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

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Fixation of Lead in Contaminated Soils by Co-agglomeration with Metal Binding Agents*

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

Abstract

Adsorption of lead from an aqueous solution by both agricultural peat moss 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 for peat, compared with ~ 250 mg/L for soil. Calculation of the isotherm parameters showed the maximum lead adsorption to be 150 mg lead/g of peat. This compared with only 12.64 mg/g of lead 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 (Environmental Protection Agency, EPA, Toxicity Characteristic Leaching Procedure, 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%.

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In addition to peat, several other agents were tested for their suitability as fixing agents in heavy-metal contaminated soils. These included: gypsum, lime, autoshredder residue, fly ash, and a sample of oil sands fines. Liquid phase agglomeration was used to coagglomerate these materials with soil as a means to fix lead in artificially contaminated samples. The agglomeration process is advantageous in that it allows concurrent fixation of heavy metals and solvent extraction of organic contaminants. In terms of material handling and equipment, a combined process will be more economical than conventional methods requiring separate extraction and leaching steps.

Introduction

Although some micro-organisms are able to change the valence state of heavy metals, they are generally 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 groundwater, 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. These include diverse inputs such as the following: vehicle emissions, mining, smelting, metal plating or finishing operations, automobile battery production, land application of sewage sludge or industrial waste, the use of fertilizers and pesticides, and the settling of fly ash from incineration or combustion processes. Concentrations of heavy metals range from below detectable levels 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 wastes [1]. 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 USEPA 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 meet regulatory limits for

leachability [1]. Washing, to remove heavy metals as stable, soluble chelates, has only been successful with coarse soils [2–5]. Natural conditions, such as low pH or variable oxidation-reduction potential, tend to solubilize metals. Metal fixation minimizes migration of these contaminants into the groundwater through hydrolysis or desorption by exposure to varying conditions in the soil. Strongly adsorbing chemical additives distributed throughout the soil minimize the migration of soluble metals into the groundwater. Metals immobilized in this way present no adverse environmental or health hazards in their treated state [6]. However, the binding agents themselves 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 groundwater.

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 soils contaminated with organics. As an extension of this work, metal binding materials have been incorporated into the 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.

Materials

Soil

A sample of Erskine soil from Alberta was used for this study. Table 1 lists the typical properties and composition of 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 1:1 [7]. An artificially contaminated sample was prepared by spiking soil with a solution of lead nitrate. In a typical test, lead nitrate (about 1500 mg) was dissolved in distilled water (100 mL). This solution was placed in a glass Waring Blender jar with uncontaminated soil (500 g). The slurry was blended at about 5000 rpm and then allowed to air dry before being broken up using a porcelain mortar and pestle.

Table 1: Typical properties of Erskine soil.

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

Peat

A sample of agricultural peat moss was ground to a particle size of about $150 \mu\text{m}$ 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 carbon 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 elsewhere [8], was from the Suncor tailings pond. A sample of automobile shredder residue (ASR) was obtained courtesy of Dr. Mike Day of our institute. A reagent grade sample of calcium sulfate from Anachemia was used as a substitute for 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.

Methods

Agglomeration Procedure

A sample of artificially contaminated soil (100 g) was mixed with amounts of ground peat depending upon the desired soil:peat ratio. This mixture was

dispersed in 250 mL of Stoddard solvent (Esso Trademark Varsol 3135), by agitating at 250 rps in a Waring Blender 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 Blender jar; agitation was stopped every five 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 and Soil

For adsorption experiments, samples of peat or soil (1 g) were added to each of a series of lead nitrate solutions (100 mL) with concentrations ranging from 100 to 15,000 mg/L. The mixtures were sealed in polypropylene jars and agitated on a reciprocal shaker. Preliminary measurements showed no significant changes in lead adsorption after agitating for periods ranging from 5 min to 24 hours, as shown for peat in Table 2. However, agitation was always continued for 24 hours in order to ensure adsorption equilibrium concentrations. Batch adsorption experiments were run at $\text{pH } 3 \pm 0.2$. Adsorption was also studied at several other pH values. Glacial acetic acid, sodium hydroxide, and in some cases nitric acid, were used for pH adjustment. During agitation, pH was measured several times and readjusted, if necessary, to the desired values by additions of acid or alkali solutions which were continuously controlled.

Suspensions were filtered using 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 concentrations, 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 (1–10 g) were added to a known amount of solution in separate jars. The remainder of the procedure was similar to the one described above.

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

Leaching Tests

The TCLP extractions were performed according to the methods described in the US Federal Register [9] and specified in SW-846 [10].

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), which has a detection limit for lead of 3 mg/L. 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

Experimental data for lead adsorption have been plotted in Figures 1–3. Inspection of the sorption isotherm, shown on Figure 1, indicates an “H” type, according to the Giles classification [11]. The amount of lead sorbed reaches saturation when the equilibrium concentration exceeds 3000 mg/L. At this concentration all possible available sites are filled with lead. The H-

Table 3: Lead mass balance in solid samples.

Test #	Sample ID	Amount of Pb (w/w % of soil)			% of Total Pb fixed	% Recovery of Pb ^a
		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

^aBased on the amount of lead determined in solid samples before leaching.

Figure 1: Adsorption isotherm for lead on peat.

curves are indicative of the adsorption of ionic micelles on oppositely charged surface or of the 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 such cases, the solute's affinity for the sorbent is so high that it is completely adsorbed in dilute solutions. Therefore, the initial part of the isotherm is vertical. The H-curves usually contain a long plateau, the length of which indicates the difficulty of formation of a second adsorbed layer because of charge repulsion between adsorbed ions and those remaining in solution.

The adsorption of lead on soil before spiking (blank soil) was also studied. The data have been plotted in the inset shown on Figure 1. There was considerably less adsorption of lead on soil than on peat. 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

Figure 2: Lead adsorption by peat as a function of initial concentration.

Figure 3: Effect of peat dosage on Pb(II) uptake [initial Pb(II) concentration = 5400 ppm; pH 2.8–3.2].

describe the aqueous phase adsorptive behavior of clay and carbon materials [12, 13]. The model can be described by the equation:

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

where q_e is the amount of solute adsorbed per unit mass of adsorbent and C_e is the equilibrium adsorbate concentration. The parameters Q^0 and b were calculated after fitting the data to eq. 1. Q^0 represents the solid-phase concentration corresponding to the adsorption maxima, and b can tentatively be related to the intensity of the adsorption reaction at low surface coverage. Table 4 summarizes the calculated Langmuir isotherm parameters for both the lead-peat and the lead-soil systems. The values of Q^0 suggest that, even in concentrated systems, peat, with a Q^0 value of 150.4 mg/g, has a much higher capacity to adsorb lead than soil alone where Q^0 is 12.6 mg/g. Consequently, peat may be a good candidate for the fixation of lead in contaminated soils/sediments.

Figure 2, 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 eq. 2:

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

where Y represents percentage of 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 of coefficient of variance (%CV) of 4.9 and 7.1, respectively. This equation can be used to calculate the amount of peat required for the removal of lead to a desired level in solution.

Effect of Adsorbent Density

Figure 3 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 eq. 2, where C 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.

Table 4: Adsorption isotherm parameters.

Parameters	Soil Pb	Peat Pb
Q^0 (mg/g)	12.6	150.4 ± 7.2
b	0.0448	0.0015 ± 0.00025
r^2	0.97	0.86

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 was 230 mg of Pb per gram of peat. This increase in removal efficiency is due to the precipitation of lead (II) ions because of the higher number of negatively charged binding sites at pH 5.2 in the adsorption medium. The lowest adsorption efficiency occurred at pH 1.6 (15 mg/g), because of the higher solubility of lead at this pH. Between pH 2.5–4.5, Pb adsorption was relatively constant at 130–150 mg/g peat. These results are listed in Table 5.

Sorption Mechanism

Humic substances are the major constituents of peat [14]. Numerous investigations of the complexation of heavy metals by humic substances have shown that they have a high affinity for metal ions [15–17]. The inorganic content of peat is relatively low (2.3%) and generally contributes little to the overall cation exchange capacity [18]. 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 Wolf [19–21] who have demonstrated that the interaction between metal ions and peat is, indeed, an ion exchange process.

Fixation of Lead in Contaminated Soil

Peat as a Binder for Lead in Soil

It has been reported that humic matter can retard heavy-metal movement in soils even under acidic conditions [22]. The ability of peat to form sta-

Table 5: Effect of pH on the adsorption of lead on peat.

pH	Amount of Pb adsorbed at equilibrium (mg/g peat)
1.6	15
2.5	130
3.0	150 $\pm$ 7
4.5	145
5.2	230

ble metal complexes with heavy metals 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 of soil as leachable lead in the absence of any peat. The amount of lead fixed by peat has been plotted in Figure 4. The amount of lead leached at pH 2.9 (TCLP) decreased with increasing amounts of peat to the extent that 100% lead fixation was achieved at a peat loading of 20%.

Figure 5 shows the effect of peat loading on the fixation of lead in soil. The data can be fitted to eq. 2, where Y is the amount of lead fixed and C is the amount of peat in the soil. The equation can be solved to determine the amount of peat required to fix the desired level of leachable lead in soil. As Environment Canada regulations [23] allow a maximum of 1000 mg/kg of insoluble lead in treated soils, this method is restricted for the fixation of relatively low levels of lead. In such cases, less than 5 w/w % peat will be required to fix all of the leachable lead.

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

Figure 4: Fixation of lead in soil using peat [amount of leachable lead in untreated soil, 1840 mg/kg soil].

Figure 5: Effect of peat loading on lead fixation in soil.

* Numbers represent amount of leachable Pb

Figure 6: Comparative efficiencies of various binders for lead fixation (amount of binder, 5 w/w % of soil in each case).

plants and Auto shredder residue (ASR). The results are shown graphically in Figure 6. 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.

Conclusion

The adsorption reaction of lead on peat appears to be complete within 5 min. The adsorption isotherm 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 soil artificially contaminated with lead, suggest that peat is a very effective material for immobilizing lead in soils or sediments. For low concentrations of lead (< 1000 mg/kg) less than 5 w/w % of peat will be sufficient to completely immobilize lead in contaminated soils or sediments.

Removal of lead from aqueous solutions by peat, was most efficient at $\text{pH} > 5$ and least efficient at $\text{pH} < 2.5$. Between $\text{pH} 2.5$ – 4.4 , lead adsorption was relatively constant at 130–150 mg/g peat.

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

Acknowledgments

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Notation

ASR	Automobile Shredder Residue
%CV	Percent of coefficient of variance
EPA	Environmental Protection Agency
ICP	Inductively Coupled Plasma
TCLP	Toxicity Characteristic Leaching Procedure
C_e	Equilibrium adsorbate concentration
q_e	Amount of solute adsorbed per unit mass of adsorbent
Q^0	Solid phase concentration corresponding to adsorption maxima
r^2	Correlation coefficient for a linear fit

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