Morel (1990) also reported that DLMs usually over predict the diffuse layer potential at high ionic strength, so for modeling purpose it is restricted to low ionic strength conditions. DDL fits better for attapulgite and kaolnite as compared to illite and montmorillonite regardless of N_S and ionic strength.

Table 4.5: Sensitivity of DLM to variation in total site density for pure clay minerals.

		Attapulgite			**Illite**			**Kaolinte**	
IS	**N_S**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**
0.001	1	5.43	-8.712	12.8	5.55	-6.76	53.6	6.64	-5.96
0.001	10	4.35	9.782	14.9	4.34	-8.14	58.5	4.86	-7.75
0.001	100	3.35	-10.78	15.1	3.32	-9.17	58.8	3.82	-8.79
0.01	1	4.54	-9.087	18.1	4.25	-7.07	51.2	4.83	-6.887
0.01	10	3.49	-10.185	22.8	2.998	-8.732	78.9	3.64	-8.407
0.01	100	2.48	-11.194	23.2	1.98	-9.782	80.7	2.62	-9.44
0.1	1	3.85	-9.505	50.5	3.23	-7.22	55.8	4.13	-7.383
0.1	10	2.776	-10.67	59.7	2.13	-9.582	106.6		
0.1	100	1.79	-11.69	60.6	1.12	-10.05	108.6		

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

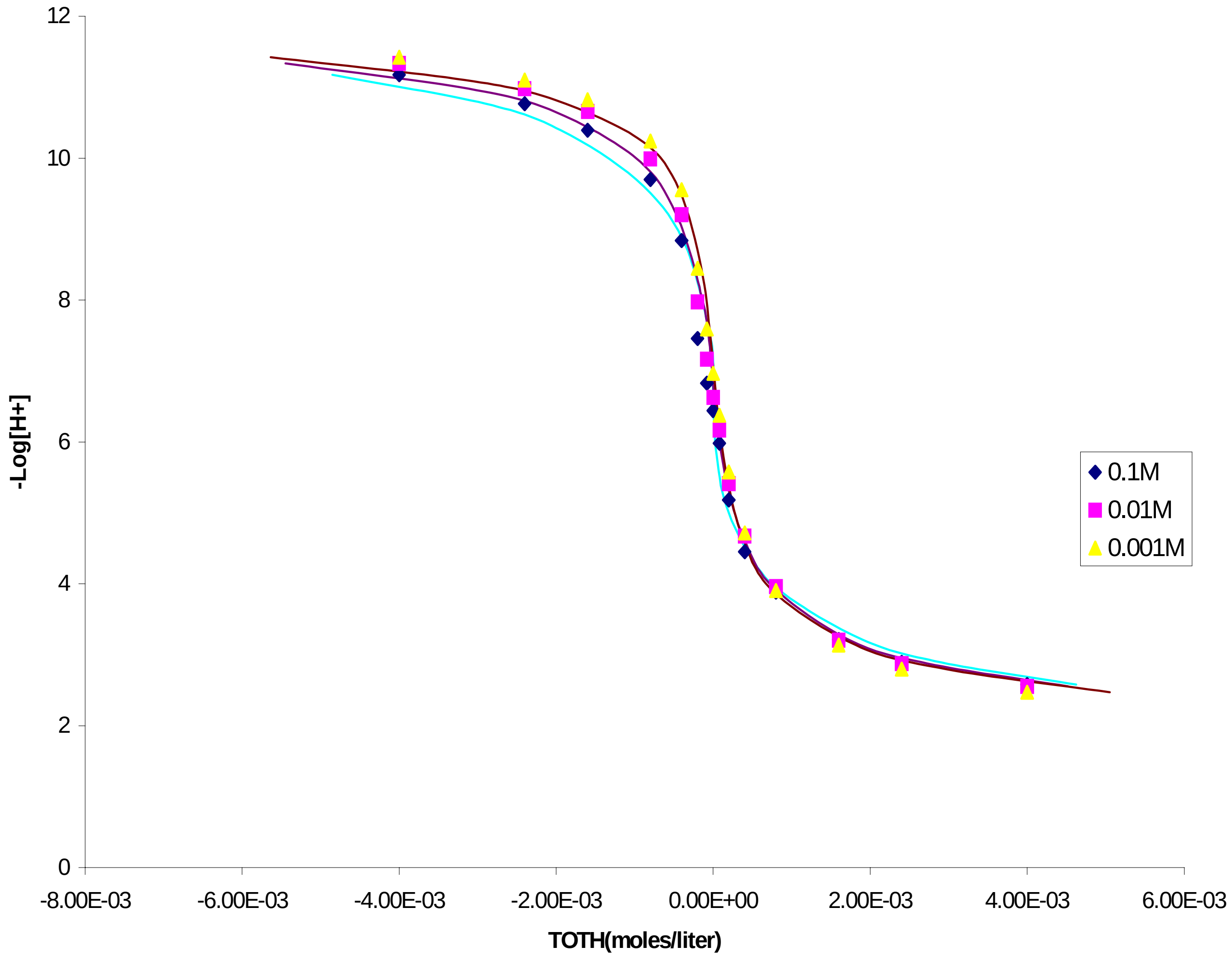

Figure 4.1 Diffuse double layer model fits of titration data for suspension of pure attapulgite

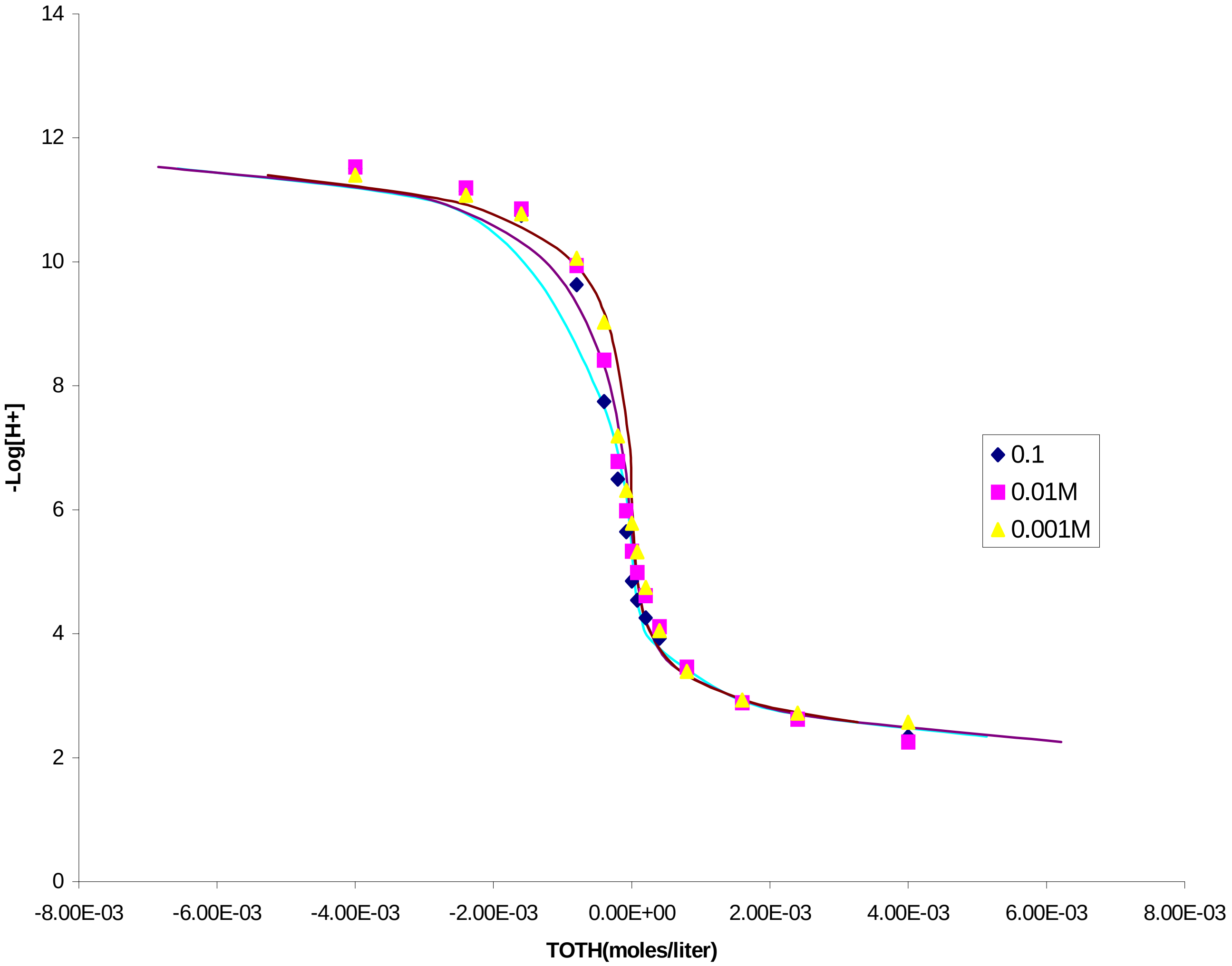

Figure 4.2: Diffuse layer model fit of titration data for suspension of pure illite

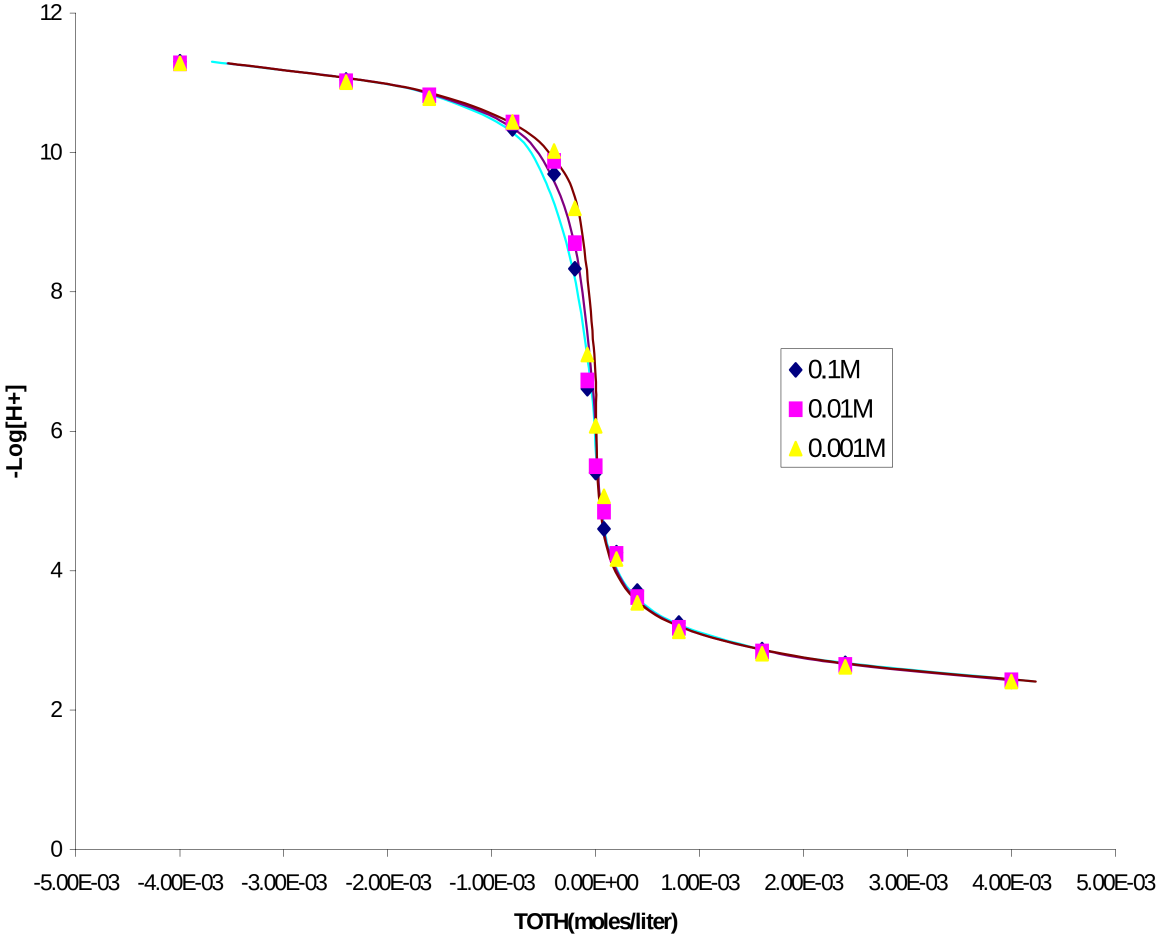

Figure 4.3: Diffuse -layer model fits of titration data for suspension of pure kaolinite

Sensitivity analysis for coated clay minerals: Same trend of decreasing log K+ and log K- with increase in the value of N_S was observed for both iron coated (4%) and aluminum coated clay minerals (Tables 4.6, 4.7, Figures 4.4-4.9). For all the coated clay minerals data set (at all ionic strength) better F values were obtained for N_S below 10 sites/nm^2 as compared to F value obtained for N_S between 10 and 100 sites/nm^2. James and Parks (1982) reported that if the range of site density value is limited to value typical of nonporous microcrystalline oxides (2 to 20 sites/nm^2), one should be able to arrive at a unique set of surface constants for DLM using FITEQL and titration data. Based on F value, the iron coated clay titration data fitted better as compared to Al coated clay titration data. The reason for this is not very obvious but it may be that the complex surface chemistry of Al coated minerals cannot be represented by simple DLM. Among Fe coated clays, there is no data convergence for attapulgite and kaolinte at 0.001 M ionic strength and best fit F values were obtained at 0.01 M ionic strength. For iron coated illite there was data convergence at 0.001 M ionic strength when the N_S value was 10 and 100. In illite good fit F value was obtained at ionic strength of 0.1 M and N_S of 1. For montmorillonite best fit F values were obtained at 0.001 M ionic strength.

Effect of Coatings on DLM best fit values: For kaolinite best fit F values were obtained for 0% coating and not to 4% iron and aluminum coatings (Table 4.10). Generally for attapulgite, illite and montmorillionite, based on the F values better fits were obtained for the 4 % iron coated clay minerals titration data compared to either pure and 4 % aluminum coated clay minerals regardless of ionic strength and site density. (Tables 4.8, 4.9, 4.11).

Table 4.6: Sensitivity of DLM to variation in total site density for 4 % iron coated clay minerals

		Attapulgite			**Illite**			**Kaolinte**			**Montmorillonite**		
IS	**N_S**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**
0.001	1	4.527	-4.73	18.5			NC			NC	6.04	-8.061	27.2
0.001	10			NC	5.41	-8.065	49.6			NC	4.91	-9.196	28.6
0.001	100			NC	4.37	-9.109	49.7			NC	3.9012	-10.207	28.7
0.01	1	5.55	-7.763	14.5	5.64	-5.8	21.6			NC	4.32	-8.841	49.6
0.01	10	4.36	-9.009	24.5	3.95	-8.008	55.8	4.59	-7.47	36.6	3.27	-9.968	57.2
0.01	100	3.34	-10.027	25.3	2.93	-9.075	58.3	3.56	-8.57	38.2	2.26	-10.97	57.9
0.1	1	4.62	-8.159	15.6	4.22	-6.341	53.9			NC	3.36	-8.676	71
0.1	10	3.47	-9.468	113.9	2.799	-8.408	70.4	4.08	-7.839	23.9	2.32	-9.79	80.3
0.1	100	2.45	-10.495	45.5	1.779	-9.532	76.9	3.02	-8.98	29	1.32	-10.8	81.1

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

Table 4.7: Sensitivity of DLM to variation in total site density for 4 % aluminum coated clay minerals

		Attapulgite			**Illite**			**Kaolinite**			**Montmorillonite**		
IS	**N_S**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^+**	**F**	**Log K^+**	**Log K^-**	**F**
0.001	1			NC			NC			NC	6.43	-7.54	162
0.001	10			NC			NC			NC	5.23	-8.77	164.2
0.001	100			NC			NC			NC	4.22	-9.79	164.4
0.01	1	5.73	-7.09	45			NC			NC	4.36	-7.78	196.8
0.01	10	4.41	-8.508	52.1	4.85	-7.31	114.1	4.85	-7451	47.4	3.16	-9.118	238.1
0.01	100	3.4	-9.535	52.8	3.79	-8.4	116.1	3.81	-8.53	48.2	2.15	-10.14	241.1
0.1	1	4.55	-7.674	68.1			NC			NC	3.08	-8.5	323.2
0.1	10	3.49	-9.043	95.6	3.573	-7.936	114.7	4.02	-7.83	49.6	2.07	-10.06	339.6
0.1	100			NC	2.51	-9.077	154.7	3.03	-8.81	83.4	1.07	-11.09	340

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

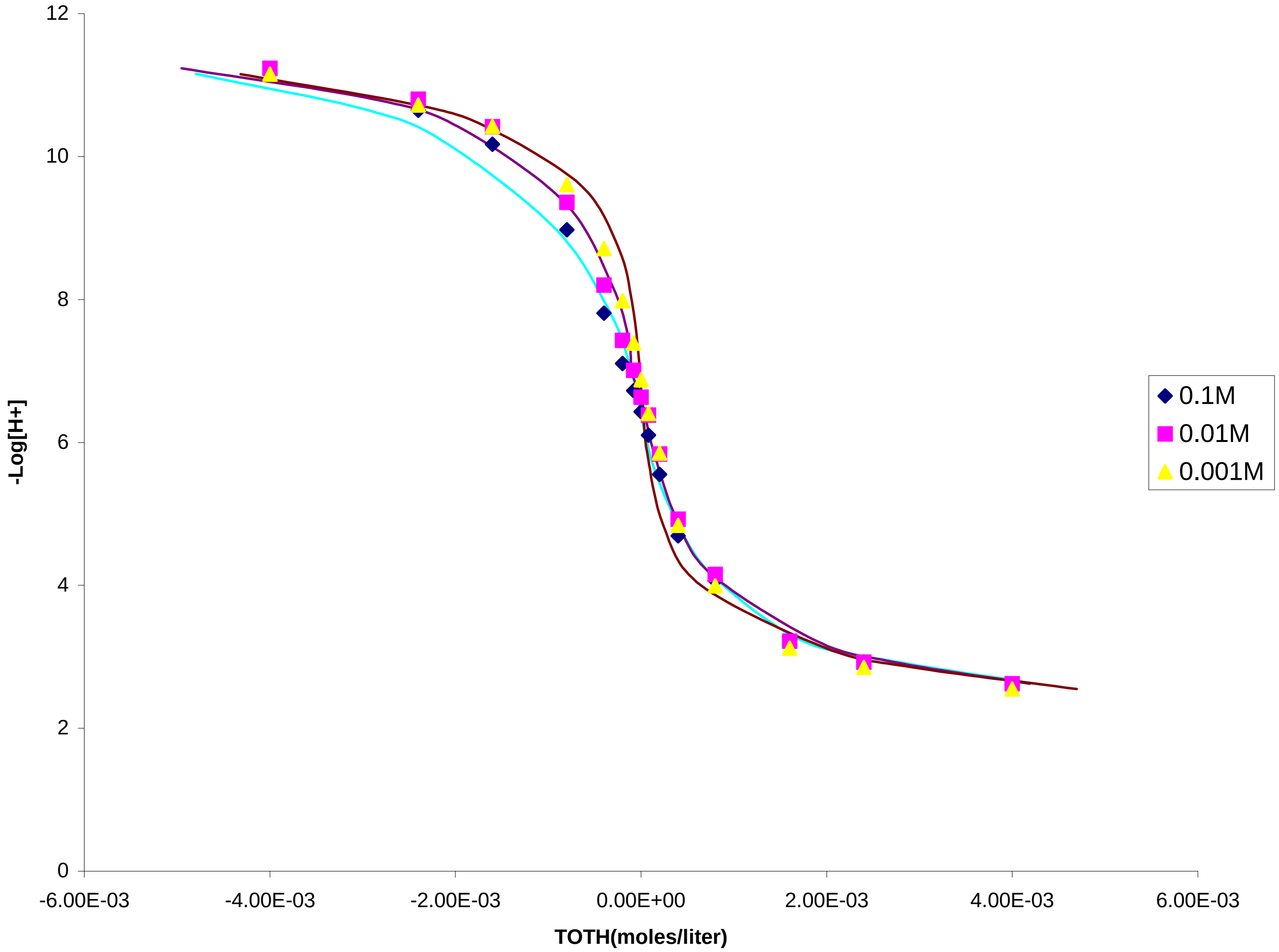

Figure 4.4 : Diffuse double layer model fit of titration data for suspension of 4% iron coated attapulgite

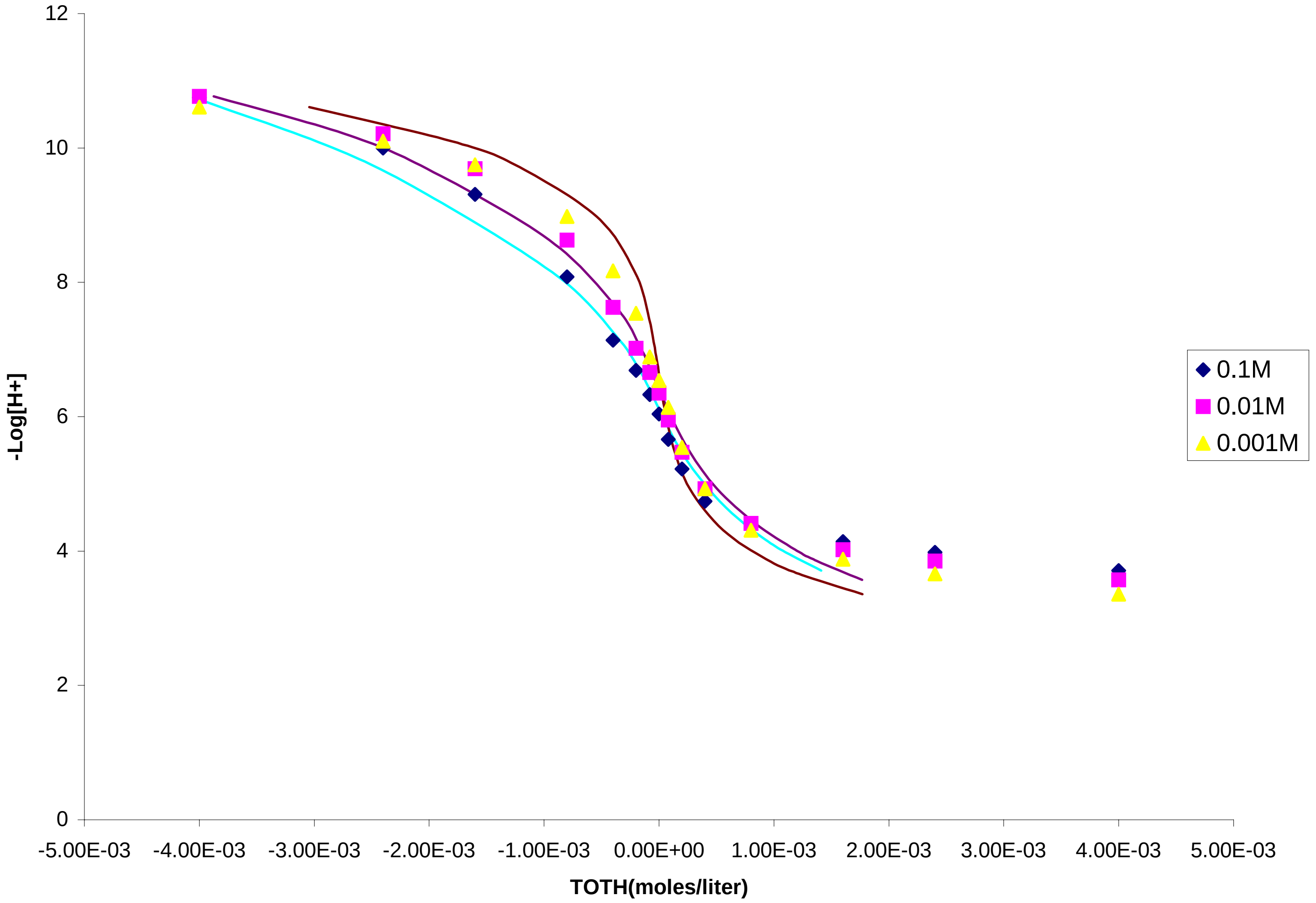

Figure 4.5: Diffuse-layer model fit of titration data for suspension of 4% aluminum coated attapulgite

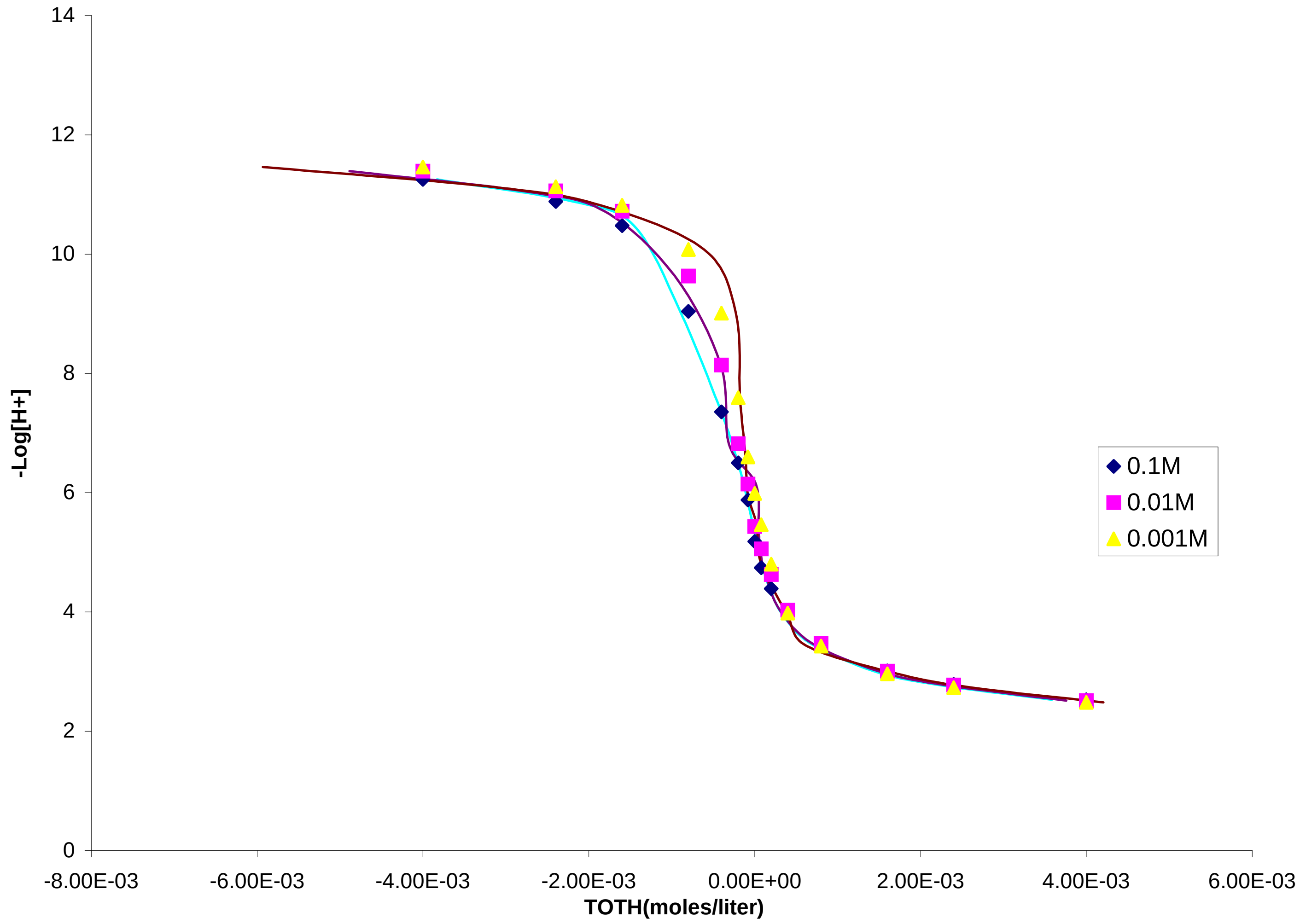

Figure 4.6: Diffuse-double layer model fit of titraiton data for suspension of 4% Fe coated illite

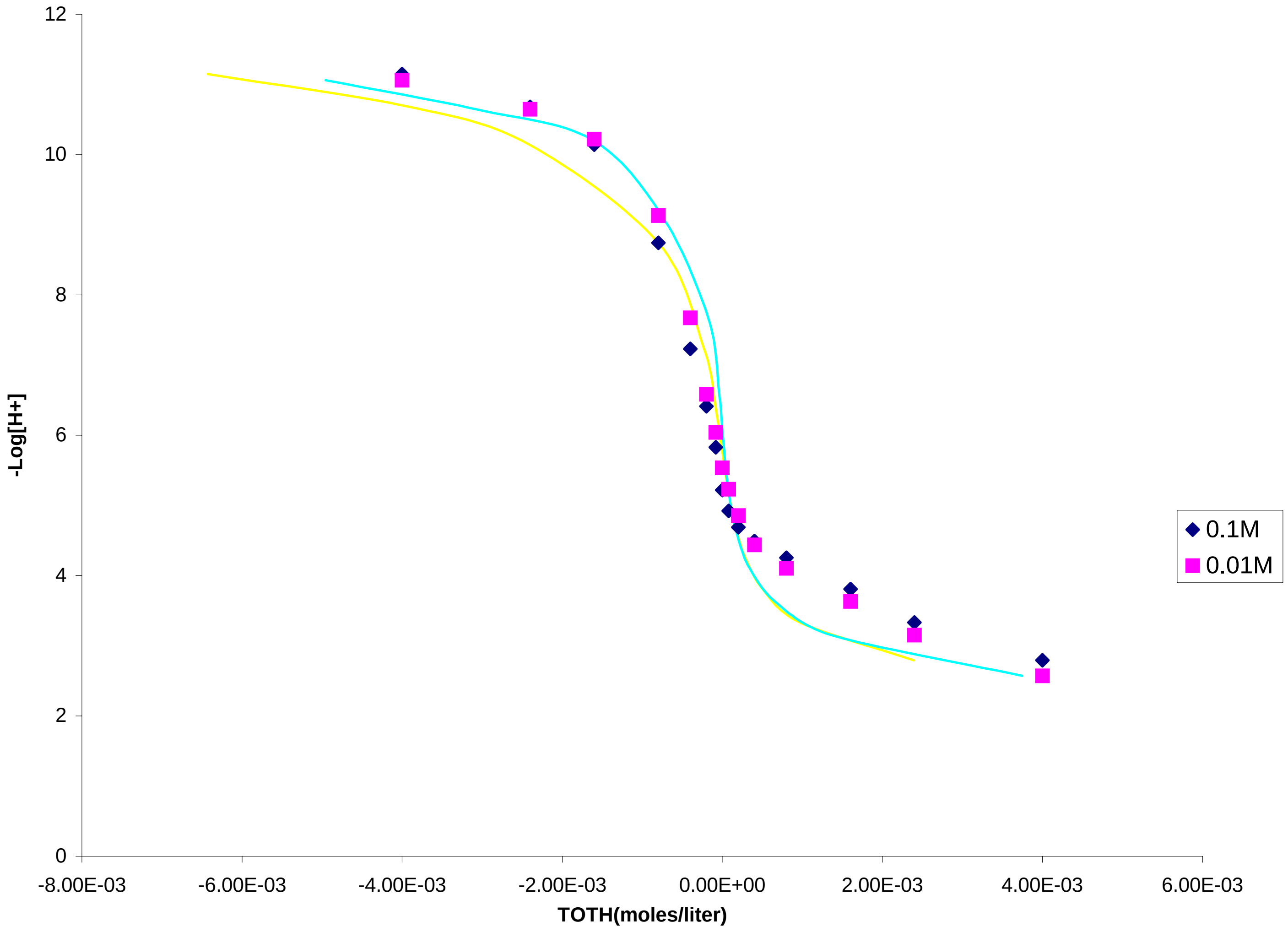

Figure 4.7: Diffuse-double layer model fit of titration data for suspension of 4% aluminum coated illite

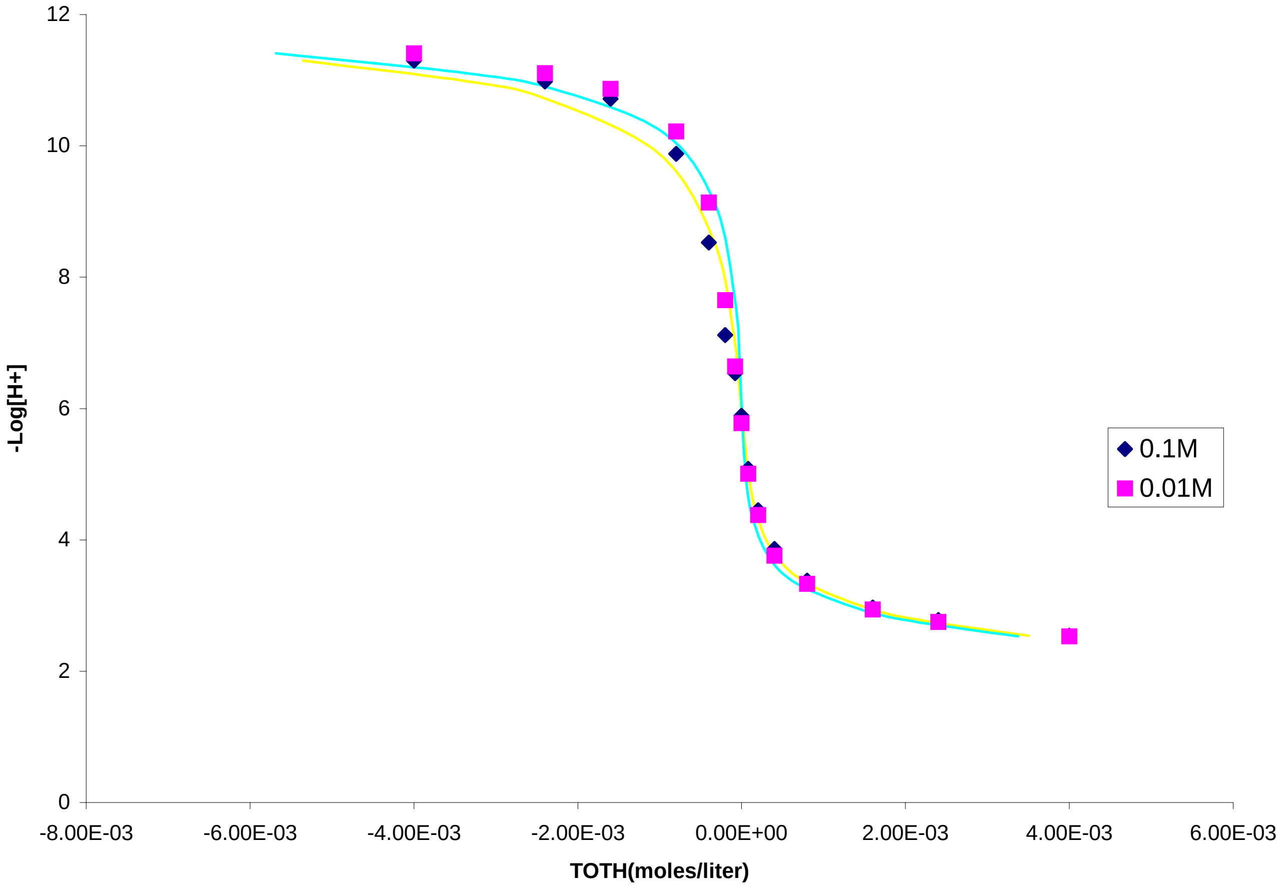

Figure 4.8: Diffuse double layer model fit of titration data for suspension of 4% iron coated kaolinite

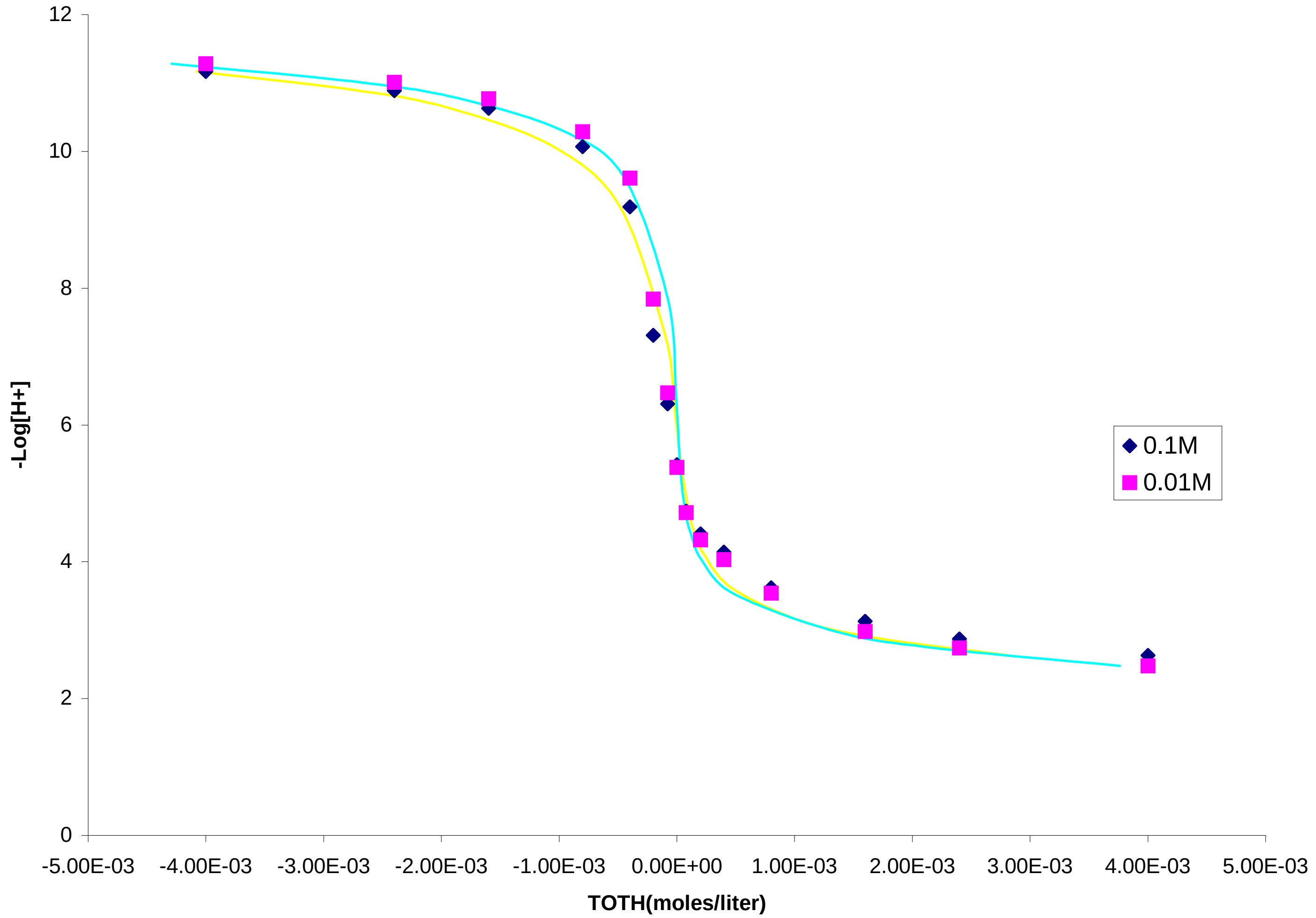

Figure 4.9: Diffuse layer model fit of titraion data for suspension of 4% aluminum coated kaolinite

Table 4.8: Effect of coatings on DLM best fit value of protolysis constants for attapulgite.

		0%			Fe 4%			Al 4%		
IS	**N_S**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**
0.001	1	5.43	-8.712	12.8	4.527	-4.73	18.5			NC
0.001	10	4.35	9.782	14.9			NC			NC
0.001	100	3.35	-10.78	15.1			NC			NC
0.01	1	4.54	-9.087	18.1	5.55	-7.763	14.5	5.73	-7.09	45
0.01	10	3.49	-10.185	22.8	4.36	-9.009	24.5	4.41	-8.508	52.1
0.01	100	2.48	-11.194	23.2	3.34	-10.027	25.3	3.4	-9.535	52.8
0.1	1	3.85	-9.505	50.5	4.62	-8.159	15.6	4.55	-7.674	68.1
0.1	10	2.776	-10.67	59.7	3.47	-9.468	113.9	3.49	-9.043	95.6
0.1	100	1.79	-11.69	60.6	2.45	-10.495	45.5			NC

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

Table 4.9: Effect of coatings on DLM best fit value of protolysis constants for illite.

		0%			Fe 4%			Al 4%		
IS	**N_S**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**
0.001	1	5.55	-6.76	53.6			NC			NC
0.001	10	4.34	-8.14	58.5	5.41	-8.065	49.6			NC
0.001	100	3.32	-9.17	58.8	4.37	-9.109	49.7			NC
0.01	1	4.25	-7.07	51.2	5.64	-5.8	21.6			NC
0.01	10	2.998	-8.732	78.9	3.95	-8.008	55.8	4.85	-7.31	114.1
0.01	100	1.98	-9.782	80.7	2.93	-9.075	58.3	3.79	-8.4	116.1
0.1	1	3.23	-7.22	55.8	4.22	-6.341	53.9			NC
0.1	10	2.13	-9.582	106.6	2.799	-8.408	70.4	3.573	-7.936	114.7
0.1	100	1.12	-10.05	108.6	1.779	-9.532	76.9	2.51	-9.077	154.7

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

Table 4.10: Effect of coatings on DLM best fit value of protolysis constants for kaolinite.

		0%			Fe 4%			Al 4%		
IS	**N$_S$**	**Log K$^+$**	**Log K$^-$**	**F**	**Log K$^+$**	**Log K$^-$**	**F**	**Log K$^+$**	**Log K$^-$**	**F**
0.001	1	6.64	-5.96	20.5			NC			NC
0.001	10	4.86	-7.75	19.9			NC			NC
0.001	100	3.82	-8.79	19.9			NC			NC
0.01	1	4.83	-6.887	12.9			NC			NC
0.01	10	3.64	-8.407	10.3	4.59	-7.47	36.6	4.85	-7451	47.4
0.01	100	2.62	-9.44	18.7	3.56	-8.57	38.2	3.81	-8.53	48.2
0.1	1	4.13	-7.383	26.4			NC			NC
0.1	10			NC	4.08	-7.839	23.9	4.02	-7836	49.6
0.1	100			NC	3.02	-8.98	29	3.03	-8.81	83.4

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

Table 4.11:Effect of Coatings on DLM best fit value of protolysis constant for montmorillonite.

		0%			Fe 4%			Al 4%		
IS	**N$_S$**	**Log K$^+$**	**Log K$^-$**	**F**	**Log K$^+$**	**Log K$^-$**	**F**	**Log K$^+$**	**Log K$^-$**	**F**
0.001	1	5.14	-8.753	36.9	6.04	-8.061	27.2	6.43	-7.54	162
0.001	10	4.099	-9.814	38.5	4.91	-9.196	28.6	5.23	-8.77	164.2
0.001	100	3.09	-10.82	38.6	3.9012	-10.207	28.7	4.22	-9.79	164.4
0.01	1	3.707	-9.23	69.3	4.32	-8.841	49.6	4.36	-7.78	196.8
0.01	10	2.69	-10.34	72.8	3.27	-9.968	57.2	3.16	-9.118	238.1
0.01	100	1.69	-11.35	73.1	2.26	-10.97	57.9	2.15	-10.14	241.1
0.1	1	1.583	-8.91	14.15	3.36	-8.676	71	3.08	-8.5	323.2
0.1	10	1.87	-10.766	104	2.32	-9.79	80.3	2.07	-10.06	339.6
0.1	100	0.813	-11.77	105	1.32	-10.8	81.1	1.07	-11.09	340

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

4.3.2 Constant Capacitance model: The effects of changes of N_S and C_1 on the best fit values of the surface hydrolysis constants were evaluated

Sensitivity analysis for pure clay minerals: For a given value of C_1 and ionic strength , the effect of site density (N_S) on the best fit values of surface protolysis constants was to the DLM computations (Table 4.12, Figures 4.10-4.12) i.e. Log K^+ and Log K^- decreased with increasing N_S. Similarly for given N_S and ionic strength Log K^+ and Log K^- decreased with increasing C_1. This can be explained (if the interfacial region is viewed as parallel- plate capacitor) by greater screening by counter ion charges as the value of C_1 increases (Hayes et al., 1991). So in terms of fitting the titration data, the value of protolysis constants, have to decrease in order to compensate for effective increase in acidity (proton release) which results from enhanced charge screening on C_1 increases. In general, for all the clay minerals, the CCM did not converge for C_1 values below 0.6 F/m^2 and above 1.2 F/m^2. Generally, for all the clay minerals for a given value of C_1 and N_S as the ionic strength of the data set increased the optimized value of log K^+ and log K^- decreased. Reasonable good fit (F <20) was observed for kaolinite at all ionic strength (0.001, 0.01,and 0.1 M) and wide range of N_S (1 to 100 sites/nm^2) and C_1 (0.2 to 1.2 F/m^2). For all the minerals at same ionic strength, as the value of N_S increased (keeping the value of C_1 constant) the F value also increased. Similarly for the same $N_{S,}$ as C_1 increased the value of F also increased. For illite and montmorillonite as the ionic strength increased for a given C_1 and $N_{S,}$ the F value also increased. For attapulgite relatively better fit was observed at 0.1M ionic strength.

Table 4.12: Sensitivity of CCM to variation in total site density, ionic strength and capacitance for titration data of pure clay minerals

			Attapulgite			**Illite**			**Kaolnite**			**Montmorillonite**		
IS	N_S	**C**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**
0.001	1	0.8	4.1	-10.16	55.1	4.08	-7.98	30.2	4.46	-7.83	9.8	4.12	-10.35	76.7
0.001	1	1	3.98	-10.31	66.8	3.98	-8.3	40.8	4.33	-8.13	13.1	4.05	-10.4	90.6
0.001	1	1.2	3.88	-10.42	75.7	3.92	-8.6	48.9	4.24	-8.41	15.9	3.99	-10.54	102.3
0.001	10	0.8	3.01	-11.2	63.2	3	-9.27	39.9	3.36	-9.09	12.3	3.07	-11.43	86.1
0.001	10	1	2.87	-11.4	76.6	2.92	-975	52.1	3.22	-9.51	16.4	2.98	-11.54	103.4
0.001	10	1.2	2.76	-11.54	86.9	2.86	-10.07	58.8	3.13	-9.82	18.9	2.9	-11.63	119.5
0.001	100	0.8	2.01	-12.27	63.9	2	-10.29	40.6	2.35	-10.11	12.6	2.07	-12.44	87
0.001	100	1	1.86	-12.43	77.5	1.92	-10.78	52.8	2.21	-10.54	16.6	1.98	-12.55	105.1
0.001	100	1.2	1.75	-12.55	87.9	1.85	-11.09	59.4	2.12	-10.85	19.1	1.89	-12.64	121.1
0.01	1	0.8	4.05	-9.8	48.3	3.8	-7.49	40.9	4.23	-7.303	8.3	3.46	-9.99	84.2
0.01	1	1	3.96	-9.972	58.9	3.72	-7.75	52.6	4.11	-7.59	10.8	3.42	-10.14	93.1
0.01	1	1.2	3.88	-10	67	3.67	-7.99	62.1	4.05	-7.82	13.4	3.39	-10.26	100.5
0.01	10	0.8	2.99	-10.92	55.7	2.74	-8.78	53.7	3.14	-8.582	10.7	2.44	-11.09	90.2
0.01	10	1	2.878	-11.1	68	2.66	-9.25	70.05	3.04	-8.99	14.8	2.39	-11.27	101
0.01	10	1.2	2.78	-11.8	77.9	2.611	-9.62	80.14	2.98	-9.31	17.8	2.35	-11.39	109.6
0.01	100	0.8	1.98	-11.9	56.4	1.73	-9.79	54.6	2.13	-9.06	10.9	1.44	-12.1	90.7
0.01	100	1	1.87	-12.11	66.8	1.65	-10.28	71	2.03	-10.01	15.1	1.39	-12.28	101.7
0.01	100	1.2	1.77	-12.33	78.8	1.6	-10.64	80.9	1.97	-10.35	18.1	1.359	-12.4	110.4
0.1	1	0.8	3.86	-9.42	46	3.27	-7.02	32.4	4.17	-6.99	5.44	2.88	-9.54	94.6
0.1	1	1	3.77	-9.61	54.9	3.21	-7.22	42.4	4.04	-7.25	7.15	2.86	-9.727	101
0.1	1	1.2	3.71	-9.76	61.5	3.17	-7.36	50.8	3.97	-7.44	8.96	2.83	-9.86	105.1
0.1	10	0.8	2.8	-10.4	52.2	2.21	-8.28	47	3.07	-8.24	7.33	1.86	-10.67	99.2
0.1	10	1	2.71	-10.74	62.3	2.14	-8.63	65.5	2.96	-8.59	10.96	1.84	-10.86	105.6
0.1	10	1.2	2.63	-10.87	70.6	2.11	-8.99	81.3	2.89	-8.88	14.5	1.81	-10.99	110.2
0.1	100	0.8	1.8	-11.56	52.8	1.2	-9.29	47.9			NC	0.86	-11.6	99.6
0.1	100	1	1.7	-11.75	63	1.14	-9.66	66.8			NC	0.83	-11.8	106
0.1	100	1.2	1.62	-11.88	71.5	1.1	-10.02	82.8			NC	0.82	-12	110.6

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

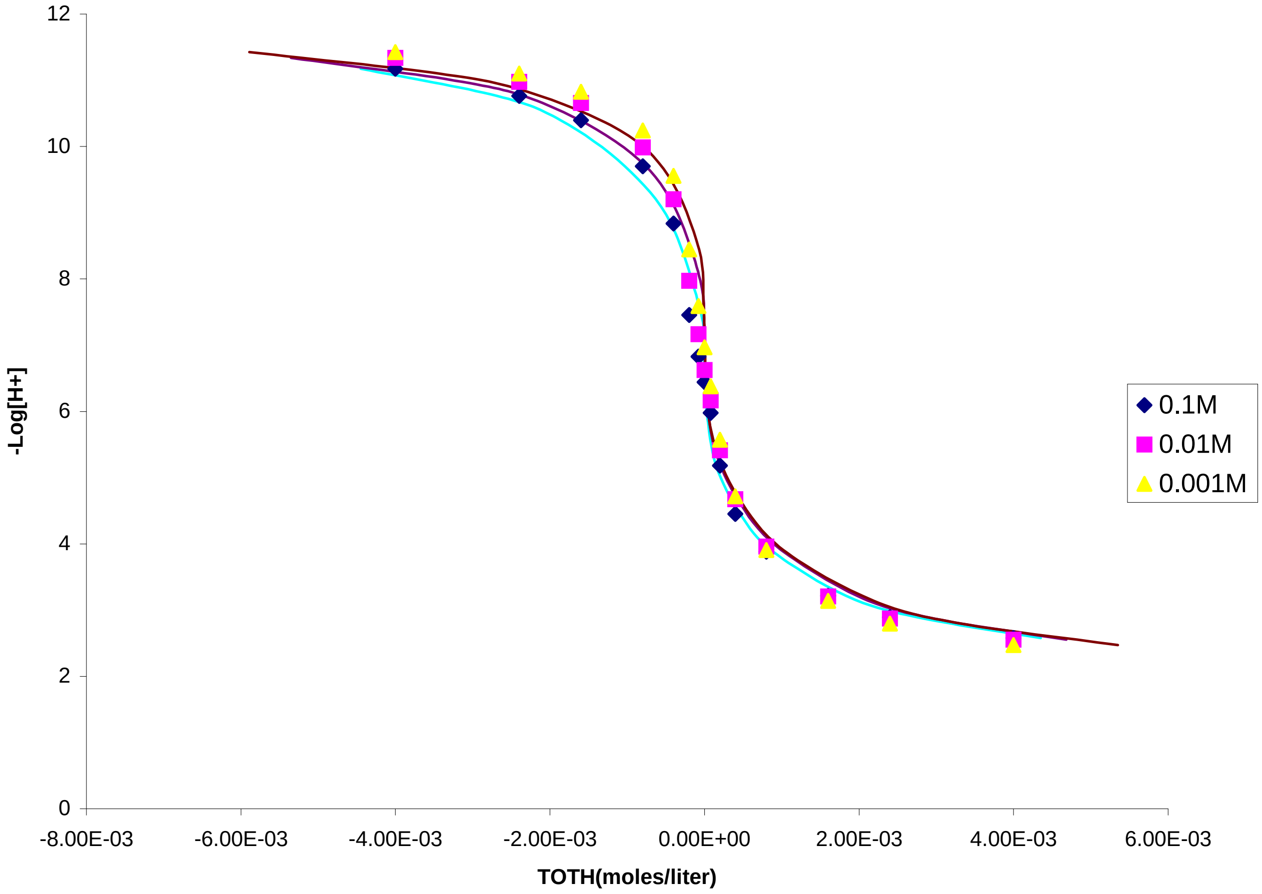

Figure 4.10 :Constant capacitance model fit of titration data suspension of pure attapulgite

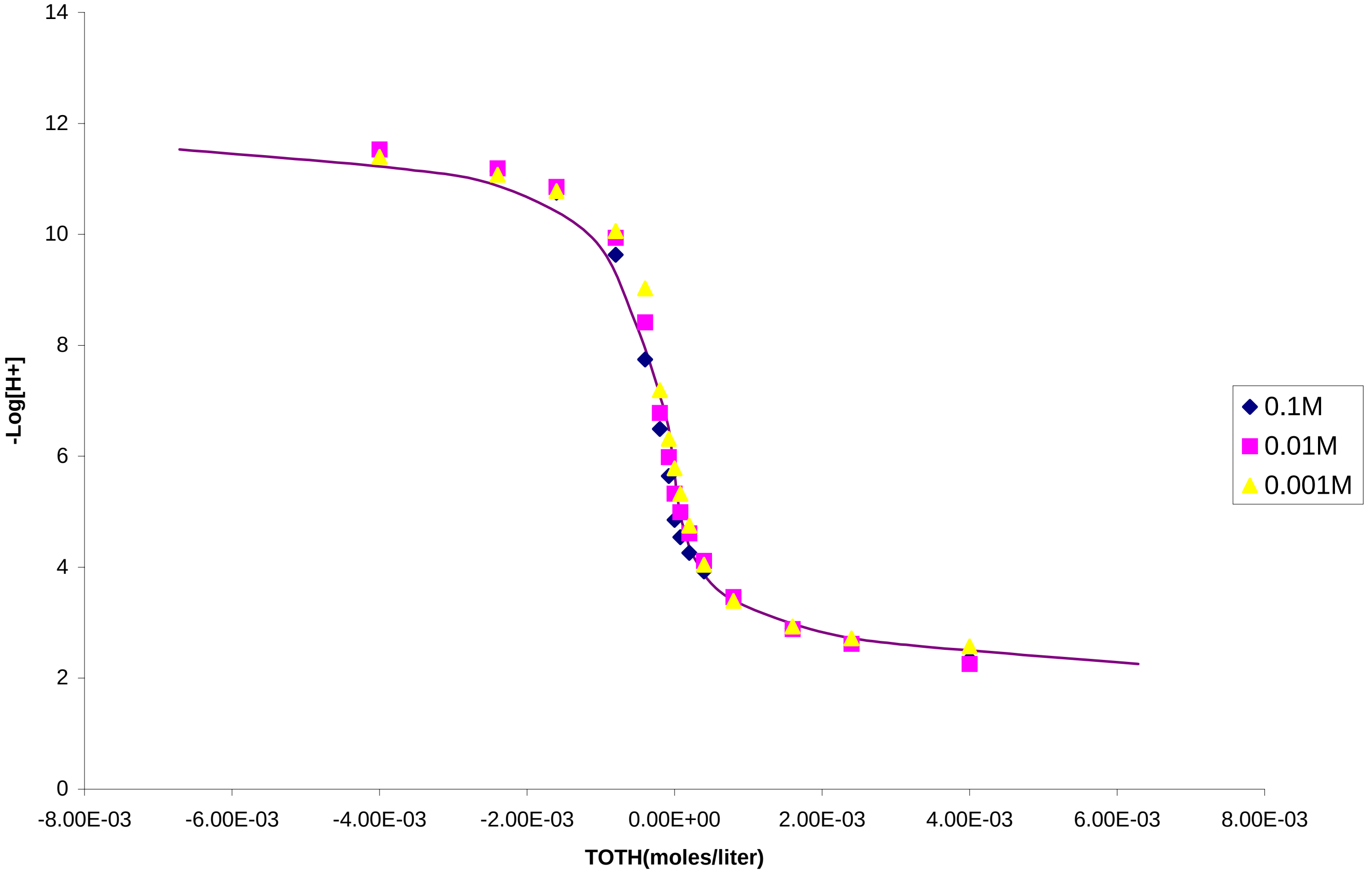

Figure 4.11: Constant capacitance model fit of titration data suspension of pure illite

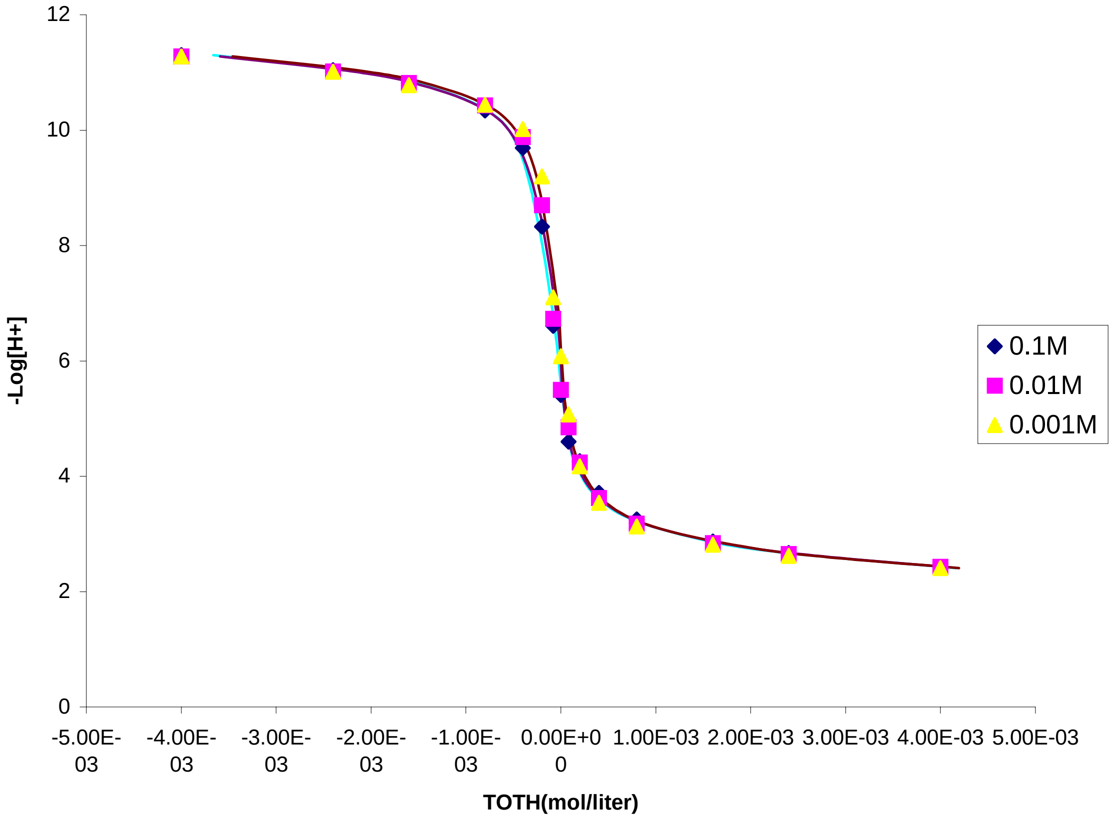

Figure 4.12: Constant capacitance model fits of titration data for suspension of pure kaolinite

Sensitivity analysis for coated clay minerals: Better fits were observed for Fe coated clay minerals as compared to Al coated clay minerals (Tables 4.13-4.14, Figures 4.13-4.18).The reason for that is high reactivity of Fe oxide coatings as compared to Al oxide coatings (Hendershot and Lavkulich,1983) Lower F values were observed for Fe coated kaolinite as compared to all other clay minerals. Generally trends were similar to pure clay minerals in the sense that as the ionic strength increased the optimized value of log K^+ and log K^- decreased for both Fe and Al coated clays. Best fit F values were observed at 0.01 M ionic strength for iron and aluminum coated kaolinite and illite.

Effect of coatings on CCM fit: Best fit F values were obtained for 0% coated kaolinite as compared to 4 % iron and aluminum coated kaolinite (Table 4.17). Optimized value of log K^+ and log K^- are insensitive to changes in Ns (1 to 100) and C (0.8 to 1.2 F/m2). In case of attapulgite, illite and montmorillionite best fit F values are obtained at 4% iron coating as compared to 0% and 4 % Al coatings (Tables 4.15,4.16,4.18). Iron coated attapulgite and montmorilionite are insensitive to change in Ns and C_1.

4.3.3 Triple layer model: The effects of changes of Ns and C_1 on the best fit values of the electrolyte surface reaction constants were evaluated.

Sensitivity analysis for pure clay minerals: Increasing the value of Ns resulted in decreasing values of Log K_{AN} and Log K_{CA} for kaolinite and illite at all the ionic strengths (Table 4.19, Figures 4.19-4.21) and the reason for that as explained in DLM and CCM is that in order for the computed number of proton released or consumed at a given pH to fit the titration data for different value of Ns, it is necessary that surface constants decrease as Ns increases. For attapulgite and montmorillonite, the titration data never converge for log K_{AN} and log K_{CA} all the ionic strengths, Ns (1 to 100 sites/nm^2) and C_1

Table 4.13: Sensitivity of CCM to variation in total site density, ionic strength and capacitance for titration data of 4 % iron coated clay minerals.

			Attapulgite			Illite			Kaolnite			Montmorillonite		
IS	N_S	**C**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**
0.001	1	0.8	4.83	-8.838	79.24	4.69	-7.475	41.66	4.97	-6.589	26.84	3.356	-8.606	64.51
0.001	1	1	4.7	-8.958	141.97	4.55	-7.663	60.22	4.711	-6.9	25.2	3.307	-8.76	79.984
0.001	1	1.2	4.59	-9.058	214.13	4.46	-7.786	80.83	4.574	-7.088	26.69	3.27	-8.89	920.917
0.001	10	0.8	3.76	-9.904	111.55	3.58	-8.667	73.23	3.75	-7.87	29.19	2.32	-9.717	750.49
0.001	10	1	3.6	-10.038	210.4	3.44	-8.915	126.84	3.56	-8.209	41.46	2.27	-9.904	925.79
0.001	10	1.2	3.46	-10.146	321.08	3.34	-9.109	190.6	3.42	-8.453	61.68	2.23	-10.05	105.7
0.001	100	0.8	2.75	-10.91	114.9	2.57	-9.681	75.53	2.74	-8.897	29.55	1.32	-10.72	759.9
0.001	100	1	2.59	-11.045	217.05	2.43	-9.931	131.14	2.53	-9.23	42.82	1.26	-10.91	936.97
0.001	100	1.2	2.45	-11.15	331.58	2.33	-10.12	198.18	2.412	-9.477	64.32	1.23	-11.06	106.9
0.01	1	0.8	4.91	-8.381	68.28	4.568	-6.728	35.7	NC			3.94	-9.525	776.14
0.01	1	1	4.77	-8.523	148.68	4.39	-6.938	44.033	5.53	-6.01	43.25	3.88	-9.72	926.6
0.01	1	1.2	4.66	-8.68	240.15	4.3	-7.07	59.04	5.11	-6.444	40.39	3.84	-9.87	1048
0.01	10	0.8	3.83	-9.465	114.65	3.43	-7.932	63.06	4.77	-6.79	25.84	2.903	-10.67	88.42
0.01	10	1	3.675	-9.628	245.12	3.27	-8.181	128.71	4.05	-7.526	22.46	2.83	-10.9	106.5
0.01	10	1.2	3.553	-9.762	393.33	3.17	-8.38	214.55	3.818	-7.799	24.56	2.788	-11.08	120.9
0.01	100	0.8	2.823	-10.472	119.15	2.42	-8.946	68.64	3.69	-7.875	25.75	1.9	-11.68	893.79
0.01	100	1	2.66	-10.637	253.94	2.26	-9.198	134.77	3.03	-8.553	22.312	1.83	-11.92	107.7
0.01	100	1.2	2.54	-10.773	406.85	2.17	-9.401	225	2.8	-8.822	25.46	1.78	-12.103	122.3
0.1	1	0.8	4.72	-8.022	111.045	4.27	-6.214	68.7			NC	4.55	-9.743	47.39
0.1	1	1	4.57	-8.165	87.85	4.08	-6.447	51.32	5.501	-6.08	157.21	4.47	-9.882	60.622
0.1	1	1.2	-4.47	-8.27	154.23	3.97	-6.578	44.99	5.16	-6.409	153.8	4.41	-9.983	72.563
0.1	10	0.8	-3.63	-9.106	66.16	3.13	-7.404	44.98	4.59	-6.97	48.4	3.49	-10.838	56.495
0.1	10	1	3.488	-9.272	161.95	2.95	-7.644	58.46	4.058	-7.517	31.2	3.41	-10.99	74.3268
0.1	10	1.2	3.37	-9.407	288.64	2.84	-7.819	104.48	3.85	-7.74	22.2	3.33	-11.1	90.887
0.1	100	0.8	2.63	-10.11	69.02	2.11	-8.418	44.77	3.52	-8.047	47.54	2.49	-11.846	57.366
0.1	100	1	2.48	-10.28	164.02	1.94	-8.659	61.09	4.06	-7.51	49.84	2.4	-12	75.616
0.1	100	1.2	2.36	-10.418	300.83	1.83	-8.836	111.25	3.23	-8.34	39.38	2.33	-12.11	92.593

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

Table 4.14: Sensitivity of CCM to variation in total site density, ionic strength and capacitance for titration data of 4 % aluminum coated clay minerals.

			Attapulgite			**Illite**			**Kaolnite**			**Montmorillonite**		
IS	N_S	**C**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**
0.001	1	0.8	4.74	-7.58	70.4	6.55	-5.11	69.4			NC	4.86	-9.08	110.2
0.001	1	1	4.44	-7.72	64.1	5.16	-6.488	69.8			NC	4.75	-9.37	138.4
0.001	1	1.2	4.38	-7.816	61.4	4.92	-6.755	68.4			NC	4.69	-9.6	156.3
0.001	10	0.8	3.48	-8.69	65.4	4.37	-7.29	60.3			NC	3.78	-10.29	132.1
0.001	10	1			NC	3.92	-7.791	56.1			NC	3.68	-10.64	159.8
0.001	10	1.2	3.3	-8.991	67.6	3.74	-8.044	53.2	4.95	-6.68	72.8	3.63	-10.85	175.3
0.001	100	0.8	2.47	-9.644	65.2	3.33	-8.336	6.01			NC	2.78	-11.31	134
0.001	100	1	2.37	-9.867	63.8	2.9	-8.815	55.8			NC	2.68	-11.66	161.2
0.001	100	1.2	2.29	-10	68.3	2.72	-9.067	53	3.37	-7.762	70.7	2.62	-11.87	176.8
0.01	1	0.8	4.69	-8.041	52.2			NC			NC	3.98	-8.42	203.3
0.01	1	1	4.59	-8.172	46.5	6.01	-5.399	55	6.023	-5.08	19.3	3.9	-8.86	236.9
0.01	1	1.2	4.52	-8.268	44.6	5.23	-6.17	55.6	5.161	-5.93	19.4	3.86	-9.2	252
0.01	10	0.8	3.62	-9.138	46.9			NC	5.47	-5.66	17.2	2.91	-9.79	235.2
0.01	10	1	3.52	-9.296	44.7	4.19	-7.246	42.2	3.99	-7.169	17.4	2.866	-10.31	257.3
0.01	10	1.2	3.44	-9.428	47.7	3.88	-7.595	40.6			NC	2.85	-10.6	261.9
0.01	100	0.8	2.62	-10.146	46.6			NC	4.08	-7.048	17.2	1.9	-10.82	236.9
0.01	100	1	2.516	-10.3	44.7	3.15	-8.284	42.1	2.96	-8.204	17.4	1.86	-11.34	258.1
0.01	100	1.2	2.44	-10.441	48.2	2.86	-8.622	40.5	2.7	-8.561	18.3	1.84	-11.65	262
0.1	1	0.8	4.68	-8.453	46.7			NC	5.34	-5.7	14.5	3.18	-7.75	251.3
0.1	1	1	4.58	-8.569	38.2			NC	4.87	-6.22	14.6	3.1	-8.38	298.3
0.1	1	1.2	4.51	-8.657	33.8	5.28	-5.69	88.9	4.66	-6.46	14.9	3.08	-8.81	309.8
0.1	10	0.8	3.62	-9.53	38.2			NC	3.87	-7.289	15.6	2.1	-9.33	298.6
0.1	10	1	3.519	-9.665	30.8	4.17	-6.82	75.8	3.56	-7.744	17.4	2.08	-9.92	314.6
0.1	10	1.2	3.4	-9.773	28.4	3.77	-7.263	75.4	3.41	-8.081	19.7	2.09	-10.17	315.5
0.1	100	0.8	2.61	-10.53	37.7			NC	2.85	-8.317	15.6	1.1	-10.38	300.8
0.1	100	1	2.51	-10.674	30.5	3.12	-7.879	75.8	2.54	-8.772	17.6	1.08	-10.95	314.8
0.1	100	1.2	2.43	-10.789	28.3	2.74	-8.294	75.4	2.403	-9.11	20	1.09	-11.19	314.5

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

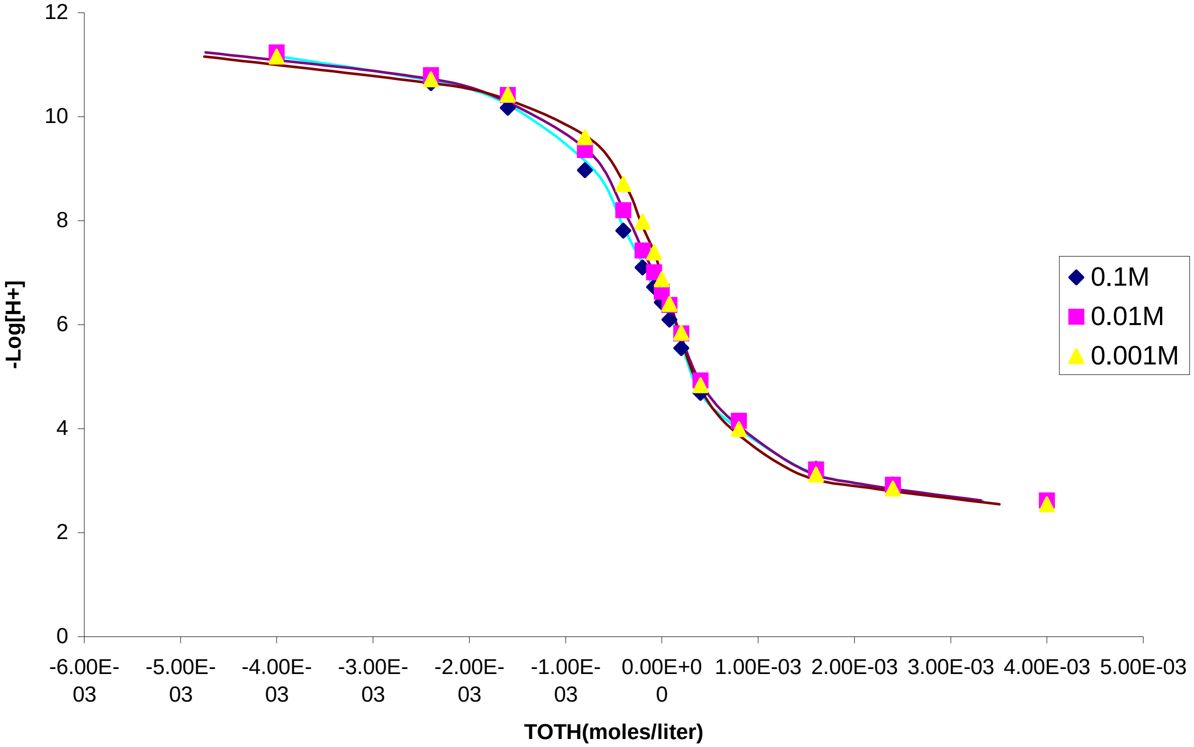

Figure 4.13: Constant capacitance model fit of titration data for suspension of 4% iron coated attapulgite

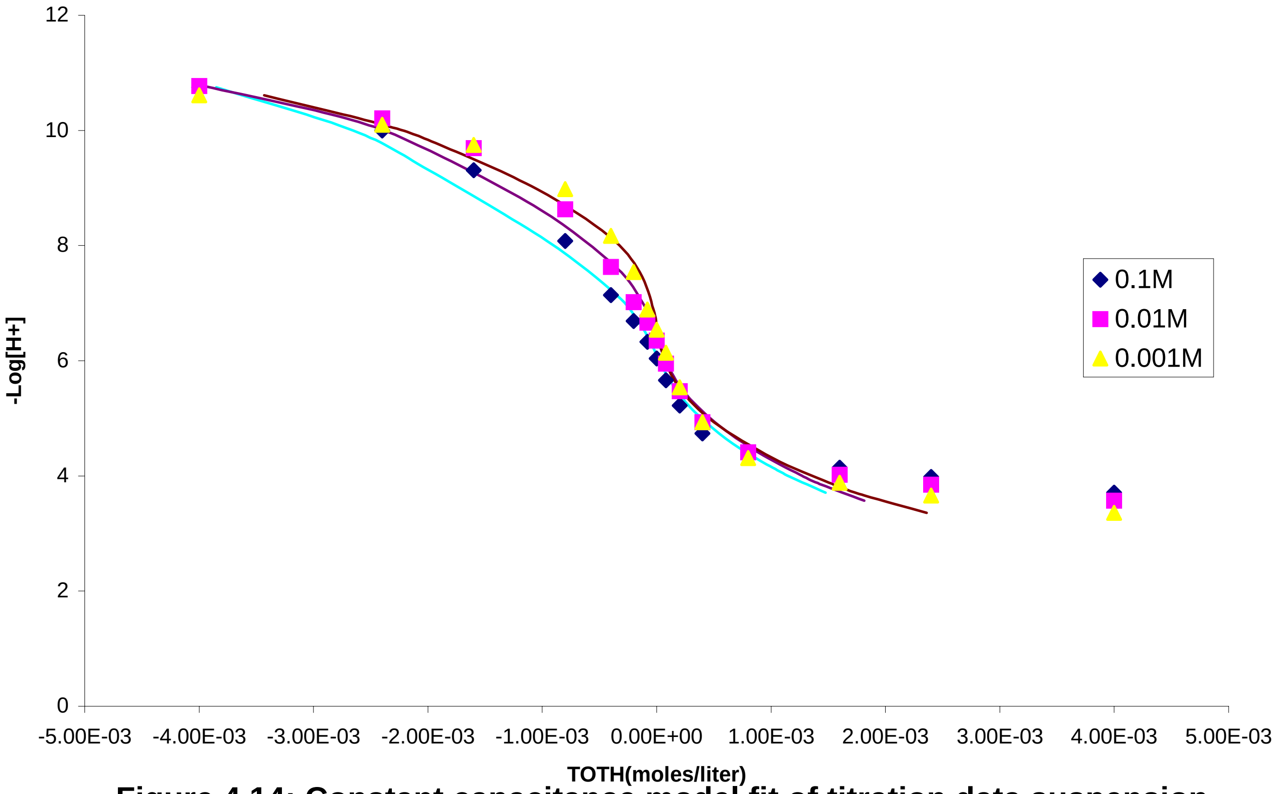

Figure 4.14: Constant capacitance model fit of titration data suspension of 4% aluminum coated attapulgite

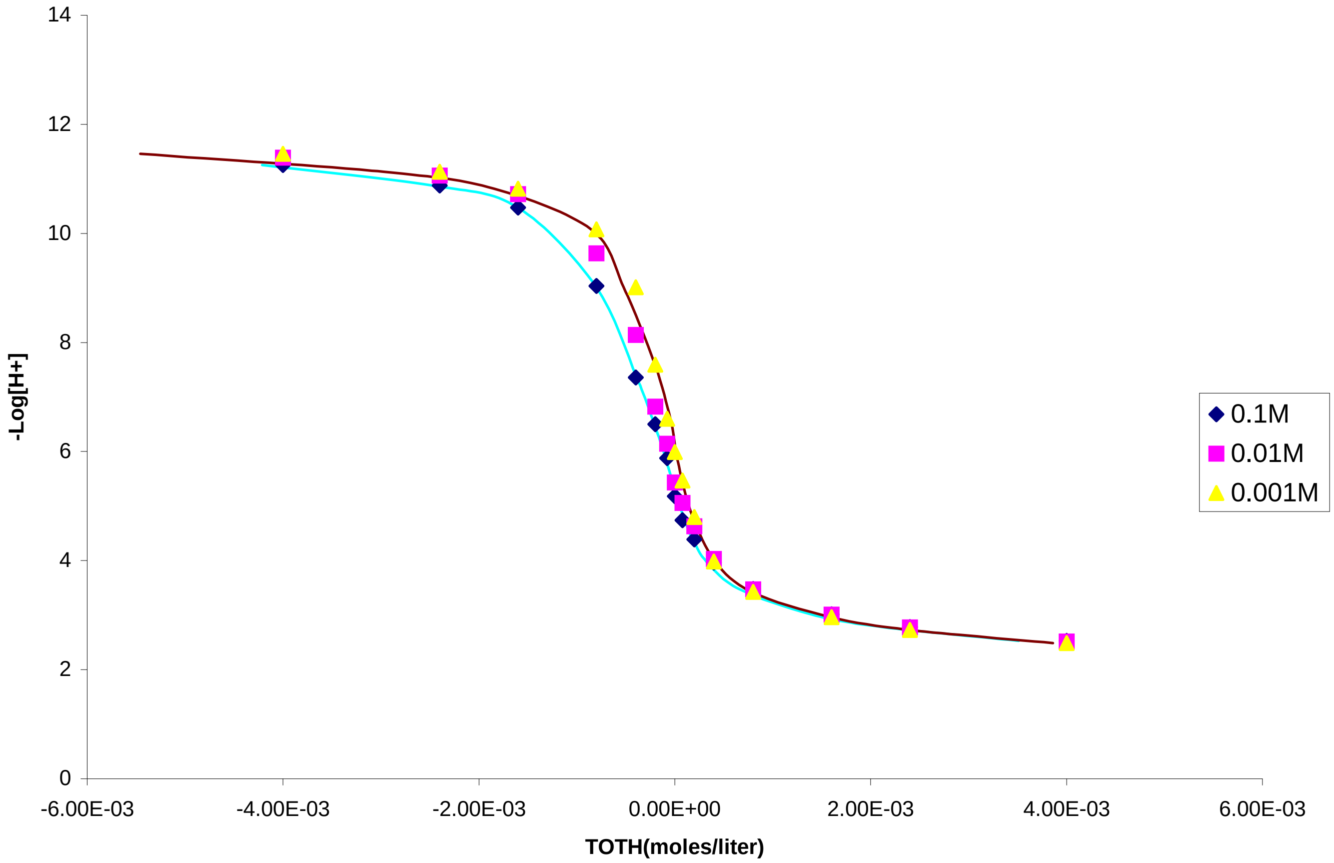

Figure 4.15: Constant capacitance model fit of titration data for suspension of 4% iron coated illite

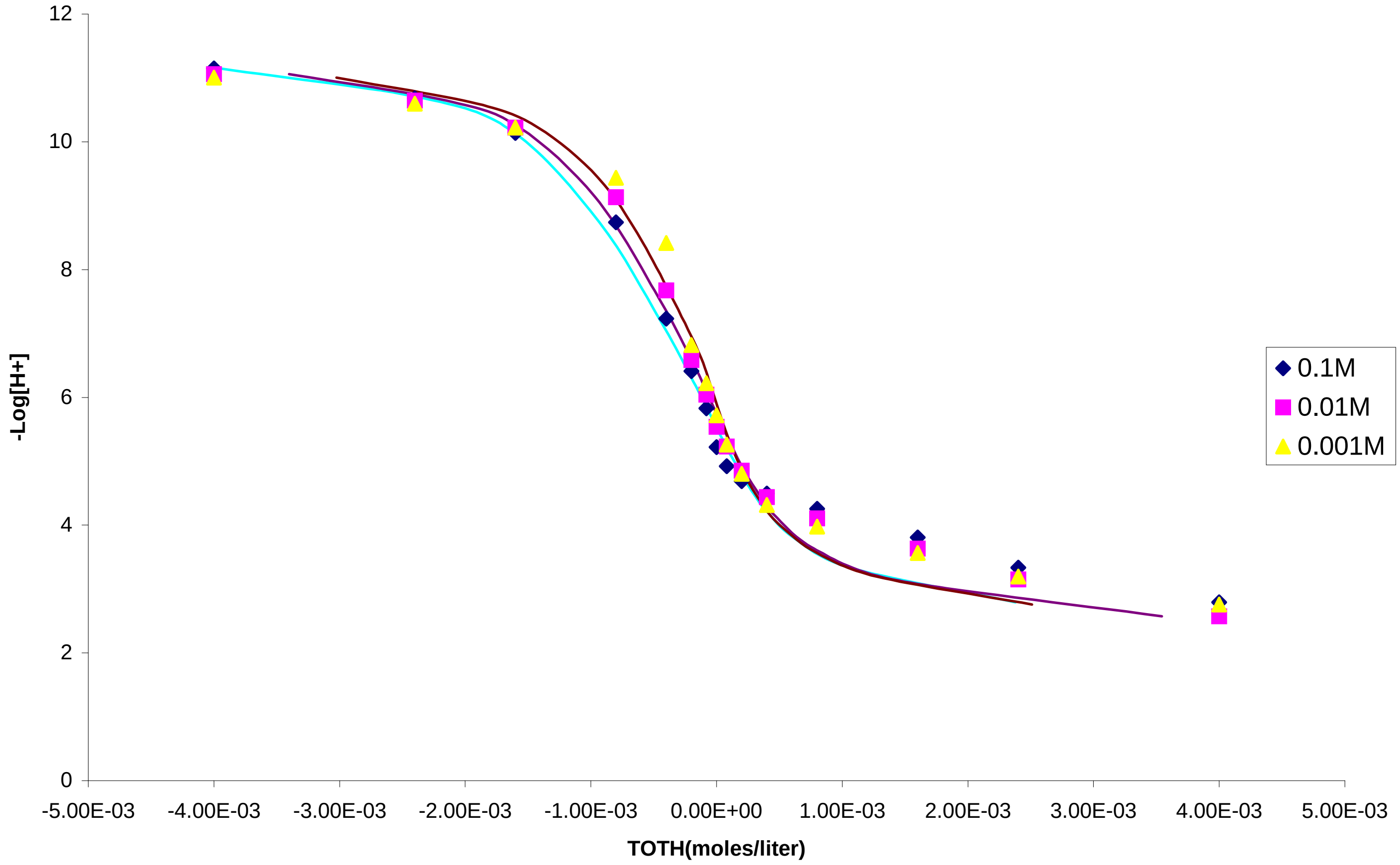

Figure 4.16: Constant capacitance model fit of titration data for suspension of 4% aluminum coated illite

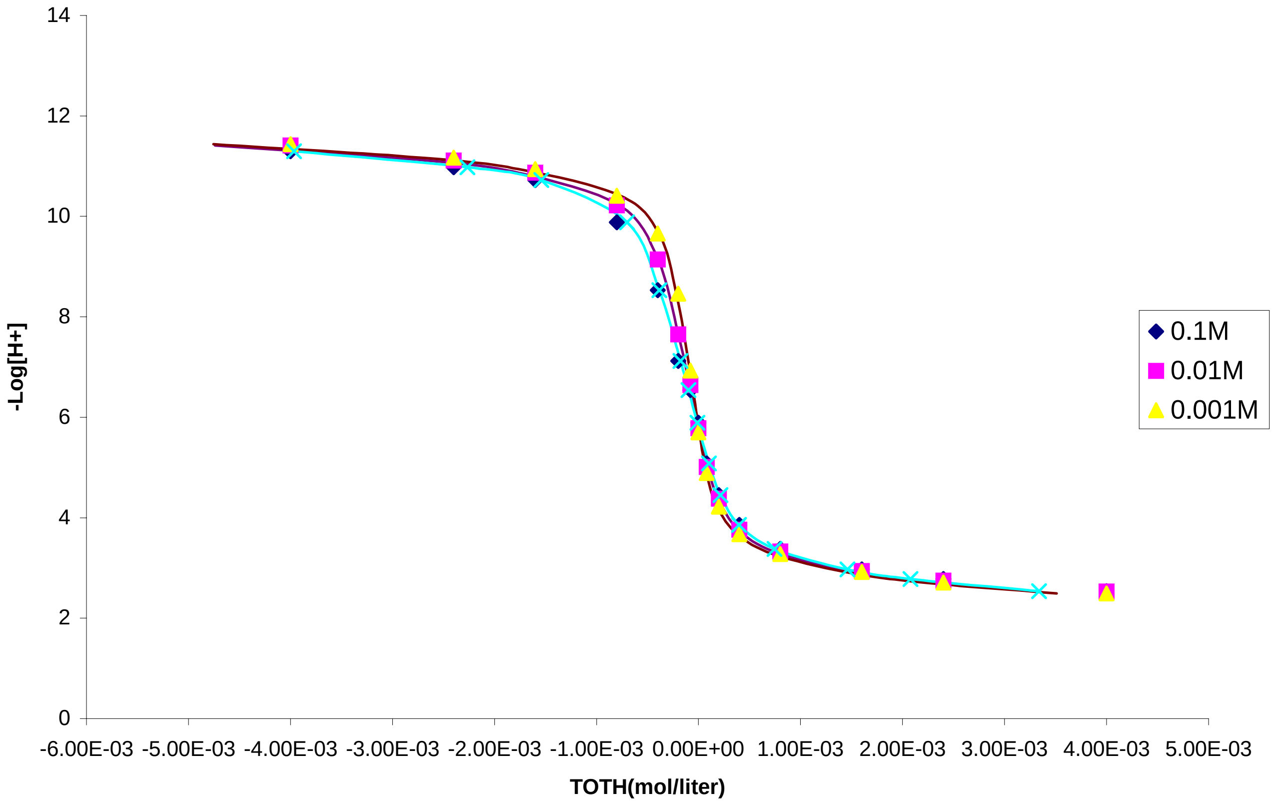

Figure 4.17: Constant capacitance model fits of titration data suspensions of 4% iron coated kaolinite

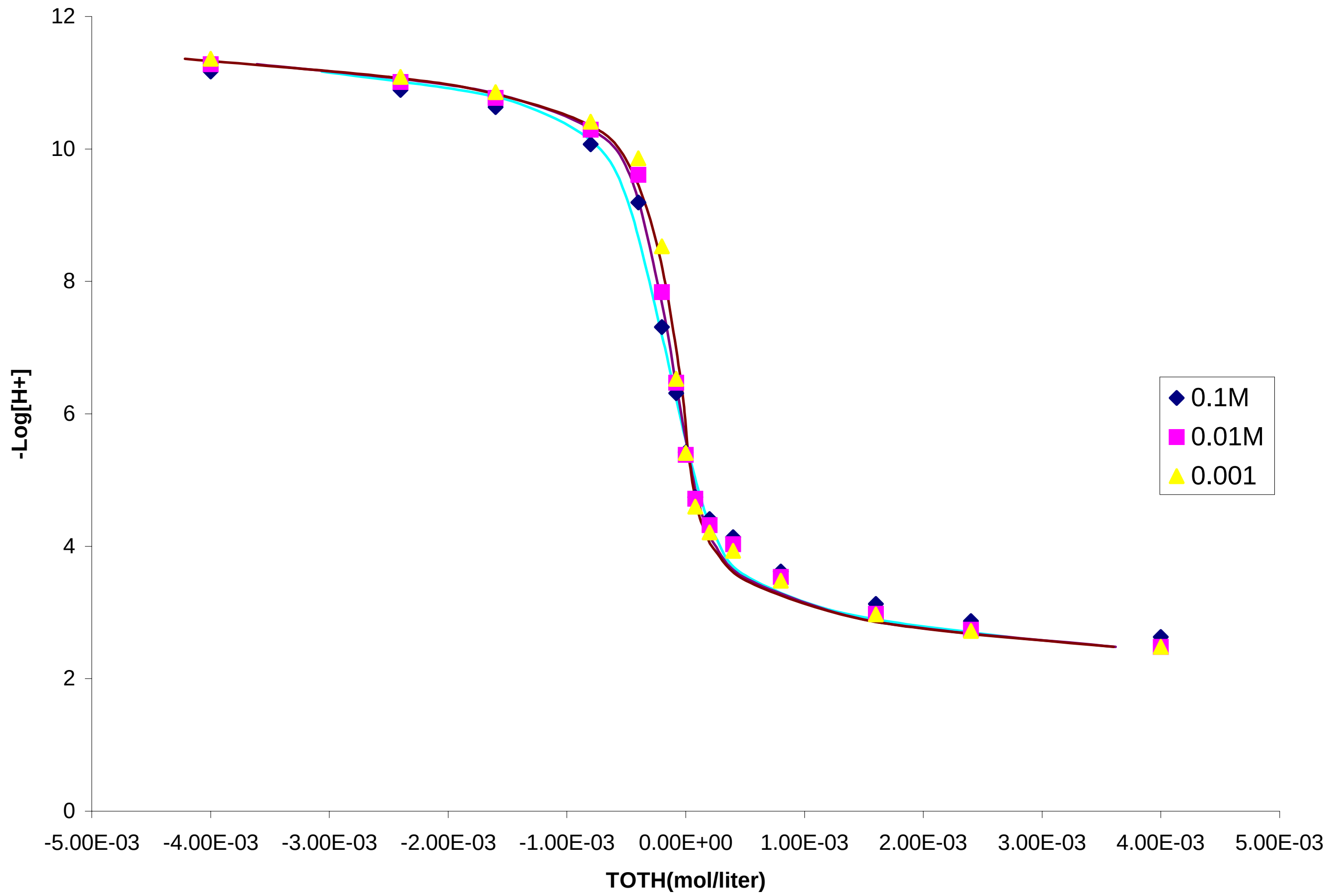

Figure 4.18: Constant capacitance model fits of titration data suspensions of 4% aluminum coated kaolinite

Table 4.15: Effect of coatings on sensitivity of CCM to variation in total site density ionic, strength and capacitance for attapulgite titration data.

			Attapulgite(0%)			**Attapulgite(4% Fe)**			**Attapulgite(4% Al)**		
IS	**N_S**	**C**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**
0.001	1	0.8	4.1	-10.16	55.1	4.83	-8.838	79.24	4.74	-7.58	70.4
0.001	1	1	3.98	-10.31	66.8	4.7	-8.958	141.97	4.44	-7.72	64.1
0.001	1	1.2	3.88	-10.42	75.7	4.59	-9.058	214.13	4.38	-7.816	61.4
0.001	10	0.8	3.01	-11.2	63.2	3.76	-9.904	111.55	3.48	-8.69	65.4
0.001	10	1	2.87	-11.4	76.6	3.6	-10.038	210.4			
0.001	10	1.2	2.76	-11.54	86.9	3.46	-10.146	321.08	3.3	-8.991	67.6
0.001	100	0.8	2.01	-12.27	63.9	2.75	-10.91	114.9	2.47	-9.644	65.2
0.001	100	1	1.86	-12.43	77.5	2.59	-11.045	217.05	2.37	-9.867	63.8
0.001	100	1.2	1.75	-12.55	87.9	2.45	-11.15	331.58	2.29	-10	68.3
0.01	1	0.8	4.05	-9.8	48.3	4.91	-8.381	68.28	4.69	-8.041	52.2
0.01	1	1	3.96	-9.972	58.9	4.77	-8.523	148.68	4.59	-8.172	46.5
0.01	1	1.2	3.88	-10	67	4.66	-8.68	240.15	4.52	-8.268	44.6
0.01	10	0.8	2.99	-10.92	55.7	3.83	-9.465	114.65	3.62	-9.138	46.9
0.01	10	1	2.878	-11.1	68	3.675	-9.628	245.12	3.52	-9.296	44.7
0.01	10	1.2	2.78	-11.8	77.9	3.553	-9.762	393.33	3.44	-9.428	47.7
0.01	100	0.8	1.98	-11.9	56.4	2.823	-10.472	119.15	2.62	-10.146	46.6
0.01	100	1	1.87	-12.11	66.8	2.66	-10.637	253.94	2.516	-10.3	44.7
0.01	100	1.2	1.77	-12.33	78.8	2.54	-10.773	406.85	2.44	-10.441	48.2
0.1	1	0.8	3.86	-9.42	46	4.72	-8.022	111.045	4.68	-8.453	46.7
0.1	1	1	3.77	-9.61	54.9	4.57	-8.165	87.85	4.58	-8.569	38.2
0.1	1	1.2	3.71	-9.76	61.5	-4.47	-8.27	154.23	4.51	-8.657	33.8
0.1	10	0.8	2.8	-10.4	52.2	-3.63	-9.106	66.16	3.62	-9.53	38.2
0.1	10	1	2.71	-10.74	62.3	3.488	-9.272	161.95	3.519	-9.665	30.8
0.1	10	1.2	2.63	-10.87	70.6	3.37	-9.407	288.64	3.4	-9.773	28.4
0.1	100	0.8	1.8	-11.56	52.8	2.63	-10.11	69.02	2.61	-10.53	37.7
0.1	100	1	1.7	-11.75	63	2.48	-10.28	164.02	2.51	-10.674	30.5
0.1	100	1.2	1.62	-11.88	71.5	2.36	-10.418	300.83	2.43	-10.789	28.3

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

Table 4.16: Effect of coatings on sensitivity of CCM to variation in total site density, ionic strength and capacitance for illite titration data.

			illite(0%)			**Illite(4%Fe)**			**Illite(4% Al)**		
IS	**N_S**	**C**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**
0.001	1	0.8	4.08	-7.98	30.2	4.69	-7.475	41.66	6.55	-5.11	69.4
0.001	1	1	3.98	-8.3	40.8	4.55	-7.663	60.22	5.16	-6.488	69.8
0.001	1	1.2	3.92	-8.6	48.9	4.46	-7.786	80.83	4.92	-6.755	68.4
0.001	10	0.8	3	-9.27	39.9	3.58	-8.667	73.23	4.37	-7.29	60.3
0.001	10	1	2.92	-975	52.1	3.44	-8.915	126.84	3.92	-7.791	56.1
0.001	10	1.2	2.86	-10.07	58.8	3.34	-9.109	190.6	3.74	-8.044	53.2
0.001	100	0.8	2	-10.29	40.6	2.57	-9.681	75.53	3.33	-8.336	6.01
0.001	100	1	1.92	-10.78	52.8	2.43	-9.931	131.14	2.9	-8.815	55.8
0.001	100	1.2	1.85	-11.09	59.4	2.33	-10.12	198.18	2.72	-9.067	53
0.01	1	0.8	3.8	-7.49	40.9	4.568	-6.728	35.7			NC
0.01	1	1	3.72	-7.75	52.6	4.39	-6.938	44.033	6.01	-5.399	55
0.01	1	1.2	3.67	-7.99	62.1	4.3	-7.07	59.04	5.23	-6.17	55.6
0.01	10	0.8	2.74	-8.78	53.7	3.43	-7.932	63.06			NC
0.01	10	1	2.66	-9.25	70.05	3.27	-8.181	128.71	4.19	-7.246	42.2
0.01	10	1.2	2.611	-9.62	80.14	3.17	-8.38	214.55	3.88	-7.595	40.6
0.01	100	0.8	1.73	-9.79	54.6	2.42	-8.946	68.64			NC
0.01	100	1	1.65	-10.28	71	2.26	-9.198	134.77	3.15	-8.284	42.1
0.01	100	1.2	1.6	-10.64	80.9	2.17	-9.401	225	2.86	-8.622	40.5
0.1	1	0.8	3.27	-7.02	32.4	4.27	-6.214	68.7			NC
0.1	1	1	3.21	-7.22	42.4	4.08	-6.447	51.32			NC
0.1	1	1.2	3.17	-7.36	50.8	3.97	-6.578	44.99	5.28	-5.69	88.9
0.1	10	0.8	2.21	-8.28	47	3.13	-7.404	44.98			NC
0.1	10	1	2.14	-8.63	65.5	2.95	-7.644	58.46	4.17	-6.82	75.8
0.1	10	1.2	2.11	-8.99	81.3	2.84	-7.819	104.48	3.77	-7.263	75.4
0.1	100	0.8	1.2	-9.29	47.9	2.11	-8.418	44.77			NC
0.1	100	1	1.14	-9.66	66.8	1.94	-8.659	61.09	3.12	-7.879	75.8
0.1	100	1.2	1.1	-10.02	82.8	1.83	-8.836	111.25	2.74	-8.294	75.4

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

Table 4.17: Effect of coatings on sensitivity of CCM to variation in total site density, ionic strength and capacitance for kaolinite titration data.

			0%			**4% Fe**			**4% Al**		
IS	**N_S**	**C**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**
0.001	1	0.8	4.46	-7.83	9.8	4.97	-6.589	26.84			NC
0.001	1	1	4.33	-8.13	13.1	4.711	-6.9	25.2			NC
0.001	1	1.2	4.24	-8.41	15.9	4.574	-7.088	26.69			NC
0.001	10	0.8	3.36	-9.09	12.3	3.75	-7.87	29.19			NC
0.001	10	1	3.22	-9.51	16.4	3.56	-8.209	41.46			NC
0.001	10	1.2	3.13	-9.82	18.9	3.42	-8.453	61.68	4.95	-6.68	72.8
0.001	100	0.8	2.35	-10.11	12.6	2.74	-8.897	29.55			NC
0.001	100	1	2.21	-10.54	16.6	2.53	-9.23	42.82			NC
0.001	100	1.2	2.12	-10.85	19.1	2.412	-9.477	64.32	3.37	-7.762	70.7
0.01	1	0.8	4.23	-7.303	8.3			NC			NC
0.01	1	1	4.11	-7.59	10.8	5.53	-6.01	43.25	6.023	-5.08	19.3
0.01	1	1.2	4.05	-7.82	13.4	5.11	-6.444	40.39	5.161	-5.93	19.4
0.01	10	0.8	3.14	-8.582	10.7	4.77	-6.79	25.84	5.47	-5.66	17.2
0.01	10	1	3.04	-8.99	14.8	4.05	-7.526	22.46	3.99	-7.169	17.4
0.01	10	1.2	2.98	-9.31	17.8	3.818	-7.799	24.56			NC
0.01	100	0.8	2.13	-9.06	10.9	3.69	-7.875	25.75	4.08	-7.048	17.2
0.01	100	1	2.03	-10.01	15.1	3.03	-8.553	22.312	2.96	-8.204	17.4
0.01	100	1.2	1.97	-10.35	18.1	2.8	-8.822	25.46	2.7	-8.561	18.3
0.1	1	0.8	4.17	-6.99	5.44			NC	5.34	-5.7	14.5
0.1	1	1	4.04	-7.25	7.15	5.501	-6.08	157.21	4.87	-6.22	14.6
0.1	1	1.2	3.97	-7.44	8.96	5.16	-6.409	153.8	4.66	-6.46	14.9
0.1	10	0.8	3.07	-8.24	7.33	4.59	-6.97	48.4	3.87	-7.289	15.6
0.1	10	1	2.96	-8.59	10.96	4.058	-7.517	31.2	3.56	-7.744	17.4
0.1	10	1.2	2.89	-8.88	14.5	3.85	-7.74	22.2	3.41	-8.081	19.7
0.1	100	0.8			NC	3.52	-8.047	47.54	2.85	-8.317	15.6
0.1	100	1			NC	4.06	-7.51	49.84	2.54	-8.772	17.6
0.1	100	1.2			NC	3.23	-8.34	39.38	2.403	-9.11	20

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

Table 4.18: Effect of coatings on sensitivity of CCM to variation in total site density, ionic strength and capacitance for montmorillonite titration data.

			Montmorillonite (0%)			Montmorillonite (4% Fe)			Montmorillonite (4% Al)		
IS	N_S	**C**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**	**Log K^+**	**Log K^-**	**F**
0.001	1	0.8	4.12	-10.35	76.7	3.356	-8.606	64.51	4.86	-9.08	110.2
0.001	1	1	4.05	-10.4	90.6	3.307	-8.76	79.984	4.75	-9.37	138.4
0.001	1	1.2	3.99	-10.54	102.3	3.27	-8.89	920.917	4.69	-9.6	156.3
0.001	10	0.8	3.07	-11.43	86.1	2.32	-9.717	750.49	3.78	-10.29	132.1
0.001	10	1	2.98	-11.54	103.4	2.27	-9.904	925.79	3.68	-10.64	159.8
0.001	10	1.2	2.9	-11.63	119.5	2.23	-10.05	105.7	3.63	-10.85	175.3
0.001	100	0.8	2.07	-12.44	87	1.32	-10.72	759.9	2.78	-11.31	134
0.001	100	1	1.98	-12.55	105.1	1.26	-10.91	936.97	2.68	-11.66	161.2
0.001	100	1.2	1.89	-12.64	121.1	1.23	-11.06	106.9	2.62	-11.87	176.8
0.01	1	0.8	3.46	-9.99	84.2	3.94	-9.525	776.14	3.98	-8.42	203.3
0.01	1	1	3.42	-10.14	93.1	3.88	-9.72	926.6	3.9	-8.86	236.9
0.01	1	1.2	3.39	-10.26	100.5	3.84	-9.87	1048	3.86	-9.2	252
0.01	10	0.8	2.44	-11.09	90.2	2.903	-10.67	88.42	2.91	-9.79	235.2
0.01	10	1	2.39	-11.27	101	2.83	-10.9	106.5	2.866	-10.31	257.3
0.01	10	1.2	2.35	-11.39	109.6	2.788	-11.08	120.9	2.85	-10.6	261.9
0.01	100	0.8	1.44	-12.1	90.7	1.9	-11.68	893.79	1.9	-10.82	236.9
0.01	100	1	1.39	-12.28	101.7	1.83	-11.92	107.7	1.86	-11.34	258.1
0.01	100	1.2	1.359	-12.4	110.4	1.78	-12.103	122.3	1.84	-11.65	262
0.1	1	0.8	2.88	-9.54	94.6	4.55	-9.743	47.39	3.18	-7.75	251.3
0.1	1	1	2.86	-9.727	101	4.47	-9.882	60.622	3.1	-8.38	298.3
0.1	1	1.2	2.83	-9.86	105.1	4.41	-9.983	72.563	3.08	-8.81	309.8
0.1	10	0.8	1.86	-10.67	99.2	3.49	-10.838	56.495	2.1	-9.33	298.6
0.1	10	1	1.84	-10.86	105.6	3.41	-10.99	74.3268	2.08	-9.92	314.6
0.1	10	1.2	1.81	-10.99	110.2	3.33	-11.1	90.887	2.09	-10.17	315.5
0.1	100	0.8	0.86	-11.6	99.6	2.49	-11.846	57.366	1.1	-10.38	300.8
0.1	100	1	0.83	-11.8	106	2.4	-12	75.616	1.08	-10.95	314.8
0.1	100	1.2	0.82	-12	110.6	2.33	-12.11	92.593	1.09	-11.19	314.5

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric sche

Table 4.19: Representative sensitivity of TLM to variation in total site density and ionic strength using pure clay titration data.

			Attapulgite.			Illite			Kaolinite			Montmorillonite.		
IS	**N_S**	**C**	**Log K_{AN}**	**Log K_{CA}**	**F**	**Log K_{AN}**	**Log K_{CA}**	**F**	**Log K_{AN}**	**Log K_{CA}**	**F**	**Log K_{AN}**	**Log K_{CA}**	**F**
0.001	1	0.8			NC	5.6	-8.12	57.9	5.71	-7.22	75.5			NC
0.001	1	1			NC	5.53	-8.4	91.8	5.59	-7.6	89.1			NC
0.001	1	1.2			NC	5.48	-8.62	127.6	5.51	-7.85	99.4			NC
0.001	10	0.8			NC	4.56	-9.4	81	4.63	-8.5	82.3			NC
0.001	10	1			NC	4.48	-9.76	137	4.5	-8.87	96.9			NC
0.001	10	1.2			NC	4.41	-10	196	4.39	-9.1	110.17			NC
0.001	100	0.8			NC			NC			NC			NC
0.001	100	1			NC			NC			NC			NC
0.001	100	1.2			NC			NC			NC			NC
0.01	1	0.8			NC	5.41	-7.91	118	5.45	-6.68	44.3			NC
0.01	1	1			NC	5.36	-8.35	138	5.37	-7.08	47.3			NC
0.01	1	1.2			NC	5.32	-8.68	161	5.31	-7.34	49.9			NC
0.01	10	0.8			NC	4.38	-9.48	133	4.4	-8.01	43.8			NC
0.01	10	1			NC	4.32	-10.13	171	4.32	-8.41	46.7			NC
0.01	10	1.2			NC			NC	4.25	-8.68	51.8			NC
0.01	100	0.8			NC			NC			NC			NC
0.01	100	1			NC			NC			NC			NC
0.01	100	1.2			NC			NC			NC			NC
0.1	1	0.8			NC	4.97	-7.42	122	5.38	-6.33	30.6			NC
0.1	1	1			NC	4.93	-7.88	142	5.29	-6.69	27.4			NC
0.1	1	1.2			NC	4.9	-8.18	162	5.23	-6.95	26.3			NC
0.1	10	0.8			NC	3.96	-8.99	148	4.33	-7.64	25.6			NC
0.1	10	1			NC	3.92	-9.53	185	4.25	-8.05	23.7			NC
0.1	10	1.2			NC			NC	4.18	-8.35	25.63			NC
0.1	100	0.8			NC			NC			NC			NC
0.1	100	1			NC			NC			NC			NC
0.1	100	1.2			NC			NC			NC			NC

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

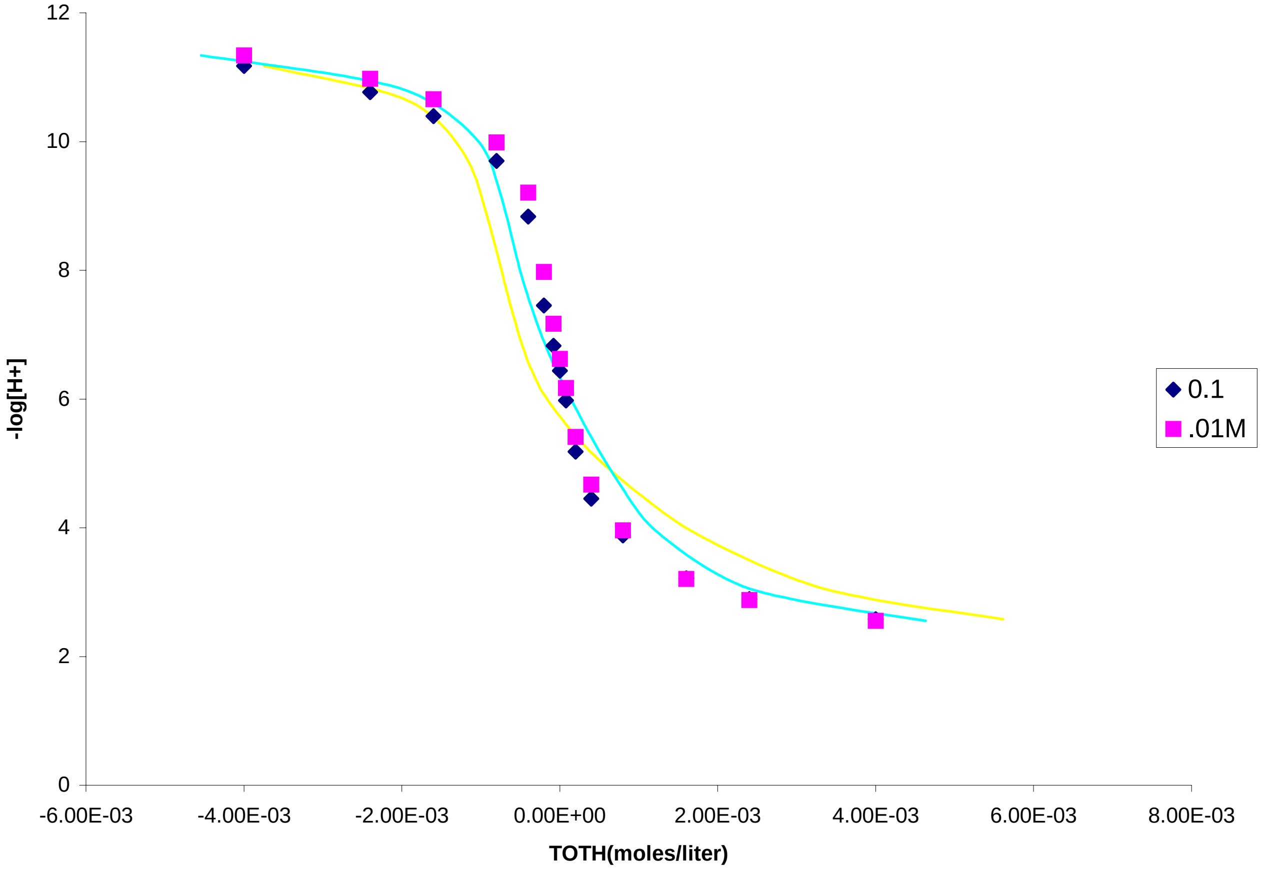

Figure 4.19: Triple layer model fits of titration data of pure attapulgite

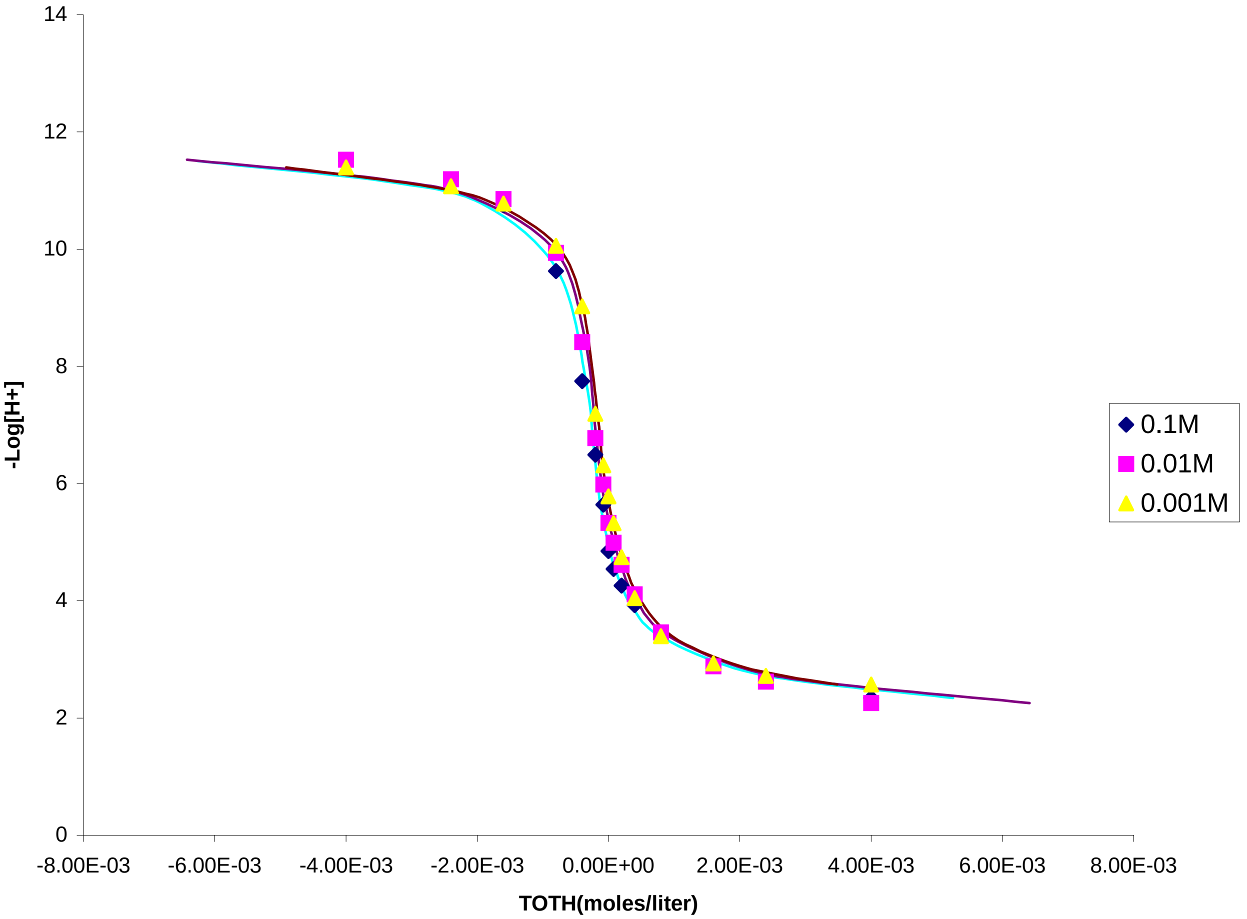

Figure 4.20: Triple-layer model fit of titration data for suspension of pure illite

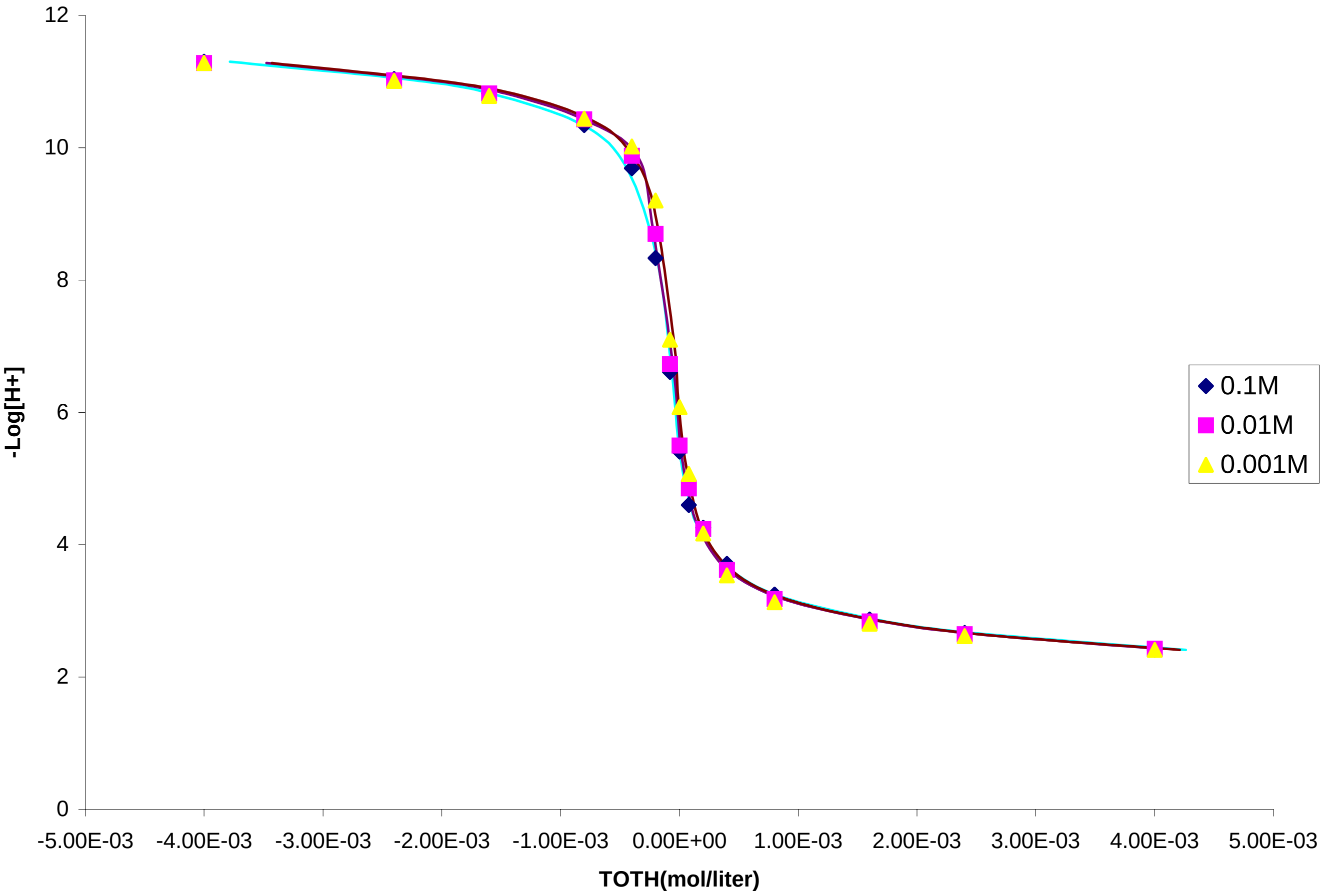

Figure 4.21: Triple-layer model fits of titration data for suspension of pure kaolinite

(0.6 to 1.2 F/m^2)values. Generally better FITEQL fits were obtained for kaolinte as compared to illite. For kaolinite better fits was obtained at 0.1M ionic strength as compared to 0.01 and 0.001M ionic strength.

Sensitivity analysis for coated clay minerals: Similar trends of decreasing log Kan and log K_{CA} with increasing value of Ns were obtained for both iron and aluminum coated clay minerals (Tables 4.20, 4.21, Figures 4.22-4.27). Titration data for Ns (100 sites/nm^2) were converged for all Fe and Al coated clay minerals. Better FITEQL fits were obtained for both iron and aluminum coated illite and kaolinite as compared to attatpulgite and montmorillonite. Generally, better FITEQL fits for Fe and Al coated clay obtained at the ionic strength of 0.1M. Better F value fits were obtained for kaolinite as compared to all other clay minerals.

Effect of Coating on TLM fits: For kaolinite, best fit values were obtained at (4% Fe) coatings at 0.01 and 0.001M ionic strength as compare to 0% and Al coated kaolinite (Table 4.24). But at ionic strength 0.1 M best fit value was obtained for 0% coating as compared to Fe and Al coated kaolinite. For attapulgite and illite, best fit values were obtained for 4% coatings as compared to 0% and 4% Al coatings at all the ionic strength values (Tables 4.22, 4.23). For montmorillonite, the values of surface constants never converge.

4.4 Summary and Conclusions

For all the models evaluated, increase in the value of total number of sites resulted in a decrease in the FITEQL best fit equilibrium log K value. Generally, better F value

Table 4.20: Representative sensitivity of TLM to variation in total site density and ionic strength using 4 % Fe coated clay titration data.

			Attapulgite.			**Illite**			**Kaolinite**			**Montmorillonite.**		
IS	**N_S**	**C**	**Log K_{AN}**	**Log K_{CA}**	**F**	**Log K_{AN}**	**Log K_{CA}**	**F**	**Log K_{AN}**	**Log K_{CA}**	**F**	**Log K_{AN}**	**Log K_{CA}**	**F**
0.001	1	0.8	6.32	-8.39	379	5.87	-6.73	37	6.4	-4.67	145			NC
0.001	1	1	6.2	-8.58	549	5.75	-7.01	56	5.93	-5.17	147			NC
0.001	1	1.2	6.11	-8.72	712	5.68	-7.21	78	5.72	-5.43	150			NC
0.001	10	0.8	5.26	-9.5	499	4.78	-7.96	57	4.94	-6.22	155			NC
0.001	10	1	5.12	-9.71	740	4.67	-8.32	94	4.63	-6.7	173			NC
0.001	10	1.2	4.99	-9.86	980	4.59	-8.61	135	4.48	-7.06	193			NC
0.001	100	0.8			NC			NC			NC			NC
0.001	100	1			NC			NC			NC			NC
0.001	100	1.2			NC			NC			NC			NC
0.01	1	0.8	6.44	-8.05	200	5.62	-5.8	41			NC			NC
0.01	1	1	5.35	-8.327	350	5.49	-6.14	36	7.05	-4.05	193			NC
0.01	1	1.2	6.28	-8.524	503	5.41	-6.33	37	6.2	-4.98	194			NC
0.01	10	0.8	5.39	-9.22	298	4.51	-7.11	52	6.55	-4.85	172			NC
0.01	10	1	5.28	-9.52	521	4.4	-7.48	69	5.06	-6.11	174			NC
0.01	10	1.2	5.19	-9.75	755	4.32	-7.79	96	4.78	-6.49	180			NC
0.01	100	0.8			NC			NC			NC			NC
0.01	100	1			NC			NC			NC			NC
0.01	100	1.2			NC			NC			NC			NC
0.1	1	0.8	6.27	-7.64	218	5.45	-5.31	66			NC			NC
0.1	1	1	6.18	-7.93	361	5.27	-5.61	45			NC			NC
0.1	1	1.2	6.12	-8.14	509	5.18	-5.8	32	5.6	-6.041	27.4			NC
0.1	10	0.8	5.23	-8.82	311	4.32	-6.52	38			NC			NC
0.1	10	1	5.13	-9.14	526	4.18	-6.87	30			NC			NC
0.1	10	1.2	5.04	-9.38	752	4.1	-7.14	42	5.35	-5.81	393			NC
0.1	100	0.8			NC			NC			NC			NC
0.1	100	1			NC			NC			NC			NC
0.1	100	1.2			NC			NC			NC			NC

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric schem

Table 4.21: Representative sensitivity of TLM to variation in total site density and ionic strength using 4 % Al coated clay titration data.

			Attapulgite.			**Illite**			**Kaolinite**			**Montmorillonite.**		
IS	**N_S**	**C**	**Log K_{AN}**	**Log K_{CA}**	**F**	**Log K_{AN}**	**Log K_{CA}**	**F**	**Log K_{AN}**	**Log K_{CA}**	**F**	**Log K_{AN}**	**Log K_{CA}**	**F**
0.001	1	0.8	6.04	-7.619	523	8.05	-3.63	693	6.02	-5.58	26.6	6.71	11.3	171
0.001	1	1	5.95	-7.77	445	6.32	-5.49	696	5.75	-5.84	25.49			NC
0.001	1	1.2	5.88	-7.89	404	6	-5.78	677	5.6	-6.04	27.47			NC
0.001	10	0.8	4.99	-8.68	454	5.44	-6.25	602	4.81	-6.8	29.4			NC
0.001	10	1	4.88	-8.86	382	5.01	-6.79	551	4.58	-7.15	41.6			NC
0.001	10	1.2	4.8	-8.99	351	4.84	-7.08	506	4.46	-7.4	60.9			NC
0.001	100	0.8			NC			NC			NC			NC
0.001	100	1			NC			NC			NC			NC
0.001	100	1.2			NC			NC			NC			NC
0.01	1	0.8	6.08	-7.32	521			NC			NC	5.92	9.9	199
0.01	1	1	6	-7.546	454	7.15	-4.29	551	6.56	-4.98	42.4	5.88	-10.4	193
0.01	1	1.2	5.93	-7.11	420	6.29	-5.2	556	6.12	-5.4	39.2	5.85	-10.9	217
0.01	10	0.8	5.04	-8.434	460			NC	5.84	-5.71	25.83			NC
0.01	10	1	4.94	-8.68	401	5.27	-6.23	419	5.1	-6.457	22.6			NC
0.01	10	1.2	4.87	-8.87	377	4.97	-6.63	389	4.85	-6.73	25			NC
0.01	100	0.8			NC			NC			NC			NC
0.01	100	1			NC			NC			NC			NC
0.01	100	1.2			NC			NC			NC			NC
0.1	1	0.8	5.9	-6.835	675			NC			NC	5.15	-9.01	437
0.1	1	1	5.81	-7.07	589			NC			NC	5.12	-9.41	398
0.1	1	1.2	5.75	-7.27	535	6.31	-4.72	892	7.14	-4.43	134.7	5.1	-9.7	383
0.1	10	0.8	4.85	-7.96	608			NC			NC	4.15	-10.61	465
0.1	10	1	4.77	-8.26	524	5.24	-5.8	758	6.16	-5.41	43.9	4.12	-11.13	464
0.1	10	1.2	4.7	-8.49	475	4.85	-6.3	740	5.29	-6.26	35.9			NC
0.1	100	0.8			NC			NC			NC			NC
0.1	100	1			NC			NC			NC			NC
0.1	100	1.2			NC			NC			NC			NC

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

were obtained when the Ns value was between 1 to 10 sites/nm^2.In the case of DL

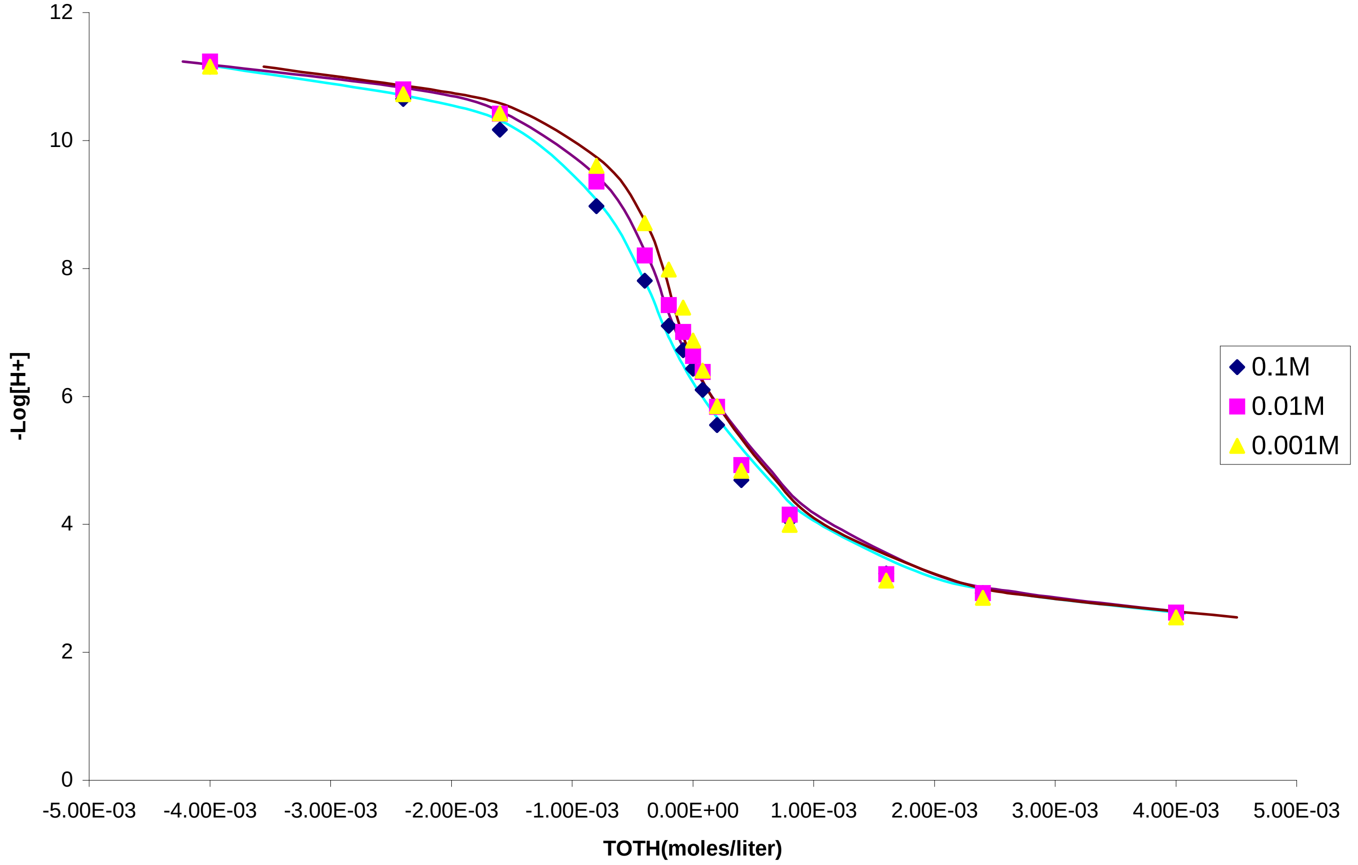

Figure 4.22: Triple-layer model fits of titration data for suspension of 4% iron coated attapulgite

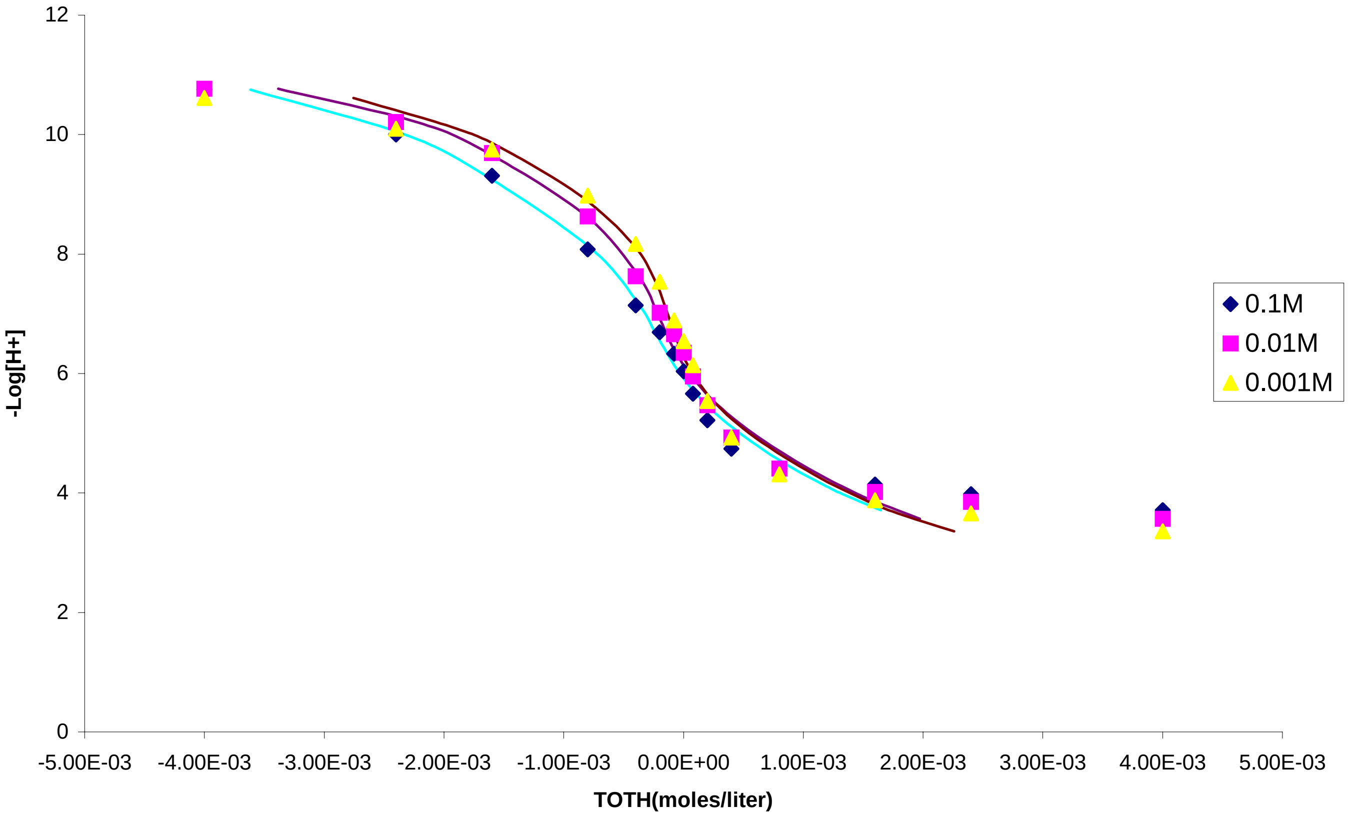

Figure 4.23: Triple-layer model fits of titration data for suspension of 4% aluminum coated attapulgite

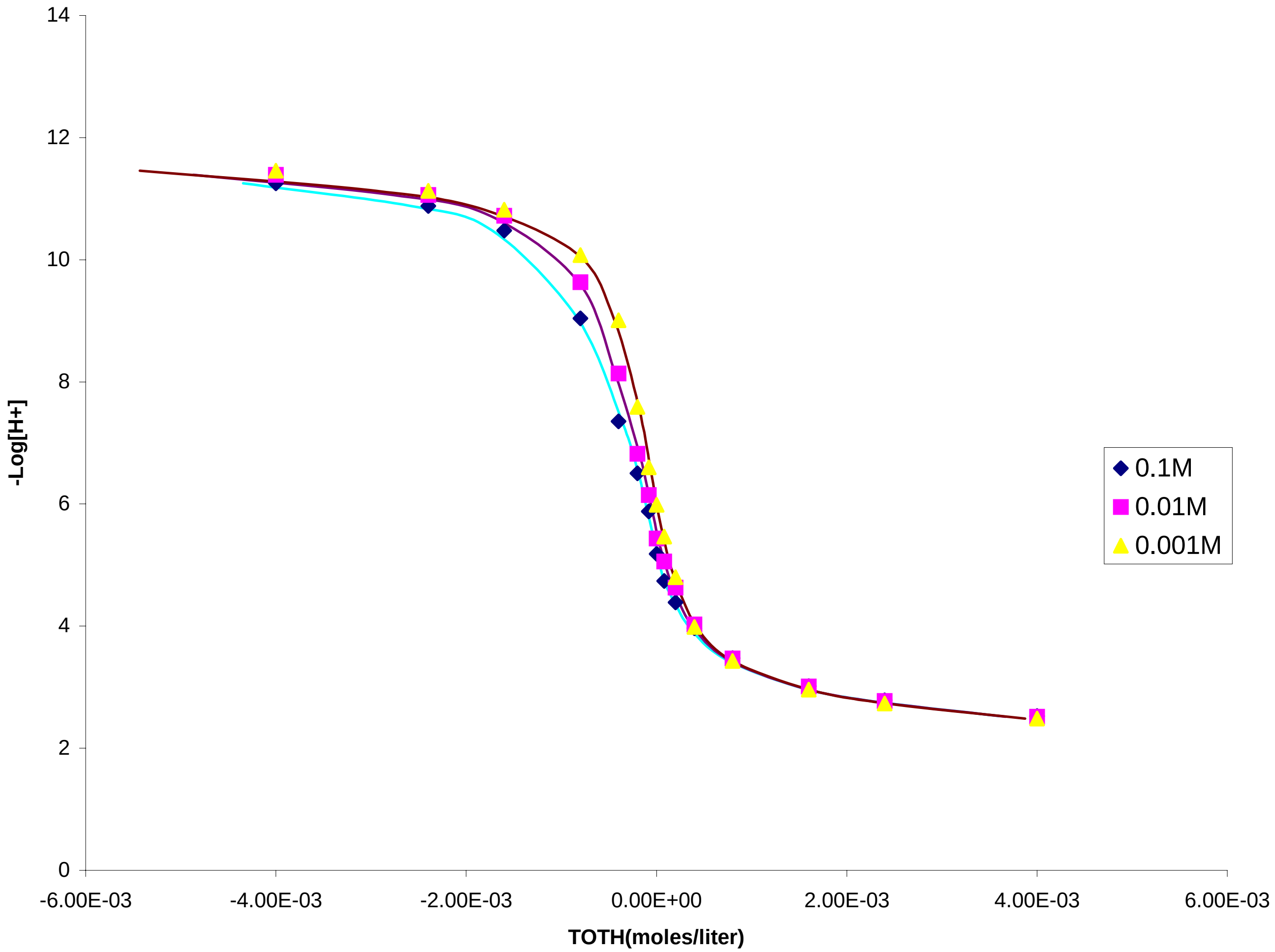

Figure 4.24: Triple layer model fit of titration data for suspension of 4% iron coated illite

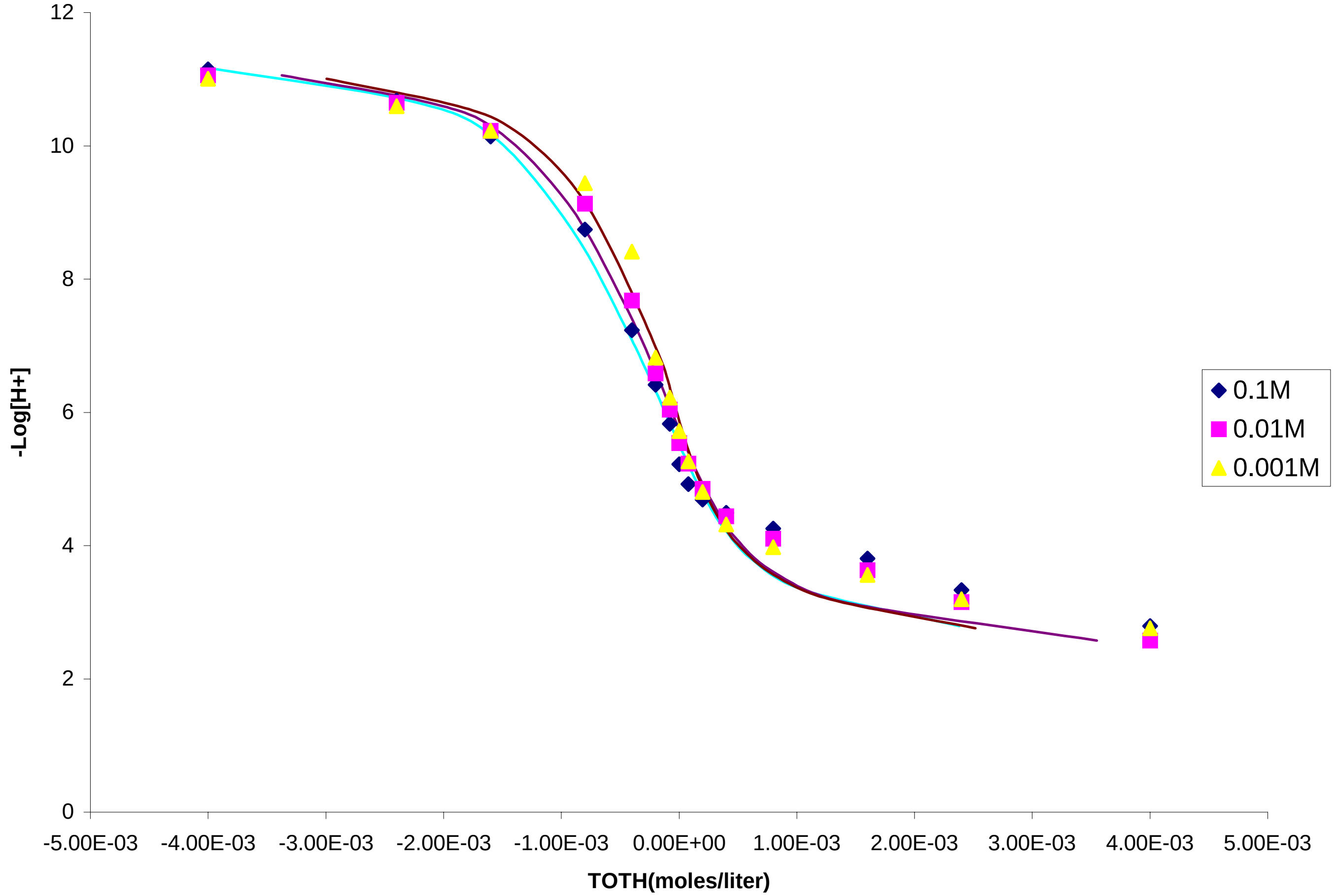

Figure 4.25: Triple-layer model fit of titration data for suspension of 4% aluminum coated illite

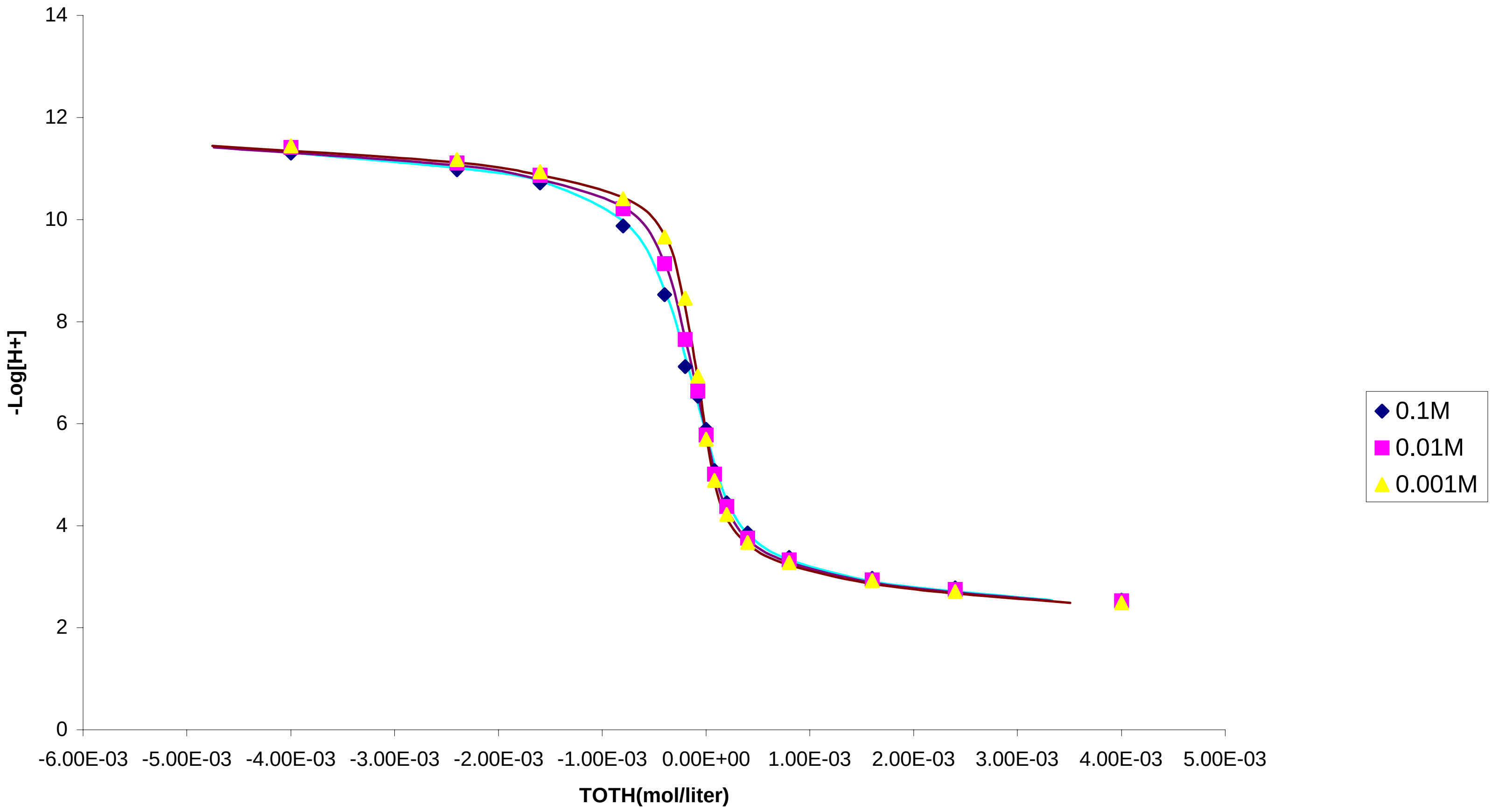

Figure 4.26: Triple-layer model fits of titration data for suspension of 4% iron coated kaolinite

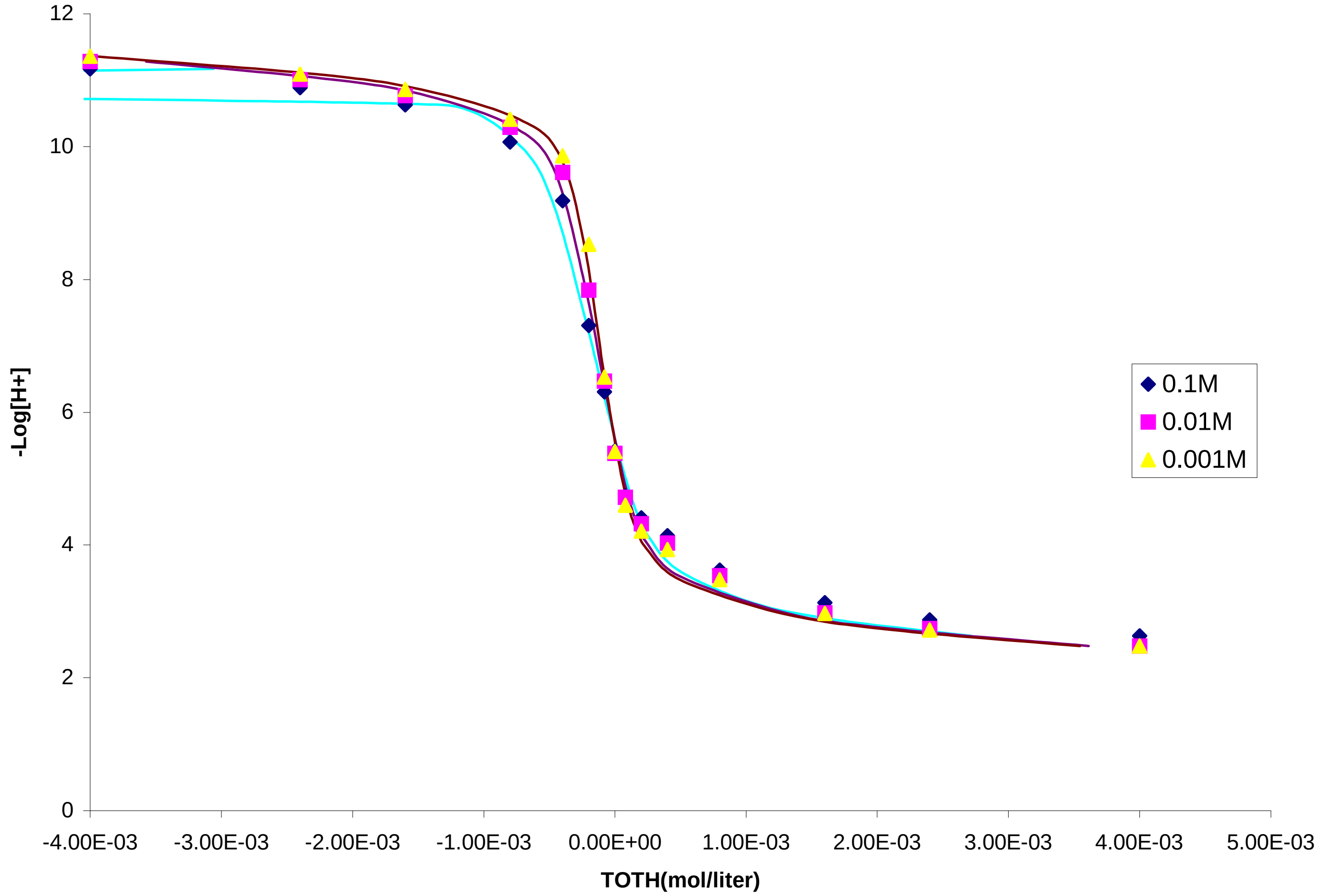

Figure 4.27:Triple layer model fits of titration data for suspensions of 4% aluminum coated kaolinite

Table 4.22: Effect of different coatings on the sensitivity of TLM for attapulgite

			0 %			**4% Fe**			**4% Al**		
IS	**N_S**	**C**	**Log K_{AN}**	**Log K_{CA}**	**F**	**Log K_{AN}**	**Log K_{CA}**	**F**	**Log K_{AN}**	**Log K_{CA}**	**F**
0.001	1	0.8			NC	6.32	-8.39	379	6.04	-7.619	523
0.001	1	1			NC	6.2	-8.58	549	5.95	-7.77	445
0.001	1	1.2			NC	6.11	-8.72	712	5.88	-7.89	404
0.001	10	0.8			NC	5.26	-9.5	499	4.99	-8.68	454
0.001	10	1			NC	5.12	-9.71	740	4.88	-8.86	382
0.001	10	1.2			NC	4.99	-9.86	980	4.8	-8.99	351
0.001	100	0.8			NC			NC			NC
0.001	100	1			NC			NC			NC
0.001	100	1.2			NC			NC			NC
0.01	1	0.8			NC	6.44	-8.05	200	6.08	-7.32	521
0.01	1	1			NC	5.35	-8.327	350	6	-7.546	454
0.01	1	1.2			NC	6.28	-8.524	503	5.93	-7.11	420
0.01	10	0.8			NC	5.39	-9.22	298	5.04	-8.434	460
0.01	10	1			NC	5.28	-9.52	521	4.94	-8.68	401
0.01	10	1.2			NC	5.19	-9.75	755	4.87	-8.87	377
0.01	100	0.8			NC			NC			NC
0.01	100	1			NC			NC			NC
0.01	100	1.2			NC			NC			NC
0.1	1	0.8			NC	6.27	-7.64	218	5.9	-6.835	675
0.1	1	1			NC	6.18	-7.93	361	5.81	-7.07	589
0.1	1	1.2			NC	6.12	-8.14	509	5.75	-7.27	535
0.1	10	0.8			NC	5.23	-8.82	311	4.85	-7.96	608
0.1	10	1			NC	5.13	-9.14	526	4.77	-8.26	524
0.1	10	1.2			NC	5.04	-9.38	752	4.7	-8.49	475
0.1	100	0.8			NC			NC			NC
0.1	100	1			NC			NC			NC
0.1	100	1.2			NC			NC			NC

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

Table 4.23: Effect of different coatings on the sensitivity of TLM for illite

			0%			**4% Fe**			**4% Al**		
IS	**N_S**	**C**	**Log K_{AN}**	**Log K_{CA}**	**F**	**Log K_{AN}**	**Log K_{CA}**	**F**	**Log K_{AN}**	**Log K_{CA}**	**F**
0.001	1	0.8	5.6	-8.12	57.9	5.87	-6.73	37	8.05	-3.63	693
0.001	1	1	5.53	-8.4	91.8	5.75	-7.01	56	6.32	-5.49	696
0.001	1	1.2	5.48	-8.62	127.6	5.68	-7.21	78	6	-5.78	677
0.001	10	0.8	4.56	-9.4	81	4.78	-7.96	57	5.44	-6.25	602
0.001	10	1	4.48	-9.76	137	4.67	-8.32	94	5.01	-6.79	551
0.001	10	1.2	4.41	-10	196	4.59	-8.61	135	4.84	-7.08	506
0.001	100	0.8			NC			NC			NC
0.001	100	1			NC			NC			NC
0.001	100	1.2			NC			NC			NC
0.01	1	0.8	5.41	-7.91	118	5.62	-5.8	41			NC
0.01	1	1	5.36	-8.35	138	5.49	-6.14	36	7.15	-4.29	551
0.01	1	1.2	5.32	-8.68	161	5.41	-6.33	37	6.29	-5.2	556
0.01	10	0.8	4.38	-9.48	133	4.51	-7.11	52			NC
0.01	10	1	4.32	-10.13	171	4.4	-7.48	69	5.27	-6.23	419
0.01	10	1.2			NC	4.32	-7.79	96	4.97	-6.63	389
0.01	100	0.8			NC			NC			NC
0.01	100	1			NC			NC			NC
0.01	100	1.2			NC			NC			NC
0.1	1	0.8	4.97	-7.42	122	5.45	-5.31	66			NC
0.1	1	1	4.93	-7.88	142	5.27	-5.61	45			NC
0.1	1	1.2	4.9	-8.18	162	5.18	-5.8	32	6.31	-4.72	892
0.1	10	0.8	3.96	-8.99	148	4.32	-6.52	38			NC
0.1	10	1	3.92	-9.53	185	4.18	-6.87	30	5.24	-5.8	758
0.1	10	1.2			NC	4.1	-7.14	42	4.85	-6.3	740
0.1	100	0.8			NC			NC			NC
0.1	100	1			NC			NC			NC
0.1	100	1.2			NC			NC			NC

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

Table 4.24: Effect of different coatings on the sensitivity of TLM for kaolinite

			0%			4% Fe			4% Al		
IS	**N_S**	**C**	**Log K_{AN}**	**Log K_{CA}**	**F**	**Log K_{AN}**	**Log K_{CA}**	**F**	**Log K_{AN}**	**Log K_{CA}**	**F**
0.001	1	0.8	5.71	-7.22	75.5	6.4	-4.67	145	6.02	-5.58	26.6
0.001	1	1	5.59	-7.6	89.1	5.93	-5.17	147	5.75	-5.84	25.49
0.001	1	1.2	5.51	-7.85	99.4	5.72	-5.43	150	5.6	-6.04	27.47
0.001	10	0.8	4.63	-8.5	82.3	4.94	-6.22	155	4.81	-6.8	29.4
0.001	10	1	4.5	-8.87	96.9	4.63	-6.7	173	4.58	-7.15	41.6
0.001	10	1.2	4.39	-9.1	110.17	4.48	-7.06	193	4.46	-7.4	60.9
0.001	100	0.8			NC			NC			NC
0.001	100	1			NC			NC			NC
0.001	100	1.2			NC			NC			NC
0.01	1	0.8	5.45	-6.68	44.3			NC			NC
0.01	1	1	5.37	-7.08	47.3	7.05	-4.05	193	6.56	-4.98	42.4
0.01	1	1.2	5.31	-7.34	49.9	6.2	-4.98	194	6.12	-5.4	39.2
0.01	10	0.8	4.4	-8.01	43.8	6.55	-4.85	172	5.84	-5.71	25.83
0.01	10	1	4.32	-8.41	46.7	5.06	-6.11	174	5.1	-6.457	22.6
0.01	10	1.2	4.25	-8.68	51.8	4.78	-6.49	180	4.85	-6.73	25
0.01	100	0.8			NC			NC			NC
0.01	100	1			NC			NC			NC
0.01	100	1.2			NC			NC			NC
0.1	1	0.8	5.38	-6.33	30.6			NC			NC
0.1	1	1	5.29	-6.69	27.4			NC			NC
0.1	1	1.2	5.23	-6.95	26.3	5.6	-6.041	27.4	7.14	-4.43	134.7
0.1	10	0.8	4.33	-7.64	25.6		NC				NC
0.1	10	1	4.25	-8.05	23.7		NC		6.16	-5.41	43.9
0.1	10	1.2	4.18	-8.35	25.63	5.35	-5.81	393	5.29	-6.26	35.9
0.1	100	0.8			NC		NC				NC
0.1	100	1			NC		NC				NC
0.1	100	1.2			NC		NC				NC

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

Table 4.25: Effect of different coatings on sensitivity of TLM for montmorillonite

			0%			4% Fe			4% Al		
IS	N_S	C	Log K_{AN}	Log K_{CA}	F	Log K_{AN}	Log K_{CA}	F	Log K_{AN}	Log K_{CA}	F
0.001	1	0.8			NC			NC	6.71	11.3	171
0.001	1	1			NC			NC			NC
0.001	1	1.2			NC			NC			NC
0.001	10	0.8			NC			NC			NC
0.001	10	1			NC			NC			NC
0.001	10	1.2			NC			NC			NC
0.001	100	0.8			NC			NC			NC
0.001	100	1			NC			NC			NC
0.001	100	1.2			NC			NC			NC
0.01	1	0.8			NC			NC	5.92	9.9	199
0.01	1	1			NC			NC	5.88	-10.4	193
0.01	1	1.2			NC			NC	5.85	-10.9	217
0.01	10	0.8			NC			NC			NC
0.01	10	1			NC			NC			NC
0.01	10	1.2			NC			NC			NC
0.01	100	0.8			NC			NC			NC
0.01	100	1			NC			NC			NC
0.01	100	1.2			NC			NC			NC
0.1	1	0.8			NC			NC	5.15	-9.01	437
0.1	1	1			NC			NC	5.12	-9.41	398
0.1	1	1.2			NC			NC	5.1	-9.7	383
0.1	10	0.8			NC			NC	4.15	-10.61	465
0.1	10	1			NC			NC	4.12	-11.13	464
0.1	10	1.2			NC			NC			NC
0.1	100	0.8			NC			NC			NC
0.1	100	1			NC			NC			NC
0.1	100	1.2			NC			NC			NC

IS= ionic strength in mol/lit, Ns= site density in sites per nm^2, C= capacitance, NC= no convergence in numeric scheme

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iron coated clay minerals showed better F value fits compared to aluminum coated clay minerals. For kaolinite, best fit F values were obtained for 0% coatings, but for attapulgite, illite and montmorillonite best fit F values were obtained at 4% iron coatings.

In the case of the CCM, generally for all clay minerals the CCM did not converge for C_1 below 0.6 F/ m^2 and above 1.2 F/ m^2 . Reasonably good fits were obtained for kaolinite (0% coatings) at all the ionic strengths and Ns values. Better F value fits were obtained for iron coated clay minerals as compared to aluminium coated clay minerals. As similar to DLM, best fit F values were obtained at 0% coatings for kaolinite and at 4% Fe coatings for attapulgite, illite and montmorillonite.

In the case of the TLM, data never converge for pure attapulgite and montmorillonite and better FITEQL fits were obtained for kaolinite as compared to illite. Better FITEQL fits were obtained for both iron and aluminum coated illite and kaolinite as compared to attapulgite and montmorillonite.

These studies focused on strategies for obtaining SCM parameters for complex natural system. As sorption of trace metals on clay and or oxide surface is a key element for better understanding transport of potentially toxic metals in the environment. It remains to be demonstrated that trace metal partitioning can be successfully modeled using the constants determined in the sensitivity analysis described above.

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Chapter 5

Pyromorphite Formation Artifact

5.1 Introduction

Lead is the most common metal pollutant at hazardous sites in the USA. Lead is potentially toxic to humans and animals, especially to young children. The major pathways of lead exposure are ingestion, inhalation, and dermal contact. Lead is rarely translocated in plants so contamination of food chain through plant uptake is a minor concern for Pb exposure. Although most of the Pb exposure occurs through involuntary dust ingestion (McBride, 1994), its extensive use and widespread disposal in the environment results in numerous lead contaminated soils (Turjoman and Fuller, 1987). In these lead-contaminated sites, there are also concerns about the contamination of surface and subsurface waters by leaching of Pb from the contaminated fractions of soils.

Lead contamination is often observed in old smelting sites. Sources of Pb at these sites are old smelting process wastes and mine wastes contaminated due to atmospheric additions of high Pb dust particles. Although total Pb concentrations in contaminated media are often used to determine potential for Pb exposure to humans, bioavailability of Pb is determined by solid phase speciation of Pb (Freeman et al., 1992). Many investigators (Ma and Rao, 1997; Ruby et al. 1994) have used sequential extraction techniques to identify the solid phases most likely to contribute to bioavailable pool of Pb.

Sequestering heavy metals in insoluble phosphate minerals has been suggested as an *in situ* remediation technique for heavy metals (Nriagu, 1973, 1974, and 1984). Lead sequestered in apatite minerals has great durability and leaching resistance, significantly exceeding other chemically stabilized forms. This is because the apatite mineral is very stable over a wide range of environmental conditions, such as from pH 2 to 12, temperature up to 1000 ^{0} C, presence of aqueous and non aqueous phase liquids, and disturbance caused by earthquakes, ground subsidence or human intrusion for geologically long time periods, i.e. hundreds of millions of years. Therefore, the lead-enriched apatites are not source of groundwater contamination. Also because of the long term stability of metal-enriched apatite (Altschuler et al., 1967; Shaw and Wasserburg, 1985; Keto and Jacobsen, 1987), the effects of gravity, soil heterogeneity, hydrology and other properties of the subsurface do not affect the performance of the remediation treatment using apatites. The bioavailability of ingested metal apatite is also greatly reduced (Davis et al., 1992; Ruby et al., 1992), making animal and human intrusion less dangerous should the metal apatite phase be ingested, and making bioremediation more effective in mixed waste environment.

Low solubility and high stability of lead phosphate minerals has spurred investigations into the mechanisms of chemical fixation of Pb by reacting Pb-contaminated soils with phosphates. Both soluble phosphates i.e. potassium phosphate (Lambert et al., 1997) and slowly dissolving phosphate minerals, i.e. rock phosphates and hydroxy apatites (Ma et al., 1994 and Ma and Rao, 1997), have been used to immobilize Pb. Amounts of phosphate application used in these studies were either empirically selected or were based on Pb concentrations in contaminated soils. Phosphate additions on the basis of level of contamination were often selected to give desired phosphate to Pb ratios. However, in soils contaminated with smelter wastes, high concentrations of iron oxides are often observed. These iron oxides become a major sink for added phosphates. Thus, all the phosphates added to remediate soils might not be available to react with Pb.

Sequential extractions of Pb have been used to determine the suitability of phosphates to immobilize Pb. Lead in many Pb-contaminated soils has been found to be associated with iron oxide phases (Xian, 1987). Phosphate additions have been reported to convert Pb associated with iron-oxide fractions of soils into pyromorphite (Ma and Rao, 1997). Pyromorphite is a very stable lead phosphate. However, there is a possibility that in the phosphate-treated lead-contaminated soils, pyromorphite does not form from reaction with Pb associated with iron oxides and the observed pyromorphite is only formed during solubilization of Fe during extraction. So it is likely that this assumption provides inaccurate information about immobilization of Pb. Therefore this study was undertaken with the objective of investigating whether lead pyromorphites are formed in the soil prior to extraction or during extraction.

5.2 Materials and Methods

5.2.1 Materials and Experimental Procedure

Three soils were collected from an area contaminated with zinc smelter waste. Total Pb concentrations (μg/g) of these materials were 714 (Soil 1), 1662 (Soil 2), and 2369 (Soil 3). The sequential extraction procedure of Ma and Rao (1997) was used to fractionate Pb into six fractions namely: water soluble, exchangeable, carbonate bound, Fe-Mn oxide, organic and residual. These fractions were extracted with deionized water, 1 M $MgCl_2$, 1M NaOAC, 0.04 M $NH_2OH.HCl$, (0.02 M HNO_3+ 30% H_2O_2+NH_2OAC) and HF, respectively. A second portion of these soils was reacted with two concentrations of phosphates (11,500 μg/g and 23,100 μg/g). After reaction with phosphates, these soils were again fractionated by using the same extraction scheme to determine the formation of lead pyromorphite.

Synthetic amorphous iron oxides were prepared by neutralizing 0.1 M $FeCl_3$ with 0.1 N NaOH. The precipitates were separated and dried to 35 ^{0}C. Dried samples were characterized by using X-ray diffraction. Ground Fe oxide materials were used to adsorb various concentration of Pb and phosphates. Various concentrations of Pb (6000 (Sample 1), 3560 (Sample 2), 2340 (Sample 3) μg/g) and lead+phosphate (6000+8000 (Sample 4), 3560+6000 (Sample 5) , 2340+4000 (Sample 6) μg/g) were adsorbed on Fe oxide to get two sets of iron oxides, i.e. iron oxides with sorbed Pb and those containing both phosphates and Pb each set having three levels of Pb and lead+phosphate additions. Phosphates and Pb were extracted from these oxides by hydroxylamine hydrochloride.

5.2.2 Analytical Method:

In this investigation, acid washed (5% HNO_3) polycarbonate labware, analytical grade chemicals and double de-ionized water were used. Total Pb concentrations of supernatant after each extraction step were analyzed using Inductively Coupled Plasma Spectrophotometer (for Pb >100 μg/L) and Graphite Furnace Atomic Absorption Spectrophotometer (for Pb < 100 μg/L). Separate Pb standards were prepared for each extraction step in the same matrix as the extracting reagent to minimize matrix effect. During analysis, standard samples were run after every 20 samples to check the accuracy of analysis.

5.3 Results and Discussions

Sequential extractions of Pb contaminated soils from a smelter site showed that most of the non-residual Pb was associated with oxide phases of the soils (Table 5.1). Exchangeable and water-soluble extractions constituted a small fraction of the total Pb in these soils. Although the water-soluble fraction was only a small fraction of the total Pb, Pb concentration in the water extracts exceeded drinking water standards (Maximum Contamination Limit (MCL) <15 μgL^{-1}). Although treatment of these soils with phosphates (11,550 μg/g) significantly reduced Pb concentration. However, Pb concentrations exceeded MCL (Table 5.2). Similar results were found when phosphate concentration was 23,100 μg/g (Table 5.3). Most of the non-residual Pb in these soils was in metal oxide fractions; this observation is consistent with the reports that Pb is predominantly associated with this fraction (Chlopeka, 1993; Jordao and Nickless, 1989; Ramos et al., 1994). Phosphate treatment of these soils reduced extractable Pb in all the fractions, including the metal oxide fraction(Table 5.2 and Table 5.3). The reason for this reduction as reported by many researchers (Ma and Rao, 1997; Davis et al., 1992) is the dissolution of phosphate minerals and the precipitation of Pb with the dissolved phosphate to form pyromorphite.

The proposed reaction suite for this mechanism the following (Lindsay,1979).

$$\underset{\text{apatite}}{Ca_{10}(PO_4)_6(OH)_2} + 14\,H^+ \xrightarrow{\text{dissolution}} 10\,Ca^{2+} + 6H_2PO_4^- + 2H_2O \quad \text{------(1)}$$

$$10\,Pb^{2+} + 6H_2PO_4^- + 2H_2O \xrightarrow{\text{precipitation}} \underset{\text{pyromorphite}}{Pb_{10}(PO_4)_6(OH)_2} + 14\,H^+ \quad \text{------(2)}$$

Table 5.1: Lead Concentration(μg/g) in different fractions of the original soils

Fractions	Soil-1	Soil-2	Soil-3
Water soluble	1.4	1.0	9.8
Exchangeable	9.5	12.8	71.4
Carbonate	44.4	97.5	383.2
Fe-Mn oxide	153.8	532.4	1180.8
Organic	50.6	167.6	184.3
Residual	459.2	779.0	985.3

Table 5.2 : Lead Concentration(μg/g) in different fractions of the soils treated with (11,550 (μg/g)) P

Fractions	Soil-1	Soil-2	Soil-3
Water soluble	0.3	0.2	0.2
Exchangeable	0.4	0.9	0.5
Carbonate	6.1	92.5	142.5
Fe-Mn oxide	68.3	499.2	573.0
Organic	30.1	17.4	14.2
Residual	543.3	943.0	1479.7

Table 5.3: Lead Concentration (μg/g) in different fractions of the soils treated with (23,100 (μg/g)) P

Fractions	Soil-1	Soil-2	Soil-3
Water soluble	0.3	0.3	0.8
Exchangeable	0.4	0.8	0.4
Carbonate	3.5	60.6	119.1
Fe-Mn oxide	51.6	408.6	514.3
Organic	38.7	16.6	19.2
Residual	545.2	1180.2	1572.3

It was hypothesized that the precipitation (reaction 2) is affected during extraction procedure; it does not actually take place in soil environment. This hypothesis was confirmed by studying Pb and lead+phosphate adsorption on synthetic iron oxides.

In synthetic iron oxides, the fact that all of the sorbed Pb could be extracted by dissolution with hydroxylamine hydrochloride (Figure 5.1) means that all the Pb was associated with Fe oxides. When iron oxides had both Pb and phosphates sorbed, there should be formation of pyromorphite to support the argument of different researchers (Nriagu, 1973; Davis et al., 1992; and Ruby et al. 1994), that addition of phosphate to Pb contaminated soils results in the formation of pyromorphite. But in our study, no pyromorphite was found by X-ray diffraction (Figure 5.2). Moreover, when iron oxides with sorbed phosphates and Pb were extracted with hydroxylamine hydrochloride, a significant fraction of Pb could not be extracted (Figure 5.3). These results suggest that in the sequential extraction procedure when a soil has both Pb and phosphate sorbed, Pb may be lost from the solution by reactions with other constituents in the extracts. Since, our system was pure, the probable cause of Pb loss was the precipitation reaction of pyromorphite. So we can conclude that there is always decrease in Pb concentration in Fe -oxide after the addition of phosphates which may not be due to the formation of pyromorphite but due to the artifact of the extraction procedure.

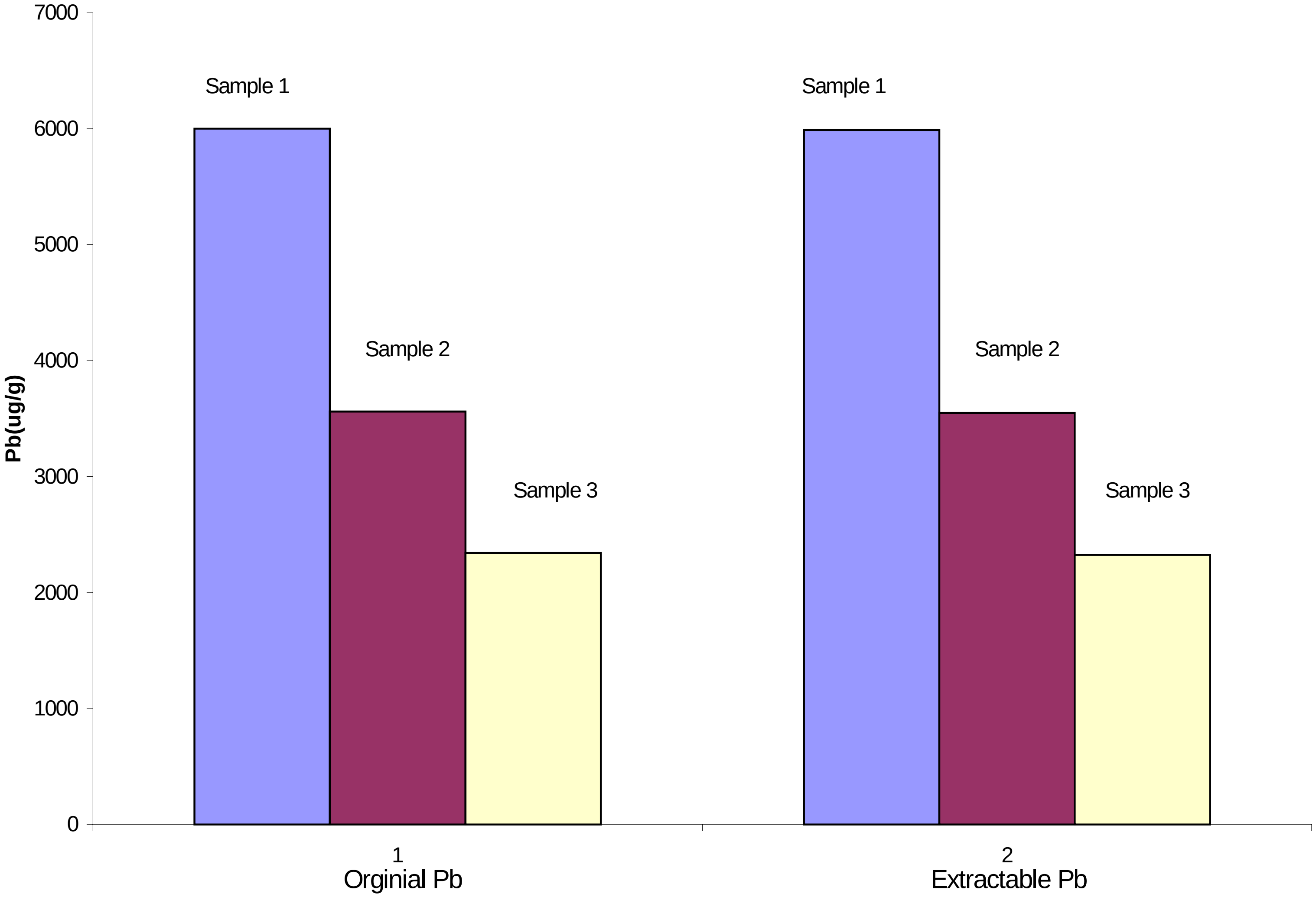

Figure 5.1: Extractable lead without phosphorus from iron-oxides

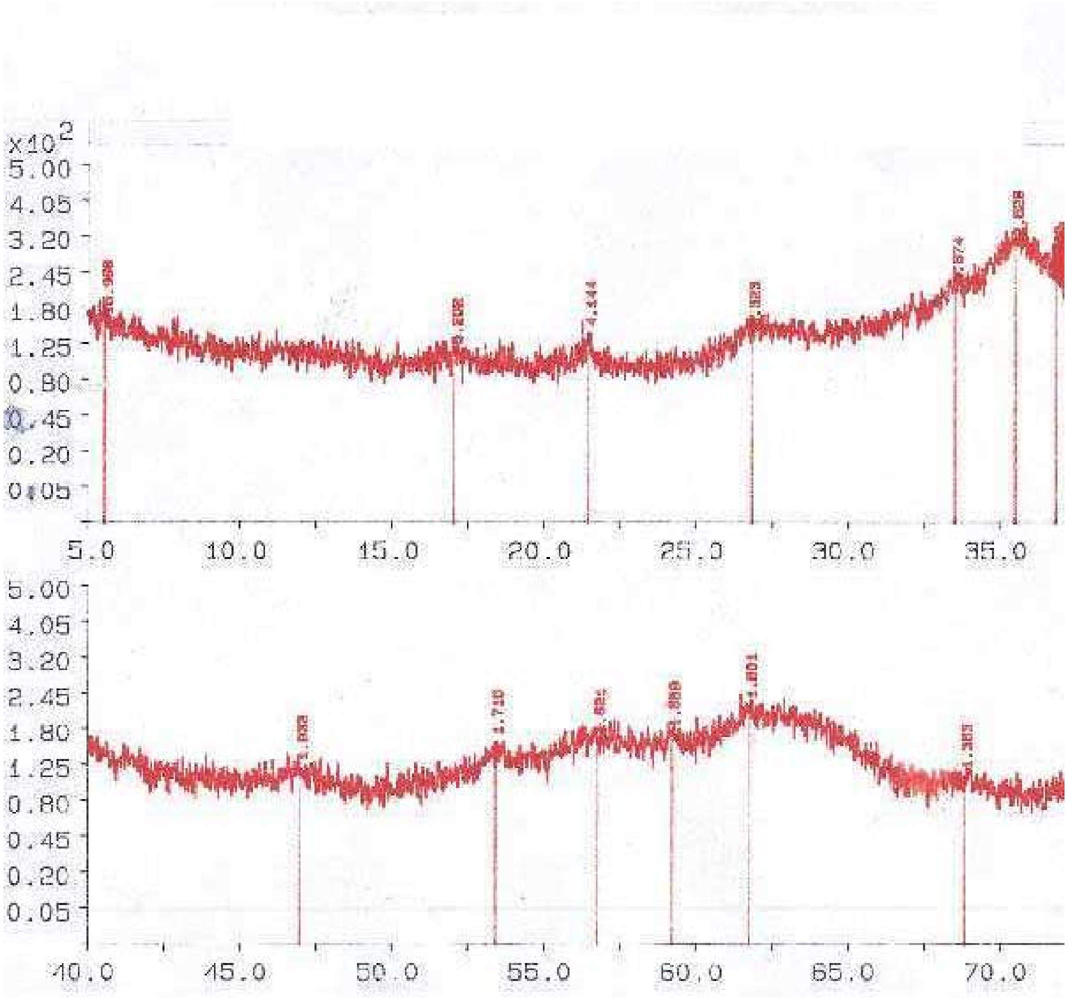

Figure 5.2: X-ray diffraction of iron oxides sorbes with lead and phosphate

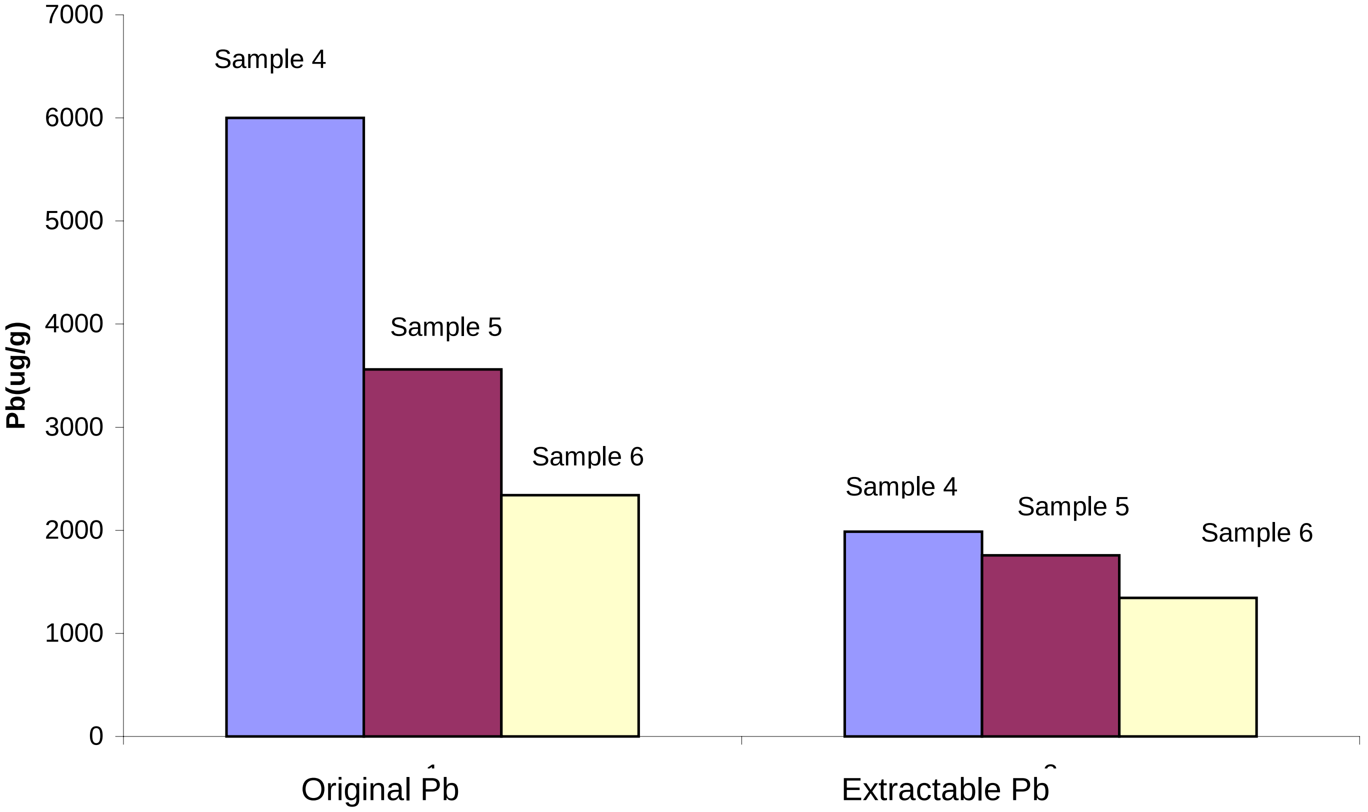

Figure 5.3: Extractable lead with phosprous from the iron-oxides

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Chapter 6

Effectiveness of Phosphate to Remediate Lead and Arsenic Contaminated Soils

6.1 Rationale and Scope for Research

Contamination of soils with toxic trace elements such as lead (Pb) and arsenic (As) represents a significant environmental threat due to their high toxicity. Excessive exposure to Pb and As is toxic to many organisms, from microbes to higher animals. Lead is the most common contaminant found at the USEPA designated superfund sites. Lead additions to the environment predate the industrial revolution. However, Pb and As contamination of the environment increased over the last century due to the extensive mining of Pb and As containing ores, use of Pb and As in industrial and agricultural products. There are many industrial and agricultural sites that are contaminated with both Pb and As.

Lead arsenate was the preferred pesticide for insect control in deciduous fruit trees before the production of DDT. Frequent application at high rates led to significant Pb and As accumulations in orchard soils (Pereyea, 1991). Lead in these soils was relatively immobile and non-phytotoxic whereas the As could be mobile and phytotoxic (Davenport and Peryea, 1991). In addition to the concerns about phytotoxicity of these two elements, there are risks of direct exposure to these toxic elements when house are constructed on soils contaminated with these elements.

Sphalerite (ZnS) is the most common ore of zinc. Galena (PbS) and arsenopyrites (FeAsS) are the most common contaminants found associated with sphalerite and consequently, Pb and As are common contaminants of zinc ores. During the smelting process, significant amounts of both Pb and As are concentrated in the silicate slag that is rich in oxides of iron and aluminum. Since Pb and As are associated with oxides of iron and aluminum, many zinc ore tailings and smelting waste disposal sites are contaminated with Pb and As. Boiling points of both Pb and As are much lower than that of Zn. During the smelting process significant amounts of both Pb and As are lost to the environment through flue gases. Because of the atmospheric additions of As and Pb, soils on the downwind direction from smelting plants often have elevated concentrations of both Pb and As.

Ingestion and inhalation are the predominant means of Pb and As contamination in humans and other animals. Ingestion is common in infants who eat contaminated soils by frequent hand to mouth activity and the subsequent ingestion of soil containing metals and other contaminants . Young children may also be exposed to these contaminants by playing on contaminated soils. Children also have the ability to absorb higher percentages of metals through the digestive system into the blood stream than adults, which may leave them susceptible to adverse health effects (Hamel et al., 1998). The incomplete development of the blood-brain barrier in very young children (up to 3 years of age) increases the risk of lead’ s entry into the developing nervous system, which can result in prolonged neurobehavioral disorders. Contamination of the food chain can also occur by bioconcentrations of these elements in plants grown on contaminated soils and from animals or human eating those plants.

Both Pb and As in soils exist as aqueous species, adsorbed components on charged surfaces, and structural components of soil materials. Lead and As are ubiquitous in the environment; however, their concentrations in uncontaminated soils are much smaller than those observed at contaminated sites. The average concentrations of Pb and As in soils around the world are estimated to be 15 mg kg $^{-1}$and 5 mg kg $^{-1}$, respectively (Zimdahl and Skogerboe, 1977). Lead and As concentrations are much higher in sites that are contaminated with smelting wastes, lead ores, or lead arsenate pesticides. In the United States, Pb contamination has been observed on 635 out of 1177 sites on the National Priorities List of Hazardous Sites (Reed and Cline, 1994). The USEPA has declared that there is a great need for remedial technologies for treating metals that are found at hazardous waste sites. In the USA, remediation is usually required when total Pb concentrations in soils exceed 300 to 500 mg kg $^{-1}$ in residential soils, or 2000 mg kg $^{-1}$ in soils used for industrial purposes (USEPA, 1996).

Remediation methods for contaminated soils attempt to reduce volume, toxicity, or mobility of contaminants in the environment. In metal contaminated sites the major thrust of remediation technologies is to reduce mobility or bioavailability of toxic trace elements. However, current remediation methods for soils contaminated with trace elements are often expensive and disruptive to the site. There are many technologies employed to clean up contaminated soils and wastes including thermal, microbiological, and physical/chemical (Ma et al., 1993). Both thermal and microbiological treatments are ineffective in removing trace elements from contaminated sites. Physical stabilization (e.g., mixing soils with cements or other solidifying agent or installation of soil or asphalt caps) is often costly and destructive. In recent years there have been a number of research reports that suggest that Pb contaminated sites can be treated with phosphates to reduce solubility and consequently, bioavailability of Pb (Ma 1996; Ma et al., 1993). Nriagu (1973) was the first to suggest that phosphate minerals have a potential to immobilize Pb in lead-contaminated soils and wastes due to low solubility of lead orthophosphates. Numerous reports from Japan suggested that hydroxy-apatite (HA) could be used to remove Pb form aqueous solutions. They suggested that apatite minerals could be used as ion exchangers for removing Pb from aqueous solutions (Ma et al., 1995). These authors provided little evidence that exchange reactions were responsible for the removal of Pb by hydroxy apatite (HA) minerals. Their results, however, showed that more Pb was removed by HA from a solution when soil pH was lowered. If exchange reactions on the surface of HA were responsible for removal of Pb, then lower pH would result in less Pb being adsorbed, as HA-surface will have less negative charge. However, the results of Takeuchi and Arai (1990) can be explained alternatively by a precipitation mechanism. More HA dissolved at low pH, and thus there was more P reacting with Pb to form hydroxypyromorphite (HP). Ma and coworkers (1993) conclusively proved that Pb was immobilized by dissolution of HA and precipitation of lead phosphate (hydroxypyromorphite).

It has been suggested that the bioavailability of soil Pb can be reduced by amending lead-contaminated soils with solid orthophosphate minerals or by adding soluble phosphates and producing Pb (II) phosphate mineral, pyromorphite ($Pb_{10}(PO_4)_6(OH)_2$). It has also been shown that formation of pyromorphite results in equilibrium Pb concentration approximately equal to EPA drinking water limits (15 $\mu g\ L^{-1}$) (Laperche et al., 1997). The hydrous oxides of Fe, Al, and Mn control, to a great extent the concentration and transport of many trace elements in soils and natural water through mechanisms of sorption and co-precipitation (Stumn and Morgan (1981). Hydrous oxides of Fe and Al can scavenge heavy metals and, thus, are believed to play an important role in retention and release of heavy metals in polluted soils. A number of Pb chemical speciation studies have shown that adsorbed Pb is the major Pb retaining solid phase in contaminated soils. Goethite is usually the dominant hydrous iron oxide mineral in soils. Interactions between goethite and Pb have been extensively investigated because they represent a common soil constituent and a typical pollutant and, therefore, are ideal candidates with which to establish a model that describes the relationship between soil matrices and pollutant for monitoring purposes and also to predict transport of metals in soils and natural waters. Zhang and Ryan (1999) observed that when stoichiometric concentrations of soluble phosphates were added directly to the suspension of Pb-adsorbed goethite, the thermodynamically stable lead phosphate mineral, chloropyromorphite, was rapidly precipitated. In their experiments approximately 60 –70 percent of the adsorbed-Pb was extractable with 1.0 M $MgCl_2$. However, additions of stoichiometric concentrations of phosphates reduced exchangeable Pb to 0.3 – 2.8 %. By contrast, when the same goethite suspension was reacted with HA, the formation of chloropyromorphite was slow and was apparently controlled by the rate of dissolution of HA. These results showed that Pb-adsorbed on oxides of Fe and Al can be desorbed from the mineral surfaces and converted into a more thermodynamically stable solid phase by reacting it with phosphates.

Arsenic exhibits varying oxidation states in natural systems; in oxidized systems As may occur As (+3) and As(+5). In smelter wastes and in orchard soils treated with lead arsenates the most common form of arsenic is As (+5). Both As (+3) and As (+5) are adsorbed to Fe oxide surfaces through inner-sphere complexation mechanisms (Jain et al., 1999). Arsenate adsorption on oxides of iron and aluminum increases when pH is decreased below 7.0. Extended x-ray absorption fine structure (EXAFS) studies have provided evidence that As (+5) adsorbs to the iron oxide and hydroxide minerals by an inner–sphere complexation mechanism. Variably charged surfaces in general, and the oxy-hydroxides of Fe, Al, and Mn in particular, are the primary solid phases that control As solubility in soils. Arsenic is retained on these clay minerals by a ligand exchange reaction where As replaces an OH^{-1} or an aqua group from the mineral surface. This ligand exchange adsorption is reversible such that both phosphates and OH^- have been used to effect the ligand displacement reactions (Chao and Salazone, 1989; Gustafsson and Jacks, 1995). Lead solubility in soils decreases with increasing soil pH. Liming is often recommended for reducing the bioavailability of Pb. However, liming an As contaminated soil may increase As concentrations in soil solution by a ligand exchange reaction. Similarly, additions of phosphate ions to solutions can displace arsenate ions from the soil solids into the soil solution, thereby increasing As solubility and bioavailability. Thus when phosphates are used to remediate soils that are contaminated with Pb and As, they may reduce bioavailability of Pb, but at the same time increase the bioavailability of As. So the objectives of this study were:

1. to conduct greenhouse investigations on the effect of treatments with iron oxides and phosphate on As concentrations in red clover grown on As contaminated soils
2. to investigate the effect of phosphate treatments on As and Pb concentrations in Japanese millet and red clover grown on soil contaminated with both Pb and As
3. to conduct laboratory investigations to determine mechanism for P induced decline in As concentrations in soil contaminated with both Pb and As.

6.2 Materials and Methods

6.2.1 Effect of Iron hydroxides and phosphate treatments on As bio-availability to red clover.

6.2.1.1 Green House Experiment 1

A bulk soil sample from a mine site in Preston County, West Virginia was collected for this experiment. The physico-chemical properties of the soil are listed in Table 6.1. Soils were limed with $Ca(OH)_2$ to a target pH of 6.5. After addition of lime, soils were incubated for 2 weeks. During that incubation period soils went through two wetting and drying cycles. After pH adjustment ,soils were divided into three subsamples. The first subsamples of soil did not receive any treatment, the second subsamples of soil was treated with $Fe(OH)_3$ that was prepared by neutralizing $Fe(NO)_3$ with NaOH to pH 6.5. Total Fe concentration in the second subsamples of soil was adjusted to 10 g kg^{-1} soil. After adjustment of Fe concentration this soil was designated

Table 6.1. Physico- chemical properties of the soil-1 used in the Greenhouse Experiment-1

	Physical Properties	
Particle size Analysis		
Sand	%	37
Silt	%	39
Clay	%	24
	Chemical Properties	
Soil pH (1:1)		4.55
Organic carbon	g kg^{-1}	9.5
Cation exchange capacity	cmol$_c$ kg^{-1}	10.1
Total Phosphorus	g kg^{-1}	0.50
Total Arsenic	mg kg^{-1}	12.5
Total Pb	mg kg^{-1}	22.7
DCB Fe	g kg^{-1}	4.5

as Soil-2 The third subsample of the soil was amended with $Fe(OH)_3$ to give a total Fe concentration of 20 g kg^{-1}. This soil was called Soil-3. Each of these soils were further divided into 3 parts each and each part was treated with $NaAsO_4$ to give As concentrations of 0, 125 and 250 mg kg^{-1}. Initial soil samples (approximately 500 g/arsenic-treatment) were collected for laboratory extraction experiments. These 9 different types of soil (550g/pot) were mixed with phosphate treatments in 3 replications. The amounts of P added were 0, 125, 250, and 375 mg kg^{-1}. Five red clover seeds were planted in each pot and after germination, two plants of red clover were retained in each pot. Above ground plant parts were harvested 60 days after sowing. Plant samples were washed with distilled de-ionized water and after washing they were dried at 60^{o} C in a forced air oven. Samples were ground with a cyclone grinder and ground samples were digested with concentrated nitric acid in a CEM (MDS-2000) microwave oven. Digested plant samples were analyzed for As on an electrothermal atomic absorption spectrophotometer.

6.2.1.2 Effect of Phosphate Concentrations on As Extraction: One-gram samples (in 12 replicates) for each As contaminated soil were transferred to 50-ml polyethylene centrifuge tubes. These soils were extracted with distilled water and KH_2PO_4 solutions with the following P concentrations:125, 250, and 375 mg kg^{-1}. Soil to solution ratio was 1:10 and equilibration time was 18 hrs. After 18 hrs of extraction, soil suspensions were centrifuged @ 12,000 rpm and the supernatant solution was filtered through a glass fiber filter paper of 0.45 μm nominal pore size. Filtered samples were analyzed for As on an electrothermal AAS.

6.2.2 Effect of Phosphate Applications on As and Pb Availability in Soils Contaminated with Both Pb and As

6.2.2.1 **Green House experiment 2**

In the second greenhouse experiment, thirteen soils were initially collected from a smelter waste disposal site. Soils were analyzed for chemical properties and three soils were selected on the basis of variation in As concentrations (Table 6.2). These soils had similar total Pb concentrations ranging from 2228 to 2485 mg/kg. Total As concentration in soil-A was 52 mg kg^{-1}, Soil –B was 238, and soil-C was 489 mg kg^{-1} (Table 6.2). These soils had very high P fixation capacity. P adsorption capacity of these soils ranged from 1250 to 1432 μg P g^{-1} soil. Soil material had 3.75 to 4.22 % organic carbon. Since the site did not support any vegetation, most of the organic carbon in these soils apparently came from unburned fuel that was used during the smelting process. These soils had a soil CEC of 16 to 18 cmol$_c$ kg^{-1}. A significant fraction of soil CEC in these waste streams originated from soil organic carbon. These soils were collected from different depths as 0 -30 cm, 30-60 cm, 60-90 cm, 90-120 cm, 120-150 cm, 150-200 cm, 200-250 cm, 250-300 cm , 300-350 cm, 350-400 cm, 400-500 cm, 500-600cm and 600-700cm. Soils were air dried and sieved for obtaining ≤ 2mm fraction. Lime was used to raise the soil pH to 6.5. For equilibration, the soils were passed through three wetting and drying cycles.

Table 6.2 Chemical properties of soils used in the Greenhouse Experiment –2

Soil Property	Units	Soil-A	Soil-B	Soil-C
Total Pb	mg kg^{-1}	2228	2485	2196
Total As	mg kg^{-1}	52	238	489
Soil pH		4.3	4.8	4.6
Organic Carbon	g kg^{-1}	42.2	38.4	37.5
CEC(pH 7.0)	$cmol_c$ kg^{-1}	18.0	17.5	16.1
Exchangeable Ca	$cmol_c$ kg^{-1}	7.2	5.9	7.8
Mg	$cmol_c$ kg^{-1}	1.21	1.15	1.73
Na	$cmol_c$ kg^{-1}	0.02	0.01	0.01
DCB Extractable Fe	g kg^{-}	52	43	58

Japanese millet(*Echinochloa crusgalli*) and red clover (*Trifolium pratense*) were grown in pots under green house conditions. These crops were chosen for their ability to accumulate metals and grow easily under greenhouse conditions. Seeds of these crops were germinated and grown in pots containing 500 g of acid washed sand. The bottom of each pot was removed and cheesecloth was inserted instead for facilitating root growth. Each pot was irrigated upon need. When a mat of roots had developed at the bottom, the pots were put back on other pots containing experimental plant growth medium described below.

Subsamples (in three replicates) of soil (500g/ pot) were mixed with phosphate materials. The amounts of phosphate were based upon the Pb content of the soil; four molar ratios (Pb/P) of 0, 0.33, 0.66, and 1.00 were used for the experiment. Aboveground plant parts were harvested 60 days after sowing and were oven dried at 60^0C. Two grams of each material were digested in CEM (MDS-2000) microwave apparatus using EPA 3051 method. The extracts were analyzed for P, As, and Pb on Perkin - Elmer Inductively Coupled Plasma Spectrophotometer and/or graphite furnace atomic absorption spectrophotometer**.**

6.2.2.2 Arsenic and P Co-precipitation Reactions (Laboratory Studies) Lead phosphates with entrained As were prepared by reacting 0.1 M $Na_3(PO_4)$ (250 mL) contaiaining 0.0001 to 0.01 M As with 250 ml of O.1 M $Pb(NO_3)_2$. Suspensions were filtered after 18 hrs through 0.2 um membrane filter paper. Filtered samples were analyzed for As and Pb on an electro-thermal AAS. Solid samples were also analyzed by

Philips X-ray diffractometer for X-ray diffraction. A second set of precipitates was prepared by reacting the following mixtures of P and As with 0.1 M $Pb(NO_3)_2$:

Molar Concentration of AS	Molar concentration of P
0.1	0.0
0.075	0.025
0.050	0.050
0.025	0.075
0.018	0.082

Solid precipitates were analyzed for their crystal structures by an X-ray diffraction spectrophotometer.

6.2.3 Basic Soil Analysis :

Soil pH: Soil pH was determined in soil samples(1:1 soil water w/v) allowing one hour equilibration using glass electrode with double junction Ag/AgCl reference electrode(McLean,1982).

Cation Exchange Capacity (CEC): Cation exchange capacity of soil was determined following the ammonium acetate method given by Soil Survey Staff (1984).

Organic Carbon(OC): A rapid titration procedure of Walkey and Black (1934) as outlined by Soil Survey Staff (1984) was used to determine Organic C.

Total Analysis: Total Analysis was done by following a procedure developed by HF digestion procedure modified from CEM corporation (CEM, 1991). Elements in digested samples were analyzed by ICP-AES (Perkin Elmer Model 400)

Exchangeable Ca, Mg, Na and DCB Extractable Fe: Exchangeable Ca, Mg, Na and Fe were determined using the standard procedures (ammonium acetate method) mentioned in Methods of Soil analysis (Sparks et al., 1996).

Particle Size Analysis: Particle size analysis was performed by pipette method proposed by Gee and Bausder (1986).

6.3 Results and Discussions

6.3.1 Effect of Iron hydroxides and phosphate treatments on As bio-availability to red clover (Greenhouse experiment –1)

In all soils increasing levels of As contamination resulted in elevated As concentrations in red clover that was grown in this pot culture experiment (Table 6.3). Arsenic concentrations of plant grown in uncontaminated soils were extremely low (< 0.14 mg kg^{-1}). In soil-1 when As concentrations were increased to 125 and 250 mg kg^{-1} corresponding As concentrations in the plant tissues were approximately 10 to 20 times larger than those observed in plants grown in uncontaminated soils. When soils contaminated with As were treated with phosphates, a significant increase in As concentrations in plant tissue were observed with increasing concentrations of P. In solution culture experiments, increasing phosphorus concentrations in nutrient solutions have been known to suppress As uptake. These results have been explained by fact that As and P have very similar chemical behavior and a single carrier facilitates uptake of these ions, consequently, high concentrations of P out-compete for sites on soil thereby making the available As for plant uptake. In our experiments, in a soil growth media, P applications enhanced As concentrations in plants. Both As and P form inner sphere

Table 6.3. Effect of four rates of phosphate treatments on As concentrations (mg kg^{-1}) in red clover plants grown on three soils that have been contaminated with 0, 125 and 250 mg kg^{-1} As.

	Soil Arsenic(mg/kg)	Arsenic concentrations in plant tissue (mg kg^{-1}) in soils treated with various concentrations of calcium phosphates				
Soil-1		P0	P125	P250	P375	
	0	0.13	0.09	0.10	0.14	
	125	1.22	1.65	1.93	2.11	
	250	2.45	2.85	3.10	2.96	
LSD(0.05)		0.19	0.25	0.37	0.39	
Soil-2	0	0.09	0.07	0.10	0.08	
	125	0.45	0.62	0.85	0.96	
	250	1.36	1.84	2.10	2.05	
LSD 0.05)		0.26	0.34	0.21	0.33	
Soil-3	0	0.0.7	0.08	0.05	0.08	
	125	0.39	0.45	0.55	0.65	
	250	0.77	0.69	0.82	0.84	
LSD(0.05)		0.22	0.35	0.29	0.23	

Note: P125, P250, P 375 refer to P concentrations of 0, 125, 250, and 375 mg L^{-1} in the soil.

complexes with metal oxides in soils. When P was added to a soil a significant amount of P participated in ligand exchange reactions that resulted in As removal from the soil surface and moving into soil solution. This transfer of As from the soil surface to the soil solution resulted in enhanced bioavailability of As. When these soils were extracted with orthophosphate solutions, As concentrations in extracts increased with increasing P concentrations of up to 250 g mL^{-1} (Table 6.4). These data support the hypothesis that amendment of soil with P increased bioavailability and potential mobility of As in the environment.

Both As uptake by plants and As extraction by phosphate containing extracting solutions decreased with increasing iron oxide concentrations in soils (Tables 6.3 and 6.4). Iron oxide concentrations in soils were: Soil-3 > Soil-2 > Soil-1. Arsenic concentrations in red clover tissue decreased from 2.45 mg kg^{-1} (Soil-1 contaminated with 250 mg kg^{-1} As) to 0.77 mg kg^{-1} (Soil-3 contaminated with 250 mg kg^{-1} As). These results suggest that iron oxides in soils not only impart As sorption capacity to soil, but they also reduce As extracting capacity of the phosphate ions. There are two possible mechanisms for these observations: 1) iron oxides may have some high energy sites where As is adsorbed so strongly that it can not be easily replaced; 2) high iron oxide concentrations in soils provide new sites for the adsorption of both As and P such that a significant fraction of orthophosphate ions in the extracting solution get adsorbed on the iron oxide surfaces thus phosphate ions are not available for extracting As.

Table 6.4. Effect of phosphate concentrations in extracting solutions on As extractions from three soils contaminated with three levels of As.

	Soil Arsenic(mg/kg)	Arsenic extracted mg kg^{-1} Soil				
		Water	P125	P250	P375	
Soil 1	0	ND*	ND	ND	ND	
	125	ND	26.2	28.6	32.1	
	250	0.19	48.3	62.5	68.7	
Soil 2	0	ND	ND	ND	ND	
	125	ND	14.2	18.7	18.2	
	250	ND	21.2	34.5	36.0	
Soil 3	0	ND	ND	ND	ND	
	125	ND	12.6	11.2	11.7	
	250	ND	19.7	21.2	21.4	

* Non determined

Note: P125, P250, P 375 refer to P concentrations of 0, 125, 250, and 375 mg L^{-1} in the extracting solution.

6.3.2 Effect of phosphate treatments on As bio-availability to red clover and Japenese millet (JM) from soils contaminated with both As and Pb (Greenhouse experiment –2)

Phosphorus concentrations in Japanese millet did not increase when P was applied @ Pb/P molar ratio 0.33. In some treatments there was a significant decline in P concentration in plant tissue when P was applied @ Pb/P Molar ratio of 0.3. This decline in P concentration was due to higher crop yield with P compared to the treatments where no P was applied. Phosphorus in JM tissue increased with fertilizer P application when P was applied @ Pb/P molar ratio of 0.66 or 1.0 (Table 6.5). Total As concentrations in the soil had no effect on the P concentrations in the JM. Lead concentrations in the JM were not affected by low application rates of P, but there were significantly lower Pb concentrations in the plants grown in pots that were treated with P application rates of @ Pb/P molar ratio of 1. There are a number of reports in the literature that indicate that P can reduce Pb availability by converting bioavailable Pb to a highly insoluble Pb phosphate mineral pyromorphite. Lead concentrations were very high in these soils and at high rates of application of water soluble P sources it is very likely that in our systems pyromorphite was formed and thus, it reduced the availability of Pb. Unlike the green house experiment–1, high rates of application of P also resulted in reduced As concentrations in the plant tissue of the crops grown on soil-B and soil-C. Thus, when soils were contaminated with both Pb and As, application of phosphate reduced plant availability of Pb.

Table 6.5. Effect of application rates of phosphates on Pb and As concentrations in Japanese millet grown on three soils contaminated with both Pb and As

Soil	Phosphate Treatments Pb/P molar ratios	Phosphorus Concentrations in Plant Tissue (mg kg^{-1} dry matter)	Lead Concentrations (mg kg^{-1} dry matter)	Arsenic Concentrations (mg kg^{-1} dry matter)
Soil 1	0.00	0.12	1.20	0.21
	0.33	.09	1.15	0.27
	0.66	0.17	0.83	0.25
	1.00	0.19	0.45	0.21
LSD(0.05)		0.04	0.12	NS
Soil 2	0.00	0..11	1.18	0.89
	0.33	0.08	1.19	0.85
	0.66	0.15	0.75	0.71
	1.00	0.18	0.82	0.35
LSD(0.05)		0.03	0.14	0.15
Soil 3	0.00	0.11	0.98	1.15
	0.33	0.13	0.95	1.06
	0.66	0.17	0.58	0.85
	1.00	0.16	0.51	0.78
LSD		0.05	0.13	0.21

In red clover tissue Pb and As concentration were much higher than those observed for JM grown on soils with same P treatment(Table 6.6). Even in this crop at high application rates of P both Pb and As concentrations in plant tissue declined. Decline in Pb concentration was expected, but no known explanation could sufficiently describe the observed antagonistic relationship between P and As. Based on the chemical structure of P and As atoms, it is possible that As and P can coprecipitate in a pyromorphite crystal where As substitutes for P atoms in the structure of a pyromorphite crystal. Soil and plant data collected from the greenhouse experiments was insufficient to conclusively prove this possibility.

6.3.3 Arsenic and P Co-precipitation Reactions (Laboratory Experiments)

When equimolar ratios of Pb and P were reacted, Pb concentrations in the equilibrium solution were less than the method detection limit for the electrothermal atomic absorption spectrophotomer of 2 g L^{-1}. When As was added along with the P, no arsenic could be detected in the equilibrium solution even when the reacting solution contained As concentrations of approximately 75 mg L^{-1} (0.001 M As) (Table 6.7). Even when As concentrations of 750 mg L^{-1} were present almost all As was incorporated into the structure of the precipitates. These experiments clearly indicated that As was removed from the solution when Pb and P reacted to form pyromorphite. Loss of a solute from a solution can occur by any of the following mechanism: 1) sorption of the solute on the surface of solid by formation of inner or outer sphere complexes; 2) surface precipitation of one solute on the surface of the solid; 3) co-precipitation of the solute with another precipitating compound. Reaction kinetics for precipitation of pyromorphite

Table 6.6. Effect of application rates of phosphates on Pb and As concentrations in red clover grown on three soils contaminated with both Pb and As

Soil	Phosphate Treatments Pb/P molar ratios	Phosphorus Concentrations in Plant Tissue(mg kg^{-1} dry matter)	Lead Concentrations (mg kg^{-1} Dry matter)	Arsenic Concentrations (mg kg^{-1} Dry matter)
Soil-A	0.00	0.14	3.15	0.31
	0.33	.09	2.78	0.32
	0.66	0.21	1.9	0.28
	1.00	0.25	0.85	0.31
LSD(0.05)		0.07	0.26	NS
Soil-B	0.00	0..16	2.75	1.13
	0.33	0.15	1.84	1.16
	0.66	0.22	1.18	0.44
	1.00	0.23	0.78	0.25
LSD(0.05)		0.05	0.27	0.21
Soil-C	0.00	0.11	2.71	1.55
	0.33	0.13	2.22	1.59
	0.66	0.21	1.69	0.92
	1.00	0.25	1.16	0.42
LSD		0.07	0.41	0.25

Table 6.7 Lead and As concentrations in equilibrium solutions when 0.1 M $Pb(NO_3)_2$ were reacted with 0.1 M phosphate solution that contained 0.0001 to 0.01 M $Na(AsO_4)_2$

Molar Concentrations of Reactants			Equilibrium Concentrations (g L^{-1})	
Pb	P	As	Pb	As
0.1	0.1	0.0	<2	ND*
0.1	0.1	0.0001	<2	ND
0.1	0.2	0.0002	<2	ND
0.1	0.1	0.001	4.5	ND
0.1	0.1	0.01	<2.0	6

* Non determined

are extremely rapid (Ma et al., 1993). Thus, in our experiments As could be removed from the solution by any of the reactions. Homogeneous inclusions of As by co-precipitation in pyromorphite can Pb to crystal distortions that can be measured by x-ray diffraction. X-ray diffraction analysis was conducted for pure pyromorphite and lead arsenate minerals . X-ray diffraction pattern showed that " d" value for 113 line was 3.34 nm for pyromorphite and it shifted to 3.38 nm when Pb was precipitated as lead arsenate (Figure 6.1). There was a linear increase in " d" value with increasing fractions of As in the precipitate. These results clearly demonstrate that As is incorporated into the crystal structure of pyromorphite and, consequently there is a distortion in the crystal structure of this mineral. Our results suggest that use of phosphates for remediation of sites that are contaminated with both Pb and As is feasible.

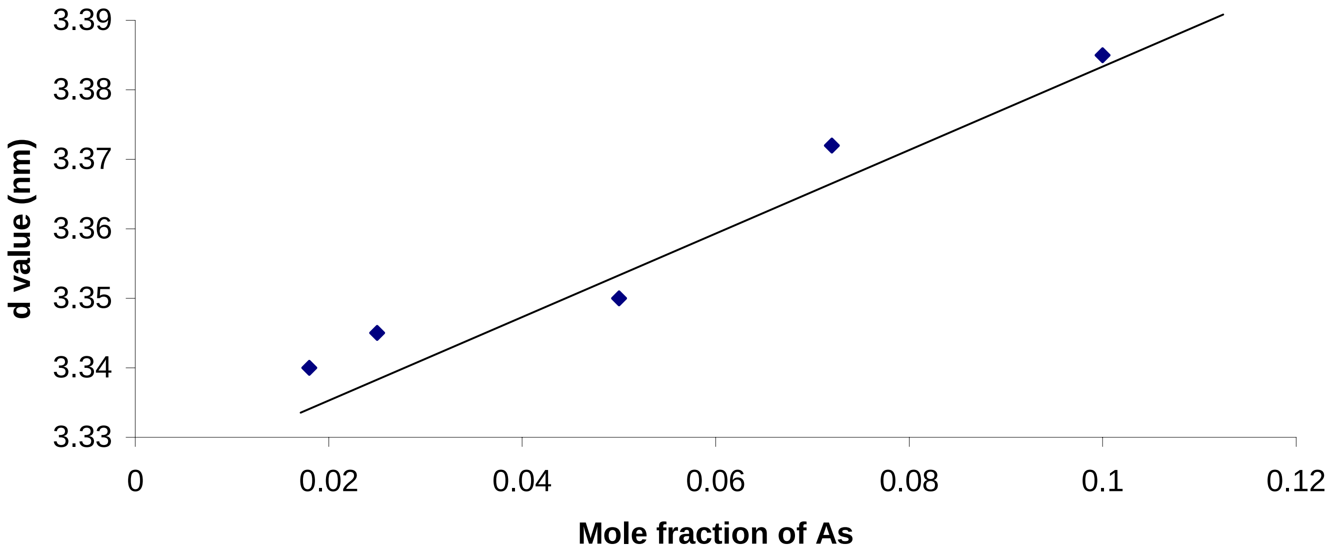

Figure 6.1: Effect of mole fraction of As in P soluton on (113) d spacing of pyromorphite crystal

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