

ADSORPTION OF MIXED METAL SYSTEMS
ON KAOLINITE

BY

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I. INTRODUCTION

Aquatic pollution by heavy metals and the fate of these metals has been the focus of considerable research in recent years. Numerous studies have demonstrated the importance of adsorption of metals by bottom muds and sediments in controlling the concentration and distribution of heavy metals in aquatic systems. Adsorption reactions in aquatic systems may be complicated by solution pH, concentration of suspended solids, the presence of ligands, and cation competition.

This study presents the results from laboratory investigations of the capacity of kaolinite to adsorb heavy metals including copper, nickel, cadmium, and lead. Kaolinite was chosen since it is a clay commonly found in suspended solids and sediments in natural water systems. Controlling factors considered included solution pH, clay dosage, and cation competition.

In any adsorption study, the amount adsorbed is usually measured as a function of adsorbate concentration in the medium surrounding the adsorbent. It is generally desirable to be able to fit the adsorption data to an adsorption isotherm equation so that parameters associated with the adsorption isotherm can be calculated for comparisons and correlation with other data. The Langmuir equation has been used extensively in the studies of adsorption of ions from solution by soils and clay minerals. This equation describes the adsorption of a single cation, not a mixed cation system.

Weber (1) has presented an equation for the simultaneous competitive adsorption of the components of a mixture of solutes. The equation for the general extent of adsorption, $q_{e,i}$ of the i th solute from a j -solute mixture is:

$$q_{e,i} = \frac{Q_i^0 b_i C_i}{1 + \sum_{j=1}^n b_j C_j} \quad (1)$$

where Q^0 and b are Langmuir constants and C_i and C_j are equilibrium concentrations.

The above equation has not been formally applied to experimental data for heavy metal adsorption on clay minerals. The objective of this study was to evaluate the validity and usefulness of the equation in describing the adsorption of mixed metal systems on kaolinite. This investigation presents the results of laboratory adsorption studies conducted for single and mixed metal systems. The preceding equation was used to predict equilibrium metal concentrations in mixed metal systems. The laboratory results, equilibrium metal concentrations in mixed systems, were compared to the equilibrium metal concentrations determined from the equation.

II. LITERATURE REVIEW

General Structure of Clays

The term clay implies a natural, earthy fine-grained material which develops plasticity when mixed with a limited amount of water. The expression clay material has no genetic significance; rather, it is used to denote material that was the product of weathering, formed by hydrothermal action, or has been deposited as a sediment. The clay fraction of a soil refers to the inorganic particles of the soil that are less than two microns in diameter (2).

Two units comprise the atomic structure of most clay minerals. One structural unit is composed of silica tetrahedrons. A silica atom is spaced equidistantly from four oxygen atoms or hydroxyls, arranged in a tetrahedron with the silica atom at the center. Each of the three oxygen atoms at the base of each tetrahedron is shared with the adjacent tetrahedron, forming a tetrahedral sheet. The second unit consists of an aluminum, iron, or magnesium ion surrounded by six equally spaced oxygen or hydroxyl ions, producing an octahedron. Each octahedron shares three hydroxyl or oxygen ions, creating an octahedral sheet which is two hydroxyl ions in thickness (3, 4).

Kaolinite is a two-layer clay commonly found in soils, stream sediments, and stream suspended matter. The structure is composed of a single tetrahedral sheet and a single alumina octahedral sheet combined in a unit so that the tetrahedral tips and one of the layers of the

octahedral sheet form a common layer. Adjacent units are held together by strong hydrogen bonds between the hydroxyl groups of the octahedral sheet and the oxygen groups of the tetrahedral sheet (3). The hydroxyl groups on the edges and outer planar surfaces are available for exchange (5).

Adsorption and Ion Exchange on Clays

Clay Characteristics Influencing Adsorption

The term adsorption is used to describe the accumulation or concentration of substances at a surface or interface (1). Cation exchange is defined as the reversible process by which cations are exchanged between a solid and liquid phase. Wiklander (6) defines ion adsorption as an increase in concentration or an accumulation of a species on a solid caused by ion exchange or some other interaction. The terms cation exchange and cation adsorption are often used interchangeably to describe the accumulation of cations at a clay mineral surface.

Clays have the capacity to adsorb cations from aqueous solution and retain them in an exchangeable state. This capacity of clays is due to the presence of a negative surface charge on the clay particles (6). There are three mechanisms by which surface charge develops:

- 1) Broken chemical bonds may be found at the edges of silica-alumina units.

- 2) Cation substitutions may occur within the lattice structure. If the valence of the substituted cation is lower, (e.g. Al^{+3} for Si^{+4} in the silica tetrahedral sheet or Mg^{+2} for Al^{+3} in the octahedral sheet), a net negative surface charge will develop.
- 3) The hydrogen of exposed hydroxyls may be replaced by a cation which would be exchangeable (2).

For kaolinite, broken bonds at the edges of the silica-alumina units are the major cause of the surface charge. The -M-O-M- (M = metal, O = oxygen) bonds in the component silica and alumina sheets can break on either side of the oxygen, which normally retains the electrons. This process gives a $-\text{M}-\text{O}^-$ group and a $-\text{M}^+$ group. As the pH is increased, adsorption of hydroxyl ions increases the negative surface charge of the clay (7).

To balance the negative surface charge, clay particles adsorb cations. These cations are exchangeable and held to the surface by Coulombic and/or Van der Waal forces, creating an electrical double layer. The cation exchange capacity (CEC) is defined as the quantity of negatively charged sites at the surface of the clay. Commonly, the CEC has been expressed in milliequivalents of exchangeable material per unit weight of exchanger (8).

The Electric Double Layer

Due to thermal motion, exchangeable cations (counterions) are distributed within a diffuse layer near the clay particle surface. These exchangeable cations are surrounded by water molecules, forming a solution that is called the micellar solution or inner solution. The solution of free ions, or electrolytes, outside of this inner layer of exchangeable ions is called the intermicellar or outer solution (6).

Van Olphen (9) summarized ion adsorption on clays in terms of the electric double layer theory. An electric double layer is created by:

- 1) Specific adsorption of certain ions which give the surface a positive or negative charge, unless the charge originates from interior crystal lattice imperfections, as in the case of the layer surface of clay, and
- 2) Accumulation of counterions close to the charged surface in the liquid. In an established double layer there may occur:
 - a. Exchange of counterions for other ions of the same sign available in solution (exchange adsorption),
 - b. Chemisorption of ions on the surface, which may lead to the destruction of the double layer or to creation of a new double layer, possibly of opposite sign, and
 - c. Exchange of exposed lattice ions at the surface by ions in solution (lattice exchange).

Three different theories of the double layer have been proposed. Helmholtz postulated that the negative surface charge of the particle formed the inner layer and the counterions in the immediate vicinity of

the surface formed the outer layer. Beyond this layer, he believed that the diffuse solution was completely at random, and balanced in charge. This was possible because the outer layer completely balanced the negative surface of the clay particle. Gouy and Chapman developed the theory of the diffuse double layer at a plane surface. In this model, the concentration of counterions is highest in the immediate vicinity of the surface and decreases with increased ionic strength. This theory is valid only for colloids having a low surface charge density, as in the plane surfaces of clays. Stern further advanced the double layer model by incorporating fundamentals of both of these models into a new theory. Stern's double layer consists of an inner layer (termed the Helmholtz layer) and an outer, diffuse layer. The inner layer is made up of closely adsorbed counterions that partially neutralize the surface charge. The thickness of this inner layer is essentially that of a molecular monolayer. The outer diffuse layer has an ionic concentration distribution due to electrostatic attractive/repulsive forces between the ion and particle surface and concentration gradient effects.

Distribution and Transport of Heavy Metals in Natural Waters and Sediments

Many studies have been conducted to determine the distribution and transport of heavy metals in aquatic systems.

Perhac (10) studied the distribution of heavy metals in two Tennessee streams. For most metals, with the exceptions of iron and manganese, the highest concentration (ppm metal in solid) was found in

the colloids and the lowest concentration was found in the dissolved state. The concentration in coarse particulates was intermediate between the colloidal and dissolved states. Even though the heavy metals were most concentrated in the colloids, Perhac found that the mass of water transported in the stream so greatly outweighed the mass of suspended particles that the greatest transport (by mass) was in the dissolved state. The concentration of metals in the bottom sediments was found to be higher than the concentrations present in the overlying waters. For example, nickel in the bottom sediments exceeded 20 parts per million (ppm), yet in the water its content was only 4 to 11 parts per billion (ppb).

Hyne and Pita (11) determined that lead, zinc, and cadmium were transported in streams in the dissolved state, either in ionic solution or as more soluble organo-metallic complexes. They also found that reservoirs located downstream from lead and zinc mining areas contained higher concentrations of the metals than reservoirs in other areas. The metals were concentrated in reservoir bottom sediments in comparison to surrounding soils and bedrock. Most of the zinc and lead content of the sediments was in the fraction with specific gravity between 2.0 and 2.9. This fraction contained significant amounts of montmorillonite, kaolinite, and illite.

Gibbs (12) investigated the transport of metals by five chemical mechanisms in the Amazon and Yukon Rivers. The mechanisms included:

- 1) Dissolved or ionic species, complexed with organic molecules in solution;

- 2) Adsorption on solids;
- 3) Incorporation in solid biological materials;
- 4) Precipitation and coprecipitation on solids;
- 5) Incorporation in crystalline sediments.

Gibbs found that the major mechanism of transport was the incorporation of metals in the crystalline structure of the sediments. The composition of the crystalline material was determined by the composition of rocks in the drainage basin.

Angino et. al. (13) studied the distribution of trace elements in Kansas streams and in the Arkansas River. They determined that the bulk of iron and manganese was transported in the suspended phase, whereas the amount of lead transported in the dissolved phase was about equal to that transported in the suspended phase. An x-ray diffraction study of the content of the suspended sediment indicated that clay minerals including kaolinite, illite, and montmorillonite were present in almost all samples.

Other investigations have shown that soluble forms of metals can be converted to insoluble particulate forms. In Indian Lake, Massachusetts, Symmes (14) showed that the conversion of copper sulfate to particulate forms was greatest within five days after treatment with the algacide. After ten days, 90 percent was converted and deposited in the sediments. Less than one percent of total sediment copper was present in interstitial water. Once attached to the sediment, the copper was not easily removed, with less than one percent being removed when sediment washing with deionized water was attempted.

Guy et. al. (15) developed a chemical model to investigate the mechanisms controlling the distribution of copper, cadmium, and zinc between soluble and particulate fractions in natural waters. Using bentonite, hydrous manganese oxides, and organic material, they found that the sorption of metals onto bentonite could be described by the Freundlich isotherm while the sorption of metals onto other solids followed the Langmuir isotherm. In a study of copper distribution, particulate components (bentonite, hydrous manganese oxides, and organic material) and soluble components (tannic acid, soluble humic acid, and bicarbonate) were combined to simulate a natural water system. The results indicated that copper distribution depended on the pH of the suspension. Above a pH of 6.0, fifty percent of the copper was sorbed onto the particulates, whereas the copper in solution was in a complexed form. Between pH 3.8 and 6.0, the soluble copper was distributed between organic complexes and free copper ion. Between pH 2.5 and 4.2, copper was desorbed from the particulates. Below pH 2.5, all of the copper was present in solution as free copper ion.

In a laboratory study, Gardiner (16) found that the adsorption of cadmium on mud solids was of major importance in controlling the concentration of cadmium in fresh waters. He found that the amount of cadmium adsorbed increased with increasing suspended-solids concentration. Concentration factors for muds varied between 5,000 and 50,000 depending on the type of solid, the concentration of metal ion present, the time of contact, and the concentration of complexing ligands present.

Buettner et. al. (17) studied the distribution and concentration of heavy metals in sediments in the Coeur d'Alene River in Northern Idaho, a river long polluted by mining and smelting operations. Mean sediment concentrations of 43 ppm, 115 ppm, and 3700 ppm were reported for cadmium, copper, and lead, respectively. The variation of metal content in different layers of core samples seemed to be related to the nature of the sediments. For example, lead was most concentrated in the clay layer of the sediment and least concentrated in the sand layer.

Aston and Thornton (18) studied the trace element composition of stream sediments and waters from eight tributaries. The greatest range of water and sediment variations occurred for mineralized/mined tributaries. For example, in one such tributary, sediments showed an annual range of 1420 - 5050 ppm copper and 1840 - 5600 ppm zinc, and for waters 150 - 515 micrograms per liter (ug/l) copper and 680 - 2000 ug/l zinc, over the same period. In contrast, an unmineralized tributary showed ranges of 48 - 150 ppm copper and 125 - 500 ppm zinc in sediments, and 2 - 8 ug/l copper and 7 - 12 ug/l zinc in waters, over the same period. High metal concentrations in mineralized/mining waters were similarly reflected in stream sediment concentrations. They suggested that average sediment metal concentrations may be useful for the predictions of areas where water concentrations of potentially toxic metals may exceed recommended limits.

Sias and Wilhn (19) found that copper levels in lake sediments can be greater in deep water sediments than in shallow ones, because the deeper sediments consist of clays having a higher cation exchange

capacity. They found that copper concentrations in the deeper areas of lakes are relatively uniform over sediment depth while concentrations in shallow water areas decreased with sediment depth because the top clay layers were constantly redeposited by surface currents and wind.

Adsorption Isotherms

Adsorption isotherms have been used for many years to investigate the nature of various types of adsorption phenomena. They provide useful models for physical adsorption; in addition, some of the equations are well suited for describing chemisorption phenomena.

Two adsorption isotherm equations have commonly been used in evaluating or comparing solution adsorption data. The Langmuir adsorption isotherm was originally derived for the adsorption of gases on solids and has since been used to describe the relationship between the adsorption of ions by a solid and the equilibrium concentration of the ion in solution. The Langmuir model is based on the assumptions that: 1) maximum adsorption corresponds to a saturated monolayer of non-interacting solute molecules on the adsorbent surface, and 2) the energy of adsorption is constant. The Langmuir adsorption equation is:

$$q_e = \frac{Q^0 b C}{(1 + b C)} \quad (2)$$

or, in linear form;

$$\frac{1}{q_e} = \frac{1}{Q^0} + \left(\frac{1}{b Q^0}\right) \left(\frac{1}{C}\right) \quad (3)$$

where,

C = measured concentration in solution at equilibrium,

Q^0 = number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface,

q_e = number of moles of solute adsorbed per unit weight at concentration C , and

b = constant related to the bonding energy or net enthalpy.

According to Weber (1), although a Q^0 value rarely represents true monolayer capacity, the value does represent a practical limiting capacity for adsorption. As long as its restrictions are recognized, the Langmuir equation is valuable for describing equilibrium data and for providing parameters, Q^0 and b , to quantitatively compare adsorption in the same or different adsorbate-adsorbent systems.

The other frequently used adsorption equation is the Freundlich isotherm equation. It was developed empirically but is often found to be useful for describing equilibrium adsorption data. The general form of the Freundlich equation is:

$$q_e = K_F C^{1/n} \quad (4)$$

or, in linear form;

$$\log q_e = \log K_F + \frac{1}{n} \log C \quad (5)$$

where K_F and n are empirical constants, and q_e and C are as defined previously. The Freundlich equation is less useful than the Langmuir

equation because no information on maximum adsorption capacities is directly obtainable. However, the intercept, the value of $\log K_F$ for $C = 1$ ($\log C = 0$), may be used roughly as an indicator of maximum sorption capacity, and the slope, $\frac{1}{n}$, of adsorption intensity (1). The Freundlich equation is most often used for the comparison of adsorption behavior in different adsorbate-adsorbent systems or in the same system under varied conditions.

Newton (20) studied the adsorption of zinc on kaolinite, illite, and bentonite over a pH range of 5 to 7. Zinc concentrations utilized ranged from 1 to 500 micromolar. The adsorption of zinc in all systems studied was pH dependent, with increased removal at higher pH values. The adsorption data showed that increasing the zinc concentration increased the amount of zinc adsorbed. However, limited adsorption data at 200 and 500 micromolar concentrations indicated that adsorption was increased very little by increasing zinc concentrations in this range.

Counts (21) investigated the adsorption of nickel and lead on kaolinite and montmorillonite at pH values of 2, 4, and 6. Metal concentrations utilized ranged from 25 to 1000 ppm. For both clays, nickel adsorption data could be adequately described by the Langmuir and Freundlich equations at all pH levels studied. Adsorption of lead on montmorillonite also conformed to both equations. However, lead adsorption data for kaolinite was adequately described by the Langmuir equation, but not the Freundlich. Adsorption of lead and nickel increased with increasing pH. In ion-competition studies, the effects of added Ca(II) or Al(III) on the adsorption of lead on kaolinite were

investigated. In these studies, the initial concentration of lead was equal to the initial concentration of either calcium or aluminum in each test suspension. Aluminum had a large reducing effect on lead adsorption. Calcium reduced lead adsorption to a lesser extent.

Various studies have been undertaken to determine whether the adsorption of heavy metals on soils conforms to the Langmuir and Freundlich equations. The Langmuir isotherm equation can be used to compute adsorption maxima and bonding energies. These coefficients are convenient capacity and intensity values which can be related to various soil properties that may influence the nature of the reaction between soils and heavy metals.

Shuman (22) investigated zinc adsorption on four soils at two different depths and found that the adsorption data could be described by the Langmuir adsorption isotherm. Soils high in clay had higher adsorption capacities and higher bonding energies for zinc than sandy soils. The slopes of the lines and, thus, the adsorption capacities were different for various soil types.

Sekhon and Trehan (23) studied zinc adsorption in suspensions of six soils of different physicochemical characteristics in zinc sulfate solutions. At low concentrations (2 to 30 ppm), zinc adsorption was described by the Langmuir equation. The calculated Langmuir adsorption maxima were positively related to clay content ($r = 0.76$) and negatively with organic matter content ($r = -0.81$) of the soils.

Adsorption of Mixed Solutes

Industrial and domestic wastewaters commonly contain a mixture of solutes to be adsorbed. According to Weber (1), the compounds may mutually enhance adsorption, may act independently, or may interfere with one another. Mutual inhibition of competing solutes will occur if:

- 1) Adsorption is confined to a single or a few molecular layers;
- 2) The adsorption affinities of the solutes do not differ by several orders of magnitude; or
- 3) There is not a specific interaction between solutes enhancing adsorption.

Further, Weber stated the degree of inhibition should be related to the relative sizes of the molecules being adsorbed, their relative adsorption affinities, and to the relative concentrations of solutes.

For adsorbates which exhibit Langmuir-type isotherms for adsorption from single-solute solutions, it is possible to define the extent of steady-state adsorption as a function of the relative equilibrium concentrations of the constituent solutes according to a monolayer adsorption model. Weber presented an equation for describing adsorption competition among the components of a mixture of solutes. By formal analogy to the Langmuir equation for adsorption of individual species from mixtures of gases, and to the expressions used by Royd et al. (24) for descriptions of competitive ion-exchange phenomena, equations for

sorption competition may be written. For the general case for extent of adsorption, $q_{e,i}$ of the i th solute from a j -solute mixture the equation is:

$$q_{e,i} = \frac{Q_i^0 b_i C_i}{1 + \sum_{j=1}^n b_j C_j} \quad (1)$$

For a two-solute mixture of substances A and B, the equation for solute A is:

$$q_{e,A} = \frac{Q_A^0 b_A C_A}{1 + b_A C_A + b_B C_B} \quad (6)$$

where Q_A^0 , b_A , and b_B are Langmuir constants determined from pure solution measurements with the respective solutes, and C_A and C_B are equilibrium concentrations.

Adsorption of Heavy Metals

The extent to which heavy metals are adsorbed from aqueous solution by clay suspensions has been shown to be a function of variables such as solution pH, the nature of the clay, competition with other heavy metals, time of contact, and the nature of any ligands present.

Stumm and Morgan (25) showed that the occurrence of metal hydroxyl species can affect the adsorption of hydrolyzable metal ions. They found that the pH at which metal hydroxyl species formed corresponded to the pH at which metal ion sorption became significant. Farrah and Pickering (7) studied the effect of pH on the adsorption of copper on

sodium-saturated kaolinite. Their results showed that the adsorptive capacity of the clay increased with pH up to a limiting value at approximately pH 7.0. In the pH region 3.0 to 6.0, the predominant aqueous copper was the hydrated, CuOH^+ , ion. Nearly complete copper removal was observed in the pH range from 6.0 to 7.0. In alkaline media, the authors suggested that the clay suspension acts as a nucleation site for hydroxy-bridged copper species. Jackson and Menzel (26) investigated the influence of pH on the uptake of copper ions by potassium-saturated kaolinite and montmorillonite. An increase in the extent of CuOH^+ adsorption was found to be directly proportional to an increase in both the pH and Cu^{+2} concentration of the soil. More than fifty percent of the copper adsorbed by these clay minerals, was in the CuOH^+ form.

Farrah and Pickering (27) later investigated the influence of pH on the adsorption of heavy metal ions (copper, lead, zinc, and cadmium) by clays. Three different clay suspensions, kaolinite, illite, and montmorillonite were utilized. The experimental results showed that the amount of each metal adsorbed increased gradually with pH over a range of 3.5 to 6.0. For all three clays, plots of the logarithm of the total millimoles of metals sorbed versus pH yielded straight lines. Farrah and Pickering suggested that the difference in slopes between montmorillonite and the other clays, kaolinite and illite, eliminated the possibility that increased uptake is due solely to the formation of MOH^+ species in solution. They proposed that the extent of metal uptake is determined in part by the relative concentrations of the various

species present, and in part by the nature of the clay. They suggested that adsorption of hydroxyl ions followed by attachment of metal ions to the clay, contributed to differences in adsorption capacity of clays at different pH levels. It was proposed that metal ions attached to the clay, either by bonding to adsorbed hydroxyl ions or to sites created by proton removal. With montmorillonite, a smaller fraction of the total capacity is associated with pH dependent sites.

Anderson (28) studied the adsorption of zinc, copper, cobalt, chromium, lead, and cadmium on kaolinite, montmorillonite, and a clay soil containing fifty-three percent illite. Adsorption of all metals by the three minerals increased as the pH increased. Virtually complete removal of copper, nickel, lead, and cadmium occurred at pH values of approximately 7.5, 7.5, 7.0, and 9.5, respectively.

Gibali (29) found that nickel adsorption by calcium-saturated montmorillonite and kaolinite was markedly affected by the pH of the equilibrium solution. In terms of percent adsorption onto kaolinite, there was an average increase of forty percent between pH 3.8 and pH 6.7. A similar trend was observed for montmorillonite, but the magnitude of the increase was only ten percent. However, montmorillonite showed a higher capacity for nickel than kaolinite at all pH values studied.

Only a limited number of studies have been performed to determine the influence of time of equilibration on heavy metal adsorption. Kardos and Sidle (30) conducted time-dependent batch equilibrium studies for copper and cadmium adsorption on a clay loam forest soil to

determine if an instantaneous equilibrium approach or a kinetic approach would be most suitable for describing the adsorption of heavy metals in natural soil systems. Major cations (Ca^{+2} , Mg^{+2} , K^+ , NH_4^+) were added to equilibrating solutions in an attempt to match the cationic matrix of a sewage sludge. The addition of cations allowed for competition with the heavy metals for adsorption sites. Essentially all of the copper was adsorbed by the soil in the first eighteen minutes, indicating that the adsorption process was kinetically rapid. Adsorption of cadmium was more time-dependent than copper. After three hours of adsorbent contact, 79 to 94 percent of the initial cadmium in solution was adsorbed. Both copper and cadmium data could be described adequately by the Freundlich and Langmuir isotherms, but lower correlation coefficients were obtained with the Langmuir isotherm.

Levi-minzi et. al. (31) studied lead adsorption on twelve soils. Experiments were conducted to select a suitable equilibration time for soils with high and low cation exchange capacity. The amount of lead adsorbed by the soils increased sharply for the first hour of mixing. Mixing longer than four hours produced minimal improvements in adsorption capacity.

Gardiner (32) observed that the adsorption of cadmium on samples of river mud occurred rapidly. Equilibrium was nearly complete two minutes after the addition of the metal solution. Gardiner concluded that either (1) vacant sites were available for rapid adsorption or (2) sites where rapid exchange with adsorbed metal ions could occur were significant.

The presence of ligands may influence metal ion adsorption behavior. Payne and Pickering (33) found that the extent of copper adsorption on kaolinite was increased by the presence of ligands. They found that the important factors for determining the extent of copper adsorption were solution pH, the nature of the ligands present, and the order of contact of the species. In the presence of organic ligands at a pH greater than 6.0, there was virtually a total removal of copper ions from solution.

Ashmead et. al. (34) found that the addition of various anions and ligands significantly increased adsorption of cadmium, copper, and lead on soils. Humic acid was most effective in this regard, followed by nitrilotriacetate, tartrate, glycine, and phosphate, respectively. They suggested that the enhanced adsorption resulted from the formation of a metal-ligand bond. The metal-ligand complex could adsorb to the solids through specific chemical bonds such as sharing of free electrons available from the metal-ligand complexes.

From the literature available on heavy metal adsorption on clay surfaces, it was apparent that no universal replacement order or cation selectivity exists. Farrah and Pickering (27) found that the affinity order for divalent cations varied with clay type. For kaolinite, the affinity order for divalent cations was found to be $Pb > Ca > Cu > Mg > Zn > Cd$. For montmorillonite, the sequence found was $Ca > Pb > Cu > Mg > Cd > Zn$, while for illite the order was $Pb > Cu > Zn > Ca > Cd > Mg$. The affinity series quoted were based on relative uptake when equal amounts of both ions were present in solution. Riemer and Toth (35)

studied copper adsorption on the same three clay minerals. Based on the absolute amounts of copper adsorbed, the clays were arranged in the following order for the aluminum-saturated forms of the clays: montmorillonite > illite > kaolinite. Kabata-Pendias (36) investigated the uptake of cobalt, zinc, copper, and nickel by clay minerals. Using 30 ppm solutions of each metal and a solution pH of 6.0, the order of uptake was found to be $Ni \geq Cu > Zn \geq Co$. The relative capacity of the clay minerals for metal uptake was illite > montmorillonite > kaolinite.

In summary, it is evident that the adsorption of heavy metals by clay minerals involves more than simple ion exchange. Adsorption reactions may be complicated by solution pH, concentration of suspended solids, the presence of ligands, and cation competition.

III. METHODS AND MATERIALS

Preparation of Clay (Adsorbent)

The clay used in this study was kaolinite (designated kaolinite hydrite UF), obtained from the Georgia Kaolin Company. The clay was size fractionated according to Jackson's procedure using a centrifuge. The procedure is outlined below.

- 1) Adjust the pH of the soil suspension to 9.5 with a 1 N sodium carbonate (Na_2CO_3) solution.
- 2) Pour the suspension into 200 milliliter centrifuge bottles to mark 10 centimeter from the bottom of the bottles.
- 3) Centrifuge at 2000 revolutions per minute (rpm) for five minutes.
- 4) Decant the supernatant into a storage container labelled < 2 microns.
- 5) Again add 1 N Na_2CO_3 to the 10 centimeter mark, stir, and centrifuge at 1000 rpm for two minutes.
- 6) Decant the supernatant into the clay storage container.
- 7) Repeat steps 5 and 6 until the supernatant liquid is about clear (37, 38, 39, 40).

The < 2 micron clay particle size fraction was retained for the adsorption studies.

After particle-size fractionation, the kaolinite was calcium-saturated by repeated washings with 1 N calcium chloride (CaCl_2).

Excess salts were removed by washing with distilled water until the chloride (Cl^-) ion tested negative to silver nitrate (AgNO_3).

Finally the clay was dried in a freeze-drier.

Preparation of Metal Solutions

Single metal ion solutions were prepared from stock atomic absorption reference solutions (Fisher, certified) containing 1000 ppm by weight test metal ion. An appropriate aliquot (10 milliliters) of each stock metal solution was diluted with distilled deionized water to make two liters of a 5 ppm solution. After preliminary adsorption studies were performed, it was necessary to modify the method of preparing two metal solutions, copper and lead. Preliminary studies indicated that when the desired metal solution was mixed with the clay, the suspension pH was greater than the experimental pH range. In making up the working solutions of copper and lead, it was necessary to adjust the solution pH levels with a minimal volume of 0.04 N hydrochloric acid (HCl) to ensure that the pH of the clay-metal suspension was within the desired range.

Mixed metal solutions contained equivalent ppm amounts of each ion. These solutions were prepared by the same procedure utilized in the preparation of the single metal solutions. For example, to prepare a mixed metal solution of copper and nickel, a ten milliliter aliquot of each stock metal solution (1000 ppm) was placed in a two liter volumetric flask and diluted with distilled deionized water. The resulting mixed metal solution contained 5 ppm copper and 5 ppm nickel.

Fresh metal solutions were prepared for each adsorption study using glassware cleaned with concentrated nitric acid and rinsed thoroughly with distilled water.

Precipitation Studies

Precipitation studies were performed using 5 ppm metal solutions and a pH range of 5.0 to 8.0. Two-hundred milliliters of the metal solution to be studied were poured into a beaker with a magnetic stirrer. The beaker was then placed on a mechanical stirrer. Each sample was adjusted to the desired pH value with 0.04 N sodium hydroxide (NaOH) and the use of a pH meter. After the desired pH value was reached, the sample was poured into centrifuge tubes (approximately 33 milliliters). Sample aliquots were centrifuged at 2000 rpm for ten minutes. Supernatants were transferred to Nalgene bottles and analyzed for metal concentrations by atomic absorption spectrophotometry (Perkin-Elmer Model 703).

Adsorption Procedure

Predetermined weight samples of kaolinite were weighed on a Mettler balance and placed in 250 milliliter acid-washed, polypropylene centrifuge bottles. Two liters of a standard metal solution were prepared as previously described. Two-hundred milliliters of the metal solution were added to each sample bottle containing the adsorbent. The clay and metal solution were mixed thoroughly by handshaking. The resulting suspensions were adjusted to the desired pH values with 0.04 N

NaOH and the use of a pH meter. After the desired pH level was reached, the samples were placed on a general purpose Eberbach shaker. The time each sample was placed on the shaker was recorded. Aliquots (approximately 33 milliliters) were taken from each sample at predetermined time intervals. The pH of each sample was determined at each time interval. The use of a combination pH electrode allowed measurement of pH directly in the centrifuge bottle. Sample aliquots were centrifuged at 2000 rpm for ten minutes. The supernatant of each sample was transferred to a Nalgene bottle, acidified to a pH value below 2.0, and analyzed for metal concentrations by atomic absorption. Blank samples containing no clay were subjected to the same procedure.

Preliminary Studies

Time studies for copper, lead, nickel, and cadmium were conducted to determine if an instantaneous equilibrium approach or a kinetic approach best described the adsorption of heavy metals in aquatic systems. Preliminary time studies were performed using a 5 ppm nickel solution and a pH range of 5.0 to 8.0. The adsorption of nickel over time and at various pHs was determined by equilibrating 0.50 grams of clay with 200 milliliters of the nickel solution. Nickel concentrations were determined after shaking periods of ten minutes, thirty minutes, one hour, two hours, four hours, and twenty-four hours. The preliminary experiments indicated that nickel was adsorbed rapidly. Shaking longer than four hours produced minimal improvement in adsorption capacity.

Single Metal Adsorption Studies

pH 5.5 - 6.0

Adsorption Rate Studies

Based upon the preliminary rate studies, time studies were initiated for nickel, cadmium, copper, and lead over the lower pH range, 5.5 to 6.0. Varying clay dosages, 0.10, 0.25, 0.50, 0.75, and 1.0 grams (per 200 milliliters) were weighed and placed in centrifuge bottles. A 5 ppm solution of the metal to be studied was prepared. The adsorption series samples were prepared and mixed according to the adsorption procedure previously outlined. The pH of each sample suspension was adjusted to 5.5 to 6.0. Samples were placed on the shaker and aliquots were taken from each sample after ten minutes, thirty minutes, two hours, four hours, and twenty-four hours. The pH of each sample was recorded at each time interval. The sample aliquots were centrifuged and the solutions analyzed for their metal concentration by atomic absorption. Blank solutions (no clay added) of each metal were subjected to the same procedure.

Adsorption Isotherm Studies

The experimental procedures for the adsorption isotherm studies were similar to those used in the kinetic studies with the exception that additional clay dosages were used. Additional dosages were chosen for each metal based on the metal uptake observed in the individual metal kinetic study.

Lead: In the lead kinetic study, a clay dosage of 0.50 grams per 200 milliliter sample removed virtually all lead from solution. Low clay dosages, 0.025, 0.05, 0.10, 0.15, 0.20, 0.25, and 0.50 grams (per 200 milliliters) were utilized in the isotherm study. A 5 ppm lead solution was prepared. The adsorption series samples were prepared according to the adsorption procedure previously outlined. The resulting suspensions were equilibrated for twenty-four hours using the shaker apparatus.

Nickel: In the kinetic study, the 0.50 gram clay dosage removed only 27 percent of the initial nickel from solution. Thus, higher clay dosages, 0.10, 0.15, 0.50, 0.75, 0.875, and 1.0 grams (per 200 milliliters) were used for the equilibrium study. A 5 ppm nickel solution was prepared. The adsorption series samples were prepared according to the adsorption procedure previously outlined. The resulting suspensions were equilibrated for twenty-four hours.

Additional nickel isotherm studies were performed using solutions containing higher initial concentrations (12.1 and 14.7 ppm) of nickel. Clay dosages ranging from 0.25 to 1.0 grams (per 200 milliliters) were used in these studies. Aliquots were taken from each sample after ten minutes, two hours, four hours, and twenty-four hours of shaking.

Copper: Clay dosages, 0.10, 0.25, 0.50, 0.625, 0.75, and 0.875 grams (per 200 milliliters) were utilized in the copper isotherm study. A 5 ppm copper solution was prepared. The adsorption series samples were prepared according to the adsorption procedure previously outlined. The resulting suspensions were equilibrated for twenty-four hours.

Additional copper isotherm studies were conducted using solutions containing higher concentrations (9.8 and 15.0 ppm) of copper. Clay dosages ranging from 0.15 to 0.75 grams (per 200 milliliters) were used in these studies. Aliquots were taken from each sample after ten minutes, two hours, four hours, and twenty-four hours of shaking.

Cadmium: In the kinetic study, the 0.50 gram clay dosage removed only 31 percent of the initial cadmium from solution. Thus, higher clay dosages of 0.05, 0.10, 0.25, 0.50, 0.75, 1.0, 1.5, 1.75, and 2.0 grams (per 200 milliliters) were utilized. A 5 ppm cadmium solution was prepared. The adsorption series samples were prepared according to the procedure previously outlined. The resulting suspensions were equilibrated for twenty-four hours.

Additional isotherm studies were conducted using solutions containing higher concentrations (9.4 and 13.7 ppm) of cadmium. Clay dosages ranging from 0.10 to 1.0 grams (per 200 milliliters) were used. Aliquots were taken from each sample after ten minutes, two hours, four hours, and twenty-four hours of shaking.

pH 7.0 - 7.5

The following paragraphs describe the procedure used to collect adsorption rate and adsorption isotherm data over the pH range 7.0 to 7.5. In the low pH studies (pH 5.5 to 6.0) rate and isotherm investigations were conducted separately.

Studies were conducted for nickel, cadmium, and copper over the pH range 7.0 to 7.5. Lead was not included since precipitation was a significant removal mechanism for lead in this pH range.

A 5 ppm solution of each metal was prepared as previously described. The literature indicated that an increase in the solution pH increased the metal uptake by clay. Based on this knowledge and the individual metal uptake indicated in the low pH isotherm studies, lower clay dosages ranging from 0.05 to 1.0 grams per 200 milliliters of sample volume, were chosen for the pH range 7.0 to 7.5. Adsorption series samples for each metal were prepared and mixed according to the adsorption procedure previously outlined. The pH of each sample suspension was adjusted to 7.0 to 7.5. Samples were placed on the shaker and aliquots were taken from each sample after thirty minutes, one hour, and two hours. The sample aliquots were centrifuged and analyzed by atomic absorption spectrophotometry. Blank solutions of each metal were carried along through the experiments.

Mixed Metal Adsorption Studies

pH 5.5 - 6.0

Mixed metal solutions contained equivalent ppm amounts (5 ppm) of each metal ion as previously described. The following mixed metal solutions were studied:

- 1) Copper and nickel;
- 2) Nickel and lead;
- 3) Cadmium and lead;

4) Copper, nickel, and cadmium; and

5) Copper, nickel, cadmium, and lead.

Clay dosages for each mixed metal study were chosen based on adsorption observed in single metal studies. The adsorption series samples for each study were prepared and mixed according to the previously defined adsorption procedure. The pH of each sample suspension was adjusted to 5.5 to 6.0. Samples were placed on the shaker and aliquots were taken from each sample after ten minutes, one hour, and two hours of shaking. The sample aliquots were centrifuged and analyzed for their metal concentrations by atomic absorption. Blank mixed metal solutions were carried through the experiments.

pH 7.0 - 7.5

Mixed metal solutions contained 5 ppm of each ion. The following mixed metal solutions were studied:

1) Copper and nickel; and

2) Nickel and cadmium.

The procedure for mixed metal studies at pH 7.0 to 7.5 was the same as previously described for studies conducted at pH 5.5 to 6.0, with one exception. Aliquots were taken from each sample after thirty minutes, one hour, and two hours of shaking.

IV. RESULTS

Precipitation Studies

Table I presents the data obtained when solutions of each metal were maintained at pH values ranging from 5.0 to 8.0. These studies were necessary to assess the potential for metal precipitation as hydroxide solids during the adsorption studies. Copper, nickel, and cadmium did not precipitate over the pH range 5.0 to 8.0. Lead precipitation was not a problem at pH 5.5 to 6.0; however, significant precipitation was noted at higher pH values. For this reason, lead was not included in the adsorption studies conducted at pH 7.0 to 7.5.

Adsorption Rate Data

Adsorption rate studies were performed to determine if an instantaneous equilibrium approach or a kinetic approach best described the adsorption of heavy metals on clay surfaces. The results for each metal for both pH ranges are included in Appendix Tables A-1 through A-4. The residual metal concentrations are also presented graphically as a function of clay dosage in Figures 1 through 7. A comparison of the data presented in graphical form indicates that the metal adsorption process was kinetically very rapid as contact times longer than thirty minutes produced minimal increases in observed adsorption capacity.

Table I. Results of Metal Precipitation Studies

pH	Residual Metal Concentration (mg/l)			
	Cu	Ni	Cd	Pb
5.0	4.92	4.96	4.67	5.04
5.5	4.91	4.94	4.68	4.90
6.0	4.88	4.95	4.66	4.79
6.5	4.45	4.93	4.64	3.41
7.0	4.14	4.93	4.68	0.62
7.5	3.96	4.90	4.67	0.34
8.0	4.02	4.88	4.55	0.24

Initial Cu Concentration = 4.98 mg/l
Initial Ni Concentration = 4.98 mg/l
Initial Cd Concentration = 4.70 mg/l
Initial Pb Concentration = 5.06 mg/l

NOTE: Values listed are averages of six independent trials.

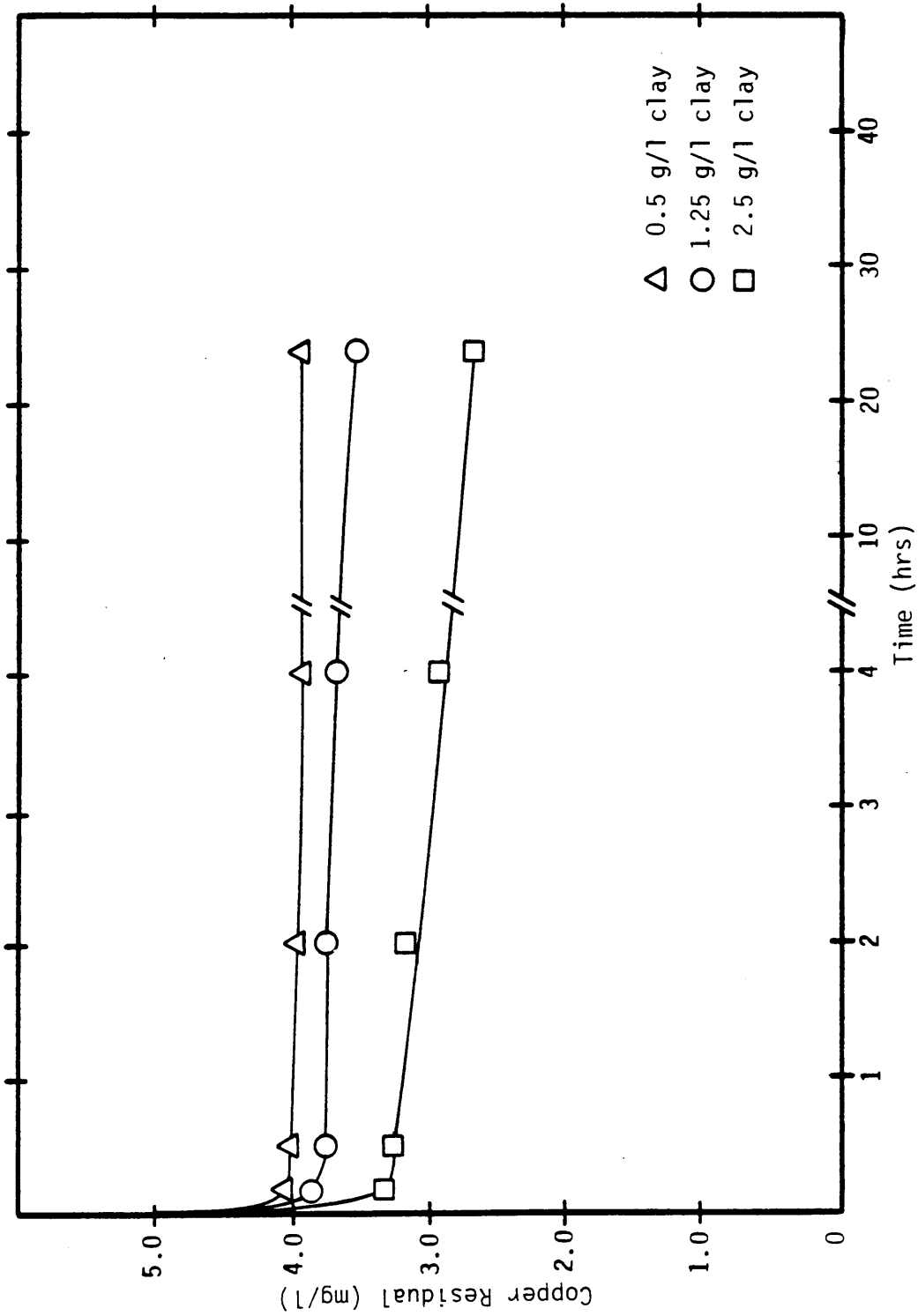


Figure 1. Copper Concentration Remaining in Solution as a Function of Time
pH = 5.5 - 6.0

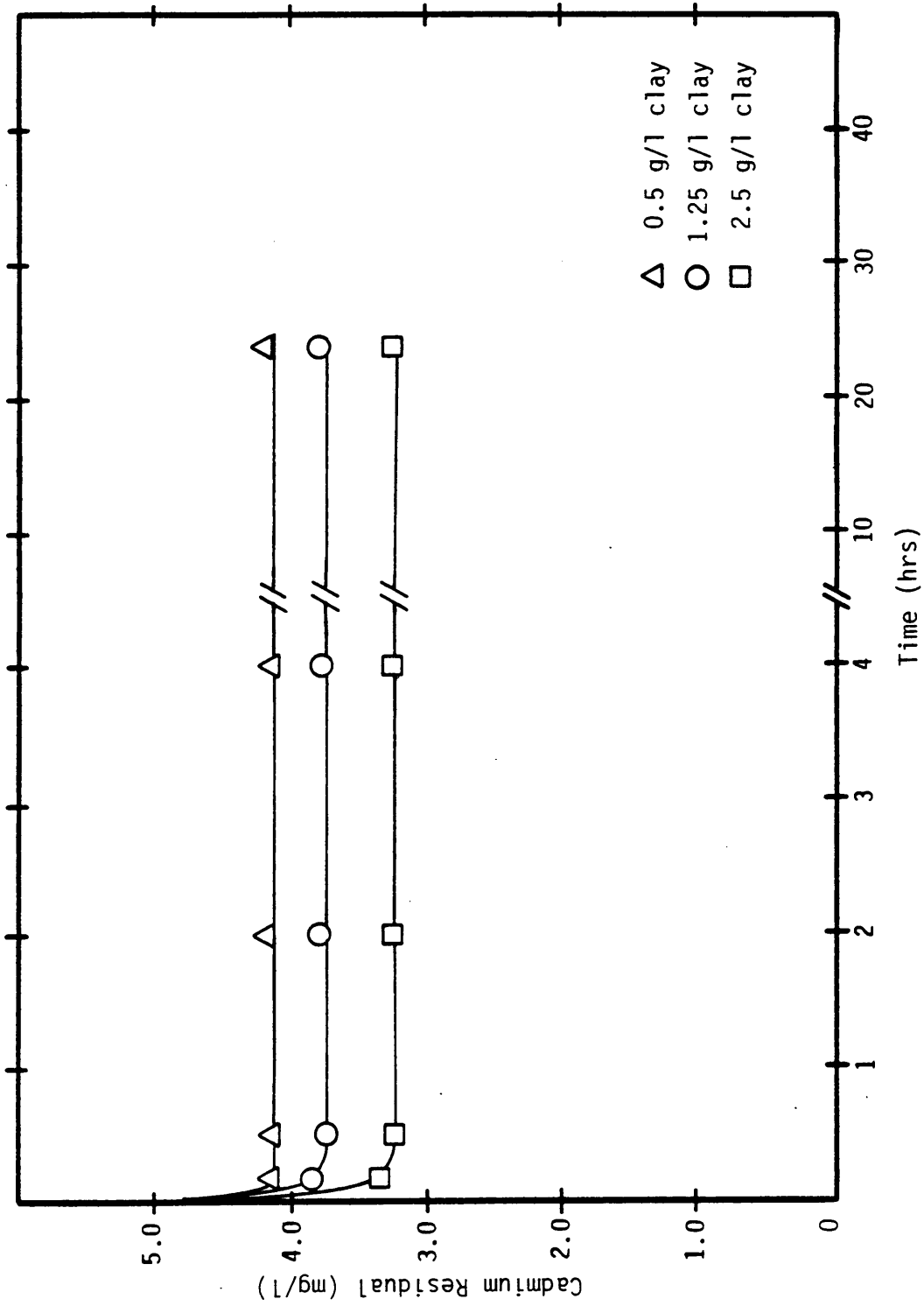


Figure 2. Cadmium Concentration Remaining in Solution as Function of Time
pH = 5.5 - 6.0

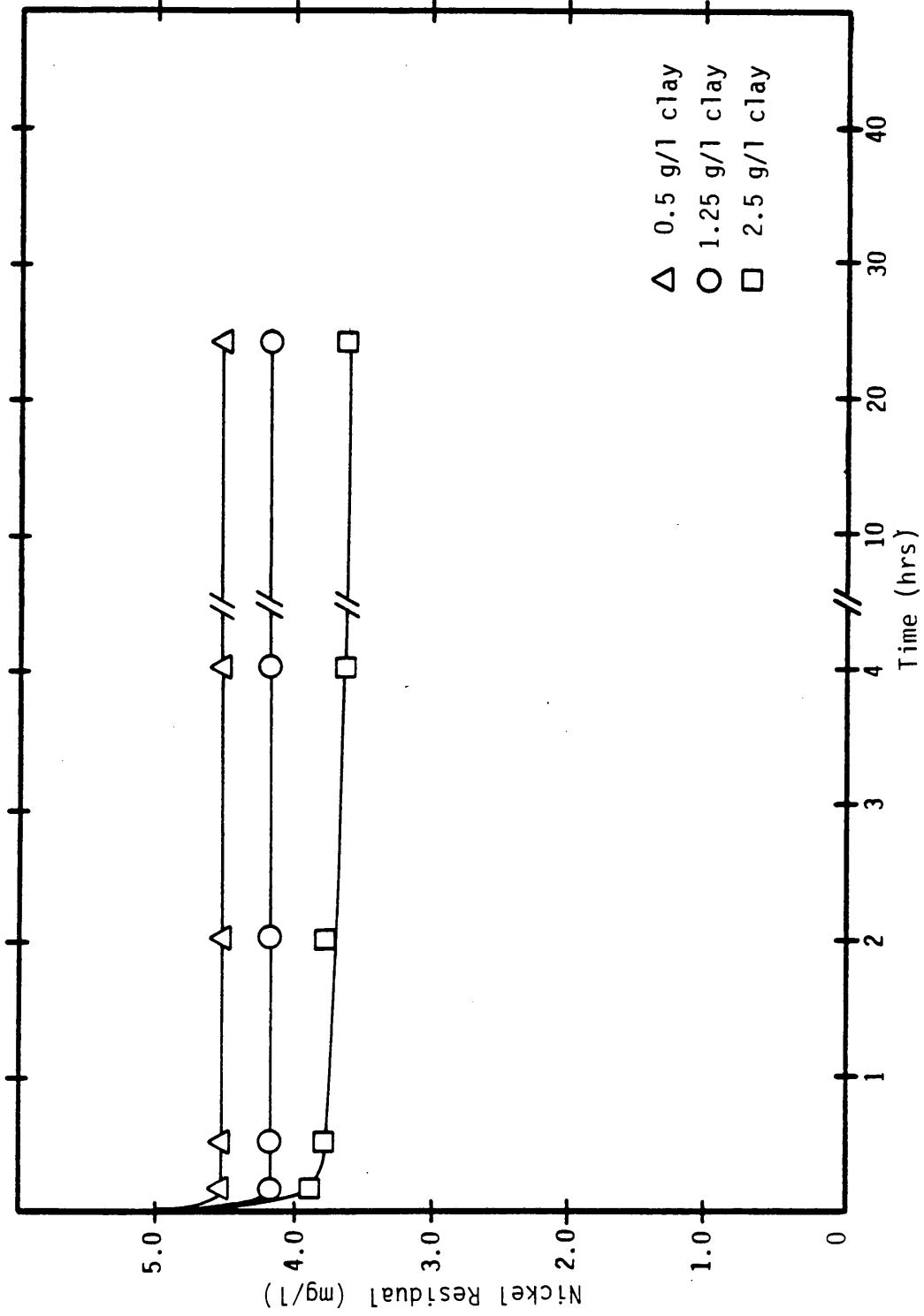


Figure 3. Nickel Concentration Remaining in Solution as a Function of Time
pH = 5.5 - 6.0

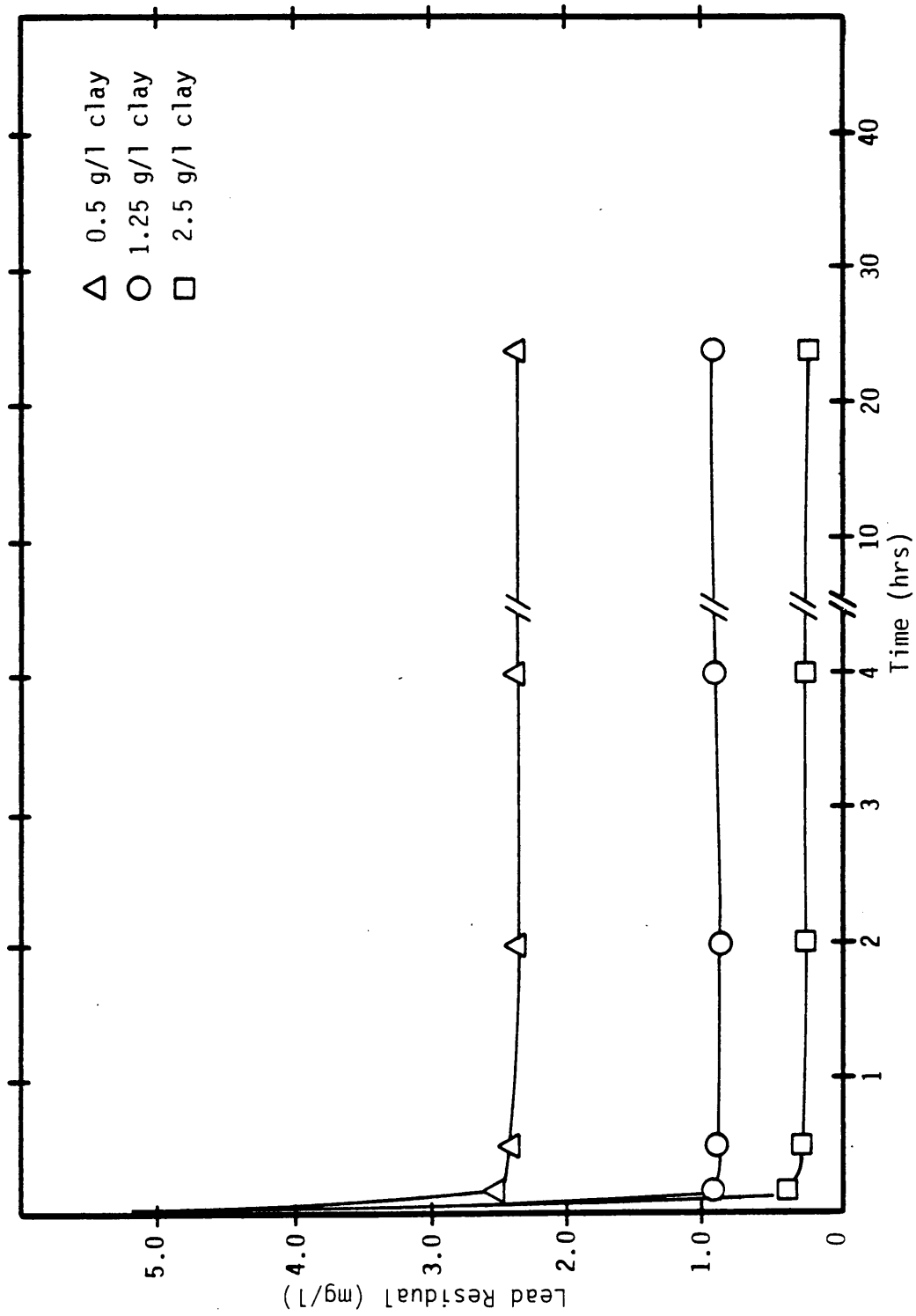


Figure 4. Lead Concentration Remaining in Solution as a Function of Time
pH = 5.5 - 6.0

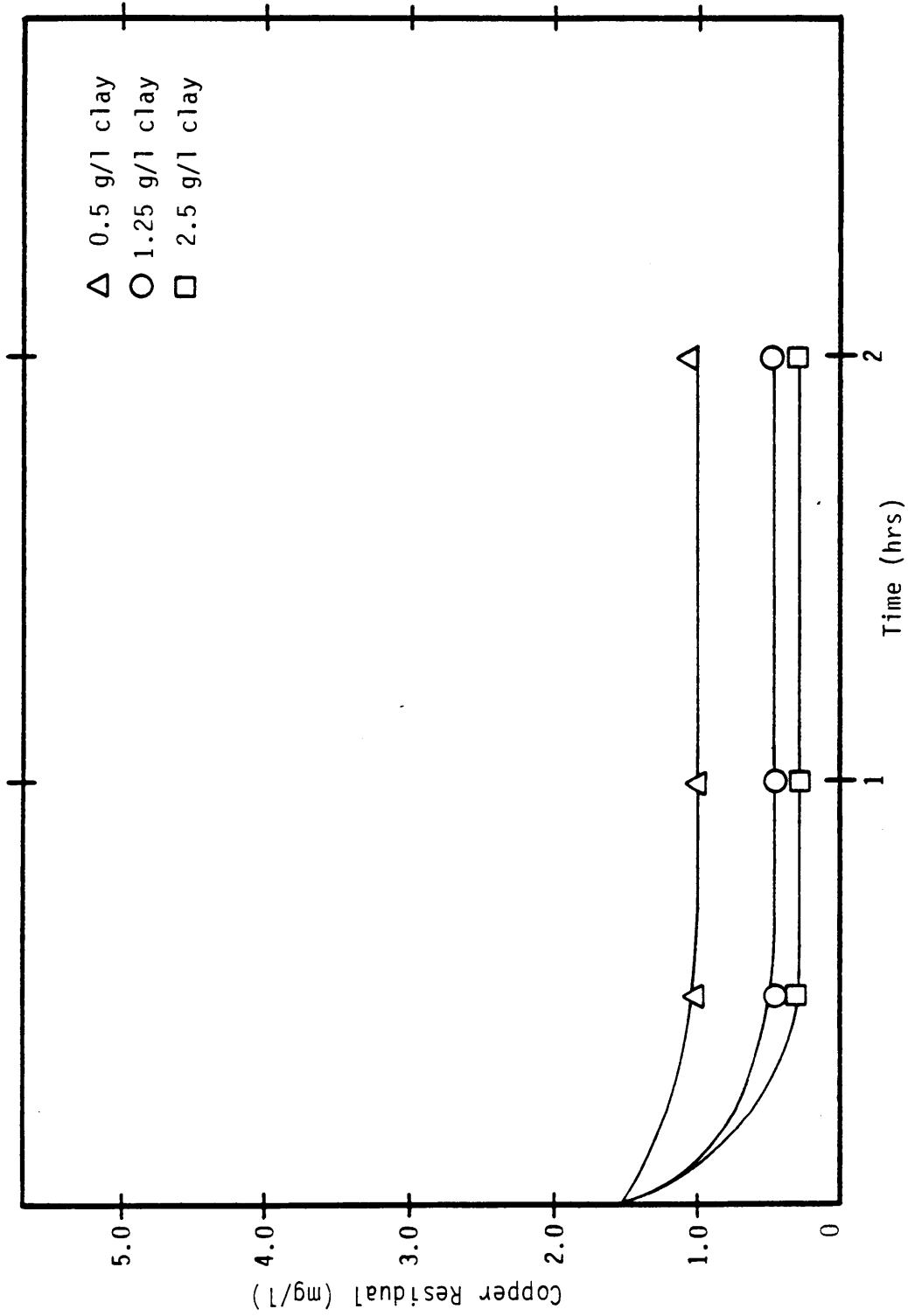


Figure 5. Copper Concentration Remaining in Solution as a Function of Time
pH = 7.0 - 7.5

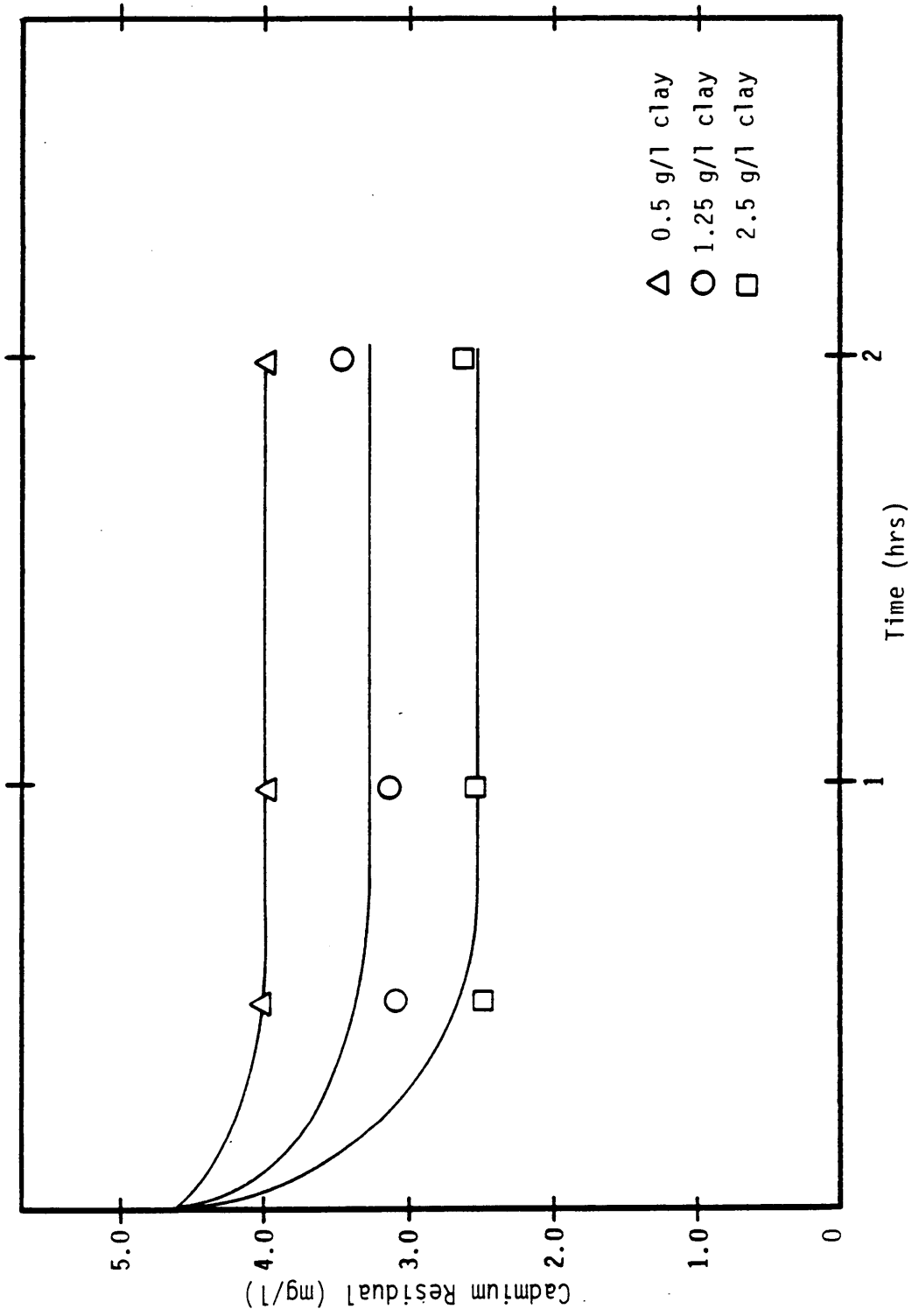


Figure 6. Cadmium Concentration Remaining in Solution as a Function of Time
pH = 7.0 - 7.5

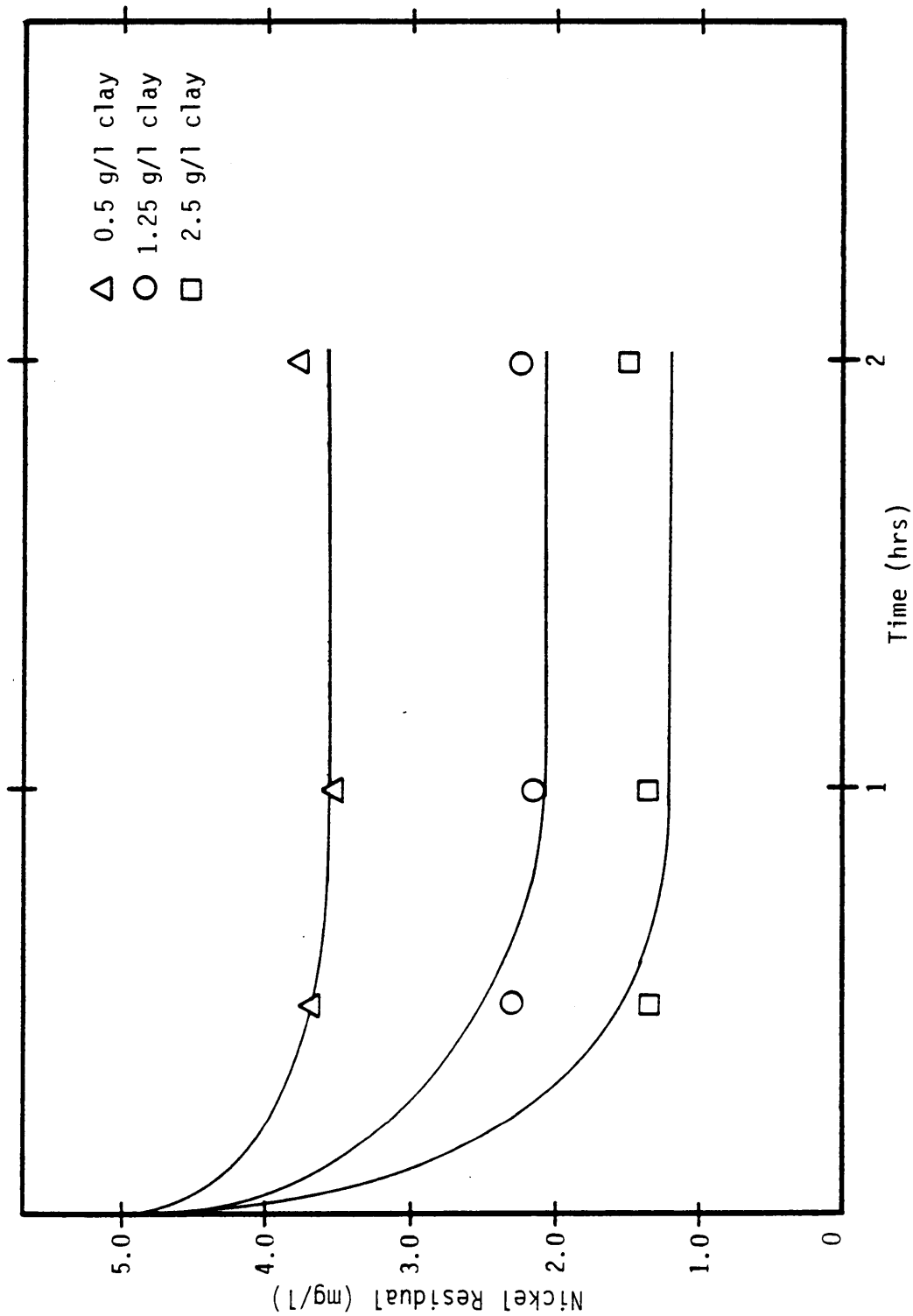


Figure 7. Nickel Concentration Remaining in Solution as a Function of Time
pH = 7.0 - 7.5

Tables II and III summarize the average percent removal at pH 5.5 to 6.0 and pH 7.0 to 7.5, respectively, for each metal as a function of clay dosage. Wide variations in removal were noted, with efficient uptake of lead observed. In comparison, removal efficiencies for nickel and cadmium were much lower. The solution pH also had a significant impact on metal uptake, with increased removal of both copper and nickel noted at pH 7.0 to 7.5 in comparison with pH 5.5 to 6.0. Cadmium was not as affected by pH, with only minimal differences in removal efficiency noted for similar clay dosages at the two pH conditions.

Adsorption Isotherm Data

Calculated adsorption capacity data and associated initial and equilibrium metal concentrations are presented in Appendix Tables B-1 through B-7. Data for the pH 5.5 to 6.0 and 7.0 to 7.5 studies are included. In these tables, C is the equilibrium metal concentration in solution expressed in moles/liter. The term q_e is the adsorption capacity observed in units of number of moles of metal adsorbed per gram of clay. The term q_e is calculated according to the following equation:

$$q_e = \frac{\text{Initial Conc. } (C_o) - \text{Equilibrium Conc. } (C_e)}{\text{Clay Dosage}}$$

The adsorption data were fitted using a linear least-squares method to the Langmuir isotherm equation. No attempt was made to fit the data to a Freundlich isotherm since this adsorption model does not provide

Table II. Average Percent Removal of Metals From Initial Solution
in Adsorption Rate Study pH = 5.5 To 6.0

	Clay Dose (g/l)				
	0.50	1.25	2.5	3.75	5.0
Ni Removal (%)	9.2	16.0	24.8	23.1	37.8
Cd Removal (%)	11.9	19.8	30.4	30.6	33.2
Cu Removal (%)	19.3	25.0	38.2	58.0	78.7
Pb Removal (%)	53.2	82.0	94.6	99.0	99.1

NOTE: Values listed are averages of five time intervals - 10 min., 30 min., 2 hrs, 4 hrs, and 24 hrs (See Appendix Table A-1).

Table III. Average Percent Removal of Metals from Initial Solution
in Adsorption Rate Study
pH = 7.0 to 7.5

	Clay Dose (g/l)									
	0.25	0.50	0.75	1.0	1.25	1.875	2.5	3.125	3.75	5.0
Ni Removal (%)	16.5	25.2	40.0	48.9	54.8	62.6	71.4	73.6	73.9	80.5
Cd Removal (%)	6.5	13.4	23.6	25.7	29.8	38.4	37.9	45.0	67.5	68.5
Cu Removal (%)	25.4	34.2	56.1	62.6	69.7	-----	81.9	-----	-----	-----

NOTE: Values listed are averages of three time intervals - 30 min., 1 hr, and 2 hrs
(See Appendix Tables A-2 through A-4).

the necessary data for Q^0 and b which are needed to utilize Weber's predictive model for adsorption from mixed solute systems. A linear regression computer program (Appendix C) was developed and used to provide best estimate values for the maximum adsorption capacity (Q^0) and the adsorption constant b . The linearized form of the Langmuir isotherm equation was used in the computer program.

Table IV summarizes the data provided by the computer model as best estimates for Q^0 and b for each metal. The correlation to the Langmuir model was excellent for the copper and lead systems under low pH conditions. The adsorption data for the high range studies also fit the Langmuir equation quite well. Significant deviation from the Langmuir model was noted only for nickel and cadmium under low pH conditions. It should be noted that the data of Counts (21) were included in the development of a Langmuir isotherm model for nickel under low pH conditions. As stated previously, Counts also studied the uptake of nickel on kaolinite. Since the experimental methods of this study were similar, the data were felt to be appropriate for use in this model development. The associated Langmuir isotherm data plots are shown in Figures 8 through 14.

For certain data sets, the inverse plotting method provided significant sources of error due to the clustering of several data points in one small locus. An attempt was made to double-check the

Table IV. Linear Regression θ^0 , b, and R^2 Values

Metal	θ^0 (mole/g)	b	R^2
I. <u>pH 5.5 - 6.0</u>			
Copper	3.9×10^{-5}	2.5×10^4	0.824
Cadmium	2.2×10^{-5}	6.0×10^3	0.500
Nickel	1.0×10^{-5}	9.5×10^4	0.358
Lead	3.8×10^{-5}	2.0×10^5	0.900
II. <u>pH 7.0 - 7.5</u>			
Copper	5.6×10^{-5}	3.9×10^4	0.931
Cadmium	1.9×10^{-5}	4.1×10^4	0.842
Nickel	6.7×10^{-4}	1.4×10^3	0.949

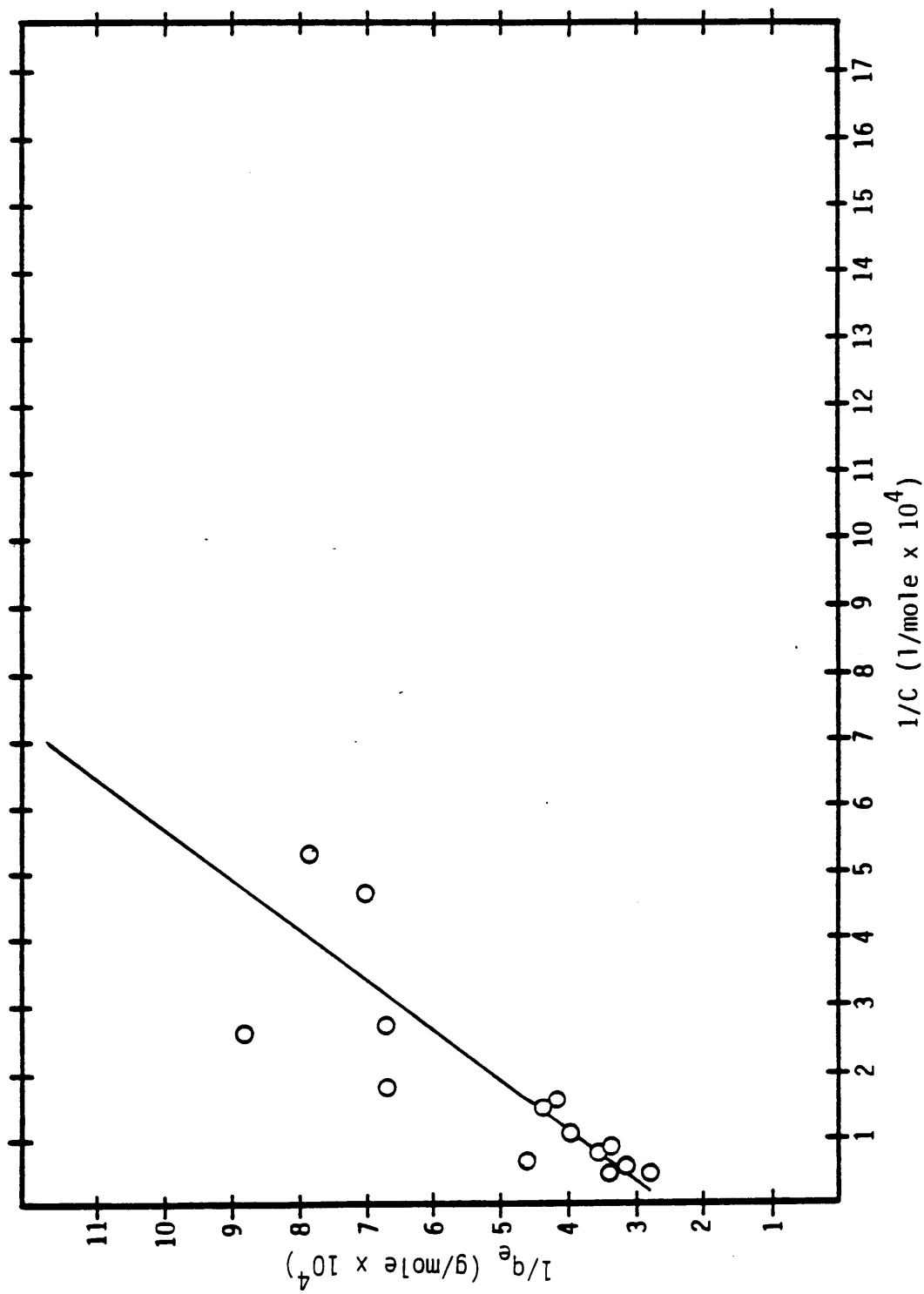


Figure 8. Langmuir Isotherm of Copper Adsorption at pH = 5.5 - 6.0

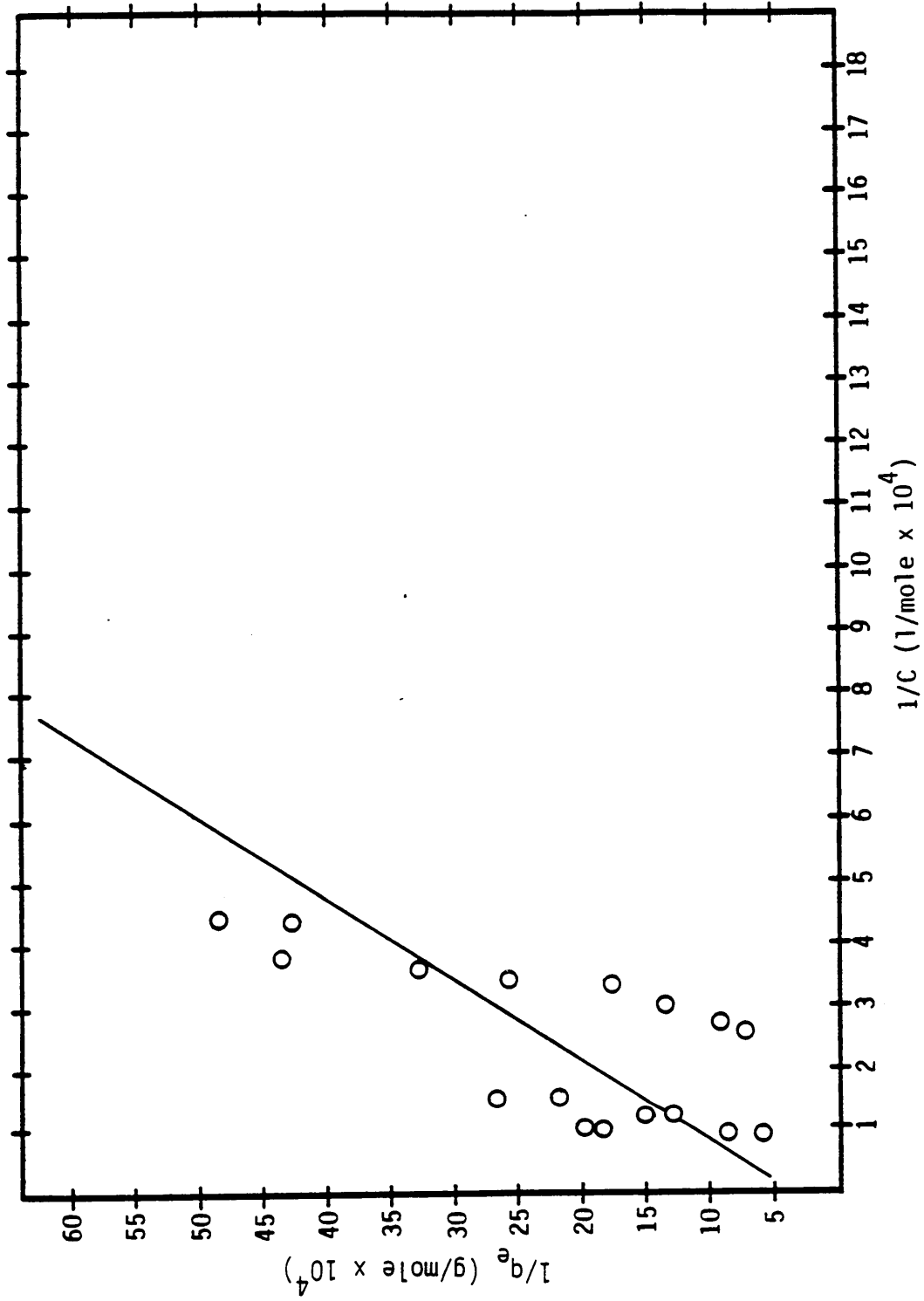


Figure 9. Langmuir Isotherm of Cadmium Adsorption at pH = 5.5 - 6.0

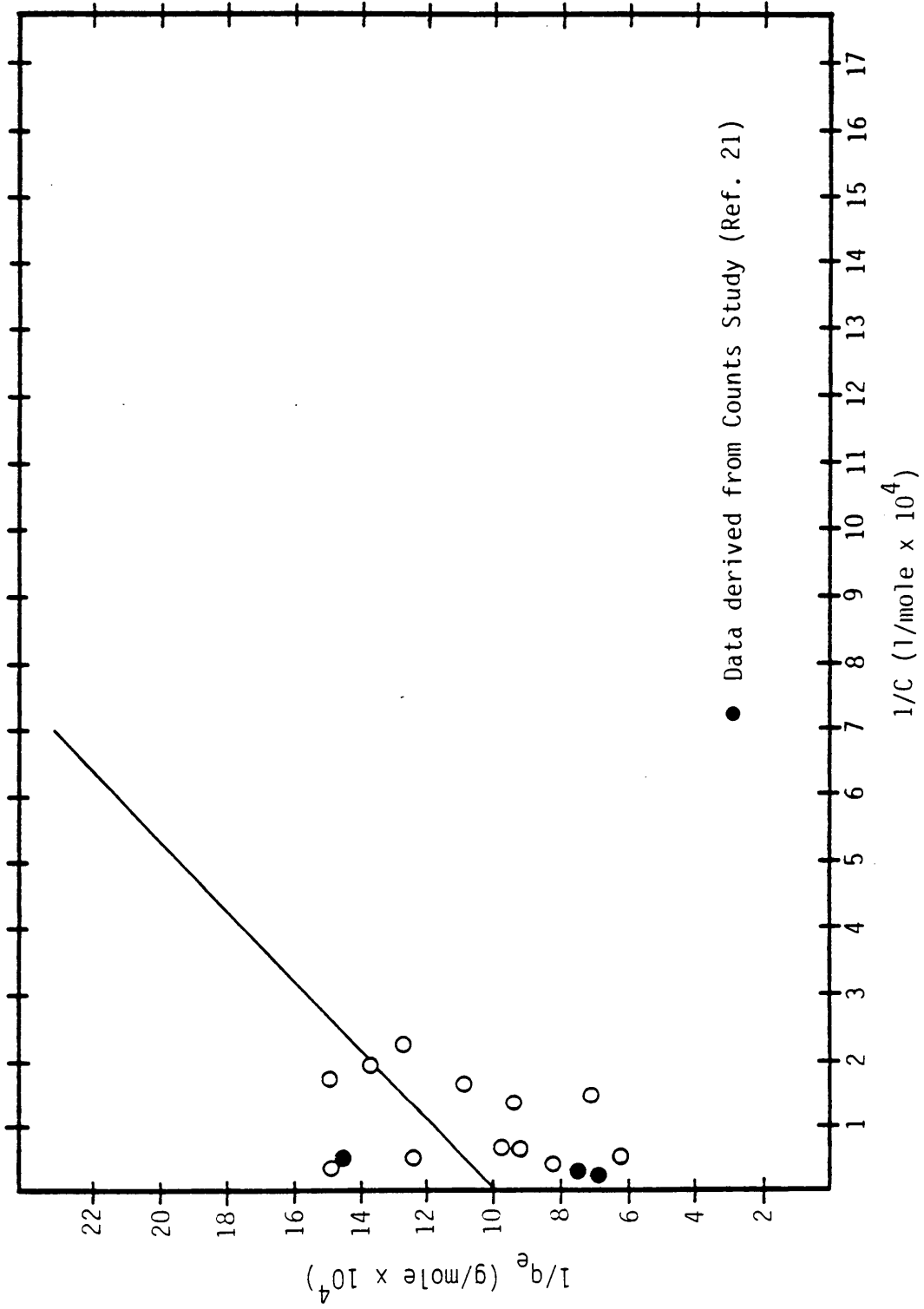


Figure 10. Langmuir Isotherm of Nickel Adsorption at pH = 5.5 - 6.0

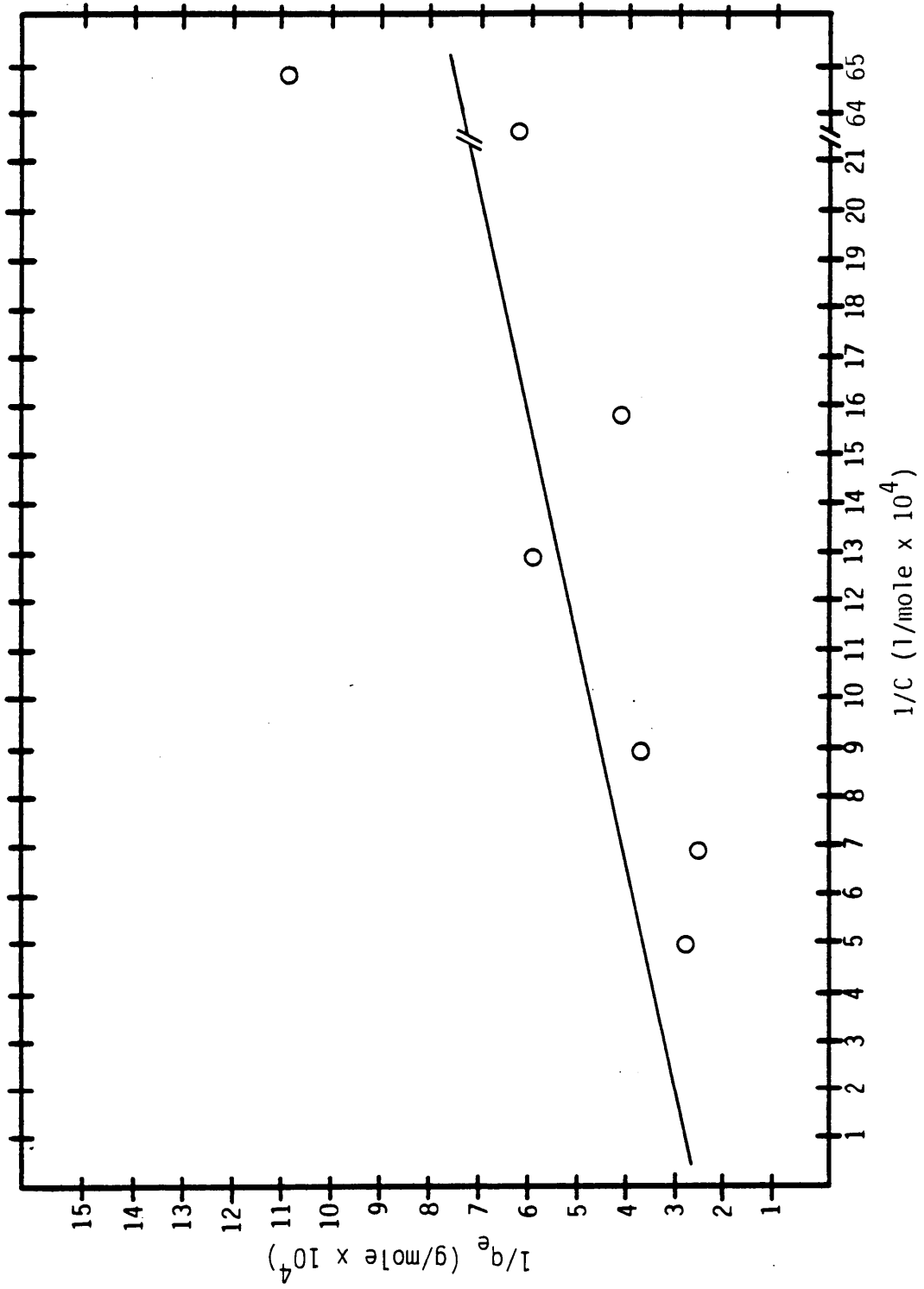


Figure 11. Langmuir Isotherm of Lead Adsorption at pH = 5.5 - 6.0

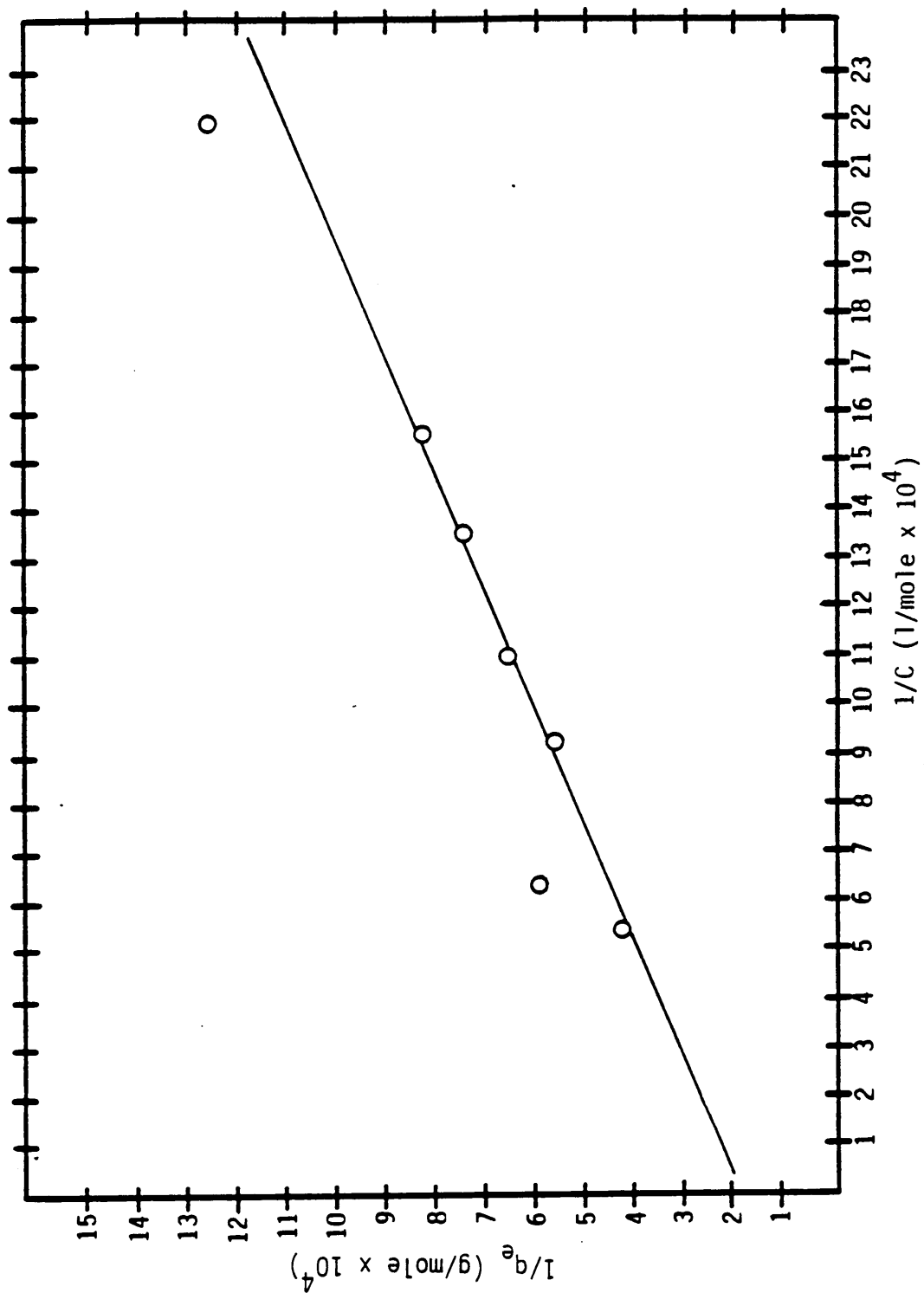


Figure 12. Langmuir Isotherm of Copper Adsorption at pH = 7.0 - 7.5

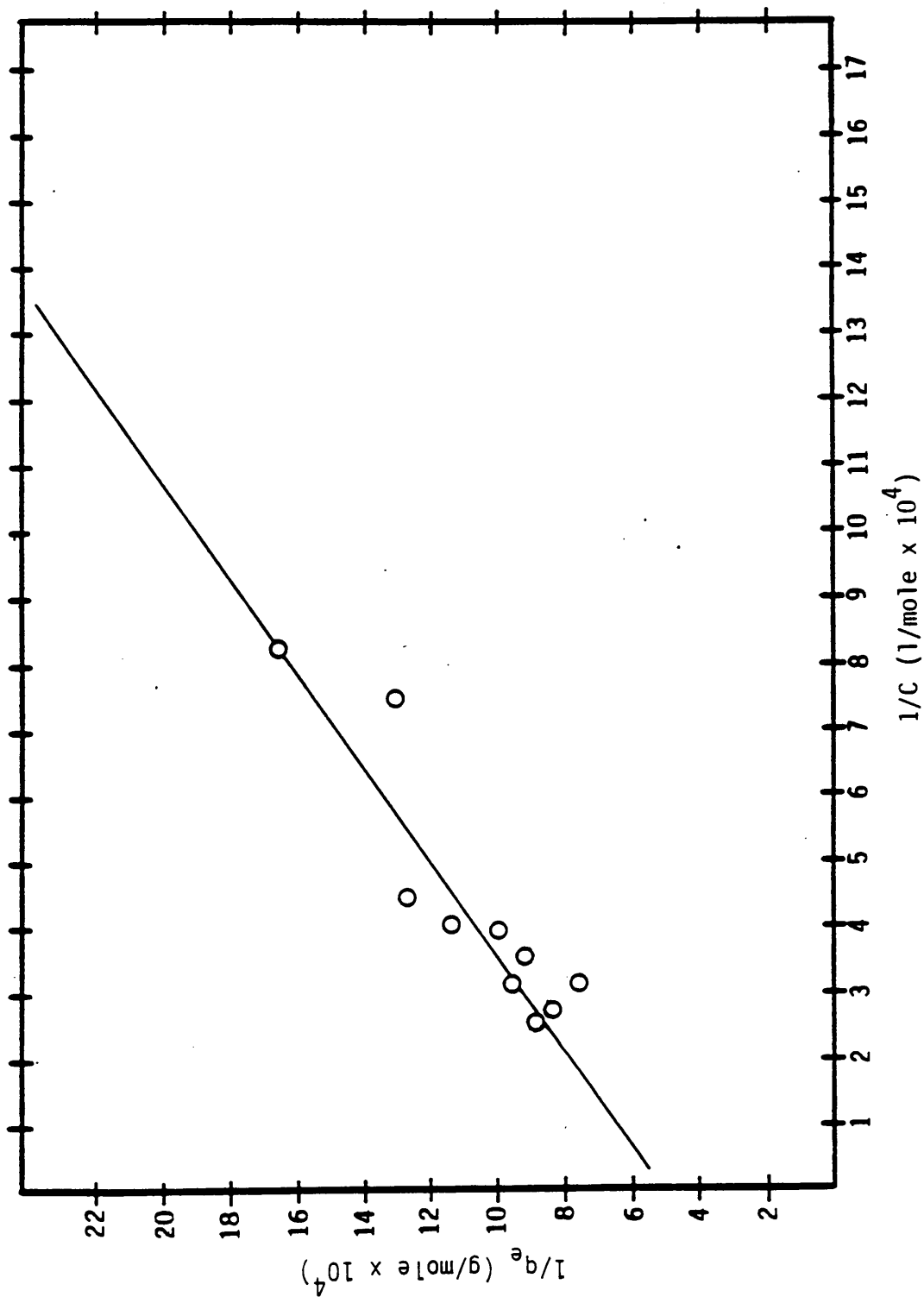


Figure 13. Langmuir Isotherm of Cadmium Adsorption at pH = 7.0 - 7.5

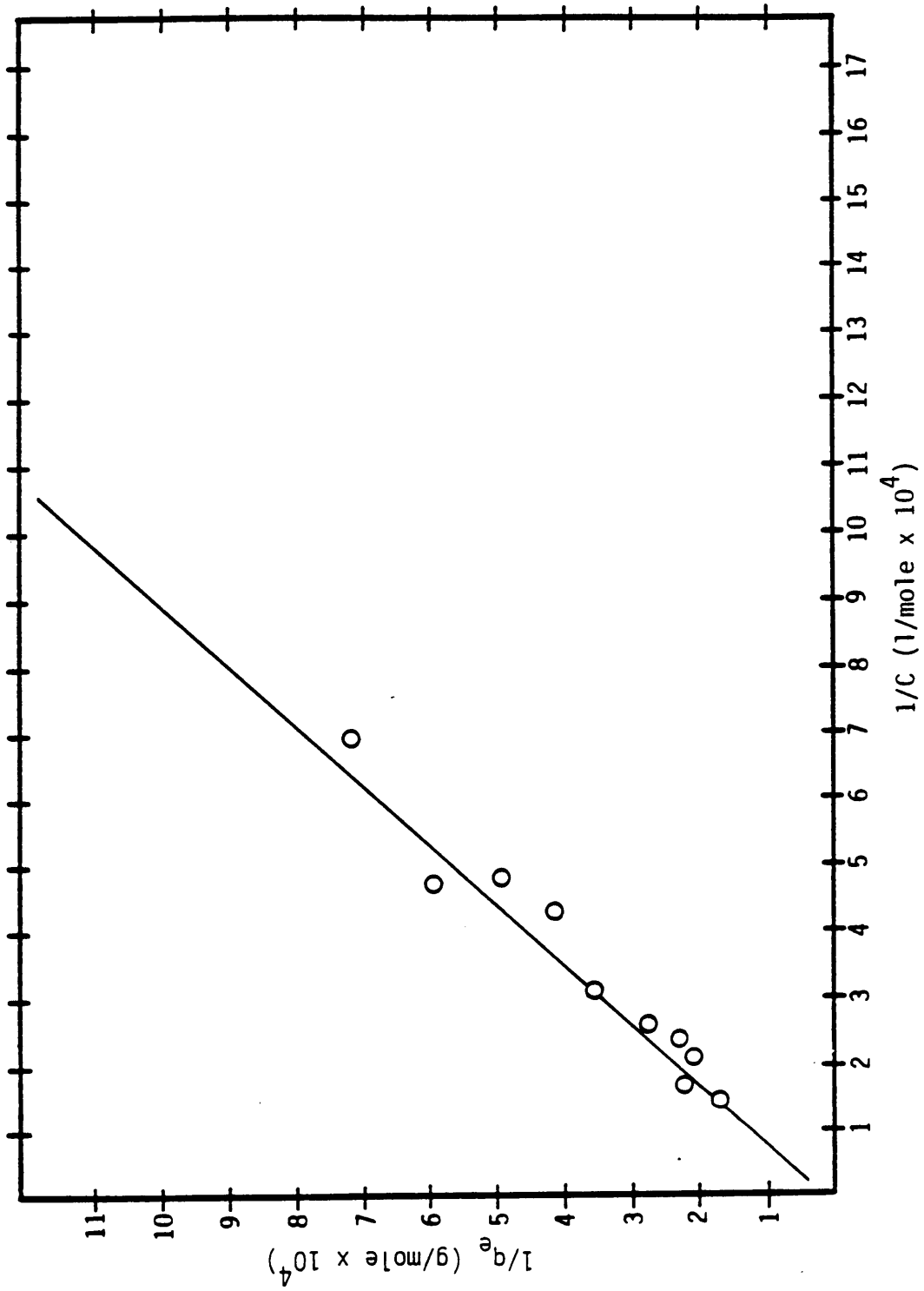


Figure 14. Langmuir Isotherm of Nickel Adsorption at pH = 7.0 - 7.5

estimated values for Q^0 and b through the use of a nonlinear regression analysis of the Langmuir equation. The computer program developed for this analysis is included in Appendix D. Table V summarizes the values for Q^0 and b estimated by the nonlinear regression analysis. The nonlinear estimates are in reasonable agreement with those obtained from the linear regression analysis. The Q^0 and b values presented in Table V from the nonlinear regression analysis were used subsequently in the development of the predictive model. Finally, Figures 15 through 21 present the observed data, plus computer-fitted adsorption plots for each metal under both pH conditions. As was seen previously, most fit the adsorption model nicely. The only exceptions were nickel and cadmium under low pH conditions.

Adsorption of Mixed Metal Systems

The experimental and predicted results of the mixed metal adsorption studies are shown in Tables VI through XII. The equation presented by Weber (1) for adsorption competition among the components of a mixture of solutes was used to predict equilibrium metal concentrations in mixed metal systems. For the general case for extent of adsorption, $q_{e,i}$ of the i th solute from a j -solute mixture the equation is:

$$q_{e,i} = \frac{Q_i^0 b_i C_i}{1 + \sum_{j=1}^n b_j C_j} \quad (1)$$

Table V. Nonlinear Regression Q^0 and b Values

Metal	Q^0 (mole/g)	b
I. <u>pH 5.5 - 6.0</u>		
Copper	3.8×10^{-5}	2.0×10^4
Cadmium	1.4×10^{-5}	1.8×10^4
Nickel	1.4×10^{-5}	2.6×10^4
Lead	6.1×10^{-5}	8.2×10^4
II. <u>pH 7.0 - 7.5</u>		
Copper	4.1×10^{-5}	6.3×10^4
Cadmium	2.1×10^{-5}	3.4×10^4
Nickel	2.9×10^{-4}	3.6×10^3

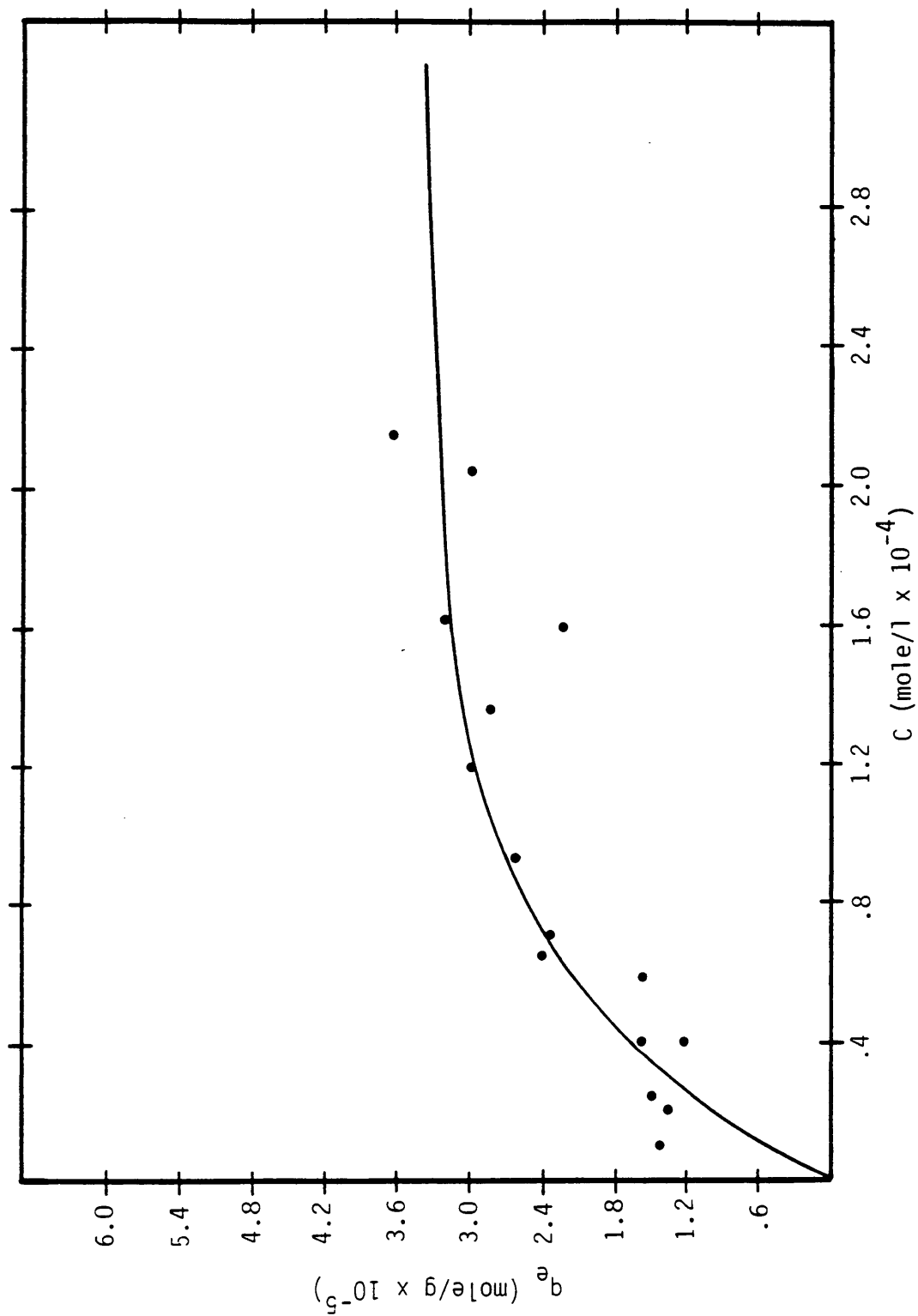


Figure 15. Amount of Copper Adsorbed per Gram of Clay Plotted as a Function of Equilibrium Concentration pH = 5.5 - 6.0

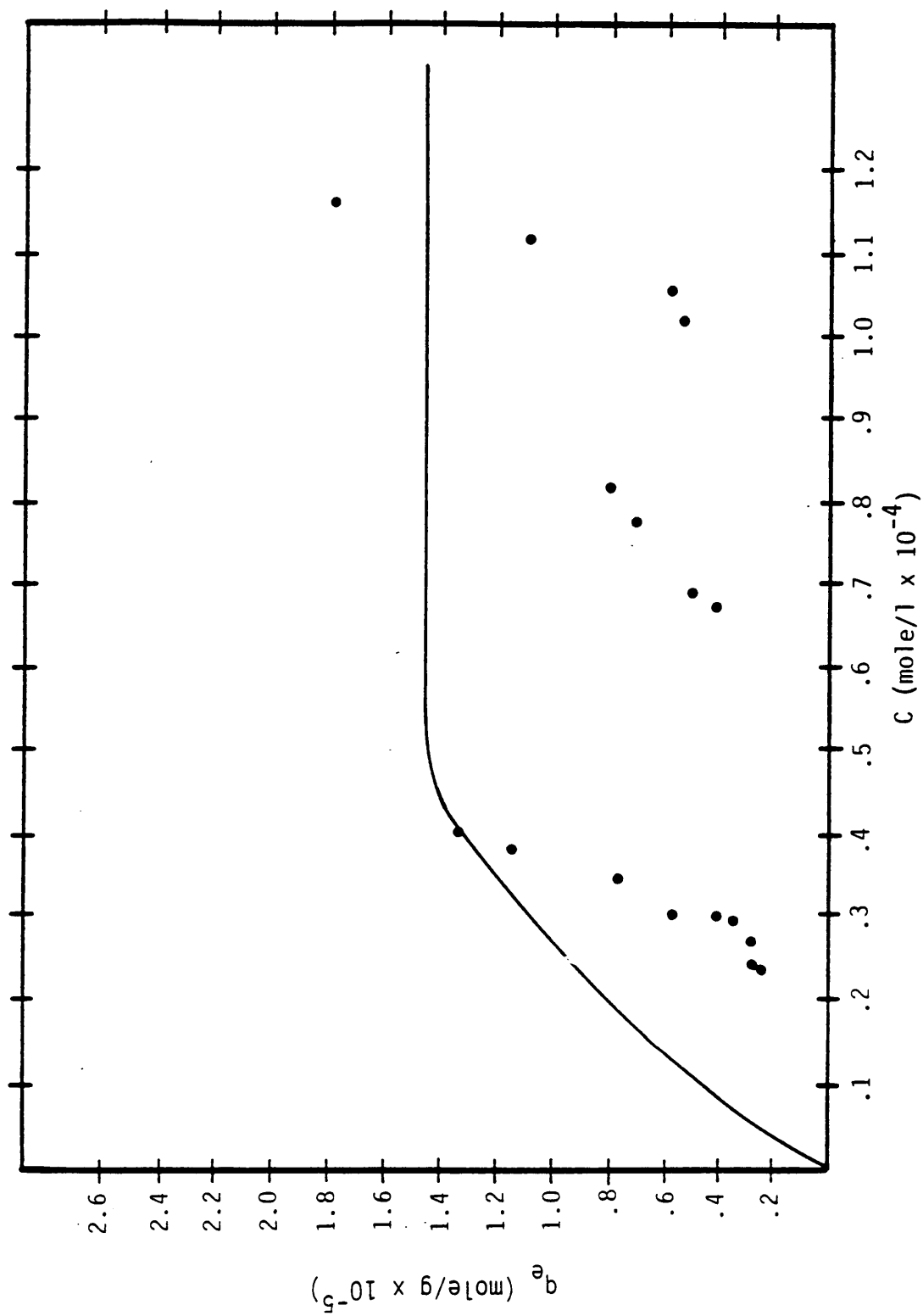


Figure 16. Amount of Cadmium Adsorbed per Gram of Clay Plotted as a Function of Equilibrium Concentration pH = 5.5 - 6.0

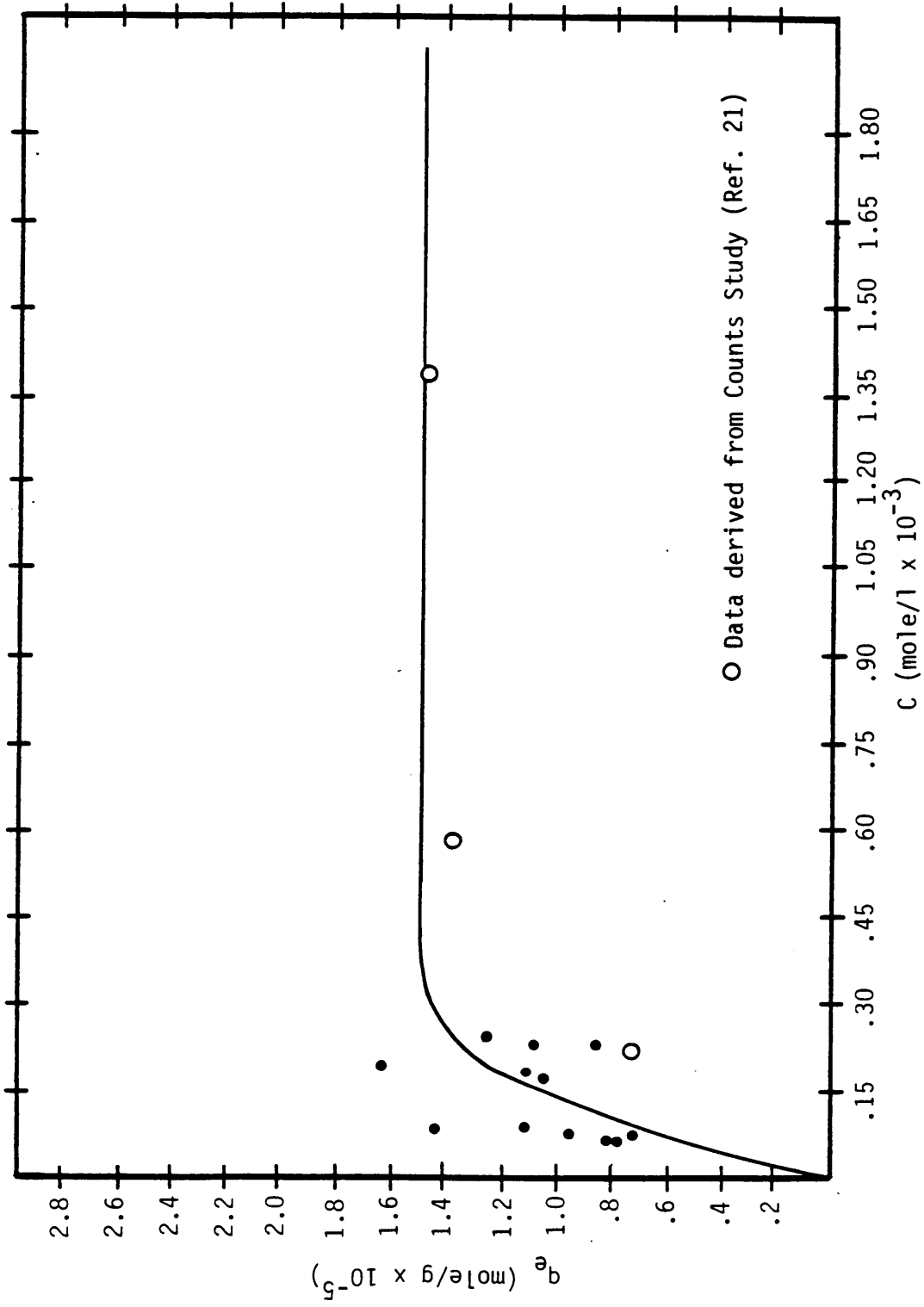


Figure 17. Amount of Nickel Adsorbed per Gram of Clay Plotted as a Function of Equilibrium Concentration pH = 5.5 - 6.0

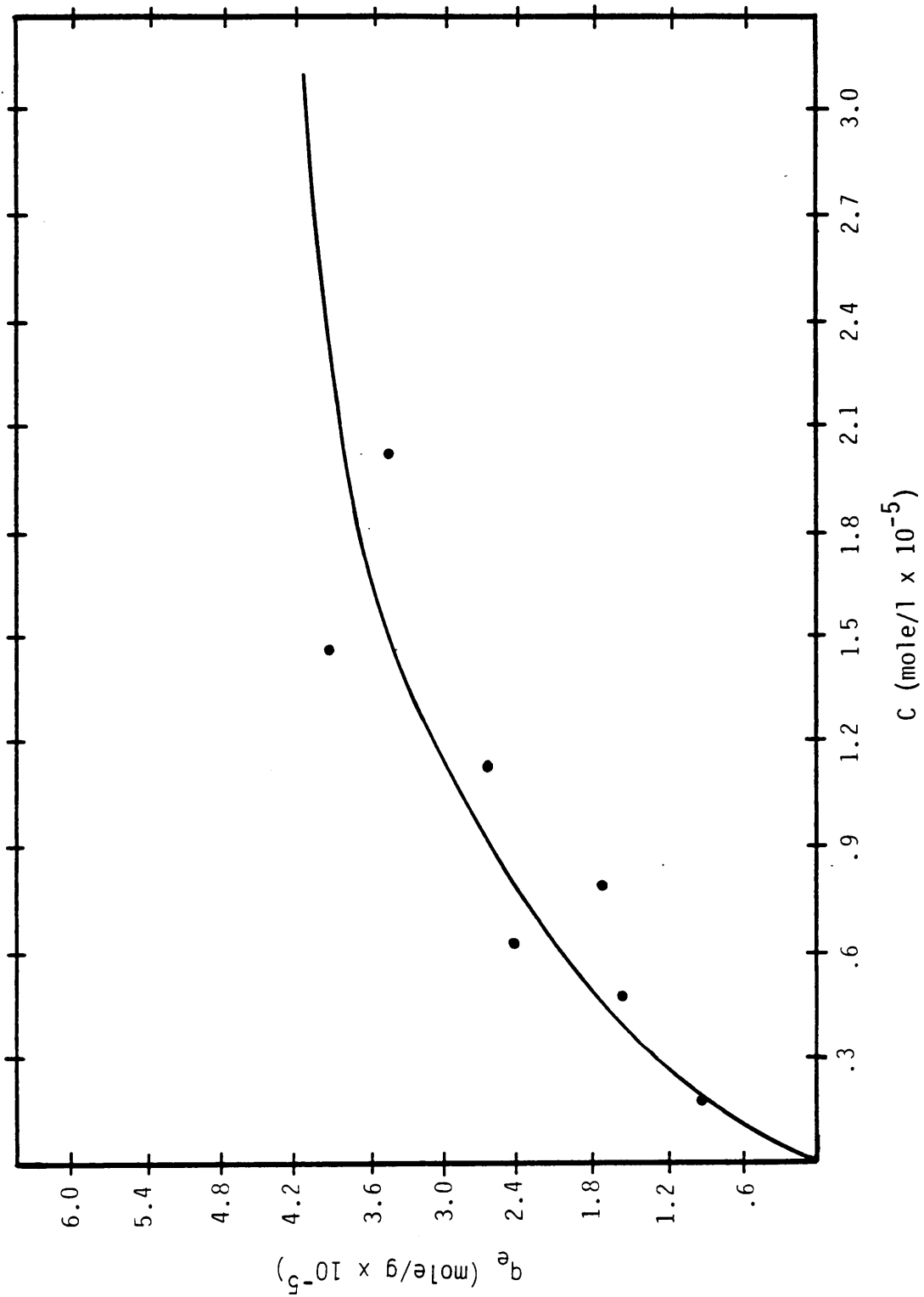


Figure 18. Amount of Lead Adsorbed per Gram of Clay Plotted as a Function of Equilibrium Concentration pH = 5.5 - 6.0

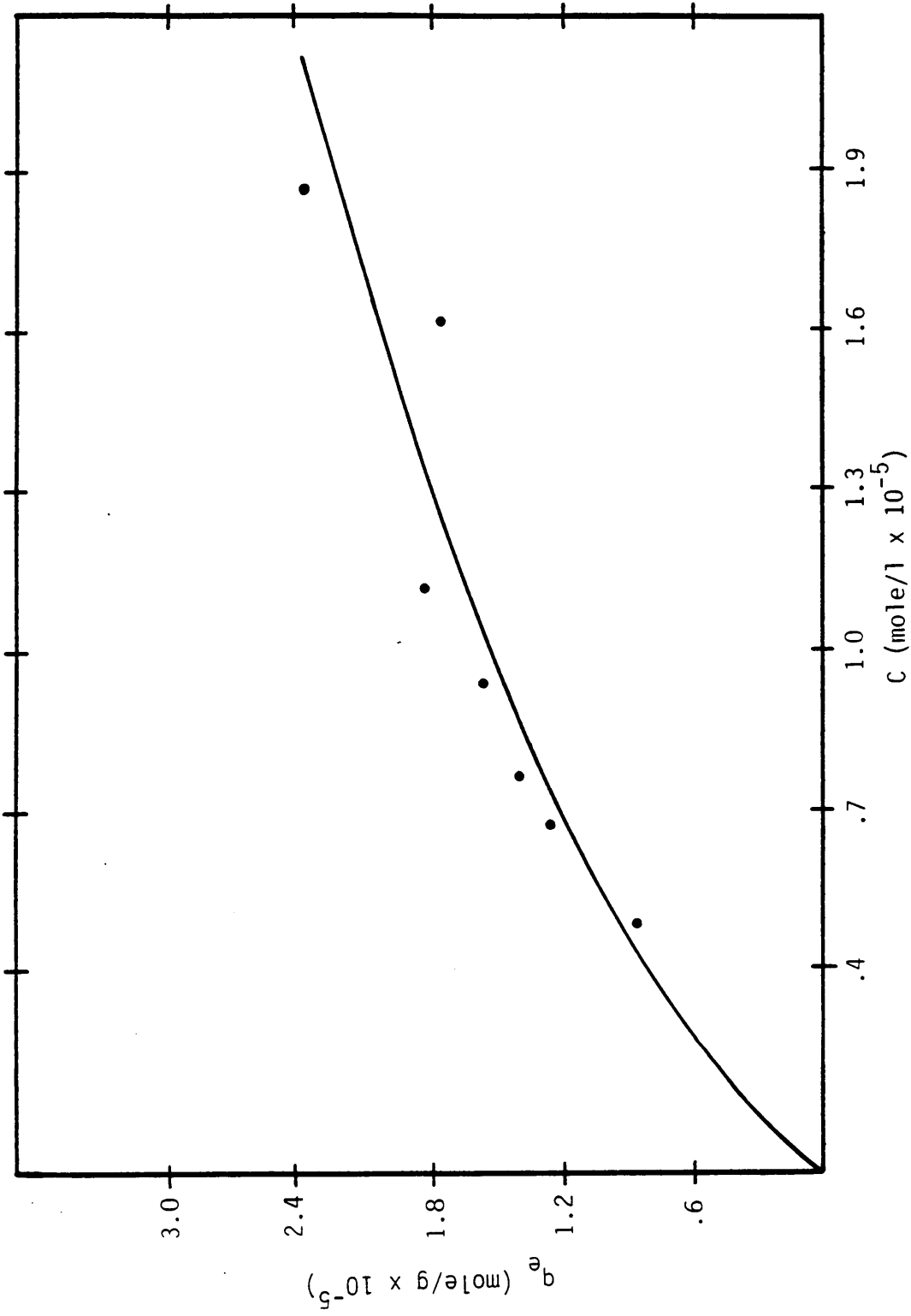


Figure 19. Amount of Copper Adsorbed per Gram of Clay Plotted as a Function of Equilibrium Concentration pH = 7.0 - 7.5

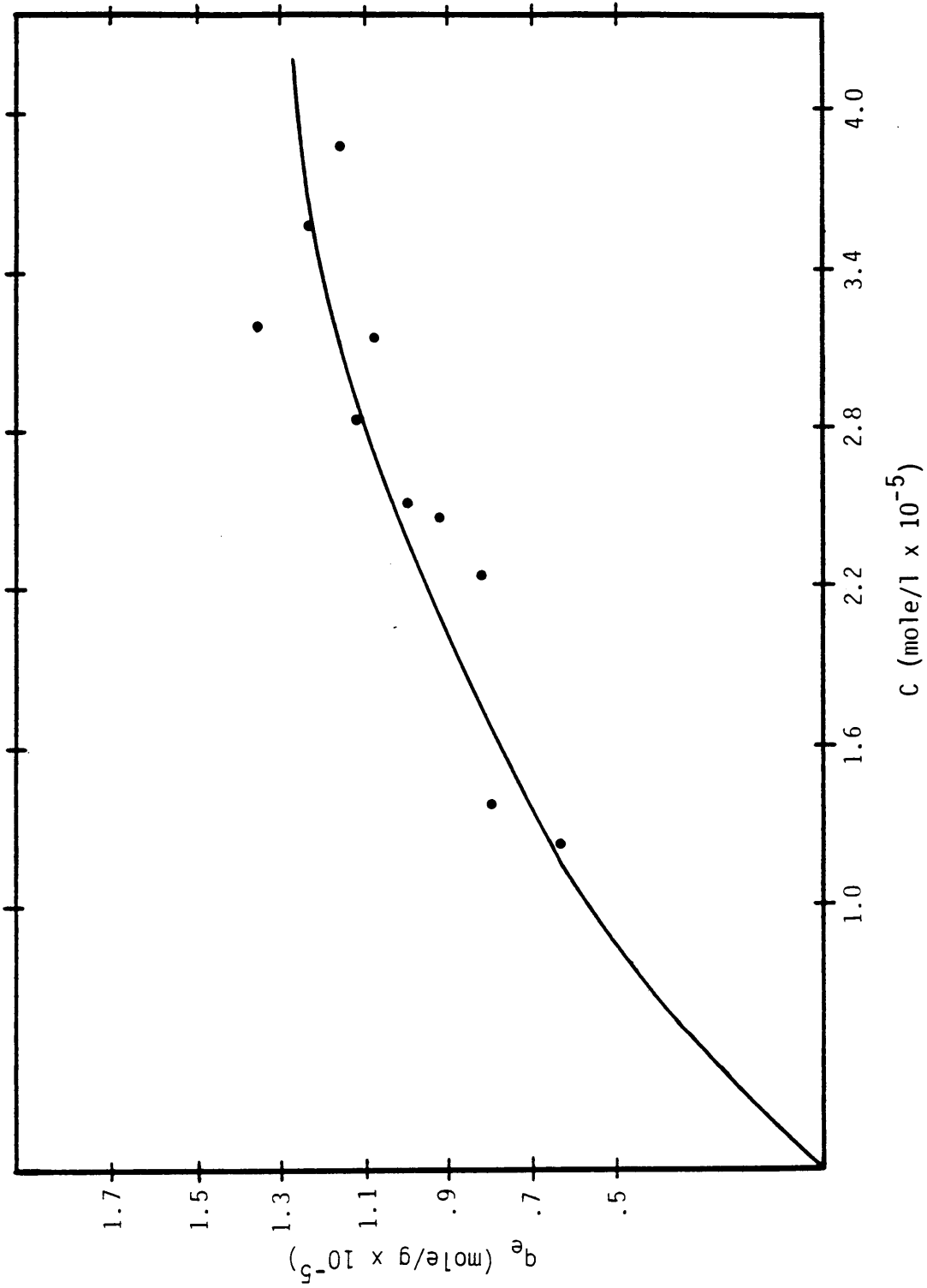


Figure 20. Amount of Cadmium Adsorbed per Gram of Clay Plotted as a Function of Equilibrium Concentration pH = 7.0 - 7.5

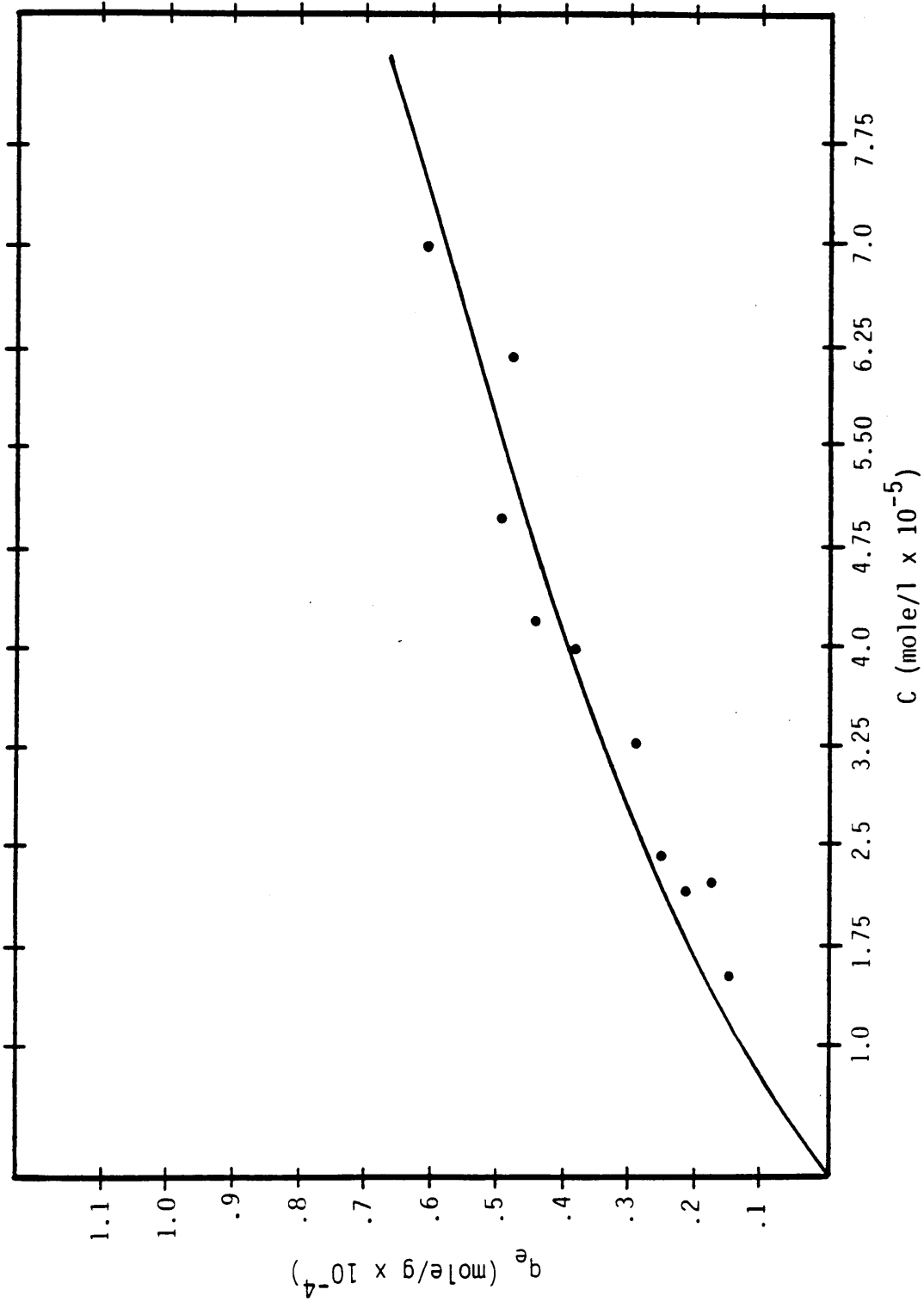


Figure 21. Amount of Nickel Adsorbed per Gram of Clay Plotted as a Function of Equilibrium Concentration pH = 7.0 - 7.5

Table VI. Mixed Metal Study - Copper And Nickel
pH = 5.5 - 6.0

Clay Dose g/l	Equilibrium Cu Concentration mg/l		Equilibrium Ni Concentration mg/l	
	<u>Observed</u>	<u>Predicted</u>	<u>Observed</u>	<u>Predicted</u>
0.500	4.33	4.49	4.80	4.78
1.000	3.82	4.14	4.69	4.59
1.250	3.82	3.97	4.59	4.49
1.875	3.39	3.58	4.42	4.25
2.500	3.06	3.22	4.33	4.00
3.750	2.66	2.62	4.12	3.54
4.375	2.10	2.37	3.91	3.32
5.000	1.62	2.14	3.84	3.10

Initial Cu Concentration = 4.87 mg/l

Initial Ni Concentration = 4.98 mg/l

Table VII. Mixed Metal Study - Nickel And Lead
pH = 5.5 - 6.0

Clay Dose g/l	Equilibrium Ni Concentration mg/l		Equilibrium Pb Concentration mg/l	
	<u>Observed</u>	<u>Predicted</u>	<u>Observed</u>	<u>Predicted</u>
0.125	4.88	4.93	4.62	4.43
0.250	4.92	4.88	3.54	3.95
0.500	4.89	4.77	3.44	3.17
0.750	4.76	4.66	2.86	2.60
1.000	4.65	4.54	2.32	2.18
1.250	4.60	4.42	2.20	1.85
2.000	4.40	4.06	1.58	1.23
2.500	4.09	3.84	0.33	0.99

Initial Ni Concentration = 4.97 mg/l

Initial Pb Concentration = 4.99 mg/l

Table VIII. Mixed Metal Study - Cadmium And Lead
pH = 5.5 - 6.0

Clay Dose g/l	Equilibrium Cd Concentration mg/l		Equilibrium Pb Concentration mg/l	
	<u>Observed</u>	<u>Predicted</u>	<u>Observed</u>	<u>Predicted</u>
0.125	4.72	4.81	3.84	3.21
0.25	4.67	4.75	3.52	2.68
0.50	4.51	4.62	2.88	1.93
0.75	4.44	4.48	2.65	1.46
1.00	4.23	4.35	1.86	1.16
1.25	4.14	4.22	1.45	0.96
1.875	3.89	3.89	0.79	0.64
2.50	3.79	3.59	0.58	0.48

Initial Cd Concentration = 4.86 mg/l
Initial Pb Concentration = 3.87 mg/l

Table IX. Mixed Metal Study - Copper, Nickel, And Cadmium
pH = 5.5 - 6.0

Clay Dose g/l	Equilibrium Cu Concentration mg/l		Equilibrium Ni Concentration mg/l		Equilibrium Cd Concentration mg/l	
	<u>Observed</u>	<u>Predicted</u>	<u>Observed</u>	<u>Predicted</u>	<u>Observed</u>	<u>Predicted</u>
0.250	4.46	4.61	4.73	4.81	4.74	4.78
1.250	4.05	4.00	4.55	4.48	4.53	4.55
1.875	3.74	3.66	4.41	4.27	4.43	4.40
3.125	3.33	3.06	4.20	3.86	4.19	4.09
3.750	3.16	2.80	4.04	3.66	4.14	3.93
4.375	2.55	2.57	3.41	3.47	4.05	3.78
5.000	1.55	2.36	3.84	3.28	3.76	3.62

Initial Cu Concentration = 4.78 mg/l
Initial Ni Concentration = 4.89 mg/l
Initial Cd Concentration = 4.83 mg/l

Table X. Mixed Metal Study - Copper, Nickel, Cadmium, And Lead
pH = 5.5 - 6.0

Clay Dose g/l	Equilibrium Cu Conc mg/l		Equilibrium Ni Conc mg/l		Equilibrium Cd Conc mg/l		Equilibrium Pb Conc mg/l	
	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted
0.50	3.84	4.56	4.90	4.80	4.72	4.77	3.82	3.61
1.00	3.80	4.29	4.73	4.66	4.64	4.66	3.37	2.74
1.25	3.40	4.16	4.70	4.58	4.58	4.62	2.98	2.42
1.875	3.60	3.83	4.58	4.39	4.46	4.47	2.32	1.84
2.50	3.00	3.52	4.43	4.19	4.34	4.34	2.03	1.45
3.75	2.95	2.97	4.31	3.80	4.16	4.04	1.70	0.97
4.375	2.96	2.72	4.25	3.61	4.11	3.88	1.56	0.82

Initial Cu Concentration = 4.82 mg/l
 Initial Ni Concentration = 4.93 mg/l
 Initial Cd Concentration = 4.86 mg/l
 Initial Pb Concentration = 4.96 mg/l

Table XI. Mixed Metal Study - Copper And Nickel
pH = 7.0 - 7.5

Clay Dose g/l	Equilibrium Cu Concentration mg/l		Equilibrium Ni Concentration mg/l	
	<u>Observed</u>	<u>Predicted</u>	<u>Observed</u>	<u>Predicted</u>
0.125	2.05	1.38	4.64	4.58
0.250	1.55	1.23	4.53	4.35
0.500	1.07	0.98	4.41	3.88
0.750	0.77	0.78	4.39	3.44
1.250	0.56	0.54	4.11	2.72
1.500	0.40	0.46	4.00	2.43
1.875	0.32	0.37	3.84	2.09
2.500	0.21	0.27	3.65	1.66
3.750	0.11	0.18	3.11	1.16

Initial Cu Concentration = 3.73 mg/l

Initial Ni Concentration = 4.81 mg/l

Table XII. Mixed Metal Study - Nickel And Cadmium
pH = 7.0 - 7.5

Clay Dose g/l	Equilibrium Ni Concentration mg/l		Equilibrium Cd Concentration mg/l	
	<u>Observed</u>	<u>Predicted</u>	<u>Observed</u>	<u>Predicted</u>
0.250	4.53	4.26	4.59	4.35
0.500	4.29	3.87	4.38	4.07
0.750	3.95	3.52	4.14	3.79
1.250	3.59	2.92	3.87	3.29
1.875	2.87	2.34	3.28	2.75
2.500	2.71	1.93	2.89	2.34
3.125	2.66	1.62	2.46	2.02
5.000	2.19	1.04	2.35	1.36

Initial Ni Concentration = 4.70 mg/l

Initial Cd Concentration = 4.66 mg/l

The computer program used to perform this analysis is shown in Appendix E. The Q^0 and b values determined from the nonlinear regression analysis of individual metal adsorption isotherm data were used to determine predicted metal concentrations. The initial metal concentration and clay dosage were also known. Since

$$\frac{\text{Initial Conc. } (C_o) - \text{Equilibrium Conc. } (C_e)}{\text{Clay Dosage (SS)}}$$

the expression $\frac{C_o - C_e}{SS}$ could be substituted in the competitive adsorption equation for q_e . Equilibrium concentrations (C_e) could then be easily predicted by the computer program.

V. DISCUSSION

Precipitation Studies

From the results of the precipitation studies, copper, nickel, and cadmium did not indicate significant precipitation over the pH range 5.0 to 8.0. Lead adsorption on kaolinite was not studied over the high pH range, 7.0 to 7.5, since precipitation was a significant removal mechanism in this pH range.

Adsorption Rate Studies

The results indicated that adsorption of heavy metals on kaolinite occurs very rapidly. This finding is in agreement with the results of Gardiner (32) who found that the adsorption of cadmium on samples of river mud was nearly complete within two minutes after the addition of the metal.

The adsorption rate studies conducted over pH range 5.5 to 6.0 indicated that equilibrium was complete within the first ten minutes of shaking. With few exceptions, metal removal after ten minutes was not significantly different than removal after twenty-four hours. For fifteen of the twenty total samples, the difference between the percent removal after ten minutes and the percent removal after twenty-four hours was less than seven percent. Two nickel samples (clay dosages = 3.75 and 5.0 grams per liter) and three copper samples (clay dosages = 2.5, 3.75, and 5.0 grams per liter) were the exceptions.

The rapid adsorption rate was further demonstrated at the high pH range, 7.0 to 7.5, studies. Metal concentrations were determined after thirty minutes, one hour, and two hours of shaking. The difference between the percent removal after thirty minutes and percent removal after two hours was less than eight percent for all samples studied.

Adsorption Isotherm Data

The first series of adsorption isotherms discussed will be the low pH range, 5.5 to 6.0, studies. Similar discussions will then be presented for the high pH range, 7.0 to 7.5, studies. Finally, a discussion of the effect of pH on adsorption will be provided.

Adsorption Studies at pH 5.5 - 6.0

Linear and nonlinear regression analyses were performed on the adsorption data. All data except that for cadmium and nickel adsorption fit the linear form of the Langmuir equation quite well. Although there was appreciable scatter in the data, reasonably straight lines could be drawn. The scatter in the experimental data may have been the result of experimental errors due to problems in precisely measuring the small changes in concentration that occurred due to adsorption. The value q_e was determined from the difference in the initial and equilibrium metal concentrations. When this difference is small, small errors in the concentration measurements will result in relatively large errors in the q_e determinations. In plotting the Langmuir data, the error is magnified in the value of $\frac{1}{q_e}$.

Less scatter was seen in the data obtained for lead which seemed to fit the linear form of the Langmuir equation reasonably well.

The low pH data for copper, nickel, cadmium, and lead were best described by nonlinear regression curves. The scatter in the experimental data points was likely best attributed to experimental error. The Q^0 and b values determined by the nonlinear regression analyses were used in the competitive adsorption equation to predict metal concentrations in mixed metal systems.

Adsorption Studies at pH 7.0 - 7.5

Adsorption results from the high pH range, 7.0 to 7.5, fit the Langmuir equation quite well. The apparent scatter about the least-squares line was much less than in the lower pH studies. Since adsorption from the higher pH solutions was greater than from the lower pH solutions, the scatter in the $\frac{1}{q_e}$ values would be expected to be less. The adsorption data for the high pH range also fit the nonlinear regression curves well. The Q^0 and b values determined from the nonlinear regression analyses were used in the competitive adsorption equation to predict metal concentrations in mixed metal systems.

Effect of pH on Adsorption

A comparison of the Q^0 values in Tables IV and V indicates that increasing the pH increased adsorption capacity. For copper, nickel, and cadmium, adsorption from the higher pH solutions was greater than from the lower pH solutions. Prior to the onset of precipitation, which

is dependent on both concentration and pH, decreasing competition from H^+ and increasing concentration of hydrolyzed ions (e.g., $CuOH^+$, $CdOH^+$) are possible reasons for the adsorption to increase as pH increases. Stumm and Morgan (25) showed that the occurrence of metal hydroxyl species can affect the adsorption of hydrolyzable metal ions. They found that the pH at which metal hydroxyl species formed corresponded to the pH at which metal ion sorption became significant. The results are in agreement with the findings of Farrah and Pickering (27) who studied the influence of pH on the adsorption of copper, lead, zinc, and cadmium on kaolinite. They found that the amount of each metal adsorbed increased gradually with pH over a range of 3.5 to 6.0. In a separate study, Farrah and Pickering (7) showed that the adsorption capacity of kaolinite for copper increased with pH up to a limiting value at approximately pH 7.0. Nearly complete removal was observed at pH 7.0, which compares quite well with the copper adsorption data in this study shown in Appendix Table B-5.

Lead was adsorbed to a greater degree than copper, nickel, and cadmium from solutions of pH 5.5 to 6.0. The copper adsorption was greater than the adsorption of cadmium and nickel. The adsorption capacities for cadmium and nickel were nearly equal. In the high pH range studies, the relative adsorption order was nickel > copper > cadmium.

Adsorption of Mixed Metal Systems

This section presents a discussion of the mixed metal adsorption studies. The observed metal concentrations are compared to the equilibrium metal concentrations predicted by the competitive adsorption equation presented by Weber (1).

Adsorption Studies at pH 5.5 - 6.0

The following paragraphs discuss the adsorption studies conducted over pH range 5.5 to 6.0.

Copper and Nickel Study

The observed concentrations compared well with the predicted equilibrium concentrations for both copper and nickel. For all clay dosages, with one exception (clay dosage = 5.0 grams per liter), the error between the observed and predicted values was less than or equal to fifteen percent. The results indicated that the copper removal was higher, though not to a great degree, than the nickel removal from solution.

Nickel and Lead Study

The observed nickel values were very close (error less than or equal to eight percent) to the predicted values. The observed and predicted values for lead were reasonably close (error less than or equal to sixteen percent) with two exceptions. The two higher clay dosage samples did not compare quite as well (error greater than twenty-two percent). The amount of nickel removal was lower than the lead removal for all clay dosages.

Cadmium and Lead Study

The observed cadmium concentrations compared extremely well with the predicted equilibrium concentrations. For all clay dosages, the error between the observed and predicted values was less than or equal to five percent. However, the observed and predicted lead concentrations did not compare as well. Three of the eight observed values were reasonably close to the predicted values. For the remaining five samples, the error between the observed and predicted concentrations was greater than twenty-four percent. The amount of lead removal from solution was greater than the cadmium removal.

Copper, Nickel, and Cadmium Study

For each metal studied, the observed concentrations were extremely close to the predicted equilibrium concentrations. For all clay dosages, with one exception, the error between the observed and predicted values was less than or equal to eleven percent. The exception was the highest clay dosage, 5.0 grams per liter. The amount of copper removal was higher than the nickel and cadmium removals for all clay dosages. Cadmium and nickel removals were nearly equal.

Copper, Nickel, Cadmium, and Lead Study

The observed and predicted cadmium concentrations were extremely close (error less than or equal to six percent). The observed nickel concentrations compared quite well with the predicted concentrations. For all clay dosages, the error between the observed and predicted copper concentrations was less than or equal to twenty percent. The lead values did not compare as well. Four of the seven observed values

were reasonably close (error less than or equal to twenty percent) to the predicted values. For the remaining samples, the error between the observed and predicted values was greater than thirty percent. The lead removal was greater than the copper, nickel, and cadmium removals. The copper removal was greater than the nickel and cadmium removals. And the nickel removal was just slightly greater than the cadmium removal.

Adsorption Studies at pH 7.0 - 7.5

The following paragraphs discuss the mixed metal adsorption studies conducted over pH range 7.0 to 7.5.

Copper and Nickel Study

The observed copper concentrations compared quite well with the predicted equilibrium concentrations. However, the observed and predicted nickel concentrations did not compare as well. Four of the nine observed values were reasonably close to the predicted values. For the remaining five samples, the error between the observed and predicted concentrations was greater than thirty-four percent. The amount of copper removal was significantly greater than the nickel removal.

Nickel and Cadmium Study

For both nickel and cadmium, the observed and predicted concentrations compared reasonably well (error less than twenty percent). Three nickel values (clay dosages = 2.5, 3.125, and 5.0 grams per liter) and one cadmium value (clay dosage = 5.0 grams per liter) were exceptions. The amount of nickel removal was slightly greater than the cadmium removal.

VI. CONCLUSIONS

The following conclusions were derived from the results of this research:

- 1) The competitive adsorption equation presented by Weber is a valid and useful equation for describing the adsorption of mixed metal systems on kaolinite. In a mixed metal system, heavy metals compete for adsorption sites. This investigation demonstrated that the competitive adsorption equation may be used to predict equilibrium metal concentrations in mixed metal systems.
- 2) Adsorption of copper, nickel, cadmium, and lead on kaolinite occurs very rapidly. Equilibrium is complete within thirty minutes after the addition of metal.

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VIII. APPENDICES

APPENDIX A
ADSORPTION RATE DATA

Table A-1. Concentration of Metals Remaining in Solution (C) and Percent Removal from Initial Solution in Adsorption Rate Study
pH = 5.5 - 6.0

Metal	Clay Dose g/l	Initial Concentration mg/l	10 Minutes		30 Minutes		2.0 Hour		4.0 Hour		24.0 Hour	
			C mg/l	Removal %	C mg/l	Removal %	C mg/l	Removal %	C mg/l	Removal %	C mg/l	Removal %
Nickel	0.50	5.00	4.53	9.4	4.54	9.2	4.54	9.2	4.54	9.2	4.54	9.2
Nickel	1.25	5.00	4.20	16.0	4.19	16.2	4.22	15.6	4.19	16.2	4.19	16.2
Nickel	2.50	5.00	3.93	21.4	3.80	24.0	3.79	24.2	3.65	27.0	3.63	27.4
Nickel	3.75	5.00	3.78	24.4	3.74	25.2	3.66	26.8	3.63	27.4	3.26	34.8
Nickel	5.00	5.00	3.41	31.8	3.36	32.8	3.22	35.6	3.03	39.4	2.54	49.2
Cadmium	0.50	4.79	4.22	11.9	4.19	12.5	4.24	11.5	4.21	12.1	4.24	11.5
Cadmium	1.25	4.79	3.88	19.0	3.81	20.5	3.85	19.6	3.83	20.0	3.84	19.8
Cadmium	2.50	4.79	3.41	28.8	3.32	30.7	3.32	30.7	3.32	30.7	3.31	30.9
Cadmium	3.75	4.79	3.34	30.3	3.33	30.5	3.33	30.5	3.32	30.7	3.31	30.9
Cadmium	5.00	4.79	3.23	32.6	3.22	32.8	3.20	33.2	3.18	33.6	3.18	33.6
Copper	0.50	4.99	4.08	18.2	4.06	18.6	4.01	19.6	3.97	20.4	4.00	19.8
Copper	1.25	4.99	3.89	22.0	3.80	23.8	3.79	24.0	3.67	26.5	3.55	28.9
Copper	2.50	4.99	3.36	32.7	3.28	34.3	3.20	35.9	2.95	40.9	2.64	47.1
Copper	3.75	4.99	2.56	48.7	2.29	54.1	2.17	56.5	1.85	62.9	1.60	67.9
Copper	5.00	4.99	1.78	64.3	1.37	72.5	0.96	80.8	0.70	86.0	0.51	89.8
Lead	0.50	5.21	2.53	51.4	2.43	53.4	2.41	53.7	2.40	53.9	2.41	53.7
Lead	1.25	5.21	0.96	81.6	0.95	81.8	0.89	82.9	0.95	81.8	0.94	82.0
Lead	2.50	5.21	0.39	92.5	0.29	94.4	0.25	95.2	0.24	95.4	0.24	95.4
Lead	3.75	5.21	0.12	97.7	0.09	98.3	0.01	99.8	0.02	99.6	0.01	99.8
Lead	5.00	5.21	0.05	99.0	0.04	99.2	0.04	99.2	0.06	98.8	0.04	99.2

Table A-2. Concentration of Copper Remaining in Solution (C) and Percent Removal of Copper from Initial Solution in Adsorption Rate Study
pH = 7.0 to 7.5

Clay Dose g/l	Initial Concentration mg/l	30 Minutes		1.0 Hour		2.0 Hour	
		C	Removal %	C	Removal %	C	Removal %
0.25	1.55	1.17	24.5	1.15	25.8	1.15	25.8
0.50	1.55	1.00	35.5	1.01	34.8	1.05	32.3
0.75	1.55	0.69	55.5	0.68	56.1	0.67	56.8
1.00	1.55	0.58	62.6	0.57	63.2	0.59	61.9
1.25	1.55	0.46	70.3	0.47	69.7	0.48	69.0
1.50	1.55	0.41	73.5	0.42	72.9	0.39	74.8
2.50	1.55	0.29	81.3	0.27	82.6	0.28	81.9

Table A-3. Concentration of Cadmium Remaining in Solution (C) and Percent Removal of Cadmium from Initial Solution in Adsorption Rate Study
pH = 7.0 to 7.5

Clay Dose g/l	Initial Concentration mg/l	30 Minutes		1.0 Hour		2.0 Hour	
		C mg/l	Removal %	C mg/l	Removal %	C mg/l	Removal %
0.25	4.61	4.31	6.5	4.34	5.9	4.28	7.2
0.50	4.61	4.03	12.6	3.97	13.9	3.98	13.7
0.75	4.61	3.54	23.2	3.52	23.6	3.50	24.1
1.00	4.61	3.35	27.3	3.45	25.2	3.48	24.5
1.25	4.61	3.11	32.5	3.15	31.7	3.45	25.2
1.75	4.61	2.79	39.5	2.72	41.0	3.01	34.7
2.00	4.61	2.72	41.0	2.92	36.7	2.95	36.0
2.50	4.61	2.48	46.2	2.52	45.3	2.61	43.4
3.75	4.61	1.51	67.2	1.49	67.7	1.50	67.5
5.00	4.61	1.35	70.7	1.48	67.9	1.52	67.0

Table A-4. Concentration of Nickel Remaining in Solution (C) and Percent Removal of Nickel from Initial Solution in Adsorption Rate Study
pH = 7.0 to 7.5

Clay Dose g/l	Initial Concentration mg/l	<u>30 Minutes</u>		<u>1.0 Hour</u>		<u>2.0 Hour</u>	
		C mg/l	Removal %	C mg/l	Removal %	C mg/l	Removal %
0.25	4.92	4.05	17.7	4.17	15.2	4.11	16.5
0.50	4.92	3.72	24.4	3.55	27.8	3.77	23.4
0.75	4.92	2.85	42.1	2.95	40.0	3.05	38.0
1.00	4.92	2.40	51.2	2.59	47.4	2.56	48.0
1.25	4.92	2.27	53.9	2.15	56.3	2.26	54.1
1.875	4.92	1.66	66.3	1.89	61.6	1.98	59.8
2.50	4.92	1.34	72.8	1.38	72.0	1.51	69.3
3.125	4.92	1.23	73.3	1.31	73.4	1.27	74.2
3.75	4.92	1.26	74.4	1.21	75.4	1.38	72.0
5.00	4.92	0.85	82.7	0.97	80.3	1.06	78.5

APPENDIX B
ADSORPTION ISOTHERM DATA

Table B-1. Copper Adsorption Isotherm Data
pH = 5.5 - 6.0

Clay Dose g/l	$[Cu]_i$ mg/l	$[Cu]_f$ mg/l	$[Cu]_f=C$ mole/l	q_e mole/g	$\frac{1}{C}$ l/mole	$\frac{1}{q_e}$ g/mole
0.50	4.74	3.97	6.26×10^{-5}	2.40×10^{-5}	1.60×10^4	4.17×10^4
1.25	4.74	3.54	5.58×10^{-5}	1.50×10^{-5}	1.80×10^4	6.67×10^4
2.50	4.74	2.35	3.70×10^{-5}	1.50×10^{-5}	2.70×10^4	6.67×10^4
3.125	4.74	2.47	3.89×10^{-5}	1.14×10^{-5}	2.57×10^4	8.77×10^4
3.75	4.74	1.34	2.11×10^{-5}	1.43×10^{-5}	4.74×10^4	6.99×10^4
4.375	4.74	1.20	1.89×10^{-5}	1.27×10^{-5}	5.29×10^4	7.87×10^4
0.75	9.76	8.45	1.33×10^{-4}	2.80×10^{-5}	7.52×10^3	3.57×10^4
1.25	9.76	7.45	1.17×10^{-4}	2.96×10^{-5}	8.55×10^3	3.38×10^4
2.50	9.76	5.76	9.07×10^{-5}	2.53×10^{-5}	1.10×10^4	3.95×10^4
3.75	9.76	4.39	6.91×10^{-5}	2.26×10^{-5}	1.45×10^4	4.42×10^4
0.75	15.03	13.35	2.10×10^{-4}	3.60×10^{-5}	4.76×10^3	2.78×10^4
1.25	15.03	12.71	2.00×10^{-4}	2.96×10^{-5}	5.00×10^3	3.38×10^4
2.50	15.03	10.02	1.58×10^{-4}	3.16×10^{-5}	6.33×10^3	3.16×10^4
3.75	15.03	9.84	1.55×10^{-4}	2.19×10^{-5}	6.45×10^3	4.57×10^4

Table B-2. Cadmium Adsorption Isotherm Data
pH = 5.5 to 6.0

Clay Dose g/l	$[Cd]_i$ mg/l	$[Cd]_f$ mg/l	$[Cd]_f=C$ mole/l	q_e mole/g	$\frac{1}{C}$ l/mole	$\frac{1}{q_e}$ g/mole
0.25	4.78	4.42	3.93×10^{-5}	1.33×10^{-5}	2.54×10^4	7.52×10^4
0.50	4.78	4.17	3.71×10^{-5}	1.12×10^{-5}	2.70×10^4	8.93×10^4
1.25	4.78	3.79	3.37×10^{-5}	7.32×10^{-6}	2.97×10^4	1.37×10^5
2.50	4.78	3.31	2.94×10^{-5}	5.45×10^{-6}	3.40×10^4	1.83×10^5
3.75	4.78	3.26	2.90×10^{-5}	3.74×10^{-6}	3.45×10^4	2.67×10^5
5.00	4.78	3.14	2.79×10^{-5}	3.04×10^{-6}	3.58×10^4	3.29×10^5
7.50	4.78	2.95	2.62×10^{-5}	2.26×10^{-6}	3.82×10^4	4.42×10^5
8.75	4.78	2.58	2.30×10^{-5}	2.32×10^{-6}	4.35×10^4	4.31×10^5
10.00	4.78	2.57	2.29×10^{-5}	2.04×10^{-6}	4.37×10^4	4.90×10^5
0.50	9.39	9.00	8.00×10^{-5}	7.60×10^{-6}	1.25×10^4	1.32×10^5
1.25	9.39	8.52	7.58×10^{-5}	6.68×10^{-6}	1.32×10^4	1.50×10^5
3.75	9.39	7.61	6.77×10^{-5}	4.57×10^{-6}	1.48×10^4	2.19×10^5
5.00	9.39	7.45	6.63×10^{-5}	3.73×10^{-6}	1.51×10^4	2.68×10^5
0.50	13.70	12.85	1.14×10^{-4}	1.80×10^{-5}	8.77×10^3	5.56×10^4
1.25	13.70	12.40	1.10×10^{-4}	1.08×10^{-5}	9.09×10^3	9.26×10^4
3.75	13.70	11.64	1.04×10^{-4}	5.40×10^{-6}	9.62×10^3	1.85×10^5
5.00	13.70	11.32	1.00×10^{-4}	4.95×10^{-6}	1.00×10^4	2.02×10^5

Table B-3. Nickel Adsorption Isotherm Data
pH = 5.5 to 6.0

Clay Dose g/l	$[\text{Ni}]_i$ mg/l	$[\text{Ni}]_f$ mg/l	$[\text{Ni}]_f = C$ mole/l	q_e mole/g	$\frac{1}{C}$ l/mole	$\frac{1}{q_e}$ g/mole
0.50	4.92	4.61	7.85×10^{-5}	1.06×10^{-5}	1.27×10^4	9.43×10^4
0.75	4.92	4.30	7.33×10^{-5}	1.40×10^{-5}	1.36×10^4	7.14×10^4
2.50	4.92	3.60	6.13×10^{-5}	9.00×10^{-6}	1.63×10^4	1.11×10^5
3.75	4.92	3.46	5.89×10^{-5}	6.64×10^{-6}	1.70×10^4	1.51×10^5
4.375	4.92	3.06	5.21×10^{-5}	7.25×10^{-6}	1.92×10^4	1.38×10^5
5.0	4.92	2.62	4.46×10^{-5}	7.84×10^{-6}	2.24×10^4	1.28×10^5
1.25	12.08	10.92	1.86×10^{-4}	1.60×10^{-5}	5.38×10^3	6.25×10^4
2.50	12.08	10.51	1.79×10^{-4}	1.08×10^{-5}	5.59×10^3	9.26×10^4
3.75	12.08	9.88	1.68×10^{-4}	1.01×10^{-5}	5.95×10^3	9.90×10^4
1.25	14.70	13.78	2.35×10^{-4}	1.20×10^{-5}	4.26×10^3	8.33×10^4
3.75	14.70	12.94	2.20×10^{-4}	8.00×10^{-6}	4.54×10^3	1.25×10^5
5.0	14.70	12.70	2.16×10^{-4}	6.80×10^{-6}	4.63×10^3	1.47×10^5

Table B-4. Lead Adsorption Isotherm Data
pH = 5.5 to 6.0

Clay Dose g/l	$[Pb]_i$ mg/l	$[Pb]_f$ mg/l	$[Pb]_f=C$ mole/l	q_e mole/g	$\frac{1}{C}$ l/mole	$\frac{1}{q_e}$ g/mole
0.125	5.11	4.21	2.03×10^{-5}	3.52×10^{-5}	4.93×10^4	2.84×10^4
0.25	5.11	3.03	1.46×10^{-5}	4.04×10^{-5}	6.85×10^4	2.48×10^4
0.50	5.11	2.33	1.12×10^{-5}	2.70×10^{-5}	8.93×10^4	3.70×10^4
0.75	5.11	1.30	6.28×10^{-6}	2.46×10^{-5}	1.59×10^5	4.07×10^4
1.0	5.11	1.61	7.78×10^{-6}	1.69×10^{-5}	1.29×10^5	5.92×10^4
1.25	5.11	0.96	4.63×10^{-6}	1.61×10^{-5}	2.16×10^5	6.21×10^4
2.50	5.11	0.32	1.54×10^{-6}	9.26×10^{-6}	6.49×10^5	1.08×10^5

Table B-5. Copper Adsorption Isotherm Data
 pH = 7.0 to 7.5

Clay Dose g/l	$[Cu]_i$ mg/l	$[Cu]_f$ mg/l	$[Cu]_f=c$ mole/l	q_e mole/g	$\frac{1}{c}$ l/mole	$\frac{1}{q_e}$ g/mole
0.25	1.55	1.17	1.84×10^{-5}	2.39×10^{-5}	5.43×10^4	4.18×10^4
0.50	1.55	1.01	1.59×10^{-5}	1.70×10^{-5}	6.29×10^4	5.88×10^4
0.75	1.55	0.69	1.09×10^{-5}	1.80×10^{-5}	9.17×10^4	5.56×10^4
1.0	1.55	0.58	9.13×10^{-6}	1.53×10^{-5}	1.10×10^5	6.54×10^4
1.25	1.55	0.47	7.40×10^{-6}	1.36×10^{-5}	1.35×10^5	7.35×10^4
1.50	1.55	0.41	6.45×10^{-6}	1.20×10^{-5}	1.55×10^5	8.33×10^4
2.50	1.55	0.29	4.56×10^{-6}	7.93×10^{-6}	2.19×10^5	1.26×10^5

Table B-6. Cadmium Adsorption Isotherm Data
pH = 7.0 to 7.5

Clay Dose g/l	$[Cd]_i$ mg/l	$[Cd]_f$ mg/l	$[Cd]_f=C$ mole/l	q_e mole/g	$\frac{1}{C}$ l/mole	$\frac{1}{q_e}$ g/mole
0.25	4.61	4.31	3.83×10^{-5}	1.12×10^{-5}	2.61×10^4	8.93×10^4
0.50	4.61	3.97	3.53×10^{-5}	1.19×10^{-5}	2.83×10^4	8.40×10^4
0.75	4.61	3.54	3.15×10^{-5}	1.32×10^{-5}	3.17×10^4	7.58×10^4
1.0	4.61	3.48	3.10×10^{-5}	1.04×10^{-5}	3.23×10^4	9.62×10^4
1.25	4.61	3.15	2.80×10^{-5}	1.08×10^{-5}	3.57×10^4	9.23×10^4
1.75	4.61	2.79	2.48×10^{-5}	9.63×10^{-6}	4.03×10^4	1.04×10^5
2.0	4.61	2.72	2.42×10^{-5}	8.74×10^{-6}	4.13×10^4	1.14×10^5
2.50	4.61	2.48	2.21×10^{-5}	7.86×10^{-6}	4.52×10^4	1.27×10^5
3.75	4.61	1.51	1.34×10^{-5}	7.65×10^{-6}	7.46×10^4	1.31×10^5
5.0	4.61	1.35	1.20×10^{-5}	6.03×10^{-6}	8.33×10^4	1.66×10^5

Table B-7. Nickel Adsorption Isotherm Data
pH = 7.0 to 7.5

Clay Dose g/l	$[Ni]_i$ mg/l	$[Ni]_f$ mg/l	$[Ni]_f=C$ mole/l	q_e mole/g	$\frac{1}{C}$ l/mole	$\frac{1}{q_e}$ g/mole
0.25	4.92	4.05	6.90×10^{-5}	5.92×10^{-5}	1.45×10^4	1.69×10^4
0.50	4.92	3.55	6.05×10^{-5}	4.66×10^{-5}	1.65×10^4	2.15×10^4
0.75	4.92	2.85	4.86×10^{-5}	4.69×10^{-5}	2.06×10^4	2.13×10^4
1.0	4.92	2.40	4.09×10^{-5}	4.29×10^{-5}	2.44×10^4	2.33×10^4
1.25	4.92	2.27	3.87×10^{-5}	3.61×10^{-5}	2.58×10^4	2.77×10^4
1.875	4.92	1.89	3.22×10^{-5}	2.75×10^{-5}	3.11×10^4	3.64×10^4
2.50	4.92	1.38	2.35×10^{-5}	2.41×10^{-5}	4.26×10^4	4.15×10^4
3.125	4.92	1.23	2.10×10^{-5}	2.00×10^{-5}	4.76×10^4	5.00×10^4
3.75	4.92	1.26	2.15×10^{-5}	1.66×10^{-5}	4.65×10^4	6.02×10^4
5.0	4.92	0.85	1.45×10^{-5}	1.39×10^{-5}	6.90×10^4	7.19×10^4

APPENDIX C
LINEAR REGRESSION COMPUTER PROGRAM USED
TO ESTIMATE θ^0 AND b VALUES

Linear Regression Computer Program Used
to Estimate Q^0 and b Values

```

DIMENSION X(30),Y(30)
READ,M
DO 4 I=1,M
SUMXY=0.0
SUMX=0.0
SUMY=0.0
SUMX2=0.0
SUMY2=0.0
READ,N,K
DO 3 J=1,N
READ5, X(J),Y(J)
5 FORMAT(2E14.3)
SUMX=SUMX+X(J)
SUMY=SUMY+Y(J)
SUMXY=SUMXY + X(J)*Y(J)
SUMX2=SUMX2 + X(J)**2
SUMY2=SUMY2 + Y(J)**2
3 CONTINUE
XBAR=SUMX/N
YBAR=SUMY/N
B=((N*SUMXY)-(SUMX*SUMY))/((N*SUMX2)-(SUMX)**2)
A=YBAR-(B*XBAR)
PRINT, K, B, A
SXX=SUMX2-((SUMX)**2)/N
SYY=SUMY2-((SUMY)**2)/N
R=B*SQRT(SXX/SYY)
R2=R**2
PRINT9,R2
9 FORMAT(' ',10X,'CORRELATION',3X,F9.3)
PRINT10
10 FORMAT(' ')
4 CONTINUE
STOP
END

```

APPENDIX D
NONLINEAR REGRESSION COMPUTER PROGRAM USED
TO ESTIMATE Q^0 AND b VALUES

Nonlinear Regression Computer Program Used
to Estimate Q^0 and b Values

```
DATA ABN;  
INPUT CC Q0;  
C=1./CC;  
Q=1./Q0;  
CARDS;  
  
PROC NLIN BEST=5;  
PARAMETERS B=8130 Q0=.00000168;  
MODEL Q=(Q0*B*C)/(1.+B*C);  
DER.B=(Q0*C)/((1+B*C)**2);  
DER.Q0=(B*C)/(1+B*C);  
OUTPUT PREDICTED=PQ;  
  
PROC PLOT; PLOT Q*C='*'PQ*C='.'/OVERLAY;
```

APPENDIX E
COMPUTER PROGRAM USED TO PREDICT EQUILIBRIUM METAL
CONCENTRATIONS IN MIXED METAL SYSTEMS

Computer Program Used to Predict Equilibrium Metal
Concentrations in Mixed Metal Systems

```
DIMENSION CE(10),B(10),O(10),CO(10),A(10),X(10)
READ,N
DO 2 I=1,N
2 READ,CO(I),B(I),O(I)
SS=.05
PER=4.0
11 DO 1 I=1,N
1 CE(1)=0.50*CO(I)
DO 3 II=1,100
DENOM=1
DO 5 K=1,N
5 DENOM=DENOM+B(K)*CE(K)
DO 6 J=1,N
X(J)=(CO(J)*DENOM)/(O(J)*B(J)*SS+DENOM)
6 CONTINUE
DO 7 I=1,N
A(I)=(ABS(X(I)-CE(I))/X(I))*100
7 CONTINUE
DO 8 I=1,N
IF (A(I).GE.PER) GO TO 10
8 CONTINUE
GO TO 12
10 DO 14 I=1,N
14 CE(I)=X(I)
3 CONTINUE
12 PRINT,SS
DO 9 J=1,N
9 PRINT,J,X(J)
SS=SS+.05
IF(SS.LE.5.0) GO TO 11
STOP
END
```

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ADSORPTION OF MIXED METAL SYSTEMS ON KAOLINITE

by

Sara Allen Irvine

(ABSTRACT)

This study presents the results from laboratory investigations of the capacity of kaolinite to adsorb heavy metals including copper, nickel, cadmium, and lead. Kaolinite is a clay commonly found in suspended solids and sediments in natural water systems. The purpose of the study was to evaluate the validity of the competitive adsorption equation presented by Weber in describing metal adsorption on kaolinite. This equation describes adsorption competition among the components of a mixture of solutes. Adsorption studies were conducted for single and mixed metal systems. Controlling factors considered include solution pH, clay dosage, and cation competition.

The investigation demonstrated that the competitive adsorption equation is a valid and useful equation for describing the adsorption of mixed metal systems on kaolinite. The equation may be used to predict equilibrium metal concentrations in mixed metal systems. The results of the study also indicated that the rate of adsorption of the metals on kaolinite was very rapid. Equilibrium was complete within thirty minutes of the addition of the metals to the clay.