

NRC Publications Archive Archives des publications du CNRC

Remediation of heavy metal contaminated solid wastes by incorporating metal binding agents : part 1. Fixation of lead in soils Majid, Abdul; Toll, Floyd; Boyko, Victor J.; Sparks, Bryan D

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.4224/21270079>

IERT-NRC Special Report; no. ER-1327-94S, 1994-10-01

NRC Publications Archive Record / Notice des Archives des publications du CNRC :

<https://nrc-publications.canada.ca/eng/view/object/?id=1b75435f-294c-49d1-8574-c015d2ca4fae>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=1b75435f-294c-49d1-8574-c015d2ca4fae>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

15



National Research Council
Canada

Conseil national de recherches
Canada

Institute for Environmental
Research and Technology

Institut de technologie et de
recherche environnementales

15

NRC-CMRC

APPROVALS

APPROBATIONS

October 1994
ER-1327-94S

**Remediation of Heavy Metal Contaminated Solid
Wastes by Incorporating Metal Binding Agents.
Part 1. Fixation of Lead in Soils**

Abdul Majid, Floyd Toll, Victor J. Boyko and Bryan D. Sparks

Submitted By
Soumis par

Project Leader

Chef de projet

Approved By
Approuvé par

Program Head

Dirigeant de programme

Approved By
Approuvé par

Director General

Directeur général

This report may not be published in whole or in
part without written consent of the
NATIONAL RESEARCH COUNCIL

La reproduction, même partielle, de ce rapport
est interdite sans autorisation écrite préalable
du CONSEIL NATIONAL DE RECHERCHES

Ottawa, Canada
K1A 0R6

Docufax: (613) 952-1275

Canada



National Research
Council Canada

Conseil national
de recherches Canada



Institute for Environmental
Research and Technology
Process Technology

Institut de technologie et de
recherche environnementales
Technologie des procédés

Remediation of Heavy Metal Contaminated Solid Wastes by Incorporating Metal Binding Agents. Part 1. Fixation of Lead in Soils

Abdul Majid, Floyd Toll, Victor J. Boyko and Bryan D. Sparks

NRC Special Report No. ER-1327-94S
October 1994

Remediation of Heavy Metal Contaminated Solid Wastes by Incorporating Metal Binding Agents

Part 1. Fixation of Lead in Soils

Abdul Majid, Floyd Toll, Victor J. Boyko and Bryan D. Sparks
Institute for Environmental Technology and Research
National Research Council of Canada,
Ottawa, Ontario
K1A 0R9

IERT-NRC Special Report No. ER-1327-94S
Date: October 1994.

EXECUTIVE SUMMARY

OBJECTIVE

Fixation of heavy metals in fine textured soils and soil like materials by incorporating peat, gypsum and other metal fixation agents into soil agglomerates. The overall goal is to integrate this option with concurrent removal of hydrocarbon contaminants using the SESR process.

ACHIEVEMENTS

100% lead fixation was achieved for a sample of high clay soil, spiked with 1840 mg/kg of leachable lead.

TECHNIQUES

- A liquid phase agglomeration technique was used to coagglomerate the metal binding agents with soil.
- EPA's Toxicity Characteristics Leaching Procedure (TCLP) was applied to determine the leachability of lead from soil agglomerates containing metal binding agents.

HIGHLIGHTS

Adsorption of Lead from Aqueous Solutions

Peat

- The adsorption of lead on the substrates investigated is complete within 5 minutes.
- Adsorption of lead from aqueous solution by both peat and soil may be described by a Langmuir isotherm model. Adsorption isotherms fitted the "H type" described in the Giles classification. Saturation adsorption was reached at equilibrium lead concentrations > 3000 mg/L, compared with ~ 250 mg/L for soil alone. Calculation of the isotherm parameters showed the maximum lead adsorption to be 150 mg/g of peat in concentrated solutions and 195 mg/g of peat in dilute solutions. These values compare with only 12.64 mg/g for soil alone.
- Removal of lead, from aqueous solutions by peat, was most efficient at pHs > 5 and least efficient at pHs < 2.5 . Between pH 2.5-4.4 Pb adsorption was relatively constant at 130-150 mg/g peat.
- Peat forms acid resistant complexes with lead.

Gypsum

- Gypsum has a greater adsorption capacity for lead from aqueous solutions than peat. One gram of gypsum removed lead from aqueous solutions almost quantitatively when the initial lead levels were less than 15000 ppm. Even when the lead concentrations were >15000 ppm over 60 % of lead was removed. The maximum adsorption was observed at pHs > 3.0.
- The data for the adsorption of lead by gypsum cannot be described by any of the three (Langmurian, Freundlich or BET) most popular adsorption models. However, the adsorption isotherm is an "H" type, suggesting a very strong interaction of the ion exchange type.

Applications to Wastewater Treatment

- Because of their strong adsorption capacity for lead from aqueous solutions, both peat and gypsum may also have applications for the removal of lead from wastewaters.

Fixation of Lead in Soil

- Results from leaching tests (EPA-TCLP at pH 2.9) on soil-peat mixtures confirmed the excellent metal binding capacity of peat in the samples tested. The amount of lead leached from a soil sample, spiked with 1840 mg/kg of water soluble lead, decreased with increasing amounts of peat loading. Total fixation was achieved at a peat loading of 20%.
- Canadian and US environmental regulations permit a maximum of 1000 ppm lead in treated soils and sediments. This level requires less than 5w/w% of peat for complete fixation of lead.

- In addition to peat several other materials were also tested for their suitability as metal fixing agents. Preliminary results from these tests suggests the following order of effectiveness:

Gypsum > peat > lime > ASR > fly ash > oil sands fines

Where ASR is auto shredder residue

FUTURE WORK

Future work is planned on the following lines:

- Concurrent solvent extraction of organic contaminants and fixation of lead.
- Evaluation of sodium metaphosphate as a lead fixation agent.
- Remediation of a naturally contaminated soil sample.

- Fixation of other heavy metals such as Cd, Cr, Hg, As, Se and Zn.
- Test for long term bioavailability of various metals after fixation in soil.

Recommendation for a New Initiative

Peat seems to have a great potential in the treatment of wastewaters for the removal of a number of impurities such as heavy metals, suspended solids, organic matter, oils, detergents, dyes, pesticides and other toxic materials. It is abundantly available and inexpensive. However, a low hydraulic loading rate limits its use for large volume wastewater treatment. Recently, there has been some progress in this regard by pelletizing peat with polymeric materials as binders. Liquid phase agglomeration may have potential applications to convert peat to a suitable physical state for specific applications. Peat blended with other materials such as gypsum, sodium metaphosphate and fly ash may result in an improved product in terms of its adsorption efficiency for various pollutants. Coagglomeration of peat with these materials in the presence of suitable binders such as sodium silicate may produce pellets having optimum porosity, strength and surface area for maximum adsorption and high hydraulic loadings.

ABSTRACT

Elevated levels of lead in soil result from such diverse inputs as vehicle emissions, fly ash deposition, land application of waste materials and other industrial activities. Because of its accumulation in plants and the possibility of ground water contamination the need to remediate this metal is critical. The ability of peat to form stable complexes with heavy metals makes it a promising fixing agent for the treatment of contaminated soils and sediments. Peat's strong metal adsorption capacity is associated with its humic matter content. The polyacidic functional groups of these humic substances are responsible for their high cation exchange capacity.

Adsorption of lead from aqueous solution by both peat and soil has been measured. The results may be described by a Langmuir isotherm model. Adsorption isotherms fitted the "H type" described in the Giles classification. Saturation adsorption was reached at equilibrium lead concentrations >3000 mg/L, compared with ~ 250 mg/L for soil. Calculation of the isotherm parameters showed the maximum lead adsorption to be 150 mg/g of peat in concentrated solutions and 195 mg/g of peat in dilute solutions. This compares with a binding capacity of only 12.64 mg of lead per gram for soil alone.

Several tests were carried out to evaluate the lead binding capacity of peat in a spiked soil sample. Results from leaching tests (EPA-TCLP at pH 2.9) on soil-peat mixtures confirmed the excellent metal binding capacity of peat in the samples tested. The amount of lead leached from a soil sample, spiked with 1840 mg/kg of water

soluble lead, decreased with increasing amounts of peat loading. Total fixation was achieved at a peat loading of 20%.

Gypsum, which is widely used for agricultural applications, was also tested for its capacity to adsorb lead from aqueous solutions as well as for fixation in soils and sediments. Gypsum was more effective than peat both for the removal of lead from aqueous solution and for its fixation in soil.

When heavy metal contamination occurs in conjunction with organic pollutants the two components must often be separated in different process steps. For example, high concentrations of heavy metals are usually toxic to the micro-organisms used for the bioremediation of organic contaminants. In this investigation, peat and gypsum have been coagglomerated with soil as a means to fix lead in artificially contaminated samples.

The agglomeration process is advantageous in that it should allow concurrent fixation of heavy metals and solvent extraction of organic contaminants. Also, Liquid phase agglomeration is capable of handling fine textured soils without adversely affecting soil fertility. In terms of material handling and equipment a combined process will be more economical than conventional methods requiring separate extraction and leaching steps.

In addition to peat and gypsum several other agents were tested for their suitability as fixing agents in heavy metal contaminated soils. The results of these tests suggest the following order of effectiveness for these materials:

Gypsum > peat > lime > ASR > fly ash > oil sands fines
where ASR is autoshredder residue.

In addition to their use as binders for lead in contaminated soils/sediments, peat and gypsum may also have potential applications in the treatment of heavy metal contaminated wastewaters.

INTRODUCTION

Although some micro-organisms are able to change the valence state of heavy metals to produce an insoluble form, metals are usually considered to be non biodegradable. Also, they have a tendency to accumulate in living material. Because soil serves as a medium for the growth of food crops and recharge of ground water, potentially dangerous health effects can be associated with elevated heavy metal levels in soils. Metals mobilized by biogeochemical processes can result in phytotoxic effects as well as contamination of edible plant parts and drinking water supplies. These serious ecological effects make it critical for soil contaminated with heavy metals to be remediated to safe levels.

Metals such as lead, cadmium, copper, zinc, nickel, chromium, and mercury constitute one of the contaminant groups considered to be most noxious with respect to human health. A variety of human activities have resulted in contamination of soil and sediments with these metals, included are such diverse inputs as; vehicle emissions, mining, smelting, metal plating or finishing operations, automobile battery production, land application of sewage sludge, industrial waste, fertilizers or pesticides and fly ash from incineration or combustion processes. Concentrations of heavy metals range from 0 to 100 ppm in municipal and agricultural waste and from 100 to 10,000 ppm in sewage sludge, mining waste, industrial (e.g. electroplating) wastes, pulp and paper sludges and chemical discharges. In particular, lead has contributed substantially to pollution and represents a ubiquitous hazard in the biosphere. Because of its widespread existence in industrial and hazardous wastes and its presence on the US EPA list of Priority Pollutants lead was chosen as the study metal for the work described here.

For remediation of heavy metal contaminated soil the metals must be either physically removed or stabilized so that they are non-leachable¹. Washing, to remove heavy metals as stable, soluble chelates, has only been successful with coarse soils²⁻⁶. Natural conditions such as low pH or variable oxidation-reduction potential tend to solubilize metals. Migration of these contaminants into the groundwater through hydrolysis, or desorption through exposure to varying conditions in the soil, may be prevented by metal fixation with strongly adsorbing, insoluble chemical additives, distributed throughout the soil. Metals immobilized in this way present no adverse environmental or health hazards in their treated state⁷. However, the binding agents must be resistant to chemical and microbial degradation in the soil environment so that the metals are not released over long periods of times. The additives themselves must not contain any leachable organic or inorganic substances that could contaminate the ground water.

Existing technologies for the cleanup of contaminated soil or sediments are poorly suited for treating fine textured soils without adversely affecting the associated humic matter or soil mineralogy. At the National Research Council of Canada liquid phase agglomeration techniques have been successfully used for the remediation of organic contaminated soils. As an extension of this work metal binding materials have been incorporated into soil agglomerates formed during solvent extraction of organic contaminants. The resulting combined process is expected to be advantageous in that it will allow concurrent removal of organics and fixation of heavy metals. The end result is a process more economical, in terms of material handling and equipment costs, than methods which require separate extraction and leaching steps for organic and heavy metals respectively.

EXPERIMENTAL METHODS

Materials. A sample of Eskine soil from Alberta was used for this study. Table 1 lists typical properties and composition for this soil. A soil pH of 7.9 was measured with a

glass combination electrode in 0.01 M CaCl_2 at a soil to solution ratio of 1:1⁸. An artificially contaminated sample was prepared by spiking soil with a solution of lead nitrate. In a typical test lead nitrate (about 1500 mgs) was dissolved in distilled water (100 mL). This solution was placed in a glass Waring Blendor jar with uncontaminated soil (500g). The slurry was blended at about 5000 rpm and then allowed to air dry before being broken up using a porcelain mortar and pestle.

Peat. A sample of agricultural peat moss was ground to about 150 μm particle size, using a Brinkman Centrifugal Grinding Mill ZM-1. A sample of this peat, suspended in distilled water, had a pH of 4 ± 0.1 . Moisture and organic contents were 25 ± 5 w/w% and 49.7 ± 1.6 w/w% (dry basis) respectively. An ash content of 2.3 w/w% (dry basis) was determined by ignition in a muffle furnace at 400 ± 10 °C. No detectable amounts of lead were found in the TCLP leachate from peat.

Other reagents. Fly ash used in this study was obtained from the Alberta Research Council sample bank. Athabasca oil sands fine clay, separated according to a procedure reported elsewhere⁹, was from the Suncor tailings pond. A sample of automobile shredder residue (ASR) was obtained courtesy of Dr. M. Day of our Institute. A reagent grade sample of calcium sulphate from Anachemia was used instead of commercial gypsum. Reagents for the spectrophotometric determination of lead were obtained from the Hach company (c/o Fryston Canada incorporated, Mississauga, Ontario). All other reagents used were of reagent grade.

Agglomeration Procedure. A sample of artificially contaminated soil (100g) was mixed with amounts of ground peat depending upon the desired soil:peat ratio. This mixture was dispersed in Varsol (250 mL), by agitating at 250 rps in a Waring Blendor jar. Distilled water was added to the vigorously agitated slurry in small increments (1 mL), at intervals of 30 seconds, until discrete agglomerates formed; a total of 15-20 mL of water was required. When the amount of peat was more than 1 w/w% the mixture tended to stick to the walls of the Blendor jar; agitation was stopped every 5 minutes and the adhering material scraped off with a spatula. The agglomerates of peat and soil were separated from the organic phase on a 100 mesh screen and then dried at 100 °C. The diameter of the roughly spherical agglomerates ranged from 0.1-1 mm. Agglomeration was also carried out in a polypropylene bottle by agitation on a paint shaker. This latter procedure gave uniformly sized agglomerates of 0.1-0.2 mm diameter.

Adsorption of Lead on Peat, Soil and Gypsum. For adsorption experiments, samples of peat, soil or gypsum (1g) were added to each of a series of lead nitrate solutions (100 mL) with concentrations ranging from 100 to 15,000 $\mu\text{g/mL}$. The mixtures were sealed in polypropylene jars and agitated on a reciprocal shaker. Preliminary measurements showed no significant changes in lead adsorption for agitation periods longer than 5 minutes, as shown for peat in Table 2. However, samples were always shaken for 24 hours in order to ensure that adsorption equilibrium

was attained. Batch adsorption experiments were run at $\text{pH } 3 \pm 0.2$; non-buffered solutions were used in order to eliminate competitive adsorption effects from the buffer components.

Suspensions were filtered using a Whatman no. 41 filter paper. The initial filtrate was discarded in order to eliminate errors due to the adsorption of lead by the filter paper. The solutions were analyzed for lead both before and after adsorption. The amount of adsorbed lead was calculated by the difference between initial and final concentration after taking into account the volume of solution entrained by the solid phase. All measurements were carried out in duplicate and only the means with standard errors of $\pm 5\%$ are reported.

In another series of tests the effect of peat loading was determined. In this case the concentration of lead in solution was kept constant and varying amounts of peat (1-10g) were added to a known amount of solution in separate jars. The remainder of the procedure was similar to the one described above.

Leaching Tests. The TCLP extractions were performed according to the methods described in the US Federal Register¹⁰ and specified in SW-846¹¹.

Analysis of Lead. For rapid screening purposes lead was analyzed spectrophotometrically, using the dithizone method, with a HACH DR/3000 spectrophotometer. However, there was considerable interference because of the color generated by peat. Therefore, final results, as reported, were obtained by analysis using Inductively Coupled Plasma Spectroscopic Analysis (ICP). Mass balances for total lead were carried out by analyzing leached as well as unleached samples of blank spiked soil and soil-peat mixtures. The results are listed in Table 3.

RESULTS AND DISCUSSION

Adsorption Studies

Case 1: Peat. Experimental data for lead adsorption have been plotted in Figures 1-4. Inspection of the isotherm, shown on Figure 1, indicates an "H type", according to the Giles classification¹². The amount of lead sorbed reaches saturation when the equilibrium concentration exceeds 3000 mg/L. At this concentration all available sites are filled with lead. "H" curves are indicative of the adsorption of ionic 'micelles' on oppositely charged surfaces or exchange of high affinity ions with low affinity ions leading to chemisorption. These curves commence at a positive value on the "concentration in solid" axis. In this case, the solute has such a high affinity that in dilute solutions it is completely adsorbed and therefore, the initial part of the isotherm is vertical. "H" curves usually contain a long plateau, the length of which is proportional to the difficulty of formation of a second adsorbed layer because of charge repulsion between adsorbed ions and those in solution.

The adsorption of lead on blank soil was also studied. The data have been plotted in the inset shown on Figure 1. Compared with peat there was considerably less adsorption of lead on soil. The adsorption isotherm was again of the "H" type.

The adsorption data for both peat and soil can be fitted by a Langmuir isotherm model. This model was used owing to its widespread application to describe the aqueous phase adsorptive behaviour of clay-carbon materials¹³⁻¹⁴. The model can be described by the equation:

$$q_e = Q_0 b C_e / (1 + b C_e) \dots \dots \dots (1)$$

where q_e is the amount of solute adsorbed per unit mass of adsorbent and C_e the equilibrium adsorbate concentration. The parameters Q_0 and b were calculated after fitting the data to equation (1). Q_0 represents the solid-phase concentration corresponding to complete coverage of available adsorption sites while b can tentatively be related to the intensity of the adsorption reaction. Table 4 summarizes the calculated Langmuir isotherm parameters for both the lead-peat and the lead-soil systems. The values of Q_0 suggests that even in concentrated solutions peat has a much higher capacity (Q_0 equals 150.4 mg/g) to adsorb lead than soil alone (Q_0 is 12.6 mg/g). Consequently, peat may be a good candidate for the fixation of lead in contaminated soils/sediments.

The data for the adsorption of lead by peat, from dilute solutions, has been plotted separately in Figure 2. This data can be fitted to a linear plot with a correlation coefficient of 0.992. Fitting this data to the Langmuir equation gives a higher value for Q_0 (194.6) than for the data from concentrated solutions, implying that lead adsorption capacity is greater in more dilute solutions. This suggests that peat will be suitable not only as a fixation agent for lead in soils and sediments, where slow leaching of lead is a problem, but could be used effectively for the treatment of waste waters containing low concentrations of dissolved lead.

The values of Langmuir parameter b for both sets of data are much higher than those reported for the adsorption of various organic pollutants on clays and activated carbons¹³. This observation suggests a very strong interaction of lead with the adsorbents, possibly by formation of a peat-lead complex through chelation with the ligands of humic matter.

Figure 3, shows the effect of initial lead concentration on its uptake by peat. It is obvious from this plot that in dilute solutions almost quantitative removal of lead by peat may be achieved. The removal efficiency decreases with the increase in lead concentration. The data can be fitted to the following equation.

$$Y = a + b \log (C) \dots \dots \dots (2)$$

Where Y represents the percentage of total lead adsorbed by peat and C is the initial lead concentration in mg/L of solution; a and b being constants. The values of a and b calculated from this equation were 169 and -0.38 with values for percent coefficient of variance (%CV) of 4.9 and 7.1 respectively. For solutions, this equation can be used to calculate the amount of peat required for the removal of lead to a desired level.

Effect of Adsorbent Density

Figure 4 shows the effect of peat suspension density on the uptake of lead; the amount of lead adsorbed increased with peat loading. The data was fitted to the following equation.

$$Y = a + b \log (D) \dots \dots \dots (3)$$

where Y is the percentage of initial lead adsorbed by peat and D is the peat dosage in g/100 mL of solution. The values of constants a and b were calculated to be 33.6 and 37.6 with %CV values of 7.3 and 9.2 respectively. Again, knowing the initial lead concentration, it is possible to determine the amount of peat required for the removal of lead to a desired level in solution.

Effect of pH

Several factors are important in the adsorption of heavy metal ions by peat. These include the specific surface area, pH and initial metal ion concentration. Adsorption studies were carried out at pH values of 1.6, 2.5, 3.0, 4.5 and 5.2. Removal of lead from aqueous solution was most efficient at pH 5.2 when adsorption of lead was 230 mg/g of peat. This level of adsorption appears to be due to the precipitation of lead (II) ions because of the high concentration of OH⁻ ions in the adsorption medium. The lowest adsorption efficiency (15 mg/g) occurred at pH 1.6 where lead solubility is highest. Between pH 2.5-4.5 Pb adsorption was relatively constant at 130-150 mg/g peat.

Sorption Mechanism

Humic substances are the major constituents of peat¹⁵. Numerous investigations of the complexation of heavy metals by humic substances have shown that they have a high affinity for metal ions¹⁶⁻¹⁸. The inorganic content of peat is relatively low (2.3%) and generally contributes little to the overall cation exchange capacity¹⁹. Therefore, it appears most likely that the polyacidic functional groups associated with the humic content of peat, are responsible for its cation exchange capacity. This is supported by the work of Coleman, Bunzl and Wolf²⁰⁻²² who have demonstrated that the interaction between metal ions and peat is, indeed, an ion exchange process.

Case 2: Gypsum. Application of gypsum on agricultural land for the prevention and correction of sodicity is widely practiced²³. For many reasons it is considered to be the

farmer's best friend. Its advantages include: greater stability of soil organic matter, more stable soil aggregates, improved water penetration into soil and more rapid seed emergence. Waste product gypsum is available in a large number of locations at very little cost. Heavy metal sulphates are insoluble in water, consequently, their stabilization through gypsum amendment may provide a cost effective method for reducing the leaching, migration and bioavailability of lead from soils. For these reasons the adsorption of lead by gypsum was investigated.

Figure 5 shows the adsorption isotherm for lead on gypsum. The data could not be fitted to any of the three most common adsorption isotherm models: Langmurian, Freundlich or BET. However, the plot can be classified as "H" type suggesting a strong interaction between lead in solution and gypsum. In Figure 6 the data has been plotted as a percentage of initial lead removed against initial lead concentration in solution. It is obvious from this plot that even at very high concentrations, over 60% of lead can be removed from solution using gypsum. At concentrations lower than 15000 ppm, lead is almost quantitatively removed by gypsum.

Fixation of Lead in Contaminated Soil

Results from the adsorption studies have clearly demonstrated that both peat and gypsum are effective for the removal of lead from aqueous solutions, implying that these materials have potential application for the treatment of contaminated soils or sediments to immobilize heavy metals. Therefore, several tests were carried out to determine the effectiveness of these materials as fixation agents for lead in an artificially contaminated soil.

Lead Fixation with Peat. It has been reported that humic matter can retard heavy metal movement in soils even under acidic conditions²⁴. The ability of peat to form stable metal complexes makes it a promising candidate for the treatment of soils or sediments contaminated with heavy metals. Several tests were carried out to test the suitability of peat for this use by coagglomerating it, in a non aqueous medium, with a soil artificially contaminated with 2200 mg of Pb/kg of soil. The leaching of lead from blank soil samples and soil-peat agglomerates was determined by EPA's TCLP leaching test. Soil alone adsorbed 360 mg of Pb/kg, leaving 1840 mg/kg leachable lead. The amount of lead fixed by peat has been plotted in Figure 7. The amount of leachable lead at pH 2.9 (TCLP) decreased with increasing peat loading to the extent that 100% lead fixation was achieved at a peat loading of 20%.

Figure 8 shows the effect of peat loading on the fixation of lead in soil. The data can be fitted to the following equation.

$$Y = a + b \log (X) \dots \dots \dots (4)$$

where Y is the amount of lead fixed and X is the amount of peat in the soil. The equation can be solved to determine the amount of peat required to fix any given

amount of leachable lead in soil. However, Environment Canada regulations²⁵ allow a maximum of 1000 ppm of lead in treated soils. At this concentration less than 5 w/w% peat is required for fixation of the leachable lead present.

Comparative Efficiencies of Various Binders for Lead Fixation

In addition to peat, several other binders were also tested for their suitability as metal fixing agents in heavy metal contaminated soils. These binders included: lime, gypsum, coke fly ash and mineral fines from Suncor oil sands plants and auto shredder residue (ASR). The results are shown graphically in Figure 9. A comparison of these data suggests the following order of effectiveness for the tested materials:

Gypsum > peat > lime > ASR > fly ash > oil sands fines

Where ASR represents Automobile Shredder Residue.

Potential Applications of Peat to Wastewater Treatment

The results from the adsorption studies, discussed in this report, have clearly demonstrated a strong adsorption capacity of peat for lead in aqueous solutions. The high adsorption capacity of peat may permit the development of methods for the removal and subsequent recovery of metals from wastewaters. This is consistent with the reported results of several workers²⁶. Peat can be modified and improved, by suitable chemical treatment, to increase its total metal sorption capacity and improve selectivity for trace or transition metals²⁷. Peat, because of its chemical composition and particulate nature has also been reported to be an effective adsorbent and filtration medium for wastewater treatment to remove other pollutants such as suspended solids, organic matter, oils, detergents, dyes and pesticides²⁸. Obviously then, peat which is a natural, inexpensive material seems to have a great potential as an alternative to several commercial ion exchange resins which range in price from \$US4.40 to 22/kg compared to peat with an average price of \$US0.09/kg²⁸. However, peat filters have a low hydraulic loading rate (0.0.15-250 Lpd/m²) and are not suitable for large volumes of wastewater treatment. Recently, attempts have been made to overcome this problem by pelletizing peat using polysulphone as a binder²⁸. It therefore appears worthwhile to explore the role of liquid phase agglomeration in developing appropriate technology to coagglomerate peat with additives for use in diverse applications. For example peat plus lime, gypsum, sodium meta-phosphate or fly ash could be used for the treatment of wastewaters.

CONCLUSIONS

The adsorption of lead on both peat and gypsum appears to be complete within 5 minutes. The isotherm for lead on peat can be classified as an "H" type, according to the Giles classification. This suggests an ion exchange mechanism and the formation of a monolayer. Adsorption data can be fitted by a Langmuir isotherm model; isotherm parameters suggest a very strong interaction of lead with peat, indicating the formation of a peat-lead complex by chelation with the ligands of humic matter.

Results from the adsorption study in aqueous solution and the TCLP tests on peat, with/and artificially contaminated soil suggest that peat is a very effective material to immobilize lead in soils or sediments. For low concentrations (<1000ppm) of lead less than 5 w/w% of peat will be sufficient to immobilize this contaminant in soils or sediments. Removal of lead from aqueous solutions was most efficient at pHs >5 and least efficient at pHs <2.5. Between pH 2.5-4.4 Pb adsorption was relatively constant at 130-150 mg/g peat.

Gypsum appears to be even more effective for the removal of lead from solution than peat. At concentrations lower than 15000 ppm, lead is almost quantitatively removed; even at very high concentrations over 60% of lead can be removed from solution by one gram of gypsum. The data for the adsorption of lead by gypsum cannot be described by any of the three more popular adsorption models, Langmurian, Freundlich or BET. However, the adsorption isotherm is of "H" type, suggesting a very strong interaction of the ion exchange type. The TCLP results on gypsum-contaminated soil are also consistent with the results from the adsorption study in solution. For gypsum, maximum adsorption was observed at pHs > 3.0.

Of the various materials tested for lead fixation ability gypsum and peat were found to be the most effective.

ACKNOWLEDGMENT

The authors are grateful to Dr. Aly Fouda for his help in the theoretical calculations related to adsorption of lead on peat. We also acknowledge technical help from V. Clancy for the determination of Hg in soil.

REFERENCES

1. R. N. Yong and N. Di Perno, " Sources and Characteristics of Waste: with Specific References to Canada"; McGill University, Geotechnical research Centre, Geo-environmental series 91-1
2. B. E. Reed and S. Arunachalam, "Hazardous and Industrial Wastes"; Proc. 24th Mid- Atlantic Industrial Waste Conference. Editors: B. E. Reed and W. A. Sack Technomic Pub.Co. 1992 pages 101-109.
3. B. J. Alloway and H. Morgan, "The Behaviour and Availability of Cadmium, Nickel and Lead in Polluted Soils"; in Contaminated Soil, Editors: W. Assink and W. J. van den Brink, 1986, Martinus Nijhoff publishers, Dordrecht, Netherlands
4. H. A. Elliott, J. H. Linn, and G. A. Shields, "Role of Fe in Extractive Decontamination of Lead Polluted Soils Hazardous Waste & Hazardous Materials", 6 (3), 223-229 (1989).

5. R. W. Peters and L. Shem, "Adsorption/Desorption Behaviour of Lead on Various Types of Soil"; Proc. 24th Mid-Atlantic Industrial Waste Conf. 1991, pages 718-730, Editors: B. E. Reed and W. A. Sack.
6. D. J. Silviera, and L. E. Sommers, "Extractability of Copper, Zinc, Cadmium, and Lead in Soils Incubated with Sewage Sludge"; Journal of Environmental Quality, 6 (1): 47-52. Jan-Mar 1977
7. G. Czupyrna, R. D. Levy, A. I. MacLean, and H. Gold, "In Situ Immobilization of Heavy-Metal-Contaminated Soils"; Noyes Data Corp., Park Ridge, NJ, 1989.
8. R. A. Storer, "Standard Test method for pH of Soils"; American Society for Testing and Materials, STP Section 4, 04.08: 1017-1018 (1991).
9. A. Majid and B. D. Sparks, "Structure Formation in Oil Sands Fine Tailings Resulting from Flocculation of Coarse Bi-Wetted Solids by Bitumen Bridging"; IEC Special Report No. EC-1281-93S, August 1993, 55 pages.
10. USEPA Federal Register. 51, (142), March 1990, Office of Solid Waste, Washington DC.
11. USEPA - "Test Methods for Evaluation of Solid Waste: Physical/Chemical Methods"; SW-846, 3rd Ed., Office of Solid Waste and Emergency Response, Washington DC, Nov. 1986.
12. C. H. Giles, T. H. MacEwan, S. N. Nakhwa, and D. Smith, "Studies in Adsorption. Part XI. A System of Classification of Solution Adsorption Isotherms, and its Use in Diagnosis of Adsorption Mechanisms and in Measurement of Specific Surface Areas of Solids"; J. Chem. Soc., London, 3973-3993 (1960).
13. S. J. T. Pollard, C. J. Sollars and R. Perry, "A Clay-Carbon Adsorbent Derived from Spent Bleaching Earth: Surface Characterization and Adsorption of Chlorophenols from Aqueous Solution"; Carbon, 30 (4), 639-645 (1992).
14. S. J. T. Pollard, C. J. Sollars, and R. Perry, "A Low-cost Adsorbent from Spent Bleaching Earth. 1. The Selection of an Activation Procedure"; J. Chem. Tech. Biotechnol. 50 (2), 265-276 (1991).
15. G. Luttig, "Plants to Peat: The Process of Humification"; in Peat and Water: C. H. Fuchsman (Ed.), Elsevier Applied Science Publishers, New York, 1986.
16. M. Schnitzer and S. U. Khan, "Humic Substances in the Environment"; Marcel Dekker, New York, 1972.

17. W. Flaig, H. Beutelspacher and E. Rietz, "Chemical Composition and Physical Properties of Humic Substances"; in *Soil Components*: J. E. Gieseking (Ed.), 1, 1-211, Springer-Verlag, New York, 1975.
18. F. J. Stevenson, "Humus Chemistry: Genesis, Composition, Reactions"; John Wiley, New York, 1980.
19. R. H. Kadlec and G. A. Keoleian, "Metal Ion Exchange on Peat"; in *Peat and Water*: C. H. Fuchsman, (Ed.), Elsevier Applied Science Publishers, New York, 1986.
20. N. T. Coleman, A. C. McClung and D. P. Moore, "Formation Constants for Cu(II)-Peat Complexes"; *Science*, **123**, 330-1(1956).
21. K. Bunzl, W. Schmidt, and B. Sansoni, "Kinetics of Ion Exchange in Soil Organic Matter. IV. Adsorption and Desorption of Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} and Ca^{2+} by Peat"; *J. Soil Sci.* **27**, 32-41 (1976).
22. A. Wolf, K. Bunzl, F. Dierl and W. F. Schmidt, "The Effect of Ca^{2+} Ions on the Absorption of Pb^{2+} , Cu^{2+} and Zn^{2+} by Humic Substances"; *Chemosphere*, **5**, 207-13 (1977).
23. G. A. Wallace and A. Wallace, "Lead and other Potentially Toxic Heavy Metals in Soil"; *Comm. Soil Sci. Plant Anal.* **25**, 109-116(1994). -
24. L. D. Tyler and M. B. McBride, "Mobility and Extractability of Cadmium, Copper, Nickel and Zinc in Organic and Mineral Soil Columns", *Soil Sci.* **134**, 198-205 (1982).
25. Proposed Guideline for the Clean-up of Contaminated Sites in Ontario, Ontario Ministry of Environment, July 1994.
26. D. Couillard, "The use of Peat in Wastewater Treatment"; *Wat. Res.* **28**(6), 1261-1274 (1994).
27. M. A. Rashid, "The Importance of Organic Compounds in Biological Oceanography"; *Ocean Science Review*, **3**, 43-51 (1975).
28. L. M. Cohn, "Asarco Relies on Peat Moss Beads for Help with its Waste Treatment"; *American Metal Market*, September 1994.

Table 1 Typical Properties of Erskine Soil

Parameter	Value
Soil pH	7.9
Loss on ignition at $400 \pm 10^\circ\text{C}$, 20 hours (w/w%)	1.1
Total carbon (w/w%)	1.0
Carbonate carbon (w/w%)	0.7
Total Sulphur (w/w%)	0.0
Clay ($\% < 2\mu\text{m}$)	38.5
Leachable lead (mg/kg of soil)	None detectable

Table 2. Adsorption of Pb by Peat as a Function of Time
(Initial Pb Concentration: 489 ± 3.3 mg/L; pH of Solution 3 ± 0.2)

Time (minutes)	Final Pb Concentration (mg/L)	Amount of Pb Adsorbed mg/g Peat
5	250 ± 3	23.9
15	266.5 ± 5.5	22.3
30	283 ± 5	20.6
60	252 ± 1.5	23.8
24 hours	256 ± 5	23.3
Average	262 ± 13.5	22.8 ± 1.2

Table 3. Lead Mass Balance in Solid Samples

Test #	Sample ID	Amount of Pb (w/w% of Soil)			Total Pb Fixed (%)	Mass Balance for Pb* (%)
		Solid Phase (a)	Leachate (b)	Total (a + b)		
1	Soil + 10% Peat (before leaching)	0.34	-	0.34	-	
1b	Soil + 10% Peat (after leaching)	0.25	0.05	0.30	83.3	88.2
2	Soil + 1% Peat (before leaching)	0.31	-	0.31	-	
2b	Soil + 1% Peat (after leaching)	0.18	0.148	0.328	54.9	105.8
3	Soil + 1% Peat (before leaching)	1.55	-	1.55	-	
3b	Soil + 1% Peat (after leaching)	0.38	1.134	1.514	25.1	97.7

* Based on the amount of lead determined in solid samples, before leaching.

Table 4. Adsorption Isotherm Parameters.

Parameters	Value	
	Pb Concentration, 1100-100ppm	Pb Concentration, 15000-100ppm
Q_0 (mg g ⁻¹)	194.6 ± 63.6	150.4 ± 7.2
b	0.00093 ± 0.0005	0.0015 ± 0.00025
r^2	0.88	0.86

Figure Captions:

- Figure 1. Adsorption Isotherm for Pb on Peat in Concentrated Solutions
- Figure 2. Adsorption Isotherm for Pb on Peat in Dilute Solutions
- Figure 3. Pb Adsorption by Peat as a Function of Initial Concentration
- Figure 4. Effect of Peat Dosage on Pb (II) Uptake
- Figure 5. Adsorption Isotherm of Pb on Gypsum
- Figure 6. Efficiency of Pb Removal by Gypsum
- Figure 7. Fixation of Pb in Soil using Peat
- Figure 8. Effect of Peat Loading on Pb Fixation in Soil
- Figure 9. Comparative Efficiencies of Various Binders for Pb Fixation

Figure 1. Adsorption Isotherm for Pb on Peat (pH 2.8-3.2).

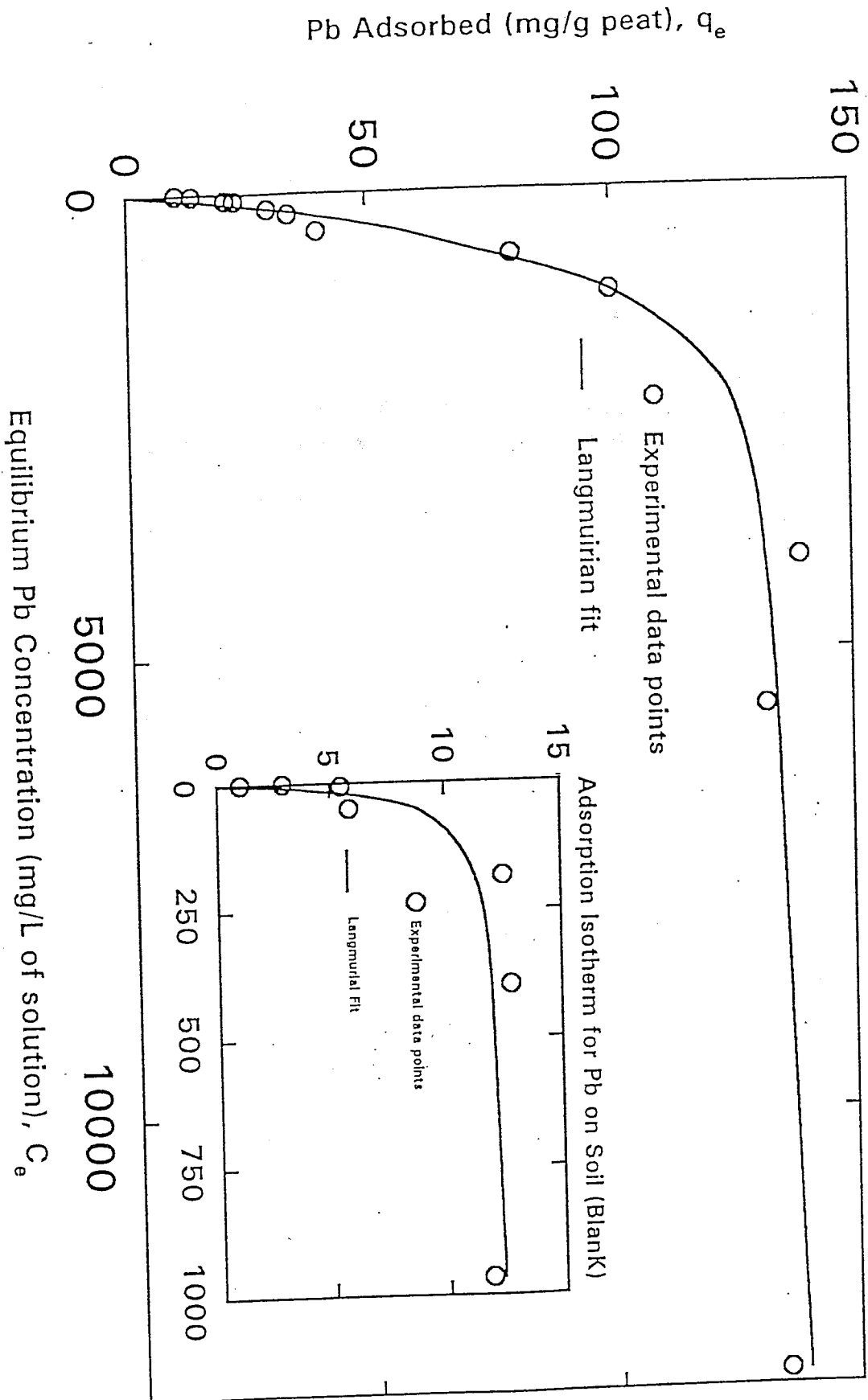


Figure 2. Adsorption Isotherm for Pb on Peat in dilute solution (pH 2.8-3.2).

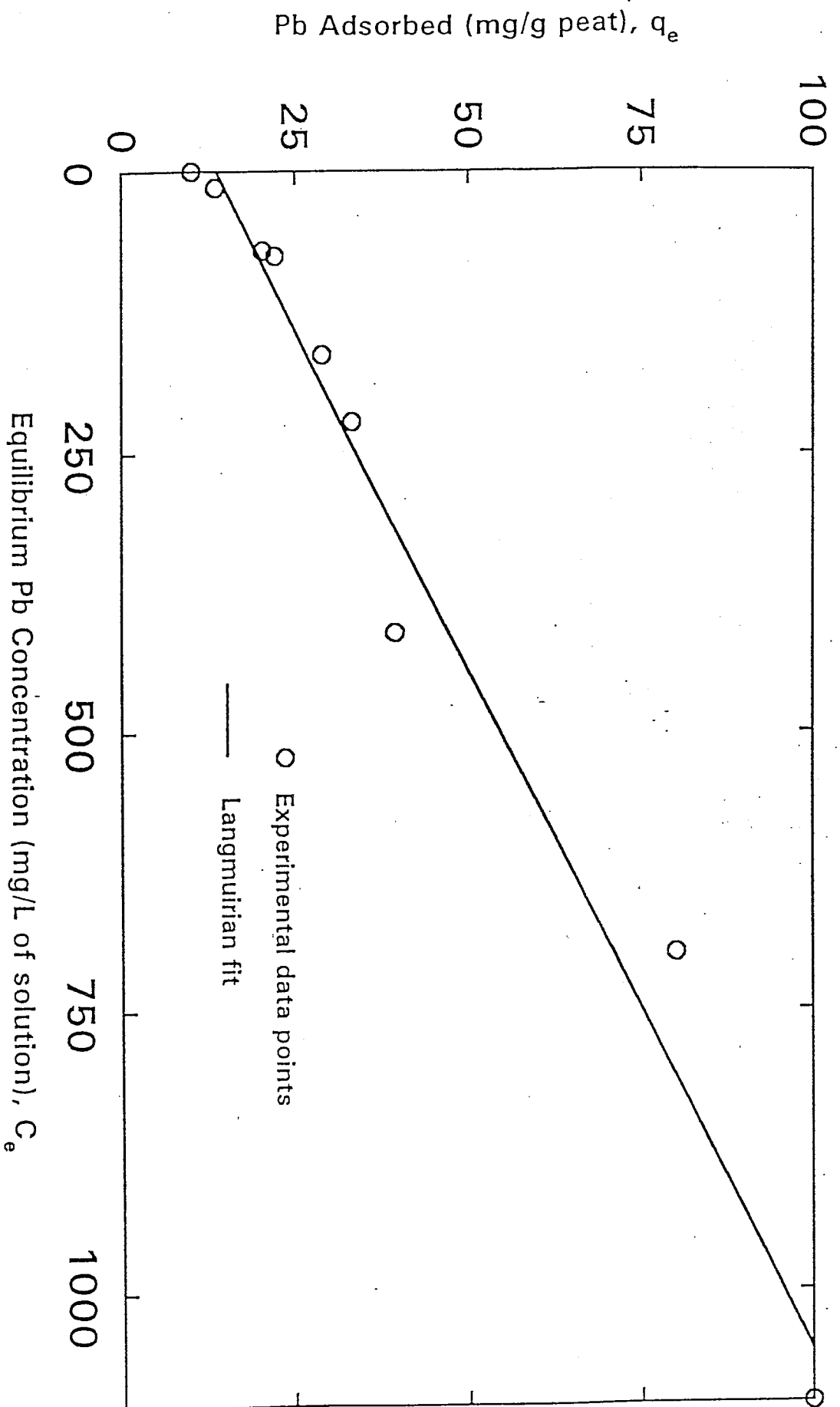
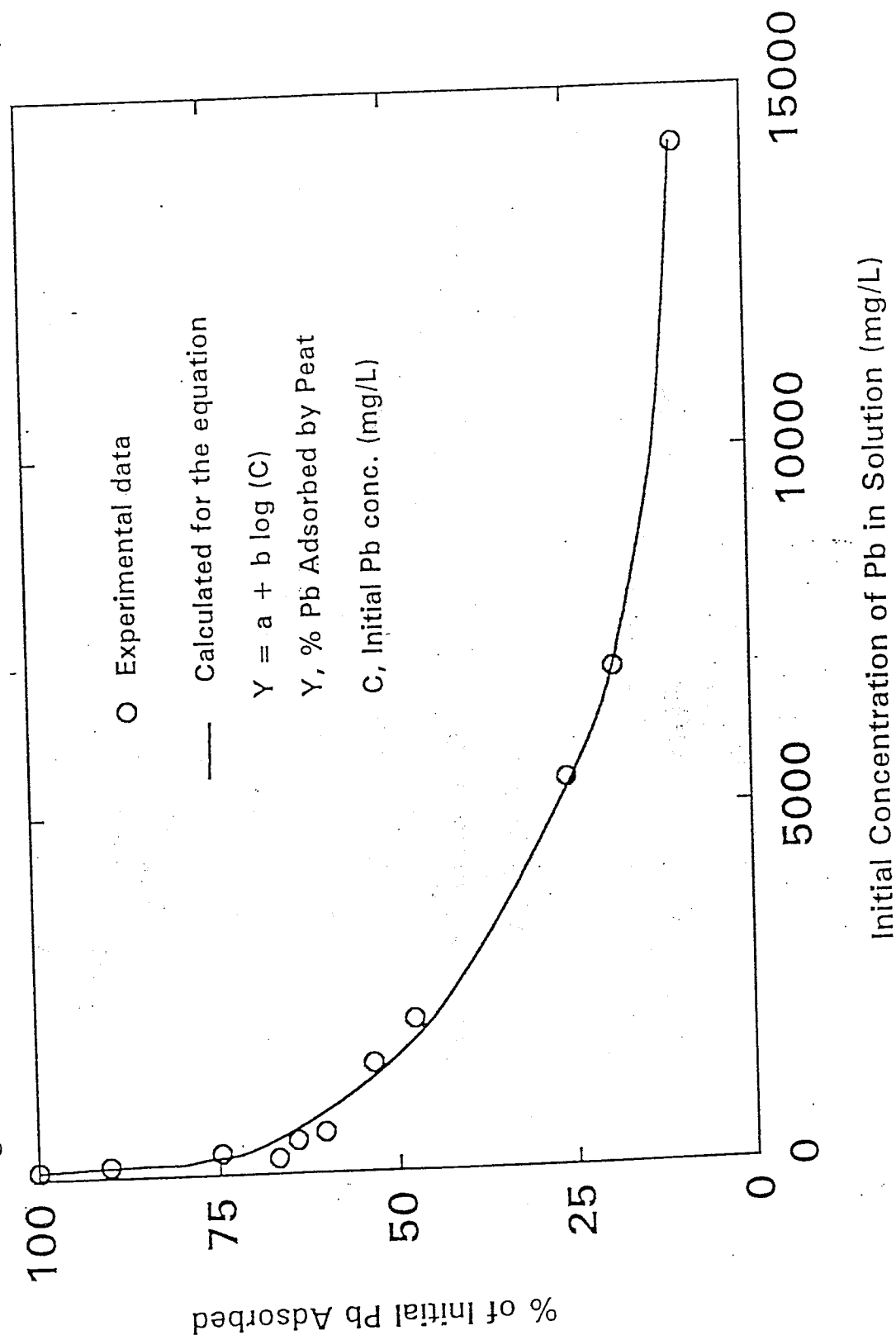
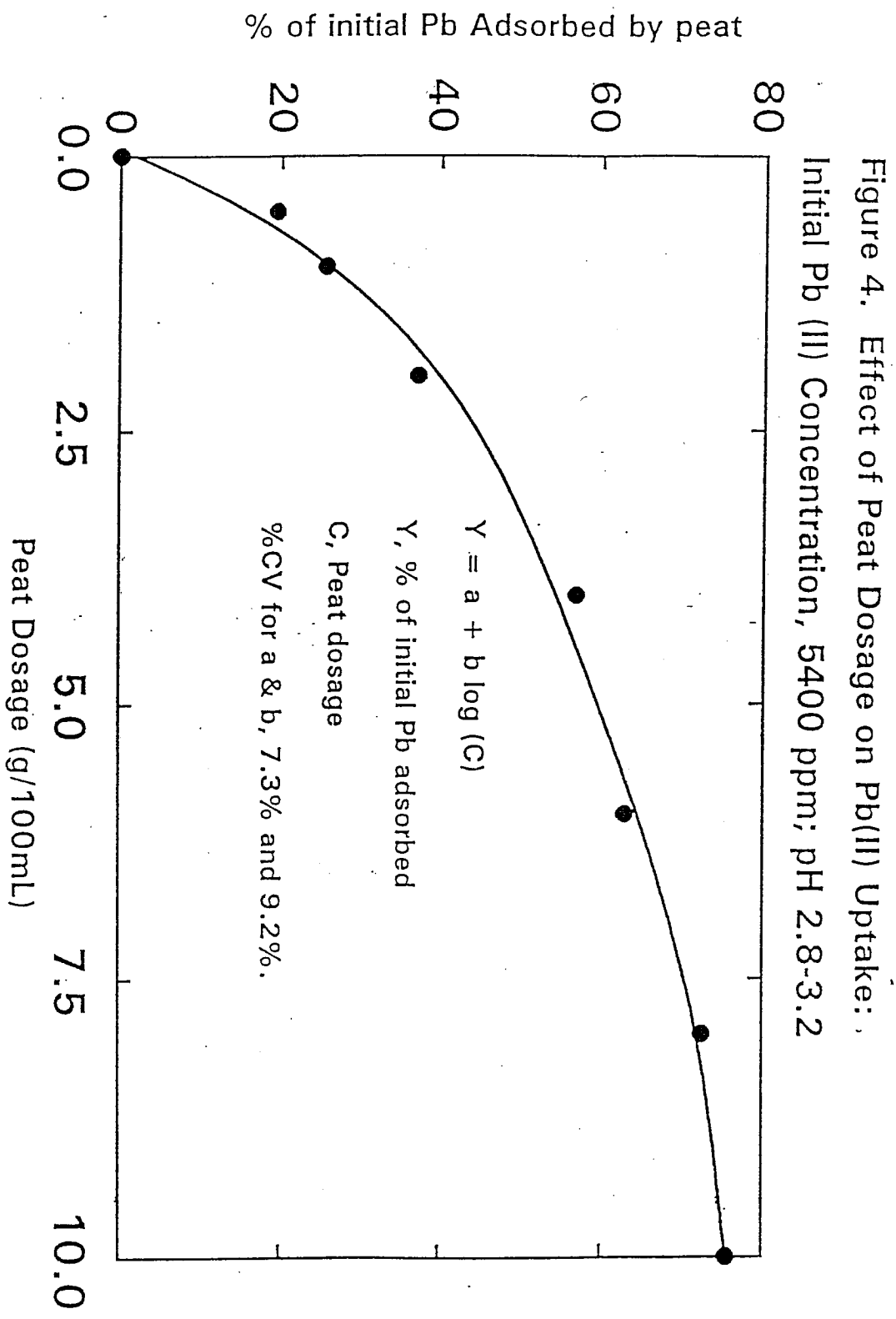


Figure 3. Pb Adsorption by Peat as a function of Initial Conc.





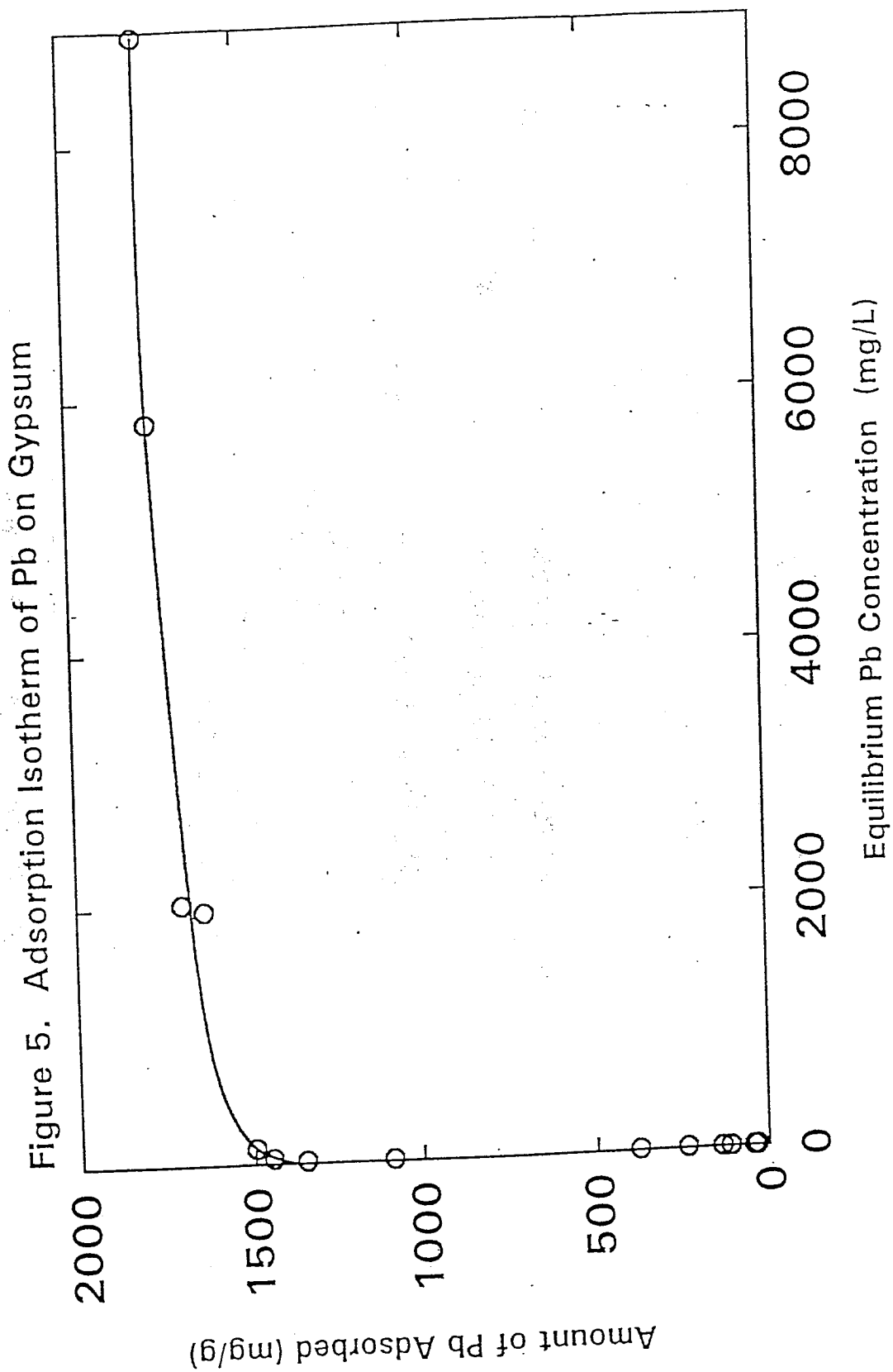


Figure 6. Efficiency of Pb Removal by Gypsum (pH 3-3.2).

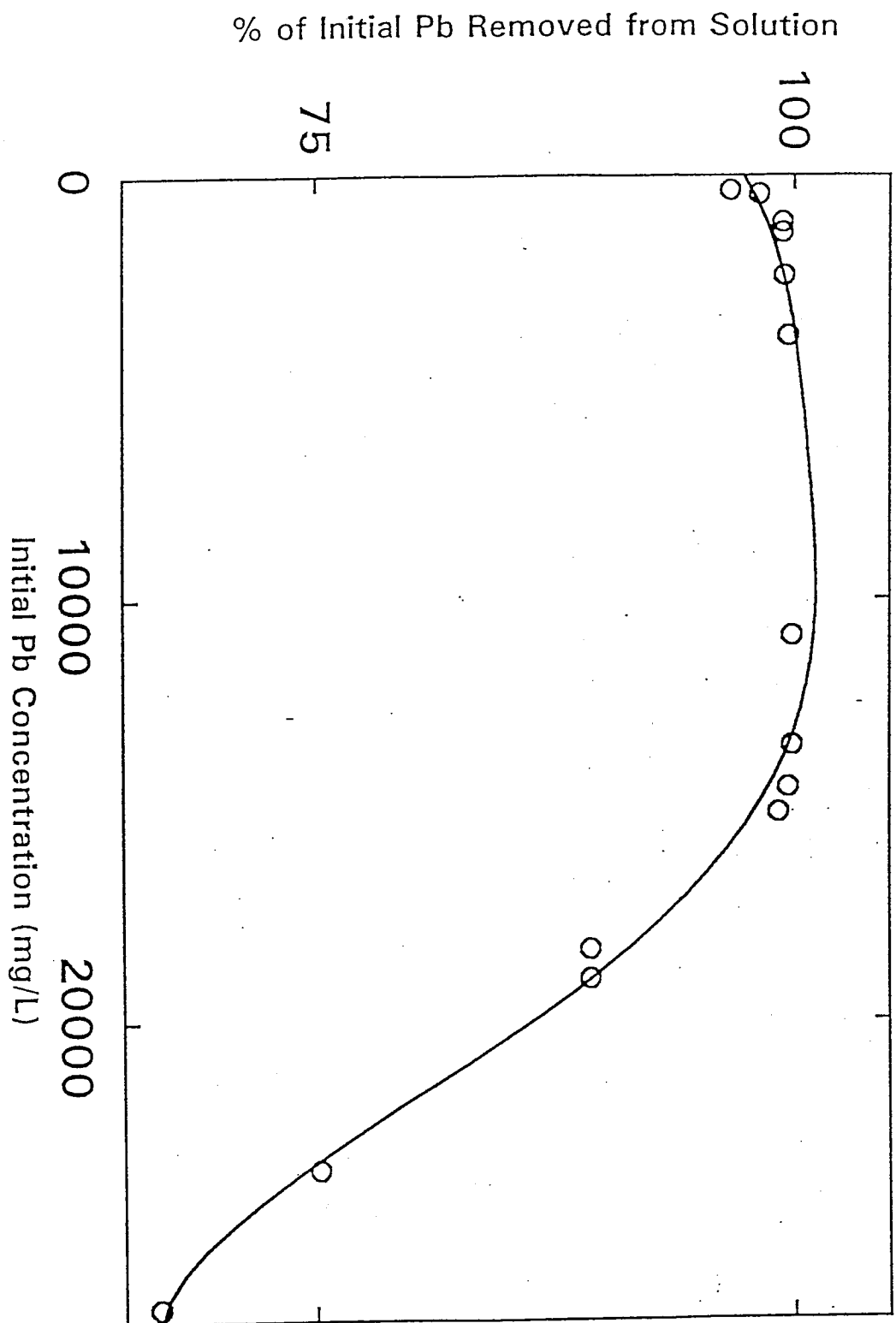
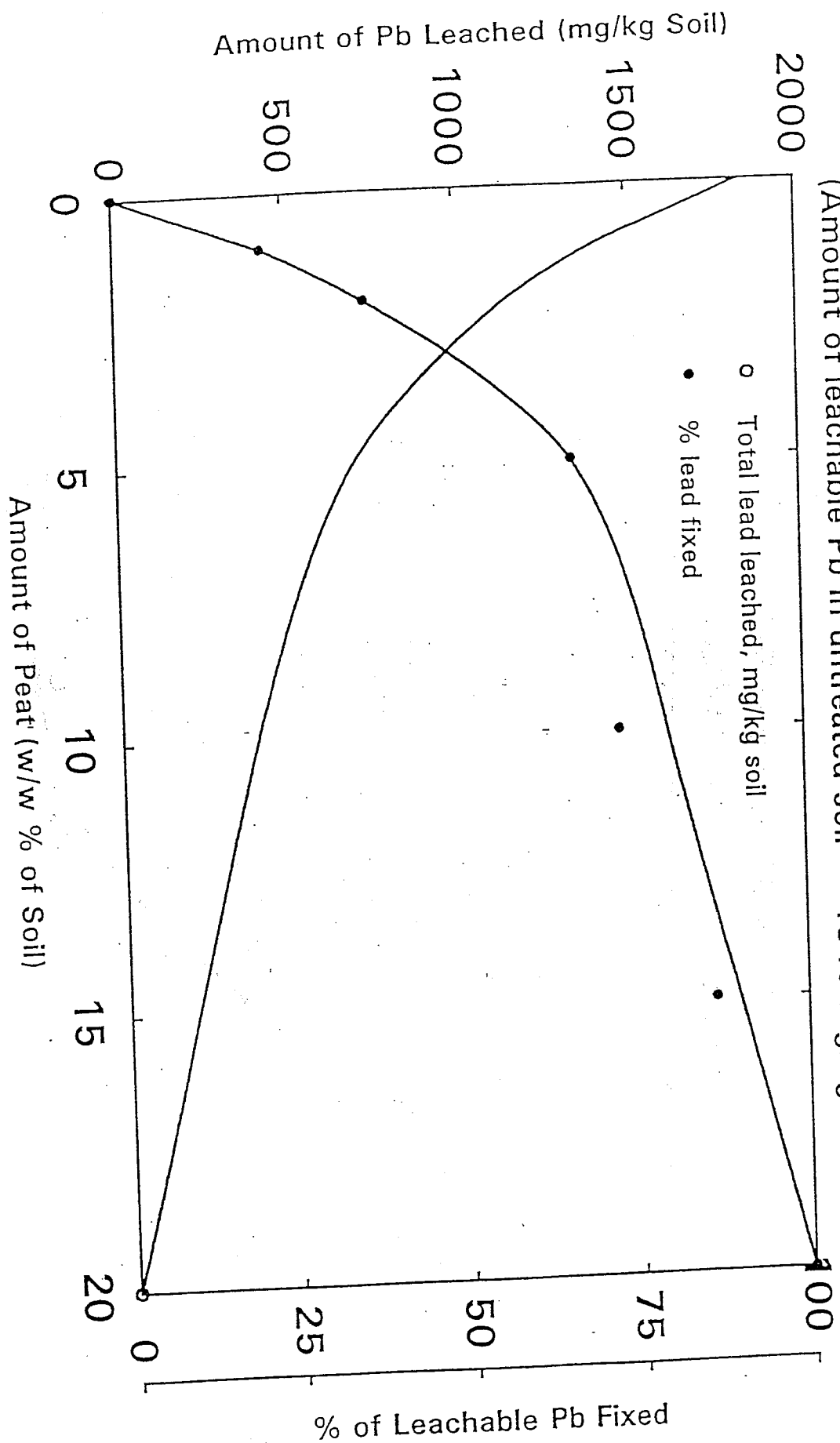


Figure 7. Fixation of Pb in Soil using Peat
 (Amount of leachable Pb in untreated soil = 1840 mg/kg soil) *



* Allowable EPA- limit for leachable Pb = 50 mg/kg soil

Figure 8. Effect of Peat Loading on Pb Fixation in Soil (pH 2.8-3.2)

