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KINETICS OF HEAVY METAL TRANSFER
FROM SLUDGE TO SOIL

By

Bahram Setoodeh

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ABSTRACT

KINETICS OF HEAVY METAL TRANSFER FROM SLUDGE TO SOIL

By

Bahram Setoodeh

Performance of an adsorption and a desorption system under field and flooding hydraulic regimes was investigated. The adsorbents were glucose, tryptophane, cellulose, clay and a combination of the clay and one of the organics. The clay was a kaolinite. The adsorbents were leached with one of two solutions of 40 mg/l of zinc and cadmium. The desorbents were raw and anaerobically treated sludges obtained from an activated sludge wastewater treatment plant. The sludges were leached with a simulated rain solution.

The leachates were collected and analyzed for their zinc and cadmium content, pH, and total carbon. It was found that the data closely fit the empirical adsorption equation proposed by Freundlich. The data, also, fit well into a logarithmic equation of type $Y = a + b \ln X$. The correlation coefficients of the fit of the data to the above logarithmic model, for different clay and clay•organic adsorbents, were found to be 0.99, in the field condition, and greater than 0.87.

It was found that the modified desorption data fit the Freundlich equation very closely. These data also were fit to a logarithmic model of the type described before. The correlation coefficients of the fit of the data to the models was 99% for both of the sludges.

The rate constants of adsorption and desorption of the cations to or from the active media were found and compared. It was found that under both, field and flooding hydraulic condition the rate of adsorption of the cations to the adsorbents always exceeded the rate of release of them from the raw and anaerobically treated sludges.

It was shown that the models can be used for prediction purposes. This can be done after a short experimental period to determine the sludge and the soil properties and the constants of the model.

To Andrew L. Simon

my academic inspirer

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CHAPTER 1

INTRODUCTION

1.1 Sludge Generation and Disposal

Wastewater sludge results from primary and secondary treatment of raw wastewater. The term "sludge" does not usually include grit, scum, and screenings. However, of all of this together sludge forms the most important by-product of the plant.[1] Primary sludge is formed as the result of gravitational settling of raw wastewater and is usually coarse and fibrous. Secondary sludge results from biological treatment of the wastewater. It is, indeed, settled flocs of organisms.

Treatment of sludge is performed in order to stabilize the organic matter and reduce its water content. Unit processes for sludge treatment and disposal are thickening, stabilization, conditioning, dewatering, heat drying, reduction volume, and final disposal.[2]

1.2 Heavy Metals in Sludge

Heavy metals are found in different concentrations in wastewater. Sources of heavy metals in wastewater may be industry, precipitation runoff, and excretion from man. Upon treatment in a conventional activated sludge or trickling filter treatment plant most of the heavy metals go into the sludge.[3–11] Retention of a high percentage of the influent heavy metals by acclimated sludge was reported by Neufeld and Hermann.[9] They indicated that such a system will continue to operate while removing heavy metals. These authors reported that the activated sludge flocs that were exposed to shock loads of mercury (Hg), cadmium (Cd), and zinc (Zn) picked up (adsorbed) these elements from the aqueous carrier. Reid[10] reported that the completely mixed aerobic treatment of wastewater is capable of removing heavy metals from the system.

1.3 Sludge Application Practices

No matter what the form of sludge dewatering or treatment may be, the final residues are normally deposited in or on soil. Land application of wastewater is the oldest method used for treatment and disposal of wastes with use by cities recorded for more than 400 years.[12] Raw sludge in the form of night soil has been used on farm land, as a fertilizer, since ancient times.[13] Land spreading of sludge as far as 180 miles from its source has been proven to be cheaper than any other alternative method of sludge disposal.[14] Reed[15] described techniques for applying sludge to soil. These include ridge-and-furrow, plough-furrow, cover and sub-sod injection methods.

Traditionally, sludges have been treated before being deposited on soil, however, application of raw sludge has been practiced.[16–18] For example, 15 communities in northern Ohio, representing a total of 600,000 people, use direct land application of wastewater sludge.[19]

1.4 Problems with Land Disposal

Heavy metals are necessary, in minute quantities, for the growth of many organisms and/or plants. However, excess amounts of these elements may have a considerable toxic effect on living matter. The threshold levels of these contaminants for each species of organism is different. It also varies with regard to other environmental factors. Heavy metals in soil can eventually enter into the human food chain. Soils that have been subjected to sludge application are subjected to heavy metals, and thus, are questionable soils for crop growth. Furthermore, the heavy metals may leach down to the ground water table and contaminate it.

Upon application of sludge to soil the liquid and some small solid particles may penetrate into or become incorporated with the soil. Adsorption from a liquid phase to a solid phase will take place more rapidly than the diffusion from a solid phase to another. The solid fraction of the sludge, also, releases its metal content into soil.

Lindsay[20] indicated that sewage sludge would decompose in the soil and release Zn, Cd, and other heavy metals with intermediate solubility. He added that under many soil conditions these products are soluble. Furthermore, he indicated the need for the quantitative studies to predict the long term fate of the heavy metals due to addition of the sewage sludge in soil.

Adjustment of the pH of acidic soils is usually done by the use of lime. This is a necessary step for limiting the availability of heavy metals to the roots, therefore, improving crop growth. The reason for the lime treatment of the acidic soil is that the solubility of macro and micronutrients increases with decreasing pH. Therefore, they may easily be carried down to the deeper strata of the soil where they are out of the reach of the crop roots. The existence of low environmental pH's generally increases the danger of groundwater pollution by leaching from surface sources.

The most toxic heavy metals of municipal sludges are zinc, cooper, nickel, and cadmium.[21-23] Between these, zinc, copper, and nickel are known for their phytotoxic effect while cadmium can accumulate in vegetation to levels which are toxic to animals before any sign of plant toxicity appears.[24]

1.5 Role of Kinetics in the Sludge-Soil System

Kinetics studies indicate how fast a reaction takes place and what factors influence the rate of the reaction. Upon application of the sludge to soil a new physical, chemical, and biological system develops which is different from either the soil or the sludge. In other words a reaction will take place such that

$$\text{SOIL} + \text{SLUDGE} \longrightarrow \text{"NEW SOIL."}$$

This is a dynamic system where time, temperature, and the moisture content of the system have great influences on its eventual stabilization.

In this system, decomposition of the sludge is followed by the release of macro and micronutrients into the soil solution. This may

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be followed by the adsorption of products by the active sites within the soil. Precipitation of these products may occur when the soil solution becomes saturated with respect to a specific matter. When the soil solution becomes unsaturated with respect to any solid phase or mineral that is present, the phase can be redissolved.[20] If enough moisture exists, a downward movement of the product will be inevitable because of the fact that the adsorption sites eventually will be exhausted. The extent of the downward movement will vary with the type and the number of adsorption sites (i.e., type of soil) and the constitutents, and their respective concentration, in the sludge. Therefore, the overall process can be summarized as:

$$\text{NEW SOIL} \longrightarrow \text{DESORPTION} \longrightarrow \text{PRODUCT} \xrightarrow{\text{Transport}}$$

$$\text{ADSORPTION + EXCESS PRODUCT}$$

If sludge application continues, the soil active sites become exhausted and all of the products escape the system. Lindsay[20] summarized the above as:

> The composition of the soil solution is ultimately controlled by the solubility of various mineral phases in soil. In many reactions the rates of precipitation and dissolution are sufficiently slow that kinetic as well as thermodynamic factors must be considered.

Kirkham[25] has discussed the discrepancy between investigators over the ultimate amount of organic matter that will be degraded once sludge is added to the soil. The reported variation is from 20 to 30% decomposition for an infinite amount of time to 60% decomposition for a short time period.

1.6 Hypothesis and Objectives

In chemical reaction engineering, reactions are classified as homogeneous and heterogeneous. The first term is used when the reaction takes place in one phase, e.g., liquid-liquid, and the second term is used in other conditions such as solid-liquid reactions.[26] In this respect the adsorption of soluble metals on solids falls in the second category. In heterogeneous systems, mass transfer becomes an important factor in rate determinations. When the reaction consists of a number of steps, the rate determining step is the slowest step which has control over the whole reaction.

Generally speaking, the rate of a reaction may be expressed as:

$$R_i = kf \text{ (system variables)}$$

where R_i is the rate of the reaction with respect to a certain species, k is the reaction constant, where its unit changes with changes in the order of the reaction. The system variables may include the volume of the reacting fluid, volume of the vessel, mass of solid in the fluid-solid system, temperature, and pressure. A rate equation is a differential equation which expresses the change in the concentration with time, i.e., the rate as a function of concentration. Even though there are ways to predict some theoretical rate equations in engineering work, they are generally of limited value. This is because it is not known before hand whether the calculated rate is close to the empirical value or off by a factor of a million.[27] Therefore, for engineering design, the experimentally found rates are generally used in all cases.

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The form of the rate equation may be found as the result of an empirical curve-fitting procedure.[27]

In natural systems the biodegradability of certain chemical species plays a rather important role in the metal adsorption process. This contribution may result because of the higher soil affinity of secondary products resulting from decomposition of the primary applied organic matter. It also could be as the result of pH changes resulting from the decomposition activities. Both of these situations, when they occur, greatly affect the kinetics of adsorption. The adsorption of organic matter, especially proteins, by clay minerals, as was shown in the early works of Esminger and Gieseking,[28-29] further complicates the whole process.

The following hypotheses were made in the light of previous studies, background information and preliminary investigations for this dissertation:

1. That some organics have ability to adsorb heavy metals and that the rate of adsorption of heavy metals is different for different organic forms.
2. That interaction between clay and organic matter (provided to the clay by application of a wastewater or wastewater sludge) may occur and thus affect the rate of adsorption of the heavy metals.
3. That upon application of a wastewater sludge to land a dynamic state will prevail in which some microorganisms can survive in the new environment. These microorganisms, then, decompose the

chelates responsible for holding the heavy metals in the sludge. This decomposition will result, eventually, in the release of the bonded heavy metals to the surrounding environment.

4. That if enough moisture exists the released heavy metals may leach down to lower strata of the soil and contaminate it. The contamination may occur if the rate of release of the heavy metal from sludge is greater than the rate of adsorption of them by the active media of the environment (i.e., mainly the clay and the organic fraction of the soil), or, if the adsorption capacity of the intermediate adsorption sites has been depleted.
5. That a dynamic system will exist until no further decomposition of the organics can occur.

The objective of this research is to find out the role of different organic forms commonly found in wastewater or wastewater sludge on the kinetics of heavy metal transfer from sludge to soil; and to investigate the rate of release of zinc and cadmium from sludge to the underlying environment.

CHAPTER 2

SYSTEM CHARACTERIZATION

2.1 Properties of Sludge

2.1.1 Physical Properties of Sludge

Sludge is a semiliquid. Its liquid fraction may be water, oil, or chemical solvents. Wastewater sludge contains water and solids. The typical water content of sludges are shown in Table 2.1.

Table 2.1 Typical Water Content of Sludges[30]

Wastewater Treatment Process	Percent Moisture of Sludge Generated	Lb water/Lb Sludge Solids
Primary sedimentation	95	19
Trickling filter		
Humus-low rate	93	13.3
Humus-high rate	97	32.3
Activated sludge	99	99

Gould and Genetelli[31] studied the solid content of an anaerobically treated sludge and reported that over 90% of the solids were in particulate form (diameter > 100 micron), whereas the colloidal, superacolloidal, and the dissolved fraction accounting for 0.1-0.3%, 5-8%, and 1-3% of the solids, respectively.

2.1.2 Chemical Composition of Sludge

Sludge contains a variety of chemical and biological substances. The chemical composition of wastewater sludge varies from one plant to another. This variation is due to the contributions received from the local industries, type of the treatment of the wastewater, and climatological factors.

2.1.3 Organic Matter in Sludge

Some authors[32, 33] have reported that cellulose and hemicellulose form a considerable portion of the organic matter of a wastewater. They may account for as much as 50% of the organic fraction. Most of the cellulose fibers are removed in primary settling tanks in the form of sludge. Degradation of cellulose, under aerobic or anaerobic conditions, has been shown to be a very slow process. In anaerobic digesters, where the temperature varies from 30-32° C, it was shown that about 90% of the cellulose was degraded after 50 days while only 50% was degraded after 20 days.[33]

Edberg and Hofsten[33] also reported that dried raw sludge contained about 23% carbohydrates, the large fraction of which was glucose. For activated sludge and digested sludge, the carbohydrate content was found to be much lower, i.e., 3 and 7%, respectively. It was reported that only one-third of the sludge going into the digesters was activated sludge.

Other authors[5, 6, 34] have reported that the settleable activated sludge organisms exist as individual cells covered by a web of rather insoluble organics. This extracellular film consists of polysaccharides, polymer fibrils, high molecular weight proteins, ribonuclic acid and deoxyribonuclic acid.

Other varieties of organic matter which might be expected to be found in wastewater and sludge are, proteins, a number of sugars, urea, aminoacids, fats, and waxes.[33,35] Vaseen[36] indicated that the conventional activated sludge from a domestic wastewater contains 43.1% protein. Table 2.2 shows the composition of typical raw and digested sludge.

2.1.4 Inorganic Matter and Heavy Metals in Sludge

2.1.4.1 Concentration of Metals in Sludge

Klein et al.[4] reported the concentration of heavy metals in the wastewater from the residential areas of New York City as shown in Table 2.3.

The typical chemical composition of treated wastewater as reported by Sank et al.[37] is given in Table 2.4. The average concentration of metals in wastewater effluents and in digested sludge were reported by Ellis[38] and by Salotto et al.,[39] and are shown in Table 2.5.

The levels of concentration of zinc, copper, nickel, and cadmium in the sludge have also been reported by others.[8,37,40] Most of these investigators, however, neglected to report the sludge moisture content. Therefore, it is extremely difficult to assume a narrow range of heavy metal concentrations for a municipal wastewater sludge.

Table 2.2 Typical Chemical Composition of Raw and Digested Sludge[1]

Item	Raw Primary Sludge		Digested Sludge	
	Range	Typical	Range	Typical
Total dry solids (TS), %	2-7	4.0	6-12	10.0
Volatile solids (% of TS)	60-80	65.0	30-60	40.0
Grease and fats (ether soluble, % of TS)	6-30	NA	5-20	NA
Protein (% of TS)	20-30	25.0	15-20	18.0
Nitrogen (N, % of TS)	1.5-4.0	2.5	1.6-6.0	3.0
Phosphorus (P_2O_5, % of TS)	0.8-2.8	1.6	1.5-4.0	2.5
Potash (K_2O, % of TS)	0.0-1.5	0.4	0.0-3.0	1.0
Cellulose (% of TS)	8-15	10.0	8-15	10.0
Iron (not as sulfide)	2-4	2.5	3-8	4.0
Silica (SiO_2, % of TS)	15-20	NA	10-20	NA
pH	5-8	6.0	6.5-7.5	7.0
Alkalinity (mg/l as $CaCO_3$)	500-1,500	600.0	2,500-3,500	3,000.0
Organic acids (mg/l as HAC)	200-2,000	500.0	100-600	200.0
Thermal content (Btu/lb)	6,800-10,000	7,600.0[a]	2,700-6,800	4,000.0[b]

[a] Based on 65% volatile matter.

[b] Based on 40% volatile matter.

Table 2.3 Heavy Metal Concentrations in Influent Wastewater[4]

Concentrations ppm	Cu	Cr	Ni	Zn	Cd
Influent wastewater	0.11-0.33	0.008-0.15	0.01-0.15	0.13-0.37	0.001-0.007
Sludge	0.46	0.16	0.15	1.6	0.025

2.1.4.2 Forms of Heavy Metal Complexes in Sludge

Generally speaking, heavy metals in sludge can be divided into: (a) soluble metals in the sludge liquid, and (b) metals that are bound to the solid particles. Chemical properties of heavy metal complexes in sludge have been the subject of many studies.[5,6,41] These studies have revealed that the existence of numerous functional groups in the extracellular film of microorganisms provides potential binding sites for heavy metals. However, it has been argued, theoretically, that under anaerobic conditions hydrolysis of the complexes may occur. This results in desorption or release of the heavy metals to the bulk of solution.[5] Cheng et al.[6] reported that the metal in wastewater are complexes composed of free metal ions and ligands of an organic or inorganic nature. Under aerobic conditions metalorganic complexes will form as the result of metal take-up by the biofloc. In addition, these authors indicated that metal ion precipitation may occur at the higher original concentrations of metals in the influent wastewater.

Table 2.4 Typical Chemical Composition of Treated Municipal Sewage Effluent[37]

Constituents	Average Concentration mg/l	Total Amount Applied[a] kg/ha
pH	8.1	NA
MBAS[b]	0.37	6
Nitrate-N	8.6	143
Organic-N	2.4	40
NH_4-N	0.9	14
P	2.65	44
Ca	25.2	420
Cl	41.3	792
Mg	12.9	215
Na	28.1	469
Fe	0.4	9
B	0.169	3.26
Mn	0.061	1.15
Cu	0.109	1.96
Zn	0.211	4.15
Cr	0.023	0.41
Pb	0.104	2.12
Cd	0.009	0.19
Co	0.062	1.24
Ni	0.093	1.82

[a] Total amount applied on areas that received 5 cm of effluent per week.

[b] Methylene blue active substance (detergent residue).

Table 2.5 Average Concentration of Metals in Digested Sludge (All Figures Are mg/kg[a] Dry Sludge Basis)[39]

	Arithmetic		Geometric		
Metal	Mean	Std. Dev. (+ and -)	Mean	Std. Dev. (+ and -)	Median 50% Value
Ag	250	230	190	1.99	100
B	430	310	380	1.58	350
Cd	75	104	43	2.47	31
Ca	36,500	23,800	31,100	1.77	30,000
Cr	1,860	1,920	1,050	3.22	1,100
Co	350	220	290	1.88	100
Cu	1,590	1,670	1,270	1.95	1,230
Hg	10	18	6.5	2.34	6.6
Mn	1,300	2,290	475	3.67	380
Ni	680	620	530	1.88	410
Pb	2,750	2,350	2,210	1.82	830
Sr	520	670	290	2.70	175
Zn	4,210	3,800	2,900	2.40	2,780

[a] mg/kg = ppm.

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2.2 Properties of Soil

Soil is a mixture of solids and water. Soil solids may be either organic or inorganic. The primary soil minerals are the parent materials such as feldspar, biotite, and apptite. Secondary minerals are formed as the result of weathering and decomposition of the primary minerals. They also are known as clay minerals. Clay minerals are that fraction of soil smaller than 2 micron in diameter. They are made up of sheets of silicon tetrahydra and aluminum octahydra.

2.2.1 Physical Properties of Soil

Bulk density, particle size distribution, porosity, permeability, temperature, moisture content, soil water potential, hysteresis, and other similar properties are known as the physical properties of soil. The physical properties of a soil are dependent upon the age, geographical location, position with respect to the ground surface, and the history man's activities on it.

2.2.2 Chemical Properties of Soil

The organic fraction of soil is composed of plant and animal residues in various stages of decomposition as well as living organisms. The organic portion of the soil has a significant effect on certain physical properties of the soil. Among the properties affected are the structure, permeability, and retention of moisture. Compounds obtained as the result of the decomposition of the organic matter cause soil particles to aggregate. Uronic compounds, along with gums and resins are believed to be effective soil binders. The organic fraction in soil is usually small averaging from 2 to 10%.[37] Obviously, the degree of decomposition of various organic fractions is different. Cellulose, proteins, and carbohydrates are found in soil. Their source being the plant tissues and dead micro and macroorganisms. Under normal conditions cellulose, fats, and waxes decompose slowly in soil. However, the rate of this decomposition under various physical, chemical, and biological conditions is not known for certain. Resistant materials are known to have little or no nitrogen and protein. This accounts, at least in part, for their resistance.[3] When the resistant substances finally decompose, they combine with the newly synthesized proteins (synthesized by soil microorganisms) and form humus.

The inorganic fraction of soil is composed of many oxides. Silicates, carbonates, sulfates, etc. are some of the different minerals that are abundant in soil.

2.2.3 Adsorption by Soil

Weber[42] indicates that all solids are able to adsorb. The exchange phenomenon is known to occur with a number of natural solids including soil, humus, cellulose, wool, protein, coal, lignin, and metal oxides.

The active portion of the soil, as far as adsorption of cations is concerned, are the clay minerals and organic matter. Organic matter, for instance, has typical exchange capacity of about 200 miliequivalents per 100 grams (me/100 g) while the cation exchange capacity (CEC) of kaolinite, which is dominant in humid areas, ranges from 5 to 15 me/100 g. The CEC of montmorillonite, which is dominant in arid areas, is about 100 me/100 g.[37]

Clay minerals are usually negatively charged. This charge is the result of charges induced by the broken edges (ionization) as well as those due to the isomorphic substitution. The attraction of ions to clay minerals could be the result of van der Walls forces, electrical forces, ion exchange forces, specific adsorption forces, or the forces causing the exchange of the coordinated metal ion with the available cation. Since adsorption is a surface phenomenon, the total available surface area of the soil granule plays a rather significant role on the overall adsorption process. Clays are known to have a very large surface area to volume ratio. Even in sandy soils more than 95% of the total surface area is associated with clay.[37]

Wetink and Etzel[43] noticed that the nature of the ion (i.e., its valence, ionic size, and polarizability) can influence the adsorption and replacement of these ions on the exchange site of a soil particle. These workers used three soil types and passed Zn, Cu, and Cr sulfite through them. They studied the rate of adsorption of these ions and concluded that the removal of Zn, Cu, and Cr were the result of an ion exchange mechanism.

Berger[44] found that the concentration of Zn in a normal soil generally falls in the range of 10-300 mg/l total Zn. He noted that very little is known about the zinc complexes in soil except that they are tightly held in soil. Furthermore, he added that some of the available zinc is held on exchange materials, namely, the clay and the organic matter of the soil.

Clays adsorb many organic substances. They can even adsorb enzymes and bacterial cells. The adsorption of organics by clay is referred to as carbon mineralization.

Ellis[45] feels that the adsorption or bonding processes responsible for the attachment of heavy metals to soil may be divided into the following categories: (1) electrostatic bonding; (2) covalent bonding; (3) hydrolysis; (4) specific adsorption; and (5) bonding to organic matter. In this classification scheme isomorphic substitution in the clay lattice is also included in the fourth category.

The removal of heavy metals from wastewater and wastewater sludges by soil is the result of biological activity as well as physico-chemical processes. The biopopulations responsible for the biological activity are expected to be different in the sludge and the soil and yet including some of those in both the soil and in the sludge. The organic portion of soil may play a significant role in the adsorption processes. Adsorption of heavy metals onto the organics is due to the availability of sites and the net attractive forces induced by electrical charges. Fair et al.[46] indicated their expectation that proteins would adsorb heavy metals to form organometalic complexes. Their reasoning relies on the fact that a protein molecule carries a net negative charge. The quantity of this charge changes with factors such as the degree of ionization and as the result of the pH of the medium. This charge may be depicted as $NH_2 - R - COO^-$,

NH_3^+ - R - COOH, or as NH_3^+ - R - COO^- (zero) at high pH, low pH, and at the isoelectric points, respectively.[1]

Based on Lahav and Hochberg,[47] it appears that the cations from a strongly chelated metal ion solution such as solutions of Zn-EDTA and Fe-EDDHA are not adsorbed by soil. These authors indicated that neither adsorption nor decomposition, aerobically or anaerobically, of Fe-EDDHA was observed in a period of two months. Other authors[27] have reported that no adsorption of cadmium was found when a solution of Cd-EDTA was applied to a soil. These types of solutions, therefore, when applied on a soil are potential sources of ground water contamination. Furthermore, adsorption of cationic species from the chelated solutions are strongly dependent upon the pH.[37]

Among the organic fractions of soil humic and fulvic acids are probably the main active group of chemical compounds responsible for the adsorption of metals. Riffaldi and Levi-Minzi[27] indicated that the presence of functional groups, chiefly COOH and OH, conduct the first stage of the adsorption or ion exchange reaction. The authors also referred to previous work that showed that the organic acids of the soil contain various types of OH groups and both aliphatic and aromatic COOH groups. It seems, therefore, that dissociation of these functional groups plays a major role in the adsorption process by providing available sites for the cations in solution.

2.3 Conclusions Based on the Background Information

In general, when sludge metal concentrations and characteristics are considered with respect to soil and its parameters, the following conclusions may be drawn.

1. Heavy metals from sludge will be released upon decomposition.
2. Heavy metals can be adsorbed by soil.
3. The adsorption process of soil includes an ion exchange process. This is due to the fixation (addition of the ion in the coordination complex form) and chelation of cations by the soil organic matter.
4. It is possible to overaccumulate some of the heavy metals by continuous and unmanaged application of sludge to soil.
5. High doses of heavy metals are toxic to plants, animals, and man.
6. A minimum metal content in sludge is desirable for the land application of sludge.
7. Pretreatment of soil by the lime application, to adjust the pH, will reduce the solubility of the metallic compounds, thus reducing the danger of ground water contamination.
8. The life expectancy of a soil disposal site may be significantly increased through a good management program, i.e., using proper crops, correct sludge application rates, etc.
9. Ground water and the crop contamination may be avoided by the proper soil testing and analysis before and during the sludge application.

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CHAPTER 3

MATERIALS AND METHODS

To test the hypothesis made in this research and to fulfill the objective of this research it was decided that a synthetic soil should be made rather than using a naturally occurring one. This was done by manually combining known amounts of organic, clay, and sand of certain characteristics. The soil was placed in adsorption columns and leached with metallic solutions. The leachates were examined for their metal content. Another set of columns was made to study the rate of release of the cations from the sludge.

3.1 Column Construction

Columns were made up of 30 centimeter (cm) long, 5 cm inside diameter glass tubing. A glass funnel acted as a base for the columns (Figure 3.1).

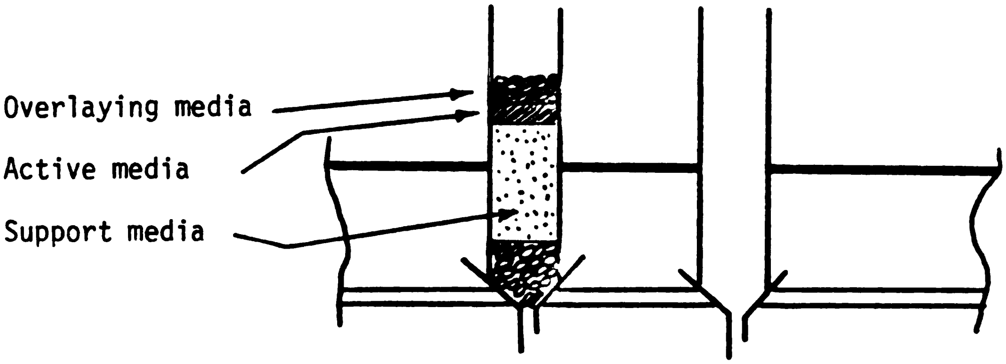

Figure 3.1 Column arrangement.

The columns were set up on wooden frames which could hold up to 32 columns. After cleaning of the columns they were packed with the supporting, active, and overlayer media.

3.1.1 Support Media

The support media is the material underlying the active media. Ideally, it is to hold, yet not interfere with the performance of the active media.

Selection of the support media, therefore, was made with respect to (a) hydraulic considerations, (b) economical reasons, and (c) inertness with respect to the elements under this study. The base of each column was filled with 6 glass raschig rings of 4 milimeter (mm) diameter purchased from Fisher Scientific Corporation. The base was then filled with 10 cm^3 (content of one 10 ml test tube) of each of 5, 4, and 3 mm solid glass beads also purchased from Fisher Scientific Corporation. Glass was used because the preliminary investigations indicated that the adsorption of zinc and cadmium by glass was negligible.

Silica sand of 99.9% purity and 4011 micron mesh was used for the subsoil make-up. Sand was purchased from Wedron, Illinois and labeled as being "thoroughly washed, bone dry, accurately graded." The volume of the sand placed in each column was 250 cm^3. This volume has an average air dried weight of 398 grams. It yielded a total depth of about 13 cm. The underlayer of glass beads was wetted with about 10 cm^3 of distilled water prior to placing the sand. This was necessary to wet the first sand grains and thus cause the sand particles to hold each other by the surface tension and other interfacial forces and, as a result, prevent the dry sand from penetrating into the glass bead phase.

The sand layer was immediately saturated with distilled water by applying from the top. The saturation of the sand was determined considering soil physics principles and visual observations (i.e., addition of each drop resulted in release of one drop). Soil has a capability to retain water against the gravitational force of leaching. The matric potential (suction or tension) also contributes to the holding of the water by the soil. This is explained as wetting front movement in classical soil physics.[3]

The entire bed was washed with distilled, deionized water a few times each day, for a week. The wash water was discarded. The bed was deaerated by virtually fluidizing it during the washings by deep injection of distilled water. It was determined that, on the average, 105 cm^3 of water was needed to saturate the dry sand (as received) after which each drop of water that was added caused one drop to leach out of the system.

3.1.2 Active Media

Organic matter and clay were used in construction of a synthetic soil in the adsorption columns. The clay was a kaolinite and the three organic compounds selected were tryptophane, dextrose (also known as D-glucose), and cellulose.

3.1.2.1 Selection of Clay

Selection of a kaolinitic clay over the other types was made based on the following: (a) kaolinitic clays are 1:1 mineral (one octahydra, one tetrahydron) as opposed to montmorilonitics and illitics (hydrous mica) clays that are 2:1 minerals. This arrangement does not allow the soil to swell and, thus, limit the drainage of the applied solution; (b) kaolinites, in general, are coarser than the montmorillonites and the illites and, thus, are more favorable for drainage; (c) kaolinitic clays are the predominant clay form in humid areas, therefore, the results of research using kaolinite might prove locally applicable whereas the others would not; and (d) the CEC of the kaolinite is usually around 5-15 me/100 g. This is much less than the values reported for the other forms of clay. This is because the cation exchange sites, in kaolinite, are the broken edges as opposed to the amorphus substitution sites found in montmorillonite.[45] With a limited amount of time available, therefore, it was felt that it would be convenient to saturate (exhaust) this soil without a need to choose unreasonably high cationic concentrations.

The clay was obtained from Western Michigan University and has the following properties, Table 3.1 (see Appendix A for more information on the clay).

3.1.2.2 Selection of Organics

Three organic compounds that are commonly found in wastewater and wastewater sludge were selected. The selections were made with

Table 3.1 Properties of Clay Used in the Experiment (Average Values)

Clay	pH	CEC
Kaolinite	5.8	4.9 me/100 g

respect to the information reported in the previous chapter. The organics chosen were those that also are found in soil. These were cellulose, glucose, and an amino acid, tryptophane. These organics are known to differ by their removal points in a wastewater treatment plant (as discussed in the introduction) and thus represent the entire plant operation. The tryptophane and dextrose were ACS reagent grade obtained from Eastman, and Fisher Scientific Corporation, respectively, and were used as received.

The cellulose sheets were obtained from Western Michigan University. The fibers were prepared by shredding the sheets to about 5 cm^2 sizes, soaking them in distilled water for about one hour, and then dispersing in water in small aliquots, using a blender. The cellulose was then freeze dried at 38° C, 65 micron mercury vacuum pressure, and 2% moisture content for 72 hours. The freeze dried fibers were finally dispersed in air using the blender.

Throughout this work the clay, tryptophane, D-glucose, and cellulose are denoted as C, T, G, and Cel, respectively. Some properties of the organic compounds used in this work may be found in Appendix A.

3.1.2.3 Selection of Mix Ratio

The quantities of the above substances that were used in each column are shown in Table 3.2. Selection of the mixing ratio of the organic to clay of 1:20 was to simulate the average condition of 5% organic matter in soil. The amount of the clay (therefore the organic matter) was chosen by trial and error to be able to reach the total exhaustion of the bed adsorption capacity in four months. This was done by assuming the average reported CEC values for kaolinite and organic matter and choosing 40 mg/l cationic solutions to be applied to the system. The reason that the amount of adsorbent in the cadmium cases is half of that in the zinc case is the fact that the miliequivalent weight of the cadmium (112/2 = 56 mg) is almost twice that of zinc (65/2 = 32.5 mg).

Table 3.2 Content of the Adsorption Columns

	Clay (g)	Organic (g)
Zn columns	20.000	1.000
Cd columns	10.000	0.500

3.1.2.4 Method of Mixing

The adsorbing substances (adsorbents) were mixed in a 125 cm^3 erlenmeyer prior to placing in columns. Twenty cubic centimeters of silica sand was added to and mixed with adsorbent in each case to facilitate drainage. The exception being the clay and clay organic columns which were leached with zinc, where 40 cm^3 of the silica sand was added during the mixing. Since the amount of sand used for the support media was relatively large (250 cm^3) in comparison to the amount added to facilitate drainage, the amount of the sand was assumed to be the same in all of the columns.

3.1.3 Desorption Active Media, Sludge

Wastewater sludge was the active media for the desorption test. Both raw and digested sludges were used for this investigation.

3.1.3.1 Selection

The objective of this study required selection of a sludge having a high zinc and cadmium content. A preliminary survey of accessible sewage treatment plants showed that the city of Grand Rapids wastewater treatment plant was a suitable place for sludge sampling.

This is a conventional activated sludge plant of 49 MGD capacity that treats municipal and industrial wastewater conveyed to the plant by a combined sewer. The plant manual (1975-76) expressed high zinc and cadmium concentrations in the raw and the anaerobically digested sludges (Table 3.3). This plant is equipped with a complete environmental engineering laboratory. The values, in Table 3.3, are the monthly averages or the values that are reported for April 1976, whichever is applicable.

The high zinc and cadmium content of these sludges is due to the contributions from the numerous metal plating shops in the city.

Table 3.3 Average Zn and Cd Concentration in Sludge for the City of Grand Rapids, Michigan[48]

Plant Product	Zinc	Cadmium	Unit
Raw inflow[a]	493	36.8	g/l
Final effluent	250	36.8	g/l
Primary sludge	3.22	NA	mg/g dry
Digested sludge	5.35	NA	mg/g dry

[a] This is not a plant product but the input.

3.1.3.2 Sampling and Characteristics

The raw and anaerobically treated sludges were obtained on Friday, April 22, 1977. Twenty liters of each of the sludges were placed in plastic containers and carried to East Lansing where they were refrigerated until use. The samples were grab samples.

The properties of sludges shown in Table 3.4 were determined in duplicate, using the procedures described in the 14th edition of Standard Methods for the Examination of Water and Wastewater[49] unless otherwise stated.

Table 3.4 Properties of the Sludges

Type of Sludge	pH	TS %	TVS %	Ash Content %
Raw	6.25	5.5	3.2	2.3
Digested	7.2	3.2	1.66	1.53

The initial concentration of zinc and cadmium in sludge were found by the digestion technique (see Appendix B) followed by measurement with an atomic Adsorption Unit (see Appendix C). The metal content of the sludges is shown in Table 3.5.

Table 3.5 Metal Content of the Sludges, mg/g dry

Sludge	Zinc	Cadmium
Raw	6.763	0.029
Digested	5.055	0.014

3.1.3.3. Preparation and Placement

The volume of the sludges that were added to the desorption* columns were chosen to satisfy a field practice condition of 22.45 dry tons/hectare (10 dry tons/acre). The volumes were computed to be 83 cm^3 and 143 cm^3 of the raw and the anaerobically digested sludges, respectively (see Appendix D for detailed calculations). They were added to the columns where they were mechanically mixed with an additional 100 cm^3 of sand and 5 cm^3 microdiameter glass beads to facilitate drainage.

The total dry sludge, zinc and cadmium content of each column is shown in Table 3.6 (see Appendix E for detailed calculations).

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*Desorption, as is used in this work, includes any process that results in the release of heavy metals, i.e., decomposition, solublization, . . .

Table 3.6 Total Zinc and Cadmium in Sludge Columns

Type of Sludge	Sludge Used per Column ml	Dry Content g	Total Zn mg	Total Cd mg
Raw	83	4.565	30.873	0.132
Digested	142	4.544	22.970	0.064

3.1.4 Control Columns

Besides the columns mentioned above, sand columns with no active media were constructed to be subjected to the same hydraulic and chemical regime as the adsorption or desorption columns. This was to detect and, therefore, take into account, any interferences by the support media.

3.1.5 Overlayer Media

Fifteen cubic centimeter each of 5 and 4 mm solid glass beads followed by 10 cm^3 of 3 mm beads were placed on top of the active media to facilitate the distribution of the flow over the entire soil surface area. They, also, were necessary to prevent local soil distrubances during the application of the liquid from some 20 cm height. In the same sense the existence of the glass beads did reduce the velocity of passage of the fluid through the media, by defusing the impact forces, thus reducing the Reynold's number. This increased the likelihood of having a laminar flow through the top portion of the active media.

3.2 Soil Adsorption

3.2.1 Selection of Adsorbate

Zinc and cadmium are known to have similar chemical properties. They are found in the same ore and are readily exchangeable in chemical reactions. However, zinc is an essential micronutrient while cadmium is one of the major environmental contaminants. Furthermore, replacement of zinc by cadmium in certain enzymes could cause diseases to man.

Zinc deficiency in the plant and crops is common, therefore, a moderate zinc application to crop land, in the form of sludge, may sometimes be beneficial. Cadmium on the other hand is reported to be a toxicant. Acute exposure to cadmium is known to cause erythrocyte destruction, tescular damage, and renal degradation in man. Chronic exposure, however, may cause respiratory disorder, anemia, osteomalcia, and hypertensive heart disease.[50]

The source of zinc in wastewater or wastewater sludge is from human excretion and industry. Many industries, such as metal and food industries, are known to use zinc or zinc compounds in their operation. Cadmium, on the other hand, is only known to be used in the metal finishing industries.

Due to the significance of these two heavy metals, they were chosen for this study. It was decided to use a cationic concentration of 40 mg/l. This level of concentration was necessary to be able to detect the changes in the concentration due to the adsorption without sample pretreatment to raise the concentration to detectable levels.

They may appear to be high; however, under the existing time and budget limitations no other reasonable alternative appeared to be available.

3.2.2 Preparation of Adsorbate

Solutions of 40 mg/l of zinc and cadmium were made up from the nitrate salt of these elements, using ACS reagent grade chemicals purchased from Fisher Scientific Corporation and distilled water. The conductivity of the distilled water was about 3 ± 1 μMHO/cm. The nitrate salts used were $Zn(NO_3)_2 \cdot 6H_2O$, and $Cd(NO_3)_2 \cdot 4H_2O$. Other properties of these compounds, as obtained from their manufacturer, are shown in Appendix A.

3.2.3 Method of Application and Sampling

Field and flooding conditions of the liquid application to the land were simulated. The liquid applications to the columns were made 3 days apart in the field condition studies while the flow was continuous in the flooding condition.

3.2.3.1 Field Condition

The field condition was defined in this work as the application of the liquid to soil (adsorption columns) at a rate comparable to that of wastewater spray irrigation.

It was intended originally to simulate a spray irrigation practice for the field condition studies. However, any sprayer for this purpose had to be made of an inert substance (preferably glass) in order to eliminate any possible interferences. This was technically hard to manufacture and economically difficult to justify. It was then decided to manually apply the solutions to the columns.

Approximatly 10 ml aliquots of the solutions were poured into a testtube which was subsequently applied over the entire surface area of each column by a rotating motion. The existence of the overlayer of glass beads (see Sec. 3.1.4) helped in the distribution of the flow over the entire area of the column. The operator had to repeat the process for a total of seven times. Having a total of 102 columns under the field condition investigation, the time necessary to finish one round of the liquid application varied between 20 and 30 minutes. The total volume of the liquid added was 65 cm^3. This volume was applied to the columns over a period of 2.5 to 4 hours.

Pouring of 10 cm^3 liquid into the columns will, mathematically, indicate an instant hydraulic loading of:

$$(10\ \text{cm}^3)/(2\cdot 2.54)^2(\pi/4)\ \text{cm}^2 = 0.49\ \text{cm}.$$

However, it was observed that the hydraulic head varied between zero (i.e., the liquid immediately entered the media) in the control, G and T columns to an accumulation of 3 cm in a few of the clay and clay-organic columns. It also was observed that the leaching process was completed in all of the columns no later than six hours after the start of the liquid application. The leachates were collected in 70 cm^3 glass bottles.

3.2.3.2 Flooding Condition

The flooding condition as referred to in this work means the continuous application of liquid to the adsorption media.

Flooding condition experiments were performed under one of the following arbitrarily adopted hydraulic conditions: (a) 5 cm of hydraulic head at all times; or (b) application of 0.12 l/cm^2-hr (0.2 gal/in^2-hr), where "a" could not be satisfied. The choice of the hydraulic condition was dictated by the type of active media in the columns. The "a" condition worked for the clay and clay•organic columns, and the "b" condition was used for the blank and the organic columns.

Three milliliter samples of the leachates were collected (see Tables G.2 to G.9 in Appendix G for time intervals) during the flooding and were tested for their metal concentrations. In the flooding experiments with the clay and the clay•organic columns, the test was stopped after the leachate concentration exceeded 95% of the applied concentration. This was necessary due to time considerations. This method proved to be justified based on the linearity observed for the last portion of the plotted data of log cumulative adsorption versus the cumulative cation applied.

The laboratory set-up of the flooding condition experiments is shown in Figure 3.2. A 2,000 cm^3 separatory funnel (C) was used as a reservoir. The stop cock (A) was adjusted to maintain the desired hydraulic condition (see Section 3.2.3.2). Reservoir (B) was a 1,000 cm^3 volumetric flask and was filled with the cationic solution

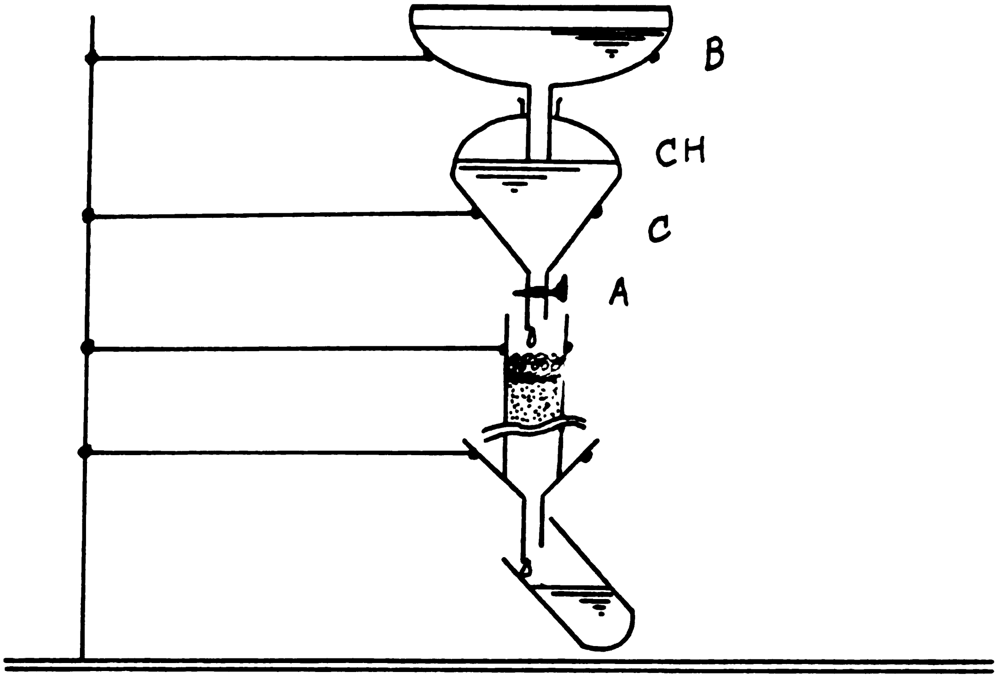

Figure 3.2 Laboratory set-up for flooding tests.

and placed as shown. A constant head (CH) was then maintained. This was necessary to produce a constant flow rate to the testing columns. It was observed that the small variations in the positions of CH did not affect the flow rate. These small variations inevitably occurred when reservoir (B) was replaced.

3.3 Sludge Desorption

Microbial activity in the sludge columns was expected to decompose the organic matter and release their heavy metal content. In order to investigate this behavior there was a need for a liquid carrier to leach the released heavy metals out of the sludge columns.

3.3.1 Selection of Leaching Solution

Simulated rain water was chosen to be the leaching solution. This selection was due to the fact that rain is naturally applied to land. Furthermore, the unique properties of the rain in the northeastern United States made it important to study.

Likens[51] reported that the precipitation falling in the northeastern United States is acidic with a pH ranging from 5.0 to 6.0 in 1966 for Michigan. This value dropped to about 4.5 in 1973. He indicated that sulfuric and nitric acids are the major sources of acidity in precipitation. The average concentration of these acids in precipitation collected at Ithaca, New York, being 4.4 and 5.1 mg/l for the nitric and sulfuric acids, respectively. In comparison, the equilibrium concentration of carbonic acid was reported to be 0.62 mg/l.

Nordel[52] investigated the chemical composition of precipitation in England. He reported, among other things, that the hardness of rain water varied between 3 and 43 mg/l as $CaCO_3$.

3.3.2 Preparation of Leaching Solution

Simulated rain water was made up using distilled water. Tap water, H_2SO_4, HNO_3, and KOH, where necessary, were used to adjust the hardness and the pH of the solutions. Selection of the above acids was made based on the reported values for the NO_3^- and $SO_4^=$ anions in rain water.[52] However, the total amount of the acid required to adjust the pH was minute, such that it was about 0.1 ml for 15 liters of distilled water.

The hardness and pH were adjusted to 20 mg/l as $CaCO_3$ and 5.4, respectively. Method No. 309B of the 14th edition of Standard Methods[49] was used for the hardness measurements.

3.3.3 Method of Application and Sampling

3.3.3.1 Field Condition

The sludge columns were leached with simulated rain water for 4.5 months. This period started in early May and went on until mid-September. The experiment was stopped when the concentration of zinc in the leachates decreased to low levels and the result indicated that the major portion of the zinc in the columns was leached out.

The sludges were leached at 3 day intervals with 70 cm^3 of the simulated rain water. The leachates were collected in glass bottles and analyzed for their zinc and cadmium content and for conductivity and pH. The method of field condition was similar to what was described in section 3.2.3.1. Observations indicated that the accumulation of the applied liquid in the sludge columns was, on some occasions, as high as 3 cm.

3.3.3.2 Flooding Condition

It was not possible to examine the flooding regime of application of the simulated rain water to the sludge columns because of the very small infiltration rates in these columns.

3.4 Sand Adsorption

The sand used in the supportive media proved to adsorb cations. The following methods, therefore, were adopted to measure the amount of adsorption of zinc and cadmium for the two different hydraulic regimes.

3.4.1 Field Condition

Two sand columns that had already been saturated with the cations (this measurement was performed on the control sand columns after the field condition experiment was stopped) were used. Each was washed with 150 ml of distilled water to replace the cationic solution retained in the columns. They were then leached with 50 ml of 25% by volume H_2SO_4 followed by a volume of distilled water to collect 125 ml of the leachate. The first 60 ml of the leachate, after the addition of the H_2SO_4 solution was discarded based on the assumption that 105 ml of solution saturated the bed. The concentration of the cations was determined and the adsorption by the columns was calculated as follows:

$$\text{Amount Adsorbed (mg)} = \text{Concentration (mg/l)}(125\ \text{ml})(1\ \text{l}/1{,}000\ \text{ml})$$

3.4.2 Flooding

In the flooding condition, the sand column was treated as an independent adsorption column. Therefore, the method used (see Sections 3.2.3.2 and 3.5.2.2) were also used for the sand.

3.5 Data Handling and Analysis

3.5.1 Rejection of Suspected Values

The results obtained for each set of columns were studied. Rejection of a suspected observation took place using the following procedure. R was calculated such that:

$$R = R_1/R_2 \tag{3.1}$$

where, R_1 is the difference between the biggest and the smallest observation, and R_2 is the difference between the biggest and the smallest observation including the suspected value. A value was rejected if $R > 2.8$ and replaced with the mean of the other four values. Using this rejection factor the chance of an extreme value being rejected when it should have been retained is equal or less than 5%.[53]

Using this procedure, a total of 51 observations out of 2,528 taken were rejected. Thus, 2% of the results were discarded as being defective.

3.5.2 Breakthrough Curves

These curves show the change in the leachate concentration versus another parameter such as time, volume, or weight from when the liquid application starts. A typical breakthrough curve is shown in Figure 3.3, where C_o is the initial concentration in the applied solution. The significance of the breakthrough curve is in their usage in rate studies. In this respect the slope of the curve gives an indication of the rate at which leaching proceeds.

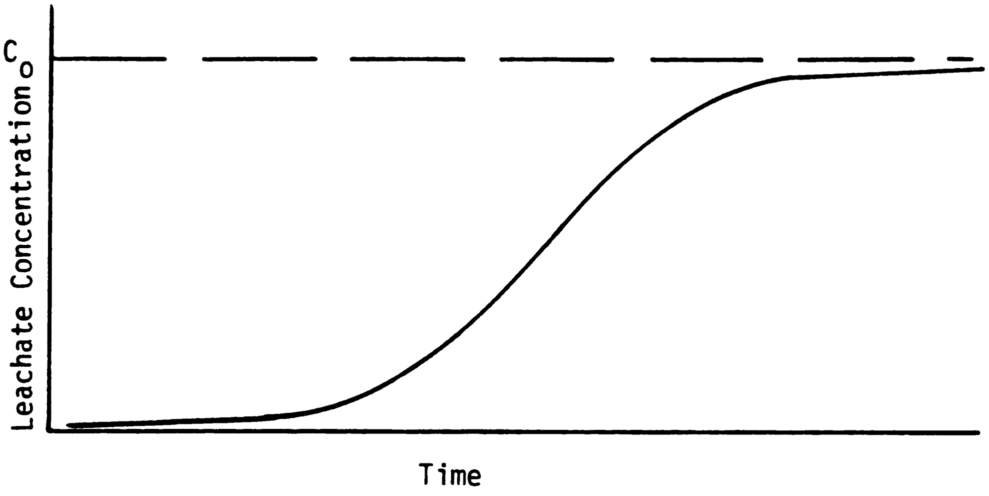

Figure 3.3 Typical breakthrough curve.

3.5.2.1 Field Condition

The leachate concentrations were plotted against the cumulative cation applied. The vertical axis (the leachate concentration) was plotted in logarithmic scale due to the wide spectrum of the results.

3.5.2.2 Flooding Condition

In this hydraulic condition adsorption was calculated with the "traposoidal rule." The amount adsorbed between two consecutive concentration measurements (p and q) when a total of $\forall$ ml was leached out between these two measurements, was calculated.

$$\text{Amount of Adsorption (mg)} = (p + (q - p)/2)(\forall/1{,}000) \qquad (3.2)$$

where, the p and q were measured in mg/l. In this method of calculation the change in concentration with time was assumed to be linear. Therefore, the total calculated adsorption will be close to the actual value.

Figure 3.4 indicates that, using the above procedure, the calculated adsorption is less than the actual value before the center, A, in the diagram and more than that after the center. This difficulty was minimized by sampling at short time intervals.

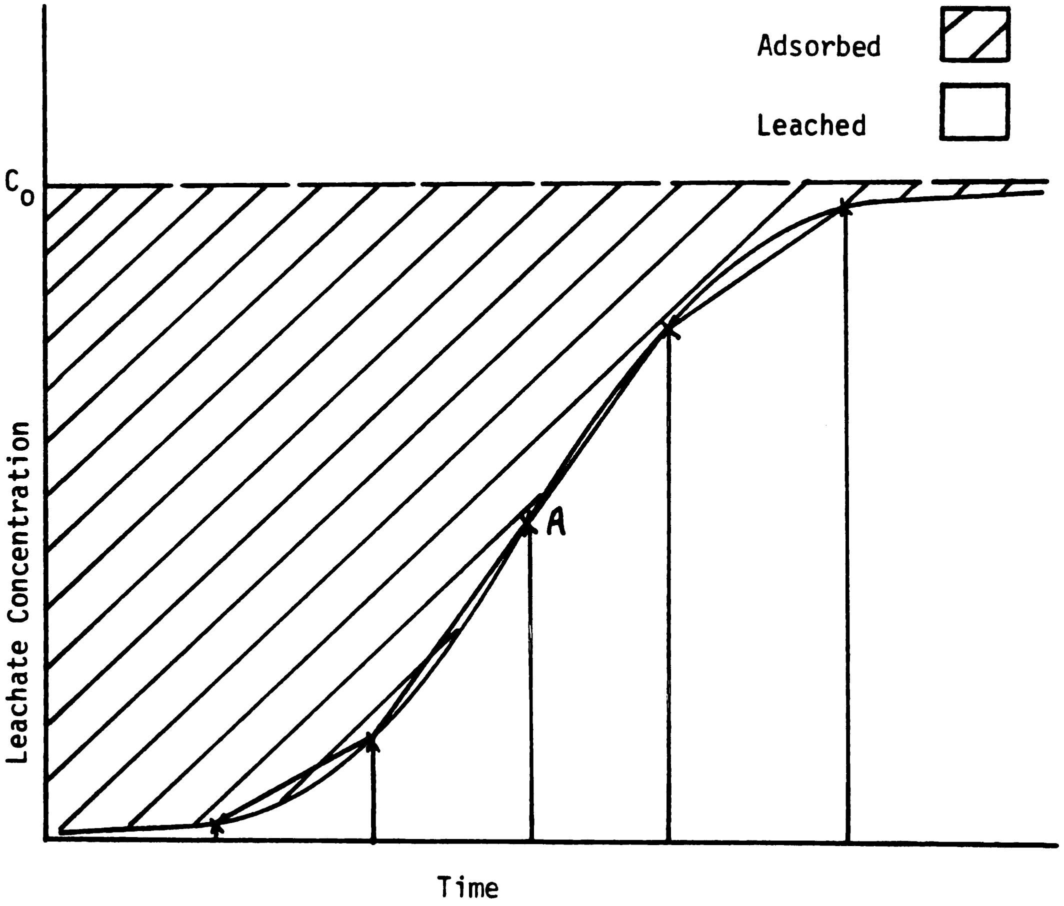

Figure 3.4 Breakthrough curve.

3.5.3 Freundlich Fitting

The well known Freundlich equation has been extensively used in experimental works for testing and interpretation of adsorption data. Other adsorption models have been proposed by different authors to suit their works.[54]

The Freundlich equation is expressed as:

$$X/M = kC^{1/n} \tag{3.3}$$

where, X = me of solute adsorbed; M = grams adsorbent; C = equilibrium concentration of solute; k and n are constants. This equation also may be written as:

$$\log (X/M) = \log k + 1/n \log C \tag{3.4}$$

Equation 3.4 represents a straight line when the values of X/M and C are plotted on a log-log system of coordinates. In other words, if the data represent a straight line on a log-log paper they may be fit to the Freundlich equation.

From the background information gathered in this work, it appears that adsorption is the likeliest reaction to be expected. Therefore the fit of the data, in each case, to the Freundlich model was examined as a means of showing that adsorption could be an explanation of the pheonomena which were occurring.

The adsorption process is a dynamic process. Therefore, a true equilibrium will not be attained until the end of reaction. Nevertheless, intermediate equilibria can be assumed if the aliquots of the product (leachate), resulting from the interaction of adsorbate and adsorbent, are separated from the system. This must be such that no further reaction occurs in the sample. Indeed, this is the way the models are developed and that any adsorption equation or isotherm may be utilized. The equilibrium concentration, C, in the Freundlich equation can be determined by analyzing samples taken at different time intervals.

In the field condition, the equilibrium concentrations, C, were normalized by dividing them by the blank values. This was necessary due to minor changes in concentration of the applied solution. The deviation from the exact concentration of 40 mg/l was due to errors of measurement and tendency of the nitrate salts of zinc and cadmium to adsorb water.

Using a regression analysis by the least squares technique, the correlation coefficient of the fit of the data to the line given by equation 3.4 was determined.

Since the adsorption and desorption mechanisms are, in fact, the same phenomenon in opposite directions, the equation for one should also suit the other. Since the Freundlich equation was originally developed for the adsorption process, it was necessary to adopt the following logic: that a hypothetical adsorption of zinc to the sludge occurred; and that it started at the end of the experiment and proceeded with the time unit having negative signs. Therefore, the very last value that was reported for the desorption becomes the first value, the one before the last value for the desorption becomes the second value and so on.

3.5.4 Determination of Kinetics

Kinetic studies are necessary to measure the rate at which a reaction proceeds toward completion. The rate of adsorption at each point of the experiment may be found by the slope of the adsorption curve at that point. Modeling of the data, therefore, greatly simplifies kinetic studies. This is because the rate studies will be reduced to the determination of the first derivative of the model, $\frac{dy}{dx}$. Then applying the coordinates of the point of interest to find the slope (if y' is not a constant).

$$\text{Slope} = \left.\frac{dy}{dx}\right|_{x,y}$$

The models can be used for predictions. They therefore reduce the amount of time spent in future studies of the same type or in actual practice.

3.5.5 Modeling of Data

For the rate analysis, an empirical curve-fitting procedure was utilized. Breakthrough curves similar to Figure 3.5 were obtained where the slope of the curve at each point, $\frac{dc}{dC}$, represents the rate of change in the concentration with respect to the cumulative cation applied (time and cumulative cation applied can be used interchangeably when the rate of application and the concentration of the cationic solution is known).

A curve fitting procedure, using the least square method, was adopted using a programmable HP 96 desk calculator. Different points of the empirically drawn curve (data points) were supplied and the parameter of the suitable model along with the coefficient of determination, r^2, for the fit were found.

CHAPTER 4

RESULTS AND CONCLUSION

4.1 Assumptions

The following assumptions were made for interpretation of the data obtained in this research:

1. That the diameter of the glass columns was large enough to assume a negligible wall effect on the outcoming solution;
2. That the applied liquid passed through the media as a complete plug flow;
3. That all of the active media was utilized in the adsorption or the desorption process;
4. That no channeling of the applied liquid occurred through the media of the column; and
5. That the support media was inert with respect to incoming cationic solutions.

4.2 Problems and Remedies

During the experiment a few major problems occurred which are described below.

4.2.1 Release of Organics

The results of a total carbon analysis of the leachates revealed that a major portion of the G and T leached out of the adsorbing columns. The amount of each organic which remained during the course of the experiment is shown in Table 4.1 (see Appendix E for details).

Table 4.1 Organics Remaining in the Adsorption Columns, mg

Columns	G	CG	T[a]	GT	Cel	C Cel
Zn column	15	41	17	102	1,000	1,000
Cd column	11	30	NA	8	500	500

[a] NA = Not available. Result of the mass balance was a negative number.

No measureable release of cellulose could be detected during the course of the experiment. Visual observation revealed no decomposition of this substance.

The releases most probably occurred as the result of solubilization. Decomposition of glucose and tryptophane was not considered as a possible explanation for their release, the reason being (a) release of the G occurred very fast; (b) lack of the necessary micro and macronutrients (i.e., P, N, Ca, and Mg) for any growth of microorganisms in the columns; (c) the toxic environment of the columns due to zinc or cadmium would limit microbial growth. This conclusion is substantiated in part by the fact that no measureable decomposition was detected in the cellulose columns during 4.5 months of the field condition portion of this experiment. The literature supports this reasoning, though not totally.

Bond et al.[55] indicated that metals in organic wastes applied to soil can be toxic to soil microorganisms and can reduce their ability to decompose organic substances. With respect to the lack of cellulose degradation, Carpenter and Owens[56] indicate that one milligram (mg) of nitrogen must be present to degrade 40 to 50 mg of cellulose. Since the soil system was prepared without any nitrogen, one would expect the cellulose degradation to be highly limited.

4.2.2 Adsorption by Support Media

The sand or impurities within the "99.9% pure"* silica sand which was used to construct the column's base were found to have adsorbing sites. In spite of washing for a week prior to use and in spite of the negative findings in the preliminary investigations, the sand adsorbed cations and tryptophane. Adsorptions of Zn and Cd by the sand is shown in Table 4.2.

Table 4.2 Adsorption of Cations by the Support Media, mg/g[a]

	Zn	Cd
Sand	0.018	0.011

[a] Average of two values.

The method of measurement was described in Section 3.4. A material balance method was used to evaluate the sand behavior in the flooding condition experiments.

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*As reported by the supplier.

Occupation of the sand adsorbing sites by tryptophane caused a reduction in the adsorption of Zn and Cd by the sand in the tryptophane columns and, perhaps, the C-T columns. Therefore, a negative adsorption of Zn and Cd was recorded for the T columns (see Table 4.3). This is because the leachates from the sand columns were treated as blanks and were used for computations of the net adsorption in the other columns.

4.2.3 Algal Growth

A minute growth of algae was observed in the sludge columns. Visual inspection indicated that the growth was only in that portion of the columns which was exposed to the laboratory fluorescent lights which were left on for about a month for security reasons. After this growth was detected the lights were turned off and were used only when necessary. Observations indicated that no further growth of algae could be seen. However, the original growth did not disappear. The effect of the algal growth on the metal release by the sludge columns was assumed to be negligible.

4.2.4 Equilibrium Investigation

As was described before, the field condition practice was conducted at 3 day intervals. However, the difference between two consecutive applications of the liquid was raised to 4 days on the third, then again on the thirteenth, fourteenth, and fifteenth application. This was done to investigate if any variation from the 3 days' results might occur. It was found that the data of both the adsorption and the descorption experiments did not indicate any change with respect to the 3 day results (see the figures on the adsorption, also the desorption--field condition, in this chapter). This implies that the equilibrium between the adsorbent or the sludge (desorbent) and their immediate solution (the media solution) maintained at or before 3 days from each solution application. This finding bears a weight later in the analysis of the data.

4.3 Adsorption

4.3.1 Field Condition

Results of the Zn and Cd adsorption by the different adsorbents are shown in Tables 4.3 and 4.4.* They are also shown in Figures 4.1 and 4.2. They indicate that all three of the organic compounds, the kaolinite, and the kaolinite • organic mixture had the ability to adsorb Zn and Cd (see Appendix G for the data).

Leaching of the glucose (G) and tryptophane (T) from the respective columns and the interaction of the T with the sand, greatly reduces the significance of the values that are reported for the G and T columns. Nevertheless, some adsorption of Zn and Cd by these substances did occur.

---

*Sample calculations for all of the tables are shown in Appendix F.

Table 4.3 Total Adsorption by Adsorbent--Field Condition (Values Are All in mg)[a]

Adsorbent Cation	G	T[b]	Cel	C	CG[c]	CT[c]	C Cel[c]
Zn	0.71	0	4.98	45.78	41.83	50.81	46.53
Cd	0.12	0	3.68	32.68	31.43	33.68	33.15

[a] The total cation applied was 92.67 and 93.95 mg for Zn and Cd columns, respectively.

[b] The apparent values were -3.03 and -0.25 mg for Zn and Cd, respectively.

[c] CG = clay • glucose; CT = clay • tryptophane; C Cel = clay • cellulose.

Table 4.4 Total Adsorption by Adsorbent and Sand--Field Condition (Values Are All in mg)

Adsorbent Cation	G	T	Cel	C	CG	CT	C Cel
Zn	8.08	4.34	12.31	53.11	49.16	58.14	53.86
Cd	4.52	4.15	8.08	37.08	35.83	38.08	37.55

4.3.2 Statistical Analysis

To determine whether the results shown in Table 4.3 for CG, CT, and C Cel were different from the values reported for the C columns, the following statistical analyses were performed: F test for differences in standard deviation and student t for differences in the means. Details are given in Appendix H.

The standard deviation of the reported results were found using the data obtained for each of five columns that were constructed for each specific adsorbent. This was done utilizing the computer program STAT 1 (see Appendix H).

The F test indicated that the standard deviations were not significantly different in the Cd cases. They were found to be significantly different from each other (clay value versus the others) in the Zn cases. The results of the test of differences of the means indicates that the adsorption values reported for the CG, CT, and C Cel are different from the values reported for the C columns with probabilities more than 99%, 99%, and 50% for Zn and 95%, 90%, and 60% for Cd columns, respectively (see Appendix H for the details). This implies that the adsorption of cations by the CG and CT columns were significantly different from those of the C columns.

The difference between the adsorption values of C and C Cel columns will be discussed further in Section 4.3.4.2.

4.3.3 Organic Adsorption

4.3.3.1 Cellulose

Figures 4.1 and 4.2 reveal that adsorption of the respective cation by cellulose occurred. This adsorption increased with time over a period of three months. The total adsorption of the cations by the cellulose are calculated to be:

[4.98 mg/(65/2)mg/me](1.0/1 g) = 0.153 me/g for Zn;

[3.68 mg/(127/2)mg/me2](1.0/0.5 g) = 0.116 me/g for Cd.

The difference between the two adsorption capacities is 27%.

The abrupt increase in adsorption for the Zn in the cellulose columns as seen in the disrupted portions of Figure 4.1 cannot be explained. Since this phenomenon occurred between two consecutive adsorbate applications and since this was not repeated for any other columns studied under this experiment, all that may be concluded is that unpredictable, unknown change or vandalism* caused the change. Nevertheless, if the first portion of the adsorption curve is continued parallel to the last portion of the curve, the ultimate adsorption of the zinc by the cellulose columns would be 3.7 mg which is

[3.7 mg/(65/2) mg/me](1.0/1 g) = 0.114 me/g

which would make it less than 2% different from the value obtained for cadmium adsorption by cellulose.

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*Some signs of trespassing were noted over the course of the experiment but no sign of disturbance were noted for these columns.

Figure 4.1 Adsorption of Zn by selected organics.

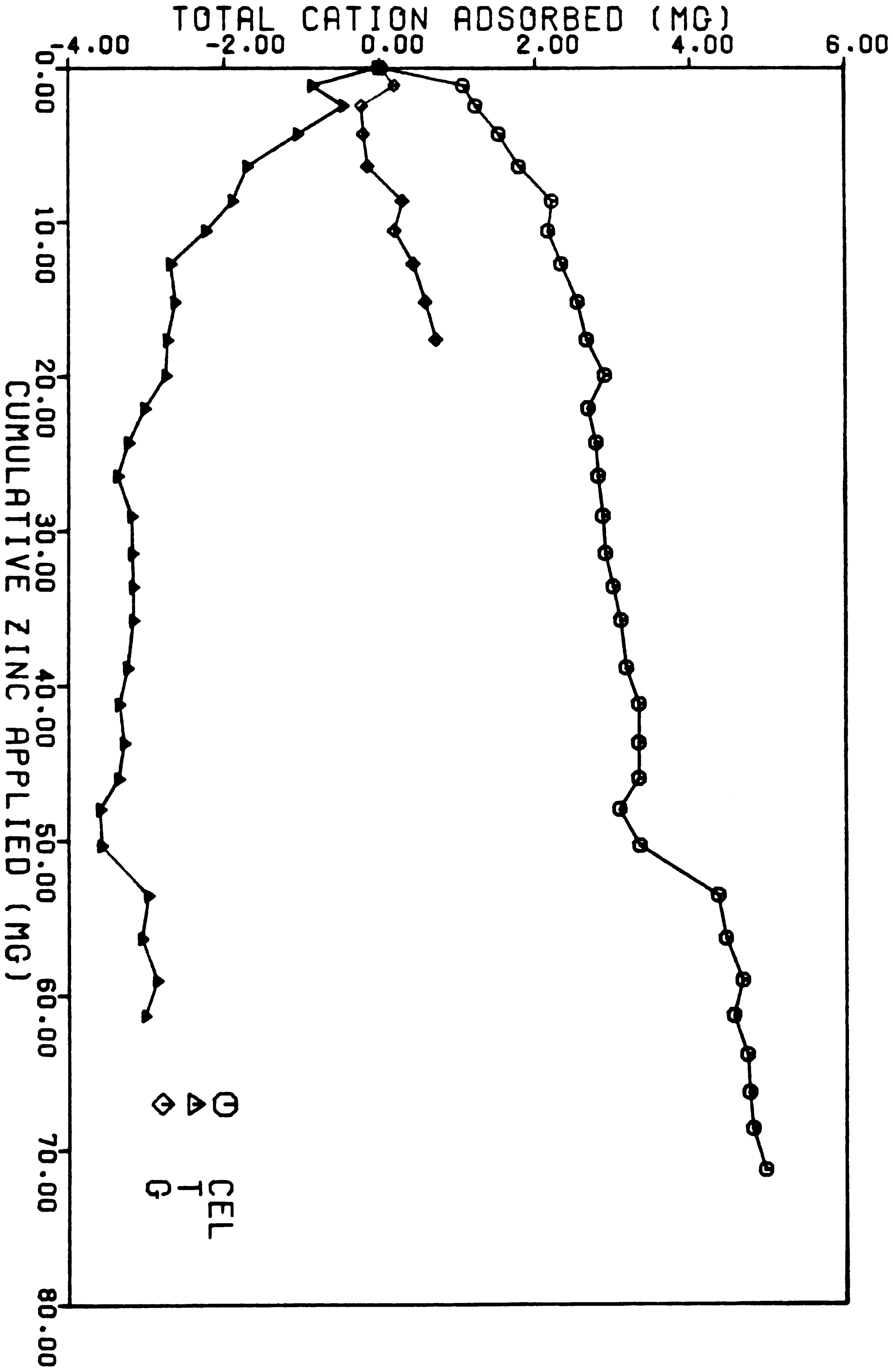
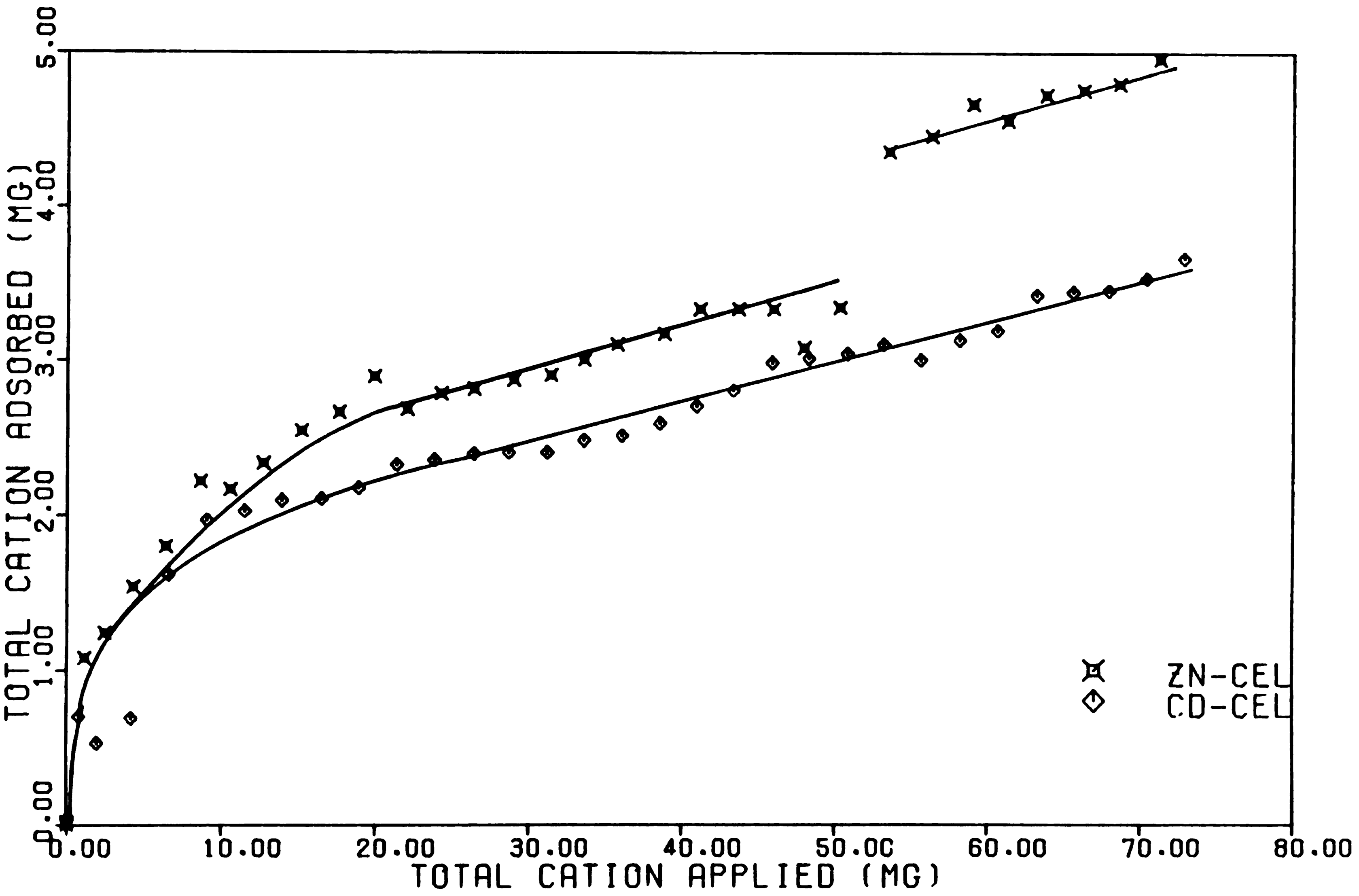
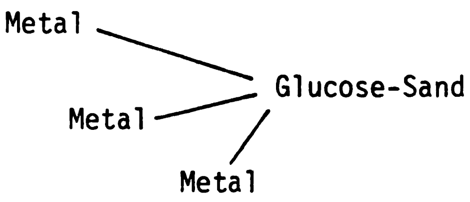

TOTAL CATION ADSORBED (MG)
-4.00
-2.00
0.00
2.00
4.00
6.00
CUMULATIVE ZINC APPLIED (MG)
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
CEL
T
G

Figure 4.2 Adsorption of Zn and Cd by cellulose.


5.00
4.00
3.00
2.00
1.00
0.00
TOTAL CATION ADSORBED (MG)
0.00
10.00
20.00
30.00
40.00
50.0C
60.00
70.00
80.00
TOTAL CATION APPLIED (MG)
ZN-CEL
CD-CEL

4.3.3.2 Glucose

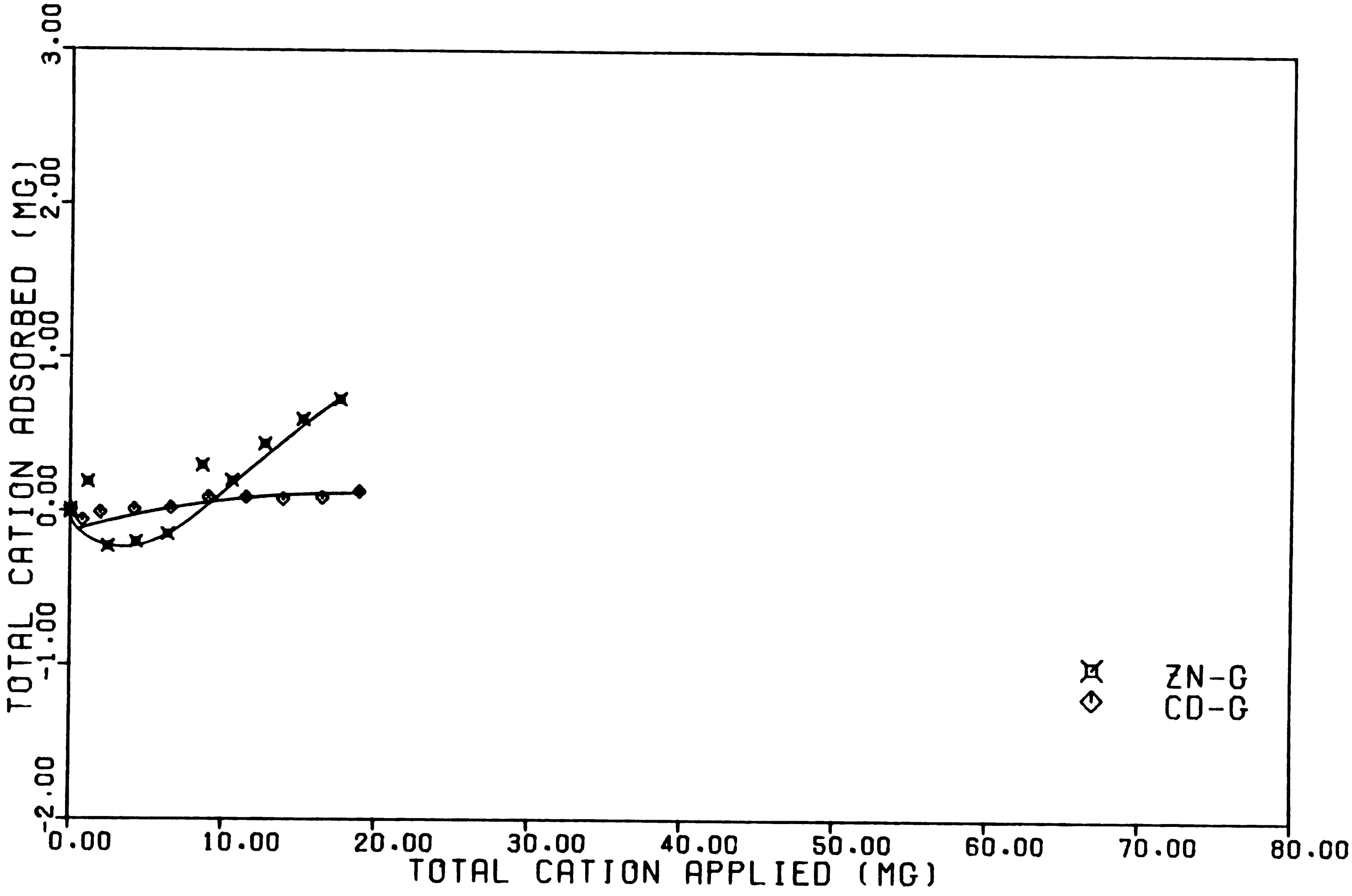
As can be seen in Table 4.1, almost all of the glucose leached out of the adsorption columns. However, based on Figure 4.3, the following conclusions may be drawn cautiously: (1) The initial negative adsorption reported for Zn and Cd suggests a reduction in the ability of the active plus the support media to adsorb. This could be explained by the competitiveness of the leaching active media (i.e., glucose) and the cations for the adsorption sites of the support media. This caused the sites to become unavailable for adsorption of the applied cations. The possession of many potential bond forming sites such as hydroxile or hydrogen as can be seen in the configuration of glucose (see Appendix A) strengthens this theory. (2) The cumulative increase in adsorption after the initial dip may be interpreted as a general adsorption of cation by the free bonds available from the adsorbed glucose, such that it formed a conglomerate such as:



therefore causing extra adsorption to occur. This adsorption would have to be of the bulk type because of the observed lag. This is out of the scope of this work.

Alternatively this might be interpreted as gradual desorption of the organic from the sand adsorption sites due to decomposition or

Figure 4.3 Adsorption of cations by glucose.



TOTAL CATION ADSORBED (MG)
3.00
2.00
1.00
0.00
-1.00
-2.00
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
TOTAL CATION APPLIED (MG)
ZN-G
CD-G

other gradual release. The increase above zero, also, could be due to the small amount of sand that was mixed with the adsorbent as was explained in Section 3.1.2.4.

4.3.3.3 Tryptophane

Section (1) of the glucose explanation would also apply here, Figure 4.4. The bond between the T and sand, however, appears to hold over the period of the experiment. The gradual deviation from zero can be explained by the way tryptophane was released from these columns (see Appendix E). Further explanation of the reaction of the tryptophane and silica sand is beyond the scope of this work.

4.3.4 Adsorption Results

Figures 4.5 and 4.6 show the unit adsorption (mg adsorbed per application) of Zn and Cd by the clay and clay•organic columns. The reduction in the amount of adsorption per application is due to exhaustion of the active media's adsorption capacity. These curves are presented to show the similarity between adsorption patterns for the different adsorbents. They indicate that adsorption starts, then decreases linearly with respect to the total cation applied. Since the cationic dose applied at varying time intervals were the same with small changes in concentration, the total cation applied or time could be used interchangeably. The total adsorption per unit weight of the adsorbents is shown in Table 4.5. These values were obtained with respect to the weight of the remaining organics (G and T) in the adsorption columns as reported in Table 4.1. The total cation mass applied to the clay and

Figure 4.4 Adsorption of cations by tryptophane.

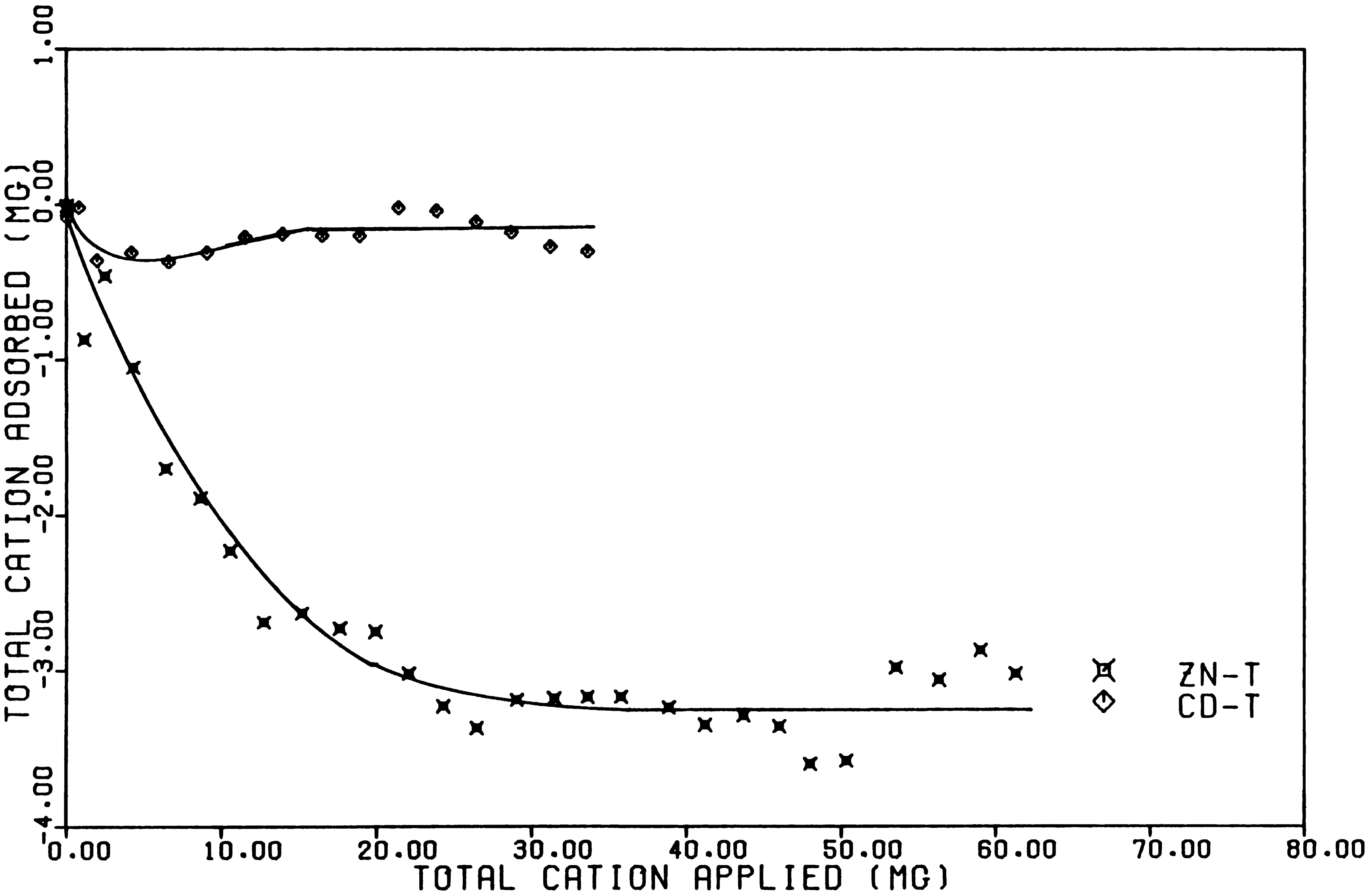

TOTAL CATION ADSORBED (MG)
1.00
0.00
-1.00
-2.00
-3.00
-4.00
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
TOTAL CATION APPLIED (MG)
ZN-T
CD-T

Figure 4.5 Unit adsorption (adsorption per application) of Zn by the clay and the clay•organic columns.

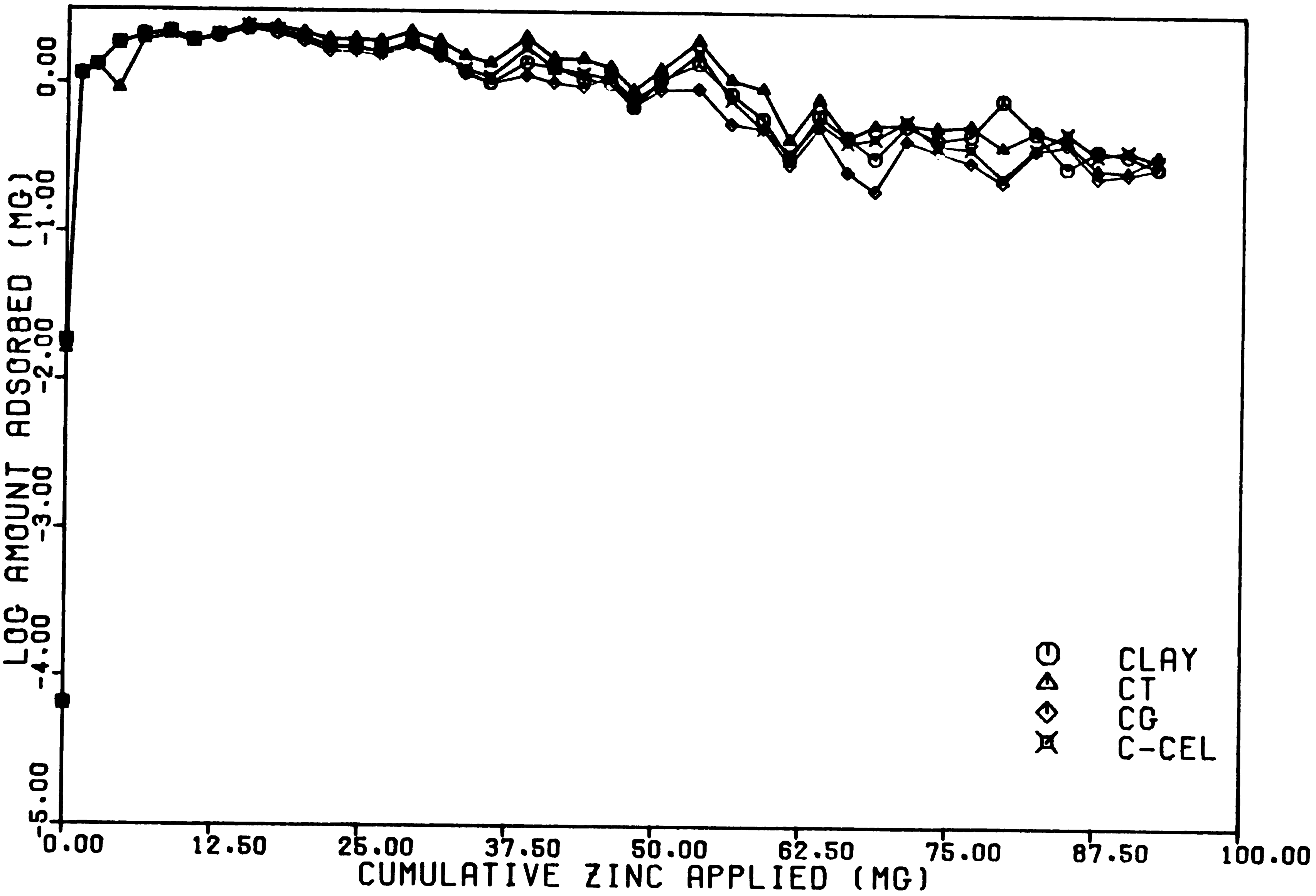

LOG AMOUNT ADSORBED (MG)
0.00
-1.00
-2.00
-3.00
-4.00
-5.00
0.00
12.50
25.00
37.50
50.00
62.50
75.00
87.50
100.00
CUMULATIVE ZINC APPLIED (MG)
CLAY
CT
CG
C-CEL

Figure 4.6 Unit adsorption (adsorption per application) of Cd by the clay and the clay•organic columns.

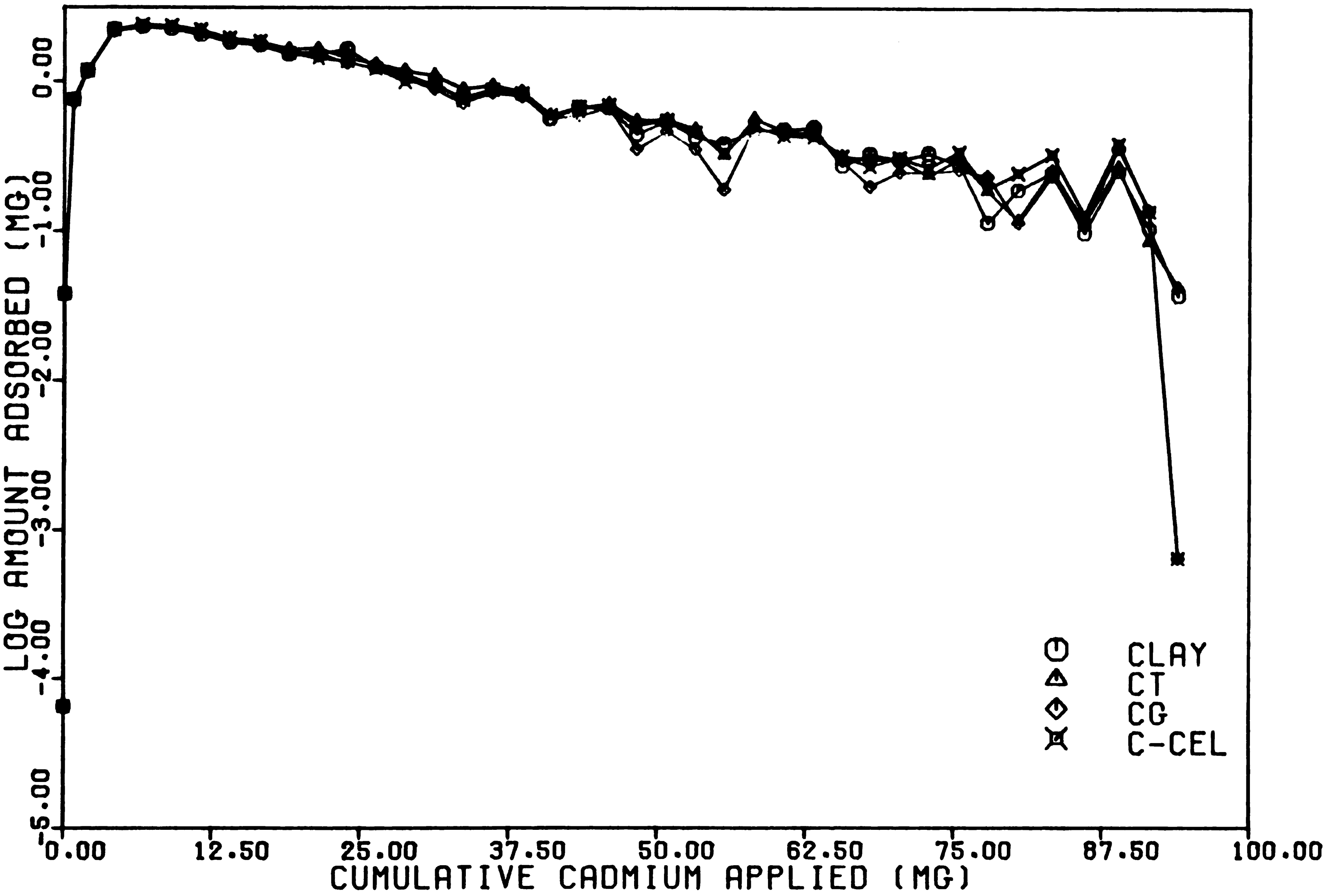

LOG AMOUNT ADSORBED (MG)
0.00
-1.00
-2.00
-3.00
-4.00
-5.00
0.00
12.50
25.00
37.50
50.00
62.50
75.00
87.50
100.00
CUMULATIVE CADMIUM APPLIED (MG)
CLAY
CT
CG
C-CEL

Table 4.5 Adsorption per Unit Weight of Adsorbent (mg/g) (Field Condition)

Adsorbent	G	T	Cel	C	CG	CT	C Cel
Zn	47.30	NA	4.98	2.289^+	2.087^+	2.528^+	2.216^+
Cd	10.91	NA	7.36	3.268^+	3.133^+	3.365^+	3.157^+

clay-organic columns was 92.67 and 93.95 mg for zinc and cadmium, respectively. A total of 17.66, 61.32, and 71.27 mg of Zn was applied to the G, T, and Cel columns while 18.94, 33.62, and 72.86 mg of CD was applied to those columns, respectively. Application of the cationic solution to the adsorption columns was terminated when no appreciable adsorption of the respective cation by the adsorbent was detected.

Table 4.5 indicates that in all cases, other than for glucose, more cadmium than zinc was adsorbed per unit weight of adsorbent. This phenomenon is reversed if the values are converted to milliequivalents per gram, Table 4.6.

Table 4.6 Adsorption per Unit Weight of Adsorbent (me/g) (Field Condition)

Adsorbent	G	T	Cel	C	CG	CT	C Cel
Zn	1.45	NA	0.153	0.070	0.064	0.078	0.068
Cd	0.17	NA	0.116	0.051	0.049	0.053	0.050

The order of adsorption for both of the cations is the same, i.e., G > Cel > CT > C > C Cel > CG. The position of T is undefined due to the leaching problems metioned previously.

Table 4.5 also reveals that in all cases adsorption by the clay • organic mixtures was less than the summation of adsorption by the respective clay and organic alone. This suggests an interaction between the clay and organic such that they occupy each other's adsorption sites which could otherwise be used to adsorb Zn and Cd. We will return to this argument later in Section 4.3.4.2 of this chapter.

Comparison of the data in Table 4.5 and what is reported by Huang[61] indicates that all the values obtained for the clay • organics fall between the values he reported for pH = 5 and pH = 8. His results are summarized in Table 4.7.

Table 4.7 Adsorption of zinc and cadmium by adsorbent, mg/g[61]

	Zn		Cd	
Adsorbent	pH = 5	pH = 8	pH = 5	pH = 8
SiO_2	1.95	12.61	-2.79	5.33
α-Al_2O_3	0.46	13.00	-2.16	15.24
Metapeak	2.00	12.60	-4.44	3.62
Evesboro	1.23	12.50	-2.10	17.78

4.3.4.1 Fitting the Adsorption Equation

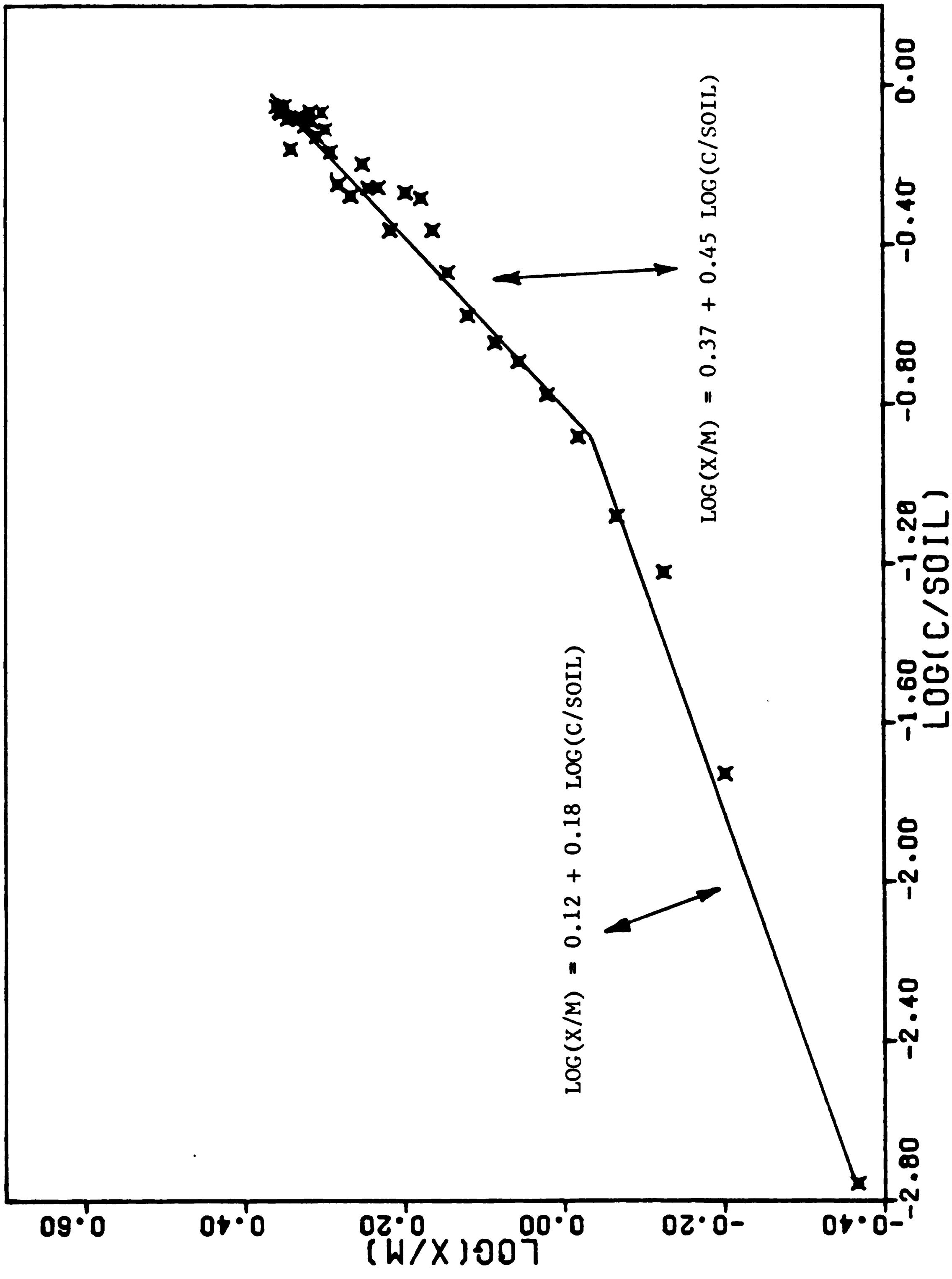
The data were fit to the Freundlich adsorption equation with the computer program FLICH (see Appendix G). The data fit the Freundlich equation very closely. The correlation coefficients are shown in Table 4.8. A typical scattered diagram of the data is shown for the data obtained as the result of the zinc adsorption by the clay in Figure 4.7. The other scatter diagrams of the data are shown in Figures I.1 to I.9 (see Appendix I). In all of these figures the equilibrium concentrations were normalized by dividing them by their respective blank concentrations. This step was necessary to eliminate the effect of variation in the input concentration to the columns. The horizontal axis of the scatter diagrams is therefore described in log (adsorbent/soil) rather than log C (where C is referred to the adsorbent as was described previously).

Table 4.8 Correlation Coefficients for Freundlich Equation Fitting[a]

	Cel	C	CG	CT	C Cel
A. For Zn:					
1st portion	-	0.990 (5)	0.980 (5)	0.460(10)	0.663 (6)
2nd portion	0.504(31)	0.970(29)	0.981(30)	0.978(30)	0.980(29)
B. For Cd:					
1st portion	-	0.990 (5)	0.100 (5)	0.950 (4)	0.985 (5)
2nd portion	0.454(31)	0.978(33)	0.986(35)	0.988(35)	0.979(33)

[a] The numbers in parentheses represent the number of the test data used in the fitting.

Figure 4.7 Freundlich equation fitting for Zn-Clay.


LOG(X/M) = 0.37 + 0.45 LOG(C/SOIL)
LOG(X/M) = 0.12 + 0.18 LOG(C/SOIL)
LOG(C/SOIL)
LOG(X/M)
-2.80
-2.40
-2.00
-1.60
-1.20
-0.80
-0.40
0.00
-0.40
-0.20
0.00
0.20
0.40
0.60

As can be seen in the scatter diagrams, two rather distinct straight lines exist for each plot. This exhibits the existence of two different adsorption bonding energies. This phenomenon has been reported by Ellis[45] for another adsorption isotherm and can be used to interpret this work. The two bond energies in this case being for the actual media and the sand. In each instance the adsorption capacity of the sand (the lower limb of the curve) had to be satisfied before adsorption by the active media could become evident.

The two bonding energies represent two types of adsorption. Existence of these two bonds appears not only in the clay • organic columns but also in the clay columns, and, as will be seen in the desorption studies (Section 4.4.2), it also appears in the sludge columns.

Since in all of the above cases the sand layer was present and since the sand layer was found to be active in adsorption of Zn and Cd (see Section 4.2.2), it is conceivable that one of the two bonds is the result of sand adsorption. This leaves the other to be the result of adsorption (or desorption) of the active media.

It is obvious that in the early stages of the adsorption experiment, a combination of sand and active media adsorption occurred simultaneously. However, the magnitude of the short term sand adsorption (as can be seen in the flooding and desorption experiments) was much greater than the active media alone. Therefore, the sand adsorption bonding overshadows the other, otherwise we should have had only one bonding energy with one straight line for each of the systems of adsorption.

In the field condition the effect of the supporting media was eliminated by comparison with the leachate from the sand alone. Some sand, however, was mixed with active media for drainage purposes as was described in Section 3.1.2.4. This sand is believed to create the extra line. Since the amount of sand was small (see Section 3.1.2.4), the amount of cation required to saturate this phase is small. The lower limbs of the curves always were comprised of a few points.

The exchange capacity of the sand (weight = 398 grams) was lower being 0.018 and 0.011 mg/g (see Table 4.2) for Zn and Cd, respectively. This does not allow the second (upper) limb to be sand adsorption because the total adsorption shown by this limb is much more than the adsorption capacity of the sand (see Section G.2 in Appendix G for an example of the adsorption in each limb).

Comparison of the sand adsorption data in the field and flooding condition (see Section 4.3.6) reveals that they are almost the same. This implies that pore and bulk diffusion do not perform a major role in the adsorption of cations by sand. As a result the adsorption capacity of the sand is expected to be depleted as soon as enough cationic solution is passed through it. Therefore, it is satisfied first.

4.3.4.2 Order of Adsorption

Cumulative adsorption versus the cumulative cations applied to the columns replotted for the portion of the experiment which was determined to be independent of the sand adsorption. The decision on the extent of these regions was made utilizing the information obtained from the fit of the Freundlich equation. The plotted curves are shown in Figures 4.8 and 4.9 . They clearly define the order of adsorption to be CT > C Cel > C > CG. The reason why this order is different from that reported in Section 4.3.4 is that they were reported on the per unit weight basis in that section.

Table 4.9 was constructed for comparison of adsorption behavior assuming that adsorption of organics by clay may be "proven" if the following order exists:

$$\text{Cation Adsorption by Organic} + \text{Adsorption by the Clay} > \text{Adsorption by Clay} \cdot \text{Organic}$$

Table 4.9 Comparison of Actual Clay • Organic and Clay + Organic Columns Adsorption (mg)--Field Condition

	Zn Columns for			Cd Columns for		
Adsorbent	G	T	Cel	G	T	Cel
Clay	45.78	45.78	45,78	32.68	32.68	32.68
Organic	0.71	NA[a]	4.98	0.12	NA[a]	3.68
Clay + organic	46.49	42.75	50.76	32.80	<32.68	36.36
Clay • organic	41.83	50.81	46.53	31.43	33.68	33.15

[a] NA = not available.

Figure 4.8 Release of zinc from the adsorption columns--field condition.

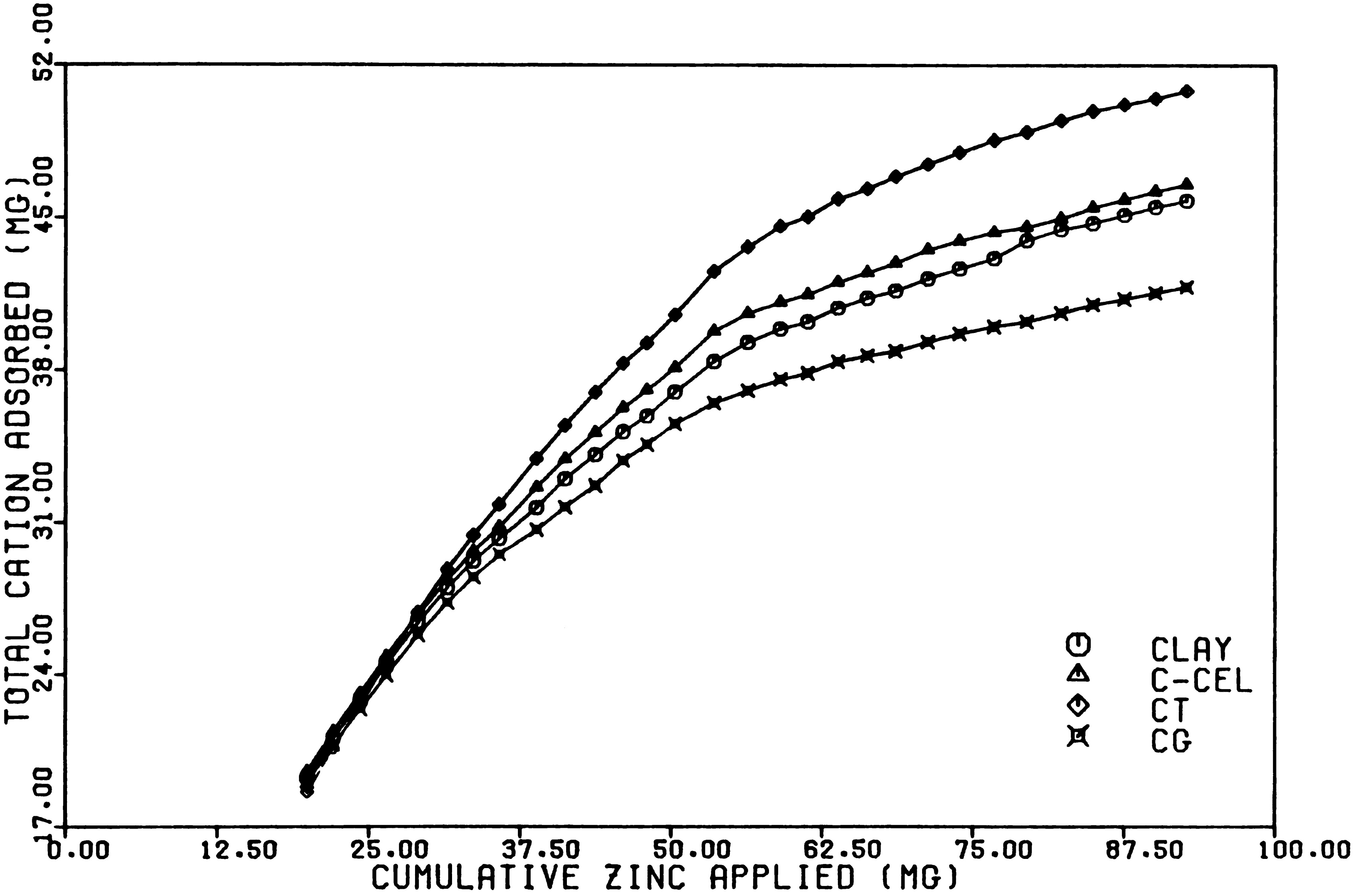
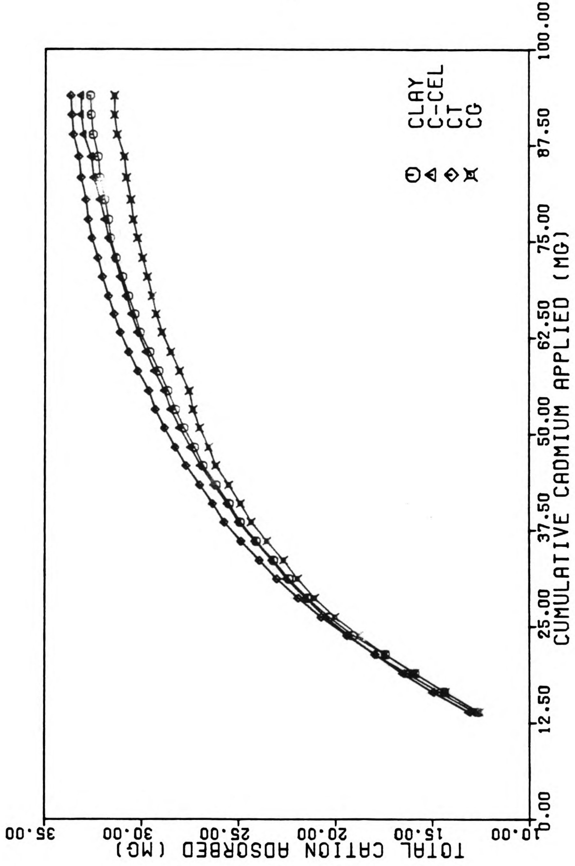

TOTAL CATION ADSORBED (MG)
52.00
45.00
38.00
31.00
24.00
17.00
0.00
12.50
25.00
37.50
50.00
62.50
75.00
87.50
100.00
CUMULATIVE ZINC APPLIED (MG)
CLAY
C-CEL
CT
CG

Figure 4.9 Release of cadmium from the adsorption columns--field condition.


TOTAL CATION ADSORBED (MG)
10.00
15.00
20.00
25.00
30.00
35.00
CUMULATIVE CADMIUM APPLIED (MG)
0.00
12.50
25.00
37.50
50.00
62.50
75.00
87.50
100.00
CLAY
C-CEL
CT
CG

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4.3.4.3 Statistical Analysis

To test the hypothesis that the adsorption results expressed in Table 4.9 for clay + organic were different from the values reported for the clay • organic columns, a statistical analysis was performed. This analysis was similar to what was described in Section 4.3.2 (see Appendix H for details). The results of the test indicated that the adsorption values reported for the clay • organic columns are significantly different from the clay + organic results with probabilities more than 99%. An exception being the CT column subjected to the zinc solution where the probability of the difference is better than 85% (see Appendix H).

4.3.4.4 Conclusions

Based on Table 4.9 and the outcome of the previous statistical analysis, the following conclusions may be drawn:

1. The total adsorption by the CG columns was less than that of the clay columns alone. Therefore, it is hypothesized that the small amount of glucose that remained in the CG column reacted mainly with the clay rather than the cations.
2. The net adsorption of cations by the CT columns was more than the adsorption by the clay alone. This suggests that most of the tryptophane that remained in the CT columns reacted with the cations rather than the clay.
3. The clay and cellulose reacted with each other, therefore occupying each other's adsorption sites. This resulted in

4.3.

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r^2.

a lower adsorption by clay•cellulose in comparison to clay + cellulose.

4.3.4.5 Kinetic Studies

Kinetic studies are necessary to find the speed with which the adsorption and desorption mechanisms proceed. A comparison of these two results would then clarify whether or not, in a system composed of both, the release of cations would be a possibility. In other words, at any particular time, if the speed at which the desorption of a cation occurred was greater than the rate of adsorption of that cation, a danger of escape of the cation to lower strata exists.

4.3.4.6 Modeling

Modeling of the adsorption and desorption curves (Figures 4.8 to 4.11 in the adsorption and 4.14 and 4.15 in the desorption cases) was performed by matching their apparent shape to different classical mathematical models. A trial and error match was made to find the most suitable form among them. The coefficient of determination of the fit, r^2 (see Tables 4.10 and 4.11) was used to judge the suitability of the models. It was found that for both the field and flooding conditions, the data were highly correlated with a lograrithmic model.* The logarithmic model was such that:

$$Y = a + b \ln x \tag{4.1}$$

---

*A program entitled "Curve Fitting" provided with the HP 97 desk calculator was used to determine the constants of the model and r^2.

Table 4.10 Modeling of Adsorption Results for Zn Columns--Field Conditions

Adsorbent	Cation	Model	Coefficient of Determination r^2	Correlation Coefficient $\|r\|$
Cel	Zn	Y = -3.36 + 1.87 ln x	0.79	0.87
C	Zn	Y = -32.48 + 17.52 ln x	0.99	0.99
CG	Zn	Y = -23.96 + 14.83 ln x	0.98	0.99
CT	Zn	Y = -46.47 + 21.94 ln x	0.99	0.99
C Cel	Zn	Y = -33.47 + 17.99 ln x	0.99	0.99

Table 4.11 Modeling of Adsorption Results for Cd Columns--Field Conditions

Adsorbent	Cation	Model	Coefficient of Determination r^2	Correlation Coefficient $\|r\|$
Cel	Cd	Y = -0.72 + 0.96 ln x	0.91	0.95
D	Cd	Y = -15.02 + 10.78 ln x	0.99	0.99
CG	Cd	Y = -12.60 + 9.93 ln x	0.99	0.99
CT	Cd	Y = -15.96 + 11.24 ln x	0.99	0.99
C Cel	Cd	Y = -14.46 + 10.70 ln x	0.99	0.99

Figure 4.10 Comparison of the models and data in Zn columns.

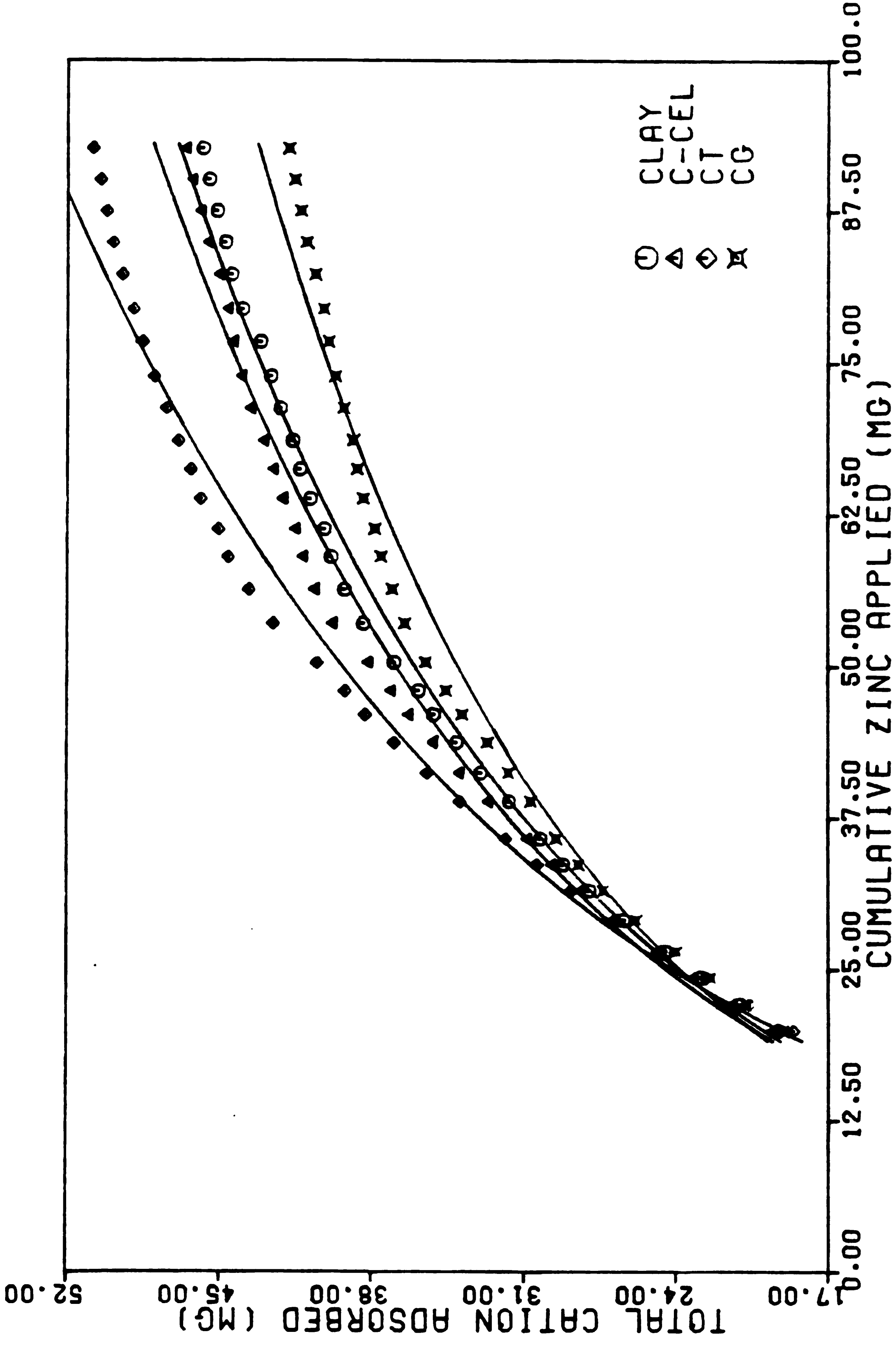
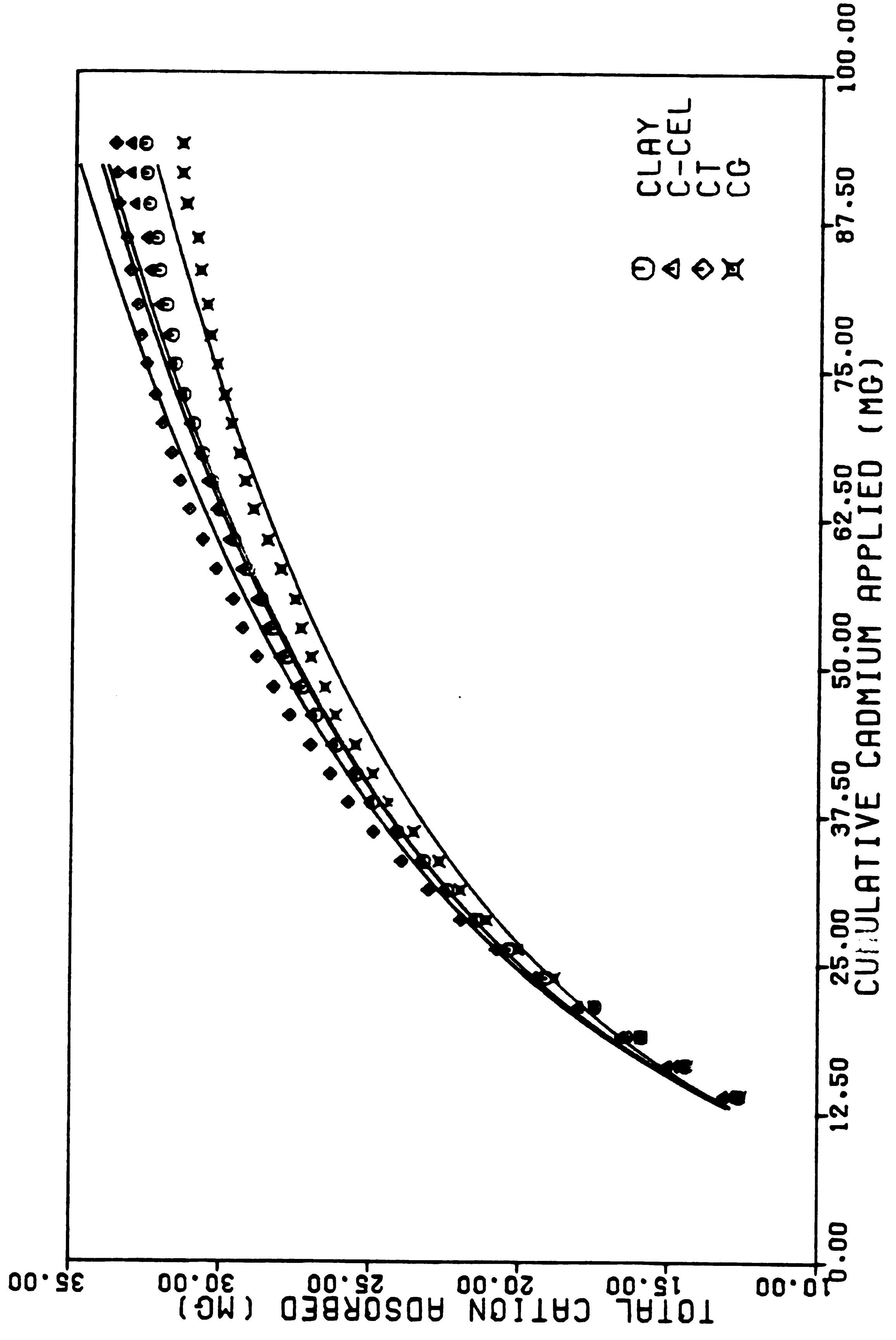

TOTAL CATION ADSORBED (MG)
17.00
24.00
31.00
38.00
45.00
52.00
CUMULATIVE ZINC APPLIED (MG)
0.00
12.50
25.00
37.50
50.00
62.50
75.00
87.50
100.00
CLAY
C-CEL
CT
CG

Figure 4.11 Comparison of the models and data in Cd columns.


TOTAL CATION ADSORBED (MG)
10.00
15.00
20.00
25.00
30.00
35.00
CUMULATIVE CADMIUM APPLIED (MG)
0.00
12.50
25.00
37.50
50.00
62.50
75.00
87.50
100.00
○ CLAY
△ C-CEL
◇ CT
⌧ CG

where x corresponded with the cumulative cations applied, mg, for adsorption, and with cumulative time, days, for desorption; Y corresponded with the cumulative cation adsorbed or desorbed for adsorption and desorption, respectively, and a and b are constants.

The models and the coefficients of determination, as well as the correlation coefficients for the field condition are shown in Tables 4.10 and 4.11. A check of the models indicated that they are highly correlated to the data (see Figures 4.10 and 4.11). The models, however, tended to predict slightly higher values than the actual data for the very beginning and the very end of the data points. This variation was at most, 8% for the very beginning point of the Cd-CG and 3.9% for the very last point of the Zn-CT value.

As it was discussed in Chapter 3 (see Section 3.5.2) the slope, b, defines the rate of adsorption. The models found can be used for the rate determinations. The rate of adsorption at each point can be found by the slope of the curvature at that point. The slope at each point on the curve can be found as:

$$Y = a + b \ln x \qquad a \text{ and } b = \text{cte}$$

$$\text{Slope} = \text{rate} = \frac{dy}{dx} = b\left(\frac{d \ln x}{dx}\right) = \frac{b}{x} = bx^{-1} \tag{4.2}$$

Equation 4.2 implies that the rate of the adsorption is an inverse function of the cation applied to the adsorbent. Since "b" of a particular adsorbent is a constant, the rate of adsorption decreases with cumulative cationic solution applied, or by increasing time at a constant cation input rate. This means that the rate of adsorption is highest when the adsorbent initially is exposed to the cationic solution. The rate decreases upon increasing exposure of the adsorbent to the cation, let's say upon approaching a saturated state. The model implies that the rate of adsorption approaches zero only when the amount of cation applied approaches infinity.

The rate of adsorption of cation at any particular applied cation concentration, x, is only dependent upon "b" (see equation 4.2). Therefore, "b" being directly proportional to the rate, it can be used, for comparison purposes, as an indicator of the rate of adsorption. In other words, the higher the magnitude of "b," the higher the adsorption rate will be.

Comparison of the models of Tables 4.10 and 4.11, based on their "b" values indicates the following: (1) the "b" values in the cadmium adsorption cases are all less than their counterparts for the zinc adsorption cases; (2) the "b" values are similar for the C and C Cel columns; (3) the "b" value is, for each cation, lowest for the CG column and highest for the CT column, excluding the cellulose column; (4) the "b" value of the adsorption by cellulose alone is considerably lower than the "b" values for the clay • organic columns for both of the cations; and (5) the correlation of the models to the actual data is more in the clay • organic columns in comparison to the cellulose alone.

The first parameter in the model expressed by equation 4.1, a, is a characteristic number for the system. This is because when Y = 0, i.e., when no adsorption of the adsorbate by the adsorbent have occurred, equation 4.1 may be written as:

$$Y = 0$$

$$0 = a + b \ln x \tag{4.3}$$

$$\ln x = - \frac{a}{b} \tag{4.4}$$

$$x_0 = e^{(-a/b)} \tag{4.5}$$

x, therefore, has a positive value. Physically, it means that x_0 milligrams of the cation has to be applied to the adsorbent before any adsorption could occur. On the other hand, if x_0 is replaced by its equivalent time value (see Section 4.3.6.1), equation 4.5 implies that x_t units of time has to pass after the application of the absorbate has started before any adsorption of the cation by the adsorbent can occur.

The above may mean a need for a potential build-up of the adsorbate for the adsorption to occur rather than an affinity by the adsorbent for the adsorbate. This is out of the context of this research. However, since the value of x_0 varies with the changes in the kind of adsorbent, adsorbate, and the hydraulic regime of the cation application, therefore, x_0 can be related to the indigenous ability of the adsorbent to adsorb a particular cation. It is a characteristic number related to the cation exchange capacity.

There is no work in the literature available to speak of this value. More work is necessary to confirm the existence of this value for different soil adsorbate systems.

The x_0 values are found, using equation 4.5, for different adsorbents, Table 4.12. The results indicate: (1) the x_0 for a

Table 4.12 Value of the Characteristic Number, x_0, mg--Field Condition

Adsorbents	Cd Columns	Zn Columns
Cel	6.03	2.11
C	4.03	6.38
CG	3.56	5.03
CT	4.13	8.30
C Cel	3.86	6.43

particular adsorbent is lower when the cation applied was cadmium than when it was zinc; and (2) the order of the magnitude of the x_0 value for the clay and clay • organic columns was such that CT > C > C Cel > CG for Cd and CT > C Cel > C > CG for Zn. Any further discussion for the x_0 values is out of the scope of this research.

4.3.5 Flooding

Results of the flooding experiments are summarized in Tables 4.13 to 4.15 and shown in Figures 4.12 to 4.15 (see Appendix G for the details) for both of the cations. Figure 4.16 is shown for illustration purposes. It shows the percent concentration of Zn in the leachate with respect to the applied concentration, i.e., $C/C_0 \cdot 100$ versus the log of the cumulative zinc applied for the sand and the cellulose columns under the flooding condition. The difference between the two curves is a measure of the adsorption by cellulose alone, whereas, the area over

Table 4.13 Adsorption of Zn and Cd, mg--Flooding Condition

Adsorbent / Adsorbate	G[a]	T[a]	Cel	C	CG	CT	C Cel
Zn	0	0	3.02	19.8	15.97	26.97	20.54
Cd	1.48	0.43	1.66	22.17	16.48	30.79	27.07

[a] The apparent values were -4.32 and -4.72 mg for G and T, respectively.

Table 4.14 Adsorption of Zn and Cd, mg/g--Flooding Condition

Adsorbent / Adsorbate	G	T	Cel	C	CG	CT	C Cel
Zn	0	0	3.02	0.994	0.795	1.337	0.978
Cd	134.5	NA	3.32	2.217	1.643	3.076	2.461

Table 4.15 Adsorption of Zn and Cd, me/g--Flooding Condition

Adsorbent / Adsorbate	G	T	Cel	C	CG	CT	C Cel
Zn	NA	NA	0.046	0.015	0.012	0.020	0.015
Cd	2.40	NA	0.059	0.040	0.029	0.055	0.044

Figure 4.12 Cumulative adsorption of Zn during flooding.

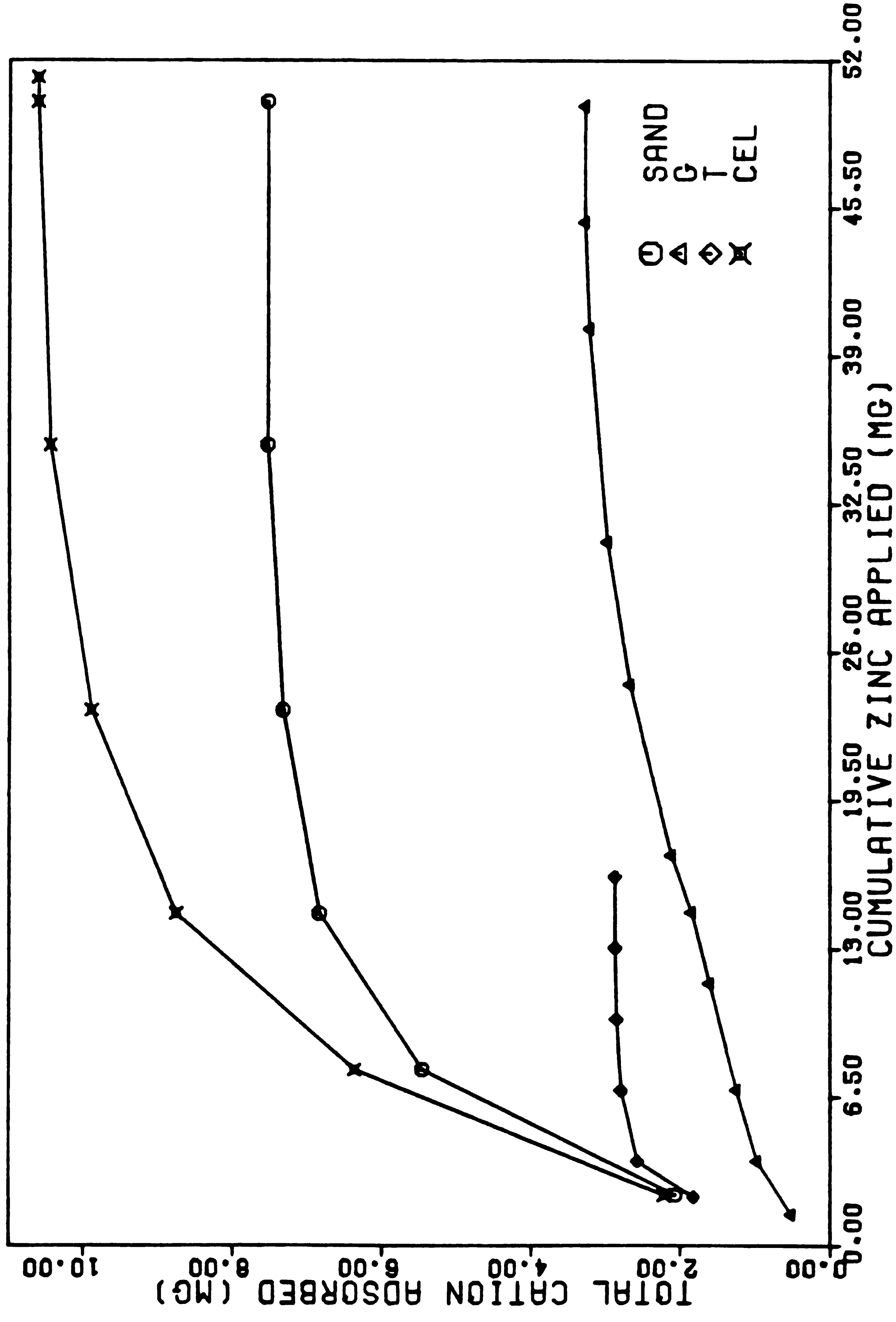

TOTAL CATION ADSORBED (MG)
0.00
2.00
4.00
6.00
8.00
10.00
CUMULATIVE ZINC APPLIED (MG)
0.00
6.50
13.00
19.50
26.00
32.50
39.00
45.50
52.00
SAND
G
T
CEL

Figure 4.13 Cumulative adsorption of Zn during flooding.

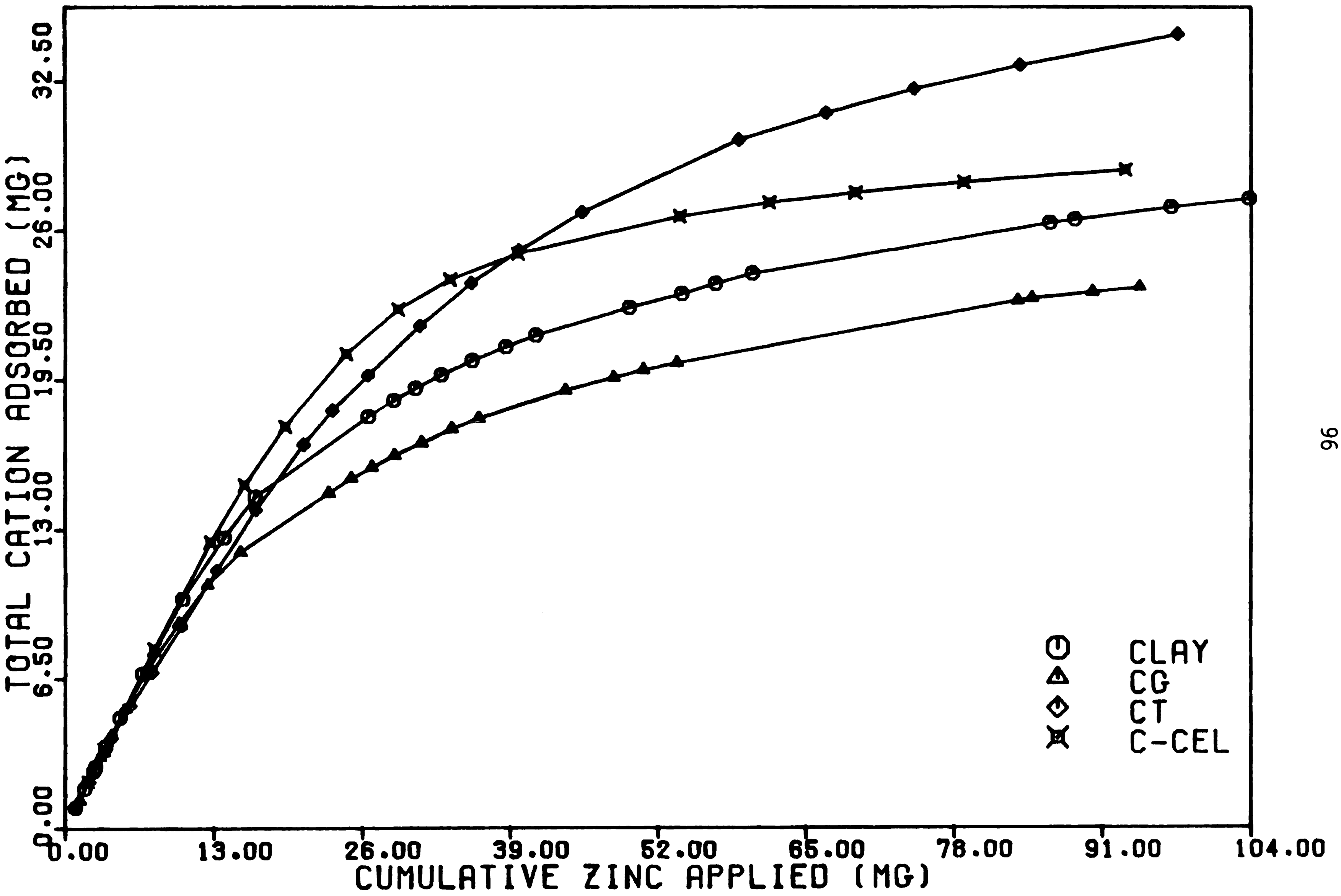

TOTAL CATION ADSORBED (MG)
0.00
6.50
13.00
19.50
26.00
32.50
CUMULATIVE ZINC APPLIED (MG)
0.00
13.00
26.00
39.00
52.00
65.00
78.00
91.00
104.00
CLAY
CG
CT
C-CEL

Figure 4.14 Cumulative adsorption of Cd during flooding.

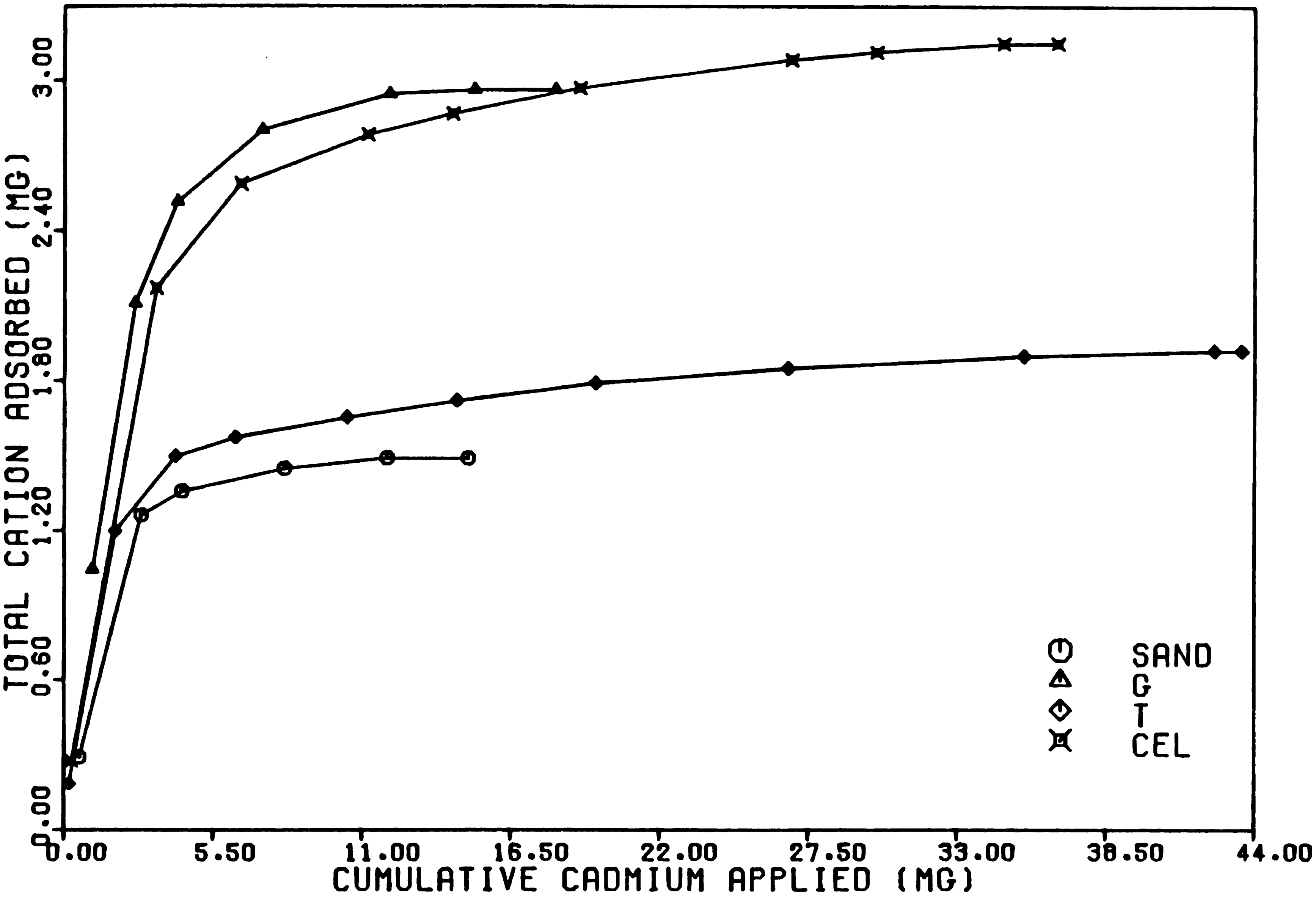

TOTAL CATION ADSORBED (MG)
0.00
0.60
1.20
1.80
2.40
3.00
CUMULATIVE CADMIUM APPLIED (MG)
0.00
5.50
11.00
16.50
22.00
27.50
33.00
38.50
44.00
SAND
G
T
CEL

Figure 4.15 Cumulative adsorption of Cd during flooding.

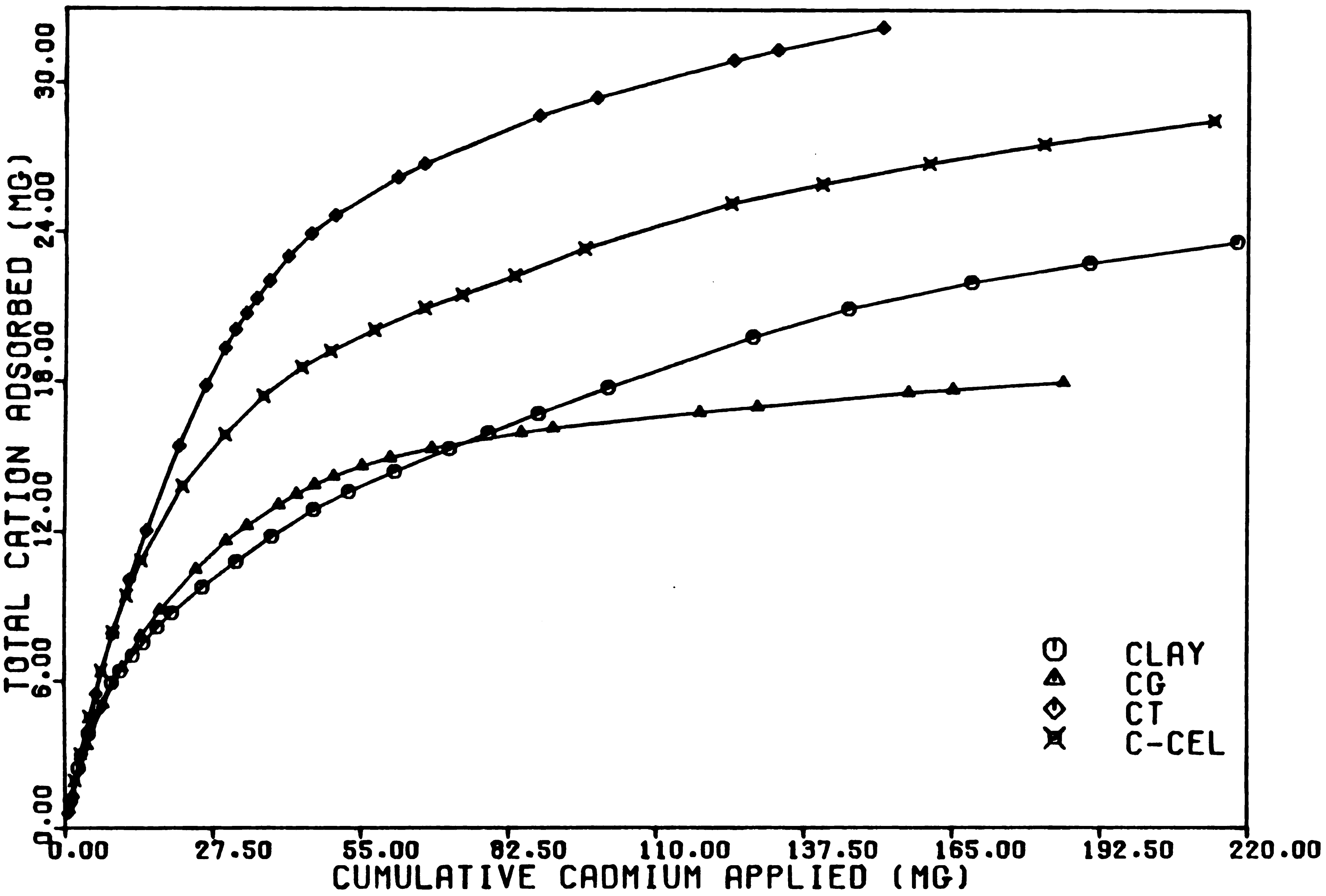
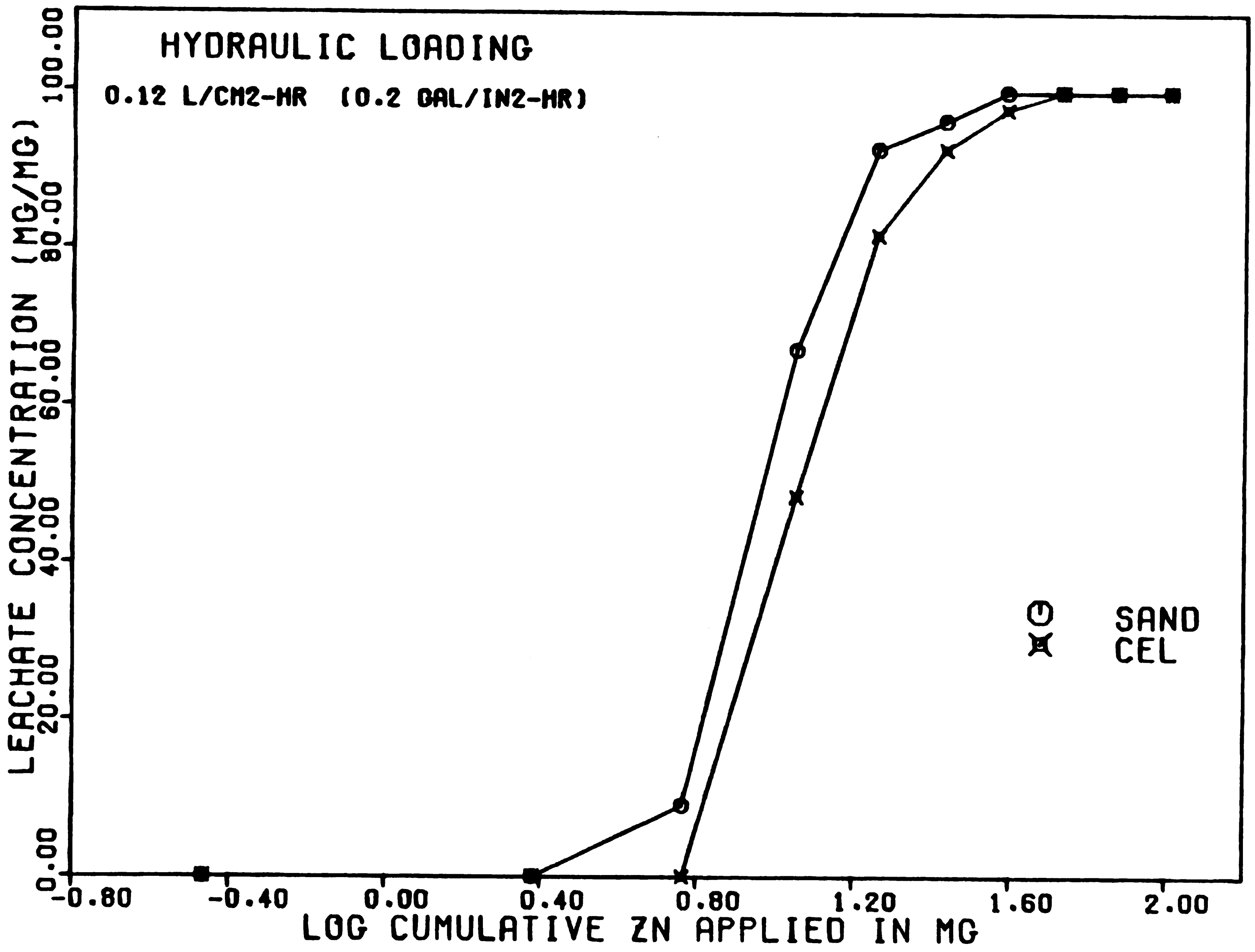

TOTAL CATION ADSORBED (MG)
0.00
6.00
12.00
18.00
24.00
30.00
CUMULATIVE CADMIUM APPLIED (MG)
0.00
27.50
55.00
82.50
110.00
137.50
165.00
192.50
220.00
CLAY
CG
CT
C-CEL

Figure 4.16 Zinc adsorption under flooding condition.


HYDRAULIC LOADING
0.12 L/CM2-HR (0.2 GAL/IN2-HR)
LEACHATE CONCENTRATION (MG/MG)
0.00
20.00
40.00
60.00
80.00
100.00
-0.80
-0.40
0.00
0.40
0.80
1.20
1.60
2.00
LOG CUMULATIVE ZN APPLIED IN MG
SAND
CEL

each curve specifies the adsorption by each of the adsorbents. Figure 4.16 also indicates that adsorption by sand occurs concurrently with the adsorption by cellulose. This is, however, for the flooding condition when the total period of flooding to saturate the adsorption capacity of the adsorbent was less than 30 minutes (see Section 4.3.4.1 for more on this subject). Furthermore, it must be mentioned here that in contrast to the field condition, the sand effect is included in the flooding results. This is because comparison of the leachate concentrations were made with concentration of the applied solutions and not the sand (blank) columns.

4.3.5.1 Modeling

The data obtained in flooding condition (see Appendix G for details) were fit to the mathematical model given in equation 4.1. It was found that they are highly correlated with the logarithmic model (see Section 4.3.4.5 for details). Tables 4.16 and 4.17 show the mathematical models of the adsorption data and the correlation coefficient of the fit for the flooding condition.

4.3.5.2 Conclusion

Due to the similarity of the models found for the data of the field and the flooding condition, the rate argument drawn in Section 4.3.4.5 also holds here. Therefore, "b" is a direct indicator of the rate at which the adsorption reaction proceeds.

Table 4.16 Modeling of Adsorption Results in Zn Columns--Flooding Condition[a]

Adsorbent	Cation	Model	Coefficient of Determination r^2	Correlation Coefficient $\|r\|$
G	Zn	$Y = -0.12 + 0.84 \ln x$	0.93	0.96
T	Zn	$Y = 1.62 + 0.55 \ln x$	0.82	0.91
Cel	Zn	$Y = 0.48 + 2.81 \ln x$	0.96	0.98
C	Zn	$Y = -3.20 + 6.51 \ln x$	0.98	0.99
CG	Zn	$Y = -3.23 + 5.81 \ln x$	0.99	0.99
CT	Zn	$Y = -6.69 + 8.45 \ln x$	0.92	0.96
C Cel	Zn	$Y = -5.78 + 7.94 \ln x$	0.97	0.98

[a] Y = cumulative cation adsorbed, mg; x = cumulative cation applied, mg.

Table 4.17 Modeling of Adsorption Results in Cd Columns--Flooding Condition[a]

Adsorbent	Cation	Model	Coefficient of Determination r^2	Correlation Coefficient $\|r\|$
G	Cd	$Y = 1.33 + 0.64 \ln x$	0.89	0.94
T	Cd	$Y = 0.89 + 0.31 \ln x$	0.95	0.97
Cel	Cd	$Y = 1.25 + 0.59 \ln x$	0.97	0.98
C	Cd	$Y = -3.50 + 4.58 \ln x$	0.94	0.97
CG	Cd	$Y = -1.73 + 3.90 \ln x$	0.98	0.99
CT	Cd	$Y = -3.51 + 6.90 \ln x$	0.93	0.96
C Cel	Cd	$Y = -2.80 + 5.66 \ln x$	0.98	0.99

[a] Y = cumulative cation adsorbed, mg; x = cumulative cation applied, mg.

Comparison of the models reported in Tables 4.16 and 4.17 reveals that (1) between the three organics under consideration in this study the "b" value which is indicative of the rate of adsorption (see Section 4.3.4.6) is lowest for T and highest for Cel in the Zn columns. It is lowest for T and highest for G in the Cd columns; (2) all of the "b" values reported for the Cd columns are smaller than their counterparts for the Zn columns; (3) the "b" values of the clay • organic columns are always higher than those reported for the organic columns alone; and (4) between the clay • organic columns the numerical value of the "b" is in an order such that CT > C Cel > C > CG for both of the cations.

For any given x value, i.e., the total cation applied, the order of the "b" remains unchanged. Therefore, the order of the "b" value automatically defines the order of maximum cation adsorbed that can be found by the model for the different adsorbents.

Following the argument drawn for x_0 in Section 4.3.4.6, the x_0 values are found in Table 4.18. It appears, from Table 4.18, that the x_0 values are higher when the cation applied was zinc than cadmium with the exception of clay column where the order was reverse. Also, the order of the x_0 for the clay • organic columns was found to be CT > C Cel > CG > C for Zn and C > CT > C Cel > CG for Cd.

Table 4.18 Value of the Characteristic Number, x_0, mg--Flooding Condition

Adsorbent	Zn	Cd
Cel	-0.17	-2.11
C	0.49	0.76
CG	0.56	0.44
CT	0.79	0.51
C Cel	0.73	0.49

4.3.6 Comparison of Field and Flooding Conditions

Results of the adsorption of Zn and Cd by the adsorbing columns were shown in Tables 4.3, 4.5, and 4.6; also in 4.13 to 4.15. Comparison of the results reveals that the adsorption of the two cations under the flooding conditions was in all cases lower than that observed in the field condition. This was to be expected because of the relatively short period of contact between the adsorbent and the adsorbate in the flooding method of cation application. The short contact does not allow for pore diffusion. Therefore, the likeliest adsorptions are those due to film diffusion and surface reactions (such as those due to coulombic attractions, van der Waals adsorption, etc.) as opposed to the pore and bulk diffusion and bulk reactions (such as isomorphic substitution).

In the field condition adsorption is through pore diffusion and as such may be categorized as bulk adsorption. This will obviously include surface adsorption and, therefore, adsorption during the flooding condition only comprizes of a portion of the long-term adsorption which occurred in the field condition. In the same sense, if the field and flooding data, for a specific adsorbent, are drawn versus the cumulative cation applied, they are expected to follow the same pattern. The flooding curve should fall on the field curve in the early stages of the adsorption and, then fall under it in the latter stages. A sample plot is shown in Figure 4.17.

The total adsorption of cadmium by the G and T columns, in the flooding condition, exceeds the values that are reported for their adsorption under the field condition. Since the amount of G and T remaining in the columns could be less in the field than in the flooding conditions because the wash out efficiency is reduced, this could account for a major portion of the discrepancy.

4.3.6.1 Comparison of the Models

Comparison of the models, found in Tables 4.10, 4.11 and 4.16, 4.17, reveals that (1) the general form of the models is identical for both of the hydraulic regimes. This is expected because although the rates at which adsorption proceeds are different, the processes are the same; (2) all the "a" values of the Model equations, in the clay and clay • organic columns found for the flooding condition are less than their corresponding values in the field condition. This indicates

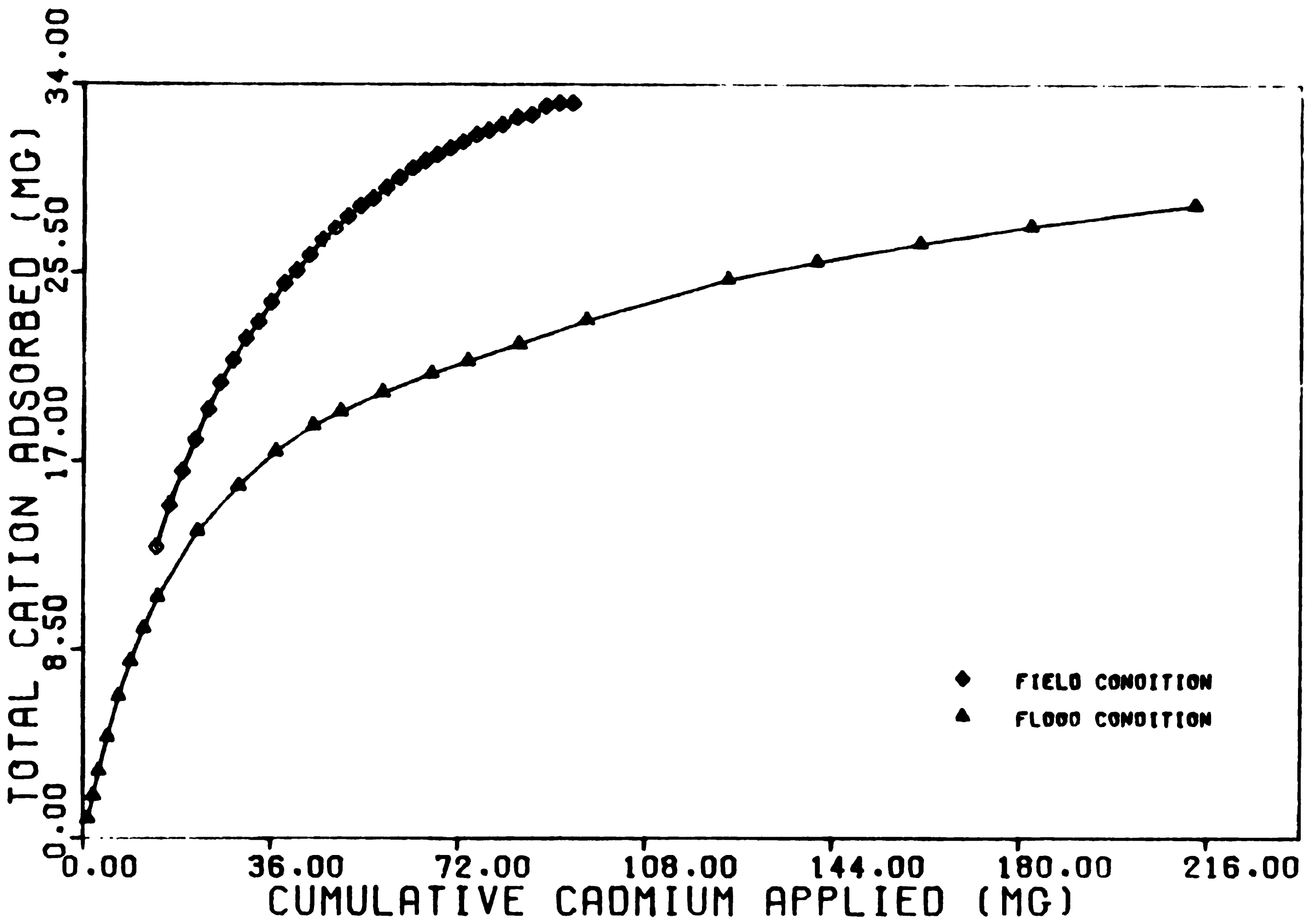


Figure 4.17 Typical position of adsorption curve

that "a" and, therefore, x_0, are related, among other factors to the hydraulic regime at which the cationic solution is applied to the adsorbents; and (3) all the "b" values of the Model equations in the clay and clay • organic columns are lower for the flooding condition than their respective values in the field condition. This implies that the adsorption processes were slower (indeed less was observed) for the flooding condition than the field situation (see Section 4.3.4.6 for more on the "b"). Furthermore, the ratio of the corresponding "b" values in the field to flooding condition varied from an average of 2.52 when zinc was applied to the columns to 2.1 for cadmium.

The reason for the higher rate of adsorption in the field condition is (1) if the total cation applied is considered (as is the case in finding the models) higher contact period facilitates more adsorption, i.e., due to the pore diffusion which otherwise cannot occur (or partially can occur); and (2) if the time period of application is considered x with units of mg in equation 4.1 and 4.2, it has to be converted to t with the units of minutes such that:

i. for the field condition and for the clay and clay • organic columns the average exchange ratio will be:

$x = 65\ \text{cm}^3$ of $40\ \text{mg/l}$ when $t = 3$ days

$x = 65 \cdot 40 \cdot 1\ \text{l}/1{,}000\ \text{cm}^3$ when $t = 3 \cdot 1{,}400$ min/d

$x = 2.6$ mg when $t = 4{,}320$ min.

or

$x/t = 2.6/4{,}320 \quad => \quad x = 6.0 \cdot 10^{-4}\ t$

ii. for the flooding condition and for the clay and clay • organic columns the average exchange ratio will be:

$x = 5 \text{ cm}^3 \text{ of } 40 \text{ mg/l}$ when $t = 1$ min

$x = 5 \cdot 40 \cdot 1 \text{ l}/1{,}000 \text{ cm}^3$

$x = 0.2$ mg

or

$x/t = 0.2/1 \quad \Rightarrow \quad x = 0.2\, t$

In the flooding condition and for the organics, flow of the cationic solution was 40 cm^3/min, therefore:

$x = 40 \text{ cm}^3 \text{ of } 40 \text{ mg/l}$ when $t = 1$ min.

$x = 1.6$ mg

or

$x/t = 1.6/1 \quad \Rightarrow \quad x = 1.6\, t$

In equation 4.1, therefore,

$$Y = a + b \ln x \tag{4.1}$$

for the field condition

$$Y = a + b \ln (6 \times 10^{-4})t \tag{4.6}$$

$$Y = a + b \, [\ln 6 \times 10^{-4} + \ln t]$$

$$Y = a + b \, (-7.42 + \ln t)$$

$$Y = a - 7.42\, b + b \ln t$$

$$Y = c + b \ln t \tag{4.7}$$

where

$$c = a - 7.42\, b \tag{4.8}$$

for the flooding condition

$$Y = a + b \ln (0.2)t \tag{4.9}$$

$$Y = c + b \ln t \tag{4.10}$$

where $$c = a - 1.61\ b \tag{4.11}$$

Equations 4.7 and 4.10 are similar to equation 4.1, therefore, the rate equation, i.e., equation 4.2 remains valid or

$$\text{Rate} = bx^{-1} \quad \text{mg/mg} \tag{4.2}$$

To convert this equation to appropriate rate equation, where x is replaced by t, we must write:

$$\text{Rate (mg/min)} = \frac{dy}{dt} = \frac{dy}{dx} \cdot \frac{dx}{dt} = \text{Rate (mg/mg)} \cdot \frac{dx}{dt} \tag{4.12}$$

i. for the field condition:

$$x = 6.0 \cdot 10^{-4}\ t \tag{4.13}$$

$$\frac{dx}{dt} = 6.0 \cdot 10^{-4} \tag{4.14}$$

$$\text{Rate (mg/min)} = (b\ x^{-1})(6.0 \cdot 10^{-4})$$

$$\text{Rate (mg/min)} = (b\ \frac{1}{6.0 \cdot 10^{-4}\ t})(6.0 \cdot 10^{-4})$$

$$\text{Rate (mg/min)} = b\ t^{-1} \tag{4.15}$$

ii. for the flooding condition and clay • organic adsorbents:

$$x = 0.2\ t \quad (4.16)$$

$$\text{Rate (mg/min)} = bt^{-1} \quad (4.17)$$

for the organic adsorbents, however:

$$x = 1.6\ t$$

$$\text{Rate (mg/min)} = bt^{-1}$$

where the "b" values of equation 4.15 are those found in Tables 4.10 and 4.11. The "b" values of equations 4.17 and 4.19 are those reported in Tables 4.16 and 4.17.

Equation 4.12 and 4.14 indicate that when, in the models, the cation applied is replaced by the appropriate time value, the rate indicator, b, remains unchanged.

Comparison of the models indicates that the "b" values for the cellulose columns, in the flooding condition, were higher than those found for the other organics. Furthermore, the similarity of the models in the field and flooding condition suggests that adsorption proceeds similarly under both the equilibrium (field) and the dynamic (flooding) conditions.

4.4 Desorption

4.4.1 Observations

Other than the very first time when some color was noted, the leachate from the sludge columns was quite clear at all times. The first few leachings from the raw sludges were odoriferous. Gas bubbles were observed in the raw sludge columns. These bubbles were small and were dissipated upon application of the liquid. In the course of the experiment growth of one plant was observed in each of two different digested sludge columns. Once observed they were cut close to the sludge surface. The entire plant was left in the column to decompose.

The total zinc released from the raw and the digested sludges was 6.53 and 3.44 mg, respectively. The percent release of these metals, with respect to their total input (see Table 3.6), can be calculated as:

for the raw sludge

$$\left(\frac{6.53}{30.873}\right) \cdot 100 = 21.1\%$$

for the treated sludge

$$\left(\frac{3.44}{22.970}\right) \cdot 100 = 15.0\%$$

This heavy release of zinc from the sludge is believed to be as the result of the following dynamic forces: (1) microbial activity in the column; (2) ion exchange of zinc in the sludge with calcium and magnesium in the simulated rain water; and (3) diffusion forces due to the concentration gradient between the content of the columns and the applied rain water.

The difference between the percent release of the zinc from the different sludge columns can be interpreted as the amount of zinc that was incorporated by the easily oxidizable organic matter. This is only in the raw sludge and is the matter that will be stabilized in the digester. This signifies the role of the volatile fraction of the sludge in chelation of the cations and is in close agreement with the studies by Gould and Genetelli.[31] These authors reported, among other things, that heavy metals of wastewater sludge are more related to the volatile fraction than the nonvolatiles.

4.4.2 Field Condition

The result of the field condition desorption are shown in Figures 4.18 and 4.19 (see Appendix G for data and analysis). The results indicate that even though no cadmium was found in the leachates, zinc release occurred at dramatic rates from both types of sludges. In fact, considering the ability of the supportive media to bond cations, as was described before, it could well be argued that the adsorption of zinc by the sand reduced, perhaps significantly, the values that are reported for the early stages of the experiment. To further investigate this effect and to investigate the quality of the desorption data, it was decided to test the fit of the Freundlich equation to the data.

4.4.2.1 Fitting the Adsorption Equation

The scatter diagrams for the raw and digested sludges may be seen in Figures 4.20 and 4.21. As can be seen in these diagrams, there are two distinct straight lines which represent two different major bonding energies (see Section 4.3.4.1 for more details). The top line,

Figure 4.18 Release of zinc from raw sludge--field condition.

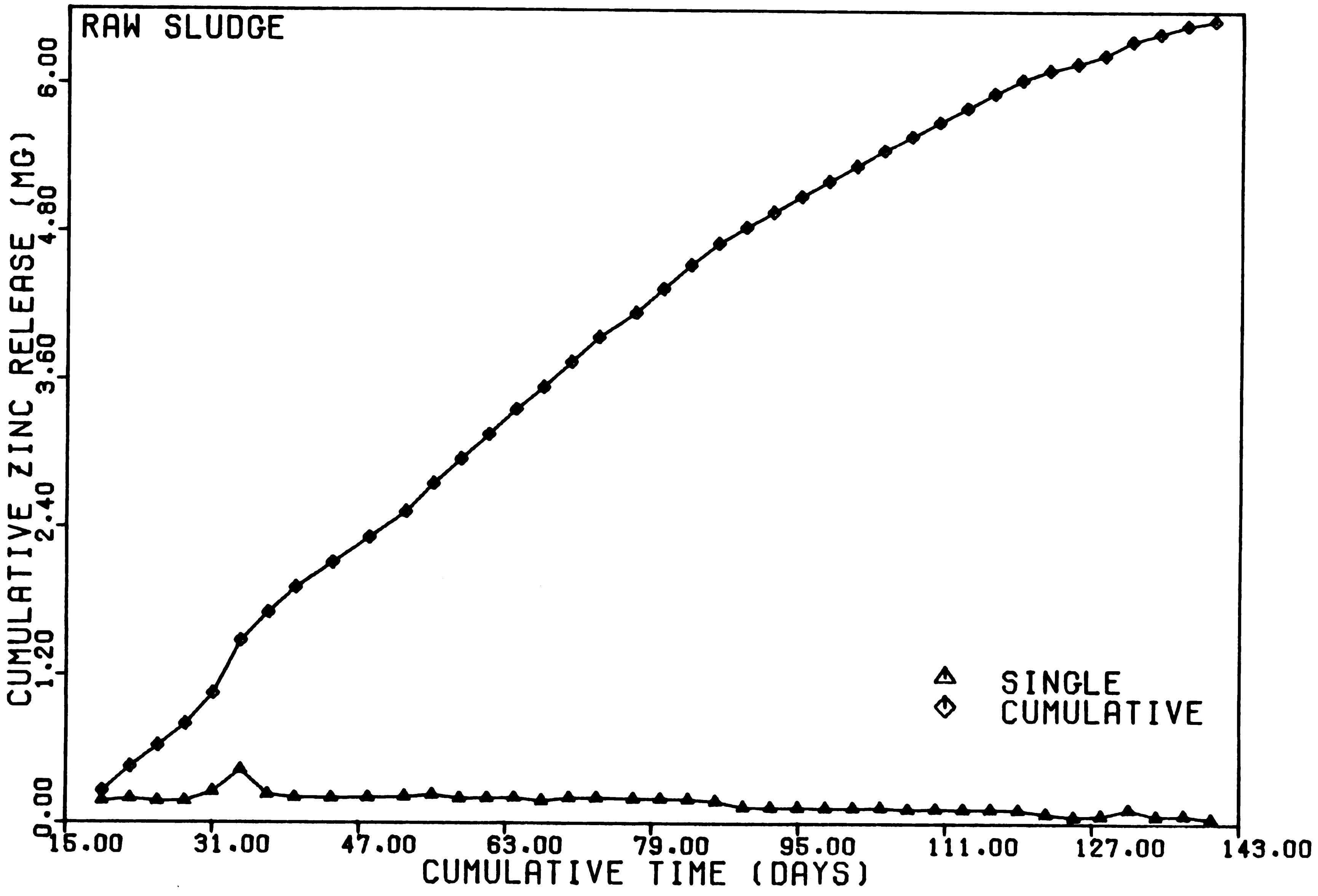

RAW SLUDGE
CUMULATIVE ZINC RELEASE (MG)
0.00
1.20
2.40
3.60
4.80
6.00
15.00
31.00
47.00
63.00
79.00
95.00
111.00
127.00
143.00
CUMULATIVE TIME (DAYS)
SINGLE
CUMULATIVE

Figure 4.19 Zinc release from the digested sludge--field condition.

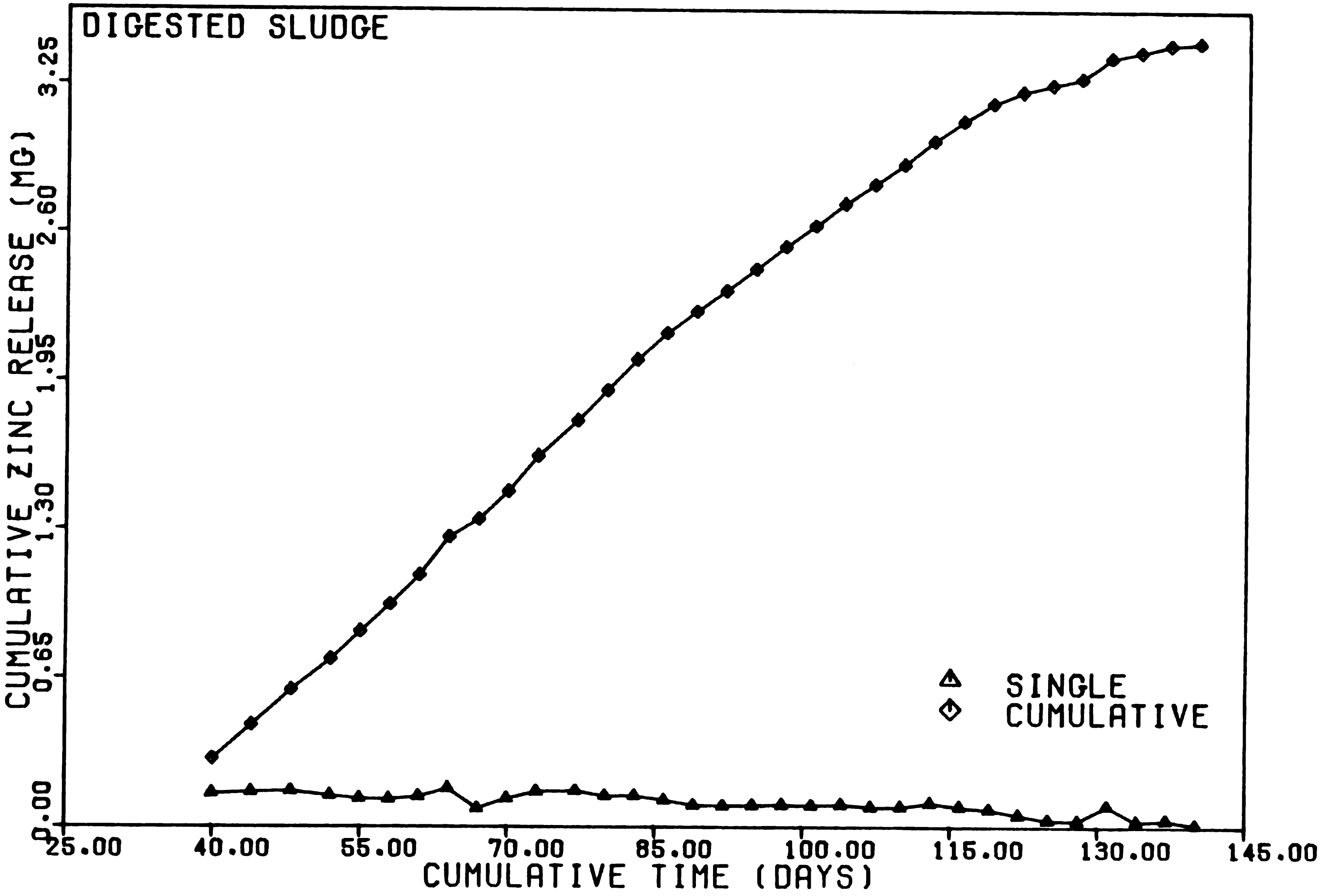

DIGESTED SLUDGE
CUMULATIVE ZINC RELEASE (MG)
0.00
0.65
1.30
1.95
2.60
3.25
CUMULATIVE TIME (DAYS)
25.00
40.00
55.00
70.00
85.00
100.00
115.00
130.00
145.00
△ SINGLE
◇ CUMULATIVE

Figure 4.20 Freundlich equation fitting for raw sludge.

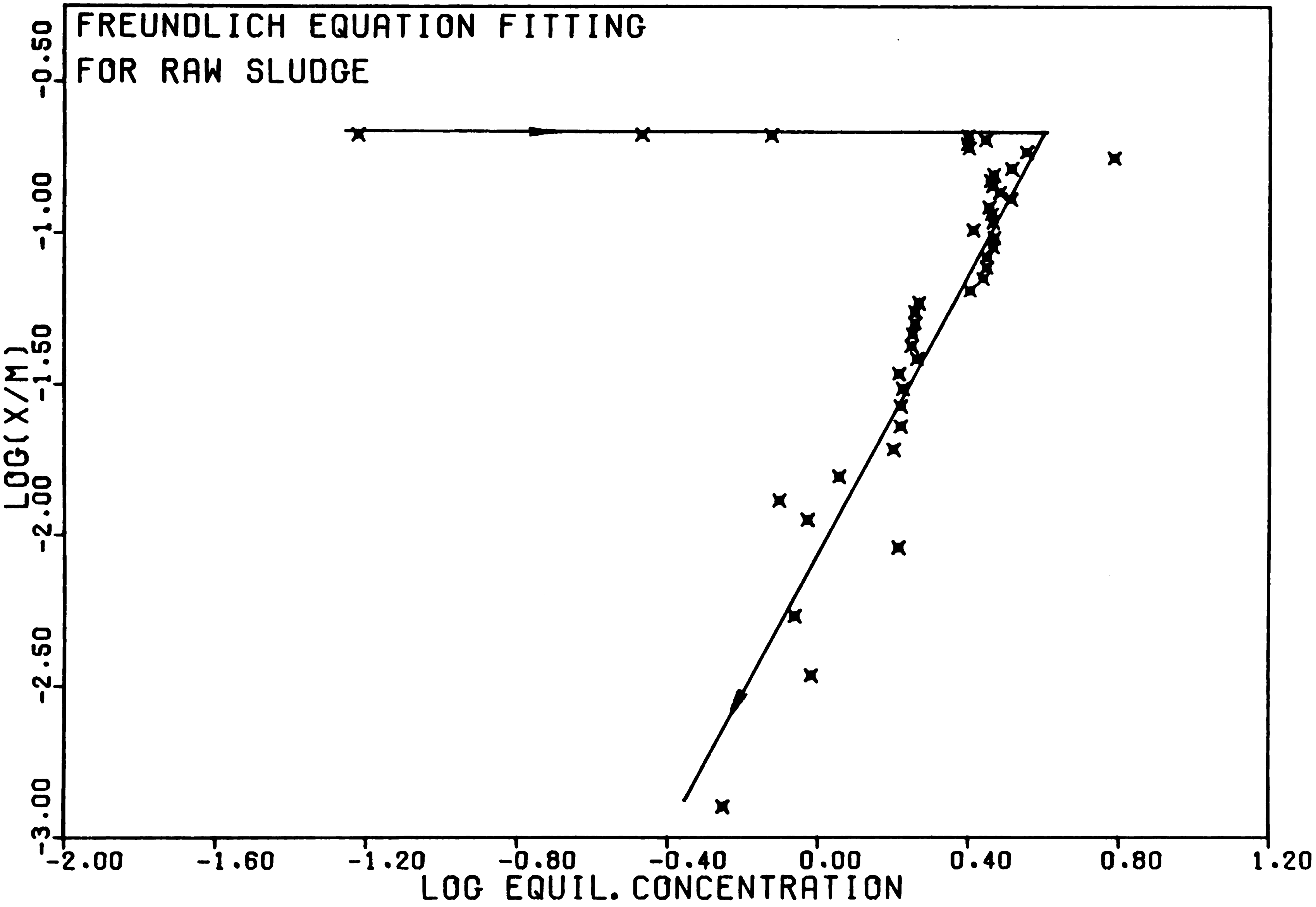
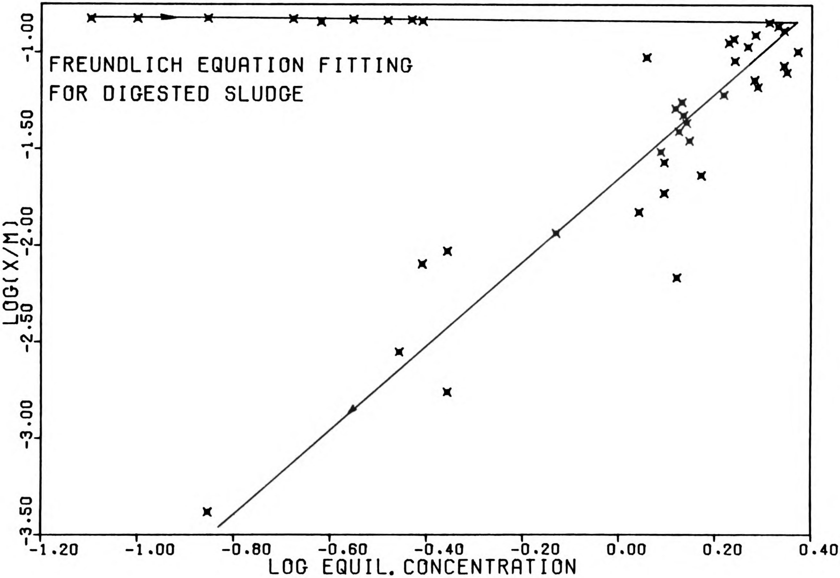

FREUNDLICH EQUATION FITTING
FOR RAW SLUDGE
LOG(X/M)
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-2.00
-1.60
-1.20
-0.80
-0.40
0.00
0.40
0.80
1.20
LOG EQUIL. CONCENTRATION

Figure 4.21 Freundlich equation fitting for digested sludge.


FREUNDLICH EQUATION FITTING
FOR DIGESTED SLUDGE
LOG(X/M)
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
-1.20
-1.00
-0.80
-0.60
-0.40
-0.20
0.00
0.20
0.40
LOG EQUIL. CONCENTRATION

which is almost parallel to the horizontal axis, belongs to the values of the release obtained at the beginning of the release processes. Following the logic expressed in the discussion of the Freundlich lines for the adsorption processes, these lines are the result of desorption from the sludge and consecutive adsorption onto the base sand. This is the same process observed in the adsorption columns. The second line, based on this argument, would be as the result of the zinc desorption.

4.4.2.2 Statistical Analysis and Discussion

The correlation coefficients obtained for the fit of the data to the Freundlich equation are listed in Table 4.19. The "first portion" refers to the horizontal section of the scatter diagrams.

Table 4.19 Correlation Coefficients for the Fit of the Freundlich Equation to the Sludge Data[a]

Sludge	1st Portion	2nd Portion
Raw	-0.69 (5)	0.91(40)
Digested	-0.79(10)	0.92(33)

[a] Values in parentheses refer to the number of data points in each portion.

The least square lines which represents the Freundlich equation are shown in Table 4.20.

Table 4.20 Least Square Equations for Freundlich Equation

Sludge	1st Portion	2nd Portion
Raw	$\log(X/M) = -0.68 - 0.02 \log C$	$\log(X/M) = -2.02 + 2.34 \log C$
Digested	$\log(X/M) = -0.84 - 0.01 \log C$	$\log(X/M) = -1.64 + 1.98 \log C$

In these equations the first and the second portions have "b" values with opposite signs. The reason being the opposite nature of the chemical reactions which produce these lines, i.e., mixed adsorption-desorption for the first portion and desorption for the second portion. The similarities between the least square lines of the scattered diagrams are due to the similar performances by the sand bed and the sludges as was described before.

Adsorption of the cations by the support media has been shown before. This requires a significant release of zinc at the early stages of the experiment. The release can be attributed to the organic and inorganic soluble zinc compounds and easily decomposable organometallic compounds which could result in formation of secondary soluble metallic compounds. Bonding of cations to the small, decomposable, organic compounds has already been reported.[31] To this we must add the exchangeable zinc which could be replaced by the calcium and/or magnesium content of the simulated rain water.

The decrease in the rate of release of the zinc at the later stages of this experiment could be as the result of the following factors which govern the system: (1) the limitation of the available macro and micronutrients necessary for growth of the microbial community; (2) reduction in the amount of the biodegradable substances in the remaining organometallic compounds of a column; and (3) the depletion of the Zn resource.

The data (see Appendix G) also indicate that no significant leaching of the cadmium was detected in the leachate of either of the sludges. Table 3.6 shows that the total Cd content of both the raw and the digested sludge was very low. Therefore, any release would have had a small magnitude. Comparison of the total Cd content of the sludge columns and the base sand's ability to adsorb this element reveals that the expected release ought to be small, if any. It is also mentionable here that in the sludge columns, in contrast to the adsorption columns, there are many cations, negatively charged organic and inorganic compounds which could effectively complete with Zn and/or Cd for binding by the sand adsorption sites. To these we must add the possible resistance of the Cd • organic compounds to decomposition under the conditions of the experiment, and the effect of pH, and E_h within the sludge columns which could cause precipitation and, thus, no release of cadmium. Therefore, a thorough investigation of the microbial, and chemical activities within the sludge columns is necessary to define the mechanism under which no cadmium leachate was detected.

4.4.2.3 Modeling and Kinetic Studies

The desorption results were modeled using the same principles, as were discussed before. The results are shown in Table 4.21. It was found that the models very closely fit the experimental results (see Figures 4.22 and 4.23). However, lower results are obtained, when the models are used, for the very early stages of the desorption.

Table 4.21 Modeling of the Desorption Results, Raw and the Digested Sludges[a]

Sludge	Cation	Model	Coefficient of Determination r^2	Correlation Coefficient $\lvert r \rvert$
Raw	Zn	$Y = -10.86 + 3.50 \ln t$	0.98	0.99
Digested	Zn	$Y = -10.26 + 2.79 \ln t$	0.99	0.99

[a] Y = cumulative cation released, mg; t = cumulative time, days.

The rate of release of zinc can be measured using the same principle as was discussed in Section 4.3.4.6.

Comparison of the rate of release of zinc from the raw and the anaerobically digested sludge, based on the models found, was done. The "b" value of the models are direct indicators of the rate of release as was shown in equation 4.2. It was found that the rate of desorption of zinc from the raw sludge was higher than that found for the digested sludge (see Table 4.21). This can be attributed to the availability of readily biodegradable metalorganic compounds in the raw sludge as was shown in the work of Gould et al.[31]

Figure 4.22. Comparison of the model and the data for desorption of zinc from the raw sludge.

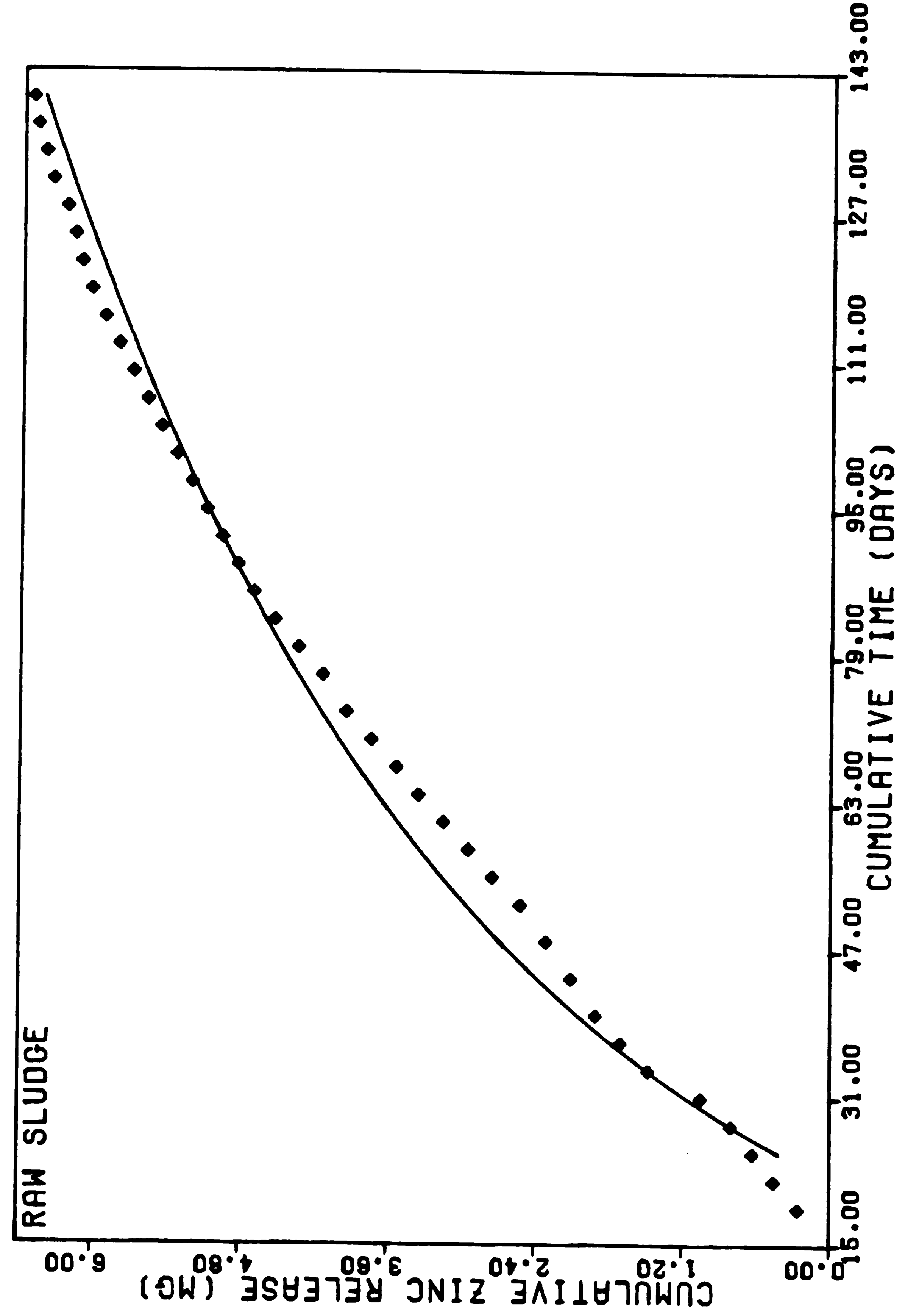
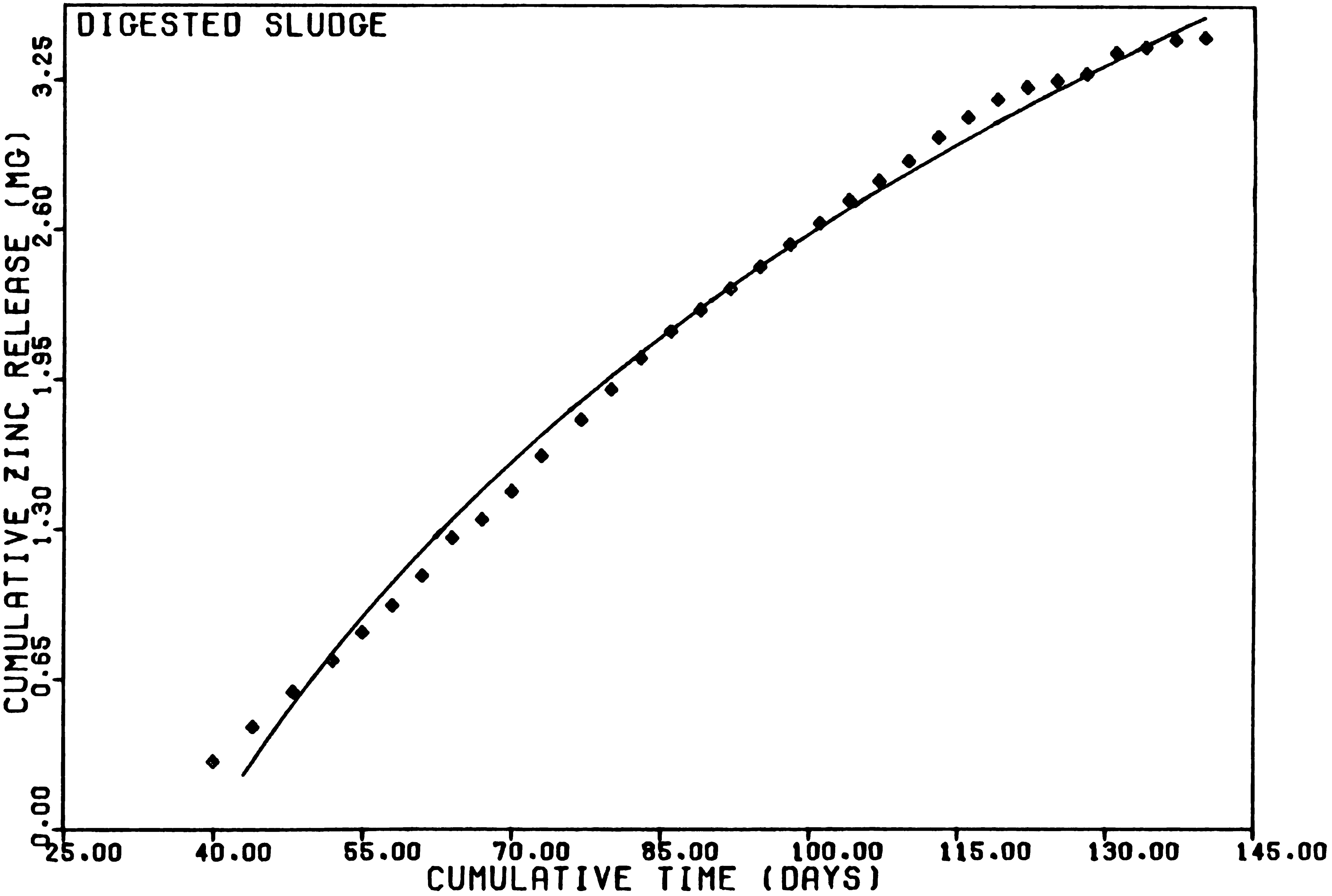

RAW SLUDGE
CUMULATIVE TIME (DAYS)
15.00
31.00
47.00
63.00
79.00
95.00
111.00
127.00
143.00
CUMULATIVE ZINC RELEASE (MG)
0.00
1.20
2.40
3.60
4.80
6.00

Figure 4.23 Comparison of the model and the data for desorption of zinc from digested sludge.


DIGESTED SLUDGE
CUMULATIVE ZINC RELEASE (MG)
0.00
0.65
1.30
1.95
2.60
3.25
25.00
40.00
55.00
70.00
85.00
100.00
115.00
130.00
145.00
CUMULATIVE TIME (DAYS)

4.5 Comparison of the Adsorption and Desorption

At present the wastewater sludge is ultimately deposited in or on soil. In such a system, therefore, adsorbents (soil), and heavy metal desorbents (substances that heavy metals could be desorbed from) are in intimate contact with each other. Comparison of the adsorption and desorption rates, therefore, is necessary to be able to make a prediction on the behavior of the system.

Comparison of the adsorption and desorption models indicates that they are exactly the same. The similarity of the models is due to the similarity of the two processes. It also greatly simplifies the rate comparisons.

For the material under this investigation, comparison of the models found in Tables 4.10, 4.11, 4.16, 4.17 and those in Table 4.21 is based on their "b" values. The "b" has a unit of $\frac{mg}{\ln t}$ for the models reported in Table 4.21 and $\frac{mg}{\ln mg}$ for others. They, therefore, have to be converted to the same unit before any comparison can be made. The cumulative cation applied, cumulative liquid applied, and time can be used interchangeably in the adsorption under the field condition. Therefore, the "b" values can be converted to the same unit and are comparable.

The rate equations were found before and are repeated here to be:

a. for either of the adsorption processes:

$$\text{Rate (mg/mg)} = bx^{-1}$$

or $$\text{Rate (mg/min)} = bt^{-1}$$

b. for the sludge desorption processes:

$$\text{Rate (mg/day)} = bT^{-1} \tag{4.18}$$

when the time is converted to minutes, the type of the models remain unchanged, however, the constant "a" will change such that

$$Y = a + b \ln T \qquad T \text{ (day)} = 1{,}440\ t \text{ (min)} \tag{4.19}$$

$$Y = a + b \ln (1{,}440\ t)$$

$$Y = c + b \ln t \tag{4.20}$$

where

$$c = a + 7.27 b \tag{4.21}$$

$$\frac{dy}{dt} = \text{rate (mg/min)} = bt^{-1} \tag{4.22}$$

Comparison of the rates, i.e., the "b" values in Table 4.22, indicates that in all cases the rate of adsorption of the cations in any hydraulic regime is higher than the rate of desorption of them from any wastewater sludge. An exception being for the organic adsorbents when the rate of release of zinc from the sludges exceeded the rate of adsorption of that by any of the three organics. This comparison is valid for the system used in this study and is subjected to limitations as will be discussed below.

4.6 Conclusion

In chemical reaction kinetics the rate of reaction is dependent upon, among other factors, the amount of the reactants. Therefore, the

Table 4.22 Values of "b" in the Adsorption and Desorption Models

Adsorbent	Hydraulic Condition	Cation	Range of "b"
C • organic	Field	Zn	14.83-21.94
C • organic	Field	Cd	9.93-11.24
Cel	Field	Zn	1.87
Cel	Field	Cd	0.96
C • organic	Flooding	Zn	5.81-8.45
C • organic	Flooding	Cd	3.90-6.90
Organics	Flooding	Zn	0.55-2.81
Organics	Flooding	Cd	0.31-0.64
Desorbent			
Raw sludge	Field	Zn	3.50
Digested sludge	Field	Zn	2.79

rate of adsorption will certainly change with the changes in the amount of adsorbent. This is such that an increase in the amount of adsorbent, when other factors remain unchanged, will increase the rate of adsorption.

Table 4.22 is useful to compare the rate of adsorption also decomposition of heavy metals in a system composed of the adsorbent and desorbent with the amounts used in this work. The volume of the sludges used in construction of the desorption columns was what is normally applied to the soil in agricultural land. Therefore, the following generalizations may be made:

1. Twenty grams of a low adsorptive clay, such as the kaolinitic clay used in this work, has a higher rate of adsorption than the rate of desorption of zinc from wastewater sludge.
2. The hydraulic regime of transferring cations to the adsorbent has a considerable effect on the rate of adsorption. Low surface loading of the liquid applied to the adsorbent-desorbent system is favored for greater adsorption rates and for higher total adsorption.
3. The rate of adsorption and desorption of heavy metals in a fixed system decreases with time. This is due to the depletion of the active site and the heavy metal resources, respectively.
4. The existence of organic matter increased the rate and the total amount of the heavy metal adsorption, an exception being the CG columns under most conditions. However, the interaction between the clay and organic matter reduced the adsorption expected if they were acting separately.

Finally, wastewater sludges are known to contain a variety of heavy metals and other cations. These cations are expected to effectively compete with each other to occupy the adsorbing sites. Therefore, a broader inventory of the negatively charged desorbates and their rate of release is necessary to judge the overall ability of a soil to accommodate a sludge. The problem of working with pure systems and then extrapolating to soil has been amply demonstrated by Lagerwerff and Brower.

4.7 Engineering Application

Engineering application of the adsorption portion of this study is limited to specific cases when the main fraction of the cationic portion of a desorbent is known. Very few other methods, such as the CEC analysis, are available to predict adsorption of cations by the soil. Therefore, in the lack of other decisive methods the prediction can be done utilizing the models developed in this work.

Although desorption of the heavy metals from sludge was expected, no previous modeling of the release of heavy metals from raw and anaerobically treated wastewater sludge has been reported. The original concentration, therefore, the total cation content (for the cation/s of interest) of a sludge can be easily found, using well known techniques. The result of the desorption study can, therefore, be used to predict the rate and the amount of the release for a known time period. The models also may be used to predict the ultimate period of time before all the cation in the sludge is released to the environment. The last is, however, a tentative methods of prediction.

The models developed can be used for the prediction purposes. This can be done by experimentally finding the first few points of an adsorption or desorption process, finding the "a" and "b" constants of the model and make prediction.

When the wastewater sludge is applied to an agricultural land, and when the metal uptake pattern of the crop is known, a material balance of the cation released to the environment and what has been picked up by the plant can describe the state of the soil pollution by the specific heavy metal.

SUMMARY

In this work finite well drained soil beds were made up of kaolinite and/or one of the three organics commonly found in the wastewater and wastewater sludge, namely, glucose, tryptophane and cellulose. A monometallic solution of zinc or cadmium was applied to the soil beds under either of the field and flooding conditions. The two hydraulic regimes simulate the ultimate adsorption condition, i.e., the equilibrium and dynamic, for field and flooding systems, respectively. The leachates were analyzed for their heavy metal contents. It was found that the adsorption data were highly correlated to the Freundlich equation. The data also fit well in a logarithmic model.

The effect of hysterises on the adsorption was not considered because the entire bed always was saturated. In the field condition, it was found that the main adsorption or desorption occurred during the period between the two liquid applications.

Two sludges known to have high metal content were studied for their heavy metal release. Simulated rain water was used as a carrier for the released cations. The leachates were analyzed for their Zn and Cd content. It was found that a combination of chemical and biological reactions occurred in the desorption columns. These reactions caused the chelated heavy metals to break up and release their cation content which subsequently was washed out of the columns.

The rate studies were performed utilizing the mathematical models. It was found, in both adsorption and desorption study, that rate is an inverse function of the time from when the process starts.

Similarity between the mathematical models found for the adsorption and desorption processes facilitated the comparative kinetic studies. It was shown that, using the quantities of the adsorbent and desorbent studied, the rate of adsorption of heavy metals by the clay and clay • organic adsorbents exceeded the rate of release of the heavy metals from either of the raw or anaerobically treated wastewater sludge. This was true for both of the hydraulic regimes that were considered.

Some experimental difficulties were encountered due to the solubility of the glucose and tryptophane, also due to the adsorption of the heavy metals by the support media.

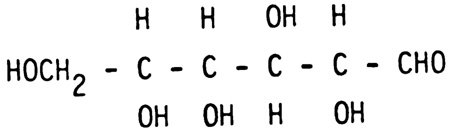
APPENDICES

APPENDIX A

PROPERTIES OF ADSORBENTS USED IN THE ADSORPTION COLUMNS

Glucose, tryptophane, and cellulose were chosen as the organics to be used in the adsorption columns. A kaolinitic clay was used as the clay source in the adsorption studies. Some properties of these selected adsorbents are as follow:

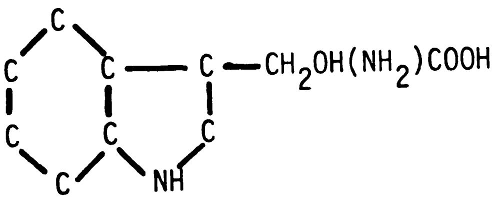
a) D-Glucose (dextrose*) $C_6H_{12}O_6 \cdot 1H_2O$



$$HOCH_2 - \underset{OH}{\overset{H}{C}} - \underset{OH}{\overset{H}{C}} - \underset{H}{\overset{OH}{C}} - \underset{OH}{\overset{H}{C}} - CHO$$

Glucose is a hexose, therefore, a monosaccharide. Dextrose is also known as grape sugar. ACS reagent grade dextrose with the properties shown in Table A.1 was used in this work.

b) Tryptophane* $C_{11}H_{12}N_2O_2$



It is, also, called α-amino- β-indolyl-proprionic acid. Its solubility in 100 g of water at 25° C is 1.136 g.

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*CRC Handbook of Chemistry and Physics, 56th edition.

Table A.1 Properties of the Selected Organic Matters

Properties	Organic Matter	
	Tryptophane	Glucose
MW	204.23	180.16
Lot No.	B719	765,944
Specific rotation [α], 25°, D	NA	+52.5
Insoluble matter	NA	0.005%
Acidity (as CH_3COOH)	NA	0.005%
Chloride (as Cl)	NA	0.002%
Starch	NA	0.08 ppm
Heavy metals (as Pb)	NA	4 ppm
Fe	NA	1 ppm

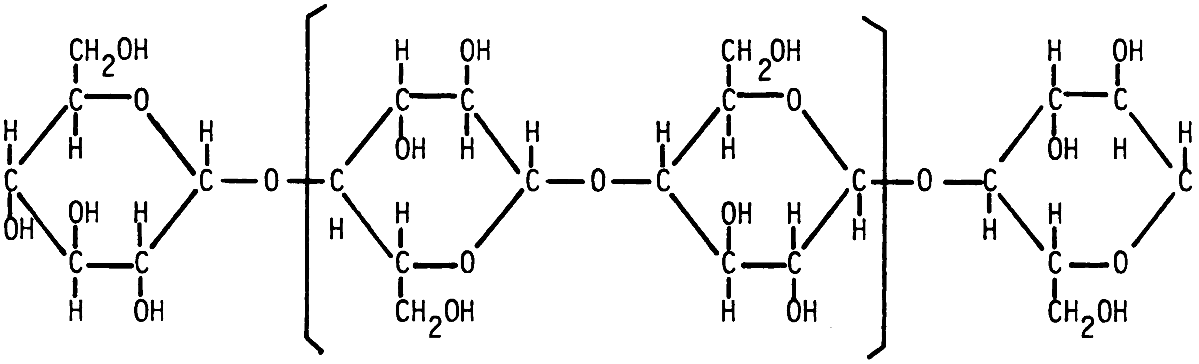
$pK_{a_1} = 9.39$

$pI = 5.88 \qquad pI = \frac{1}{2}(pK_{a_1} + pK_{b_1} + pK_w)$

$pK_{b_1} = 11.62$

where pI is the pH at the isoelectric point. ACS reagent grade tryptophane with the properties shown in Table A.1 was used in this work.

c) Cellulose $(C_6H_{10}O_5)_x$ - Glucose, in particular the form known as β-glucose is the unit break from which the cellulose is built. One of the most favorable arrangement of cellulose is proposed to be:[60]



Cellulose,therefore, could indeed be assumed to be a polymer of glucose. Furthermore, the ultimate product of the hydrolysis of cellulose by acids is glucose.

d) Kaolinite

This type of kaolinite is usually used in the pulp and paper industry. The grain size distribution of the kaolinite is obtained as the result of a hydrometer testing and is shown in Figure A.1. It could be seen in the figure, that more than 60% of the particles are smaller than 2 micron, therefore are clays.

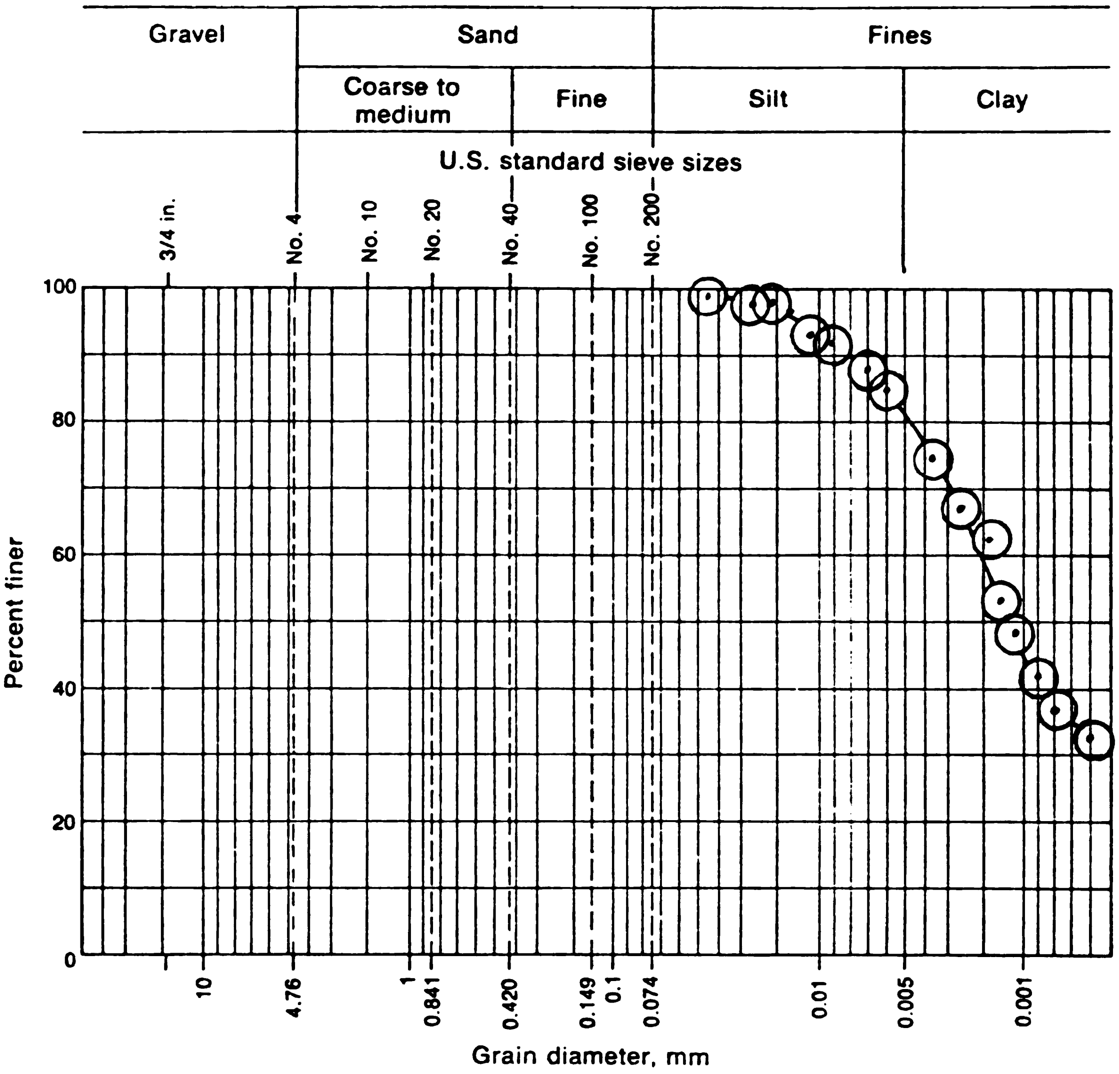


Figure A.1 Grain size distribution curve for clay (kaolinite).[62]

Table A.2 Properties of Zinc and Cadmium Compounds*

Parameters	$Zn(NO_3)_2$, $6H_2O$	$Cd(NO_3)_2$, $4H_2O$
Formula weight	297.47	308.47
Lot number	762191	755409
Insoluble matter	0.001%	0.002%
Acidity as (HNO_3)	0.006%	NA
Cl	0.002%	0.0003%
PO_4	0.0005%	NA
SO_4	0.008%	0.003%
Alkalies and earth	0.2%	0.03%
Pb	0.002%	0.001%
Fe	0.0005%	0.0003%
Cu	NA	0.0005%
Zn	NA	0.05%
NH_3	NA	0.003%

* NA = Not available

APPENDIX B

SLUDGE DIGESTION AND METAL MEASUREMENT

The following procedure was adopted to measure the zinc and cadmium in sludge.

B.1 Digestion Procedure

Digestion of the sludges was necessary for measurement of the zinc and cadmium by atomic adsorption spectroscopy (See Appendix C for the analytical procedure). The moisture content of the sludges was reduced by placing them on silica sand beds and allowing them to drain for 24 hours. This was necessary to reduce the volume that had to be digested. After 24 hours the moisture content of the raw and treated sludges reduced to 81.35% and 77.1%, respectively. The following steps were then followed:

1. A sample of the sludge having about 0.5 g dry weight was placed in a 50 ml all teflon beaker. A blank consisting of 10 ml of distilled water was also prepared to be carried through all the remaining steps.
2. 25 ml concentrated ACS Reagent grade HNO_3 was added.
3. The beaker was then placed on a hot silica sand bed having a temperature of 160° C and left to dry (4-6 hrs.).
4. Steps 2 and 3 were repeated.
5. The beaker was then cooled in air and 20 ml concentrated

Reagent grade HF was added followed by 10 ml concentrated $HClO_4$.

6. The beaker was then placed back on the hot sand bed for 24 hours to dry.
7. The contents of the beaker was then washed with 5 ml 6N HCl while still warm to dissolve the residues.
8. The washings were transferred to a 50 ml volumetric flask.
9. The washings were then made up to 50.0 ml by adding distilled water.
10. The samples were then analyzed for metal content by Atomic Adsorption Spectroscopy (See Appendix C for the method).

B.2 Measurement Result

Result of the measurement are shown in Tables B.1 and B.2 where the raw, digested and blank samples are denoted as R, D, and B.

Table B.1 Zinc and Cadmium Content of Digested Sludges

Sludge[a]	Wet Wt. g	Dry Wt.[b] g	Zn Conc. mg/l	Cd Conc. mg/l
R_1	1.8244	0.3402	50.5	0.35
R_2	2.2592	0.4213	56.0	0.40
D_1	1.5663	0.3587	39.5	0.24
D_2	1.7962	0.4113	4.25	0.28
B_1			1.94	0.15
B_2			2.13	0.15

[a] Subscripts refer to the sample numbers.

[b] Dry Wt. = wet wt. • dry content.

Table B.2 Zinc and Cadmium Content of Sludge (with blank correction)

Sludge	Zn Conc.[a] mg/l	Zn Conc.[b] mg/g dry	Cd Conc.[a] mg/l	Cd Conc.[b] mg/g dry
R_1	48.46	7.122	0.2	0.029
R_2	53.96	6.404	0.25	0.030
D_1	37.46	5.222	0.09	0.013
D_2	40.21	4.888	0.13	0.016

[a] Conc. = Conc. - blank conc. (Table B.1).

[b] Total metal in sample = Conc. (mg)/1,000 ml • 50 ml = 0.05 • Conc. (mg)
Conc. in dry state = Total metal in sample/Dry wt. of the sample.

As the result of the Table B.2 information the average zinc and cadmium content of the samples are 6.763 and 0.029 mg/g dry for the raw, and 5.055 and 0.014 mg/g dry for the digested sludges, respectively.

APPENDIX C

ANALYTICAL PROCEDURES

All synthetic feed solutions were prepared with reagent grade chemicals and distilled deionized water. All glassware and operation materials were rinsed with tap water, cleaned with either dichromate acid, acetone, or soap cleaning solution, rinsed three times with tap water, and three times with distilled water.

The zinc and cadmium standard solutions were reagent grade 1,000 mg/l purchased from Fisher Scientific Incorporation.

C.1 Equipment

Cadmium and zinc ion concentration of the samples were determined utilizing an Atomic Adsorption Spectrophotometry unit. The unit was an Instrument Laboratories Model 151 with a premixed burner. An acetelene flame was used as recommended in the Standard Method for Examination of Water, and Wastewater.[49] Readings were made at the conditions summarized in Table C.1. These operational factors were so chosen to achieve an optimum sensitivity. In addition, the position of the nebulizer was adjusted to obtain a minimum operational noise.

All of the standard solutions, used to obtain standard curves, were made from the 1,000 mg/l zinc and cadmium solutions and distilled water.

Table C.1 Operational Conditions in the Atomic Adsorption Measurement of Zn and Cd

Parameter Description	Zn	Cd
Wave length, Å	2,139	2,288
Hollow cathod current, mA	5-7	5
Voltage, volts	530	460
Burner height, machine unit	12	12
Slid width, micron	320	320

APPENDIX D

MEASUREMENT OF REQUIRED SLUDGE

The volume of sludge that was used in each column was based on an assumed application rate of 10 dry tons/acre and was calculated as follows:

Converting dry ton/acre to grams per 2 inch diameter column:

$(10 \text{ tons/ac})(2{,}000 \text{ lbs/ton})(454 \text{ g/lb})(1 \text{ ac}/43{,}560 \text{ ft}^2)$

$(1 \text{ ft}^2/144 \text{ in}^2)(2 \text{ in})^2 (\pi/4) = 4.55 \text{ g/column}$

For the raw sludge which had a dry solids content of 5.5 g/100 ml:

$(4.55 \text{ g})/(5.5 \text{ g}/100 \text{ ml}) = 83 \text{ ml}$

For the treated sludge which had a dry solids content of 3.29 g/100 ml:

$(4.55 \text{ g})/(3.2 \text{ g}/100 \text{ ml}) = 142 \text{ ml}$

APPENDIX E

ORGANIC RELEASE

As was described before glucose and tryptophane leached out of the adsorption columns, the results of the total carbon measurement, T_c, which are expressed as mg/l Carbon, were converted back to the respective organics as follows:

$$\alpha = \frac{\text{Molecular wt of the organic}}{12 \cdot \text{number of C in the molecule}}$$

Therefore,

$$\text{organic concentration in the leachate in mg/l} = T_{cL} = \alpha T_c$$

where α is 2.75 and 1.545 for glucose and the tryptophane, respectively. The average amount of glucose and tryptophane that were left in the columns, T_{Cr}, were calculated as:

$$T_{Cr} = \text{Initial organic added} - \Sigma 0.065\ (T_{cL} + e)$$
$$e = 5N\alpha$$

where e is the error due to the dissolved CO_2 (measured from the blank cationic solution to be 5 mg/l) and N is the number of times carbon was detected (and measured) in the leachate.

The release of organics from the adsorption columns were calculated, using the procedures described before, in this appendix.

The results are shown in Table E.1 to E.8.* The net cumulative release of glucose and tryptophane from the adsorption columns versus the cumulative volume of the cationic solution are shown in Figures E.1 and E.2. The total glucose and tryptophane remaining in the system are shown in Table E.9. The value reported for the release of the tryptophane in the cadmium-T columns has exceeded the amount originally added to these columns, therefore, is meaningless. The actual number is, therefore, not available.

Table E.1 Release of Glucose from the Cadmium Columns

CdG	Cumulative G Concentration (ppm)	Cumulative G Release (mg)	Error (mg)	Net Cumulative Release (mg)
60	60	3.9	.9	3.0
5,500	5,560	361.4	1.8	359.6
2,002	7,562	491.5	2.7	488.8

---

*For the sample calculations see the end of this appendix.

Table E.2 Release of Glucose from the Cadmium Columns

CdCG	Cumulative G Concentration (ppm)	Cumulative G Release (mg)	Error (mg)	Net Cumulative Release (mg)
65	65	4.2	.9	3.3
1,168	1,233	80.1	1.8	78.3
5,005	6,238	405.5	2.7	402.8
1,042	7,280	473.2	3.6	469.6

Table E.3 Release of Tryptophane from the Cadmium Columns (T)

CdT	Cumulative T Concentration (ppm)	Cumulative T Release (mg)	Error (mg)	Net Cumulative Release (mg)
35	35	2.3	.5	1.8
1,062	1,097	71.3	1.0	70.3
1,275	2,372	154.2	1.5	152.7
1,579	3,951	256.8	2.0	254.8
1,635	5,586	363.1	2.5	360.6
1,392	6,978	453.6	3.0	450.6
1,210	8,188	532.2	3.5	528.7
669	8,857	575.7	4.0	571.7
202	9,059	588.8	4.5	584.3
34	9,093	591.0	5.0	586.0

Table E.4 Release of Tryptophane from the Cadmium Columns (CT)

CdCT	Cumulative T Concentration (ppm)	Cumulative T Release (mg)	Error (mg)	Net Cumulative Release (mg)
55	55	3.6	.5	3.1
970	1,025	66.6	1.0	65.6
1,335	2,360	153.4	1.5	151.9
1,477	3,837	249.4	2.0	247.4
1,416	5,253	341.4	2.5	338.9
1,025	6,278	408.1	3.0	405.1
601	6,879	447.1	3.5	443.6
384	7,263	472.1	4.0	468.1
182	7,445	483.9	4.5	479.4
104	7,549	490.7	5.0	485.7
61	7,610	494.6	5.5	489.1
34	7,644	496.9	6.0	490.9
20	7,664	498.2	6.5	491.7

Table E.5 Release of Glucose from the Zinc Columns (G)

ZnG	Cumulative G Concentration (ppm)	Cumulative G Release (mg)	Error (mg)	Net Cumulative Release (mg)
96	96	6.2	.9	5.3
7,830	7,926	515.2	1.8	513.4
7,012	14,938	971.0	2.7	968.3
271	15,209	988.6	3.6	985.0

Table E.6 Release of Glucose from the Zinc Columns (CG)

ZnCG	Cumulative G Concentration (ppm)	Cumulative G Release (mg)	Error (mg)	Net Cumulative Release (mg)
78	78	5.1	.9	4.2
5,250	5,328	346.3	1.8	344.5
7,947	13,275	862.9	2.7	860.2
1,474	14,749	958.7	3.6	955.1
64	14,823	963.5	4.5	959.0

Table E.7 Release of Tryptophane from the Zinc Columns (CT)

ZnCT	Cumulative T Concentration (ppm)	Cumulative T Release (mg)	Error (mg)	Net Cumulative Release (mg)
68	68	4.4	.5	3.9
1,093	1,161	75.5	1.0	74.5
1,261	2,422	157.4	1.5	155.9
2,157	4,579	297.6	2.0	295.6
2,340	6,919	449.7	2.5	447.2
2,386	9,305	604.8	3.0	601.8
2,030	11,335	736.1	3.5	732.6
1,438	12,773	830.2	4.0	826.2
737	13,510	878.1	4.5	873.6
262	13,772	895.2	5.0	890.2
98	13,870	901.5	5.5	896.0
36	13,906	903.9	6.0	897.9
15	13,921	904.9	6.5	898.4

Table E.8 Release of Tryptophane from the Zinc Columns (T)

ZnT	Cumulative T Concentration (ppm)	Cumulative T Release (mg)	Error (mg)	Net Cumulative Release (mg)
31	31	2.0	.5	1.5
862	893	58.0	1.0	57.0
1,208	2,101	136.6	1.5	135.1
1,444	3,545	230.4	2.0	228.4
1,285	4,830	313.9	2.5	311.4
1,074	5,904	383.8	3.0	380.8
1,069	6,973	453.2	3.5	449.7
1,043	8,016	521.0	4.0	517.0
978	8,994	584.6	4.5	580.1
819	9,813	637.8	5.0	632.8
754	10,567	686.8	5.5	681.3
652	11,219	729.2	6.0	723.2
708	11,927	775.2	6.5	768.7
596	12,523	814.0	7.0	807.0
487	13,010	845.6	7.5	838.1
503	13,513	878.3	8.0	870.3
445	13,958	907.3	8.5	898.8
348	14,306	929.9	9.0	920.9
276	14,582	947.8	9.5	938.3
215	14,797	961.8	10.0	951.8
157	14,954	972.0	10.5	961.5
147	15,101	981.6	11.0	970.6
99	15,200	988.0	11.5	976.5
54	15,254	991.51	12.0	979.5
37	15,291	993.9	12.5	981.4
21	15,312	995.3	13.0	982.3
15	15,327	996.2	13.5	982.7

Figure E.1 Total release of the glucose and tryptophane from the cadmium columns

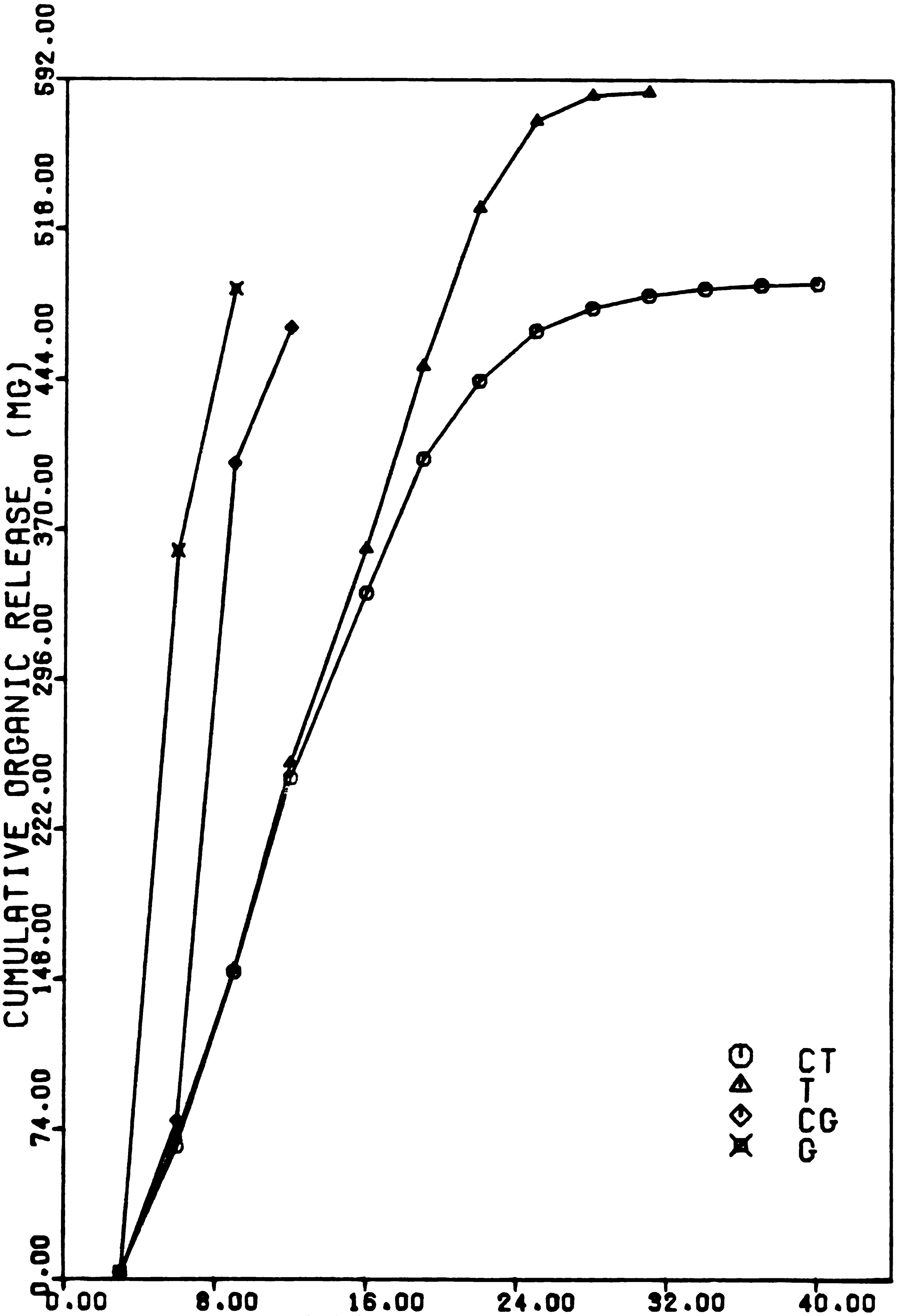

CUMULATIVE ORGANIC RELEASE (MG)
LIQUID APPLIED*65 (ML)
0.00
74.00
148.00
222.00
296.00
370.00
444.00
518.00
592.00
0.00
8.00
16.00
24.00
32.00
40.00
CT
T
CG
G

Figure E.2 Total release of the glucose and tryptophane from the zinc columns

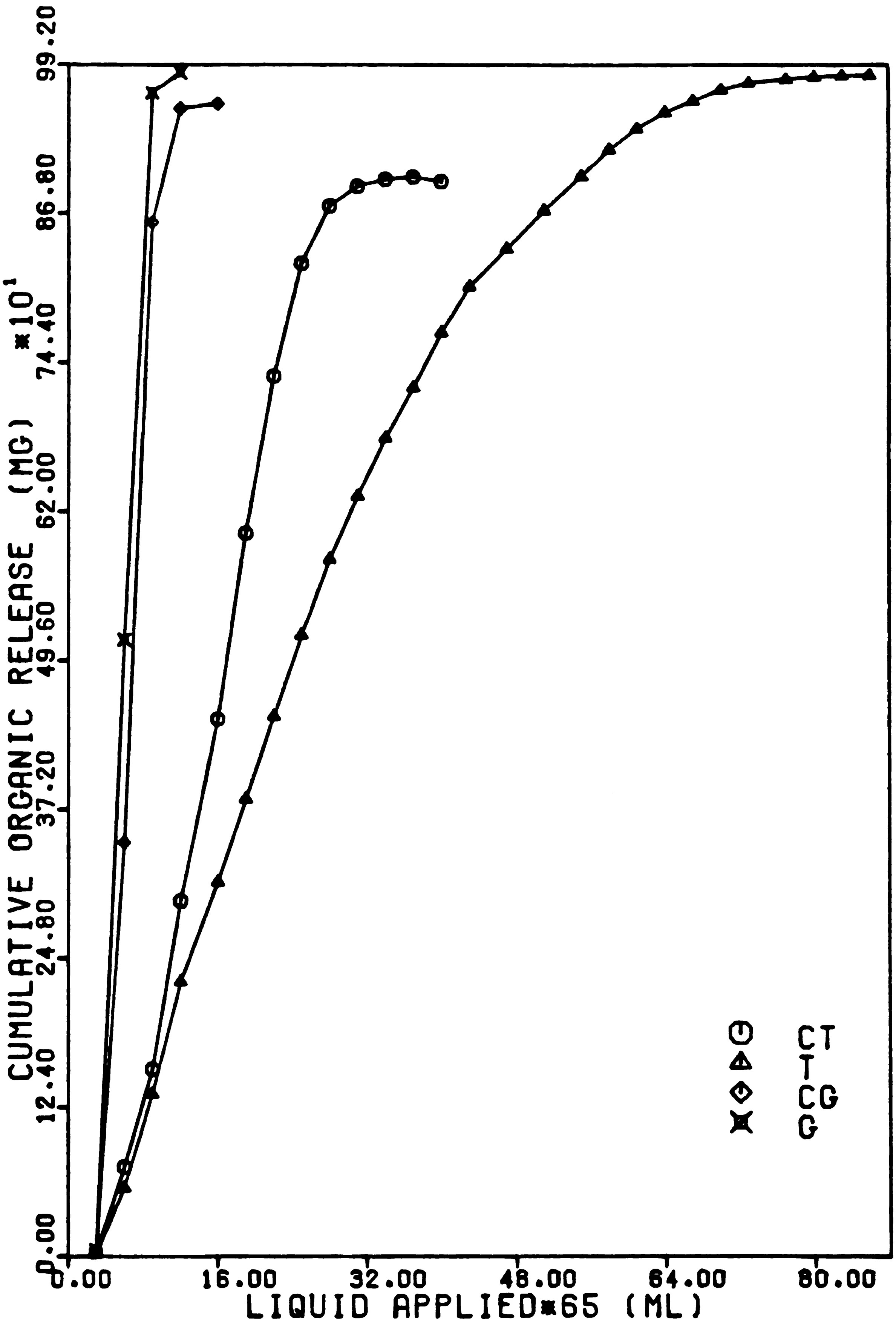

CUMULATIVE ORGANIC RELEASE (MG) *10¹
0.00
12.40
24.80
37.20
49.60
62.00
74.40
86.80
99.20
0.00
16.00
32.00
48.00
64.00
80.00
LIQUID APPLIED*65 (ML)
CT
T
CG
G

Table E.9 Glucose and Tryptophane Remained in the Adsorption Columns, mg

	G	CG	T	CT
Cd columns	11	30	NA	8
Zn columns	15	41	17	102

Sample calculations for Tables E.1 to E.8

The sample calculation is given for Table E.1, i.e., CdG:

Col. 1 - Concentration of glucose measured in the leachate sample mg/l, for example 60 mg/l, 5,500 mg/l, etc.

Col. 2 - The cumulative concentration of glucose = ΣCol. 1.

Col. 3 - (0.065 l)(Col. 2), example:

$$(0.065)(60) = 3.9$$

The 65 ml is the volume applied, and collected to and from a particular adsorption column.

Col. 4 - Error = (5 mg/l)(α)(65 ml)(1 l/1,000 ml)(N)

N = 1 for the first measurement, therefore:

Error = 0.9 mg, where α = 2.75 for glucose (see below)

Col. 5 - Net cumulative release = Col. 3 - Col. 4, example

3.9 - .9 = 3.0 mg.

α, the correction factor to convert the total carbon measured to the appropriate organic was found as below:

For glucose

$$\alpha = \frac{\text{MW } C_6H_{12}O_6 \cdot H_2O}{6\ C} = \frac{198}{72} = 2.75$$

For tryptophane

$$\alpha = \frac{\text{MW } C_{11}H_{12}O_2N_2}{11\ C} = \frac{204}{132} = 1.545$$

For cellulose

$$\alpha = \frac{n(C_6H_{10}O_5)}{6nC} = \frac{162}{72} = 2.25$$

APPENDIX F

SAMPLE CALCULATIONS

Columns in each table is numbered, starting from the first data column, Col., in the left side of the table.

Table 3.6

Col. 1 See Appendix D

Col. 2 (83 ml)(5.5g/100 ml dry content) = 4.565 g

Col. 4, Col. 3 (Col. 2)(Cation content from Table 3.6)

(4.565 g)(6.763 mg/g dry) = 30.873 mg

Table 4.4

Values are all those from Table 4.3 plus 7.37 and 4.4 for the zinc and cadmium columns, respectively.

Example for Zn-G columns:

0.71 (from Table 4.3) + 7.32 = 8.03 mg

Table 4.5

Values of Table 4.3 divided by their weight left in the adsorption columns (from Table 4.1).

Example

0.71 mg/0.015 g = 47.3 mg/g

Table 4.6

Values of Table 4.5 divided by equivalent weight of zinc or cadmium.

$$\text{me Zn} = \frac{\text{atomic wt (mg)}}{\text{valance}} = \frac{65}{2} = 32.5 \text{ mg}$$

$$\text{me Cd} = \frac{112}{2} = 56 \text{ mg}$$

example: 47.3 / 32.5 = 1.45 me/g

Table 4.14

See Table 4.5.

Table 4.15

See Table 4.6.

APPENDIX G

EXPERIMENTAL DATA

G.1 Field Condition

The result of the adsorption tests under the field condition are shown in Tables G.1 to G.4. The adsorption values that are reported are calculated in comparison to the leachates from the columns. The procedure adopted for this calculation was as follows:

1. Find the average of the cation effluent concentration (i.e., the average of 5 values) for the sand, AVGS, and the test column (AVG X, with X being G, T, Cel, C, CG, CT and CCel).
2. Calculate the total applied cation as

   mg applied = [Volume applied (l)][AVGS (mg/l)]

   where the volume applied each time was 65 ml.
3. Calculate the amount adsorbed, at each particular time, for each adsorbent as:

   mg adsorbed = (mg applied) - [(Volume applied)(AVGX)]

   or

   mg adsorbed = 0.065 (AVGS - AVGX)

The total period of the experiment was 4.5 months. The experiment started in early May and continued until mid September.

Table G.1--Adsorption of Zinc--Field Condition

	MG ZN APPLIED	ADSORPTION CLAY MG	ADSORPTION T MG	ADSORPTION CT MG	ADSORPTION G MG	ADSORPTION CG MG	ADSORPTION CEL MG	ADSORPTION CCEL MG
1	.07	.00	-.01	.00	-.01	.00	.00	.00
2	18.20	.02	-.02	.02	.02	.02	.02	.02
3	1142.05	1.14	-.84	1.12	.18	1.13	1.06	1.14
4	1313.00	1.31	.41	1.30	-.42	1.31	.16	1.31
5	1846.00	1.85	-.59	.92	.03	1.85	.30	1.85
6	2099.50	2.10	-.65	1.93	.05	2.10	.26	2.10
7	2232.75	2.23	-.19	2.10	.45	2.23	.42	2.23
8	1943.50	1.94	-.34	1.92	-.10	1.92	-.05	1.94
9	2135.25	2.10	-.46	2.12	.24	2.06	.17	2.13
10	2496.00	2.35	.06	2.49	.16	2.35	.21	2.45
11	2437.50	2.24	-.10	2.43	.13	2.19	.12	2.30
12	2294.50	1.99	-.02	2.24	0.00	1.93	.23	2.06
13	2151.50	1.79	-.27	2.00	0.00	1.66	-.21	1.81
14	2203.50	1.76	-.21	2.02	0.00	1.65	.10	1.78
15	2164.50	1.68	-.14	1.97	0.00	1.56	.03	1.68
16	2587.00	1.90	.18	2.27	0.00	1.84	.06	1.93
17	2424.50	1.60	.01	1.96	0.00	1.52	.03	1.62
18	2159.00	1.23	.01	1.58	0.00	1.16	.10	1.29
19	2145.00	1.03	0.00	1.41	0.00	1.02	.10	1.13
20	3087.50	1.43	-.07	2.10	0.00	1.16	.07	1.81
21	2340.00	1.33	-.11	1.52	0.00	1.04	.16	1.32
22	2502.50	1.12	.06	1.52	0.00	.98	0.00	1.20
23	2307.50	1.03	-.07	1.34	0.00	1.15	0.00	1.13
24	1966.25	.72	-.24	.93	0.00	.73	-.25	.81
25	2340.00	1.11	.02	1.29	0.00	.94	.26	1.05
26	3217.50	1.40	.60	2.02	0.00	.96	1.01	1.67
27	2795.00	.89	-.08	1.11	0.00	.56	.10	.81
28	2697.50	.61	.19	.96	0.00	.52	.21	.52
29	2275.00	.33	-.15	.44	0.00	.30	-.11	.36
30	2502.50	.64	0.00	.82	0.00	.53	.17	.58
31	2437.50	.46	0.00	.46	0.00	.27	.03	.42
32	2340.00	.33	0.00	.56	0.00	.20	.04	.46
33	2665.00	.56	0.00	.57	0.00	.44	.18	.60
34	2632.50	.45	0.00	.54	0.00	.37	0.00	.41
35	2860.00	.48	0.00	.56	0.00	.32	0.00	.39
36	2691.00	.83	0.00	.40	0.00	.23	0.00	.25
37	2840.50	.50	0.00	.51	0.00	.38	0.00	.40
38	2626.00	.29	0.00	.44	0.00	.41	0.00	.50
39	2600.00	.38	0.00	.29	0.00	.25	0.00	.36
40	2587.00	.36	0.00	.28	0.00	.27	0.00	.38
41	2567.50	.29	0.00	.35	0.00	.29	0.00	.33

Table G.2 Adsorption of Cadmium--Field Condition

	MG CD APPLIED	ADSOPPTION CLAY MG	ADSORFTION T MG	ADSORP TION CT MG	ADSORPTION G MG	ADSORPTION CG MG	ACSOPPTICN CEL MG	ADSORPTICN CCFL MG
1	.07	.00	.00	.00	.00	.00	.00	.00
2	37.83	.04	-.09	.04	.01	.04	.04	.04
3	754.00	.75	.07	.75	-.07	.72	.66	.75
4	1173.25	1.17	-.34	1.16	.05	1.15	-.17	1.17
5	2223.00	2.22	.05	2.17	.02	2.18	.16	2.22
6	2414.75	2.32	-.06	2.29	.01	2.31	.93	2.41
7	2447.25	2.24	.06	2.28	.07	2.23	.35	2.36
8	2470.00	2.04	.10	2.20	0.00	2.09	.06	2.21
9	2421.25	1.83	.02	1.93	-.01	1.84	.07	1.95
10	2580.50	1.75	-.01	1.84	.01	1.76	.01	1.86
11	2421.25	1.52	0.00	1.66	.04	1.57	.07	1.55
12	2486.25	1.55	.18	1.57	0.00	1.56	.15	1.42
13	2447.25	1.65	-.02	1.45	0.00	1.33	.03	1.36
14	2372.50	1.25	-.07	1.32	0.00	1.24	.04	1.21
15	2476.50	1.12	-.07	1.19	0.00	1.05	.01	1.00
16	2459.50	.95	-.09	1.10	0.00	.89	0.00	.99
17	2408.25	.79	.03	.90	0.00	.72	.09	.75
18	2470.00	.89	0.00	.95	0.00	.85	.03	.89
19	2486.25	.83	0.00	.96	0.00	.81	.08	.84
20	2405.00	.57	0.00	.60	0.00	.56	.11	.59
21	2405.00	.68	0.00	.66	0.00	.60	.10	.68
22	2522.00	.67	0.00	.71	0.00	.67	.18	.70
23	2372.50	.45	0.00	.55	0.00	.36	.03	.51
24	2518.75	.55	0.00	.56	0.00	.47	.03	.56
25	2388.75	.43	0.00	.48	0.00	.36	.06	.46
26	2437.50	.39	0.00	.33	0.00	.19	-.10	.34
27	2535.00	.47	0.00	.57	0.00	.50	.13	.51
28	2476.50	.48	0.00	.47	0.00	.44	.06	.43
29	2567.50	.49	0.00	.44	0.00	.47	.23	.43
30	2372.50	.28	0.00	.32	0.00	.30	.02	.32
31	2320.50	.33	0.00	.31	0.00	.20	.01	.27
32	2502.50	.30	0.00	.30	0.00	.25	.09	.31
33	2453.75	.33	0.00	.24	0.00	.25	.13	.27
34	2567.50	.28	0.00	.31	0.00	.26	0.00	.34
35	2405.00	.12	0.00	.19	0.00	.23	0.00	.19
36	2567.50	.19	0.00	.12	0.00	.12	0.00	.25
37	2882.75	.25	0.00	.26	0.00	.23	0.00	.33
38	2730.00	.10	0.00	.12	0.00	.11	0.00	.13
39	2860.00	.26	0.00	.28	0.00	.37	0.00	.39
40	2574.00	.11	0.00	.09	0.00	.14	0.00	.14
41	2502.50	.04	0.00	.04	0.00	.00	0.00	.00

Table G.3 Cumulative Adsorption of Zinc--Field Condition

	MG ZN APPLIED	ADSORPTION CLAY MG	ADSORPTION T MG	ADSORPTION CT MG	ADSORPTION G MG	ADSORPTION CG MG	ADSORPTION CFL MG	ADSORPTION CCFL MG
1	.00	.00	-.01	.00	-.01	.00	.00	.00
2	.02	.02	-.03	.02	.01	.02	.02	.02
3	1.16	1.16	-.37	1.13	.20	1.15	1.08	1.16
4	2.47	2.47	-.46	2.44	-.23	2.46	1.24	2.47
5	4.32	4.32	-1.05	3.36	-.20	4.31	1.53	4.32
6	6.42	6.42	-1.70	5.29	-.16	6.41	1.80	6.42
7	8.65	8.65	-1.89	7.40	.29	8.64	2.22	8.65
8	10.60	10.59	-2.23	9.31	.19	10.56	2.18	10.59
9	12.73	12.69	-2.69	11.43	.43	12.62	2.35	12.72
10	15.23	15.03	-2.63	13.92	.59	14.97	2.56	15.18
11	17.66	17.27	-2.74	16.35	.71	17.15	2.68	17.48
12	19.96	19.26	-2.76	18.60	.71	19.08	2.92	19.54
13	22.11	21.05	-3.02	20.60	.71	20.74	2.71	21.35
14	24.31	22.81	-3.23	22.62	.71	22.39	2.81	23.14
15	26.48	24.48	-3.37	24.59	.71	23.95	2.84	24.81
16	29.06	26.39	-3.19	26.86	.71	25.80	2.90	26.74
17	31.49	27.99	-3.18	28.82	.71	27.32	2.92	28.37
18	33.65	29.21	-3.17	30.40	.71	28.48	3.02	29.65
19	35.79	30.24	-3.17	31.81	.71	29.50	3.12	30.79
20	38.88	31.67	-3.24	33.91	.71	30.66	3.18	32.59
21	41.22	32.99	-3.35	35.43	.71	31.71	3.34	33.91
22	43.72	34.11	-3.29	36.95	.71	32.68	3.34	35.11
23	46.03	35.15	-3.36	38.29	.71	33.83	3.34	36.24
24	48.00	35.86	-3.60	39.22	.71	34.57	3.09	37.05
25	50.34	36.97	-3.59	40.51	.71	35.51	3.35	38.10
26	53.55	38.37	-2.99	42.52	.71	36.47	4.36	39.77
27	56.35	39.26	-3.06	43.53	.71	37.03	4.46	40.58
28	59.85	39.87	-2.87	44.59	.71	37.55	4.67	41.10
29	61.32	40.20	-3.03	45.03	.71	37.85	4.56	41.46
30	63.82	40.84	-3.03	45.85	.71	38.39	4.73	42.04
31	66.26	41.30	-3.03	46.31	.71	38.65	4.76	42.46
32	68.60	41.64	-3.03	46.87	.71	38.86	4.80	42.92
33	71.27	42.19	-3.03	47.44	.71	39.29	4.98	43.51
34	73.90	42.64	-3.03	47.98	.71	39.67	4.98	43.93
35	76.76	43.12	-3.03	48.54	.71	39.99	4.98	44.32
36	79.45	43.95	-3.03	48.94	.71	40.22	4.98	44.57
37	82.29	44.46	-3.03	49.45	.71	40.50	4.98	44.96
38	84.92	44.75	-3.03	49.99	.71	41.02	4.98	45.47
39	87.52	45.13	-3.03	50.19	.71	41.27	4.98	45.82
40	90.10	45.49	-3.03	50.45	.71	41.54	4.98	46.21
41	92.67	45.78	-3.03	50.81	.71	41.83	4.99	46.53

Table G.4 Cumulative Adsorption of Cadmium--Field Condition

	MG CD APPLIED	ADSOPPTION CLAY MG	ADSORPTION T MG	ADSCRPTION CT MG	ADSORPTION G MG	ADSORPTICN CG MG	ADSOFPTION CFL MG	ADSOPPTICN CCFL MG
1	.00	.00	.00	.00	.00	.00	.00	.00
2	.04	.04	-.09	.04	.01	.04	.04	.04
3	.79	.79	-.02	.78	-.07	.76	.70	.79
4	1.97	1.97	-.36	1.94	-.01	1.91	.53	1.97
5	4.19	4.19	-.31	4.11	.01	4.09	.70	4.19
6	6.60	6.51	-.37	6.40	.02	6.40	1.62	6.59
7	9.05	8.75	-.32	8.58	.09	8.63	1.97	8.06
8	11.52	10.79	-.22	10.87	.09	10.73	2.03	11.17
9	13.94	12.62	-.19	12.81	.07	12.57	2.09	13.12
10	16.52	14.37	-.21	14.65	.09	14.33	2.11	14.99
11	18.94	15.99	-.21	16.30	.12	15.90	2.19	16.54
12	21.43	17.43	-.03	17.97	.12	17.46	2.33	17.96
13	23.88	19.09	-.05	19.42	.12	18.79	2.36	19.32
14	26.25	20.34	-.12	20.74	.12	20.03	2.40	20.53
15	28.73	21.46	-.19	21.93	.12	21.08	2.41	21.53
16	31.22	22.41	-.28	23.03	.12	21.97	2.41	22.53
17	33.62	23.20	-.25	23.93	.12	22.69	2.49	23.28
18	36.09	24.09	-.25	24.88	.12	23.54	2.52	24.16
19	38.58	24.92	-.25	25.74	.12	24.35	2.60	25.00
20	40.98	25.49	-.25	26.34	.12	24.91	2.71	25.59
21	43.39	26.16	-.25	27.01	.12	25.51	2.81	26.28
22	45.91	26.84	-.25	27.72	.12	26.18	2.99	26.97
23	48.28	27.28	-.25	28.27	.12	26.54	3.02	27.48
24	50.80	27.83	-.25	28.83	.12	27.01	3.05	28.04
25	53.19	28.26	-.25	29.31	.12	27.36	3.11	28.50
26	55.63	28.65	-.25	29.64	.12	27.56	3.01	28.84
27	58.16	29.12	-.25	30.21	.12	28.05	3.14	29.35
28	60.64	29.60	-.25	30.68	.12	28.50	3.20	29.78
29	63.21	30.10	-.25	31.12	.12	28.97	3.43	30.21
30	65.58	30.37	-.25	31.44	.12	29.27	3.45	30.53
31	67.90	30.70	-.25	31.74	.12	29.47	3.47	30.80
32	70.40	31.01	-.25	32.05	.12	29.72	3.55	31.12
33	72.86	31.34	-.25	32.28	.12	29.97	3.63	31.39
34	75.42	31.63	-.25	32.59	.12	30.23	3.68	31.73
35	77.83	31.74	-.25	32.78	.12	30.46	3.68	31.92
36	80.40	31.93	-.25	32.90	.12	30.58	3.69	32.17
37	83.28	32.18	-.25	33.15	.12	30.81	3.69	32.50
38	86.01	32.28	-.25	33.27	.12	30.92	3.69	32.63
39	88.87	32.54	-.25	33.55	.12	31.29	3.68	33.02
40	91.44	32.64	-.25	33.63	.12	31.43	3.68	33.15
41	93.95	32.68	-.25	33.69	.12	31.43	3.69	33.15

G.2 Adsorption Measurement Based on Freundlich Equation

Table G.1 indicates that the amount of adsorptions in the Zn-clay column were 6.42 mg for the first 5 points (see Figure 4.), excluding the zero value of adsorption. It was 39.36 mg for the remaining measurements.

G.3 Flooding Condition

Data of the flooding condition are shown in Tables G.5 to G.20.

G.4 Desorption Data

The leachate of the sludge columns were analyzed for both zinc and cadmium. The results are shown in Table G.21. The concentrations are the average of 5 values. The total zinc and cadmium content of the sludge columns may be calculated using the information furnished in Table 3.6, Table G.22.

Sample Calculations

Raw sludge - Cd

$$(10 \text{ dry ton/ac})(2{,}000 \text{ lbs/ton})(454 \text{ gr/lb})(1 \text{ ac}/43{,}560 \text{ ft}^2)$$

$$(1 \text{ ft}^2/144 \text{ in}^2) \cdot (2^2 \cdot \pi/4)(0.029 \text{ mg/g}) = 0.132$$

Table G.5 Flooding of the Sand Column with Cd Solution

Cumulative ml Applied	Cumulative Cd Applied mg	Release of Cd µg	Cumulative Release mg	Cumulative Adsorption mg
60	0.569	279.	0.279	0.290
120	2.844	1,306.8	1.585	1.261
160	4.361	1,418.6	3.004	1.357
260	8.153	3,729.5	6.734	1.448
360	11.945	3,782.0	10.519	1.492

First 105 ml had no Cd content and was discarded.

Rate of the flow was measured to be 40 ml/min.

Concentration of the Cd solution input was 37.92 mg/l.

Table G.6 Flooding of Glucose Column with Cd Solution

Cumulative ml Applied	Cumulative Cd Applied mg	Release of Cd µg	Cumulative Release mg	Cumulative Adsorption mg
32	1.058	16	0.016	1.042
72	2.626	500	0.516	2.110
112	4.194	1,160	1.676	2.518
192	7.330	2,848	4.524	2.806
312	12.034	4,560	9.084	2.950
392	15.170	3,120	12.204	2.966
512	19.872	4,704	16.908	2.966

Rate of the flow was measured to be 40.37 ml/min.

Concentration of the Cd solution input was 39.2 mg/l.

Table G.7 Flooding of Tryptophane Column with Cd Solution

Cumulative Volume Applied (ml)	Cumulative Cd Applied (mg)	Release of Cd (μg)	Cumulative Release (mg)	Cumulative Adsorption (mg)
5	.185	3.125	.003	.182
51	1.891	690.000	.693	1.198
111	4.116	1,925.100	2.618	1.498
171	6.341	2,150.100	4.768	1.573
282	10.457	4,035.405	8.804	1.653
392	14.535	4,010.600	12.814	1.721
530	19.652	5,045.970	17.860	1.792
722	26.772	7,059.84	24.920	1.852
957	35.486	8,664.45	33.585	1.901
1,147	42.531	7,025.25	40.610	1.921

Rate of the flow was measured to be 37.94 ml/min.

Concentration of the Cd solution input was 37.08 mg/l.

Table G.8 Flooding of Cellulose Column with Cd Solution

Cumulative Volume Applied (ml)	Cumulative Cd Applied (mg)	Release of Cd (μg)	Cumulative Release (mg)	Cumulative Adsorption (mg)
5	.274	0	0	.274
87	3.406	1,234.4	1.234	2.172
167	6.538	2,712.4	3.947	2.591
287	11.236	4,502.4	8.449	2.787
367	14.368	3,047.6	11.497	2.871
487	19.066	4,594.8	16.092	2.974
687	26.896	7,716	23.808	3.088
767	30.028	3,101.6	26.909	3.119
887	34.726	4,664.8	31.574	3.152
1,313	51.412			3.152

Rate of the flow was measured to be 39.7 ml/min.

Concentration of the Cd solution input was 39.15 mg/l.

Table G.9 Flooding of Clay Column with Cd Solution

Cumulative Volume Applied (ml)	Cumulative Cd Applied (mg)	Release of Cd (μg)	Cumulative Release (mg)	Cumulative Adsorption (mg)
28	1.098	1.82	.002	1.096
65	2.548	124.505	.126	2.422
115	4.508	545.000	.671	3.837
165	6.468	872.500	1.544	4.924
225	8.820	1,367.400	2.911	5.909
265	10.388	1,090.200	4.001	6.387
324	12.701	1,692.120	5.693	7.008
374	14.661	1,456.750	7.150	7.511
441	17.287	1,988.560	9.139	8.148
509	19.953	2,089.640	11.228	8.725
654	25.637	4,646.525	15.875	9.762
814	31.909	5,250.400	21.125	10.784
982	38.494	5,567.520	26.693	11.801
1,182	46.334	6,764.000	33.457	12.877
1,347	52.802	5,763.450	39.220	13.582
1,565	61.348	7,730.280	46.951	14.397
1,825	71.540	9,275.500	56.226	15.314
2,009	78.753	6,587.200	62.813	15.940
2,247	88.082	8,550.150	71.363	16.719
2,577	101.018	11,908.050	83.271	17.747
3,263	127.910	24,960.110	108.128	19.782
3,718	145.746	16,748.550	124.809	20.937
4,300	168.560	21,792.990	146.544	22.016
4,860	190.512	21,277.200	167.695	22.817
5,560	217.952	26,747.000	194.291	23.661

Rate of the flow was measured to be 6.10 ml/min.

Concentration of the Cd solution input was 39.2 mg/l.

Table G.10 Flooding of Clay • Glucose Column with Cd Solution

Cumulative Cd Applied (ml)	Release of Cd (μg)	Cumulative Release (mg)	Cumulative Adsorption (mg)
1.564	225.	.225	1.339
4.223	669.8	.895	3.338
7.233	1,316.7	2.211	5.022
10.725	1,981.35	4.193	6.532
14.271	2,292.3	6.485	7.786
17.790	2,461.9	8.947	8.843
24.477	5,048.8	13.996	10.481
30.029	4,416.2	18.412	11.617
33.939	3,283.	21.695	12.244
39.804	5,037.75	26.733	13.071
43.127	2,902.75	29.635	13.492
46.451	2,950.8	32.586	13.865
49.970	3,183.75	35.770	14.200
55.248	4,864.7	40.635	14.613
60.527	4,953.8	45.589	14.938
68.269	7,359.7	52.948	15.321
84.886	15,992.75	68.941	15.945
90.751	5,686.5	74.627	16.124
118.004	26,628.9	101.256	16.748
128.756	10,532.5	111.789	16.967
156.908	27,576	139.365	17.543
165.119	8,086.	147.451	17.668
185.647	20,230.9	167.682	17.965

Rate of the flow was measured to be 7.07 ml/min.

Concentration of the Cd solution input was 39.1 mg/l.

Table G.11 Flooding of Clay • Tryptophane Column with Cd Solution

Cumulative Cd Applied (ml)	Release of Cd (μg)	Cumulative Release (mg)	Cumulative Adsorption (mg)
.586	4.	.004	.582
3.089	81.6	.086	3.003
5.904	354.	.440	5.464
9.032	684	1.124	7.908
12.160	960	2.084	10.076
15.288	1,164	3.248	12.040
21.270	2,595	5.843	15.427
26.236	2,559.	8.402	17.834
29.794	2,056.6	10.458	19.336
31.749	1,220.	11.678	20.071
33.704	1,302.5	12.981	20.723
35.659	1,354.	14.335	21.324
38.005	1,635.	15.970	22.035
41.524	2,551.5	18.521	23.003
45.747	3,309.7	21.831	23.916
50.204	3,701.	25.532	24.672
61.934	10,207.5	35.739	26.195
66.900	4,429.	40.168	26.732
88.210	19,355.7	59.524	28.686
98.962	10,014.1	69.538	29.424
124.377	23,907.	93.445	30.932
132.588	7,783.6	101.229	31.359
152.138	18,625	119.854	32.284

Rate of the flow was measured to be 8.59 ml/min.

Concentration of the Cd solution input was 39.1 mg/l.

Table G.12 Flooding of Clay • Cellulose Column with Cd Solution

Cumulative Volume Applied (ml)	Cumulative Cd Applied (mg)	Release of Cd (µg)	Cumulative Release (mg)	Cumulative Adsorption (mg)
22	0.868	1.1	0.002	0.867
49	1.934	4.32	0.006	1.928
77	3.039	18.48	0.025	3.014
118	4.657	91.84	0.117	4.540
174	6.868	356.44	0.473	6.395
230	9.078	651.00	1.124	7.954
293	11.565	1,004.85	2.129	9.436
362	14.288	1,311.00	3.440	10.848
556	21.945	4,675.40	8.115	13.830
756	29.838	5,840.00	13.955	15.883
936	36.944	5,564.70	19.520	17.424
1,118	44.127	6,016.92	25.537	18.590
1,253	49.456	4,697.32	30.234	19.222
1,458	57.547	7,236.50	37.471	20.076
1,695	66.902	8,492.89	45.964	20.938
2,871	73.848	6,403.76	52.368	21.480
2,119	83.637	9,023.48	61.391	22.246
2,449	96.662	11,936.10	73.327	23.335
3,139	123.896	25,398.90	98.726	25.170
3,569	140.868	16,172.30	114.898	25.970
4,073	160.761	19,068.84	133.967	26.794
4,613	182.075	20,520.00	154.487	27.588
5,413	213.651	30,600.00	185.087	28.564

Rate of the flow was measured to be 5.9 ml/min.

Concentration of the Cd solution input was 39.47 mg/l.

Table G.13 Flooding of Sand with Zn Solution

Cumulative Volume Applied (ml)	Cumulative Zn Applied (mg)	Release of Zn (μg)	Cumulative Release (mg)	Cumulative Adsorption (mg)
65	2.226		0.156	2.070
225	7.706		2.247	5.459
425	14.556		7.722	6.834
685	23.461		16.139	7.322
1,025	35.106		27.572	7.534
1,465	50.176			7.534

Rate of the flow was measured to be 40 ml/min.

Concentration of the Zn solution input was 34.25 mg/l.

Table G.14 Flooding of Glucose Column with Zn Solution

Cumulative Volume Applied (ml)	Cumulative Zn Applied (mg)	Release of Zn (μg)	Cumulative Release (mg)	Cumulative Adsorption (mg)
35.4	1.365		0.848	0.517
96.0	3.705		2.738	0.967
176.8	6.825		5.578	1.247
298.	11.505		9.898	1.607
378.9	14.625		12.778	1.847
443.5	17.121		15.007	2.114
637.5	24.609		21.938	2.671
799.2	30.849		27.874	2.975
1,041.7	40.209		36.994	3.215
1,162.9	44.889		41.614	3.275

Rate of the flow was measured to be 33.7 ml/min.

Concentration of the Zn solution input was 38.6 mg/l.

Table G.15 Flooding of Tryptophane Column with Zn Solution

Cumulative Volume Applied (ml)	Cumulative Zn Applied (mg)	Release of Zn (μg)	Cumulative Release (mg)	Cumulative Adsorption (mg)
55.6	2.145		0.324	1.821
96.	3.705		1.130	2.575
176.8	6.825		4.030	2.795
257.6	9.945		7.090	2.855
338.5	13.065		10.190	2.875
419.3	16.185		13.310	2.875

Rate of the flow was measured to be 40 ml/min.

Concentration of the Zn solution input was 38.6 mg/l.

Table G.16 Flooding of Cellulose Column with Zn Solution

Cumulative Volume Applied (ml)	Cumulative Zn Applied (mg)	Release of Zn (μg)	Cumulative Release (mg)	Cumulative Adsorption (mg)
65	2.226	5	0.005	2.221
225	7.706	1,336	1.341	6.365
425	14.556	4,460	5.801	8.755
685	23.461	7,767	13.568	9.893
1,025	35.106	11,092	24.660	10.446
1,465	50.176	14,905	39.565	10.611

Rate of the flow was measured to be 40 ml/min.

Concentration of the Zn solution input was 34.25 mg/l.

Table G.17 Flooding of Clay Column with Zn Solution

Cumulative Volume Applied (ml)	Cumulative Zn Applied (mg)	Release of Zn (μg)	Cumulative Release (mg)	Cumulative Adsorption (mg)
24	.902	.002	.002	.900
46	1.730	.005	.007	1.723
67	2.519	.002	.009	2.510
71	2.670	.000	.009	2.661
95	3.572	.003	.012	3.560
128	4.813	.010	.022	4.791
180	6.768	.028	.050	6.718
274	10.302	.282	.332	9.970
370	13.912	.936	1.268	12.644
442	16.619	.936	2.204	14.415
706	26.546	6.442	8.646	17.900
715	28.764	1.510	10.156	18.608
816	30.682	1.387	11.543	19.139
876	32.938	1.680	13.223	19.715
948	35.645	2.074	15.297	20.348
1,027	38.615	2.370	17.667	20.948
1,097	41.247	2.128	19.795	21.452
1,315	49.444	6.976	26.771	22.673
1,438	54.069	4.034	30.805	23.264
1,517	57.039	2.528	33.333	23.706
1,603	60.273	2.786	36.119	24.154
2,298	86.405	23.908	60.027	26.378
2,356	88.586	2.042	62.069	26.517
2,580	97.008	7.885	69.954	27.054
2,762	103.851	6.479	76.433	27.418

Rate of the flow was measured to be 1.85 ml/min.

Concentration of the Zn solution input was 37.5 mg/l.

Table G.18 Flooding of Clay • Glucose Column with Zn Solution

Cumulative Volume Applied (ml)	Cumulative Zn Applied (mg)	Release of Zn (μg)	Cumulative Release (mg)	Cumulative Adsorption (mg)
33	1.237	11.55	.011	1.226
57	2.137	6.72	.018	2.119
83	3.112	9.36	.028	3.084
88	3.3	1.95	.030	3.270
109	4.087	8.4	.038	4.049
139	5.212	26.7	.065	5.147
196	7.35	256.5	.321	7.029
266	9.975	742.	1.063	8.912
333	12.487	837.5	1.901	10.586
409	15.337	1,406.	3.307	12.030
616	23.1	5,212.26	8.519	14.581
668	25.05	1,309.36	9.828	15.222
716	26.85	1,315.68	11.144	15.706
769	28.837	1,472.34	12.616	16.221
833	31.237	1,848.96	14.465	16.772
903	33.862	2,022.3	16.488	17.374
966	36.225	1,913.31	18.401	17.824
1,169	43.837	6,390.44	24.791	19.046
1,282	48.075	3,682.67	28.474	19.601
1,352	50.7	2,281.3	30.755	19.945
1,431	53.662	2,662.3	33.418	20.244
2,229	83.587	27,187.86	60.605	22.982
2,262	84.825	1,148.73	61.754	23.071
2,403	90.1125	5,013.96	66.768	23.344
2,513	94.237	3,911.6	70.680	23.557

Rate of the flow was measured to be 1.69 ml/min.

Concentration of the Zn solution input was 37.5 mg/l.

Table G.19 Flooding of Clay Tryptophane Column with Zn Solution

Cumulative Volume Applied (ml)	Cumulative Zn Applied (mg)	Release of Zn (μg)	Cumulative Release (mg)	Cumulative Adsorption (mg)
25	.946	1.25	.001	.945
55	2.082	16.5	.018	2.064
105	3.974	87.5	.105	3.869
152	5.753	304.3	.410	5.343
202	7.646	455	.865	6.781
270	10.219	561	1.426	8.793
350	13.247	616	2.042	11.205
441	16.692	796	2.838	13.854
551	20.855	1,320	4.158	16.697
618	23.391	1,075	5.233	18.158
700	26.495	1,566	6.799	19.696
820	31.037	2,382	9.181	21.856
940	35.579	2,672	11.854	23.725
1,050	39.742	2,749	14.603	25.139
1,197	45.306	3,897	18.500	26.806
1,559	59.10	10,639	29.139	29.961
1,764	66.767	6,491	35.631	31.136
1,968	74.489	6,676	42.307	32.182
2,213	83.762	8,240	50.547	33.215
2,578	97.577	12,472	63.019	34.558

Rate of the flow was measured to be 2.91 ml/min.

Concentration of the Zn solution input was 37.85 mg/l.

Table G.20 Flooding of Clay • Cellulose Column with Zn Solution

Cumulative Volume Applied (ml)	Cumulative Zn Ayplied (mg)	Release of Zn (μg)	Cumulative Release (mg)	Cumulative Adsorption (mg)
58	2.03	1.45	.001	2.029
98	3.43	3.00	.004	3.426
223	7.805	12.50	.017	7.788
363	12.705	252.00	.269	12.436
448	15.680	488.75	.758	14.922
550	19.250	1,020.00	1.778	17.472
703	24.605	2,195.55	3.973	20.632
833	29.155	2,601.95	6.575	22.580
963	33.705	3,250.00	9.825	23.880
1,133	39.655	4,816.95	14.642	25.013
1,540	53.900	12,617.00	27.259	26.641
1,765	61.775	7,275.00	34.534	27.241
1,981	69.335	7,128.00	41.662	27.673
2,253	78.855	9,065.76	50.728	28.127
2,657	92.995	13,600.66	64.335	28.660

Rate of the flow was measured to be 3.00 ml/min.

Concentration of the Zn solution input was 35.0 mg/l.

Table G.21 Desorption of Zinc from the Raw and Digested Sludges

RAW SLUDGE					DIGESTED SLUDGE			
LOG RELEASE	LOG CUM. RELEASE	SINGLE RELEASE mg	CUM RELEASE mg	TIME (DAY)	LOG RELEASE	LOG CUM. RELEASE	SINGLE RELEASE mg	CUM RELEASE mg
		0.000	0.000	3.			0.000	0.000
		0.000	0.000	6.			0.000	0.000
		.004	.004	9.			0.000	0.000
		.024	.028	12.			.010	.010
		.053	.081	15.			.007	.017
.175	.256	.175	.256	19.			.005	.022
.195	.450	.195	.450	22.			.015	.037
.174	.624	.174	.624	25.			.020	.057
.176	.799	.176	.799	28.			.026	.083
.250	1.049	.250	1.049	31.			.023	.106
.427	1.476	.427	1.476	34.			.027	.133
.228	1.705	.228	1.705	37.			.017	.150
.204	1.909	.204	1.909	40.	.144	.293	.144	.293
.201	2.110	.201	2.110	44.	.150	.443	.150	.443
.203	2.313	.203	2.313	49.	.154	.597	.154	.597
.212	2.525	.212	2.525	52.	.134	.732	.134	.732
.228	2.752	.228	2.752	55.	.121	.853	.121	.853
.199	2.951	.199	2.951	58.	.118	.971	.118	.971
.202	3.154	.202	3.154	61.	.130	1.100	.130	1.100
.204	3.357	.204	3.357	64.	.165	1.265	.165	1.265
.181	3.539	.181	3.539	67.	.080	1.345	.080	1.345
.205	3.743	.205	3.743	70.	.122	1.467	.122	1.467
.204	3.947	.204	3.947	73.	.154	1.621	.154	1.621
.196	4.143	.196	4.143	77.	.156	1.777	.156	1.777
.196	4.339	.196	4.339	80.	.134	1.910	.134	1.910
.192	4.530	.192	4.530	83.	.136	2.046	.136	2.046
.177	4.707	.177	4.707	86.	.116	2.162	.116	2.162
.130	4.837	.130	4.837	89.	.095	2.256	.095	2.256
.127	4.964	.127	4.964	92.	.092	2.348	.092	2.348
.127	5.090	.127	5.090	95.	.095	2.443	.095	2.443
.125	5.215	.125	5.215	98.	.097	2.540	.097	2.540
.124	5.339	.124	5.339	101.	.093	2.633	.093	2.633
.128	5.467	.128	5.467	104.	.098	2.731	.098	2.731
.115	5.582	.115	5.582	107.	.085	2.816	.085	2.816
.118	5.699	.118	5.699	110.	.087	2.903	.087	2.903
.116	5.816	.116	5.816	113.	.104	3.007	.104	3.007
.116	5.932	.116	5.932	116.	.087	3.093	.087	3.093
.111	6.043	.111	6.043	119.	.077	3.170	.077	3.170
.080	6.123	.080	6.123	122.	.052	3.222	.052	3.222
.055	6.178	.055	6.179	125.	.031	3.253	.031	3.253
.066	6.244	.066	6.244	128.	.027	3.280	.027	3.280
.115	6.359	.115	6.359	131.	.092	3.373	.092	3.373
.061	6.420	.061	6.420	134.	.025	3.397	.025	3.397
.067	6.487	.067	6.487	137.	.031	3.428	.031	3.428
.039	6.526	.039	6.526	140.	.010	3.438	.010	3.438

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      PROGRAM FLICH(INPUT,OUTPUT)
C     THIS PROGRAM IS TO SEE IF OUR CATA WCULD FOLLOW THE FREUNDLICH
C     ISCTHERM.  IT WOULD MAKE 4 PLOTS OF LOGC  VS  LOGX/M WHERE X/M =
C     SOLID ADSORBED/GR OF ADSORBING SUBSTANCES  C=EQUIV. CONC.  HERE
C     X/M=(B/WT+AORG) AND C=(AVGC/AVGSL) FOR C WE NOTMALIZED THE VALUES.
      DIMENSION SL(5),C(5),ADC(43,7)
      DIMENSION A(43),CT(43),CG(43),CCEL(43),GGG(43,7),CEL(43)
      READ 17,WT,AC,AT,AG,ACEL,ACT,ACG
  17  FORMAT(7F10.5)
      K=1
    2 READ 10,(SL(I),I=1,5)
   10 FORMAT(5F5.2)
      IF(SL(1).EQ.1111.)GO TO 101
      AVGSL=(SL(1)+SL(2)+SL(3)+SL(4)+SL(5))/5
      DO 20 L=1,7
      READ 10,(C(J),J=1,5)          $  IF(C(1).EQ.999.)GO TO 18
      AVGC=(C(1)+C(2)+C(3)+C(4)+C(5))/5
      GGG(K,L)=AVGC/AVGSL
      ADC(K,L)=0.065*(AVGSL-AVGC)           $  GO TO 20
   18 ADC(K,L)=0.0
   20 CONTINUE
      K=K+1      $  GO TO 2
  100 CONTINUE
  101     B1=B2=B3=B4=S1=S2=S3=0.0
      PRINT 11
  11  FORMAT(*1*,8X,5HCEL/M,8X,8HCEL/SOIL)
          DO 40 KA=1,41
        B1=B1+ADC(KA,1)         $    B2=B2+ADC(KA,3)
        B3=B3+ADC(KA,5) $ B4=B4+ADC(KA,7)
      CT(KA)=B1/AC
      CG(KA)=B4/(AC+ACEL)
          IF(KA.GT.33)GO TO 40
          S1=S1+ADC(KA,6)
          CEL(KA)=S1/ACEL
          PRINT 9,CEL(KA),GGG(KA,6)
   40 CONTINUE
    9         FORMAT(* *,(8X,F6.2,6X,F10.5))
      SIXY1=SIXY2=SXI1=SXI2=SYI1=SYI2=SXI1SQ=SXI2SQ=SYI1SQ=SYI2SQ=0.0
      SIXY3=SXI3=SYI3=SXI3SQ=SYI3SQ=0.0
      PRINT 114
  114 FORMAT(*1*,2HKC,2(14X,4HSIXY,8X,3HSXI,8X,3HSYI,6X,5HSXISQ,10X,5HSY
     +ISQ))
C     ********** FOR CEL PORTION OF BOTH ZN AND CO ********************
          DO 112 KC=4,33,1
      SIXY1=SIXY1+(ALOG10(CEL(KC)))*(ALOG10(GGG(KC,6)))
      SXI1=SXI1+ALOG10(GGG(KC,6))
      SYI1=SYI1+ALOG10(CEL(KC))
      SXI1SQ=SXI1SQ+(ALOG10(GGG(KC,6)))**2.0
      SYI1SQ=SYI1SQ+(ALOG10(CEL(KC)))**2.0
      PRINT 113,KC,SIXY1,SXI1,SYI1,SXI1SQ,SYI1SQ
  113 FORMAT(* *,I2, (7X,4(4X,F7.3),4X,F11.3))
      IF(KC.EQ.33)GO TO 115
  112     CONTINUE
  115 BB1=(30.0*SIXY1-SXI1*SYI1)/(30.0*SXI1SQ-SXI1**2.0)
      AA1=SYI1/30.0-BB1*(SXI1/30.0)
      CCOEF1=(SIXY1-(SXI1*SYI1/30.0))/SQRT((SXI1SQ-(SXI1**2.0/30.0))*(
     +SYI1SQ-(SYI1**2.0/30.0)))
      PRINT 111,AA1,BB1,CCOEF1
  111 FORMAT(//20X,*A...*,F5.2,5X,*B...*,F5.2,15X,*R.....*,F6.4/)
      PRINT 99999
99999 FORMAT(* *,20X,*... FOR ZN-CELLULOSE  ................*)
      END
```

Table G.22 Total Zinc and Cadmium in Sludges

Sludge	Zn	Cd
Raw	30.873	0.132
Digested	22.970	0.064

APPENDIX H

STATISTICAL ANALYSIS

Program STAT1 was written in Fortran language and is used in CDC6500 computer. Inputing the data obtained for each adsorption column throughout the field condition study, the program then, compute and print the following: (i) the cumulative adsorption by each individual clay and clay·organic column; (ii) the average adsorption for each set of 5 columns; and (iii) the standard deviation of each average value. A copy of this program is included in this appendix.

H.1 Statistical Analysis for Table 4.3

The F test, $F = (S_1^2)/(S_2^2)$, was performed to determine whether or not the variables, or the standard deviations, s, are significantly different from each other. The comparison was made to the standard deviation of the clay columns, Table H.1.

Table H.1 Standard Deviation of the Total Adsorption by the Clay and Clay·Organic Adsorbents--Field Condition*

Cation	C	CG	CT	CCel
Zn	2.13	0.94	0.53	0.2
Cd	0.79	0.58	0.87	0.78

*Values are all in mg.

Table H.2 shows the values of $(S_1^2)/(S_2^2)$, where S_1 and S_2 are chosen to obtain a ratio of greater than one (see Table 4.5 for the standard deviations).

Table H.2 Variance Analysis--Ratio of $(S_1^2)/(S_2^2)$

Cation	C	CT	CG	CCel
Zn	1	16.15	5.13	113.4
Cd	1	1.21	1.85	1.02

The F value, for 4 and 4 degrees of freedom, was obtained from the F test table* and is found to be 6.39. Since all the ratios reported for cadmium, in Table H.1 are less than 6.39, therefore, the standard deviations are not significantly different. For the zinc columns, however, they are significantly different from the value reported for the clay columns.

H.1.1 Student t Statistics

Using the famous Student t test for the equality of means of two set of data having the same standard deviation, s, the cadmium results were tested. Table H.3 expresses the result where the average values are obtained from Table 4.3.

$$t = \frac{|\bar{X}_1 - \bar{X}_2|}{s} \sqrt{\frac{n_1 n_2}{n_1 + n_2}} \quad , \; n_1 + n_2 - 2 \text{ d.f.}$$

---

*CRC Mathematics Handbook.

Table H.3 Student t Analysis for the Cadmium

Adsorbent	Average Adsorption Values (mg)	t	Degrees of Freedom	t*
CG	31.43	2.61	8	2.31 (95%)
CT	33.68	2.1	8	1.86 (90%)
CCel	33.15	0.98	8	0.71 (60%)

t* = t Statistic from statistical tables

Therefore, the means are different from the Cd-clay adsorption by the probabilities equal or exceeding the values that are shown in the parentheses (see Table H.3).

H.1.2 Student t Test for the Zinc Data

Since the variances are different from each other, the following statistical analysis was used. Table H.4 expresses the results where the average values are obtained from Table 4.3.

$$t = \frac{|\overline{X}_1 - \overline{X}_2|}{\sqrt{\frac{(n_1-1)S_1^2 + (n_2-1)S_2^2}{n_1+n_2-2}}\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \qquad n_1+n_2-2 \text{ d.f.}$$

Table H.4 Comparison of the Means for the Zinc Data

Adsorbent	Average Adsorption Values (mg)	t	Degrees of Freedom	t*
CG	41.83	4.02	8	3.355 (99%)
CT	50.81	4.83	8	3.355 (99%)
CCel	46.53	0.784	8	0.71 (60%)

t* = t Statistic from statistical tables

Study of Table H.4 indicates that the means of the zinc clay•organic columns are different from the Zn-clay adsorption by the probabilities equal or exceeding the values that are shown in the parentheses (see Table H.4).

H.2 Statistical Analysis for Table 4.9

The adsorption results obtained for organic columns (e.g., for G: $G_1, G_2 \ldots G_5$) were added to the adsorption results obtained for the clay columns (i.e., C_1, $C_2 \ldots C_5$) in a random fashion such that G_1 was added to C_1, G_2 to C_2, and so on. The standard deviations of the products (i.e., for the 5 points) were found, Table H.5, utilizing the computer program STAT1. To test whether or not the standard deviations of the clay + organic columns, found in Table H.5 are significantly different from those of the clay organic columns, reported in Table H.1, Table H.6 was constructed.

Table H.5 Standard Deviation of Clay + Organic Columns (mg), Field Condition

Cation	C	CG	CT	CCel
Zn	2.13	2.23	2.40	1.91
Cd	0.79	0.68	0.74	0.69

Table H.6 Variance Ratios $(S_1^2)/(S_2^2)$ $(S_1 > S_2)$

Cation	CG	CT	Ccel
Zn	5.63	20.51	91.20
Cd	1.37	1.38	1.28

The F value for 4 and 4 degrees of freedom (5 - 1 = 4 for S_1^2, and 5 - 1 = 4 for S_2^2) was found using a F statistical table to be 6.39. Therefore, it is concluded that the standard deviations of the clay + organic columns and clay•organic columns were not significantly different from each other for cadmium columns, also the CG column of the zinc columns. They are different for the CT and CCel columns of the zinc applied columns.

H.2.1 Student t Analysis

The same method of analysis as was described in section H.1 of this appendix was used for the cadmium data, also for the CG column of the zinc columns, Table H.7 and H.8.

Table H.7 Student t Analysis of Cd Data

Adsorbent	Cation	Clay + Organic (mg)	Clay • Organic (mg)	AVG S (mg)	t	d.f.*	t**
CG	Cd	32.80	31.43	0.63	3.44	8	3.35 (99%)
CT	Cd	<32.80	33.68	0.81	1.72	8	1.63 (85%)
Ccel	Cd	36.36	33.15	0.74	6.86	8	3.35 (99%)

* degrees of freedom = n_1+n_2-2 = 5+5-2=8

**t* = t statistic from statistical tables

Therefore, the values are different from each other by the probabilities equal or exceeding the values that are shown in the parentheses, see Table H7 and H8.

Table H.8 Student t Analysis of Zn Data

Adsorbent	Cation	Clay + Organic (mg)	Clay • Organic (mg)	t	d.f.*	t**
CG	Zn	46.49	41.83	4.63	8	3.35 (99%)
CT	Zn	42.75	50.81	7.33	8	3.55 (99%)
CCel	Zn	50.76	46.53	6.09	8	3.55 (99%)

* d.f. = degrees of freedom

**t* = t statistic from statistical table

PROGRAM STAT1

```
      PROGRAM STAT1(INPUT,OUTPUT)
      DIMENSION SL(5),A(5,7),ADC(50,7,5)
      DIMENSION CC(5),CT(5),CG(5),CCEL(5)
      K=1
    2 READ 10,(SL(I),I=1,5)
   10 FORMAT(5F5.2)
      IF(SL(1).EQ.1111.)GO TO 101
      AVGSL=(SL(1)+SL(2)+SL(3)+SL(4)+SL(5))/5.0
          DO 20 L=1,7
          READ 10,(A(J,L),J=1,5)
          IF(A(1,L).EQ.999.)GO TO 11
      JA=0
   30 JA=JA+1
      IF(JA.GT.5)GO TO 20
  11  IF(A(1,L).EQ.999.)12,22
  22        ADC(K,L,JA)=0.065*(AVGSL-A(JA,L))
      GO TO 30
  12    CONTINUE
      DO 13 JC=1,5
      ADC(K,L,JC)=0.0
  13  CONTINUE
   20 CONTINUE
      K=K+1
      GO TO 2
  101 CONTINUE
      JJ=0
 111  C=T=G=CEL=0.0
      JJ=JJ+1
      IF(JJ.GT.5)GO TO 91
         DO 50  JB=1,41
      T=ADC(JB,1,JJ)+ADC(JB,2,JJ)+T
      G=ADC(JB,1,JJ)+ADC(JB,4,JJ)+G
      CEL=ADC(JB,1,JJ)+ADC(JB,6,JJ)+CEL
  50    CONTINUE
      PRINT 1
                     CT(JJ)=T   $   CG(JJ)=G   $   CCEL(JJ)=CEL
        PRINT 90,  T,G,CEL
  90   FORMAT(* *,30X,3F10.4)
      GO TO 111
   91 CONTINUE
         CTAVG=(CT(1)+CT(2)+CT(3)+CT(4)+CT(5))/5.0
         CGAVG=(CG(1)+CG(2)+CG(3)+CG(4)+CG(5))/5.0
        CCELAVG=(CCEL(1)+CCEL(2)+CCEL(3)+CCEL(4)+CCEL(5))/5.0
      PRINT 92
      PRINT 90,       CTAVG,CGAVG,CCELAVG
   92  FORMAT(*1*,20X,7X,         5X,5HAVGCT,5X,5HAVGCG,5X,
      +7HAVGCCEL)
      SQC=SCT=SQG=SQCEL=0.0
          DO 112 IA=1,5
         IF(CT(IA).EQ.CTAVG)GO TO 114
         SQT=SQT+(CT(IA)-CTAVG)**2.
  114    IF(CG(IA).EQ.CGAVG)GO TO 115
         SQG=SQG+(CG(IA)-CGAVG)**2.
  115    IF(CCEL(IA).EQ.CCELAVG)GO TO 112
         SQCEL=SQCEL+(CCEL(IA)-CCELAVG)**2.
 112  CONTINUE
  1   FORMAT(* *,*...PROGRAM IS WORKING TO HERE...........*)
      ST=SQRT(SQT/4.0)
      SG=SQRT(SQG/4.0)
      SCEL=SQRT(SQCEL/4.0)
      PRINT 210
  210 FORMAT(*1*,20X,2X  ,8X,2HST,8X,2HSG,6X,4HSCEL)
      PRINT 211,    ST,SG,SCEL
  211 FORMAT(* *,20X,3F10.5)
      END
```

APPENDIX I

FIT OF FREUNDLICH EQUATION

The computer program FLICH is written in Fortran language and was used to find the least square line parameters, correlation coefficients of the fit of the data to a straight line, and also to plot the scattered diagrams.

A typical scattered diagram was shown in Figure 4.7. Other scattered diagrams are shown in Figures I.1 to I.9.

Figure I.1 Freundlich Equation fitting for Zn-Cel

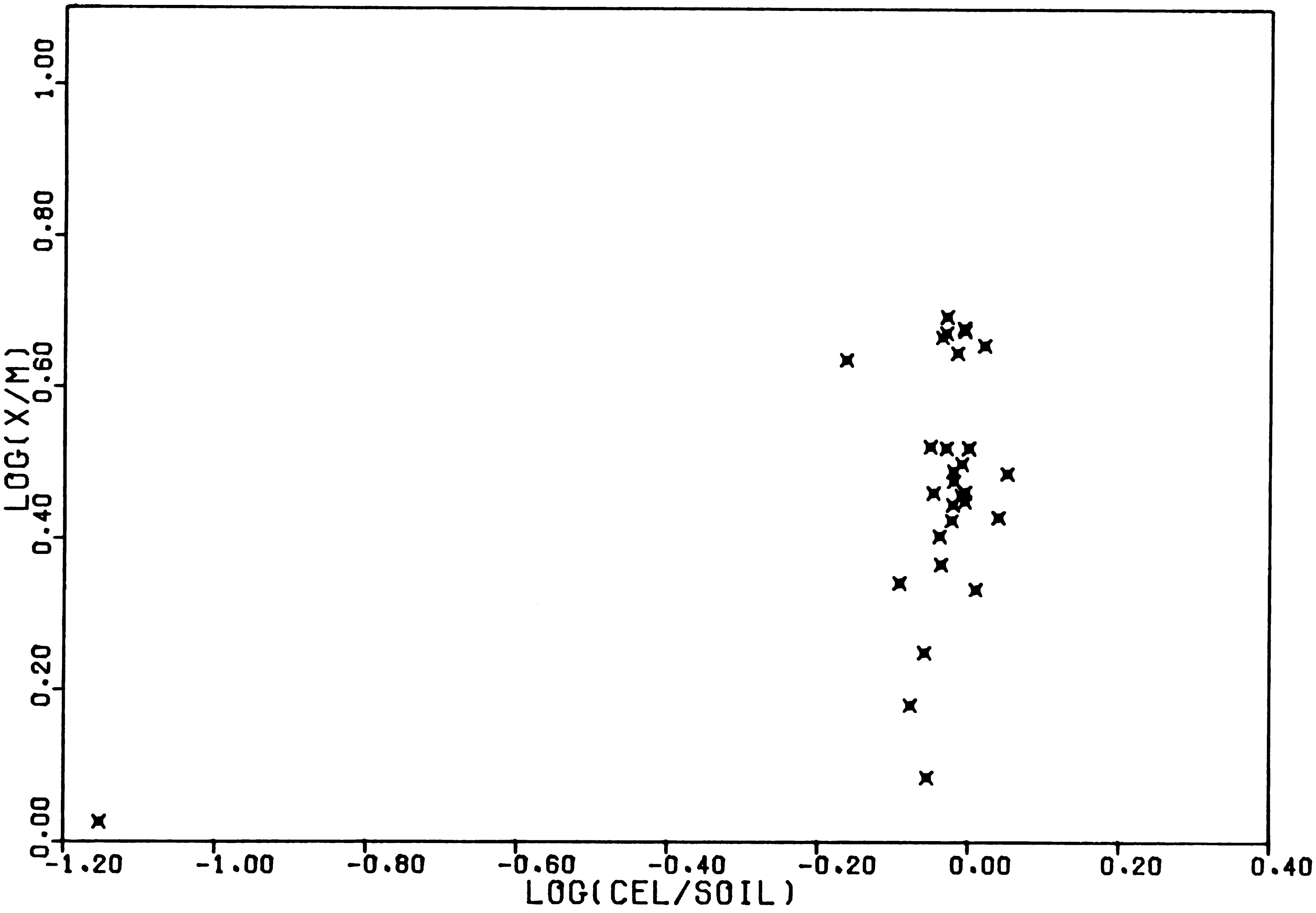

LOG(X/M)
0.00
0.20
0.40
0.60
0.80
1.00
-1.20
-1.00
-0.80
-0.60
-0.40
-0.20
0.00
0.20
0.40
LOG(CEL/SOIL)

Figure I.2 Freundlich Equation fitting for Zn-CG

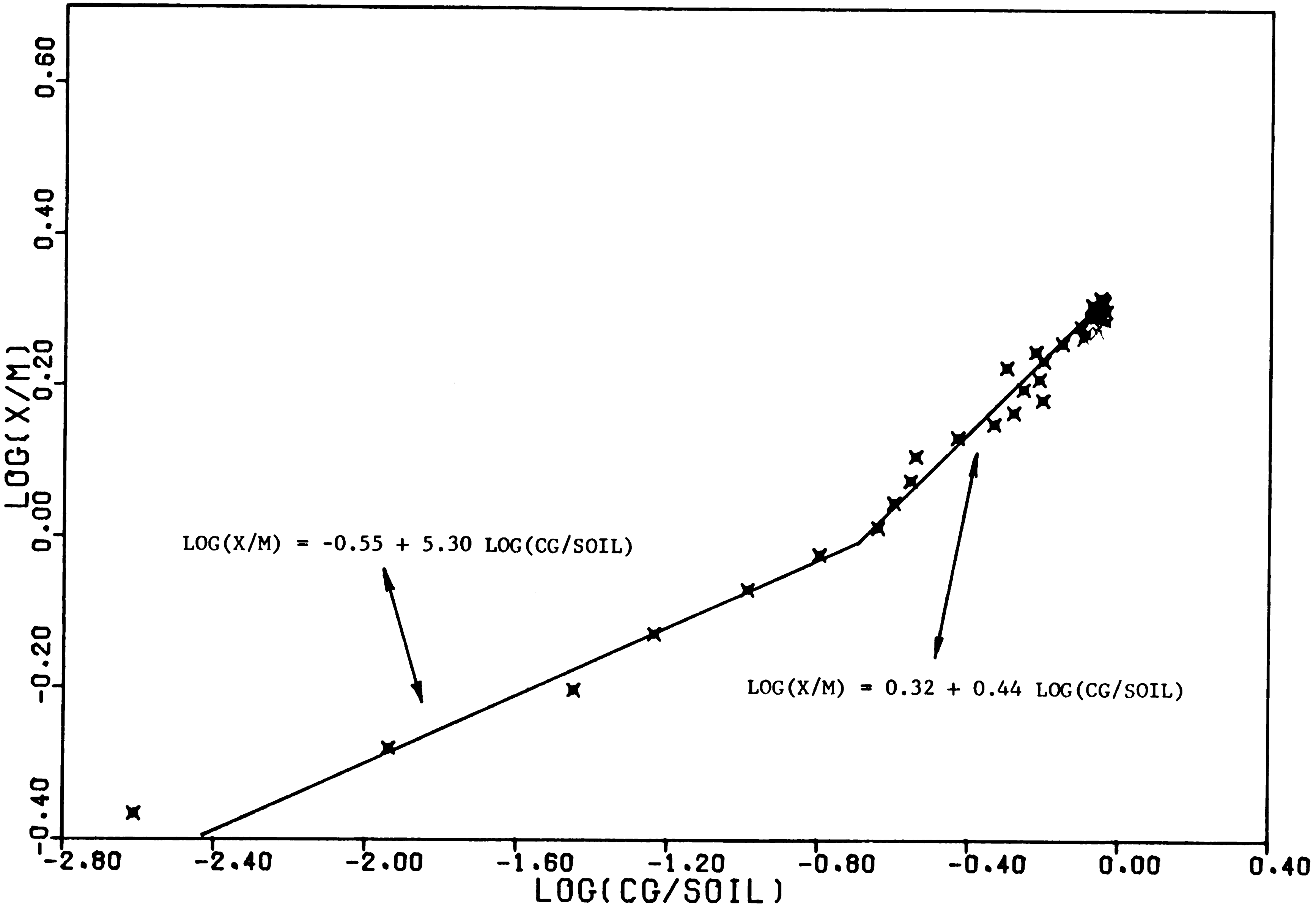

LOG(X/M)
LOG(CG/SOIL)
0.60
0.40
0.20
0.00
-0.20
-0.40
-2.80
-2.40
-2.00
-1.60
-1.20
-0.80
-0.40
0.00
0.40
LOG(X/M) = -0.55 + 5.30 LOG(CG/SOIL)
LOG(X/M) = 0.32 + 0.44 LOG(CG/SOIL)

Figure I.3 Freundlich Equation fitting for Zn-CT

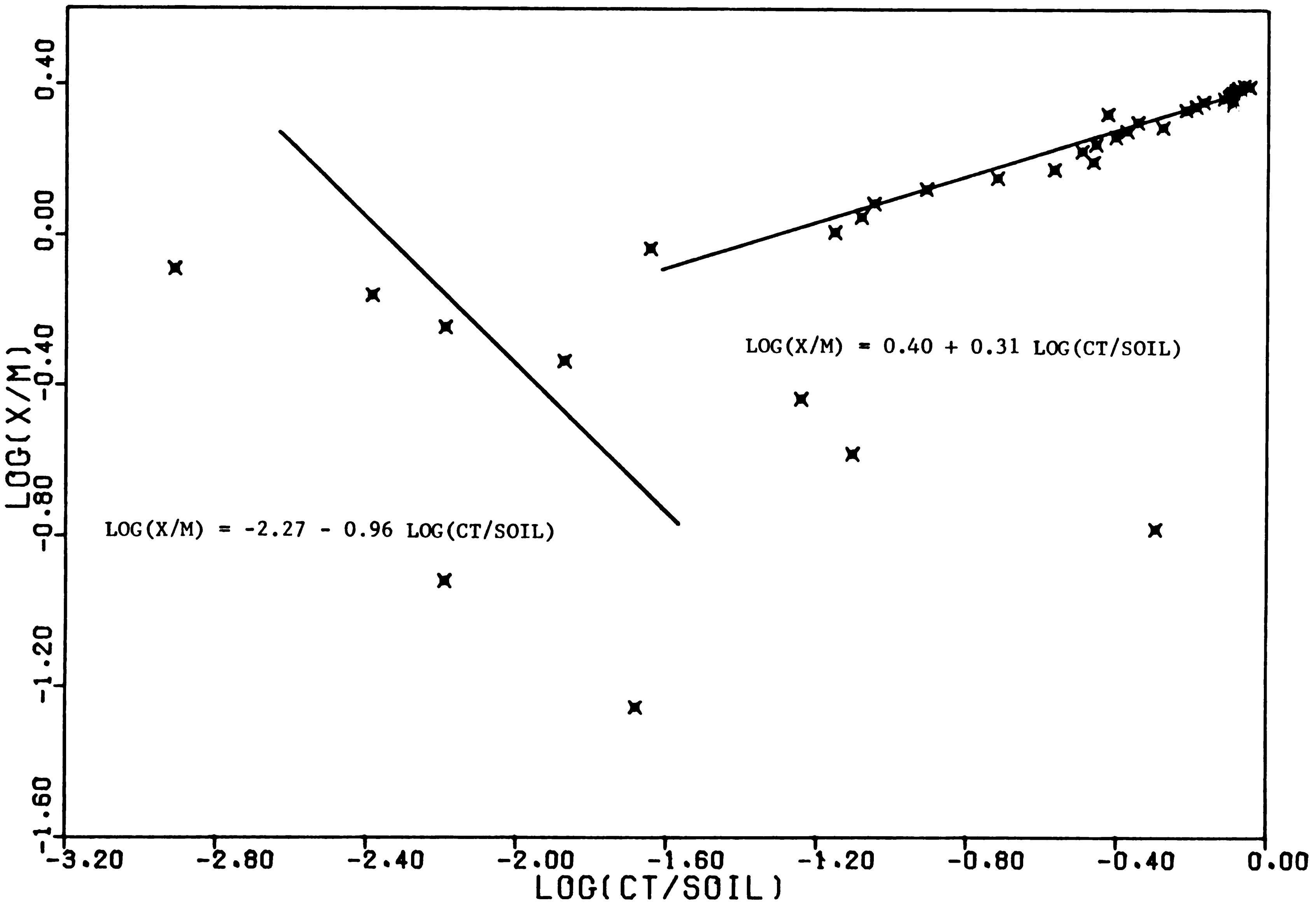

LOG(X/M) = 0.40 + 0.31 LOG(CT/SOIL)
LOG(X/M) = -2.27 - 0.96 LOG(CT/SOIL)
LOG(X/M)
0.40
0.00
-0.40
-0.80
-1.20
-1.60
LOG(CT/SOIL)
-3.20
-2.80
-2.40
-2.00
-1.60
-1.20
-0.80
-0.40
0.00

Figure I.4 Freundlich Equation fitting for Zn-Clay Cellulose

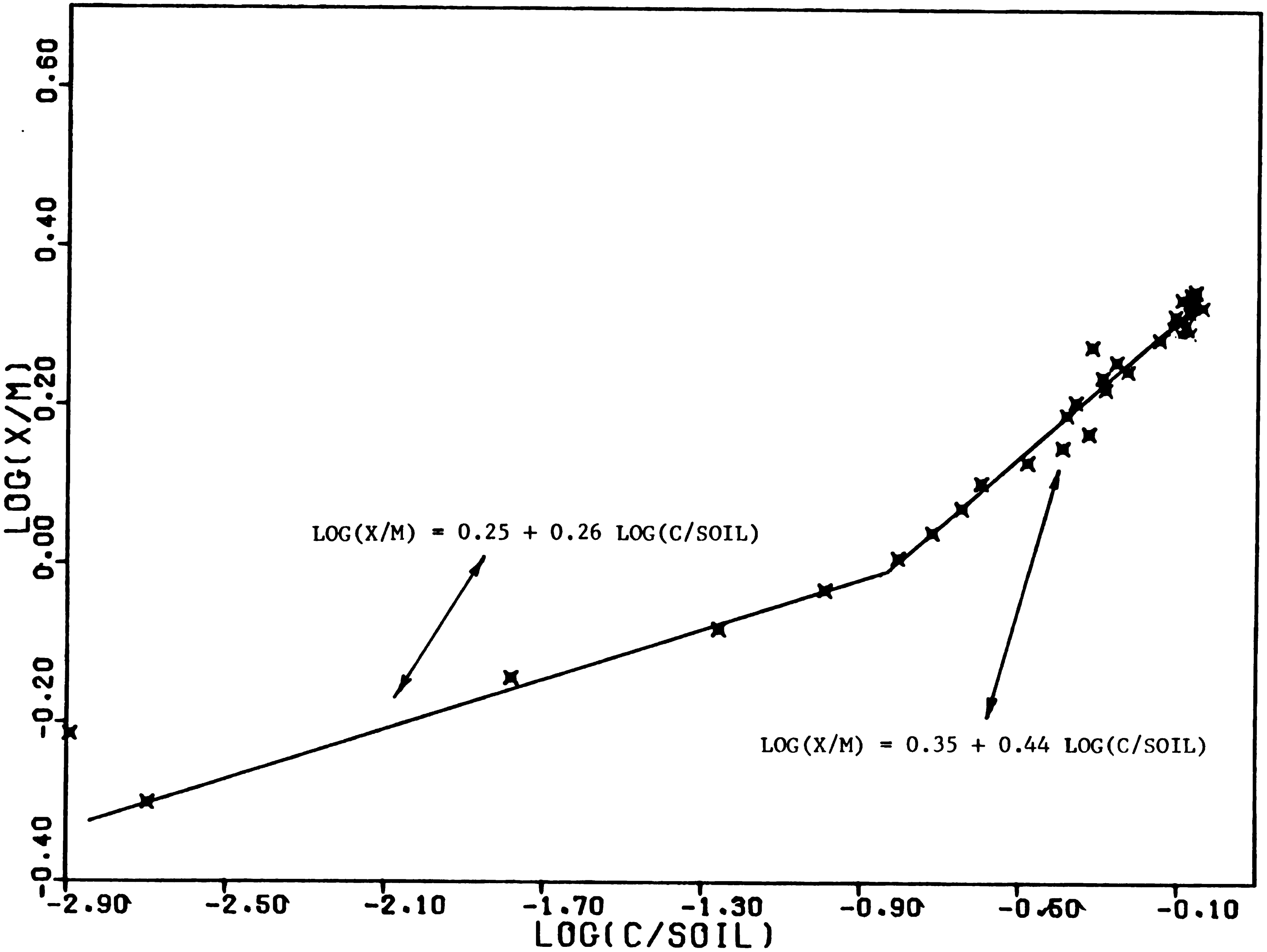

LOG(X/M) = 0.25 + 0.26 LOG(C/SOIL)
LOG(X/M) = 0.35 + 0.44 LOG(C/SOIL)
LOG(X/M)
0.60
0.40
0.20
0.00
-0.20
-0.40
-2.90
-2.50
-2.10
-1.70
-1.30
-0.90
-0.50
-0.10
LOG(C/SOIL)

Figure I.5 Freundlich Equation fitting for Cd-Cel

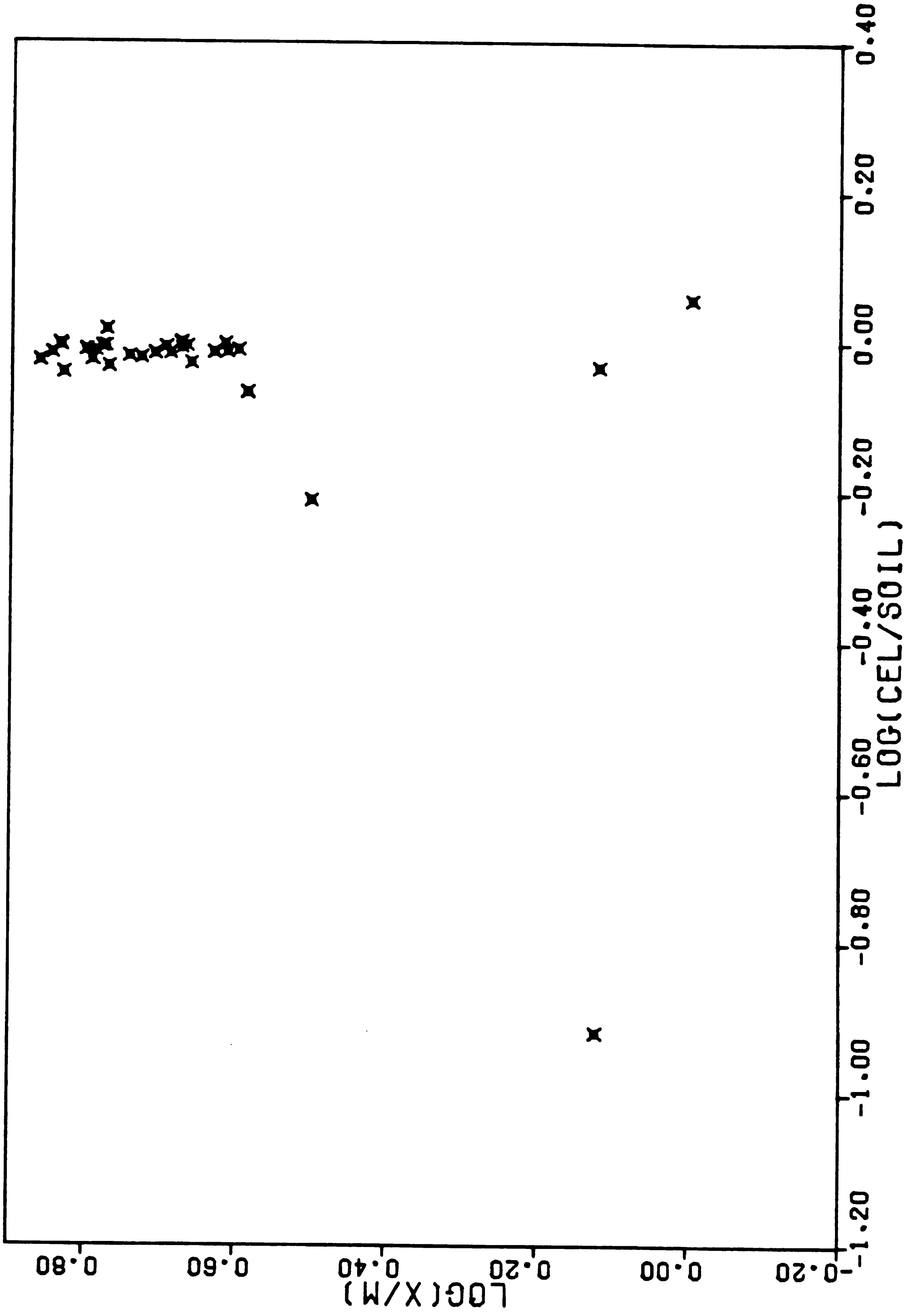

LOG(CEL/SOIL)
0.40
0.20
0.00
-0.20
-0.40
-0.60
-0.80
-1.00
-1.20
LOG(X/M)
-0.20
0.00
0.20
0.40
0.60
0.80

Figure I.6 Freundlich Equation fitting for Cd Clay

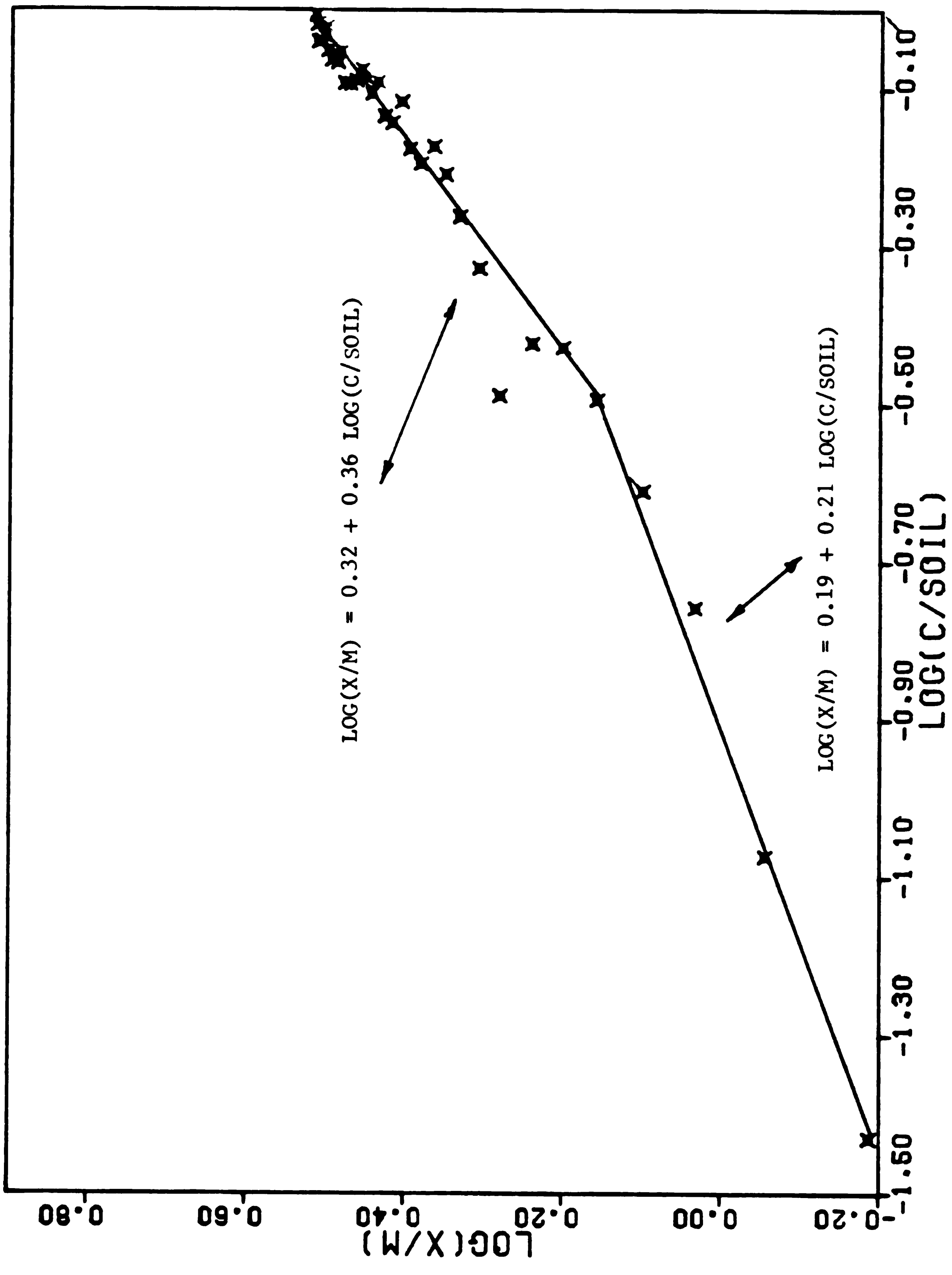

LOG(X/M) = 0.32 + 0.36 LOG(C/SOIL)
LOG(X/M) = 0.19 + 0.21 LOG(C/SOIL)
LOG(C/SOIL)
-1.50
-1.30
-1.10
-0.90
-0.70
-0.50
-0.30
-0.10
LOG(X/M)
-0.20
0.00
0.20
0.40
0.60
0.80

Figure I.7 Freundlich Equation fitting for Cd-CG

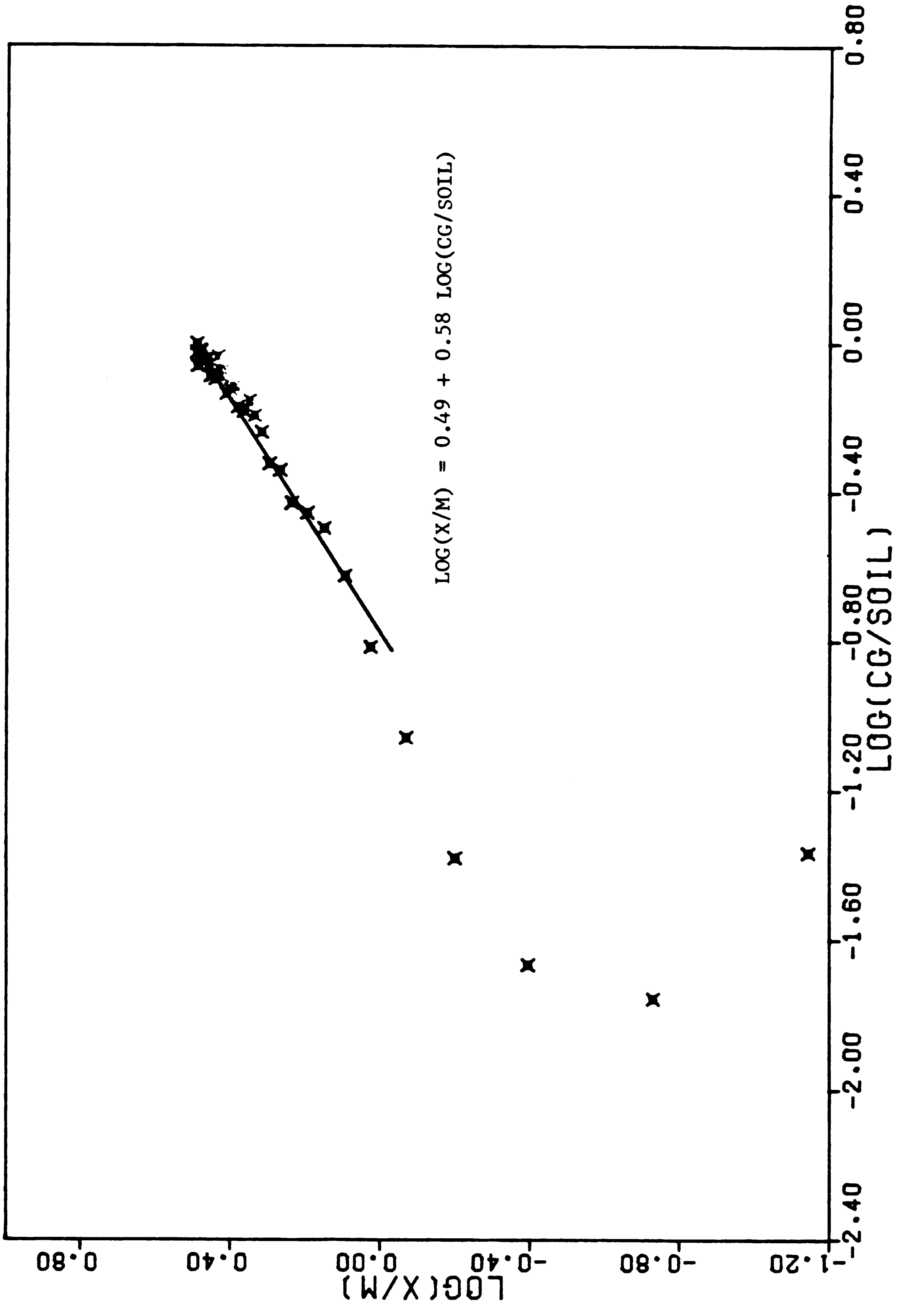

LOG(X/M) = 0.49 + 0.58 LOG(CG/SOIL)
LOG(CG/SOIL)
-2.40
-2.00
-1.60
-1.20
-0.80
-0.40
0.00
0.40
0.80
LOG(X/M)
-1.20
-0.80
-0.40
0.00
0.40
0.80

Figure I.8 Freundlich Equation fitting for Cd-CT

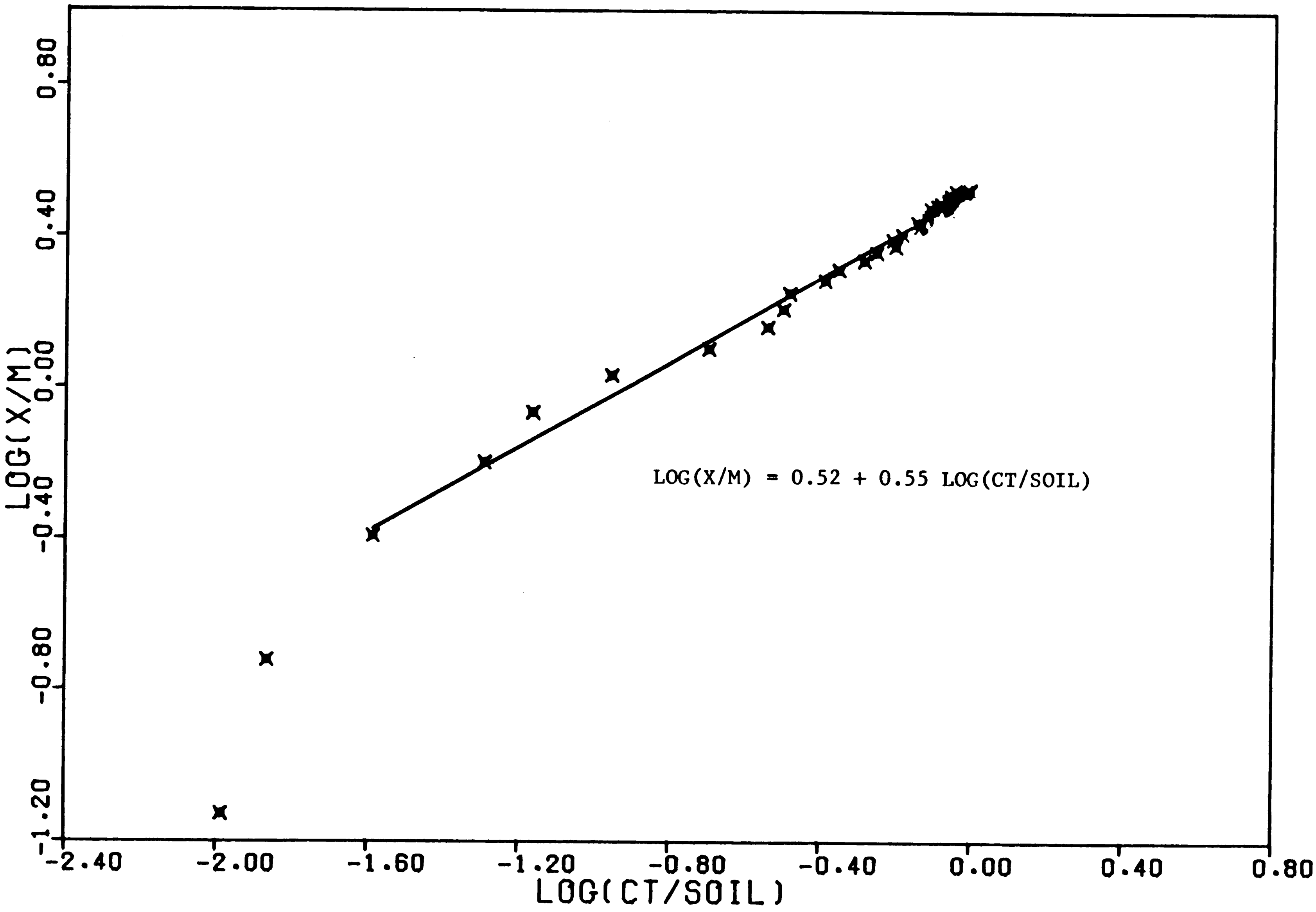
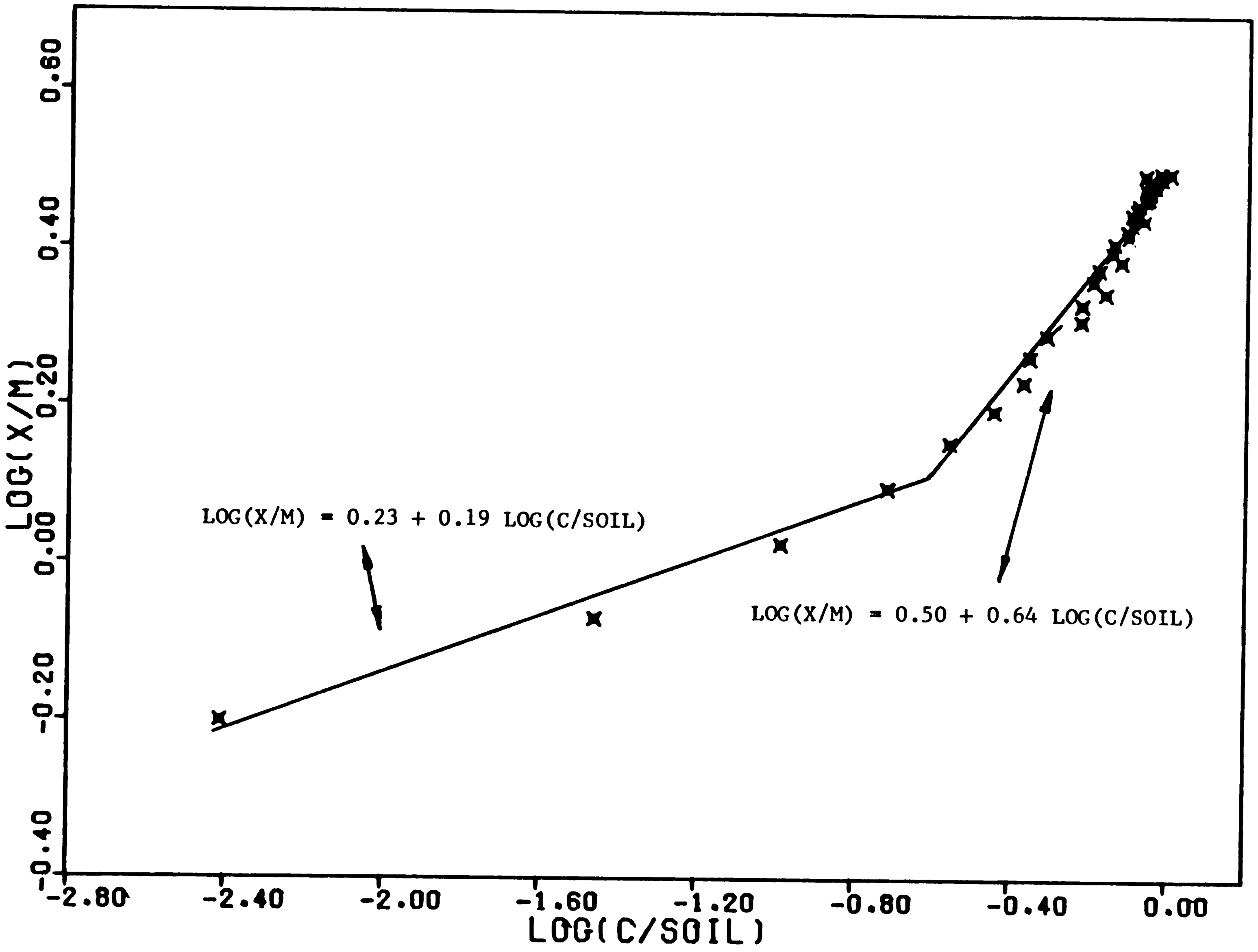

LOG(X/M) = 0.52 + 0.55 LOG(CT/SOIL)
LOG(X/M)
0.80
0.40
0.00
-0.40
-0.80
-1.20
LOG(CT/SOIL)
-2.40
-2.00
-1.60
-1.20
-0.80
-0.40
0.00
0.40
0.80

Figure I.9 Freundlich Equation fitting for Cd leached Clay-Cellulose


LOG(X/M) = 0.23 + 0.19 LOG(C/SOIL)
LOG(X/M) = 0.50 + 0.64 LOG(C/SOIL)
LOG(X/M)
-0.40
-0.20
0.00
0.20
0.40
0.60
LOG(C/SOIL)
-2.80
-2.40
-2.00
-1.60
-1.20
-0.80
-0.40
0.00

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