ASSESSMENT OF THE BIOSORPTIVE CAPACITY OF BIOLOGICAL SLUDGES FOR METAL CATIONS

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Project A-074-PR
Grant Agreement No. 14-34-0001-2141

FINAL TECHNICAL REPORT
TO
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D.C. 20240

"The research on which this report is based was financed in part by the U.S. Department of the Interior, as authorized by the Water Research and Development Act of 1978 (P.L.-95-467)".

June 1984

Table of Contents

List of Figures

Page

FIGURES:

List of figures...(con'd)

List of figures...(con'd)

List of figures...(con'd)

List of Tables

ACKNOWLEDGMENTS

Special recognition is given to Mrs. Alicia Balseira and Professor Félix Santiago for their role in the preliminary experiment of this study.

Mr. Jorge Pagán assumed most of the burden in all of the experiments but one. His dedication, enthusiasm, and interest, as well as the analytical skills he developed were crucial to the successful execution and completion of this project. I am deeply indebted to Mr. Pagán.

Mr. José Davis work and quiet dedication was very important to the successful completion of the project.

Mr. Luis Grajales aid in the laboratory and in all phases of work enabled us to finish our work properly on time.

A special note of thanks must be given to Mr. Johnny Pérez for his assistance with the equipment we needed.

Our very special thanks to Ms. Aida Feliciano for her excellent typing of the manuscript.

Finally, our heartfelt thanks to the Civil Engineering Department, to Dr. Rafael Muñoz Candelario, the Water Resources Research Institute and the Department of the Interior, for having supplied the facilities and the funds that made this study possible.

Introduction:

Large amounts of heavy metal ions find their way to the waters of the nation either through 1) domestic wastewaters, 2) stormwaters or 3) industrial wastewaters. The presence of heavy metal ions poses a serious threat to human health due to their toxic properties. The problem is compounded by the fact that normal biological treatment is generally incompatible with waste streams containing significant amounts of metal cations due to this toxicity. These difficulties, among others, stand in the way of increased water reuse both in Puerto Rico and in the continental United States.

Removal of heavy metal cations is possible through ion exchange, reverse osmosis, electrodyalisis and chemical precipitation. All of these alternatives involve the commitment of resources which are fairly expensive, thus discouraging their use. The discovery of an abundant, cheap matrix that could be used as a sorption matrix to remove these metals could therefore be of tremendous value and give a much needed push to the field of water reuse.

Recent research results by several investigators have indicated the ability of microbes to bind and concentrate heavy metals. This property has been designated biosorption and has been found to be based on the chemical composition of cell walls. This fact implies that even dead cell wall materials will exhibit good biosorptive properties. It has also been established in several cases that biosorptive capacity equals or exceeds the sorptive capacity of ion exchange resins or activated carbon.

There arises the interesting question as to whether treated wastewater sludges possess such a significant biosorptive capacity that it will permit them to substitute ion exchange resins, membranes, and expensive chemicals in the task of removing heavy metals from water cheaply and efficiently.

Research Objectives:

The objectives of this study are as follows:

1. To determine for which common heavy metallic cations there exists a significance biosorptive affinity in municipal wastewater sludges.
2. To determine the optimum pH range for the biosorptive capacity of sludge for a specific metal.
3. To determine the effect of different types of sludge treatment on biosorption.
4. To estimate biosorption capacity of sludge for specific metal cations at optimal conditions.
5. To compare biosorption capacities of sludge with the adsorption capacities of ion exchange resins.

Related Research:

Microorganisms have been shown to concentrate cations from their aquatic environment and, specifically, to concentrate heavy metal ions. Beveridge et al (1) has shown this phenomenon for Bacillus subtilis in particular and for bacterial walls in general (2). Chiu (3) documented the uptake of heavy metals by microbes. Elsabee et. al. (4) illustrated the relationship between cupric complexes and cell wall related structures. Paskins-Hurlburt et. al. (5) documented the relationship between biosorption of lead and a specific kind of microorganism.

Volesky et. al. (6) showed that biosorbent activity is not associated exclusively with living organisms but that it is present in dead biomass as well to perhaps an even greater degree. Biosorption has been specifically linked to the cell wall.

Volesky (7), and other workers (8,9,10) have gone beyond and demonstrated the feasibility of concentrating uranium, thorium, actinides and other valuable heavy metals from dilute radioactive wastes or seawater. This constitutes a discovery which opens up applications of immense potential.

The work done so far suggests that perphaps this biosorption property may be present in wastewater sludges and that therefore these may be useful in sequestering heavy metals from waters. It is intent of this proposal to investigate such a connection and to elucidate some of the parameters that enhance the biosorption phenomenon.

Research Procedure:

The following activities were performed as part of the experimental protocol:

1. A source of dried sludge was selected from a municipal wastewater treatment plant.
2. Information was collected on the operational characteristics of the plant and on the wet sludge characteristics before it was dried.
3. The dry sludge was then sifted to remove sand and other foreign matter, and then hand ground and passed through a sieve with 425 mm openings to insure uniform size particles. An appropiate number of samples was collected and weighted. Duplicates of each kind of experimental treatment were run.
4. Solutions of the desired metal were prepared by dissolving exact quantities of atomic absorption grade metal standard in redistilled deionized water to obtain the desired metal concentrations. Solution pH was adjusted as needed. Two

hundred milliliters of the above solutions were then added to the sludges samples in 250 ml erlenmeyer flasks. Blanks were utilized consisting of redistilled deionized water with the same initial concentration of metal as in the treated samples. These blanks were utilized to correct for changes in solubility due to pH and hydrolysis effects. Initial concentrations actually used for the treated samples were in fact the equilibrium concentrations of the dissolved metal species in the controls after the desired contact time for treatment.

5. A series of isotherm experiments were performed, utilizing a constant temperature water bath (Fisher Model 129) equipped with a shaker with capacity for 24 Erlenmeyer flasks (250 ml).

<u>Description of the Experiments</u>:

A description of the experiments performed is given in the following tables.

Table 1: Experiment X-1, Preliminary Identification of Most Significant Experimental Variables

Initial Concentration (mg/liter)	Mass of Sludge (grams)			
0.0	0.0000	2.0400	4.2783	8.0052
0.5	1.0777	2.0529	4.0538	8.0530
1.0	1.0774	2.0270	4.0123	8.2285
2.0	1.0140	2.2014	4.0367	8.2550
Contact Time (hrs)	1	2	4	8

pH = 3.0

The first experiment was meant to be a preliminary screening to get rough estimates of operational parameters, such as initial concentration, contact time, and sludge concentration. The results of this experiment were expected to help decide on the initial values for the significant parameters in the subsequent experiments. Initial metal concentration, sludge mass and contact time were all varied in order to get a rough idea of the most effective values for these parameter. In order to minimize hydrolysis effects, all samples were treated at pH 3.0. Volesky (7,8,9, 10) has used pH 3 extensively.

The sludge utilized in the first experiment was dried, aerobically digested sludge from the San Germãn municipal wastewater treatment plant. San Germãn is a town of about 50,000 people located about 20 minutes Southeast of Mayaguez (Fig. 1). The plant has a mean daily flow of about 1.1 million gallons per day (MGD) and treats an essentially domestic sewage. There is at least one significant industrial contributor, however. The Digital Equipment Corporation plant, every few days discharges a slug of dissolved metals into the system. The plant is a completely mixed activated sludge system with low speed surface aerators, without primary clarification.

The other experiments were designed partly on the basis of this first preliminary test. Their description is given in Table 2, which is self-explanatory.

Time was running out after the experimental series with Cadmium, so in order to proceed as fast as possible three mutually compatible metals were combined into a single series of experiments: nickel, zinc, and chromium. This combination was judged not to be detrimental in terms of competitive adsorption since the previous experiments with Cadmium had established the adsorption capacity of the sludge to be about 2 orders of magnitude above the 1 mg/l level.

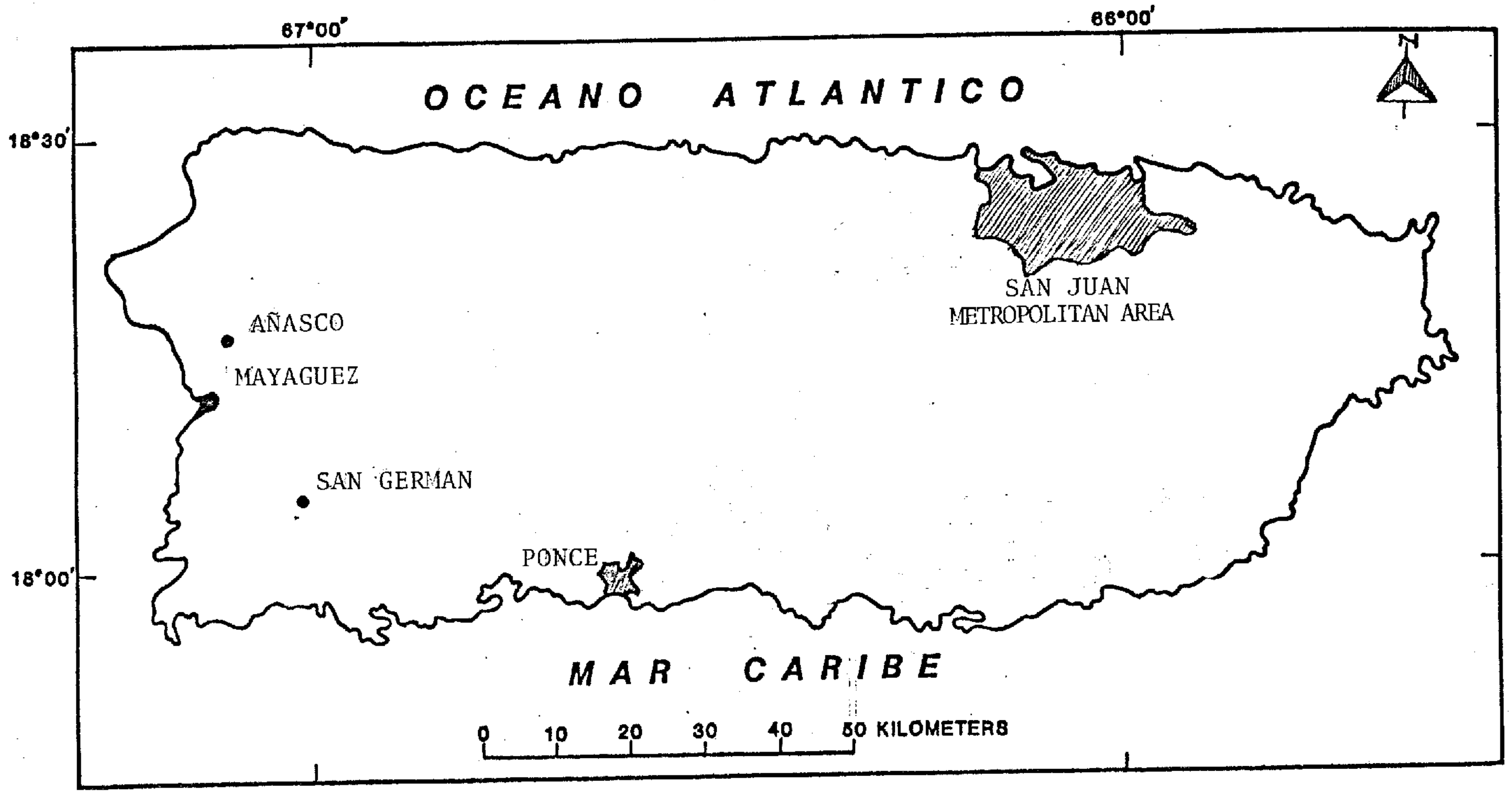

FIGURE 1. LOCATION MAP

Table 2: Description of Experiments

Experiment No.	Title	Temp. (°C)	Metal	Nominal* Initial Metal Conc. (mg/l)	Controls	Sludge Concent. (%)	Independent Variable	Values of Independent Variable	Dependent Variable	Contact Time (hrs)	pH
1	Effect of Hydrolysis and pH on the Solubility of Cadmium	20	Cd	0.5	aqueous solution w/o sludge	2	pH	3.0 4.5 5.5 7.0	Equilibrium dissolved Cd. concent.	4	Variable
2	Effect of Hydrolysis and pH on the Removal of Cadmium	20	Cd	0.5	experiment 1	2	pH	3.0 4.5 5.5 7.0	Equilibrium dissolved Cd. concent.	4	Variable
3	Effect of Contact Time on the Removal of Cadmium	20	Cd	0.5	aqueous solution w/o sludge	2	Contact Time	1 hr 2 hr 4 hr 8 hr	Equilibrium dissolved Cd. concent.	Variable	7.0
4	Effect of Initial Concentration on the Removal of Cadmium	20	Cd	Variable	aqueous solution w/o sludge	2	Initial Concentration	1 mg/l 10 mg/l 100 mg/l 1000 mg/l	Equilibrium dissolved	4	5.0
5	Analysis of Metal Content of Añasco Sludge	-	all	N.A.	N.A.	dry sludge	Constant sludge weight for all samples	3.0441 g. 3.1910 g. 2.8997 g. 2.5808 g.	mass of metal present on sludge	N.A.	N.A.
6A	Effect of Sludge Concentration on the Removal of Cadmium, Contact Time = 4 hours	20	Cd	0.1	aqueous solution w/o sludge	Variable	sludge concentration	1 % 2 4 8	Equlibrium dissolved metal concentration	4	7.0

*Initial metal concentration was actually taken to be the equilibrium concentration of the dissolved metal in the controls, in order to accurately correct for hydrolysis and pH effects.

Table 2: Cont'd.

Experiment No.	Title	Temp. (°C)	Metal	Nominal Initial Metal Conc. (mg/1)	Controls	Sludge Concent. (%)	Independent Variable	Values of Independent Variable	Dependent Variable	Contact Time (hrs)	pH
6B	Effect of Sludge Concentration on the Removal of Cadmium, Contact Time - 1 hour	20	Cd	0.1	aqueous solution w/o sludge	variable	Sludge concentration	1 % 2 4 8	Equilibrium dissolved metal concentration	1	7.0
6C	Effect of Sludge Concentration on the Removal of Cadmium, Contact Time = 2 hours	20	Cd	0.1	aqueous solution w/o sludge	Variable	Sludge concentration	1 % 2 4 8	Equilibrium dissolved metal concentration	2	7.0
7	Effect of Hydrolysis and pH on the Solubility of Nickel, Chromium, and Zinc	20	Ni, Cr,Zn	0.5	samples	2	pH	3.0 4.5 5.5 7.0	Equilibrium dissolved metal concentration	4	Variable
8	Effect of Hydrolysis and pH on the Removal of Nickel, Chromium, and Zinc	20	Ni Cr,Zn	0.5	experiment 7	2	pH	3.0 4.5 5.5 7.0	Equilibrium dissolved metal concentration	4	Variable
9	Effect of Contact Time on the Removal of Nickel, Chromium, and Zinc	20	Ni, Cr,Zn	0.5	aqueous solution w/o sludge	2	Contact Time	1 hrs 2 " 4 " 8 "	Equilibrium dissolved metal concentration	Variable	7.0
10	Effect of Initial Concentration on the Removal of Nickel, Chromium, and Zinc	20	Ni, Cr,Zn	Variable	aqueous solution w/o sludge	2	Initial Concentration	1 mg/1 10 " 100 " 1000 "	Equilibrium dissolved metal concentration	4	7.0
11	Effect os Sludge Concentration on the Removal of Nickel, Chromium, and Zinc, Contact Time = 4 hours	20	Ni, Cr,Zn	0.5	aqueous solution w/o sludge	Variable	Sludge Concentration	1 % 2 4 8	Equilibrium dissolved metal concentration	4	7.0

Table 2: Cont'd.

Experiment No.	Title	Temp. (°C)	Metal	Nominal Initial Metal Concent. (mg/l)	Controls	Sludge Concent. (%)	Independent Variable	Values of Independent Variable	Dependent Variable	Contact Time (hrs)	pH
12	Effect of Sludge Concentration on the Removal of Nickel, Chromium and Zinc, Contact Time = 1 hr	20	Ni, Cr,Zn	0.5	aqueous solution w/o sludge	Variable	Sludge Concentration	1 % 2 4 8	Equilibrium dissolved metal concentration	1	7.0
13	Effect of Sludge Concentration on the Removal of Nickel, Chromium and Zinc, Contact Time = 2 hours	20	Ni, Cr,Zn	0.5	aqueous solution w/o sludge	Variable	Sludge Concentration	1 % 2 4 8	Equilibrium dissolved metal concentration	2	7.0
14	Effects of Hydrolysis and pH on the Solubility of Lead	20	Pb	0.5	samples themselves	2	pH	3.0 4.5 5.5 7.0	Equilibrium dissolved metal concentration	4	Variable
15	Effect of Hydrolysis and pH on the Removal of Lead	20	Pb	0.5	experiment 14	2	pH	3.0 4.5 5.5 7.0	Equilibrium dissolved metal contration	4	7.0
16	Effect of Initial Concentration on the Removal of Lead	20	Pb	Variable	aqueous solution w/o sludge	2	Initial Concentration	1 mg/l 10 " 100 " 1000 "	same as above	4	7.0
17	Effect of Contact Time on the Removal of Lead	20	Pb	0.5	aqueous solution w/o sludge	2	Contact Time	1 hrs 2 " 4 8	same as above	Variable	7.0
18	Effect of Sludge Concentration on the Removal of Lead, Contact Time = 4 hrs.	20	Pb	0.5	Aqueous solution w/o sludge	Variable	Sludge Concentration	1 % 2 4 8	Same as	4.0	7.0

Table 2: Cont'd.

Experiment No.	Title	Temp. (°C)	Metal	Nominals Initial Metal Conc. (mg/l)	Controls	Sludge Content. (%)	Independent Variable	Values of Independent Variable	Dependent Variable	Contact Time (hrs)	pH
19	Effect of Sludge Concentration on the Removal of Lead, Contact Time = 1 hr.	20	Pb	0.5	aqueous solutions w/o sludge	Variable	Sludge Concentration	1 % 2 4 8	Same as above	1.0	7.0
20	Effect of Sludge Concentration on the Removal of Lead, Contact Time = 2 hrs.	20	Pb	0.5	aqueous solutions w/o sludge	Variable	Sludge Concentration	1 % 2 4 8	Same as above	2.0	7.0
21	Comparative Analysis between Equal Masses of Sludge and Ion Exchange	20	Ni, Cd,Zn	0.5	aqueous solutions w/o sludge or resin	Variable	Sludge and Ion Exchange Resin Conc.	1 % 2 4	Same as above	4.0	7.0

One last experiment was performed in which adsorption with Añasco sludge was to be compared to an ion exchange resin (Duolite C-20), in order to get an idea of the relative efficiency of the sludge.

The sludge utilized from experiment one onwards, was collected at the Añasco municipal wastewater treatment plant. Añasco is a town about 15 minutes north of Mayaguez with a population of about 30,000 people. The Añasco plant consists of primary clarification followed by a trickling filter, secondary clarification, and secondary effluent recycle. The sludge is anaerobically digested in an Imhoff-tank-like digester compartment underneath the primary clarifier. The dried digested sludge is a non-odorous, well stabilized product. The Añasco area has several industries none of which seem to discharge any harmful liquid wastes into the municipal sewage collection system. The Añasco plant exhibits a more stable treatment performance than the San Germán Plant, and there are no known industrial discharges of metals. It was for these reasons that Añasco sludge was utilized for the remainder of the project instead of San Germán sludge (Experiments 1 through 21).

Analytical Methods

After the required contact time, each sample was subdivided into two well-mixed equal portions. One portion was immediately filtered using a standard 0.45 micron (μ) membrane filter and then acified to below pH 2.0. These samples were then analyzed for dissolved metal content utilizing standard Atomic Absorption (AA) spectrophotometry methods (13). These results represented the soluble fraction of the metal species at equilibrium. The other portion of sample was immediately acidified and processed through an EPA recommended acid digestion procedure (14). The digested sample was then filtered using the standard 0.45μ filter, and analyzed for dissolved metal species content. These results represented the total metal content of the sample, including both dissolved and suspended species.

The Atomic Absorption spectrophotometer that was utilized was a Perkin Elmer 2380, which has double beam, automatic calibration, digitizing, and data integration capabilities.

Experimental Results

The results of each experiment are summarized in Tables A-1 to A- in the Appendix, which contain the raw data.

Figures 2 through 60 graphically summarize the most significant results of the experiments. The discussion that follows examines the results in depth and organizes them by experimental theme rather than by experiment number.

Preliminary Experiment:

Cadmium was selected at random as the subject of the first experiments. Table 3 shows the results of experiment X-1. The initial concentration, contact time, and sludge mass were varied in a single experiment at constant pH 3.0 in an attempt to identify appropiate values for these parameters to be used in subsequent experiments. There was not a noticeable improvement in the removal of Cadmium at a contact time of 8 hours, so 4 hours was judged as a good estimate for "optimal" contact time. A sludge mass of 4g coincided with this "optimal" removal. This is equivalent to a sludge concentration of 2 g/l, or 2 percent, which then became the selected value for the experiments that followed.

Table 3. Effect of Initial Concentration, Sludge Mass and Contact Time on the Adsorption of Cadmium.

Initial Concentration (mg/liter)	Equilibrium Concentration of Samples, mg/l			
	Sludge Mass (g)			
	1	2	4	8
0.000	0.000	0.000	0.000	0.000
0.505	0.004	0.000	0.002	0.004
0.992	0.015	0.010	0.003	0.003
1.897	0.042	0.019	0.010	0.012
	1	2	4	8
	Contact Time (hrs)			

Removal of Cadmium Through Biosorption:

The first two experiments of each series involving different metals were performed with the following objectives in mind:

1. Determine whether reasonably good removals could be obtained at pH 7.0, since this is the pH of natural wastewaters so that addition of chemicals for pH adjustment could be avoided.
2. Identify which pH closest to the neutral region would yield a reasonably good removal rate, in case poor removal was exhibited at pH 7.0.
3. Account for the reduction in solubility due to metal hydrolysis at all pH levels. This was accomplished through the first experiment, which consisted of solutions at the same pH levels and with the same initial concentrations of the dissolved metal, but without any sludge in them. The equilibrium dissolved metal concentrations of these controls (after the required contact time) then became the "initial" concentrations utilized for the samples with sludge at each pH level, for purposes of calculating the metal removed due to adsorption only. These pairs of experiments were performed simultaneously so as to minimize differences between samples and controls due to laboratory errors.

Figure 2 show the results of these experiments for Cadmium. The decrease in solubility varied linearly with increasing pH, and its magnitude was rather small. Removal, however, was shown to increase with increasing pH which suggests that Cadmium removal can be a maximum at the neutral range, which is an unexpected but very good result in terms of

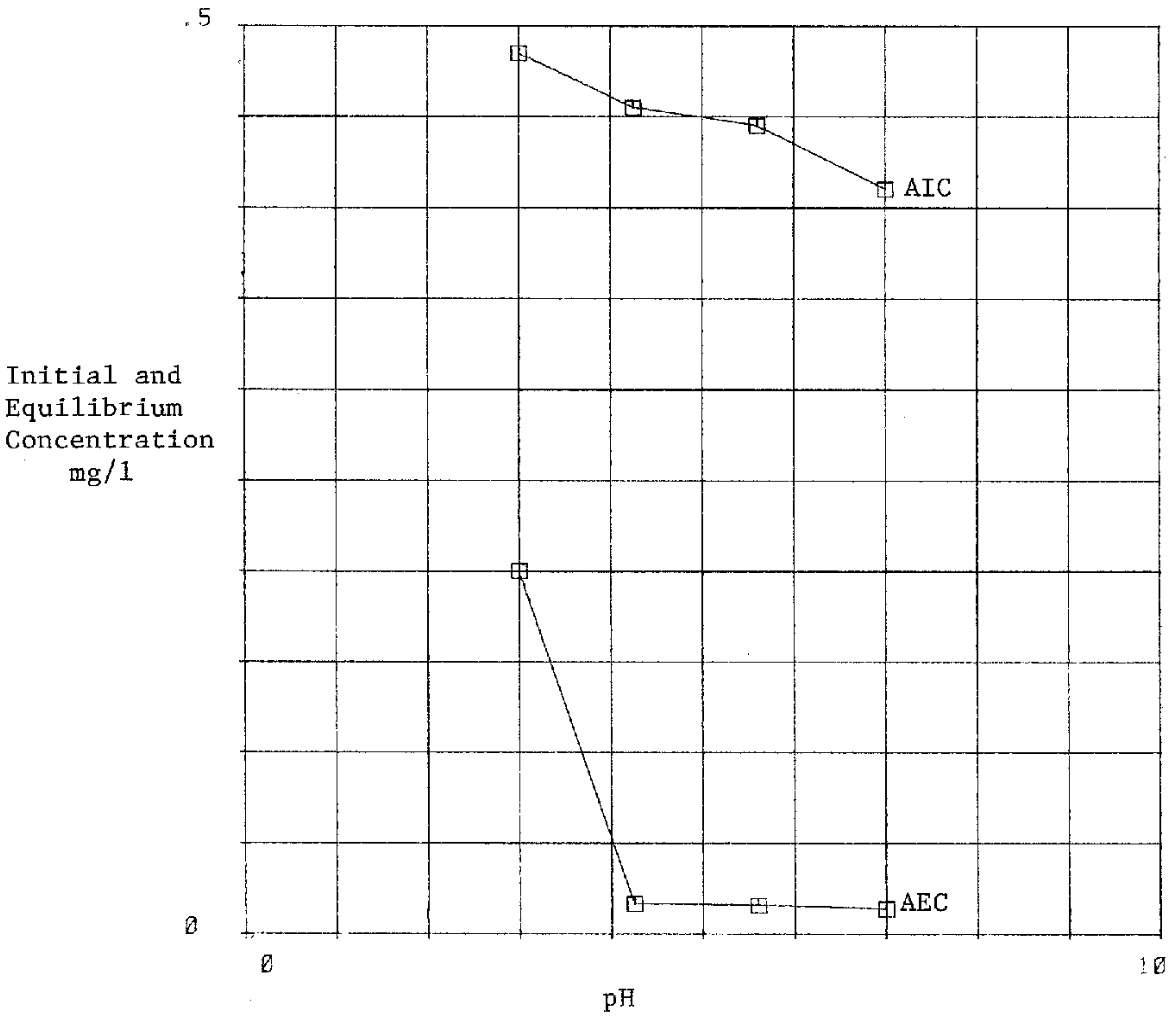

Fig. 2: Effect of Hydrolysis and pH on the Removal of Cadmium.

its possible applications. Removal efficiency was indeed observed to be a maximum in the Remaining Fraction Curve (see Figure 3). This is very encouraging, since it suggests that the sludge will exercise maximum adsorption potential for Cadmium at the neutral pH regions of wastewaters.

Figures 4and 5 show the results of the experiment measuring the effect of contact time on the Removal of Cadmium. As can be seen, after 4 hours the improvement in removal is minimal, so it seems that a 4 hour contact time is indeed optimal for removing Cadmium at a pH 7.0.

Figures 6 and 7 show the effects of increasing initial concentration on the removal of Cadmium. The remaining fraction can be interpreted to be essentially constant for all cases, which means that in order to improve removal in the face of increasing influent concentrations the contact time must be increased accordingly. All samples in this experiment had a 4 hour contact time. Thus removal of Cadmium as a function of increasing initial concentration seems to be controlled by contact time.

Figures 8,10, and 12 show the effect of sludge concentration, expressed as percent by weight, on the equilibrium concentration of Cadmium at contact time of 1, 2 and 4 hours, respectively. Figures 9, 11, and 13 show remaining fraction at the same respective contact times.

Cadmium was in all cases reduced to concentrations very close to the water quality standards established by the U.S. Environmental Protection Agency, as can be seen in Tables A-11, A-12, A-13 in the Appendix and in Table 4 below. At the very least, its concentration was reduced to a point where a minimal dilution ratio of 2:1 would bring the metal concentration into compliance with the water quality standards.

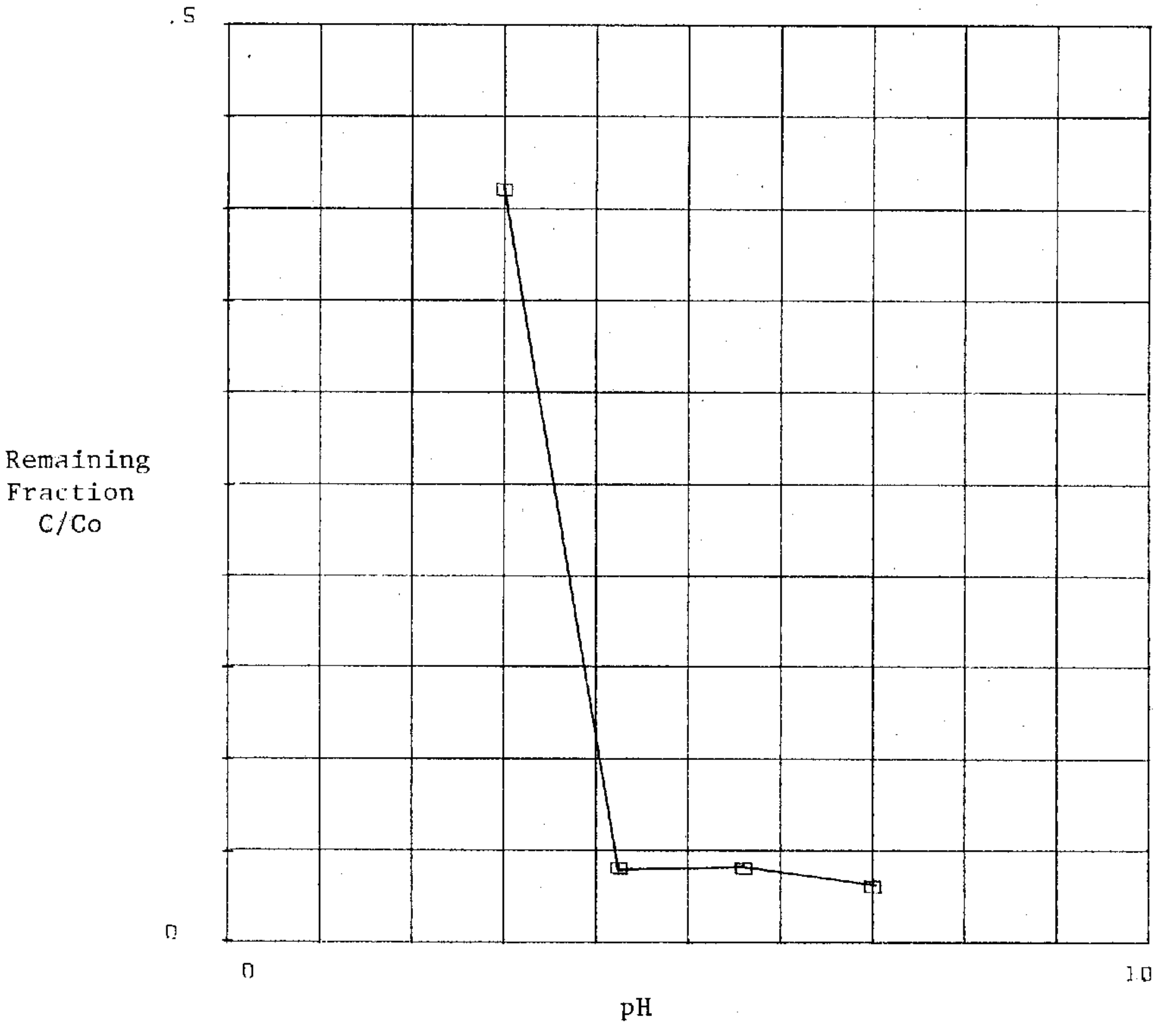

Fig. 3: Effect of Hydrolysis and pH on the Remaining Fraction of Cadmium.

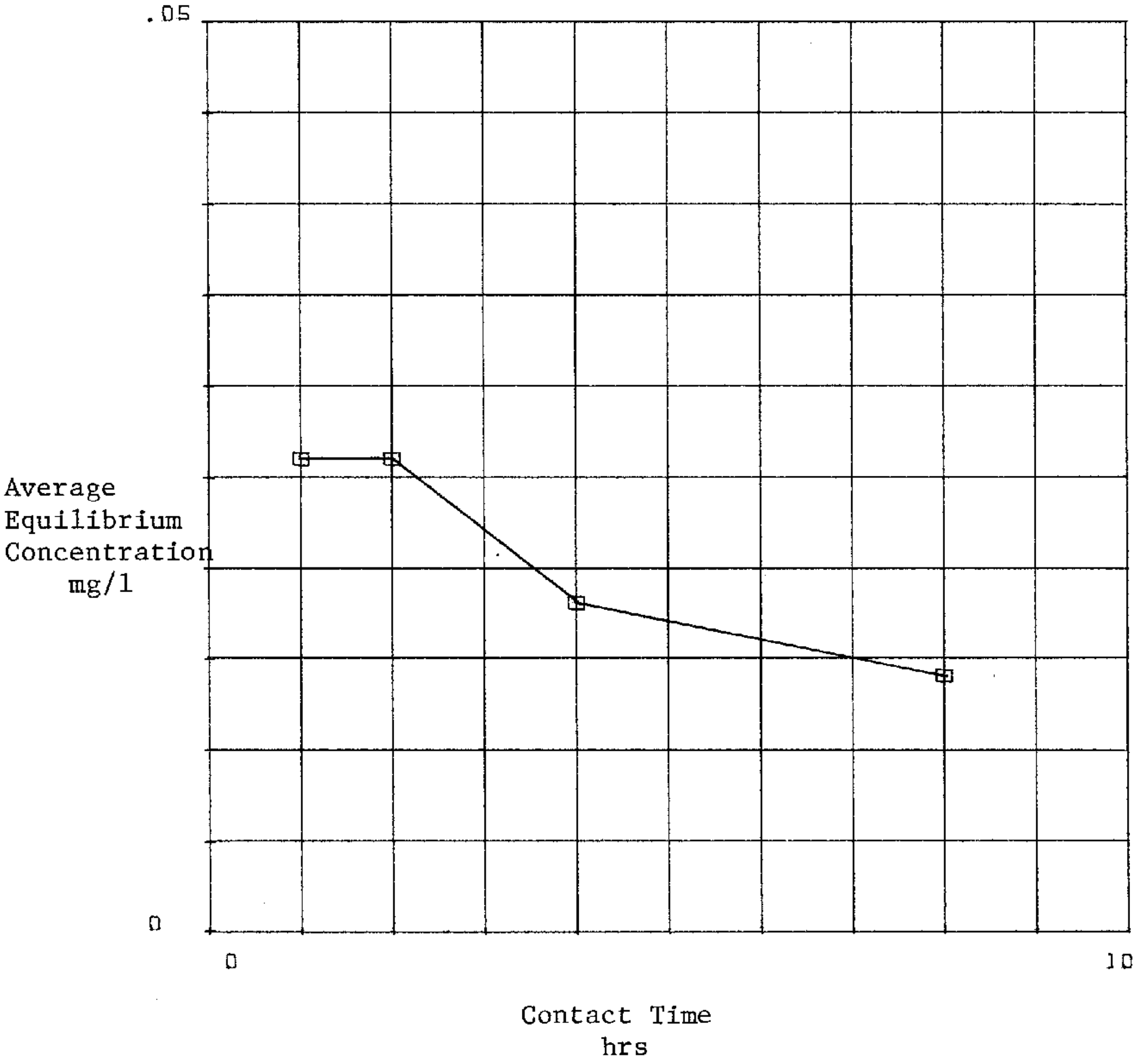

Fig. 4: Effect of Contact Time on the Removal of Cadmium.

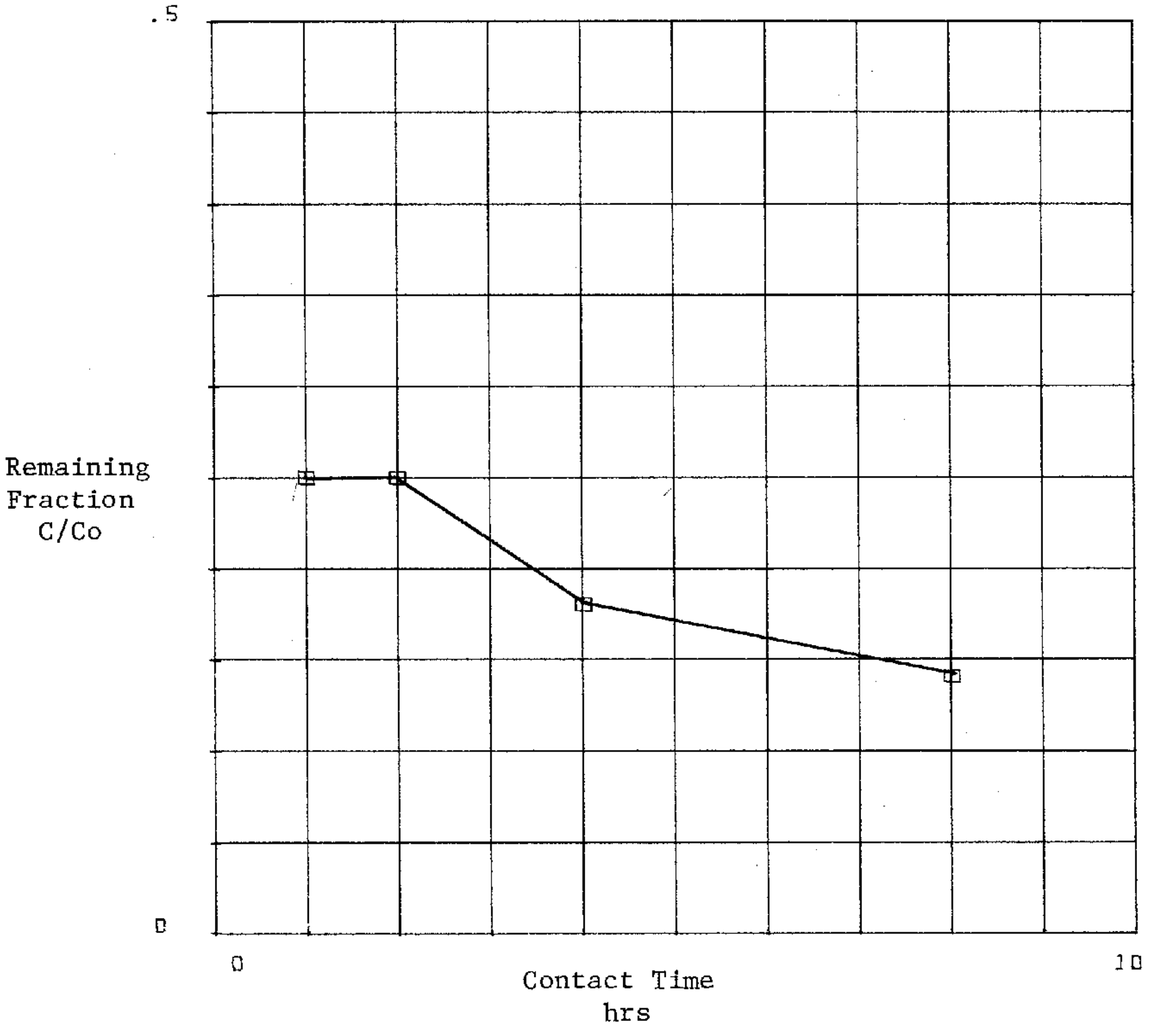

Fig. 5: Effect of Contact Time on the Remaining Fraction of Cadmium.

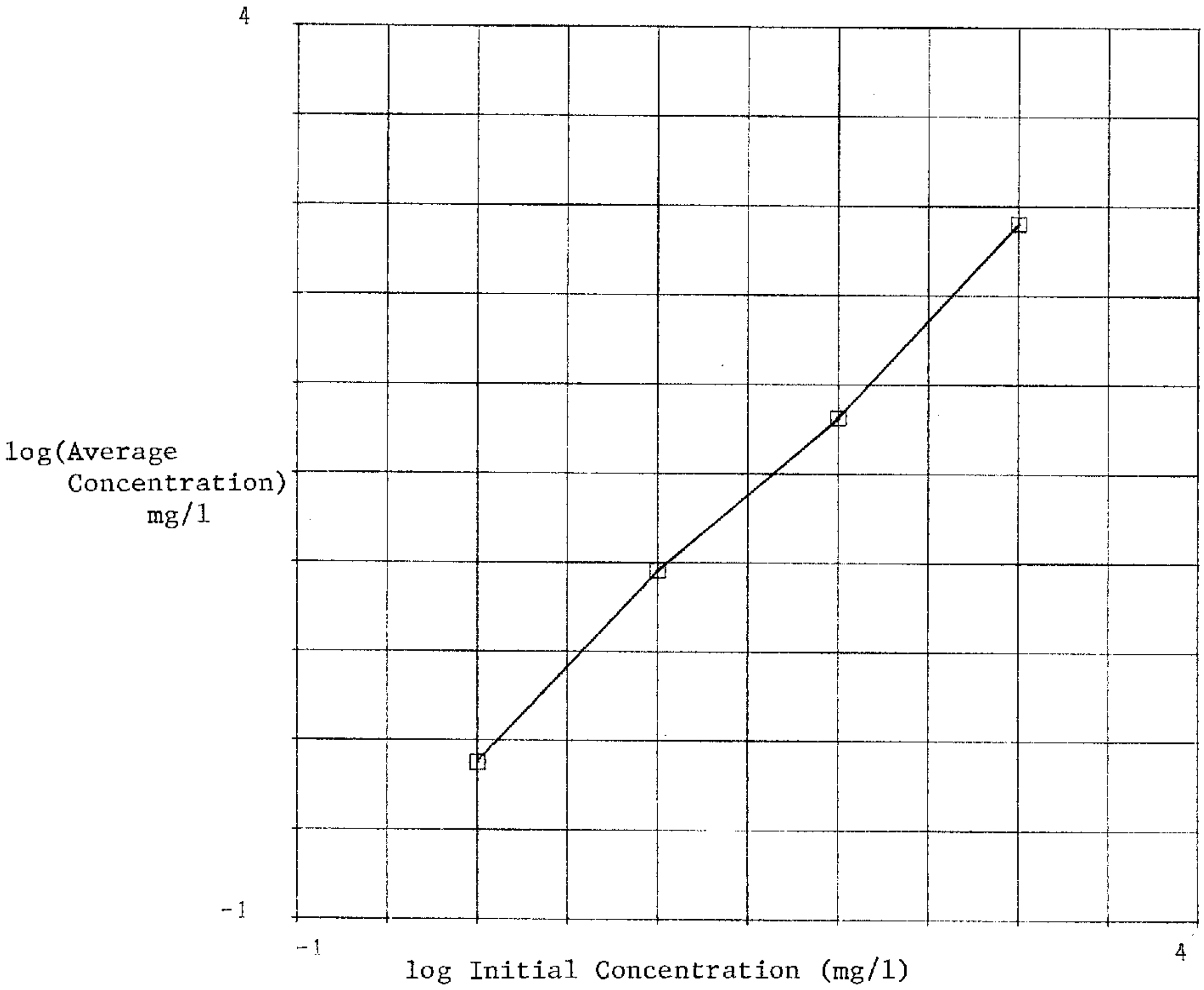

Fig. 6: Effects of Initial Concentration on the Removal of Cadmium.

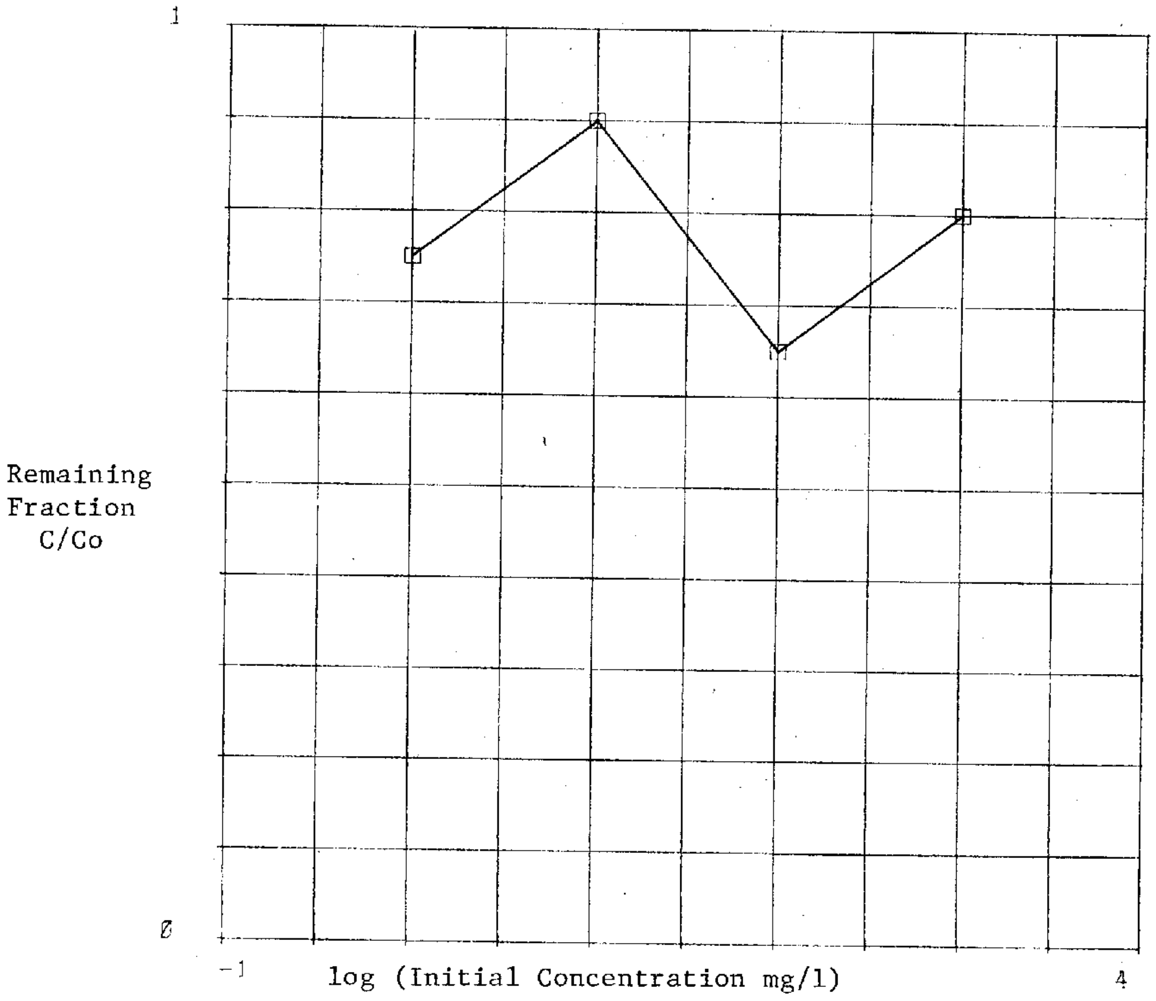

Fig. 7: Effect of Initial Concentration on the Remaining Fraction of Cadmium.

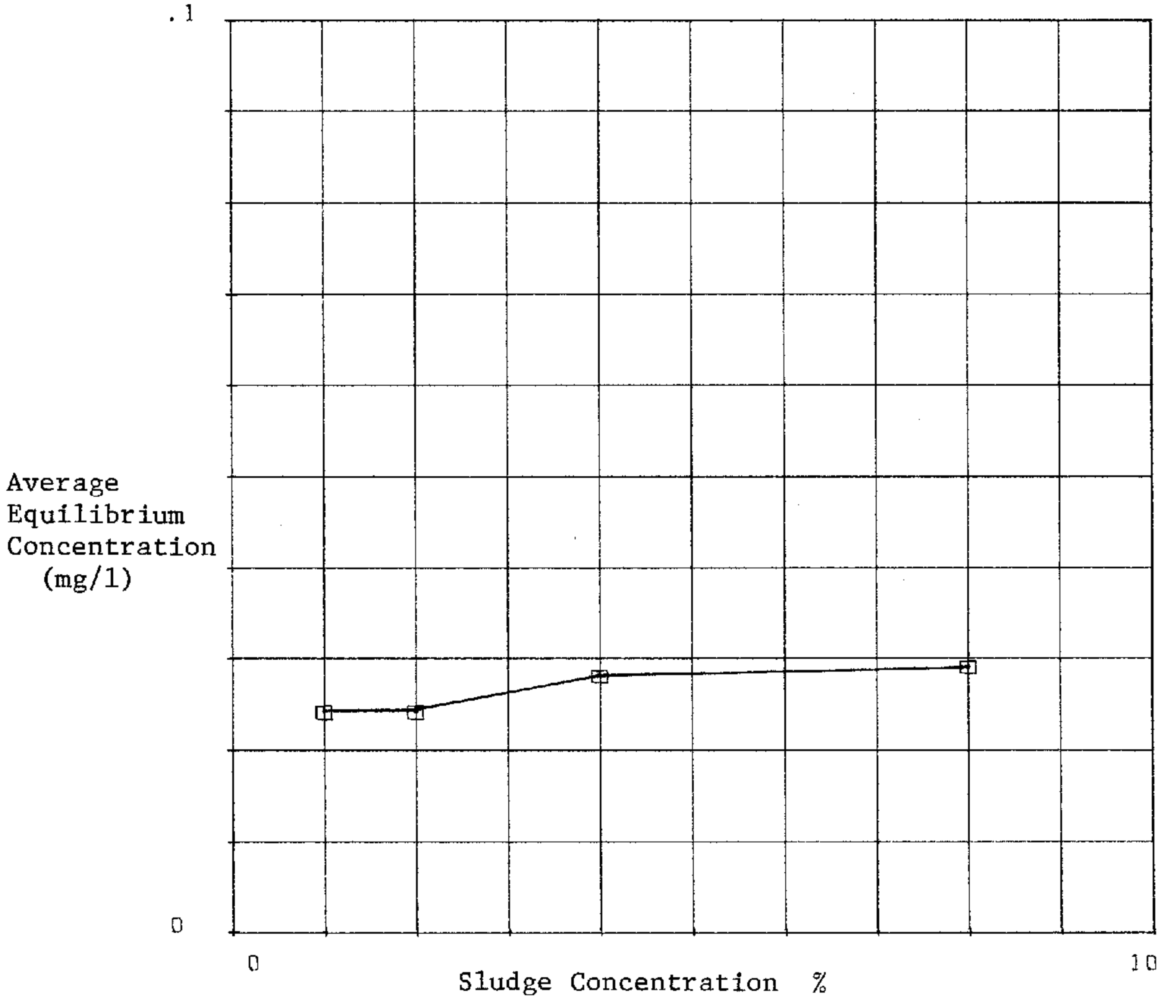

Fig. 8: Effect of Sludge Concentration on the Removal of Cadmium, Contact Time = 1 hour.

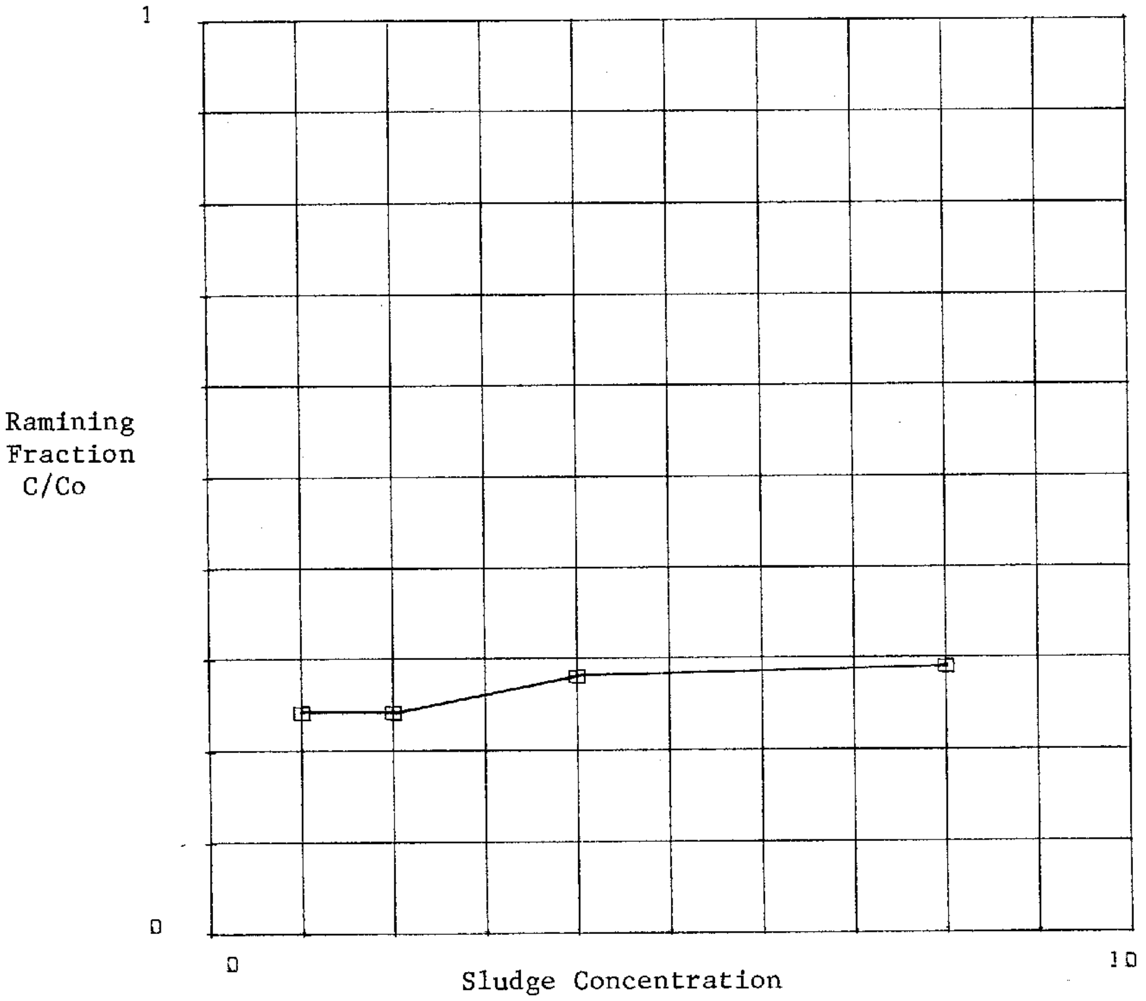

Fig. 9: Effect of Sludge Concentration on the Remaining Fraction of Cadmium, Contact Time = 1 hour.

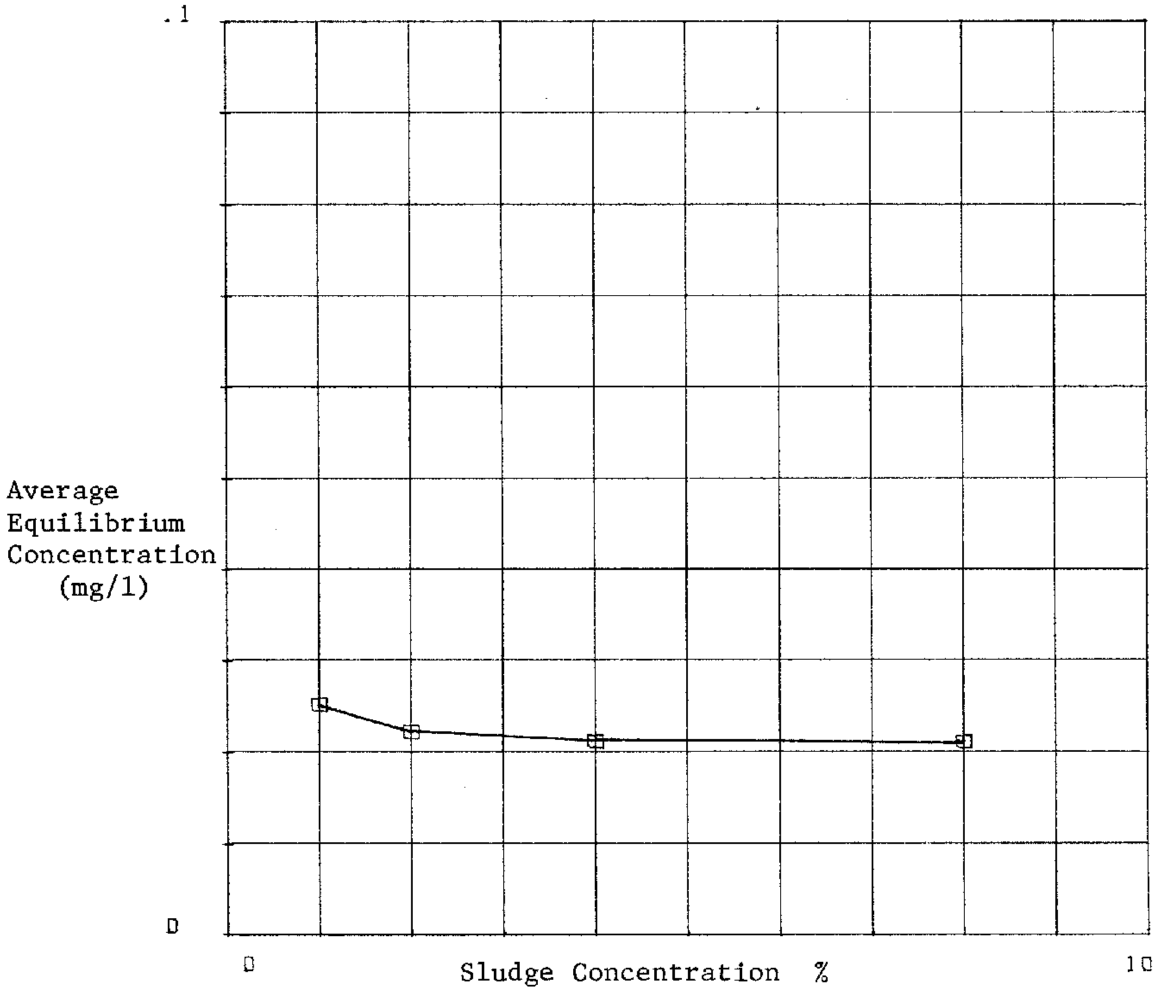

Fig. 10: Effect of Sludge Concentration on the Removal of Cadmium, Contact Time = 2 hours.

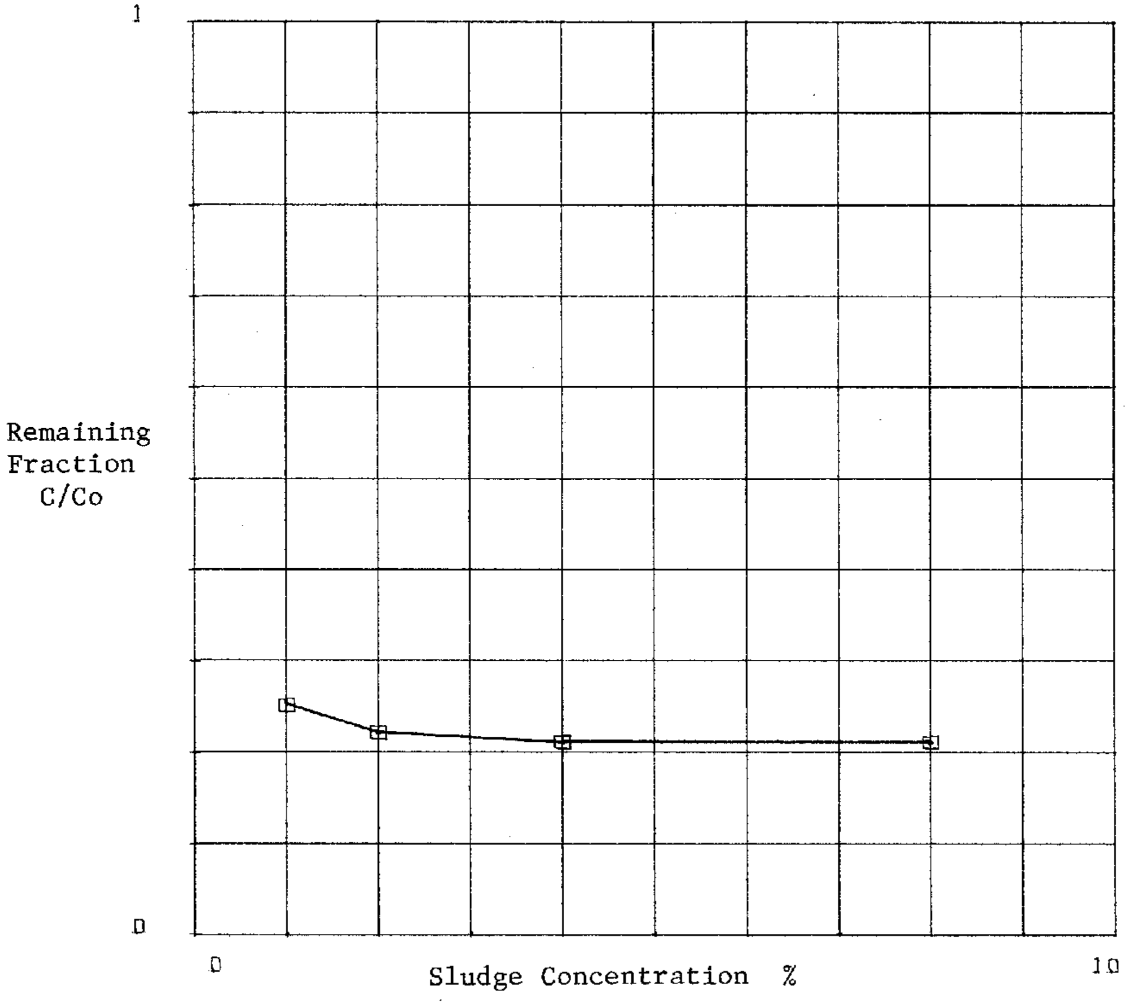

Fig. 11: Effects of Sludge Concentration on the Remaining Fraction of Cadmium, Contact Time = 2 hours.

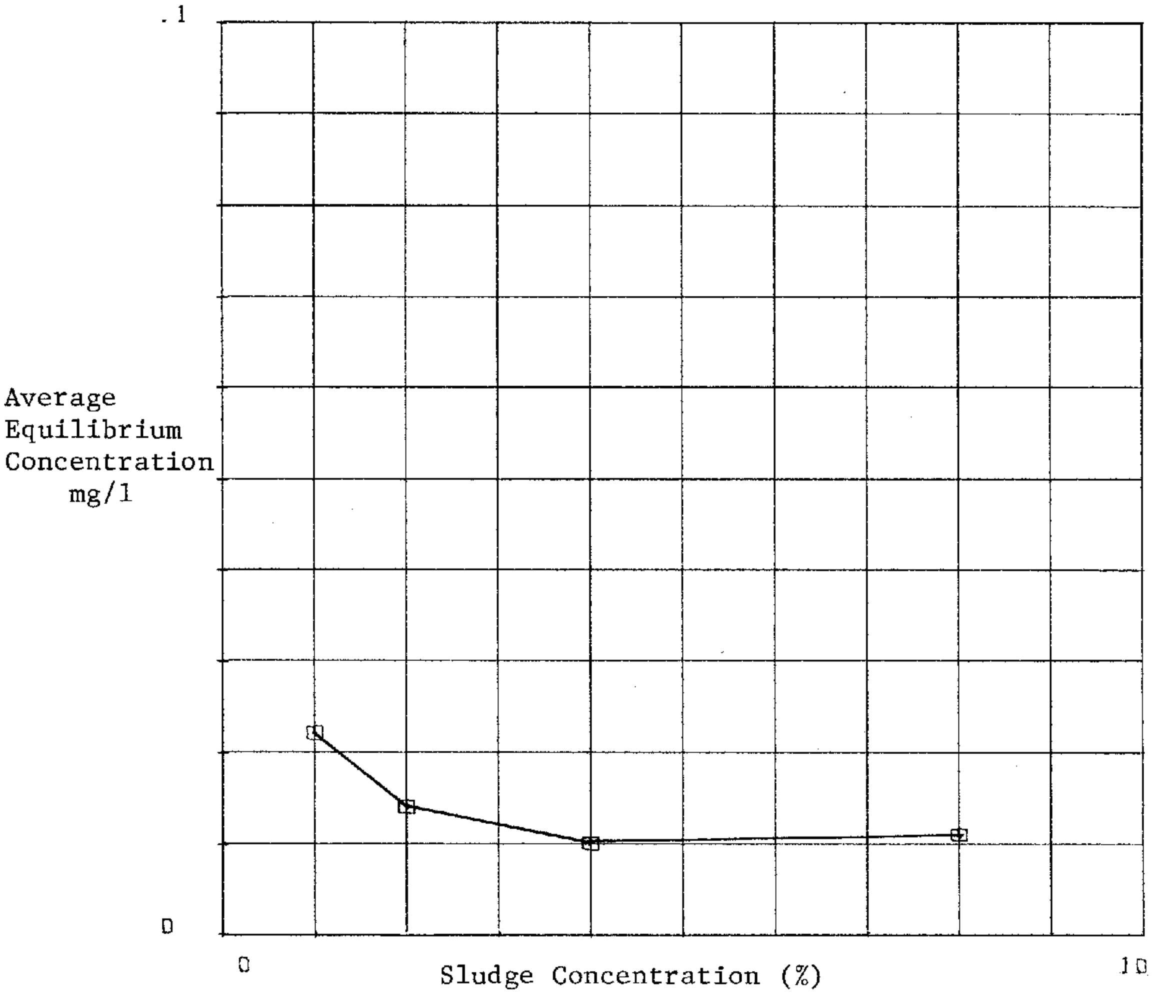

Fig. 12: Effect of Sludge Concentration on the Removal of Cadmium, Contact Time = 4 hours.

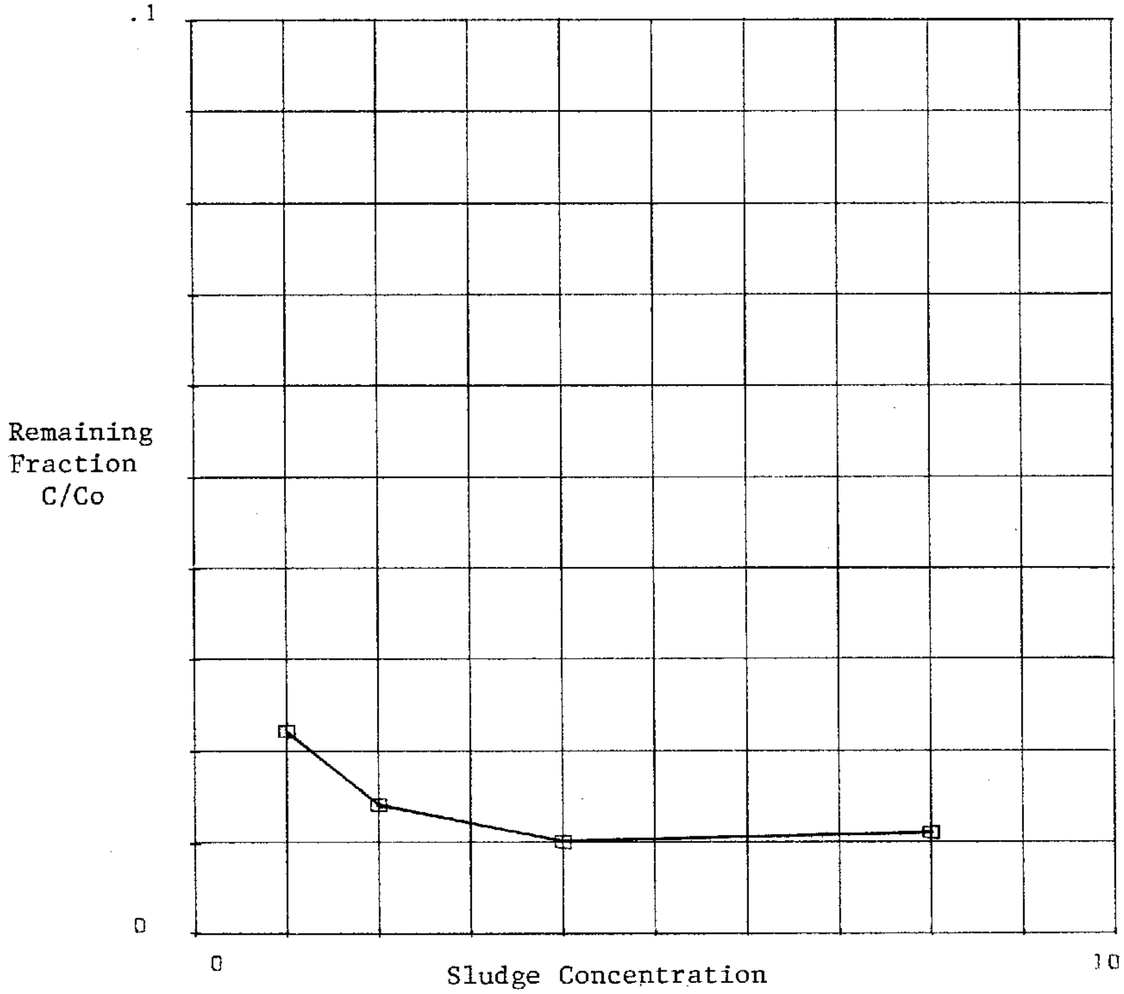

Fig. 13: Effect of Sludge Concentration on the Remaining Fraction of Cadmium, Contact Time = 4 hours.

Table 4: EPA Maximum Contaminant Levels for Water Quality Protection

Metal	Primary Standard (mg/1)
Cadmium	0.01
Chromium (total)	0.05
Lead	0.05
Zinc	5.00
Nickel	-

Table 5 and Figures 14A, 14B, 15A, 15B show a summary of the effect of sludge concentration and contact time on the removal of Cadmium. It seems that a contact time of 1 hour is too short for the increase in sludge concentration to operate any appreciable reduction in metal concentration. At contact times of 2 and 4 hours the effect of sludge concentration definitely causes a decrease in equilibrium concentration and in the remaining fraction. Removal efficiency ranged from 78 percent at sludge concentrations of 2 percent and contact times of 2 hours to a maximum of 90 percent at sludge concentrations of 4 and 8 percent at contact times of 4 hours.

Table 5: Effect of Contact Time and Sludge Concentration on the Remaining Fraction of Cadmium.

Sludge Concentration (%)	REMAINING FRACTION, C/Co Contact Time, Hours 1	 2	 4
1	0.24	0.25	0.22
2	0.24	0.22	0.14
4	0.28	0.21	0.10
8	0.29	0.21	0.11

TEMP. = 20°C pH = 7.0

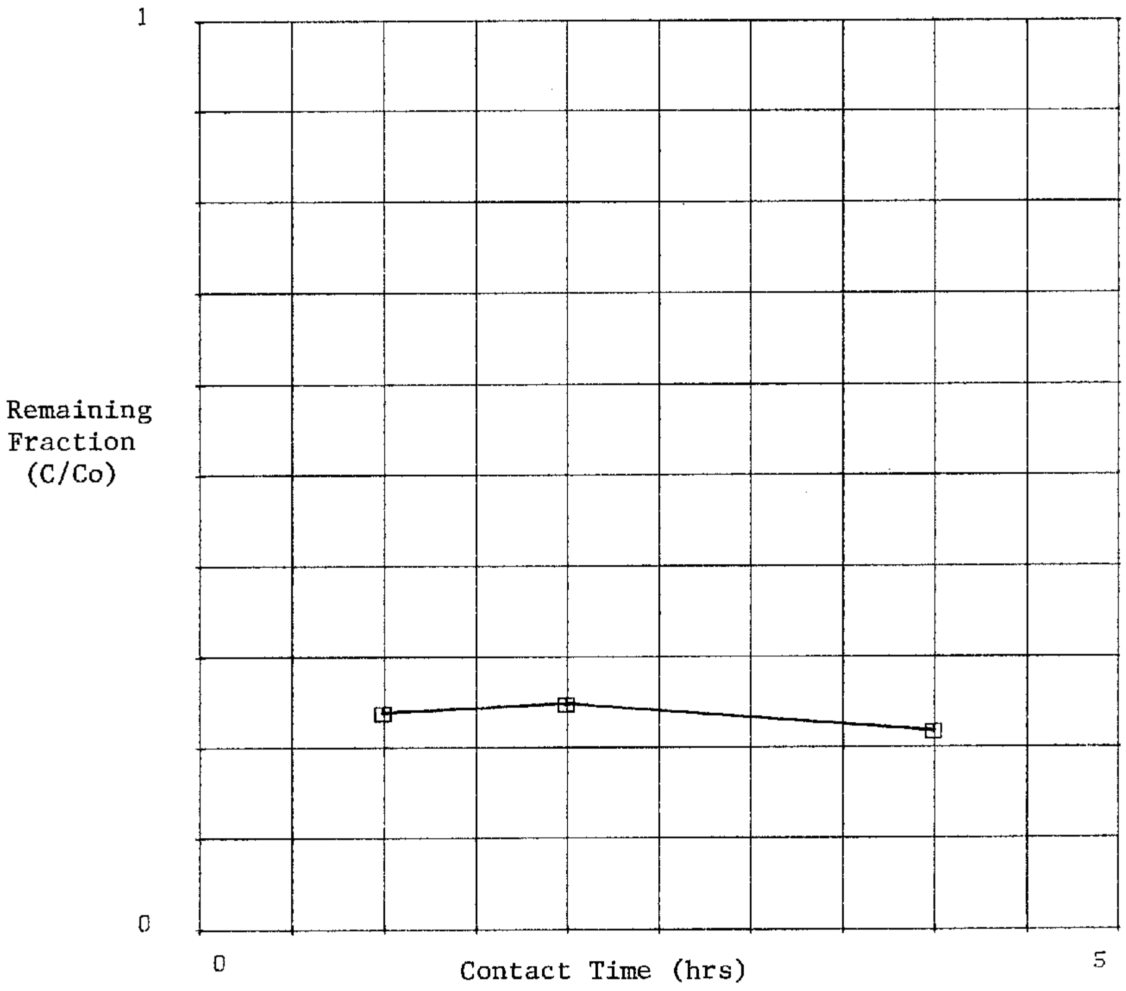

Fig. 14A: Correlation of emaining Fraction of Cadmium with Contact Time and Sludge Concentration (1 & 2%).

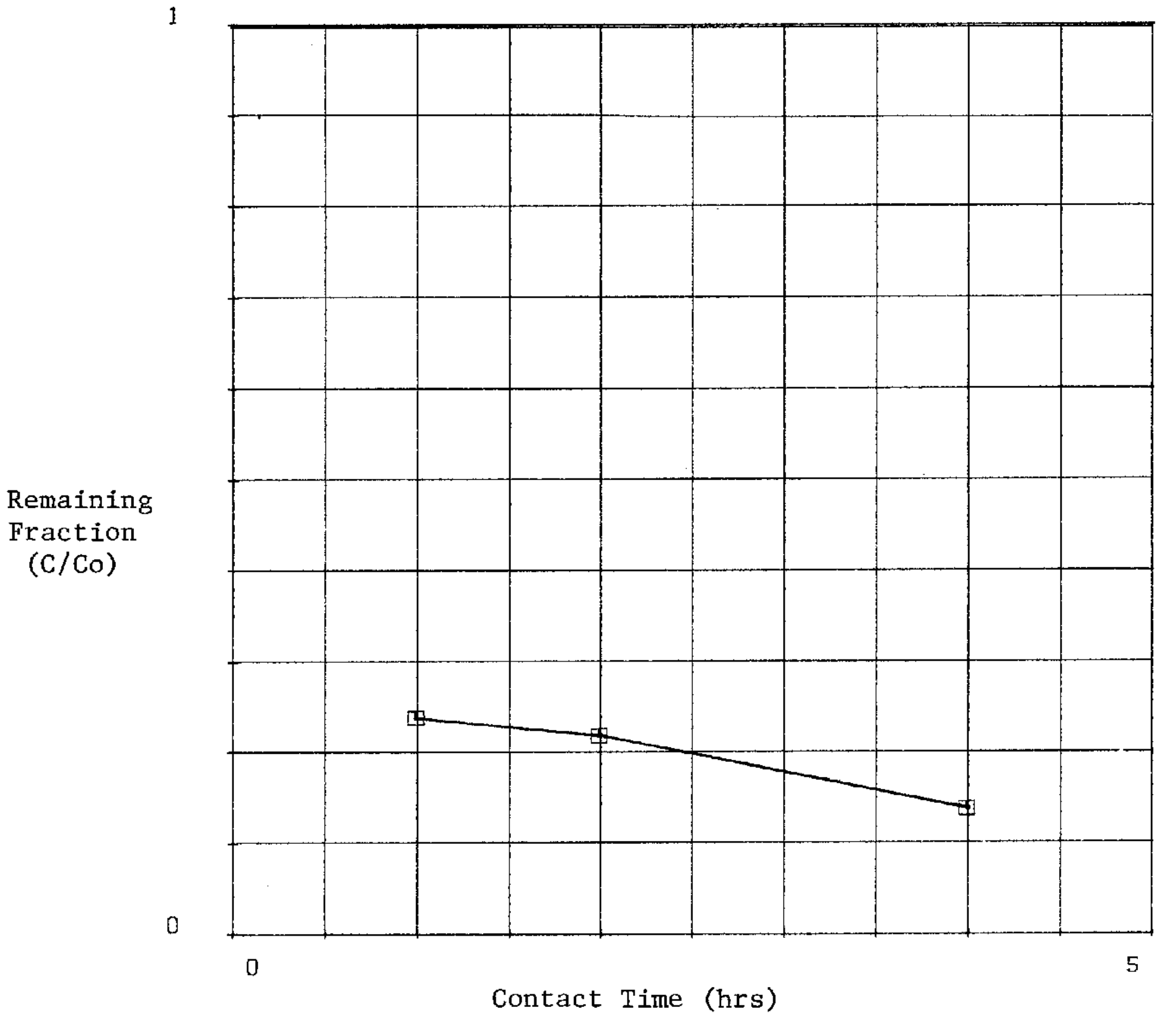

Fig. 14B: Correlation of Remaining Fraction of cadmium with Contact Time and Sludge Concentration (2%).

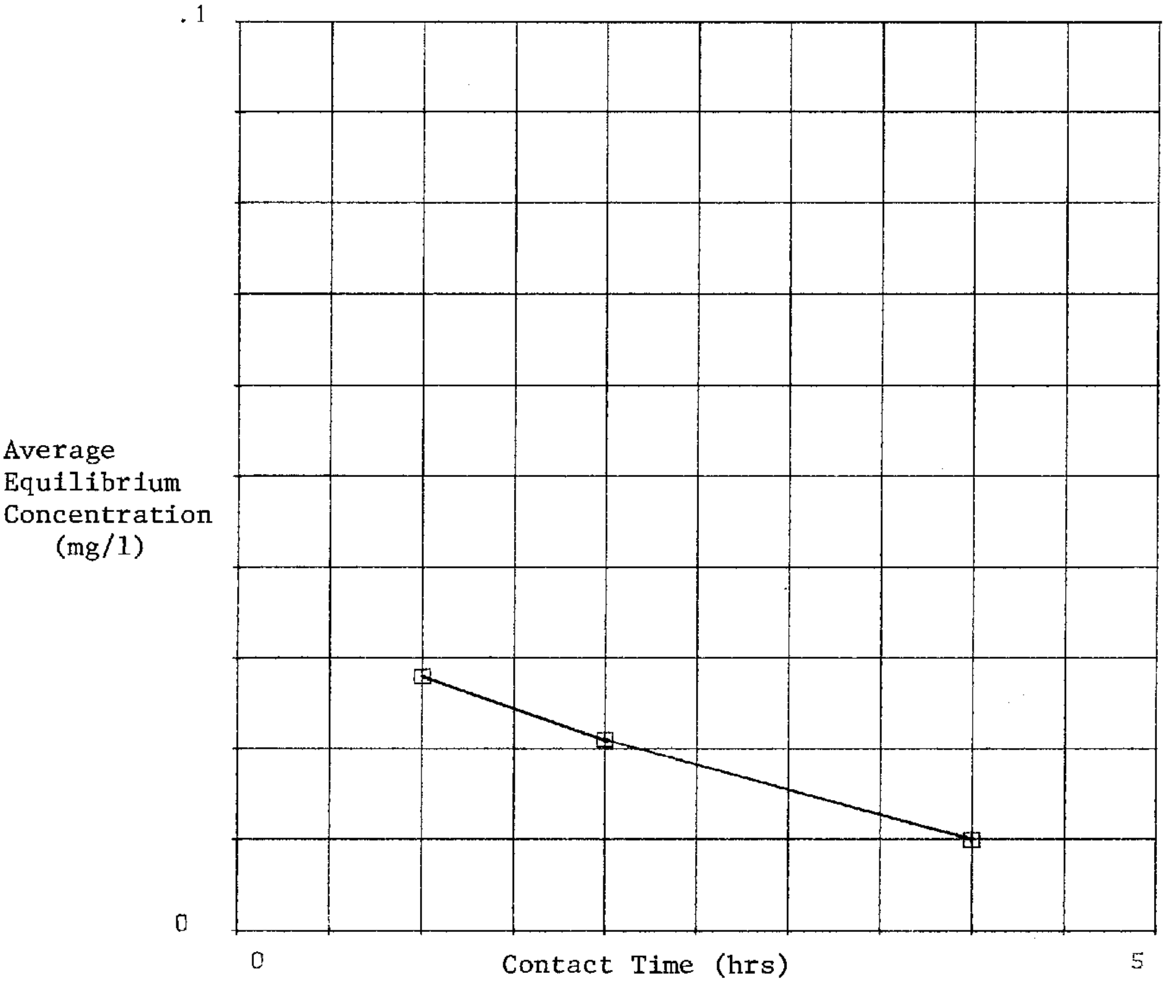

Fig. 15A: Correlation of Remaining Fraction of Cadmium, with Contact Time and Sludge Concentration (4%).

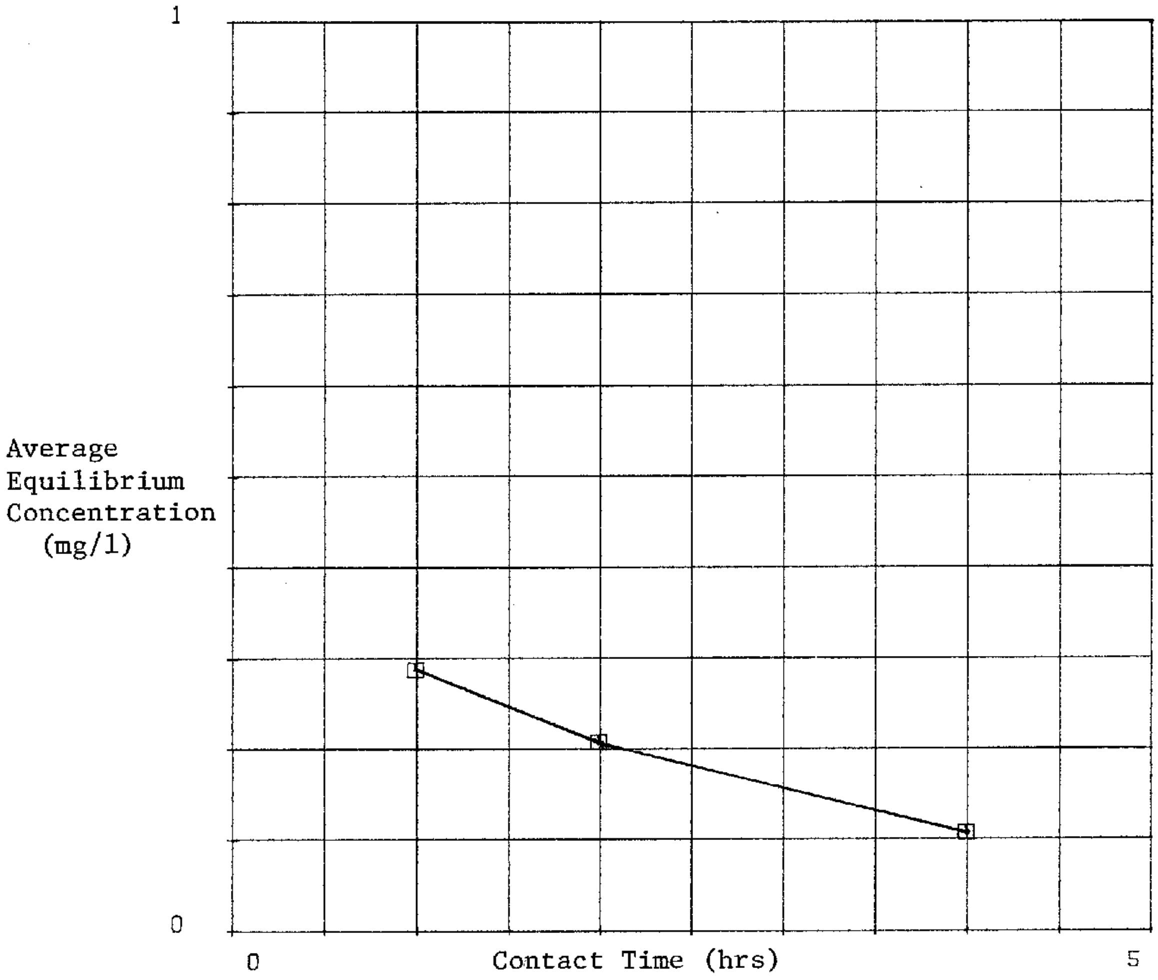

Fig. 15B: Correlation of Remaining Fraction of Cadmium with Contact Time and Sludge Concentration (8%).

The general results with Cadmium point to a very promising potential for biosorption as an innovative and possibly cheap removal technology. The results for Nickel will be now examined.

Removal of Nickel Through Biosorption:

Figures 16 and 17 illustrate the effect of hydrolysis and pH on the removal of dissolved nickel through biosorption with an inert sludge. It can be seen that the solubility of Nickel varies little with increasing pH, as shown in Figure 16, but the removal efficiency increases dramatically with increasing pH, from virtually none at pH 3.0 to approximately 66 percent at pH 7.0. The increase in removal efficiency with pH for Nickel is consistent with the results obtained for Cadmium, which is very encouraging.

An increase in removal efficiency with pH suggests that the adsorption mechanism may be electrostatic in nature. Electrical sites in the cell walls may be either positive or less negative at lower pH's. The increase in pH may cause interactions which increase the electronegativity at these sites, thereby increasing their affinity for polyvalent metallic ions. These changes in the polarity of charged sites with pH is a fairly common phenomenon in water chemistry, with polyelectrolytes being one of the most obvious examples (15). This conclusion is entirely consistent with the well known property of biological sludges for flocculating colloids and therefore could be one of the most important, if rather unexpected, contributions of this study.

The equilibrium concentration and remaining fraction of Nickel (Figures 18 and 19) was observed to remain essentially constant with increase in contact time, which is contrary to expectations. This suggests that the adsorption sites may be exhausted, yet Figure 6 (for Cadmium) showed that the sludge accepted dramatic increases in the metal

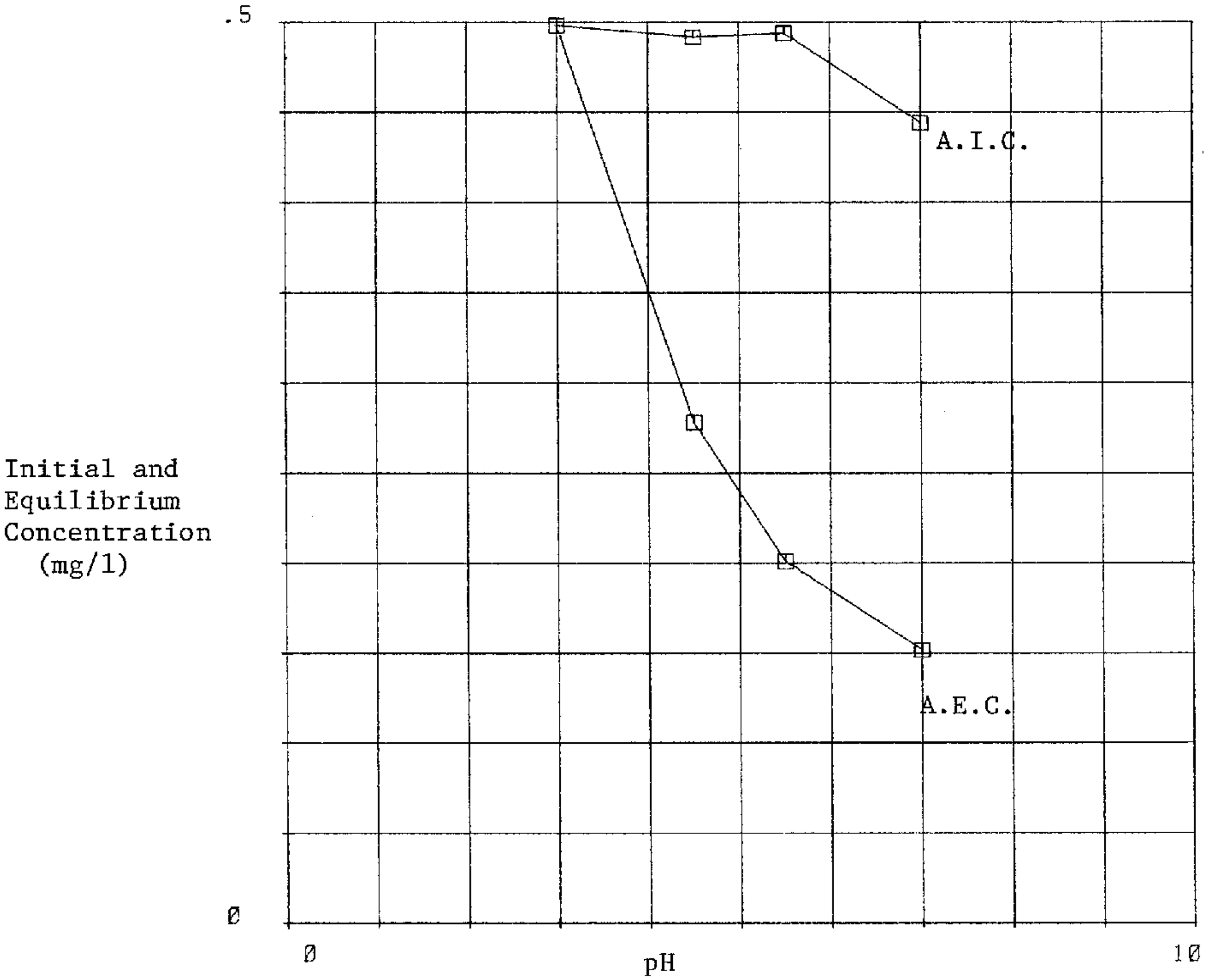

Fig. 16: Effect of Hydrolysis and pH on the
Removal of Nickel

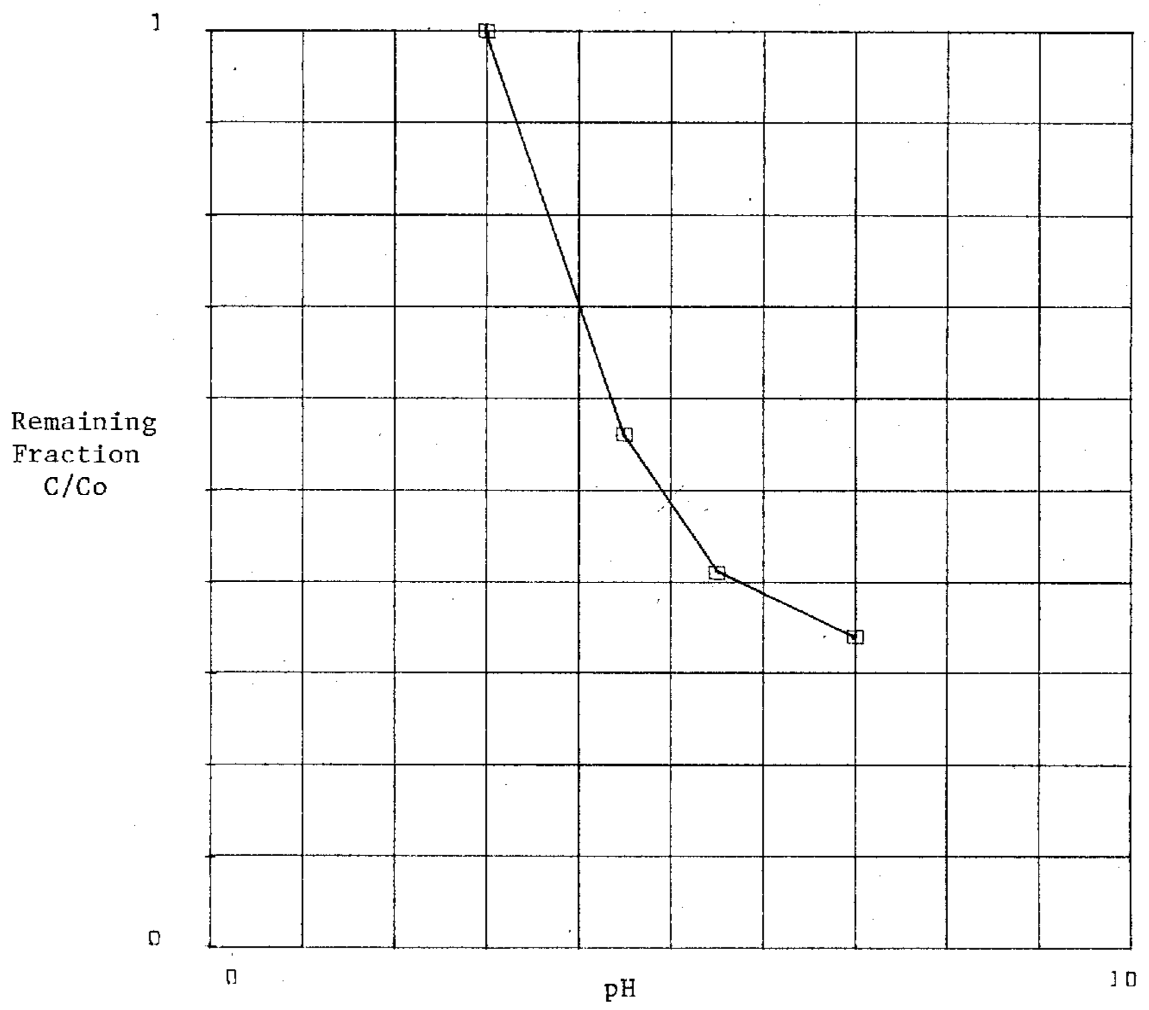

Fig. 17: Effects of Hydrolysis and pH on the Remaining Fraction of Nickel.

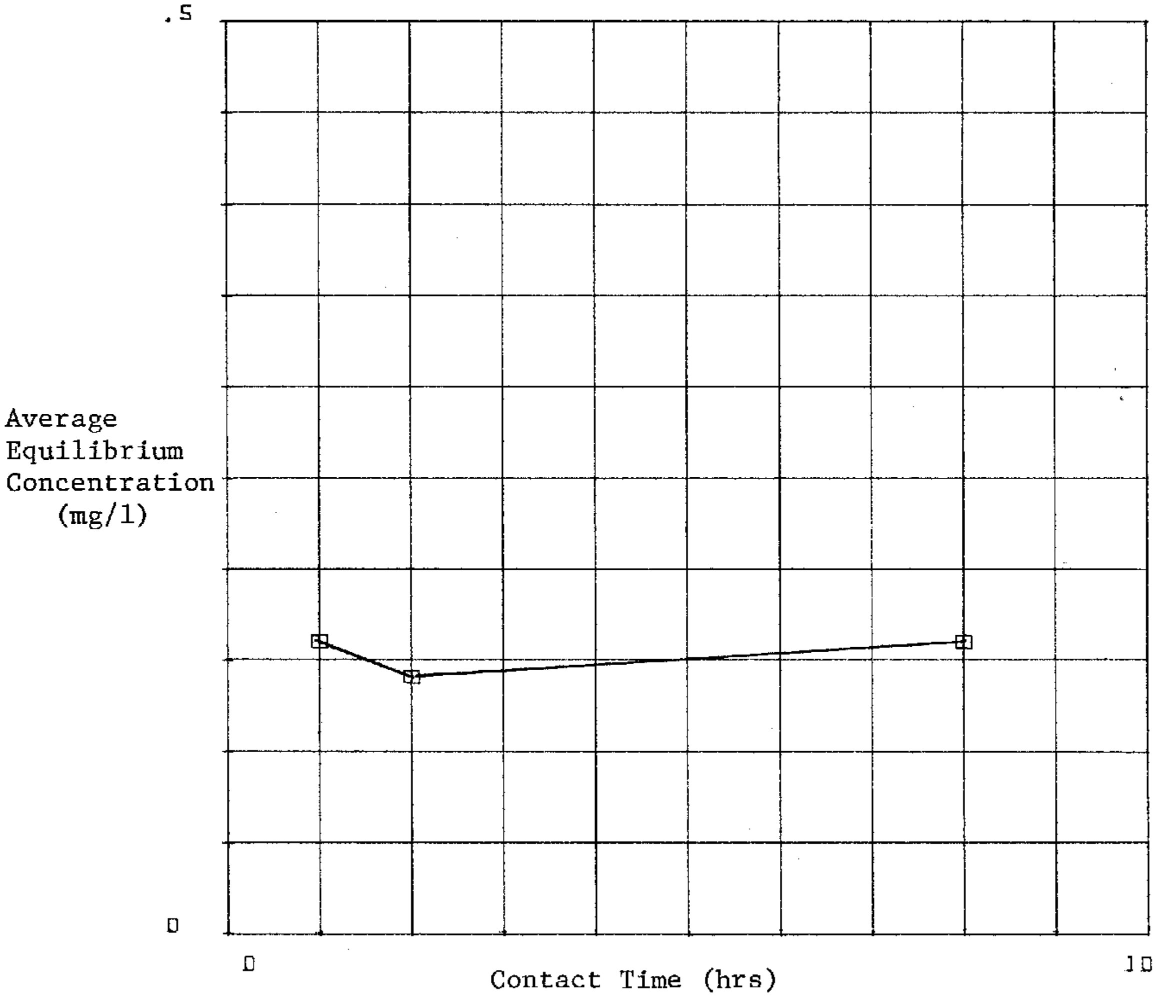

Fig. 18: Effect of Contact Time on the Removal of Nickel

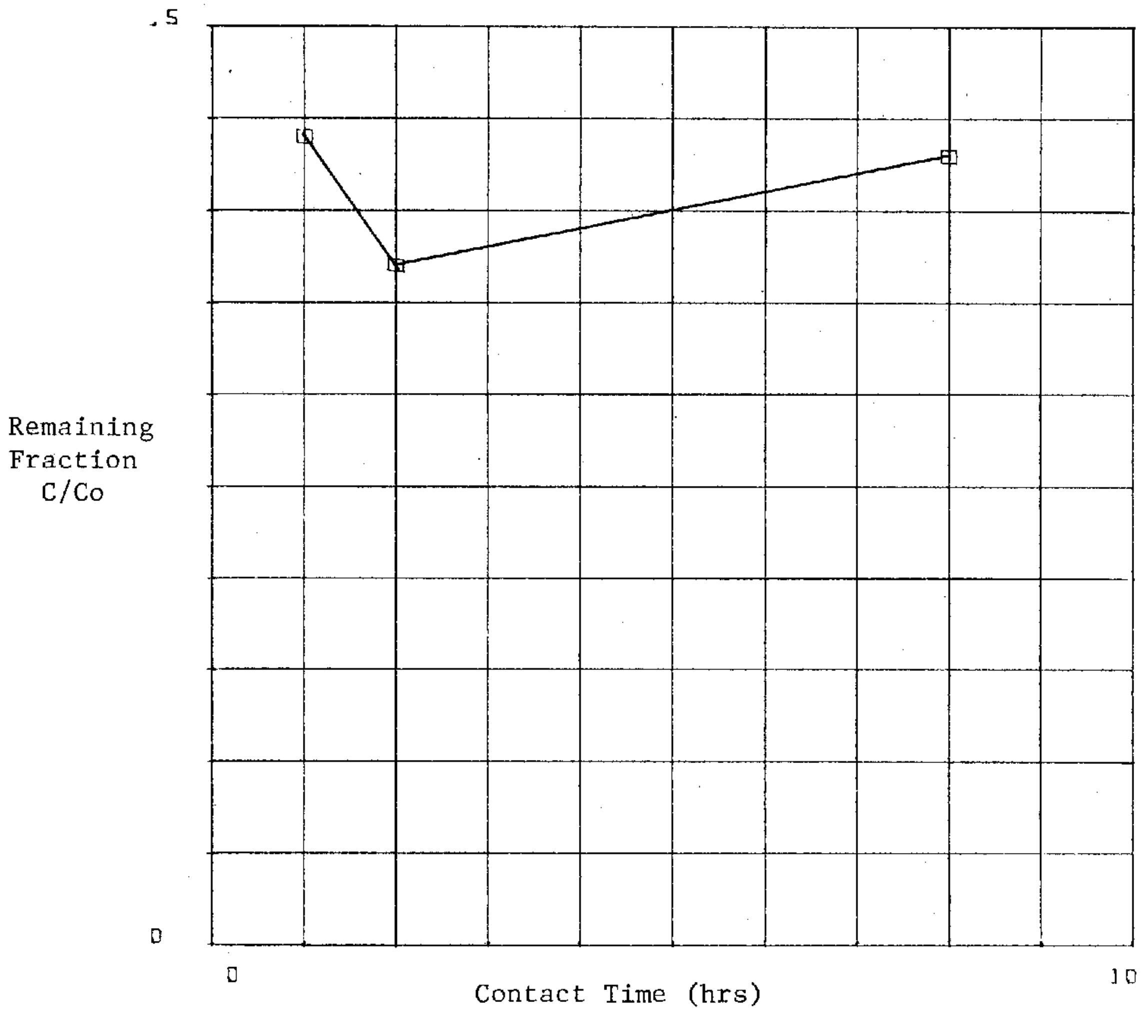

Fig. 19: Effect of Contact Time on the Remaining Fraction of Nickel.

concentration. Had there been a finite number of sites that were quickly exhausted, the increase in concentration should have caused a marked decrease and deterioration in the removal efficiency with increasing initial concentration. This is certainly not what was observed, since the remaining fraction was constant for all cases (Figure 7, Cadmium).

The explanation could lie in an ion exchange model for the adsorption mechanism. If other ions are held at these sites, then a given concentration of metal will have the capacity of replacing only a certain fraction of the other ion. As the bulk concentration of metal increases, its capacity to replace ions at a greater number of sites may increase proportionately. A linear increase can certainly account for the uniform removal efficiency observed for Cadmium with increasing initial concentration.

Figures 20, 22, and 24 show the effect of increase in sludge concentration on the equilibrium concentration of Nickel. Figures 21, 23, and 25 show the results for the remaining fraction. The results seem to suggest that there is no significant effect. Table 6 below and Figures 26 and 27 that follow confirm this conclusion.

Table 6: Effect of Contact Time and Sludge Concentration on the Remaining Fraction of Nickel

Sludge Concentration (%)	REMAINING FRACTION, C/Co		
	Contact Time, Hours		
	1	2	4
1	0.39	0.39	0.48
2	0.36	0.38	0.41
4	0.41	0.42	0.37
8	0.44	0.45	0.43

In fact, there appears to be slightly better removal at the two lower

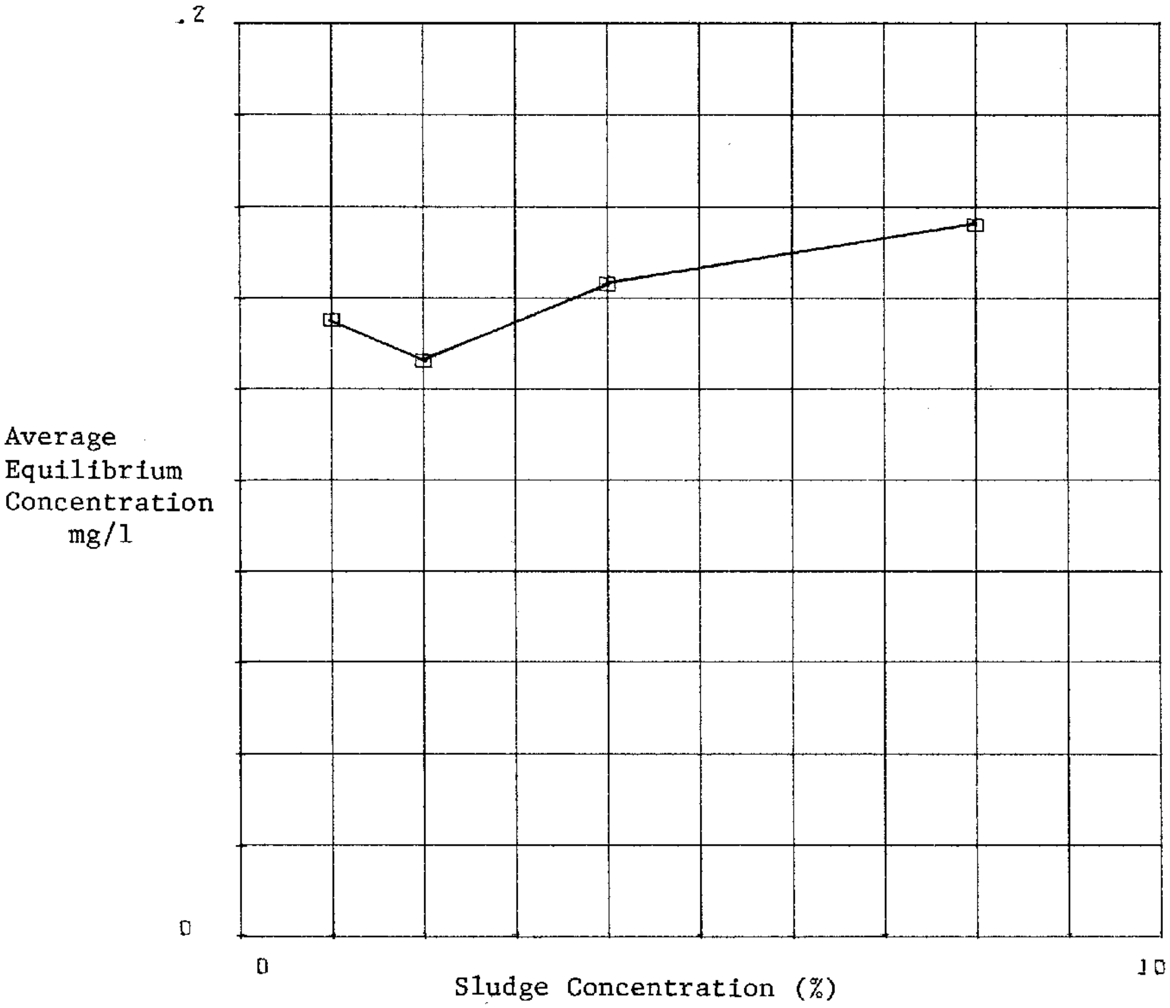

Fig. 20: Effect of Sludge Concentration on the Removal of Nickel, Contact Time = 1 hour.

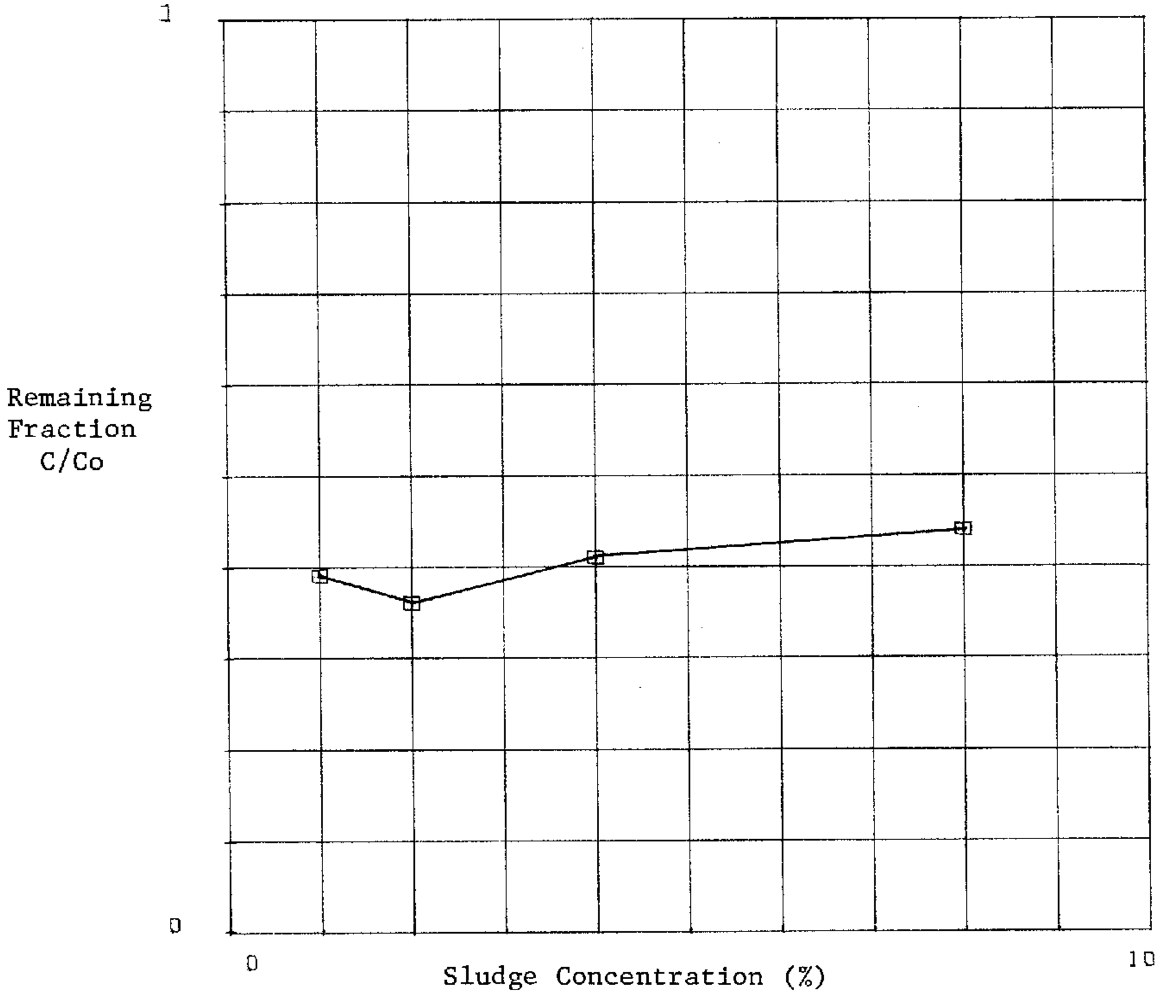

Fig. 21: Effect of Sludge Concentration on the Remaining Fraction of Nickel, Contact Time = 1 hour.

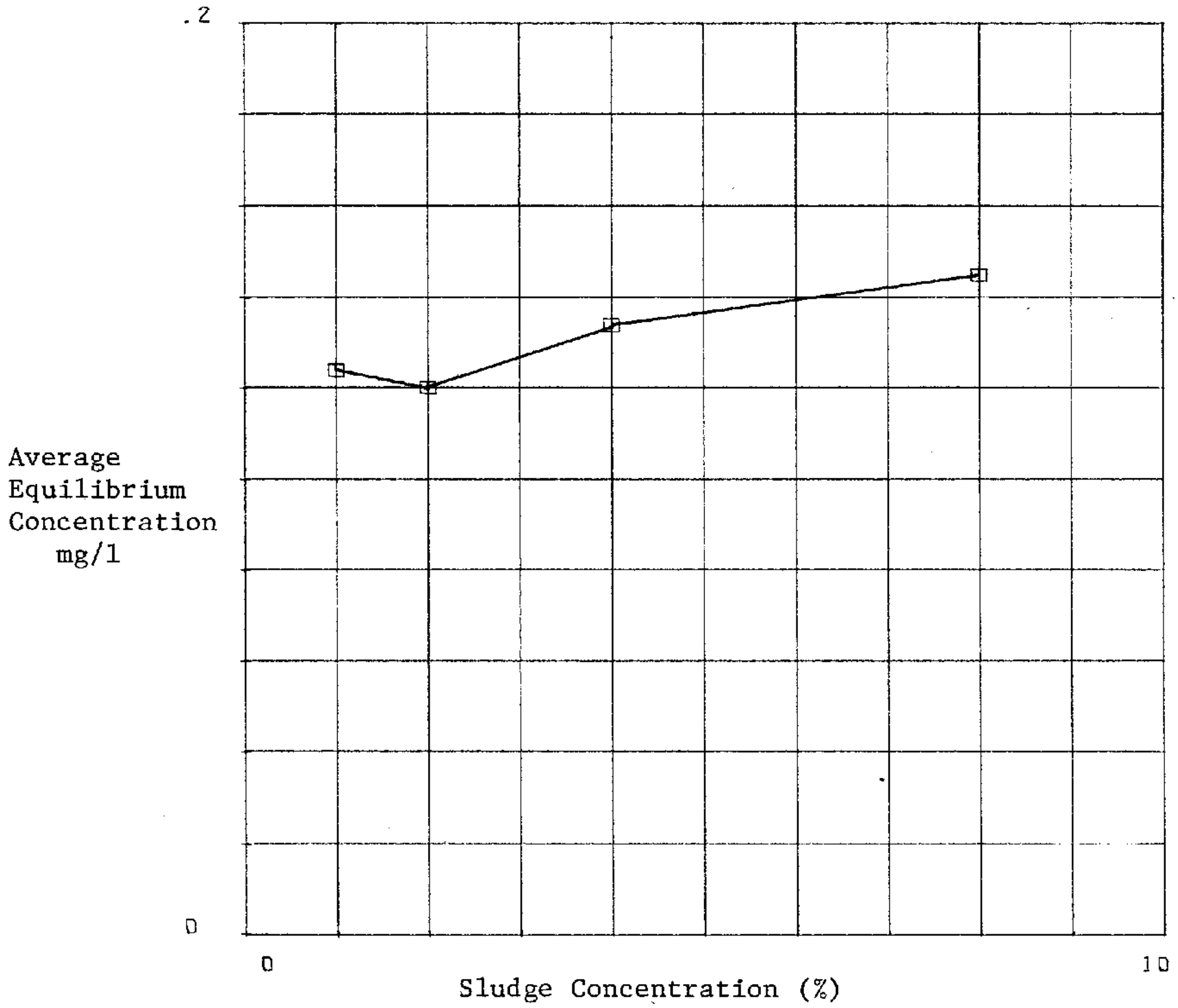

Fig. 22: Effect of Sludge Concentration on the Removal of Nickel, Contact Time = 2 hours.

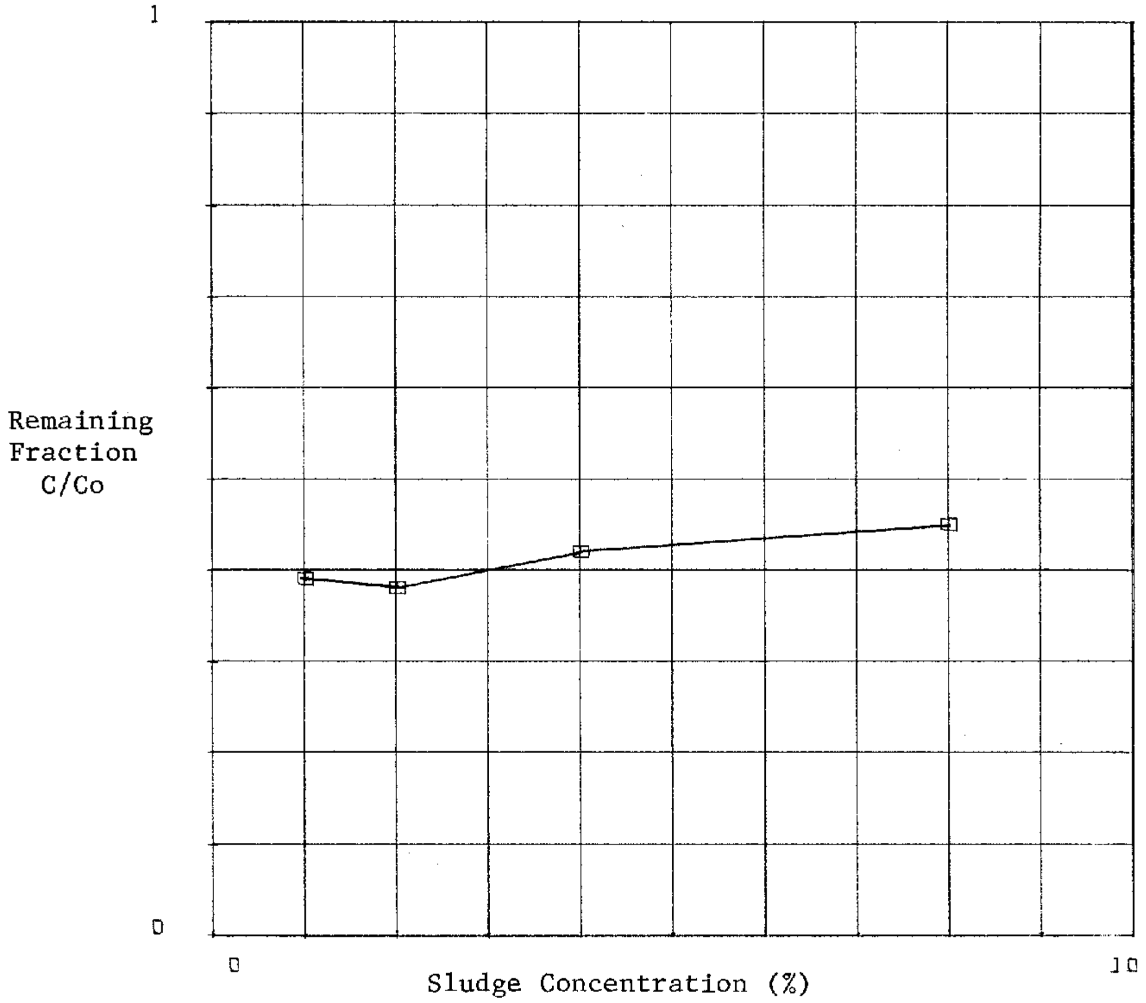

Fig. 23: Effect of Sludge Concentration on the Remaining Fraction of Nickel, Contact Time = 2 hours.

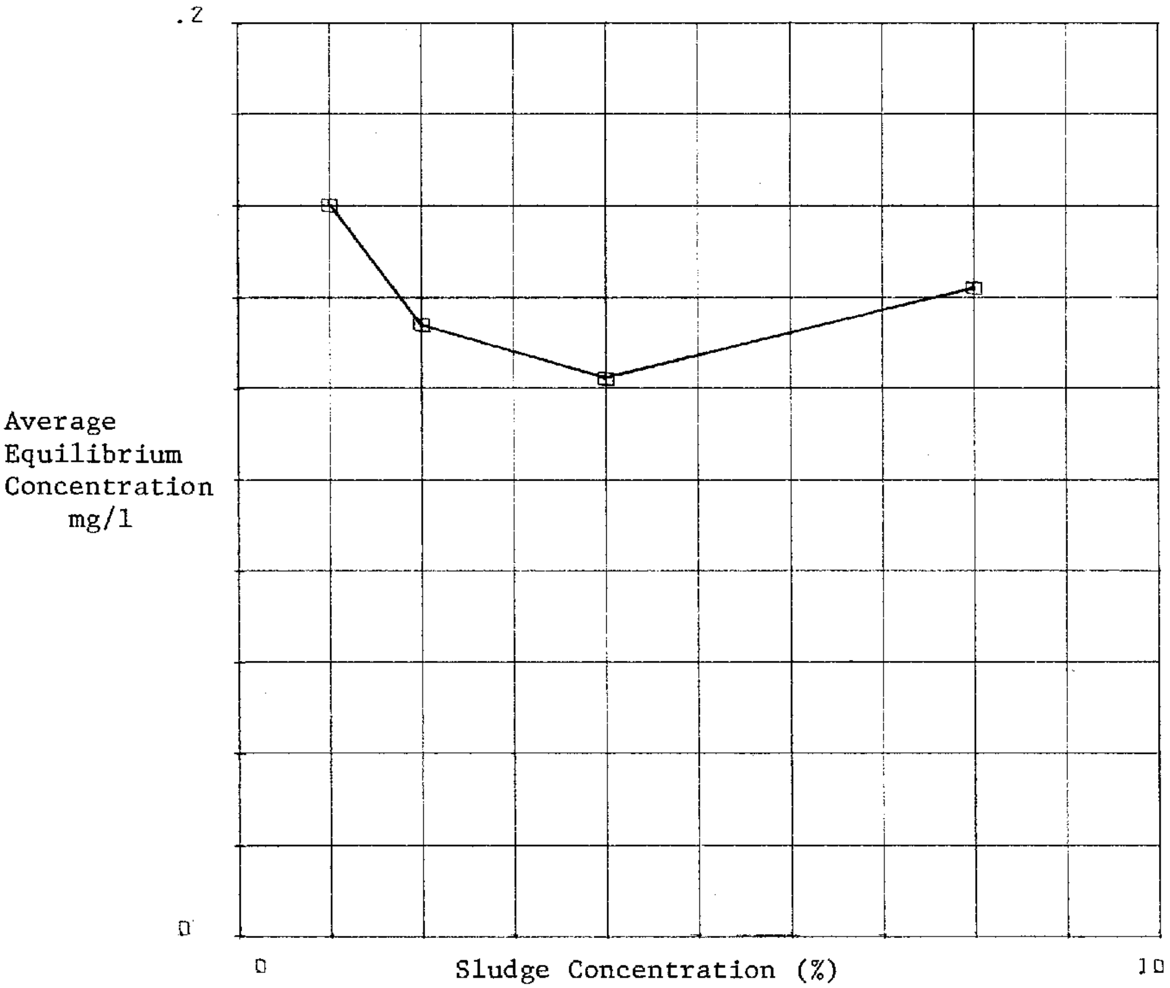

Fig. 24: Effect of Sludge Concentration on the Removal of Nickel, Contact Time = 4 hours.

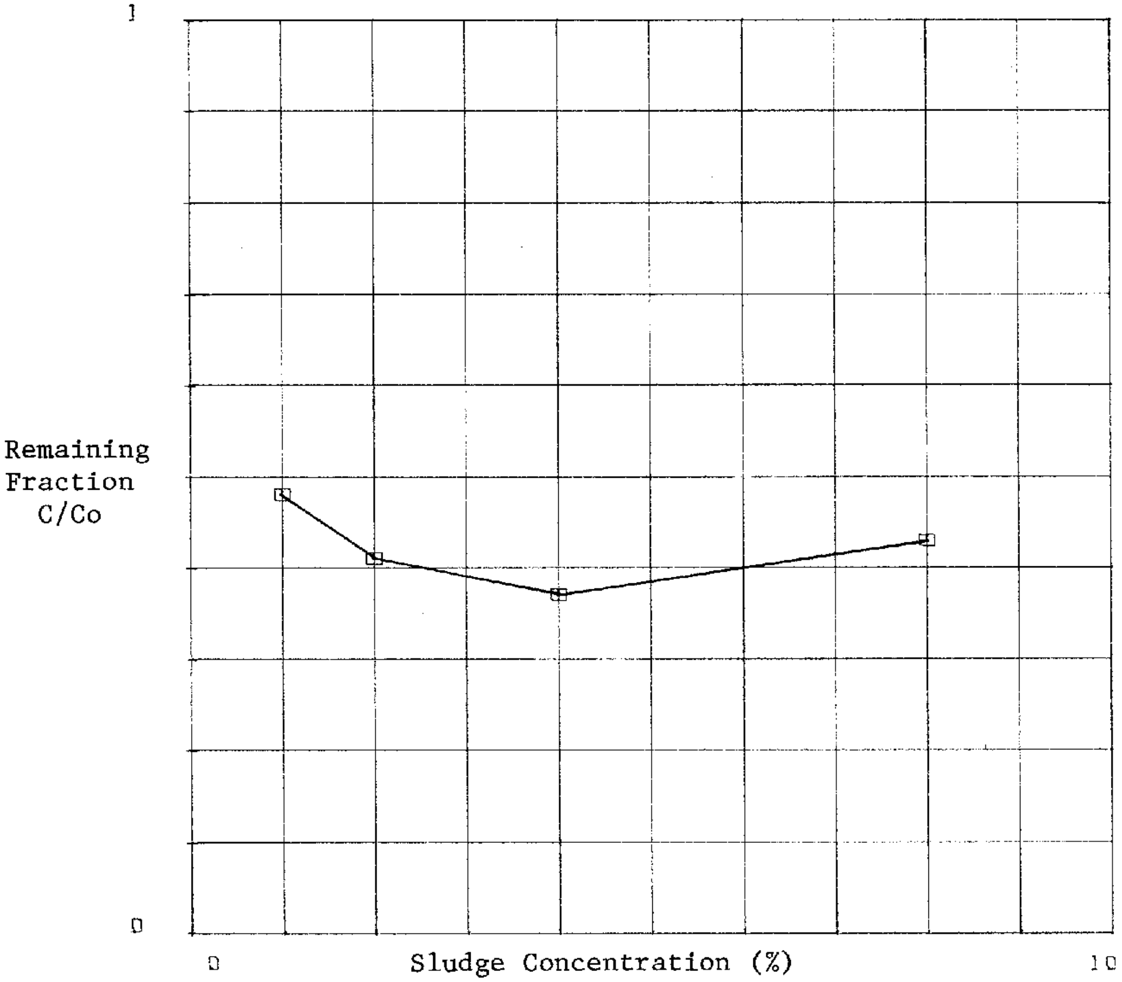

Fig. 25: Effect of Sludge Concentration on the Remaining Fraction of Nickel, Contact Time = 4 hours.

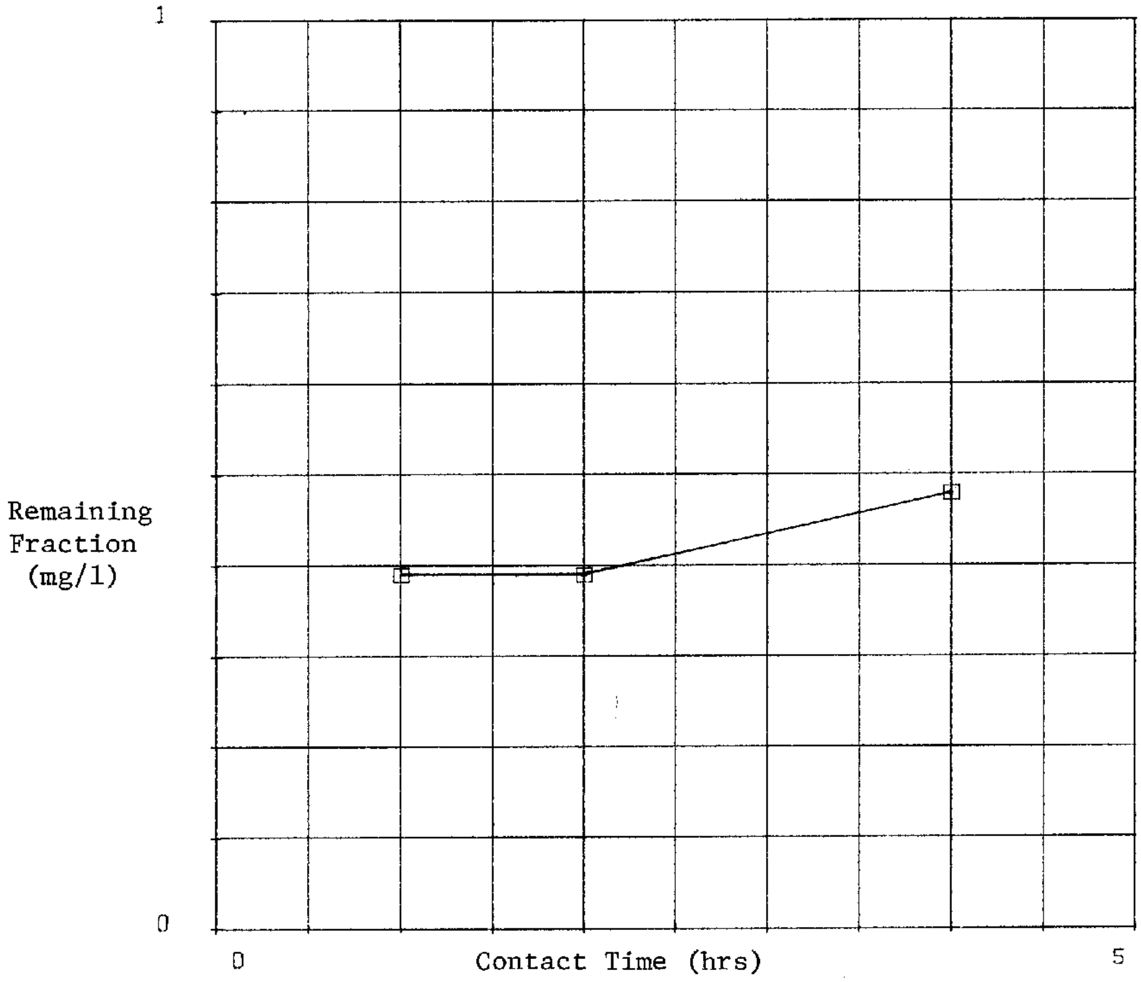

Fig. 26A: Correlation of Remaining Fraction of Nickel with Contact Time and Sludge Concentration (1%).

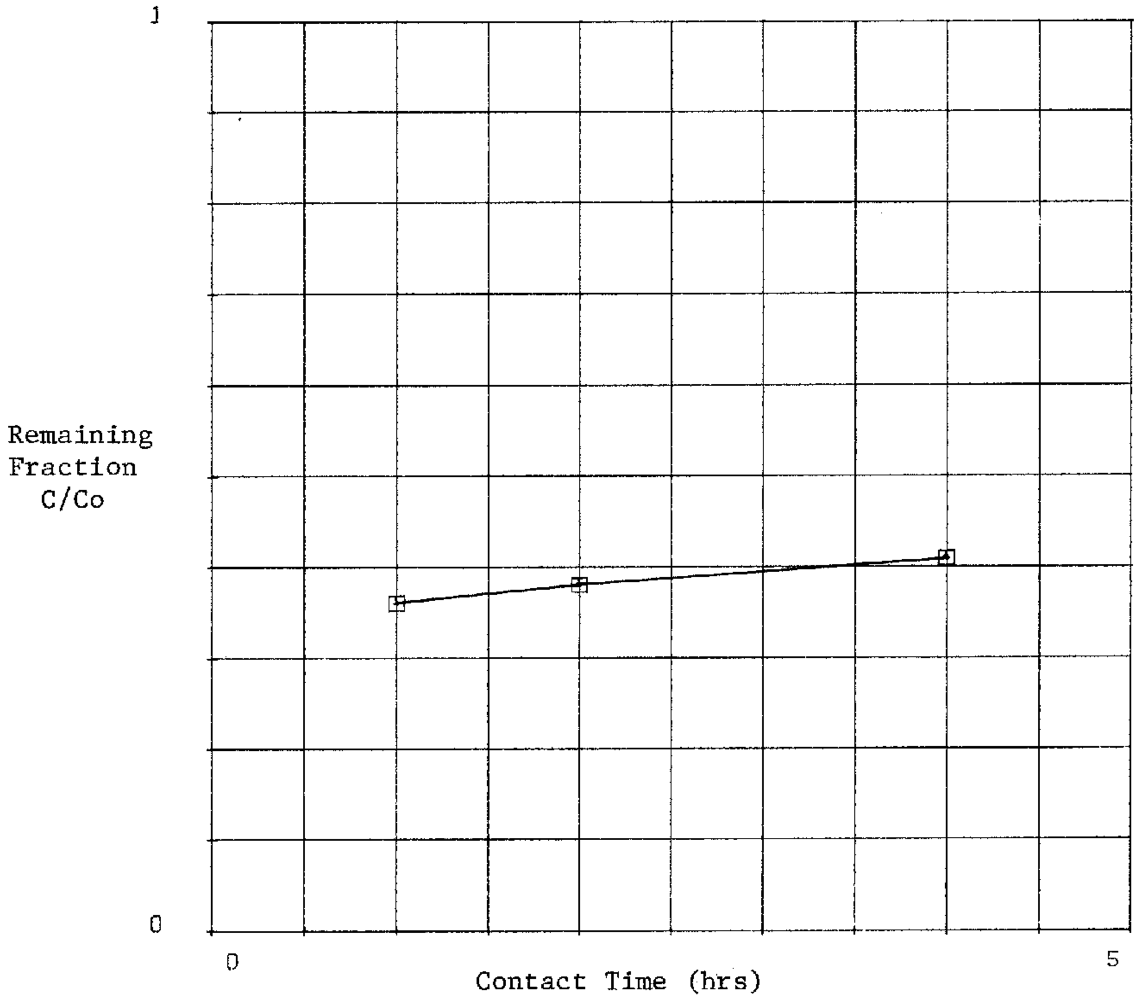

Fig. 26B: Correlation of Remaining Fraction of Nickel with Contact Time and Sludge Concentration (2%).

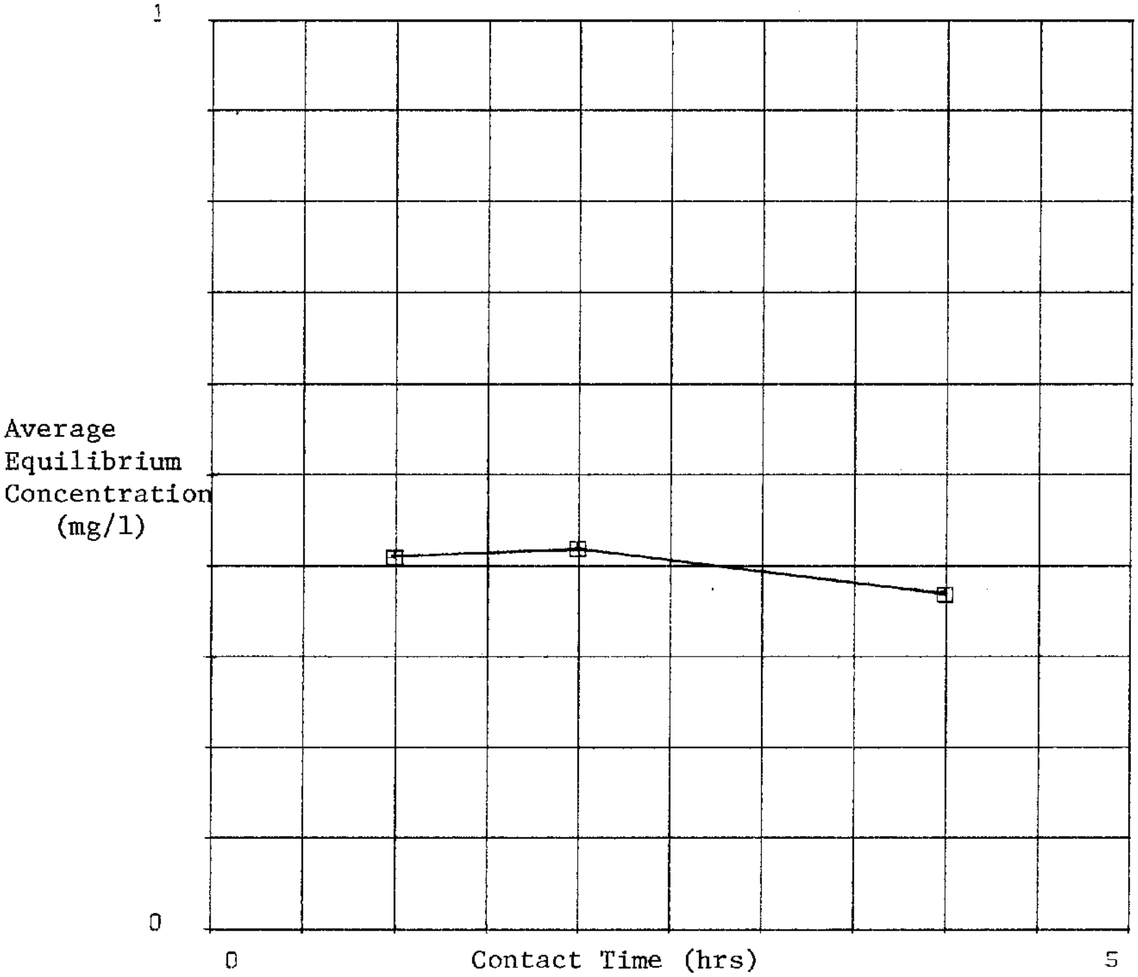

Fig. 27A: Correlation of Remaining Fraction of Nickel with Contact Time and Sludge Concentration (4%).

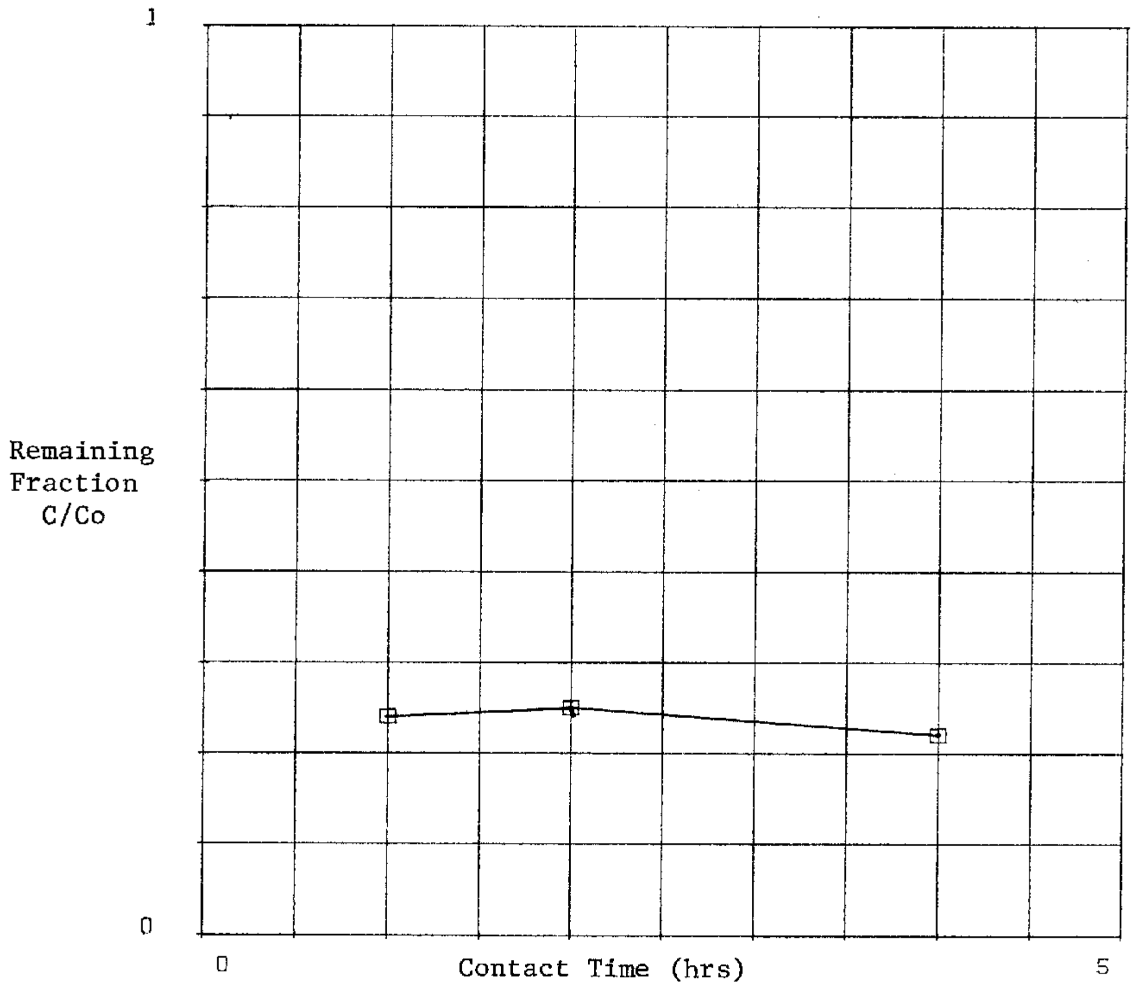

Fig. 27B: Correlation of Remaining Fraction of Nickel with Contact Time and Sludge Concentration (8%).

sludge concentration than at the higher ones. The apparent differences were found not to be statistically significant at the 0.95 level of confidence, using a standard one-tailed "t" test (16).

The above results are consistent with the ion exchange model. If the bulk metal concentration is the driving force behind the exchange, which then causes successful removals events, there is no reason why an increase in sludge concentration should increase removal. If, however, a standard adsorption site without an ion to exchange were the responsible removal mechanism, then an increase in removal efficiency should accompany an increase in sludge concentration.

Another possible explanation to what was observed is the existence of a transport limiting condition in the cell wall. Since cell walls are selectively permeable to proteins and other very large molecules, there is no reason why there should be a transport limiting condition for polyvalent cations. The results for Lead will be now examined.

Removal of Lead Through Biosorption:

Figures 28 and 29 illustrate the effect of pH on the equilibrium concentration and removal efficiency of Lead. There seems to be initially a similar trend of increased removal with pH as with the other metals. At pH 7, however, there is a slight deterioration in the removal efficiency. This effect may be explained by the dramatic decrease in the solubility of lead at pH 7. It could be argued that the decrease in solubility effect predominates over the removal effect, thereby showing a decrease in soluble metal species removal. This argument is supported by the fact that the equilibrium concentration of lead was lower at pH 7 than at the other pH's. Thus the electrical ion exchange model previously proposed may still be considered a valid one.

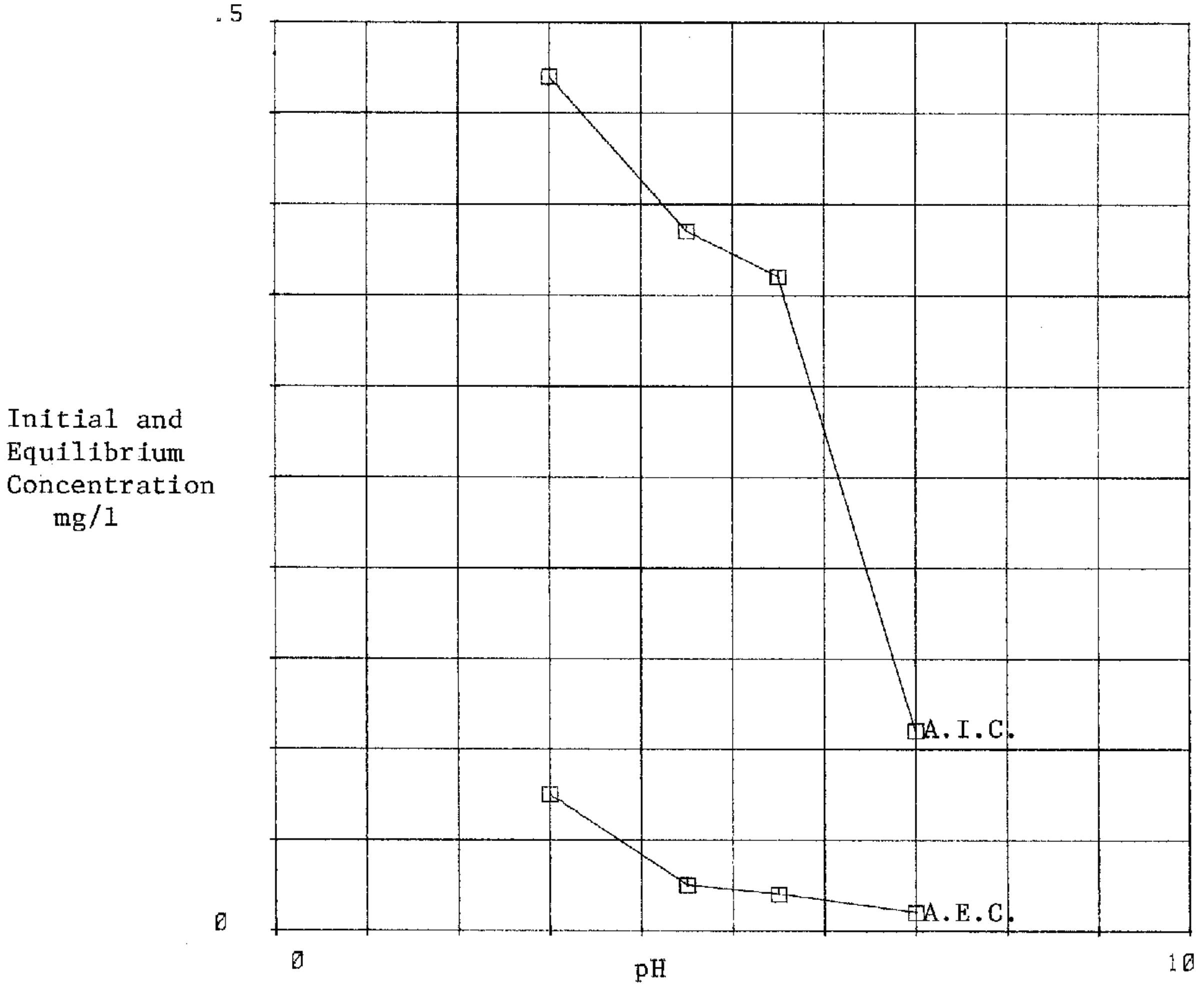

Fig. 28: Effect of Hydrolysis and pH on the Removal of Lead.

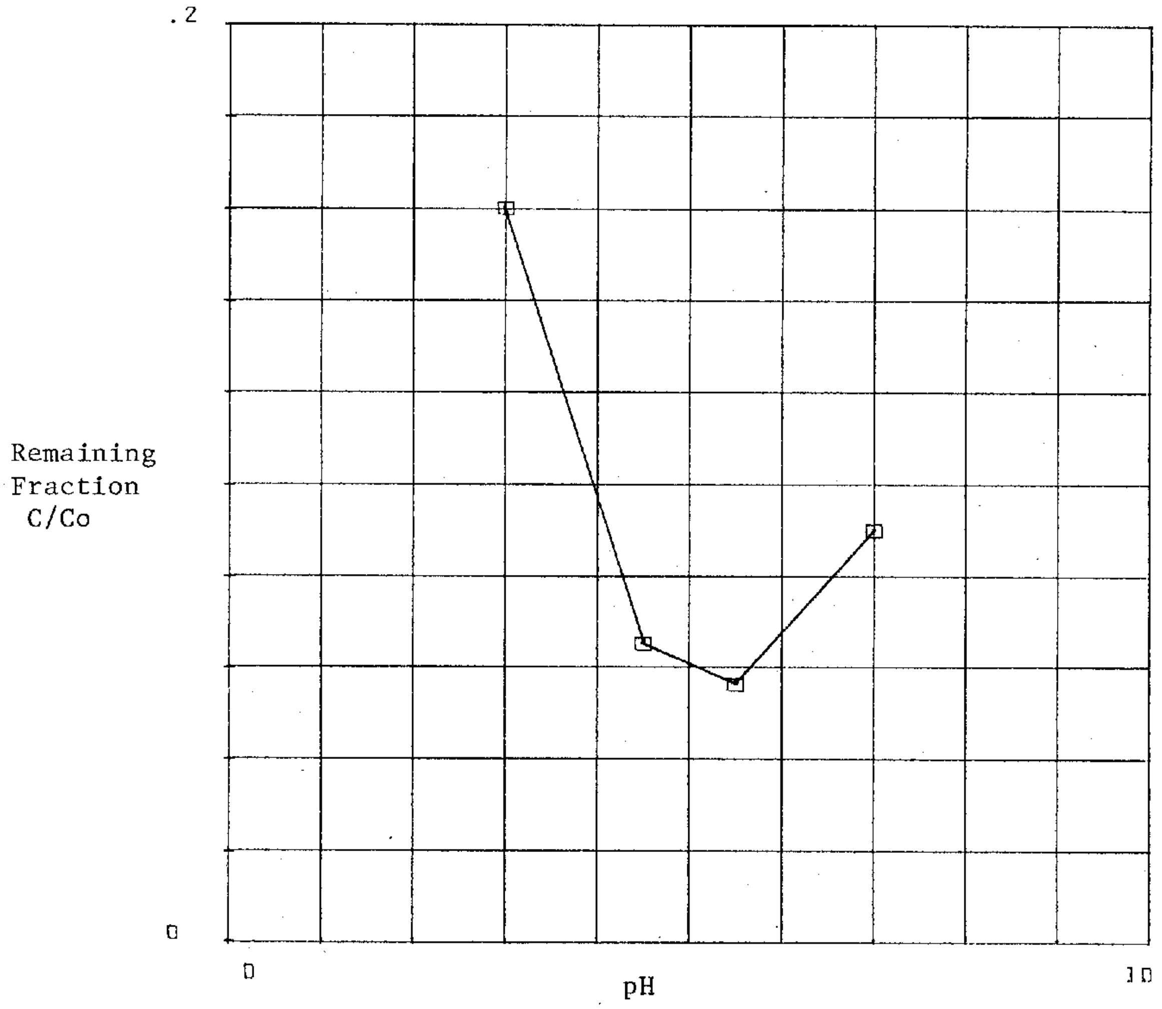

Fig. 29: Effects of Hydrolysis and pH on the Remaining Fraction of Lead.

Contact time is once more observed to have no effect in removal efficiency, for constant initial concentration of lead (∿0.28 mg/1) and constant sludge concentration (∿2 percent). This result is consistent with those for Nickel. If an ion exchange mechanism were responsible for the removal, contact time would them not be expected to have any impact. If a transport limiting condition existed, increased contact time should reveal an improvement in metal removal, which is certainly not what was observed. Thus the conclusion that no transport limiting conditions were present seems to be supported by the experimental results for lead, as presented in Figures 30 and 31.

The effects of sludge concentration on the removal of lead are illustrated in Figures 32, 34, and 36 for contact times of 1, 2 and 4 hours. The correlation with the remaining fraction is shown in Figures 33, 35 and 37. The removal efficiency was a maximum at sludge concentration of 2 percent for contact times of 1 and 2 hours. Only at a contact time of 4 hours did an increase in sludge concentration cause a corresponding increase in the removal efficiency of lead. If the electrical-ion exchange thesis is correct, then there should be no reason why an increase in sludge concentration should cause a decrease in dissolved metal concentration.

A correlation was performed of the effect of sludge concentration and contact time in the remaining fraction of lead. This correlation is summarized in Table 7 and illustrated in Figures 38A, 38B and 39A, 39B. Only at contact times of 4 hours and sludge concentrations of 4 and 8 percent does there appear a consistent pattern of reduction of soluble metal species.

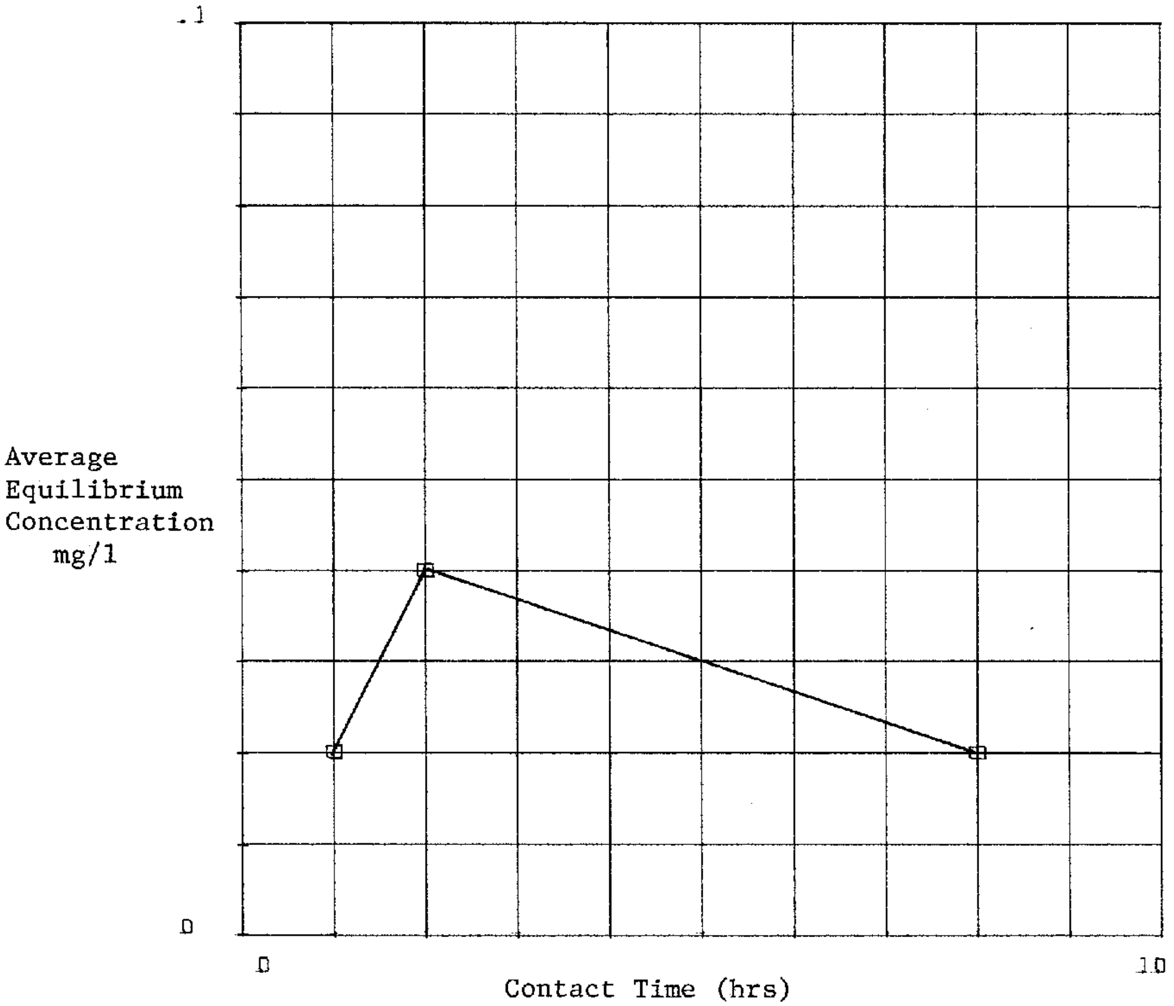

Fig. 30: Effect of Contact Time on the Removal of Lead

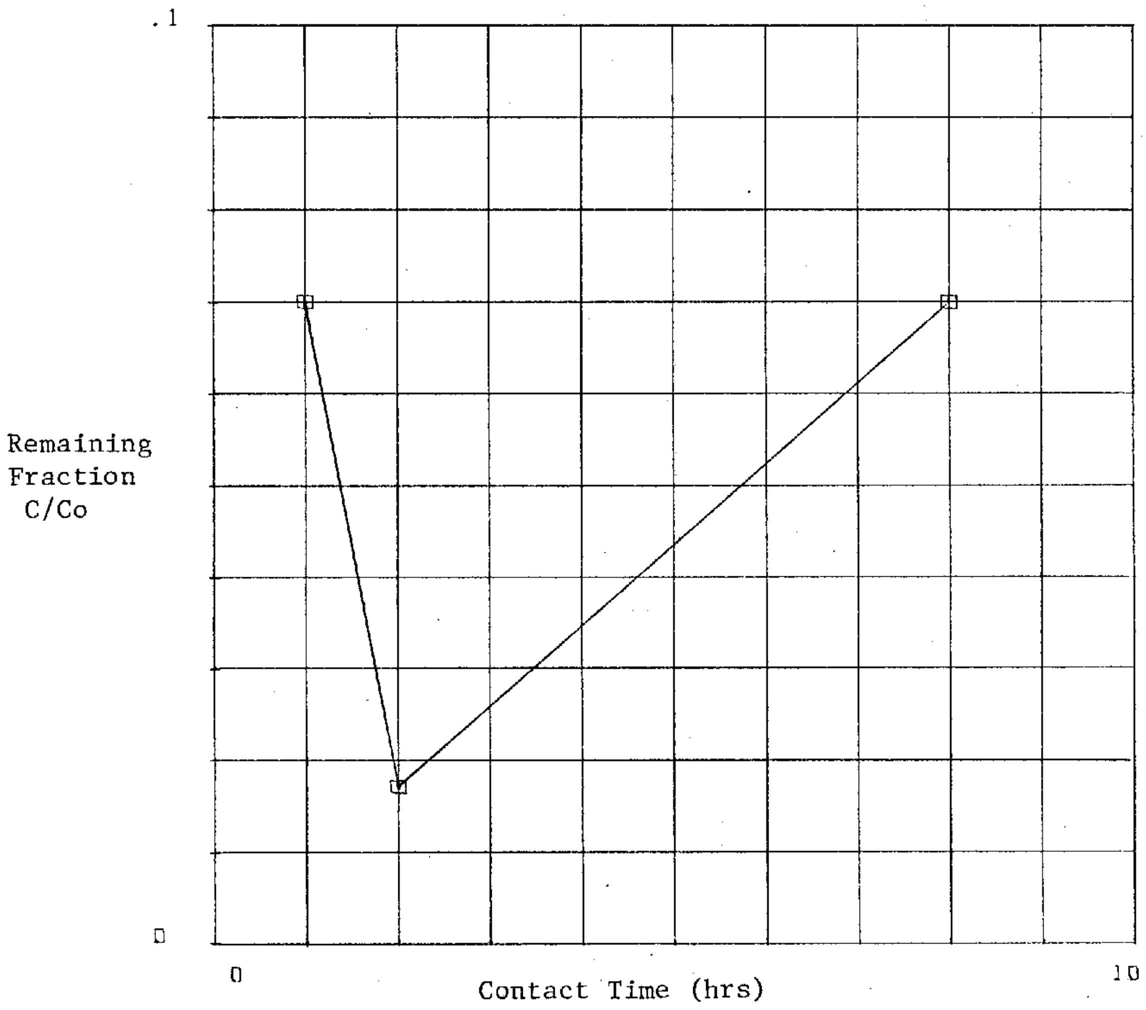

Fig. 31: Effect of Contact Time on the Remaining Fraction of Lead.

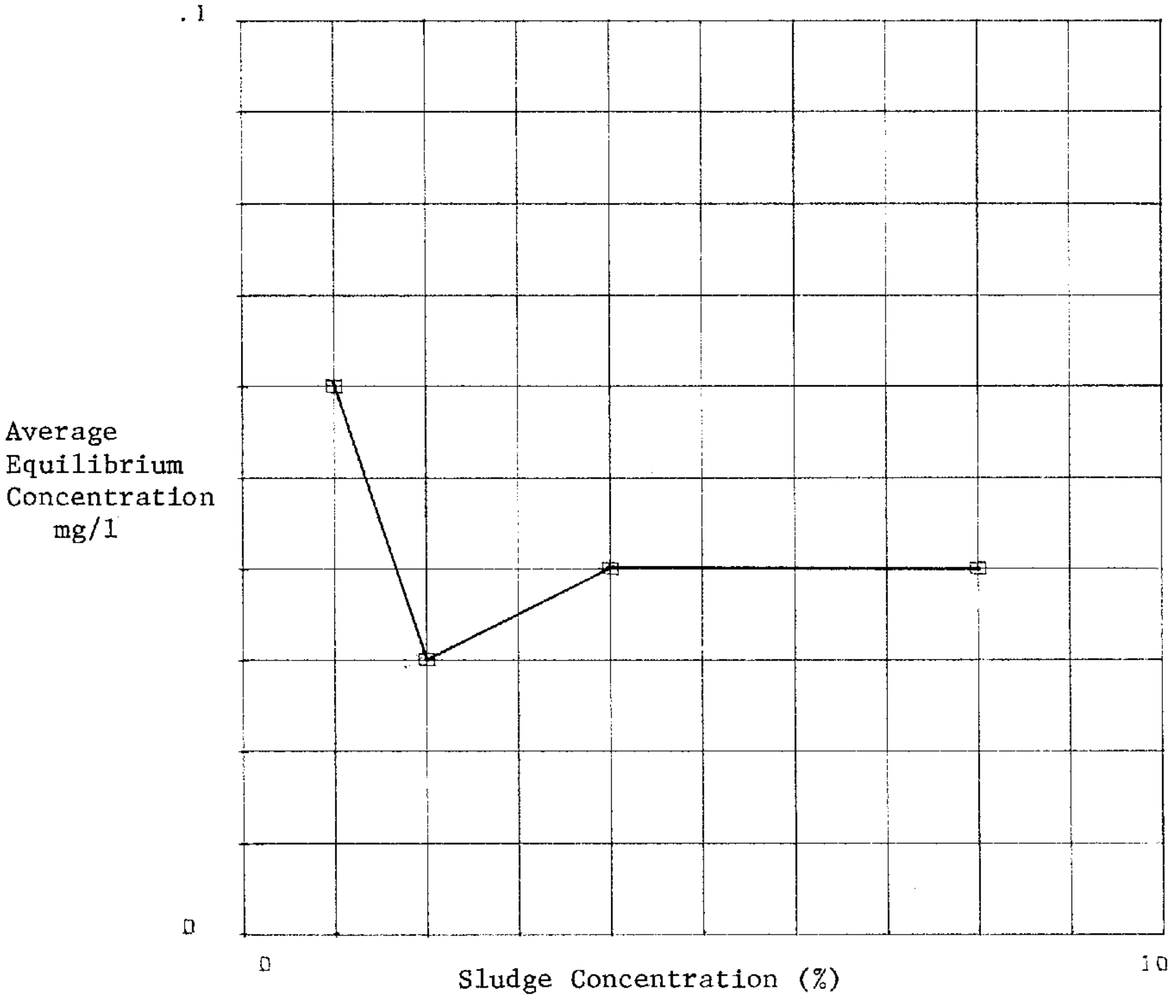

Fig. 32: Effect of Sludge Concentration on the Removal of Lead, Contact Time = 1 hour.

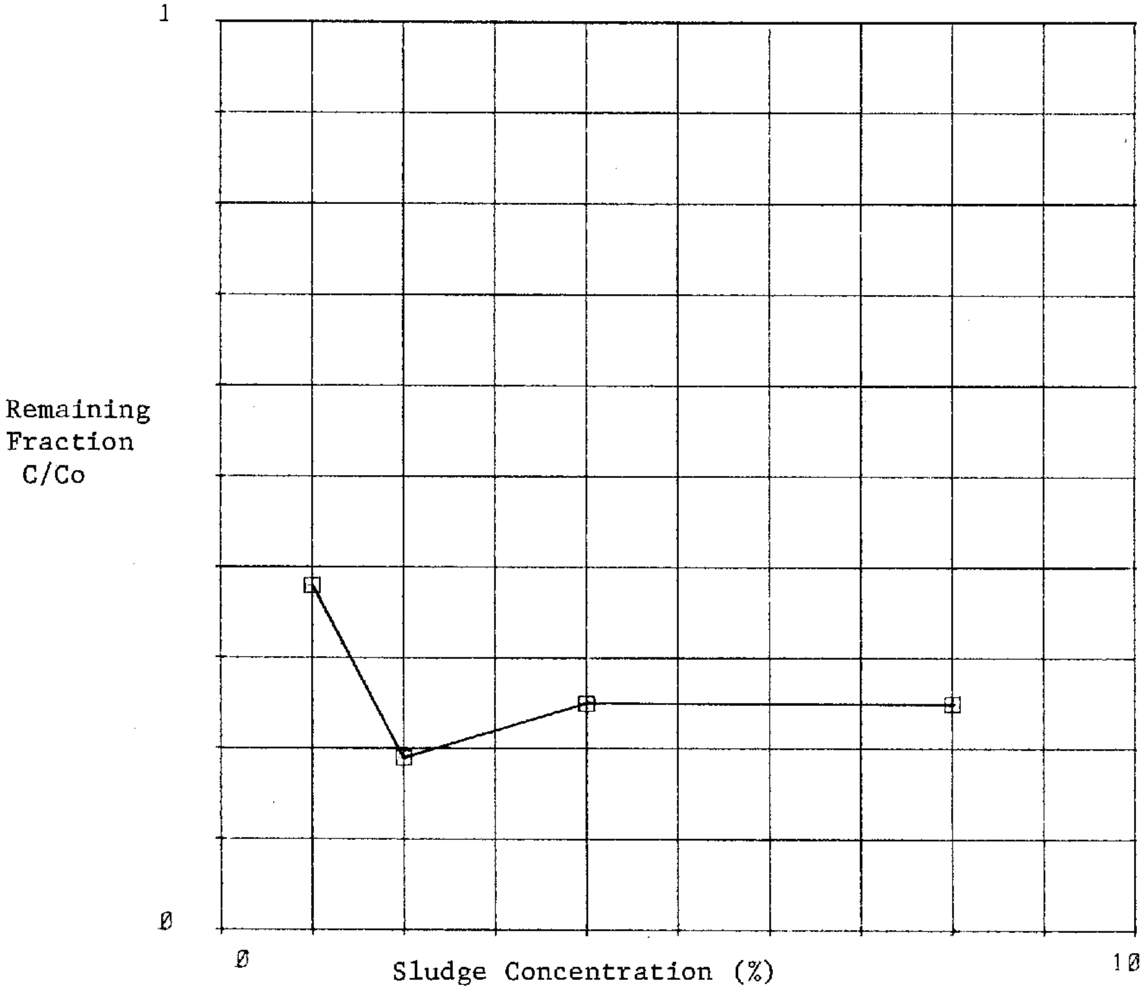

Fig. 33: Effect of Sludge Concentration on the Remaining Fraction of Lead, Contact Time = 1 hour.

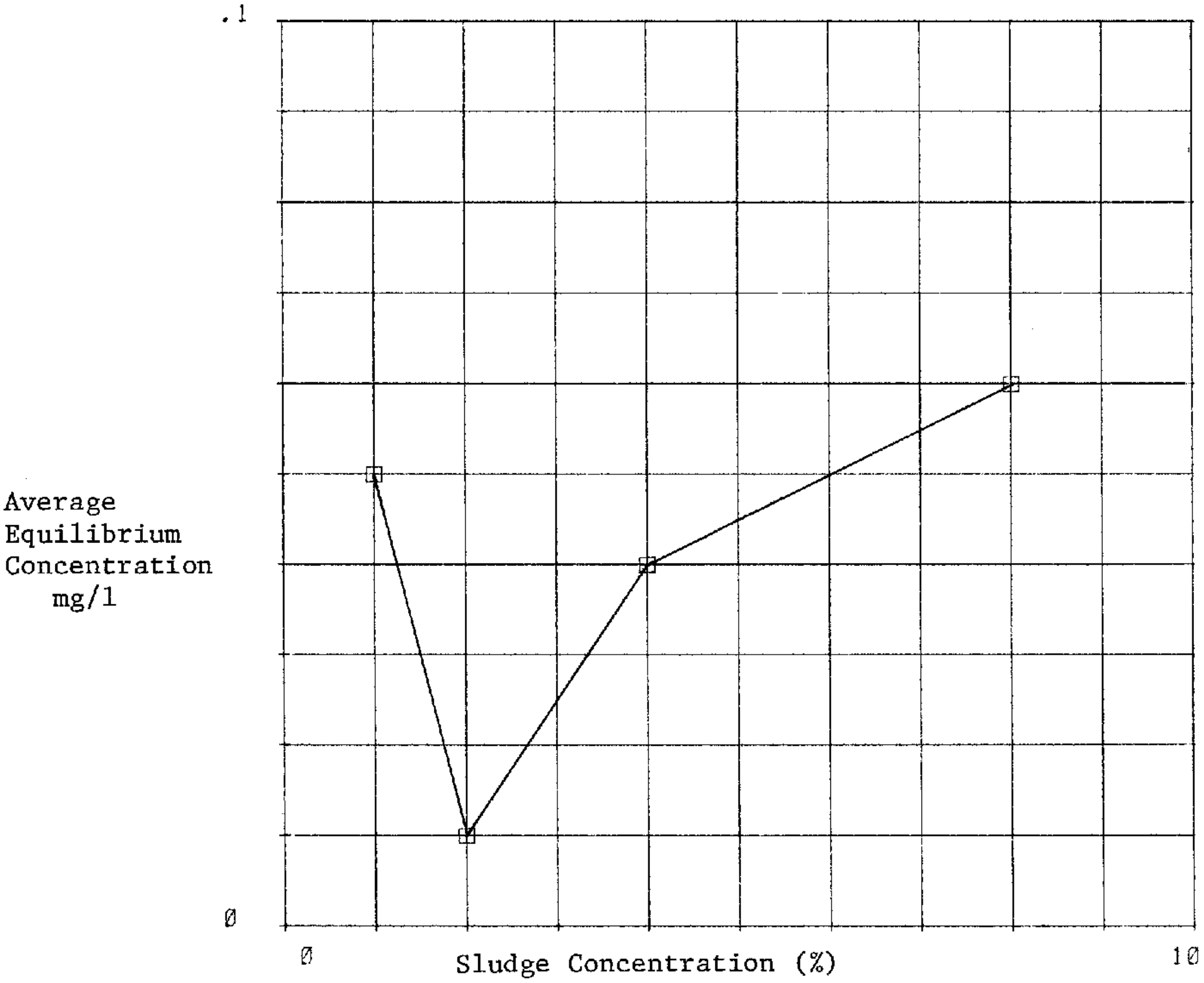

Fig. 34: Effect of Sludge Concentration on the Removal of Lead, Contact Time = 2 hours.

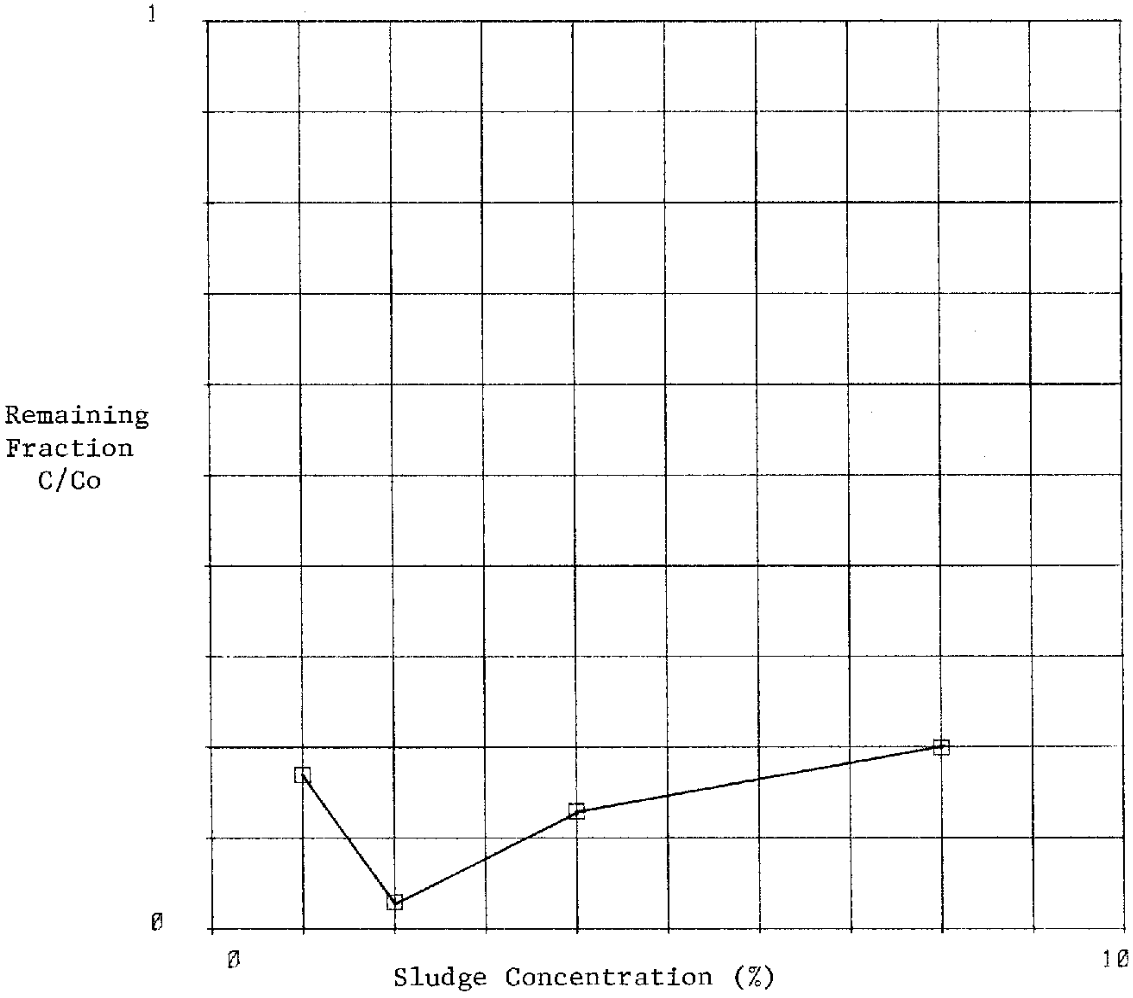

Fig. 35: Effect of Sludge Concentration on the Remaining Fraction of Lead, Contact Time = 2 hours.

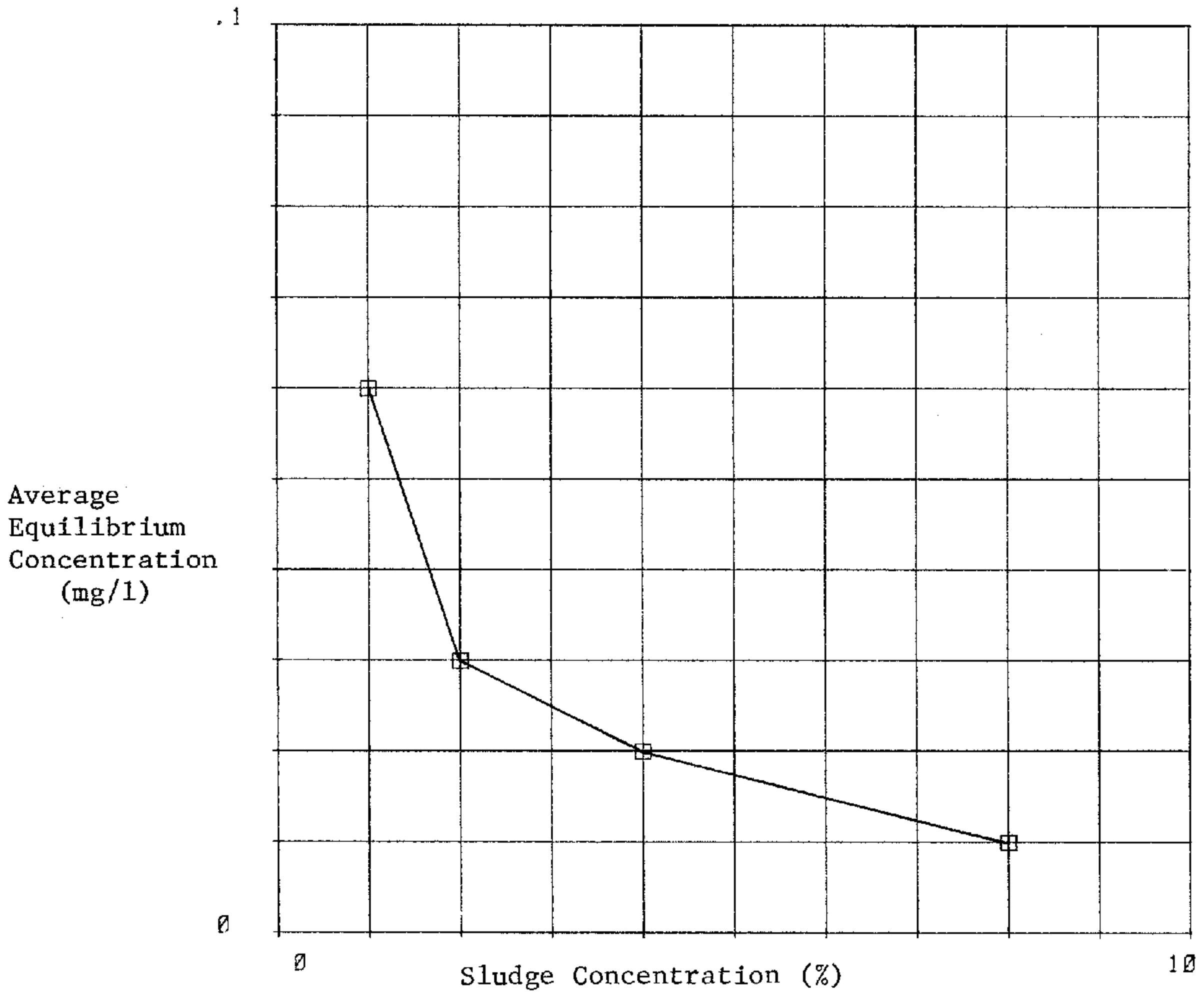

Fig. 36: Effect of Sludge Concentration on the Removal of Lead, Contact Time = 4 hours.

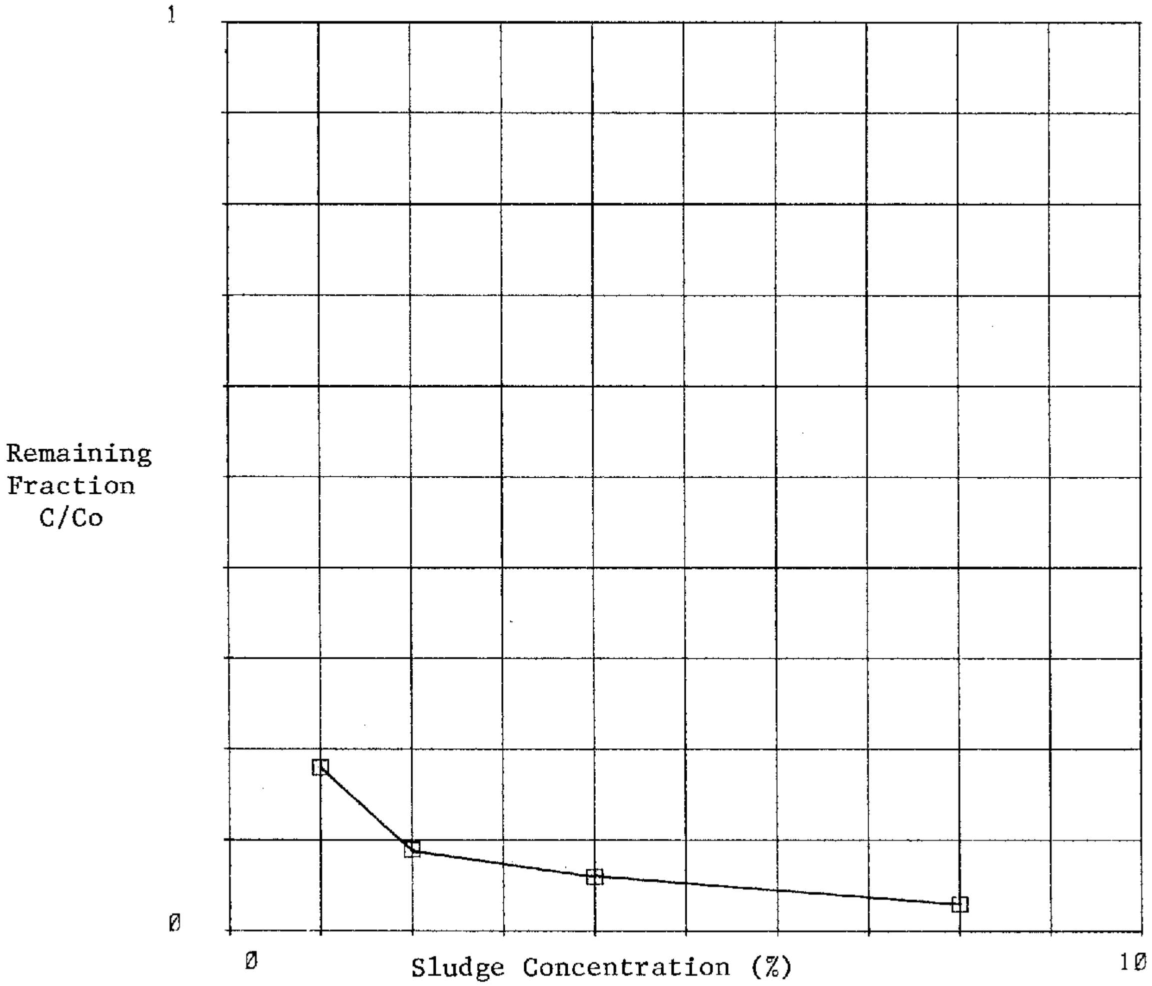

Fig. 37: Effect of Sludge Concentration on the Remaining Fraction of Lead, Contact Time = 4 hours.

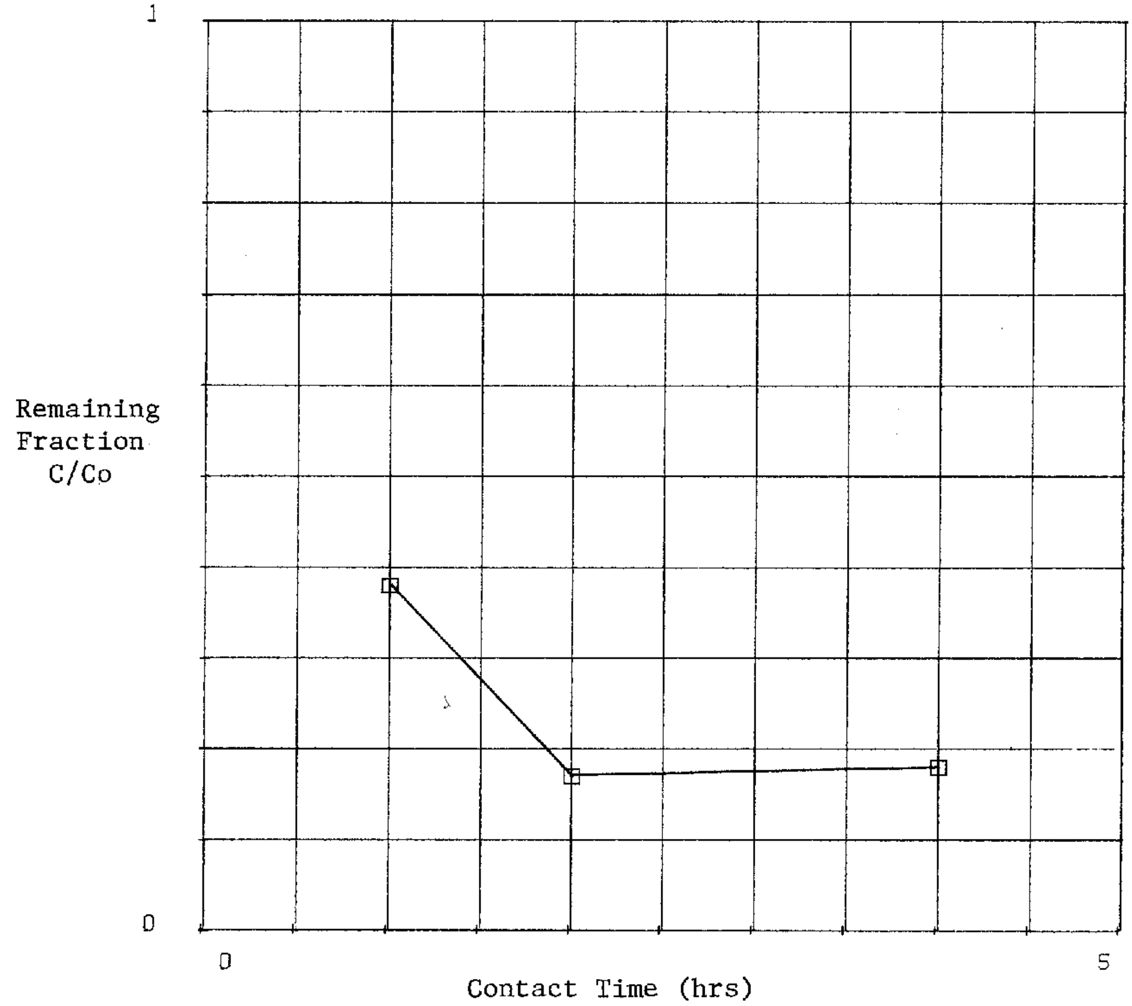

Fig. 38A: Correlation of Remaining Fraction of Lead with Contact Time and Sludge Concentration (1%).

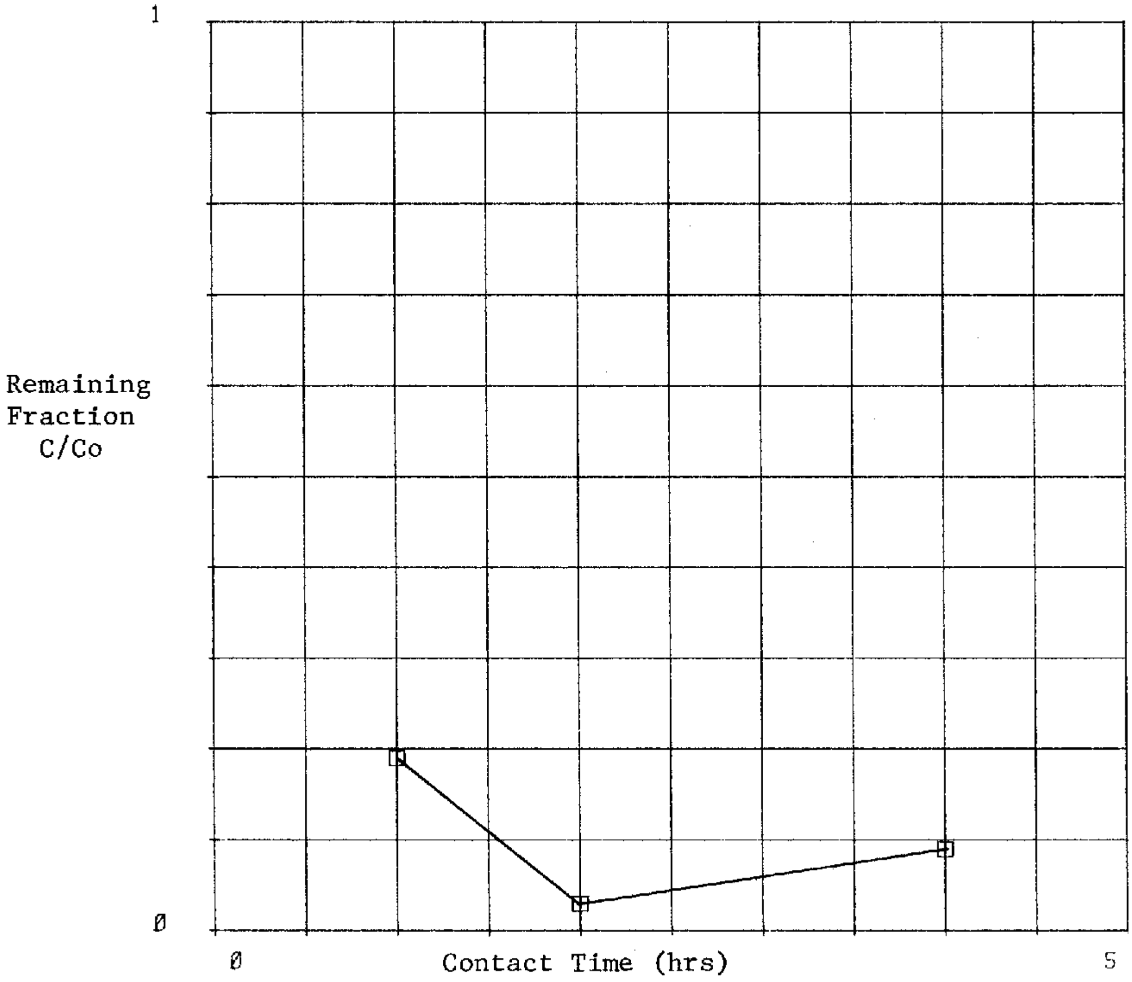

Fig. 38B: Correlation of Remaining Fraction of Lead with Contact Time and Sludge Concentration (2%).

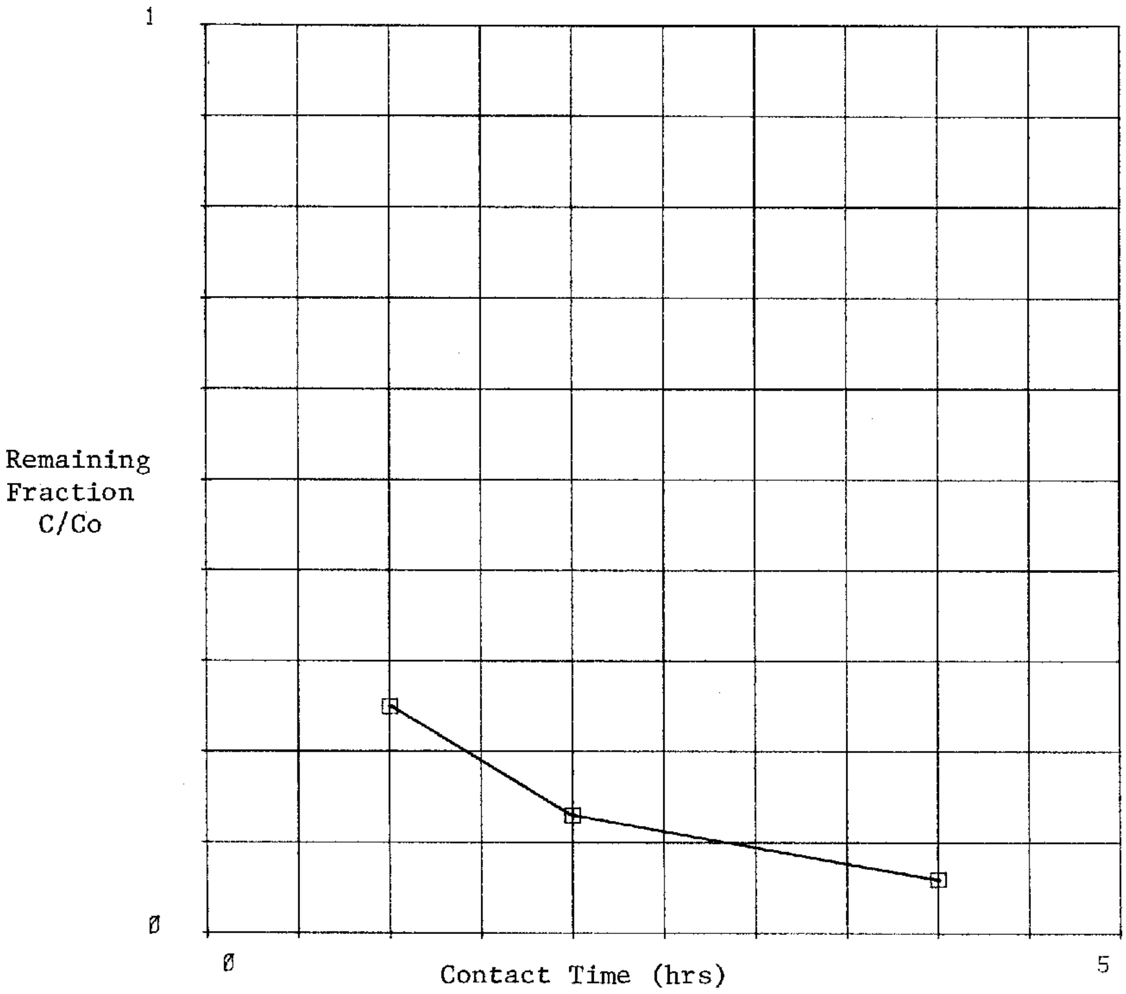

Fig. 39A: Correlation of Remaining Fraction of Lead with Contact Time and Sludge Concentration (4%).

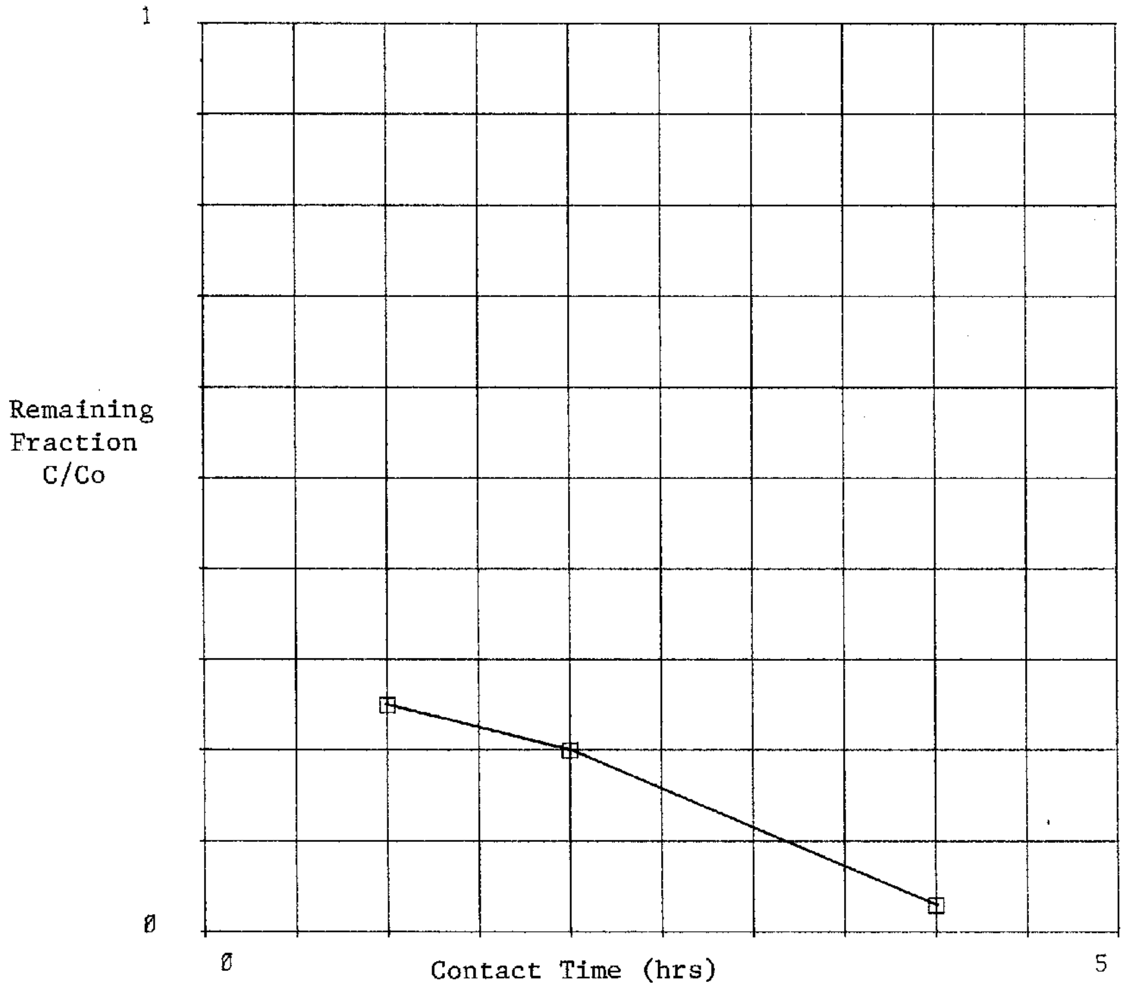

Fig. 39B: Correlation of Remaining Fraction of Lead with Contact Time and Sludge Concentration (8%).

Table 7: Effect of Contact Time and Sludge Concentration on the Remaining Fraction of Lead.

Sludge Concentration (%)	REMAINING FRACTION, C/Co		
	Contact Time, Hours		
	1	2	4
1	0.38	0.17	0.18
2	0.19	0.03	0.09
4	0.25	0.13	0.06
8	0.25	0.20	0.03

Removal of Chromium Through Biosorption:

The solubility of Chromium stayed almost constant throughout the observed pH range of 3.0 to 7.0, as seen in Figure 40. A maximum removal efficiency was observed at a pH of 4.5, (Figure 41), unlike the results obtained for Cadmium, Nickel and Lead. At pH 7.0, the remaining fraction was even higher than at pH 3.0, with a correspondingly low removal efficiency of only 38 percent (compared to 72 percent at pH 4.5 and 61 percent at pH 5.5). These results suggest that removal of Chromium through biological adsorption may not be feasible at neutral pH levels.

Removal of Zinc Through Biosorption:

The results with Zinc are the least promising of all the metals tested (Figure 42). Zinc seems like a potentially good candidate for removal through biosorption, since its solubility was not observed to decrease very much at pH 7.0. Unfortunately, the results for the experiments studying the removal of Zinc by biological sludge turned out to be completely unreliable and were therefore not reported. There was no time to repeat these experiments. The only experiment that could be reported was the one showing the effect of contact time on the removal of Zinc (Figure 43). As with other metal, contact time seemed to have no effect, but there also seemed to be no-

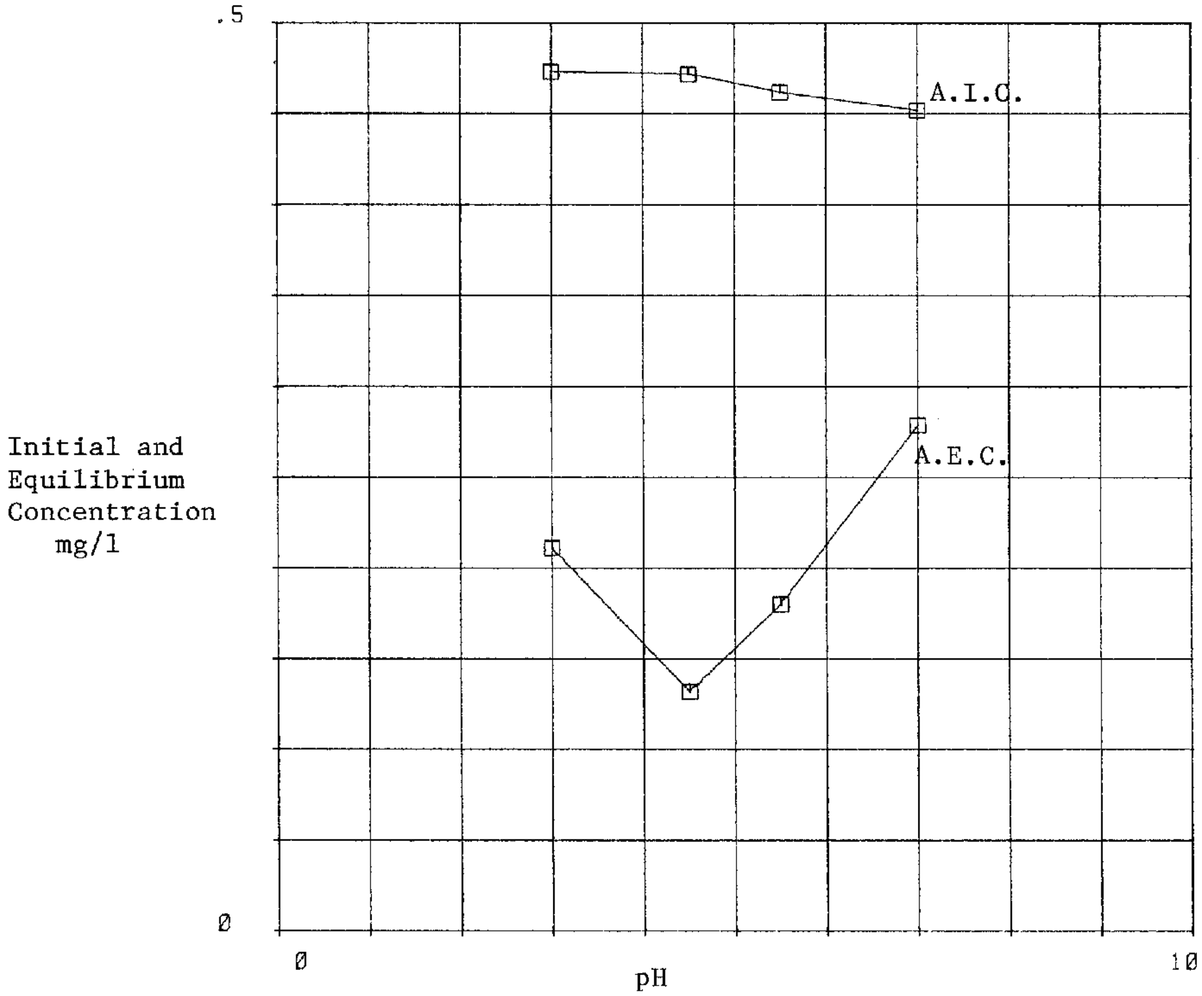

Fig. 40: Effect of Hydrolysis and pH on the Removal of Chromium.

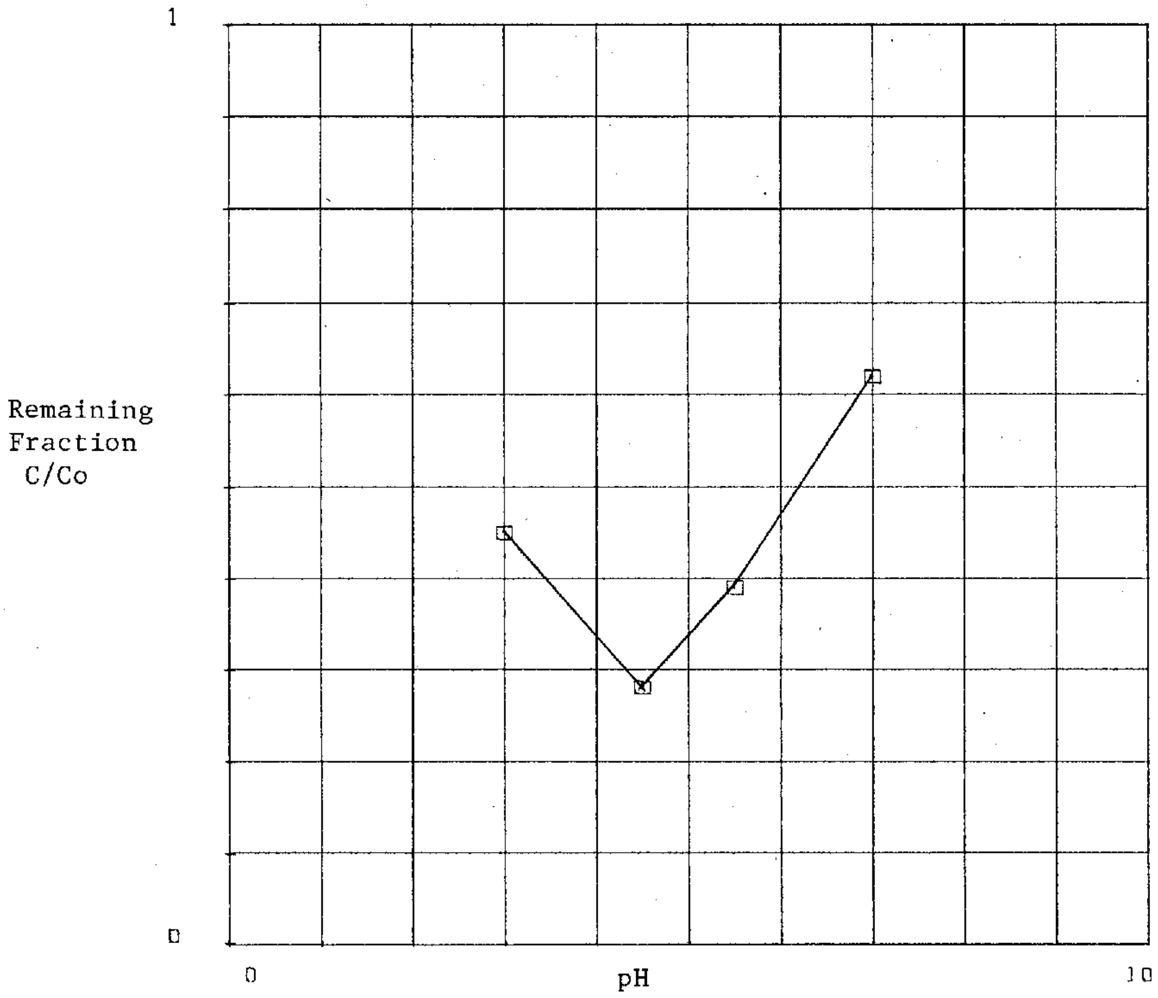

Fig. 41: Effects of Hydrolysis and pH on the Remaining Fraction of Chromium.

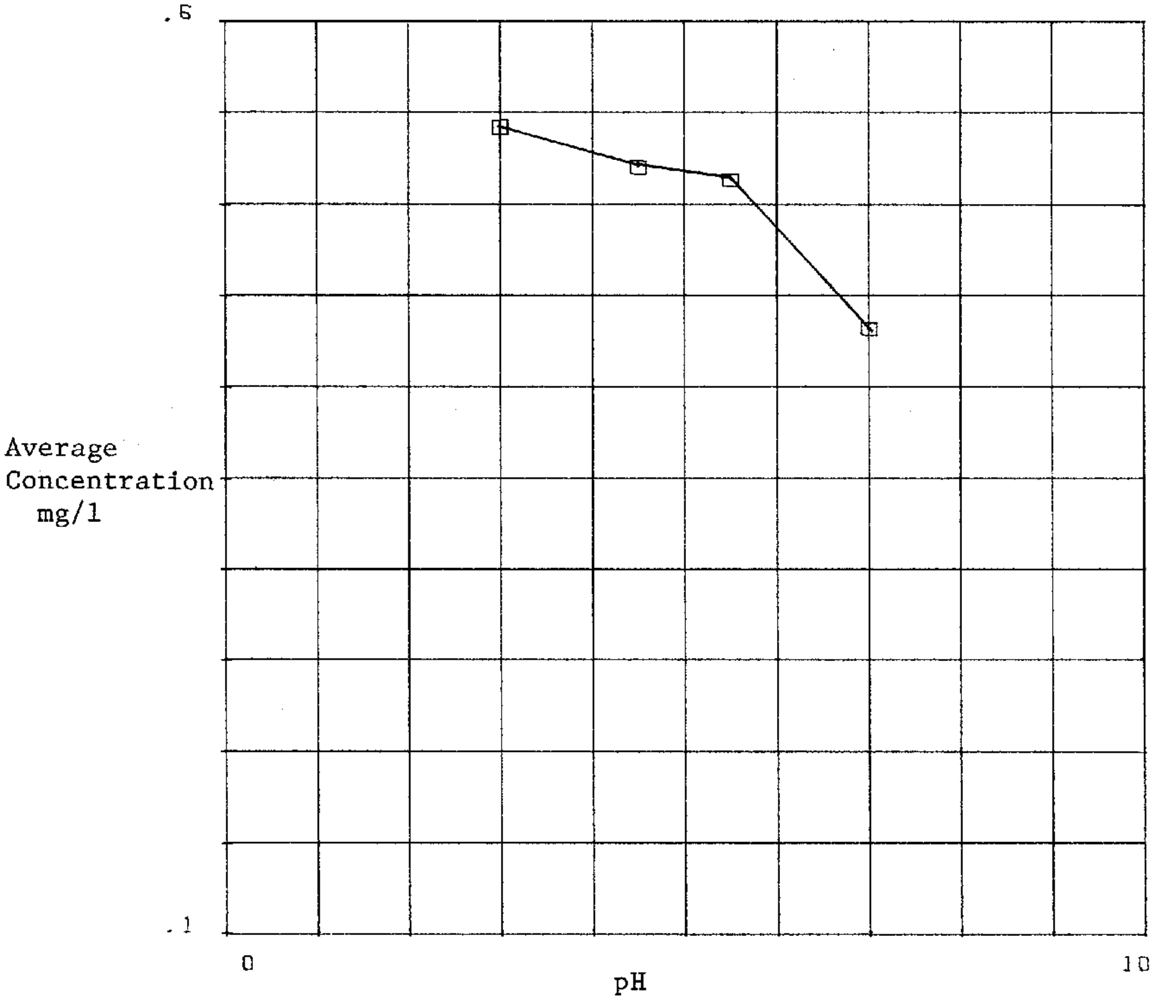

Fig. 42: Effects of Hydrolysis and pH on the Solubility of Zinc.

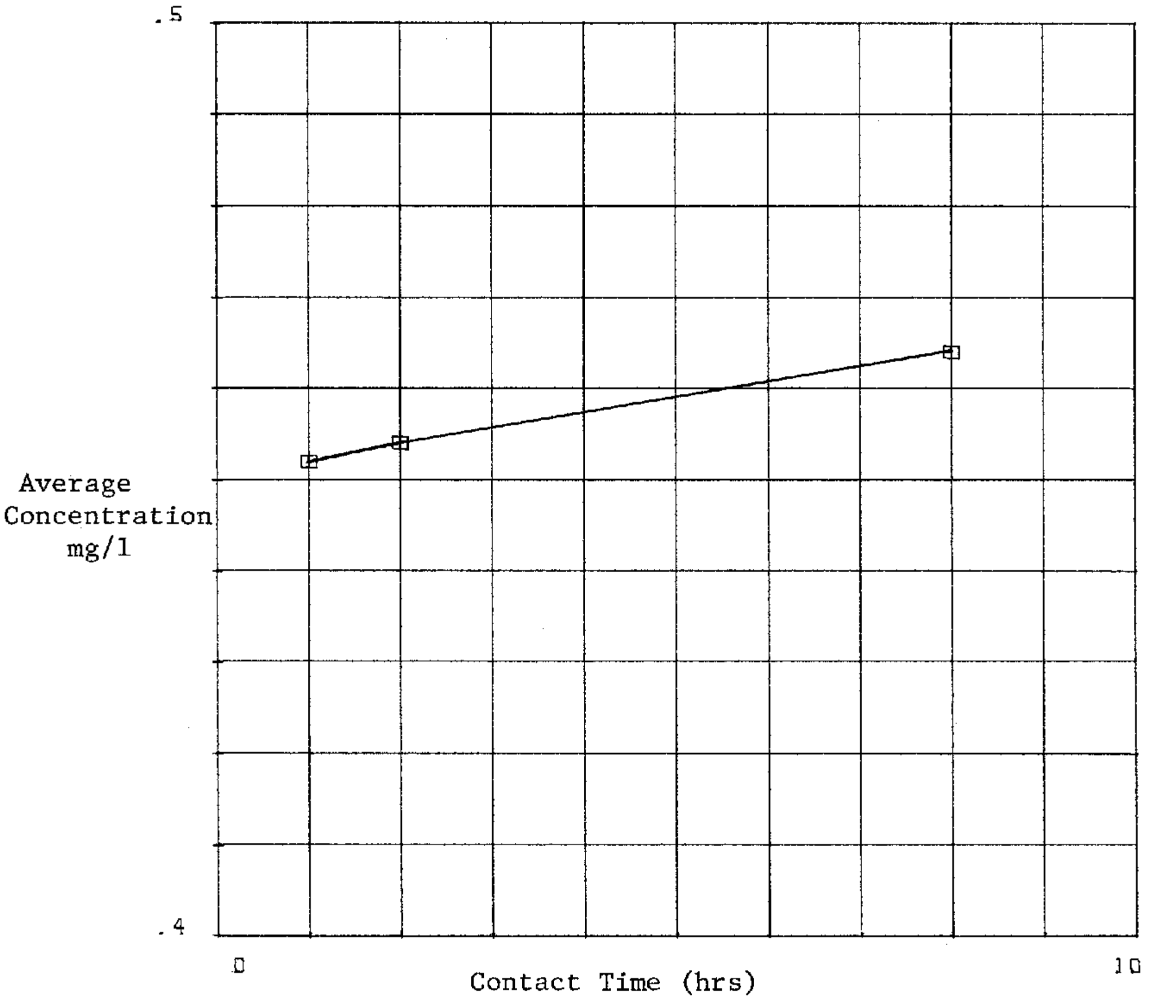

Fig. 43: Effect of Contact Time on the Removal of Zinc

removal of metal, which was completely contrary to expectations and to previous results with other metals. We do not feel that these results are trustworthy and thus discard the results with zinc in its entirety.

Adsorption Behavior by the Biological Sludge:

An attempt was made to characterize the adsorption properties of the biological sludge by correlating some of the data through the Langmuir and Freundlich isotherm models.

Langmuir Correlation:

The Langmuir model assumes that (17):

1. maximum adsorption of solute molecules occur on the surface of the adsorber.
2. the energy of adsorption is constant.
3. there is no transmigration of adsorbate in the surface of the adsorber.

The equation for the Langmuir model is

$$q_e = \frac{Q^\circ bC}{1 + bC} \qquad (1)$$

where qe = amount of solute adsorbed per unit weight of solid adsorbent, moles/g or g/g.

C = concentration of solute remaining in solution at equilibrium, moles/1 or g/1.

b = constant related to the net enthalpy (ΔH) of adsorption, $b \alpha e^{-\Delta H/RT}$.

Q°= maximum no. of moles or mass of solute possible to complete a saturated monolayer.

The linearized form of equation (1) is

$$\frac{1}{q_e} = \frac{1}{Q^\circ} + \left(\frac{1}{bQ^\circ}\right)\left(\frac{1}{C}\right) \qquad (2)$$

where a plot of 1/qe versus 1/C should yield a linear relationship.

The mass of metal adsorbed per unit mass of sludge was calculated from the experiments studying the effect of sludge concentration in metal removal. The reciprocal of said quantity was plotted against the reciprocal of the equilibrium concentration of the metal.

Freundlich Correlation:

The Freundlich model (17) assumes that:

a) adsorption has heterogeneous surface energies

b) the energy term of the Freundlich model (b) varies as a function of surface coverage, q_e, strictly due to variations in heat of adsorption.

The Freundlich model is basically an empirical relation which is often useful to describe and characterize data. The equation is of the form

$$qe = K\ C^{1/m} \qquad (3)$$

where K = is a constant characteristic of the solute -solvent-adsorber system. $K \alpha RT_n b e^{\Delta H/RT}$

n = is a constant greater than 1.

The linearized form of the equation is

$$\log qe = \log K + \frac{1}{n} \log C \qquad (4)$$

where a plot of log qe versus log C should yield a straight line with intercept log K and slope 1/n.

Correlation of data:

Figures 44, 46, and 48 illustrate the Langmuir correlation for Cadmium at contact times of 1, 2, and 4 hours, respectively. The data does not fit the Langmuir model well.

Figures 45, 47, and 49 illustrate the Freundlich correlation for Cadmium at the same contact time as before. Again the data does not seem to fit the model at all. Only the data corresponding to a contact time of four hours approximates something that could correlate with the model,

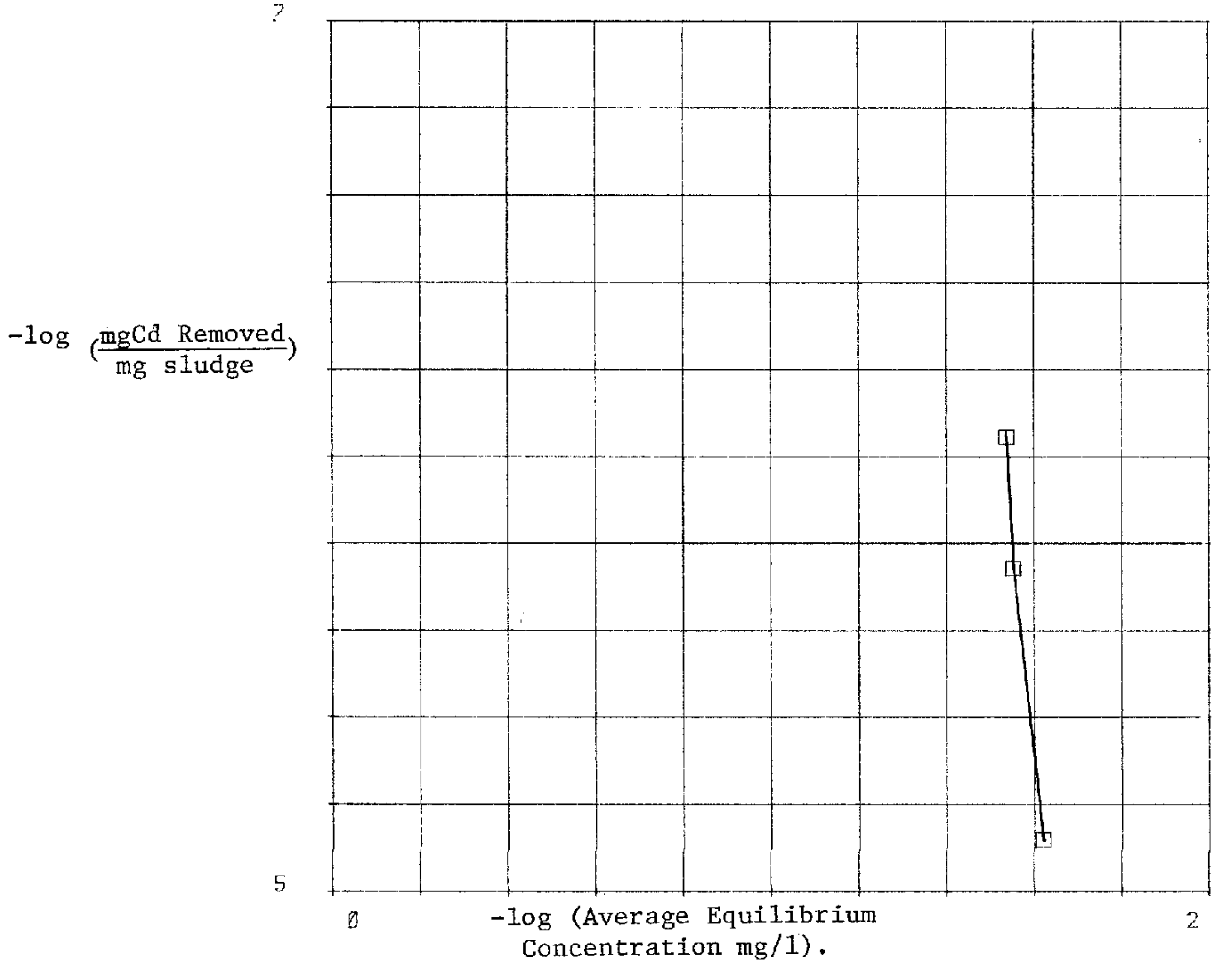

Fig. 44: Langmuir Isotherm for Cadmium, Contact Time = 1 hour.

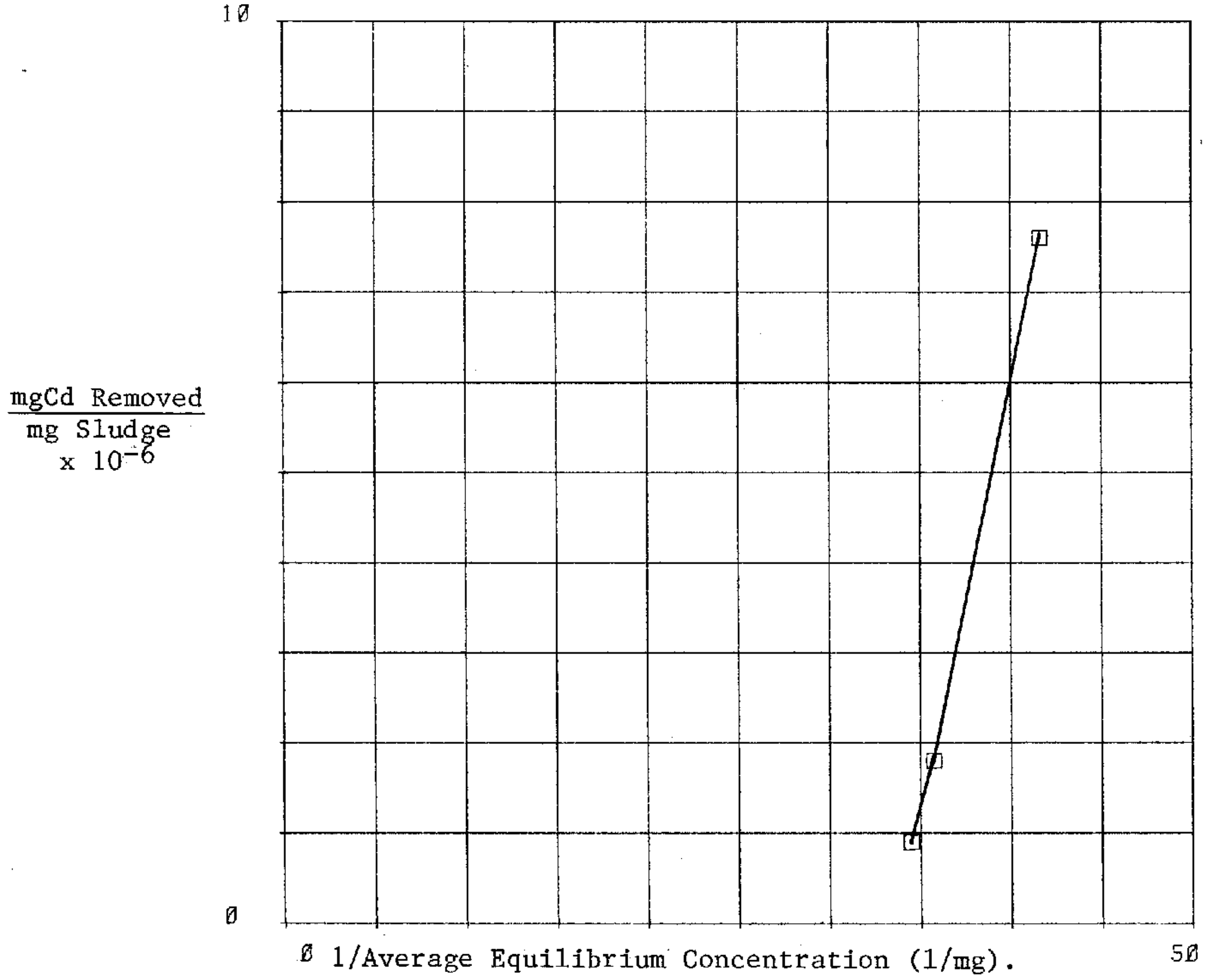

Fig. 45: Freundlich Isotherm for Cadmium, Contact Time = 1 hour.

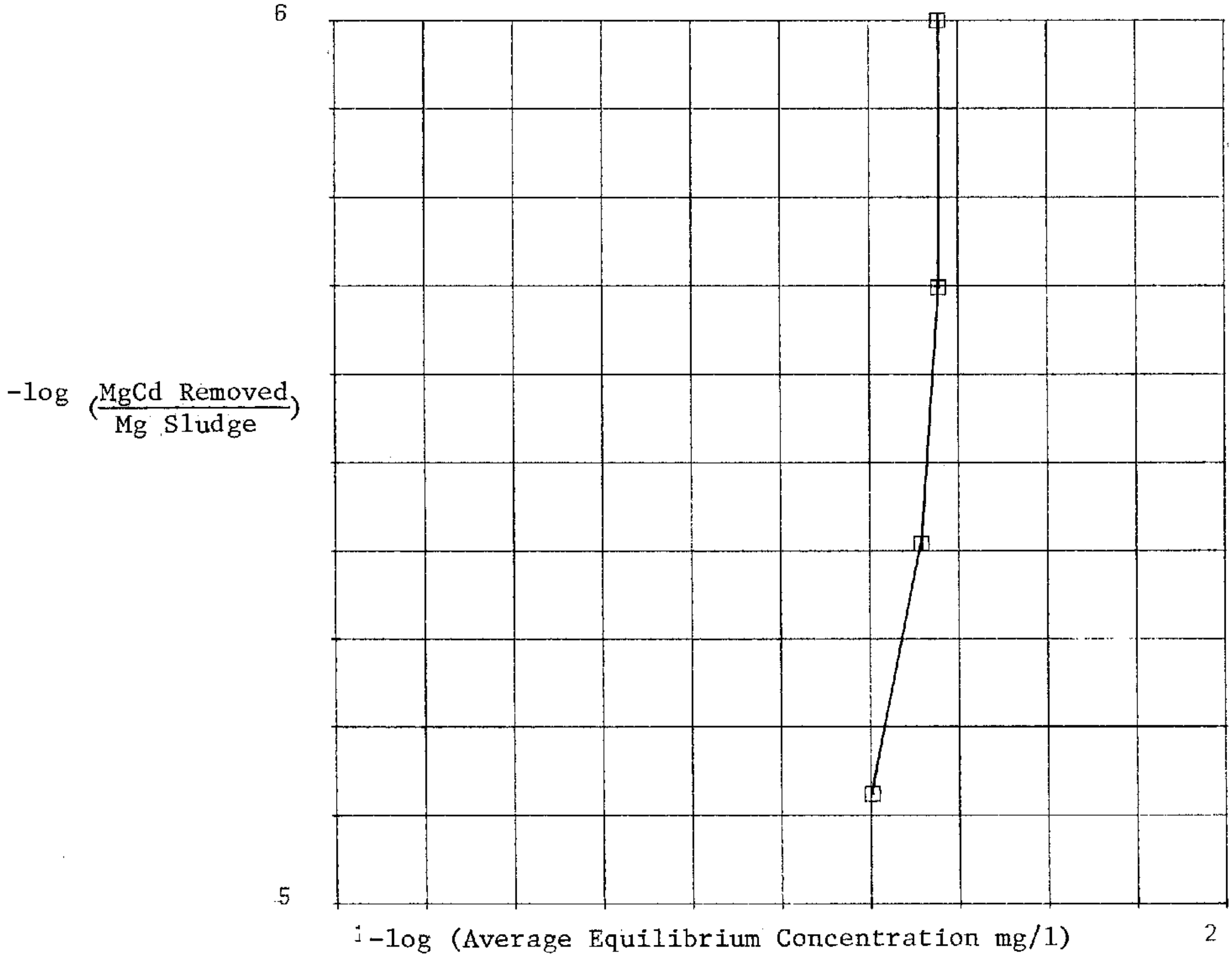

Fig. 46: Langmuir Isotherm for Cadmium,
Contact Time = 2 hours.

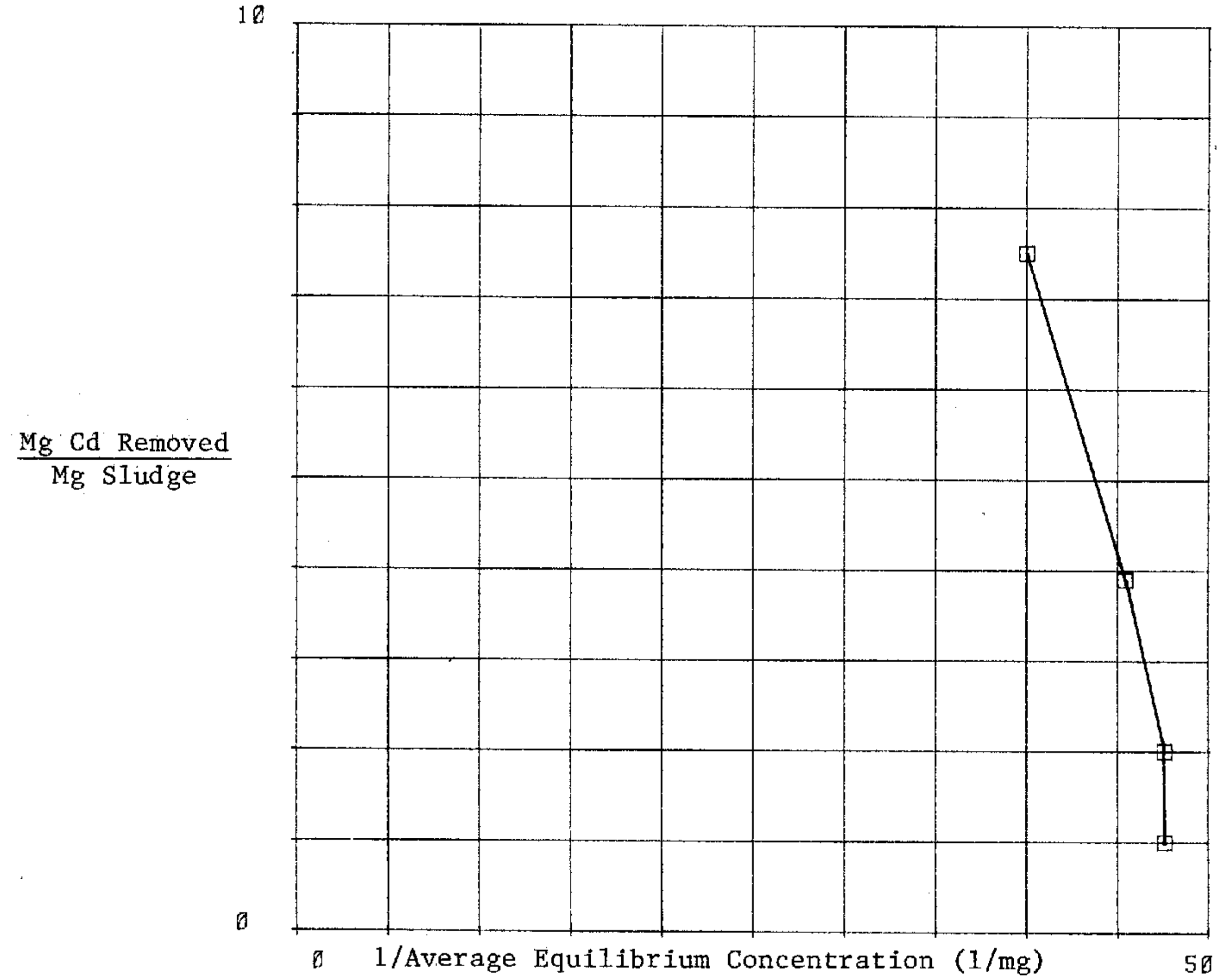

Fig. 47: Freundlich Isotherm for Cadmium,
Contact Time = 2 hours.

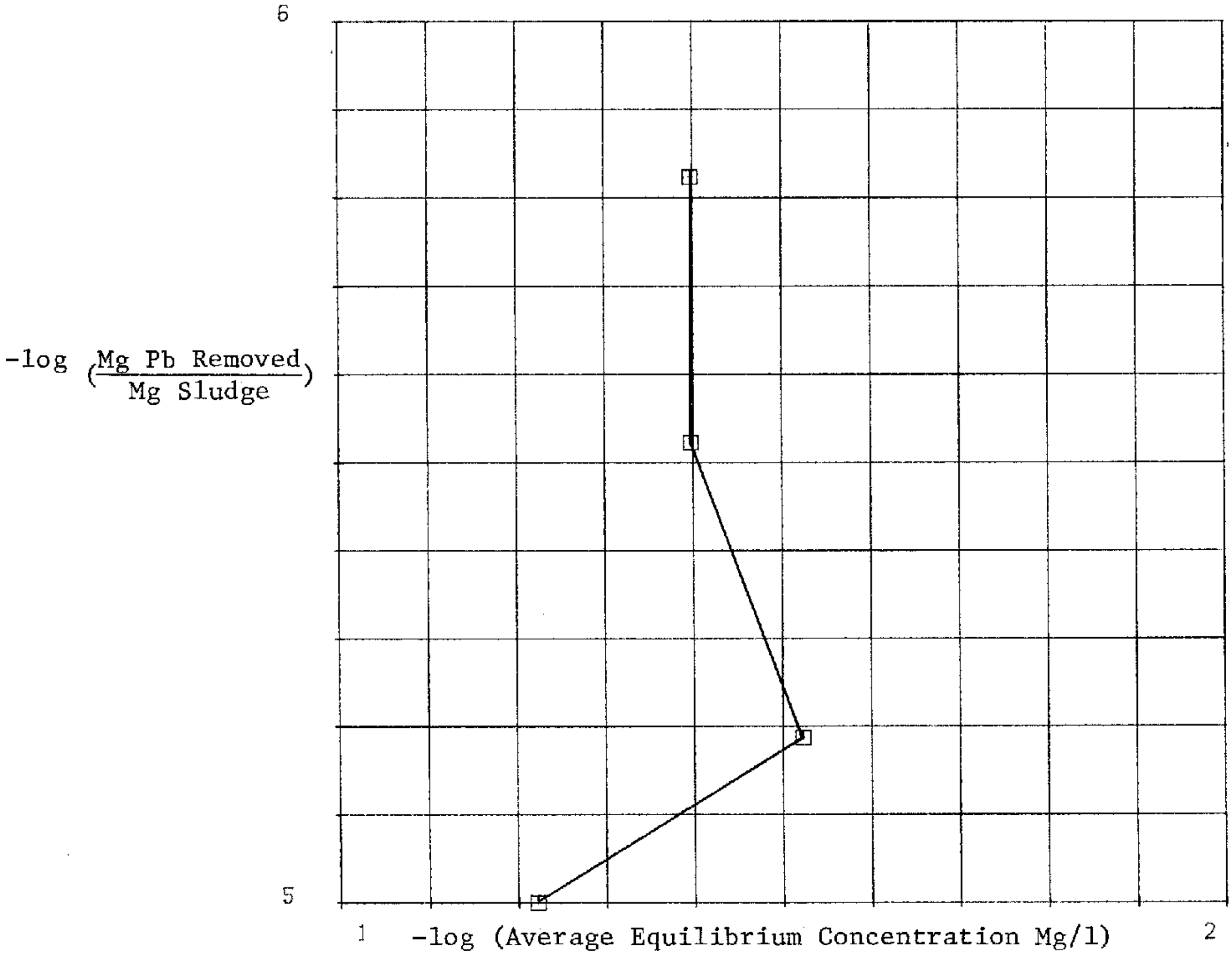

Fig. 56: Langmuir Isotherm for Lead,
Contact Time = 1 hour.

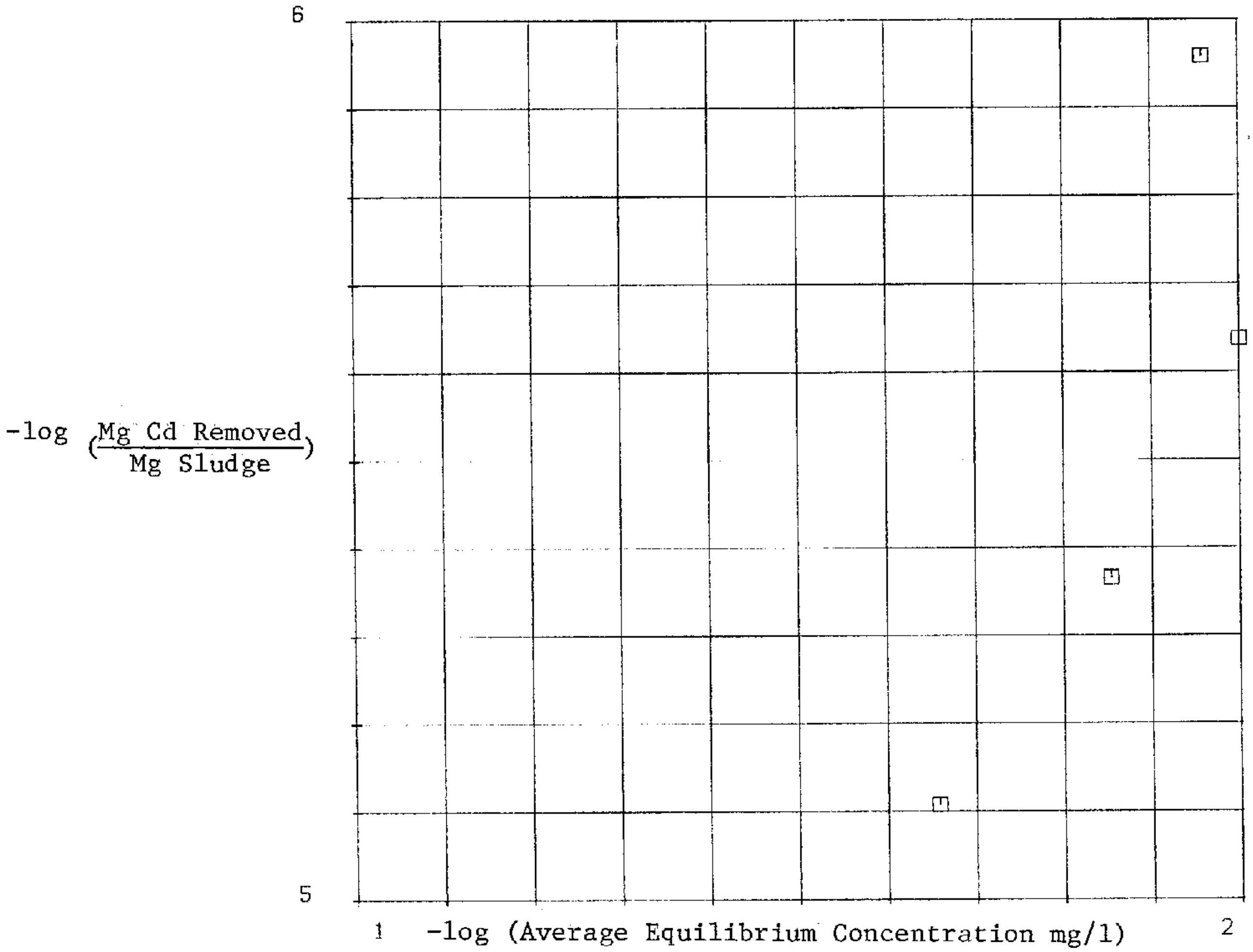

Fig. 48: Langmuir Isotherm for Cadmium,
Contact Time = 4 hours.

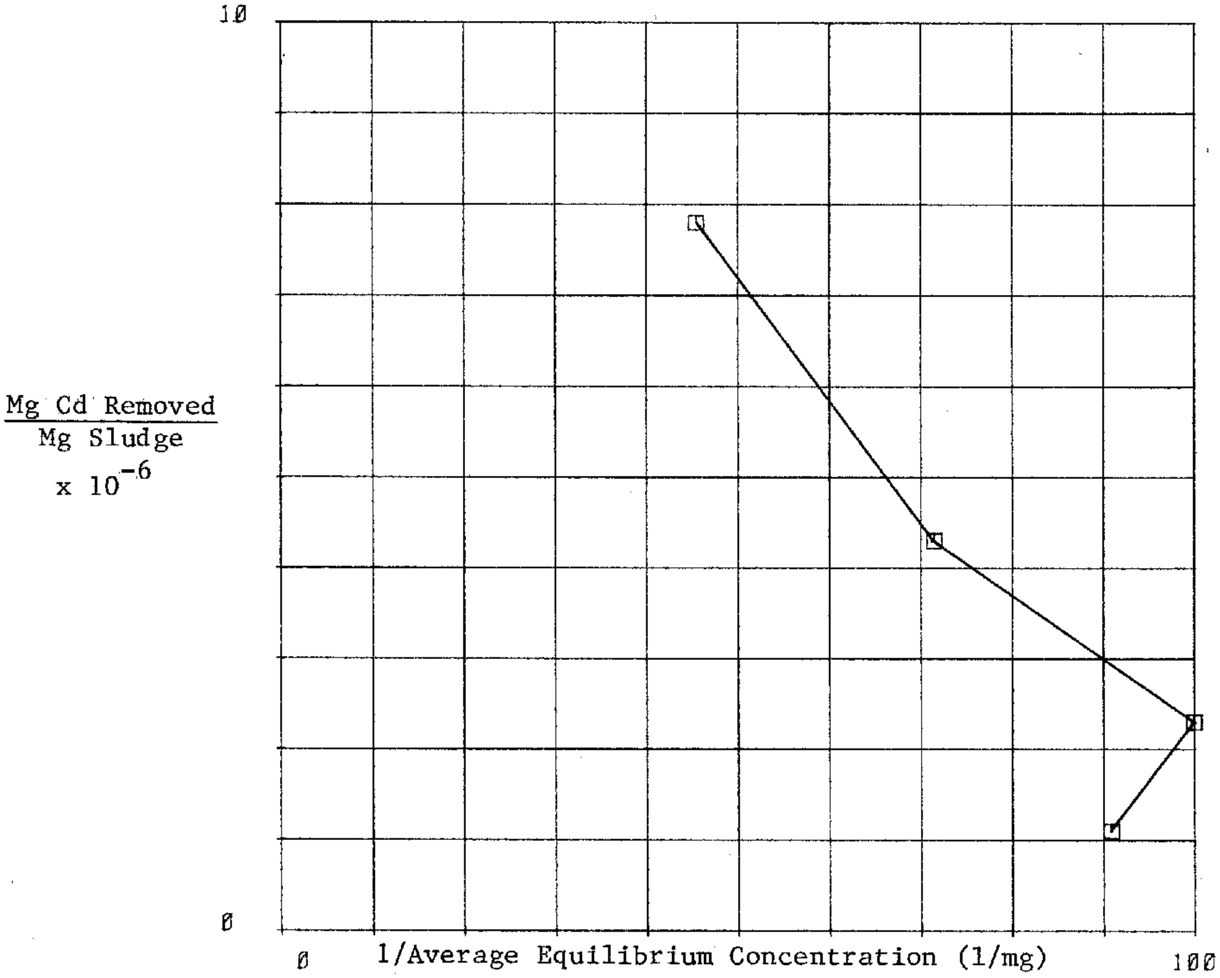

Fig. 49: Freundlich Isotherm for Cadmium, Contact Time = 4 hours.

assuming that one point is an outlier.

Figures 50, 52, and 54 illustrate the Langmuir correlation for Nickel and contact times of 1, 2, and 4 hours, respectively. None of these correlations is a useful one.

Figures 51, 53, and 55 illustrate the Freundlich correlation for Nickel at these same contact times. Again, none of the correlations is a good one.

Similar correlations were obtained for lead at the same contact times. Figures 56, 58, and 60 show these results. The correlation for lead at a contact time of 4 hours is definitely linear and can be fitted to the model. The value for b is -4.07, and for Q° is -0.000096. The correlation coefficient was 0.996. Both b and Q° should be positive.

Figures 57, 59, and 61 illustrate the corresponding Freundlich correlation for lead. The results for a contact time of 4 hours are again linear, with a value of K of 0.000675 and for n of 0.887. The correlation coefficient was 0.976. The value for n should be greater than 1.

Although these results could be fitted to the models, the values for the constants are considered meaningless. In addition, the measured levels of lead fall below what is the reliable detection level (Table 8) for an atomic absorption spectrophotometer such as the one used for the analyses. Thus we cannot be totally sure that even this one good correlation is a valid one.

Table 8: Detection Limits of Atomic Absorption Analysis for Various Metals (14)

Metal	Detection Limit (mg/1)
Cadmium	0.002
Chromium	0.02
Lead	0.05
Nickel	0.02
Zinc	0.005

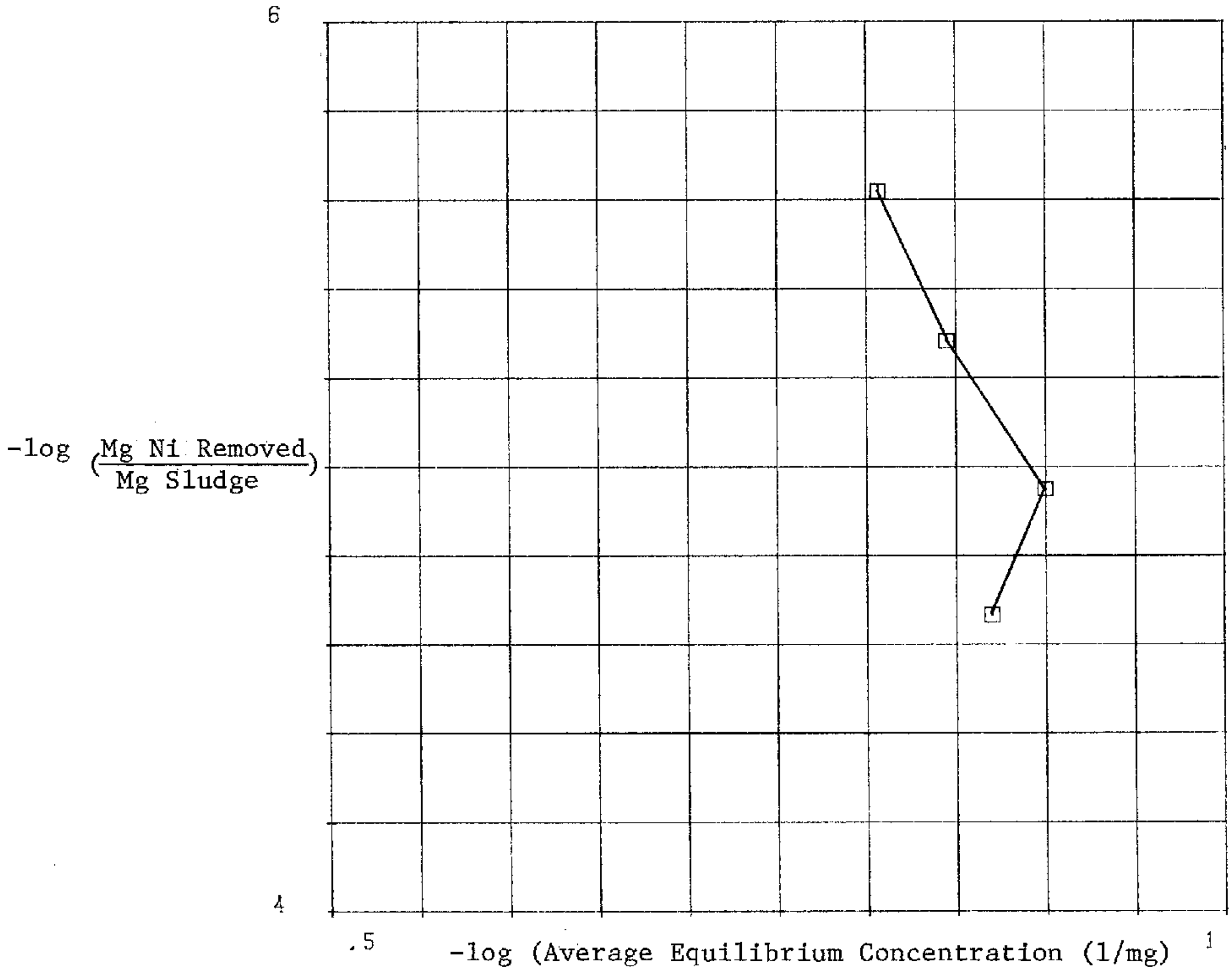

Fig. 50: Langmuir Isotherm for Nickel,
Contact Time = 1 hour.

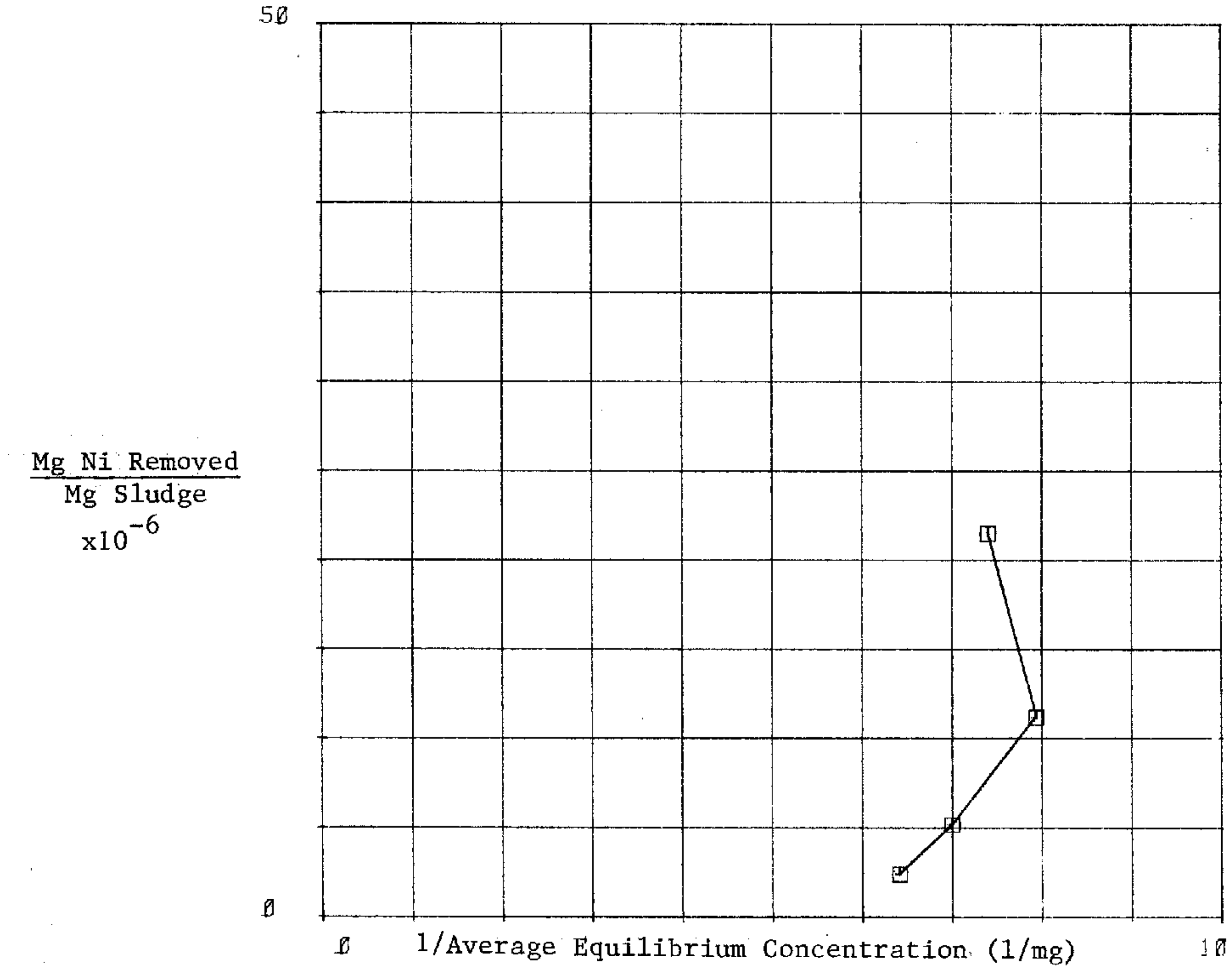

Fig. 51: Freundlich Isotherm for Nickel, Contact Time = 1 hour.

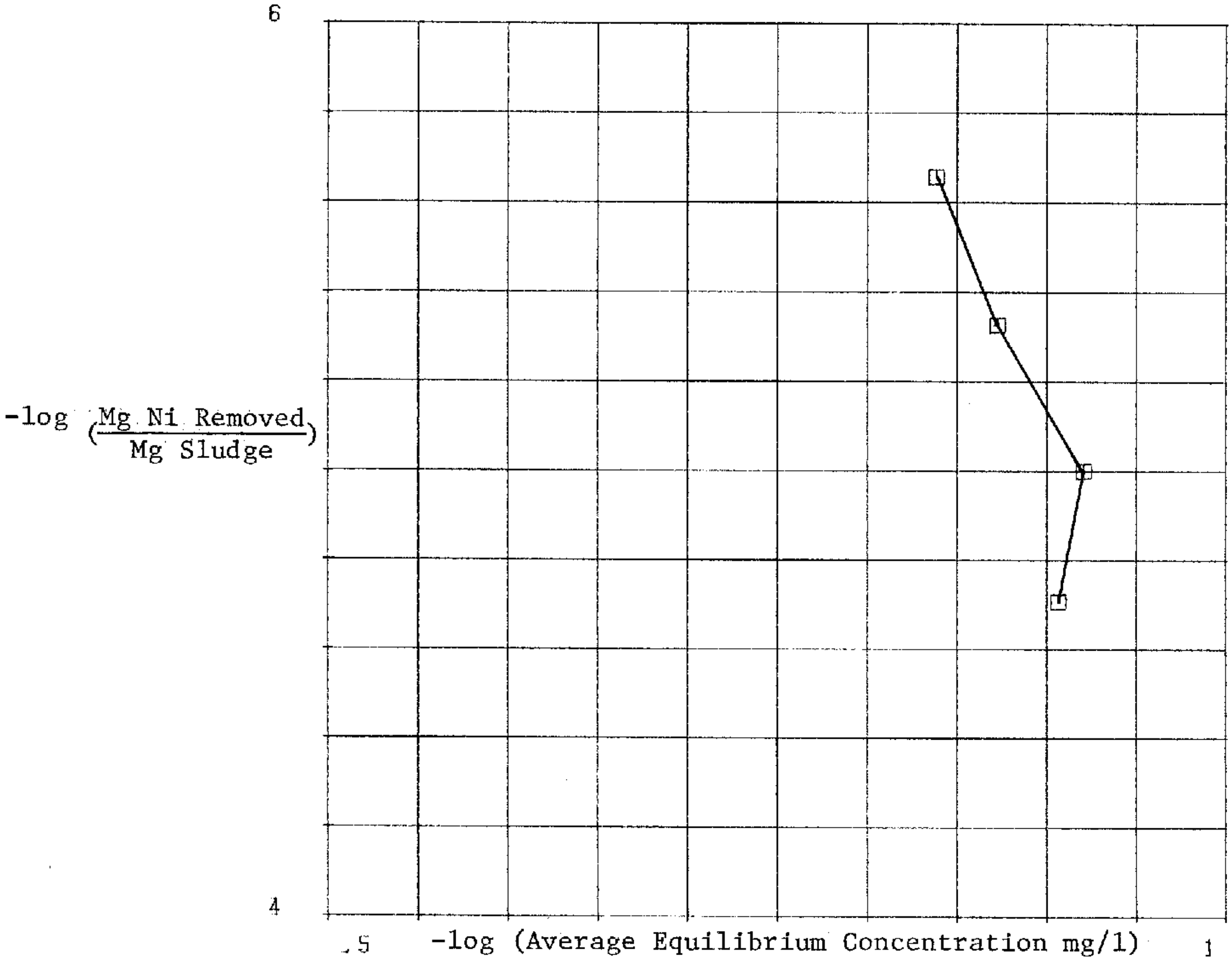

Fig. 52: Langmuir Isotherm for Nickel, Contact Time = 2 hours.

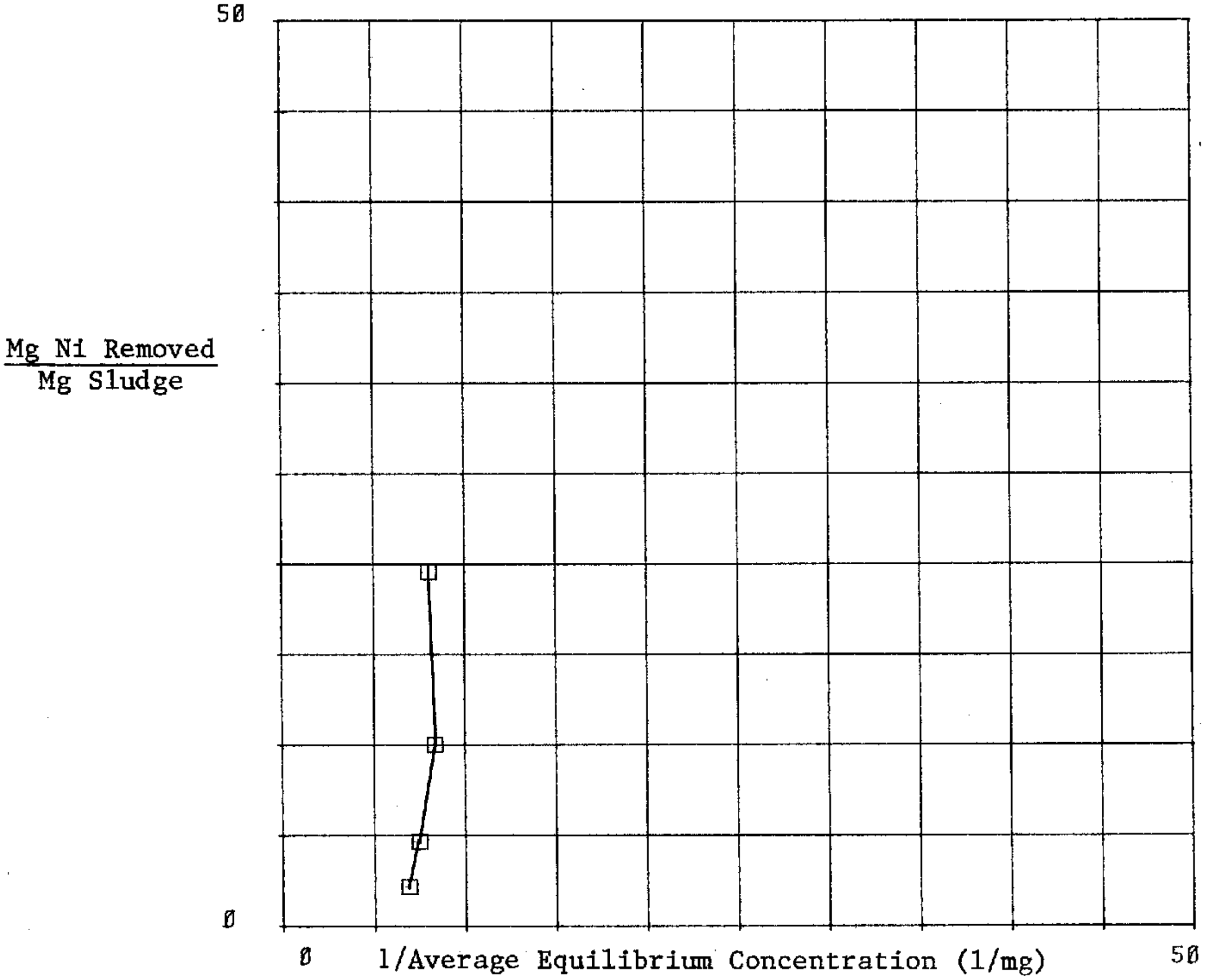

Fig. 53: Freundlich Isotherm for Nickel,
Contact Time = 2 hours.

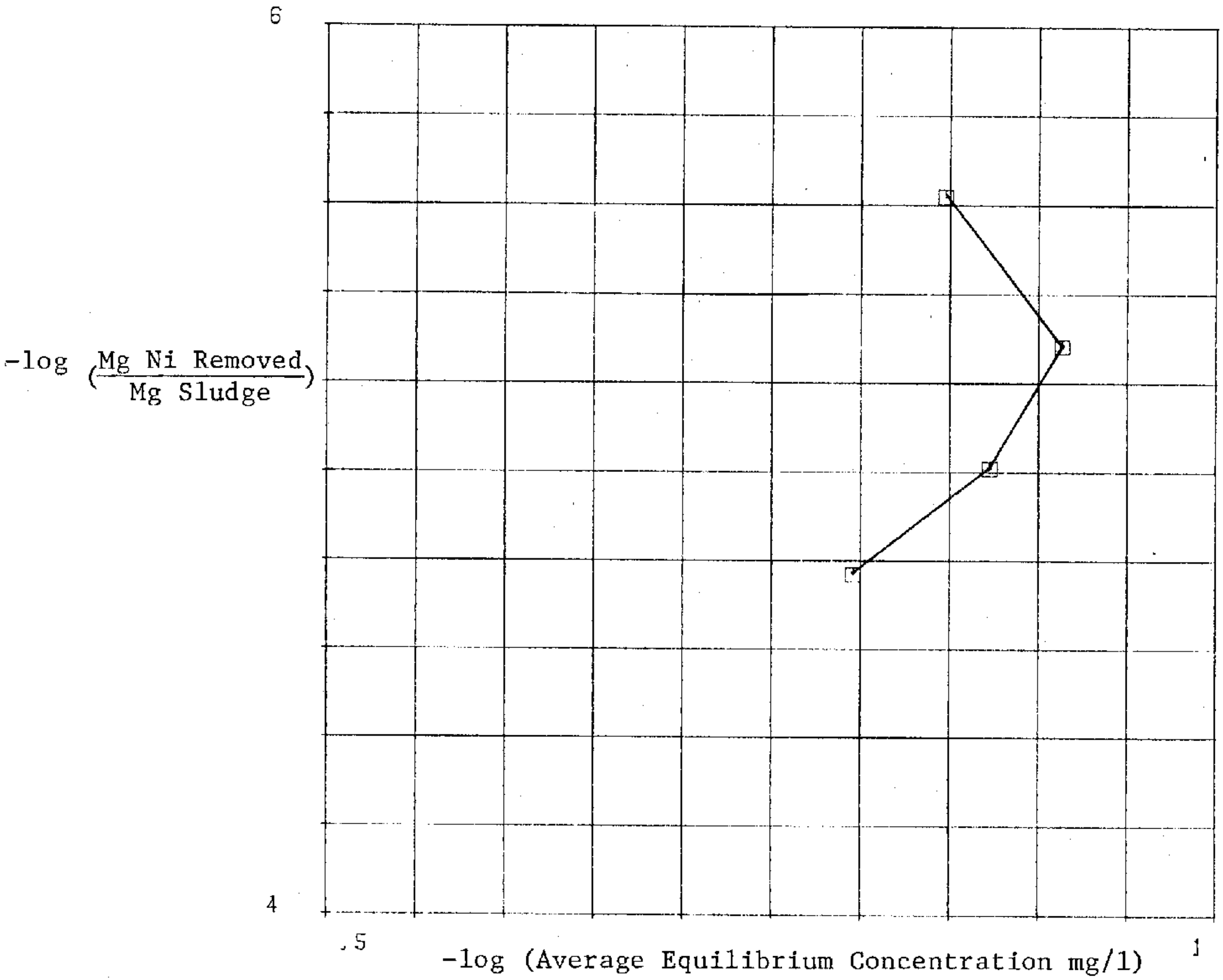

Fig. 54: Langmuir Isotherm for Nickel,
Contact Time = 4 hours.

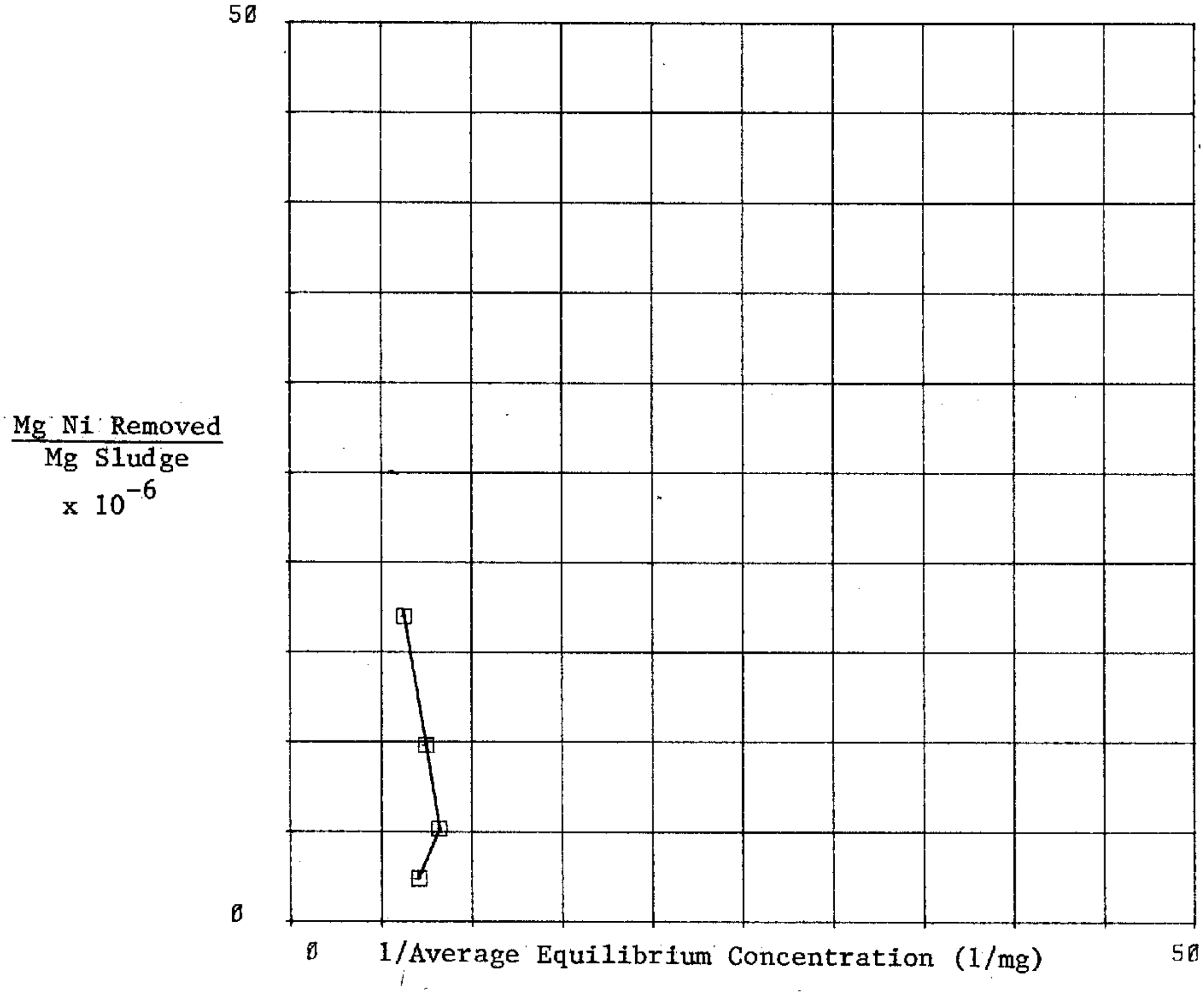

Fig. 55: Freundlich Isotherm for Nickel, Contact Time = 4 hours.

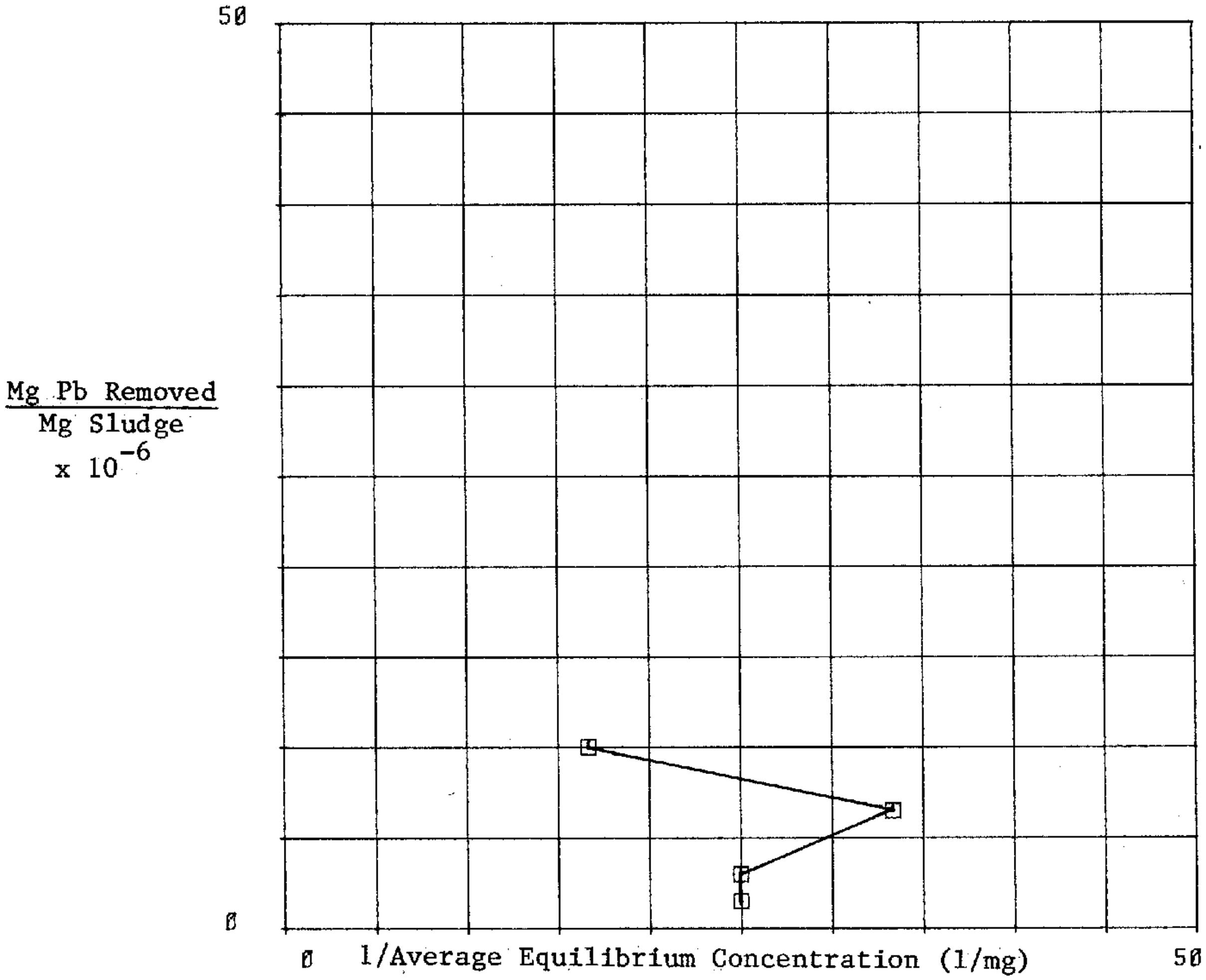

Fig. 57: Freundlich Isotherm for Lead,
Contact Time = 1 hour.

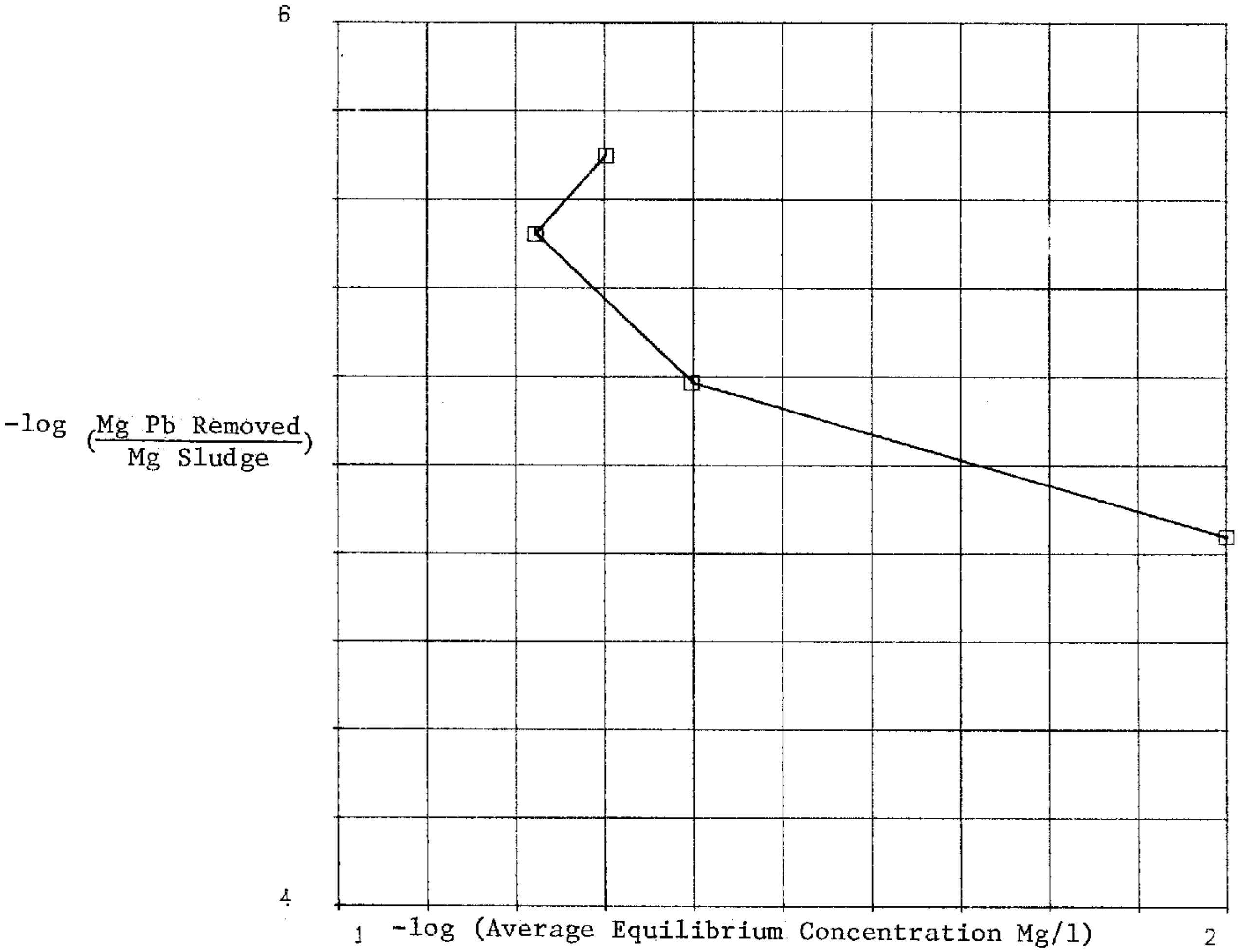

Fig. 58: Langmuir Isotherm for Lead,
Contact Time = 2 hours.

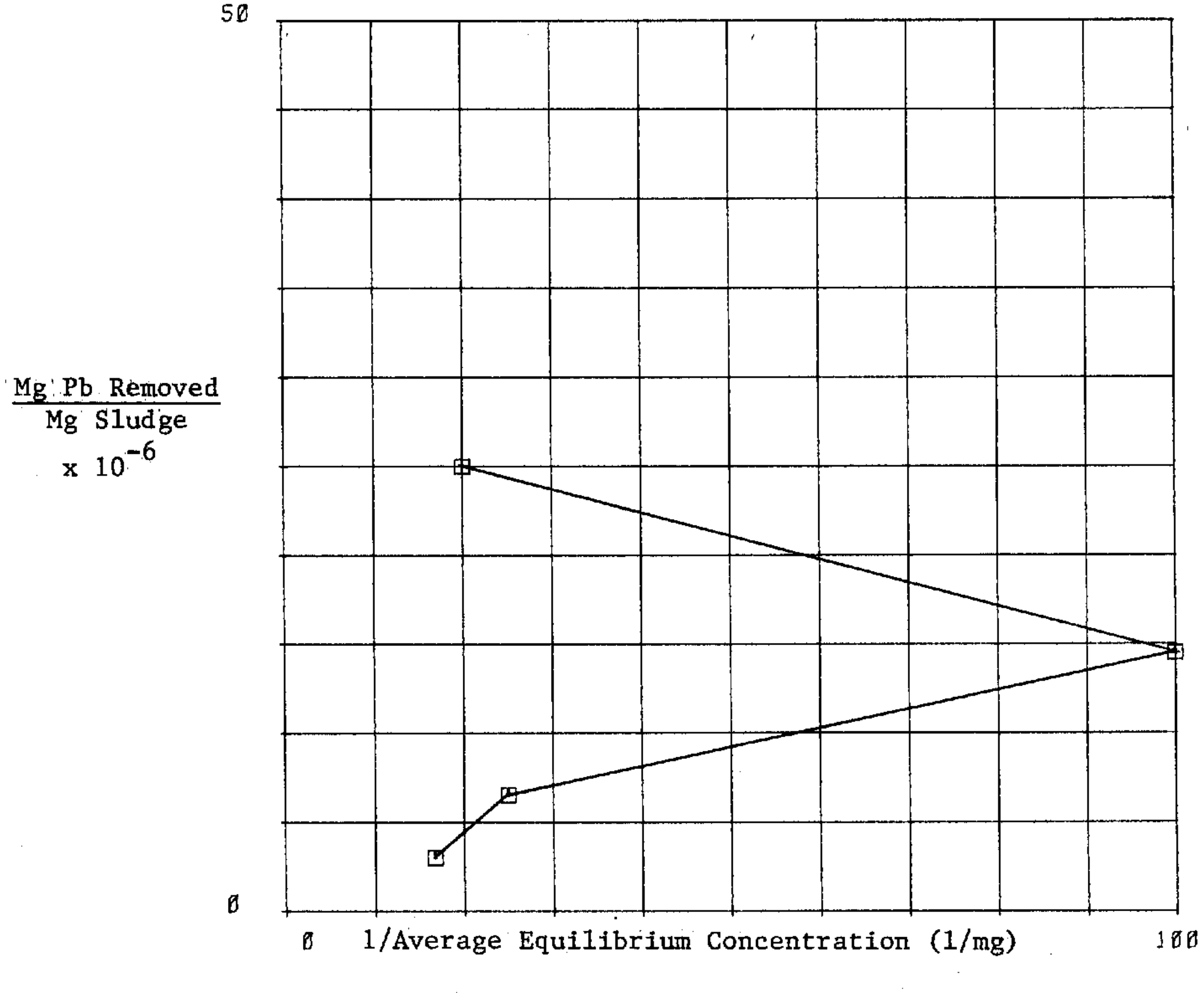

Fig. 59: Freundlich Isotherm for Lead,
Contact Time = 2 hours.

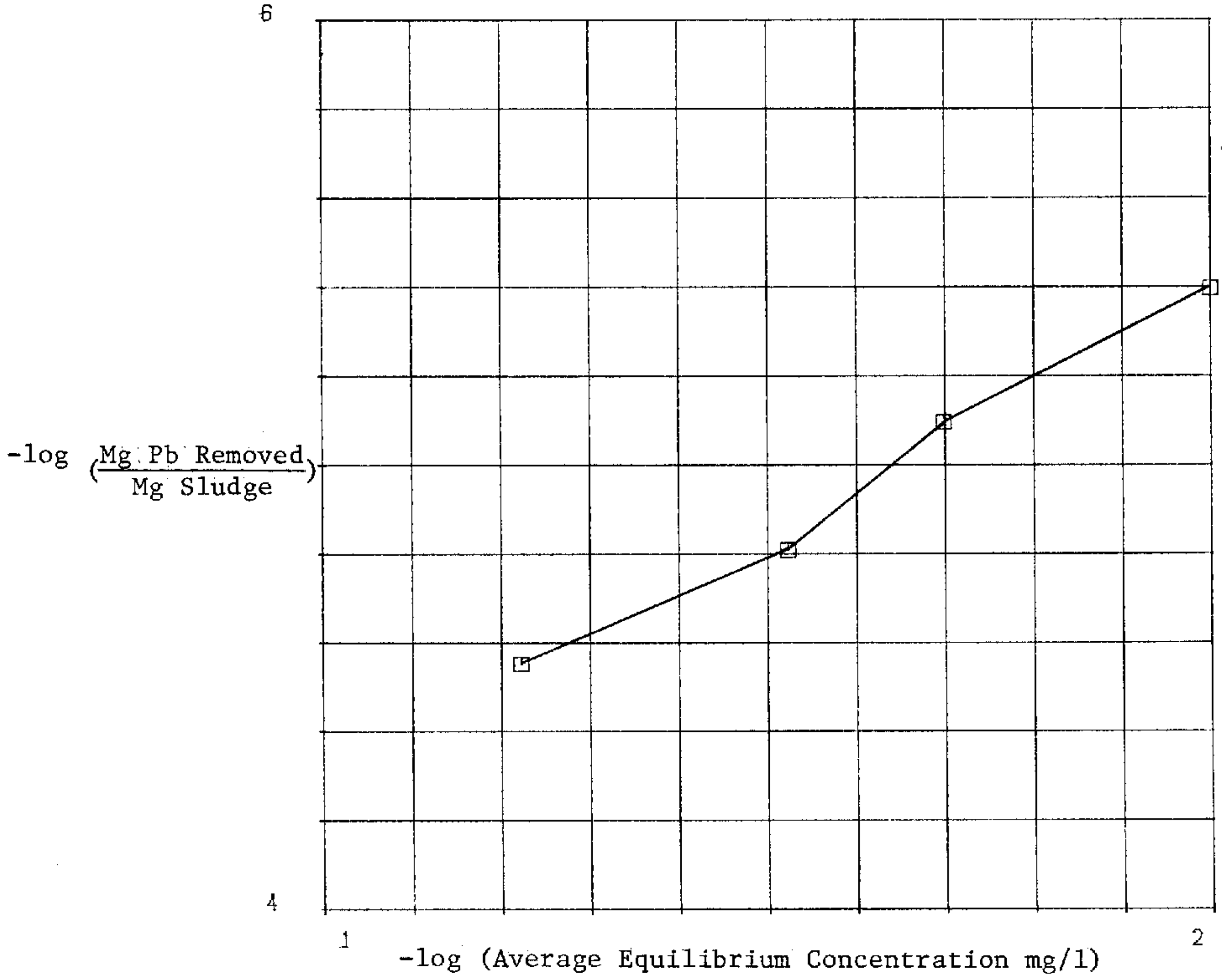

Fig. 60: Langmuir Isotherm for Lead, Contact Time = 4 hours.

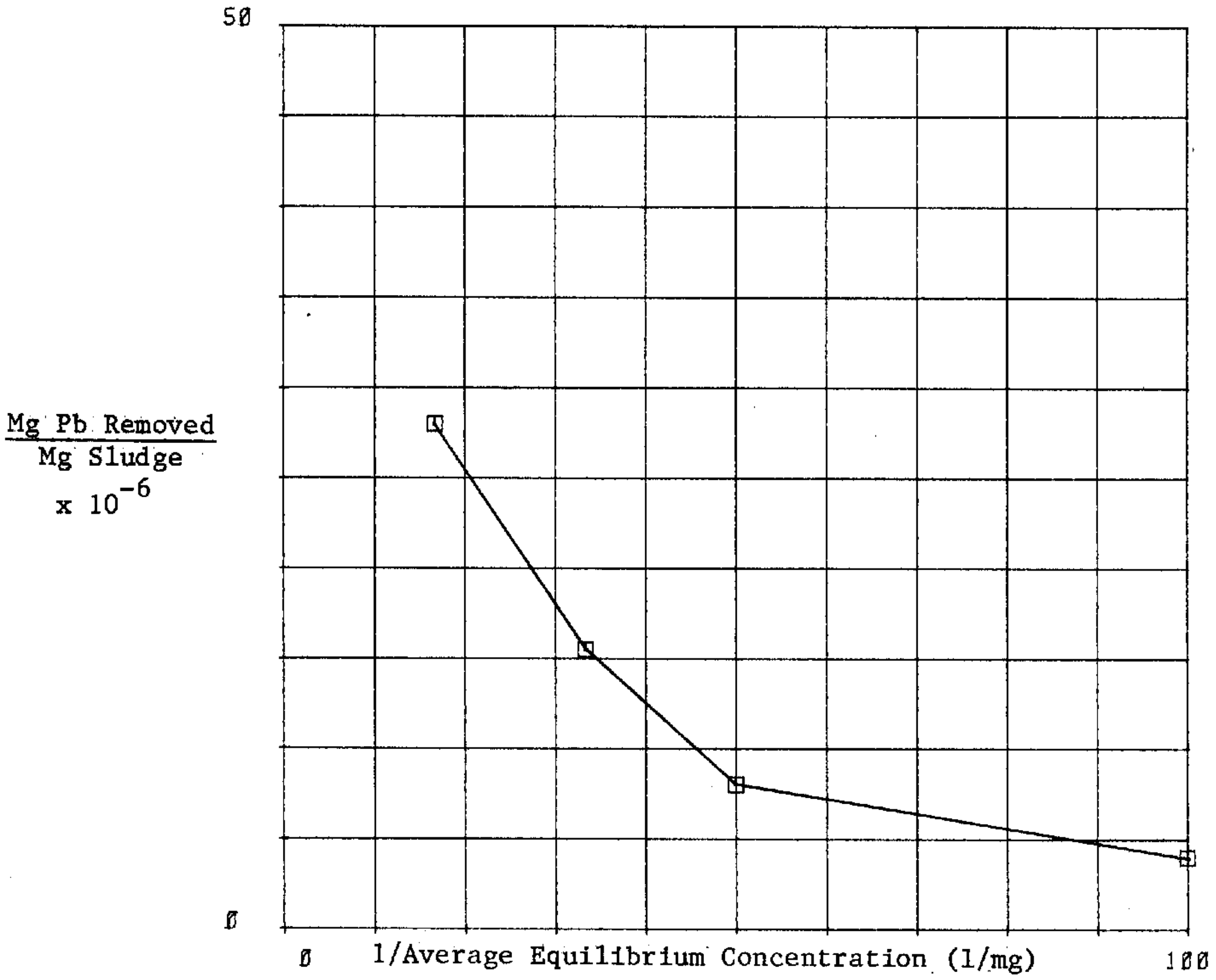

Fig. 61: Freundlich Isotherm for Lead,
Contact Time = 4 hours.

It is clear that none of the adsorption models tested was adequate. These models assume an adsorber surface where more or less uniform accumulation in layers takes place. A cell wall is not a surface but rather a mesh of complex molecular chains cross linked in very complicated arrangements. The adsorption sites are in all probability discrete points or nodes in a scattered, random distribution throughout the cell wall. This large discrepancy between the physical model of where adsorption is actually taking place and the assumptions of the mathematical model probably explains why the observed data cannot fit the Langmuir or Freundlich models well. In addition, ion exchange may be an incompatible mechanism with those assumed by the models.

An attempt to correlate the data with the Brunauer, Emmett, Teller (BET) Model (17) was not possible since we did not have information on the saturation concentration of the metals for the biological adsorber.

Sludge Characteristics:

The sludge from San Germān was analyzed for its metal content. The results are summarized in Table 9. Cadmium was barely detectable in the samples tested. Copper, chromium, iron, lead, and nickel were present in significant amounts. The sludge had a 34 percent moisture content, was aerobically digested for about 30 days and air dried. It originated in a completely mixed, activated sludge system. The San Germān plant is hydraulically overloaded, with a consequent erratic behavior of the plant. Thus it was not possible to obtain more precise information about the sludge characteristics.

The sludge from Añasco was also analyzed for its metal content. The results are shown in Table 10.

Cobalt, Iron, Manganese, Lead, Nickel, Zinc, and Magnesium, were present in significant amounts. Cadmium was below detection limits, and chromium was at its detection limit.

Table 9: Metal Content of San Germán Sludge

Element	Total Metal Content, mg/l				
	Samples				
	A	B	C	D	Average
Cadmium	0.00486	0.00514	0.00498	0.00518	0.00504
Cobalt	0.00913	0.01029	0.01035	0.01072	0.01012
Copper	4.2121	4.5647	4.5757	4.9917	4.5860
Chromium	1.0604	1.0608	1.1356	1.3311	1.1470
Iron	9.5906	9.9331	10.4873	12.6530	10.6660
Lead	1.1155	1.2302	1.2267	1.2930	1.2164
Nickel	0.2651	0.2893	0.2672	0.2958	0.2794

Table 10: Metal Content of Añasco Sludge

METAL	CONCENTRATION (MG/G)	CONCENTRATION (MEQ/G)	% METAL CONTENT
COBALT	0.1622	0.0055	0.32
CHROMIUM	0.0268	0.0015	0.09
COPPER	0.0819	0.0013	0.07
IRON	10.3759	0.5574	31.95
MANGANESE	0.4558	0.0166	0.92
LEAD	0.1229	0.0012	0.07
NICKEL	0.6863	0.0234	1.34
ZINC	1.1847	0.0362	2.07
SILVER	0.0060	0.0093	0.53
MAGNESSIUM	0.9765	0.0803	4.60
SODIUM	0.2697	0.0117	0.67
POTASSIUM	0.4916	0.0126	0.72
CALCIUM	19.7951	0.9878	56.64
CADMIUM	0.0003	0.000005	ND*
TOTAL METAL CONTENT:		1.7848 meq/g	100.00

*Not Detectable; below detection limits.

Traces of silver were found to be present. A quick calculation showed that it would take 83.2 tons of dry sludge (assuming a uniform distribution of silver) to produce one pound of silver. We are not knowledgeable in mining, but that does not seem like a profitable yield.

The Añasco sludge was anaerobically digested together with primary sludge. This may lead us to expect the Añasco sludge to have a higher fraction of inorganic substances and a smaller percent of active adsorber. In spite of this, the Añasco sludge performed very well.

Conclusions:

The results from this study have shown the following:

1. Maximum or near maximum removal efficiencies can be expected for cadmium, nickel, and lead at the neutral pH region. Thus there exists a definite potential for the removal of these metals with biological adsorbers. Industries with chronic concentrations of these metals in their wastewaters may benefit by using cheap or perhaps even free, dried or digested wet sludges to remove them.
2. Maximum removal efficiencies for chromium were observed at pH 4.5 to 5.5. This would require pH adjustment. The costs of chemicals might not make the bioadsorbers an economical alternative.
3. Cadmium was reduced to a little over twice the concentration required by the water quality standards (Table 4). This definitely establishes the bioadsorbers as a viable alternative from the water quality standpoint.
4. Lead was reduced to at or below its detection limit with atomic adsorption analysis, which coincides with the water quality standard. Again this establishes the capability

of bioadsorber technology.

4. Nickel was reduced sixty six percent at pH 7.0, to a concentration of 0.15 mg/l. There is at present no water quality standard for nickel, since there are presumably no known associated health effects.
5. For constant sludge concentrations of 2 percent, contact time was seen to have little effect on overall removal efficiency for nickel and lead. Cadmium showed some improvement up to 4 hours, but very little after that. This can be interpreted to mean that whatever removal is going to take place will occur at small contact times. This could make a bioadsorption system an economical one for applications.
6. There was some improvement in removal efficiency at higher contact times (2 and 4 hours) at higher sludge concentrations (4 and 8 percent). Nevertheless, the improvements were not very large. These results seem to indicate that maximum removals can be obtained with sludge concentrations of 2 percent, which is not an excessively high concentration and should therefore not require higher than usual levels of power for mixing purposes.
7. The absence of sensitivity to changes in contact time and sludge concentration point to the possibility of an ion exchange mechanism for the adsorption of the biological sludge. If simple electrical interaction at appropiate sites had been responsible, then increases in sludge concentrations should have effected a reduction in equilibrium concentrations. Such reductions were not observed.

Also, if randomly located electrical sites are the responsible mechanisms for the removal, then an increased contact time should have increased removal. Otherwise, a limited amount of these sites may have been present in the sludge. But adding more sludge would have made fresh sites available and removal should have therefore increased. Again such increase was not observed.

Ion exchange is a phenomenon for which it has been demonstrated that there exists a quantitative affinity of the metal species to be removed for the exchange sites and exchange ions. It can be mathematically shown (18) that for a given concentration of metal species only a fraction of it will be exchanged in the presence of a given mass of exchange resin. In addition, the ability to replace ions is dependent in part to the concentration of the dissolved metal species. Exchange is one of the recognized forms of adsorption mechanisms (17).

8. The Langmuir and Freundlich adsorption models do not do an adequate job of describing the removal of metals from water through biosorption. The BET model was not tested due to the absence of saturation concentration data of the metals for the biological sludges.
9. Both sludges tested had fairly high contents of various metals. This implies that the adsorptive capacity of the sludge is very high, since all of our experiments were performed with adsorbers already having a high metal content. Precise data was not available on sludge characteristics due to improper and erratic plant operation and

inadequate records.

10. Time did not permit obtaining data for a comparison between an ion exchange resin and the biological sludges.

Recommendations:

Biosorption has been found to have a very promising potential for removing heavy metals from wastewaters. Further studies should be performed in order to:

1. Establish the removal potential and operational characteristics for metals which were not tested adequately or which were not tested at all.
2. Establish the potential for removal and the significant operational characteristics for continuous flow systems using a) previously dried inert sludges and b) wet digested sludges.
3. Correlate in a very precise manner sludge characteristics and original microbiological composition with removal characteristics for specific metals.
4. Elucidate the specific removal mechanisms responsible for the adsorption properties.
5. Establish the relationship between the original microbial ecology and an enhanced selective removal of specific metals. Establish the methodology to maximize the adsorptive properties of biological sludges by manipulating the dynamic equilibrium of the microbial populations.

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APPENDIX

Table A-1: Effect of Hydrolisis and pH on the Removal of Cadmium

pH	Equilibrium Concentration of Controls (mg/l)	Average Initial Concentration (mg/l)	Equilibrium Concentration for Samples (mg/l)	Average Equilibrium Concentration (mg/l)	Remaining Fraction C/Co
3.0	0.49	0.485	0.20*	0.20*	0.41
	0.48		0.20*		
4.25	0.49	0.455	0.018	0.017	0.04
	0.42		0.016		
5.60	0.40	0.445	0.016	0.016	0.04
	0.49		0.016		
7.0	0.32*	0.410	0.014	0.014	0.03
	0.41		0.014		

Temperature = 20°C Contact Time = 4 hrs. Sludge Concentration = 20 g/l

*Outliers

Table A-2: Effect of Hydrolysis and pH on the Removal of Chromium

pH	Equilibrium Concentration of Controls (mg/l)	Average Initial Concentration (mg/l)	Equilibrium Concentration for Samples (mg/l)	Average Equilibrium Concentration (mg/l)	Remaining Fraction C/Co
3	0.466	0.473	0.206	0.211	0.45
	0.480		0.216		
4.5	0.479	0.472	0.129	0.132	0.28
	0.464		0.134		
5.5	0.465	0.462	0.163	0.180	0.39
	0.459		0.196		
7.0	0.451	0.452	0.282	0.279	0.62
	0.454		0.276		

Temperature = 20°C Contact Time = 4 hrs.

Sludge Concentration = 20 g/l

Table A-3: Effects of Hydrolysis and pH on the Removal of Nickel

pH	Equilibrium Concentration of Controls (mg/l)	Average Initial Concentration (mg/l)	Equilibrium Concentration for Samples (mg/l)	Average Equilibrium Concentration (mg/l)	Remaining Fraction C/Co
3	0.473	0.498	0.508	0.498	1.0
	0.522		0.489		
4.5	0.501	0.492	0.282	0.278	0.56
	0.482		0.274		
5.5	0.495	0.494	0.204	0.201	0.41
	0.493		0.198		
7.0	0.438	0.444	0.166	0.152	0.34
	0.451		0.139		

Temperature = 20°C Contact Time = 4 hrs.

Sludge Concentration = 20 g/l

Table A-4: Effects of Hydrolysis and pH on the Removal of Lead

pH	Equilibrium Concentration of Controls (mg/1)	Average Initial Concentration (mg/1)	Equilibrium Concentration of Samples (mg/1)	Average Equilibrium Concentration (mg/1)	Remaining Fraction C/Co
3.0	0.450	0.470	0.110	0.075	0.16
	0.490		0.040		
4.5	0.380	0.385	0.020	0.025	0.065
	0.370		0.030		
5.5	0.330	0.360	0.020	0.020	0.056
	0.390		0.020		
7.0	0.080	0.110	N.D.*	0.010	0.09
	0.140		0.020		

Temperature: 20°C Contact Time = 4 hrs.

Sludge Concentration = 20 g/1

Table A-5: Effects of Hydrolysis on the Removal of Zinc

pH	Equilibrium Concentration (mg/1)	Average Concentration (mg/1)
3	0.518	0.542
	0.565	
4.5	0.529	0.520
	0.511	
5.5	0.616	0.513
	0.510	
7.0	0.457	0.432
	0.407	

Temperature = 20°C Contact Time = 4 hrs.

Table A-6: Effect of Contact Time on the Removal of Cadmium

Contact Time (hrs)	Initial Concentration (mg/l)	Equilibrium Concentration of Samples (mg/l)	Average Equilibrium Concentration (mg/l)	Remaining Fraction C/Co
1	0.102	0.022 0.030	0.026	0.25
2	0.102	0.030 0.021	0.026	0.25
4	0.102	0.018 0.017	0.018	0.18
8	0.102	0.015 0.014	0.014	0.14

Temperature = 20°C pH = 7.0 Sludge Concentration = 2 g/l

Table A-7: Effect of Contact Time on the Removal of Nickel

Contact Time (hrs)	Equilibrium Concentration of Controls (mg/1	Average Initial Concentration (mg/1)	Equilibrium Concentration of Samples (mg/1)	Avera Equilibrium Concentration (mg/1)	Remaining Fraction C/Co
1	0.354	0.365	0.179	0.16	0.44
	0.375		0.140		
2	0.355	0.374	0.132	0.14	0.37
	0.393		0.141		
4	-	-	-	-	-
	-		-		
8	0.388	0.375	0.166	0.16	0.43
	0.361		0.153		

Temperature = 20°C pH = 7.0 Sludge Concentration = 20 g/1

Table A-8: Effect of Contact Time on the Removal of Lead

Contact Time (hrs)	Equilibrium Concentration of Controls (mg/1)	Average Initial Concentration (mg/1)	Equilibrium Concentration of Samples (mg/1)	Average Equilibrium Concentration (mg/1)	Remaining Fraction C/Co
1	0.09*	0.27	0.02	0.02	0.07
	0.27		0.03		
2	0.22	0.24	0.03	0.04	0.17
	0.26		0.04		
4	0.29	0.29	-	-	-
	0.29		-		
8	0.29	0.29	0.01	0.02	0.07
	0.29		0.02		

*Outlier

Temperature = 20° C pH = 7.0 Sludge Contration = 20 g/1

Table A-9: Effect of Contact Time on the Removal of Zinc

Contact Time (hrs)	Initial Concentration (mg/l)	Equilibrium Concentration (mg/l)	Average Concentration (mg/l)
1	0.5	0.440 0.464	0.452
2	0.5	0.452 0.456	0.454
8	0.5	0.459 0.468	0.464

Table A-10: Effect of Initial Concentration on the Removal of Cadmium

Initial Concentration (mg/l)	Equilibrium Concentration of Samples (mg/l)	Average Equilibrium Concentration (mg/l)	Remaining Fraction, C/Co
1	0.7	0.75	0.75
	0.8		
10	9.0	9.05	0.90
	9.1		
100	70.0	65.0	0.65
	60.0		
1000	820.0	800.0	0.80
	780.0		

Temperature: 20°C pH = 7.0 Sludge Concentration = 20 g/l

Table A-11: Effect of Sludge Concentration on the Removal of Cadmium, Contact Time = 1 hour

Sludge Concentration (%)	Initial Concentration (mg/)	Equilibrium Concentration of Samples (mg/)	Average Equilibrium Concentration (mg/)	Remaining Fraction C/Co	$\frac{\text{mgCd Removed}}{\text{mg Sludge}}$
1	0.1	0.021 0.028	0.024	0.24	7.6×10^{-6}
2	0.1	0.025 0.022	0.024	0.24	7.6×10^{-6}
4	0.1	0.032 0.025	0.028	0.28	1.8×10^{-6}
8	0.1	0.032 0.026	0.029	0.29	0.9×10^{-6}

Temperature = 20°C pH = 7.0

Table A-12: Effect of Sludge Concentration on the Removal of Cadmium
Contact Time = 2 hours

Sludge Concentration (%)	Initial Concentration (mg/l)	Equilibrium Concentration of Samples (mg/l)	Average Equilibrium Concentration (mg/l)	Remaining Fraction C/Co	$\frac{\text{mg Cd Removed}}{\text{mg Sludge}}$
1	0.1	0.025 0.026	0.025	0.25	7.5×10^{-6}
2	0.1	0.022 0.021	0.022	0.22	3.9×10^{-6}
4	0.1	0.021 0.021	0.021	0.21	2.0×10^{-6}
8	0.1	0.021 0.021	0.021	0.21	1.0×10^{-6}

Temperature = 20°C pH = 7.0

Table A-13: Effect of Sludge Concentration on the Removal of Cadmium
Contact Time = 4 hours

Sludge Concentration (%)	Initial Concentration (mg/l)	Equilibrium Concentration of Samples (mg/l)	Average Equilibrium Concentration (mg/l)	Remaining Fraction C/Co	$\frac{\text{mg Cd Removed}}{\text{mg Sludge}}$
1	0.1	0.022 0.023	0.022	0.22	7.8×10^{-6}
2	0.1	0.015 0.012	0.014	0.14	4.3×10^{-6}
4	0.1	0.009 0.011	0.010	0.10	2.3×10^{-6}
8	0.1	0.010 0.012	0.011	0.11	1.1×10^{-6}

Temperature = 20°C pH = 7.0

Table A-14: Effect of Sludge Concentration on the Removal of Nickel
Contact Time = 1 hour

Sludge Concentration (%)	Initial Concentration (mg/l)	Equilibrium Concentration of Samples (mg/l)	Average Equilibrium Concentration (mg/l)	Remaining Fraction C/Co	mg Ni Removed / mg Sludge
1	0.35	0.152 0.118	0.135	0.39	21.5×10^{-6}
2	0.35	0.123 0.129	0.126	0.36	11.2×10^{-6}
4	0.35	0.138 0.148	0.143	0.41	5.2×10^{-6}
8	0.35	0.153 0.158	0.156	0.44	2.4×10^{-6}

Temperature = 20°C pH = 7.0

Table A-15: Effect of Sludge Concentration on the Removal of Nickel
Contact Time = 2 hours.

Sludge Concentration (%)	Initial Concentration (mg/1)	Equilibrium Concentration of Samples (mg/1)	Average Equilibrium Concentration (mg/1)	Remaining Fraction C/Co	$\frac{\text{mg Ni Removed}}{\text{mg Sludge}}$
1	0.32	0.126 0.122	0.124	0.39	$19.6\text{x}10^{-6}$
2	0.32	0.114 0.126	0.120	0.38	$10.0\text{x}10^{-6}$
4	0.32	0.140 0.139	0.134	0.42	$4.7\text{x}10^{-6}$
8	0.32	0.140 0.149	0.145	0.45	$2.2\text{x}10^{-6}$

Temperature = 20°C pH = 7.0

Table A-16: Effect of Sludge Concentration on the Removal of Nickel
Contact Time = 4 hours.

Sludge Concentration (%)	Initial Concentration (mg/l)	Equilibrium Concentration of Samples (mg/l)	Average Equilibrium Concentration (mg/l)	Remaining Fraction C/Co	$\frac{\text{mg Ni Removed}}{\text{mg Sludge}}$
1	0.33	0.158 0.162	0.160	0.48	$17.0\text{x}10^{-6}$
2	0.33	0.130 0.137	0.134	0.41	$9.8\text{x}10^{-6}$
4	0.33	0.130 0.115	0.122	0.37	$5.2\text{x}10^{-6}$
8	0.33	0.137 0.146	0.142	0.43	$2.4\text{x}10^{-6}$

Temperature = 20°C   pH = 7.0

Table A-17: Effect of Sludge Concentration on the Removal of Lead
Contact Time = 1 hour

Sludge Concentration (%)	Initial Concentration* (mg/l)	Equilibrium Concentration of Samples (mg/l)	Average Equilibrium Concentration (mg/l)	Remaining Fraction C/Co	$\frac{\text{mg Pb Removed}}{\text{mg Sludge}}$
1	0.16	0.06 0.06	0.06	0.38	10×10^{-6}
2	0.16	0.04 0.02	0.03	0.19	6.5×10^{-6}
4	0.16	0.03 0.04	0.04	0.25	3.0×10^{-6}
8	0.16	0.04 0.04	0.04	0.25	1.5×10^{-6}

*Final equilibrium concentration of dissolved lead in controls.

Temperature = 20°C pH = 7.0

Table A-18: Effect of Sludge Concentration on the Removal of Lead
Contact Time = 2 hours

Sludge Concentration (%)	Initial Concentration* (mg/l)	Equilibrium Concentration of Samples (mg/l)	Average Equilibrium Concentration (mg/l)	Remaining Fraction C/Co	mg Pb Removed / mg Sludge
1	0.3	0.06 0.04	0.05	0.17	25.0×10^{-6}
2	0.3	0.01 N.D.**	0.01	0.03	14.5×10^{-6}
4	0.3	0.02 0.05	0.04	0.13	6.5×10^{-6}
8	0.3	0.05 0.06	0.06	0.20	3.0×10^{-6}

* Final average equilibrium concentration of dissolved lead in controls.

** ND = not detectable; below detection limits.

Table A-19: Effect of Sludge Concentration on the Removal of Lead
Contact Time = 4 hours

Sludge Concentration (%)	Initial Concentration (mg/1)	Equilibrium Concentration of Samples (mg/1)	Average Equilibrium Concentration (mg/1)	Remaining Fraction C/Co	$\frac{\text{mg Pb Removed}}{\text{mg Sludge}}$
1	0.34	0.06 ND*	0.06	0.18	$28.0\text{x}10^{-6}$
2	0.34	0.01 0.05	0.03	0.09	$15.5\text{x}10^{-6}$
4	0.34	0.01 0.03	0.02	0.06	$8.0\text{x}10^{-6}$
8	0.34	0.02 0.01	0.01	0.03	$4.1\text{x}10^{-6}$

*ND = not detectable, below detection limits.

Temperature = 20°C, pH = 7.0