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Comparison of soluble and immobilized acetate for removing Pb from contaminated soil

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Abstract

Five lead (Pb) contaminated soils were used in a laboratory and modeling study to examine the effects of soluble and immobilized acetate on Pb removal from a contaminated soil as a function of pH. Soluble acetate was added as sodium acetate; immobilized acetate was added in the form of a cation exchange resin. For comparative purposes, Pb adsorption with no acetate also was measured as a function of pH. A surface complexation modeling framework was used to interpret experimental data. Experimental results showed the cation exchange resin was much more effective than soluble acetate in removing Pb from soils due to a strong affinity of the resin for Pb. In addition, concentrations of soluble Pb in resin/soil slurry were very low, minimizing the pollution threat if discharged. As deduced from modeling studies, soluble acetate performed poorly compared to the resin, in part, due to adsorption of the soluble $PbAc^+$ complex. The effectiveness of both soluble and immobilized acetate was diminished below pH 4 as a result of competition by H^+ for acetate. Modeling results based on resin affinity for Pb compare well with experimental data for resin/soil mixtures, suggesting that Pb partitioning in resin/soil mixtures may be predicted reasonably well if soil/Pb and resin/Pb partitioning are known. Thus, the modeling approach may be used as a screening tool to determine the performance of alternative resins.

Keywords: Soil remediation; Resin; Lead; Modeling

1. Introduction

One of the strategies available to remediate metal-contaminated soils is chemical extraction. Aqueous extraction agents may include mineral acids [1], complexing ligands [2],

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chelants [3–5], oxidizing and reducing agents [6,7], and surfactants [8]. The metal-containing liquid then is separated from the clean soil and either reused or treated to remove soluble metal ions prior to reuse or disposal.

For use with contaminated soils, mineral acids have been shown to be effective in metal removal, but the low pH that may be required for effective treatment is undesirable for reasons including nonselectivity, potential for destruction of the soil matrix, and high corrosivity to processing equipment [1]. Chelants have advantages in terms of their strong metal complexation ability and, for some chelants, a high selectivity for particular contaminant species. However, since reactivity in solution often is correlated with surface reactivity [9], complexing ligands and chelants would be expected to adsorb to mineral surfaces, a reaction that would diminish their effectiveness. For example, Evanko and Dzombak [10] studied the adsorption organic acids to goethite and showed that the sorption characteristics of most aromatic organic acids were typical for anionic sorbates, with higher sorption as pH decreases. Structural features of the organic acids important in their sorption behavior included the relative position of carboxylic and phenolic groups and overall acidity.

Another type of chemical extraction involves the use of ion exchange resins or other sorbents in a soil slurry (a process referred to as 'resin-in-pulp'). Ion exchange resins have been used in soil applications since the 1950s in a variety of ways [11,12]. For uranium recovery from ores, anion exchange resins have been used in a slurry to remove the uranyl-sulfate complex formed by addition of surfuric acid. Separation of the resin particles from the ore particles in the slurry is achieved by filtering, using screens with air agitation, sieving, or centrifugation [12,13]. After separation of the resin beads, uranium is eluted with concentrated chloride or nitrate solutions. Similar processes have been developed for extracting gold from ores. Anion exchange resins again are used due to the ease of extracting anionic complexes of gold. Gold can be leached from ores using cyanide to form the anionic complex of gold with cyanide called aurocyanide. Most of the anion exchange resins used for gold recovery have been strong base resins [14,15].

Applications of ion exchange resins to remediate contaminated soils and sludges also have been investigated. Sengupta and Sengupta [16] tested a composite membrane made of small resin beads (with iminodiacetate functional groups) enmeshed in a polytetrafluoroethylene membrane. Studies were conducted with the resin to examine uptake of Cu, Ni, and Pb from solution and from a synthesized sludge suspension. Results showed that resin effectiveness was not diminished by the presence of solids, high pH, or the presence of high concentrations of oxalate. Sengupta and Shi [17] have also reported the recovery of Al from drinking water sludges using a resin-based process.

A full-scale resin-in-pulp operation is used by Tallon Technology (Tallon Environnement, Inc., Montreal, Canada). Contaminated soil is excavated, washed, and separated by particle size through the use of vibrating sieves, rotary screens, and magnetic separators. The fine particles, where the contaminants are usually concentrated, are mixed with a polystyrene based chelating resin and water under acidic conditions to promote desorption of heavy metals from the soil particles. The metal-laden resin beads are separated by sieving and regenerated with the appropriate solvent.

The purpose of this study was to compare removal of Pb from several contaminated soils by soluble and immobilized acetate. A design-oriented surface complexation modeling framework is used to help interpret the experimental data. The results of the work add to the relatively limited literature on the use of resin-in-pulp applications for environmental remediation and provide insights to differences in performance between soluble and immobilized ligands.

2. Materials and methods

Five soils were used in the study. Soil 1, provided by the National Aeronautics and Space Administration (NASA), was from a shooting test range at Cleveland, Ohio. Due to the historical use of the site, the soil was heavily contaminated with Pb. In preliminary tests, the soil was found to be highly heterogeneous in Pb contamination, making representative sampling of the soil for the bench scale study difficult. Therefore, the soil was wet-sieved using a No. 40 mesh sieve. The sieved soil was air dried (~7–10 days) and then ground to pass a 14 mesh sieve. The purpose of grinding the soil was to produce a small particle size that could be separated from the ion exchange resin (see below). Soil 2 also was provided by NASA. This soil was used for a pilot scale soil washing demonstration program by NASA. The soil was pretreated on site for removal of the soil fraction larger than No. 18 mesh and was used as received for this study. Soil 3 is a Minoa sandy loam native to western New York that previously was used in a study by Reed et al. [18]. The soil was sieved with a No. 10 mesh (2 mm) sieve to screen out stones and large debris. This soil was spiked with Pb following the procedure described by Garland [19]. Soil 4 was provided by National Risk Management Research Laboratory (Edison, New Jersey). The soil was from a firing range and was contaminated with lead from munitions testing. The soil was used as received. Soil 5 was provided by the Northeast Hazardous Substance Research Center. The site characteristics where the sample was collected are unknown. The soil was contaminated with a high level of lead and also polyaromatic hydrocarbons. The soil was sieved using a No. 10 mesh to remove large stones and debris. All of the soils were dried and stored in sealed plastic storage bags at room temperature.

The resin used in the study was a high capacity ion exchange material consisting of polyvinyl alcohol (PVA), polyacrylic acid (PAA), and a crosslinking agent, such as formaldelyde or gluteraldehyde. The resin contains acetate functional groups and was developed and patented by the NASA Lewis Research Center [20]. The resin is water insoluble and is made in the acid form. The resin was converted to the calcium form following procedures recommended by the manufacturer. There are many physical forms of the resin including spherical beads, irregular granules, powder, thin films and fibers. The granular form (between 20 to 35 mesh) was used in this study. The cation exchange capacity of the granular form of the resin is reported as 3.5–4 meq/g.

Soil characterization tests were conducted for soil pH, cation exchange capacity, water content, total organic matter, TCLP for Pb, total Pb, and iron oxide content. The characteristics of the study soils are shown in Table 1.

Soil 'desorption' experiments were conducted in batch using 500 ml beakers. Soil was added to Nanopure water at a liquid-to-solid ratio of 20 to 1 (300 ml/15 g soil). The pH was controlled with pH/ORP controllers (Cole–Parmer Model 5652-10 or Jenco Model 3675). Soil suspensions were allowed to equilibrate for 72 h at constant pH (approximate pH range from 1 to 8) maintained by automatic addition of nitric acid or sodium

Table 1
Soil characterization data[a]

Parameter	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
Total Pb (mg/kg)	997	3091 ± 753 (3)	685.5	10137	75805 ± 4674 (4)
TCLP for Pb (mg/kg)	80.8 ± 6.9 (2)	484.8 ± 18.1 (3)		842.7 ± 190.9 (3)	9591 ± 179 (3)
pH	5.56 (1)	6.61 ± 0.27 (2)	5.55 (1)	7.22 ± 0.01 (2)	6.37 ± 0.09 (2)
CEC (meq/100 g)	21.79 ± 6.65 (2)	33.89 ± 5.05 (2)	6.37 ± 0.88 (2)	22.14 ± 1.23 (2)	7.45 ± 0.49 (3)
Water content (%)	2.92 ± 0.02 (2)	12.59 ± 0.13 (3)	0.17 ± 0.01 (2)	0.82 ± 0.01 (3)	0.72 ± 0.01 (3)
Total organic matter (%)	8.33 ± 3.93 (2)	3.53 ± 4.66 (2)	6.05 ± 4.79 (2)	4.25 ± 0.29 (2)	2.96 ± 0.73 (4)
Iron oxide (mg Fe/kg)	452 ± 68 (3)	748 ± 21 (3)	130 ± 11 (3)	775 ± 99 (3)	882 ± 115 (3)

[a] Values given represent mean ± standard deviation and number of replicates.

hydroxide. Mixing was provided by magnetic stirrer. In those experiments involving soluble acetate, sodium acetate was added at 0.3 or 1 M. At the end of each test, the final pH and conductivity was recorded and the soil suspension was filtered with 2.0 μm membrane filter (MSI Inc.). Pb in the filtrate was analyzed by flame atomic absorption spectrophotometry (AAS).

Resin/soil experiments were conducted for soils 1 and 2. Tests were conducted at fixed pH as described above and involved addition of the resin (3.6 g) to the soil slurry (15 g soil in 300 ml Nanopure water). After equilibration, separation of the soil and resin was performed by sieving the soil/resin slurry through a nylon mesh which retained the resin granules and allowed passage of the smaller size soil particles. The separated resin was first washed four times with the filtrate (using 2.2 μm filters) and then Pb was desorbed using 7% HNO_3 for 1 h at a ratio of 100 ml of acid per gram of resin. Pb in the aqueous phase and in the nitric acid extract from the resin was measured by AAS.

Experiments to determine partitioning between aqueous Pb and the resin were performed by adding 1.5 g resin in a 300 ml solution of $PbNO_3$ at 50 or 150 mg Pb/l. Experiments were conducted at pH 2–5 with an equilibration time of 3.5 h. Resin was separated from the liquid by sieving and then rinsed with Nanopure water. Pb in the aqueous phase then was measured by AAS.

3. Modeling approach

The modeling approach included equations for selected chemical species in the aqueous phase, resin phase, and sorbed to soils. Aqueous phase chemical speciation considered included Pb complexation with nitrate and acetate, and acetate acid/base chemistry. The relevant reactions and equilibrium constants are presented in Table 2.

Ion exchange equilibria was simulated as competitive reactions between Ca^{2+}, Pb^{2+} and H^+ using the convention of Gaines and Thomas [21] where resin-bound species are expressed as equivalent fractions. The reactions for ion exchange sites (X^-) are as follows

$$CaX_2 + 2H^+ = Ca^{2+} + 2HX \qquad K_{X_1} \tag{1}$$

$$CaX_2 + Pb^{2+} = Ca^{2+} + PbX_2 \qquad K_{X_2} \tag{2}$$

Table 2
Aqueous phase reactions included in the model (log K values from [27])

Reaction	log K
$HAc = H^+ + Ac^-$	−4.76
$Pb^{2+} + Ac^- = PbAc^+$	2.87
$Pb^{2+} + 2Ac^- = PbAc_2$	4.08
$Pb^{2+} + 3Ac^- = PbAc_3{}^-$	3.59
$Pb^{2+} + 4Ac^- = PbAc_4{}^{2-}$	3.40
$Pb^{2+} + NO_3{}^- = PbNO_3{}^+$	1.17
$H_2O = H^+ + OH^-$	−14

with equilibrium constants

$$K_{X_1} = \frac{\{Ca^{2+}\}\, y_{HX}^2}{\{H^+\}^2\, y_{CaX_2}} \tag{3}$$

and

$$K_{X_2} = \frac{\{Ca^{2+}\}\, y_{PbX_2}}{\{Pb^{2+}\}^2\, y_{CaX_2}} \tag{4}$$

where y_i are the equivalent fraction of species i. The equivalent fractions are defined as

$$Y_{PbX_2} = \frac{2[PbX_2]}{CEC}, \qquad y_{CaX_2} = \frac{2[CaX_2]}{CEC}, \qquad Y_{HX} = \frac{HX}{CEC} \tag{5}$$

where CEC is the total cation exchange capacity with CEC $= 2[PbX_2] + 2[CaX_2] + [HX]$. In Eqs. (3)–(5) and elsewhere, { } deote activities and [ ] indicate molar concentrations. Activity coefficients were calculated using the Davies equation. The equilibrium constants K_{X_1} and K_{X_2} were used as fitting parameters.

Soil phase reactions were simulated using the variable reactivity modeling approach as reported by Ganguly et al. [22] and Ganguly and Van Benschoten [23]. In the model, proton and metal binding reactions to heterogeneous surfaces are conceptualized as reactions with a single, composite 'site', with empirical correction factors to the equilibrium constants that are represented as simple power functions of hydrogen ion concentration, metal-to-site concentration ratio (M_T/S_T), and ionic strength (I). That is, the observed metal-binding equilibrium constant, $K_{Me,app}$, is represented as $K_{Me,\,app} = K_{Me}\{H^+\}^{\alpha}(M_T/S_T)^{\beta} I^{\phi}$. The observed proton-binding equilibrium constant is represented with a single correction that is a power function of hydrogen ion concentration. In an application of the model to metal and proton binding to humic substances [22], titration data were used to determine total site density and acid/base model parameters while isotherm and pH sorption edge data were used to adjust metal binding parameters. For contaminated soils, titration of the pristine soil is not possible. So it is difficult to unambiguously estimate surface site concentration. This is relatively unimportant, however, when desorption studies are conducted since there is no need to estimate the total capacity of the sorbent. In this work, total site density was arbitrarily set at 1.5 Pb_T and the acid/base chemistry part of the model was omitted. Another simplification is that for contaminated soils M_T/S_T is constant and so this correction factor (and estimation of model parameter β) is unnecessary. The form of the model used in this work to describe metal binding was

$$SOH + Pb^{2+} = SOPb^+ + H^+ \tag{6}$$

where SOH is a protonated surface site. The apparent equilibrium constant for this reaction ($K_{Pb,app}$) is given as

$$K_{SOPb,app} = K_{SOPb}\{H^+\}^{\alpha_1} I^{\Phi} = \frac{[SOPb^+]\{H^+\}}{[SOH]\{Pb^{2+}\}} \tag{7}$$

K_{SOPb} and α_1 are fitting parameters and $\Phi = 0.5$ assuming surface reactions exhibit the same functional dependence on ionic strength as do solution phase reactions

[22]. Adsorption of the $PbAc^+$ species was also hypothesized to occur according to the reaction

$$\mathrm{SOH} + \mathrm{PbAc}^+ = \mathrm{SO\,PbAc} + \mathrm{H}^+ \tag{8}$$

with the apparent equilibrium constant

$$K_{\mathrm{SOPbAc,app}} = K_{\mathrm{SOPbAc}} \left\{\mathrm{H}^+\right\}^{\alpha_2} I^{\Phi} = \frac{[\mathrm{SOPbAc}]\left\{\mathrm{H}^+\right\}}{[\mathrm{SOH}]\left\{\mathrm{PbAc}^+\right\}} \tag{9}$$

In applying the model to data sets with acetate present, K_{SOPbAc} and α_2 were used as fitting parameters.

The equation set was completed by writing the following mass balance equations

$$\begin{aligned}\mathrm{Pb}_T &= \mathrm{Pb}^{2+} + \mathrm{PbAc}^+ + \mathrm{PbAc}_2 + \mathrm{PbAc}_3{}^- + \mathrm{PbAc}_4{}^{2-} + \mathrm{PbNO}_3{}^+ + \mathrm{X}_2\mathrm{Pb} \\ &\quad + \mathrm{SOPb}^+ + \mathrm{SOPbAc}\end{aligned} \tag{10}$$

$$\mathrm{Ac}_T = \mathrm{HAc} + \mathrm{Ac}^- + \mathrm{PbAc}^+ + 2\mathrm{PbAc}_2 + 3\mathrm{PbAc}_3{}^- + 4\mathrm{PbAc}_4{}^{2-} + \mathrm{SOPbAc} \tag{11}$$

$$\mathrm{Ca}_T = \mathrm{Ca}^{2+} + \mathrm{CaX}_2 \tag{12}$$

$$\mathrm{X}_T = 2\mathrm{PbX}_2 + 2\mathrm{CaX}_2 + \mathrm{HX} \tag{13}$$

$$\mathrm{S}_T = \mathrm{SOH} + \mathrm{SOPb}^+ + \mathrm{SOPbAc} \tag{14}$$

As described elsewhere [22,23], the model was implemented on a standard spreadsheet (EXCEL) and model parameters were determined by minimizing the error sum of squares (SSE) between fitted and experimental data for the sorbed species. Model parameter estimates were made in the following steps: (1) experimental data for Pb sorption as a function of pH (without acetate present) were used to fit the model parameters K_{SOPb} and α_1. (2) Experimental data for Pb sorption in the presence of acetate were used to fit model parameters K_{SOPbAc} and α_2. (3) Experimental data for Pb binding to the ion exchange resin (for experiments without soils) were used to estimate the parameter K_{X_1} and K_{X_2}. Thus, no more than two parameters were fitted simultaneously to a given experimental data set. Performance of the soil/resin mixtures was predicted based on these independent estimates of model parameters. Acceptable predictions would imply that resin performance may be predicted if soil/Pb and resin/Pb partitioning are known without performing actual resin/soil experiments.

The implementation of the modeling approach on a standard spreadsheet is a matter of convenience. Users may choose to implement the approach using other computational frameworks including standard chemical equilibrium models. All aqueous phase reactions are based on standard mass action laws, and standard ion exchange conventions sometimes are included in such models. The sorption reactions used in this work (e.g. Eqs. (7) and (9)) are semi-empirical expressions that attempt to capture effects of electrostatic interactions and heterogeneity. While fundamental surface complexation models exist and constants have been determined for some pure minerals of environmental significance (e.g. hydrous ferric oxide), these models often do not work very well for simulating metal binding to field soils. As a result, semi-empirical models including the approach used in this work or affinity distribution models [24] often are used. While these models are capable of simulating heterogeneous sorption phenomena, they must be calibrated to experimental data.

4. Results and discussion

Pb adsorption to the ion exchange resin as a function of pH at two Pb_T levels is shown in Fig. 1. When soluble Pb is expressed as a percentage of Pb_T, the experimental data (symbols) at two Pb_T levels are virtually identical and are well described by the competitive ion exchange model (solid line). Fitted values for the ion exchange constants were $\log K_{X_1} = 5.93$ and $\log K_{X_2} = 2.05$. The total CEC was set at 3.5 meq/g.

Soil Pb desorption experimental data (symbols) and modeling results (lines) are shown in Figs. 2–6. Fitted model parameter values are shown in Table 3. Also shown in Table 3

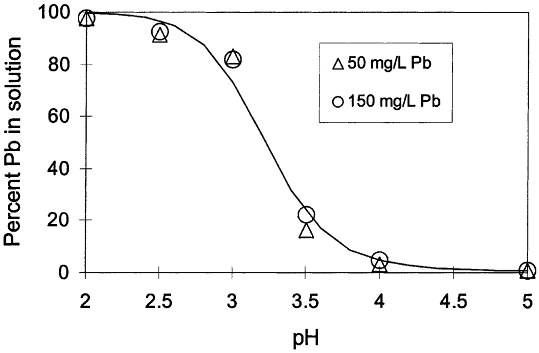

Fig. 1. Experimental data (symbols) and model simulations (lines) for Pb removal from aqueous solution by ion exchange resin.

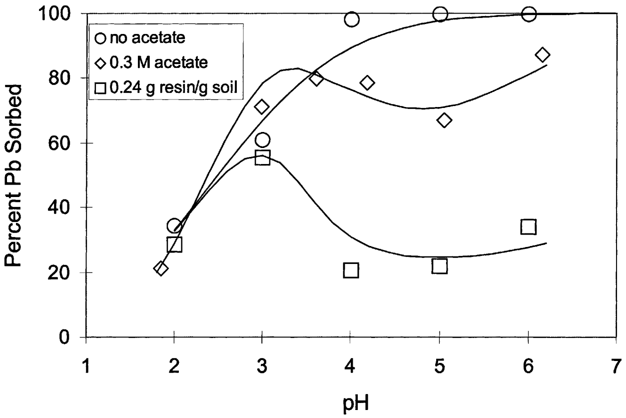

Fig. 2. Experimental data (symbols) and model simulations (lines) for Pb removal from soil 1.

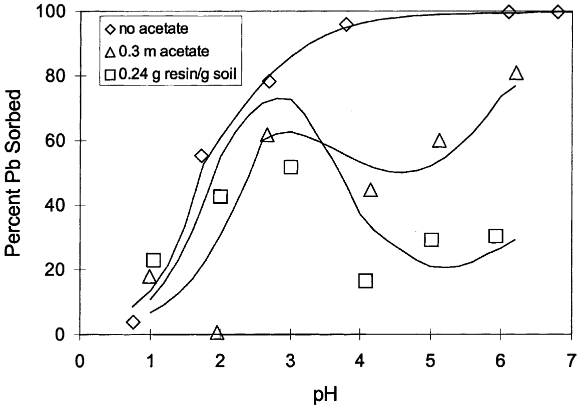

Fig. 3. Experimental data (symbols) and model simulations (lines) for Pb removal from soil 2.

are apparent equilibrium constants at pH 4 and $I = 0.01$ which are presented to facilitate comparisons between soils. As expected, Pb sorption decreased as pH decreased as a result of competition of protons for surface sites and/or dissolution of Pb precipitates. Soluble acetate was somewhat effective in removing Pb at pH 4–6, but was ineffective at more acidic pH. Immobilized acetate groups on the ion exchange resin were much more effective than soluble acetate in removing Pb at higher pH, but were also ineffective at low pH.

Model results for no acetate and with soluble acetate show good agreement with experimental data. It should be noted that Pb sorption in the presence of acetate could not be simulated correctly without considering adsorption of the PbAc complex (see Eq. (8)).

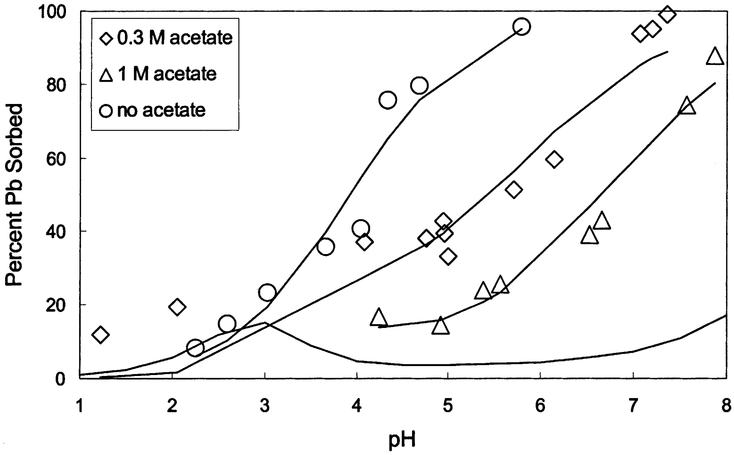

Fig. 4. Experimental data (symbols) and model simulations (lines) for Pb removal from soil 3. Solid line with no symbols is predictions of removal for 0.24 g resin/g soil.

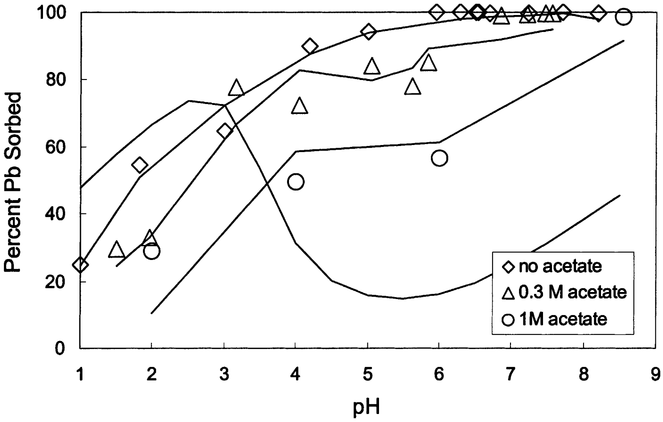

Fig. 5. Experimental data (symbols) and model simulations (lines) for Pb removal from soil 4. Solid line with no symbols is predictions of removal for 0.24 g resin/g soil.

Model predictions for the results for soil/resin experimental data (soils 1 and 2) are reasonably good. Note that the same ion exchange equilibrium constants were used for all model simulations involving the resin. Model predictions for the effects of the cation exchange resin for soils 3–5 are included although resin experiments for these soils were not conducted.

Fitted constants for adsorption of Pb^{2+} or $PbAc^{+}$ (Eqs. (6) and (8)) at pH 4 and $I = 0.01$ (Table 3) are ordered approximately inversely with Pb_T and are linearly correlated with organic matter content. Poor correlations exist between fitted constants and CEC and or iron oxide content. An inverse relationship of fitted constants with Pb_T is expected for

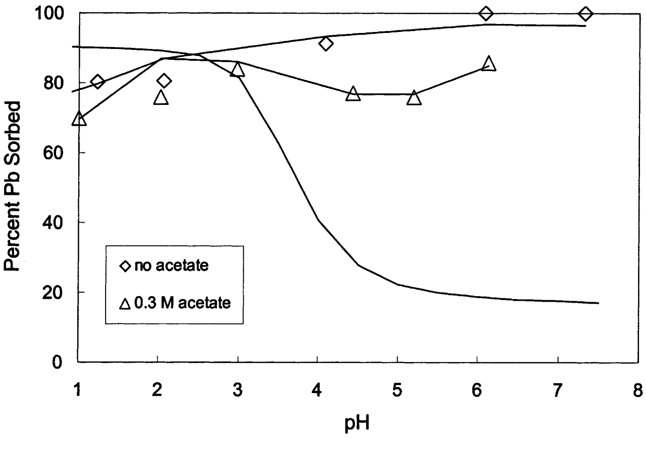

Fig. 6. Experimental data (symbols) and model simulations (lines) for Pb removal from soil 5. Solid line with no symbols is predictions of removal for 0.24 g resin/g soil.

Table 3
Fitted model parameter values for soil desorption experiments

Soil	$\log K_{\mathrm{SOPb}}$ ($\mathrm{M_2}^{0.5-\alpha}$)	α_1	$\log K_{\mathrm{SOPb,app}}$ (pH = 4, I = 0.01)	$\log K_{\mathrm{SOPbAc}}$ ($\mathrm{M_2}^{0.5-\alpha}$)	α_2	$\log K_{\mathrm{SOPbAc,app}}$ (pH = 4, I = 0.01)
1	1.78	0.241	1.81	1.86	0.530	0.745
2	2.16	0.487	1.21	0.985	0.539	−0.173
3	0.769	0.201	0.963	1.08	0.402	0.477
4	2.05	0.567	0.781	2.17	0.651	0.569
5	2.89	1.05	−0.309	0.476	0.583	−0.856

a heterogeneous sorbent since at higher metal loadings progressively weaker sites would be involved in metal binding. Since organic coatings would be expected to bind metals, it also seems reasonable that higher organic content would result in higher apparent binding constants. The poor and approximately inverse correlation with iron oxide content was unexpected since iron oxides are known to have a high affinity for metal ions [25]. However, in this study, all soils except soil 1 had higher Pb levels than Fe on a mol/kg basis, suggesting that for heavily contaminated soils binding mechanisms other than iron oxide sorption must be operative. In the final analysis, the complexity of field soils may be such that the use of simple parameters as indicators of metal binding are simply not informative and that actual leaching data coupled with models provide more insight to soil sorption behavior.

Leaching data (e.g. Figs. 2 and 3) show superior performance for the resin compared to soluble acetate. Because of differences in experimental conditions, however, direct comparisons are best made by model simulations under identical conditions. Shown in Fig. 7 are separate model simulations (solid lines) for soil 1 with soluble acetate or resin sites at a concentration of 0.1 M and at constant ionic strength of 0.1 M. For comparative purposes, Pb sorption as a function of pH with no acetate or resin present also is shown. Also shown

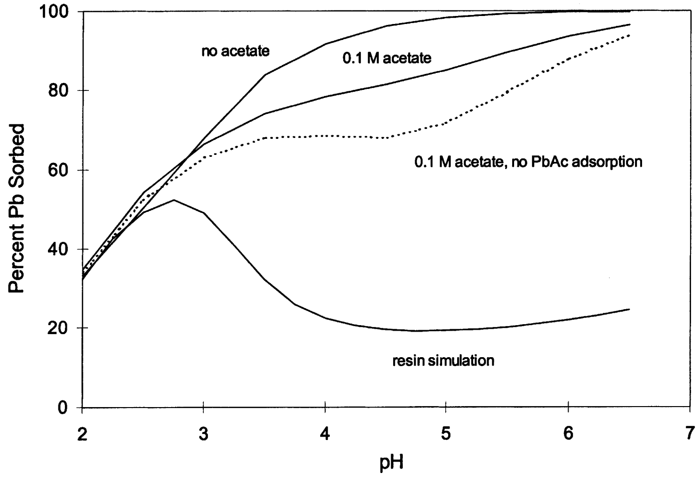

Fig. 7. Model prediction for Pb removal from soil 1 at eqimolar acetate and resin concentrations.

are simulation results (dotted line) for 0.1 M acetate but with no adsorption of the $PbAc^+$ species. It is clear that immobilized acetate in the resin is far superior to soluble acetate, even if adsorption of the $PbAc^+$ species is not considered.

While the results of this study clearly show the ability of the resin to remove Pb from contaminated soils, it also is of interest to use the model to explore how strong a complexing ligand would be required for effective Pb removal. Again using the calibrated model parameters for soil 1 and assuming only 1:1 complexes and also that complexed Pb does not adsorb, $\log K$ values for complexed Pb were varied and Pb sorption to the soil predicted using the model (Fig. 8). For this contaminated soil, $\log K$ values on the order of 4–5 would be required to remove Pb from the soil to a comparable degree achieved by the resin. Under this type of remediation strategy, nearly all the Pb would be in a soluble form and treatment of this waste stream may be difficult. If the resin used in this work were used in an attempt to treat an aqueous waste stream where Pb was complexed with a ligand of $\log K = 5$, model simulations show adsorption of the Pb to the resin would be minimal (no more than about 15%). This highlights the potential difficulty of waste stream treatment when using strong complexing ligands for soil remediation.

In terms of waste stream treatment, a desirable attribute of using an immobilized ligand is that aqueous phase metal concentrations are kept to a minimum. For example, based on the resin simulation shown in Fig. 2 at pH 5, the aqueous phase Pb concentration is predicted to be only about 0.3 uM (67 ug/l). If the same amount of Pb could be removed from the soil without using the resin, the aqueous phase concentration would be about 0.2 mm (40 mg/l). Thus, problems associated with treatment or disposal of a contaminated liquid waste are minimized with use of the resin.

For practical application, a key aspect of resin use in soil remediation is the successful recovery of resin from the soil/resin slurry. In this study, resin and soil particle size was controlled so separation by seiving could be used. In a parallel study [26], resins were held in a special cell with mesh covers to allow circulation of water but keep separate the soil

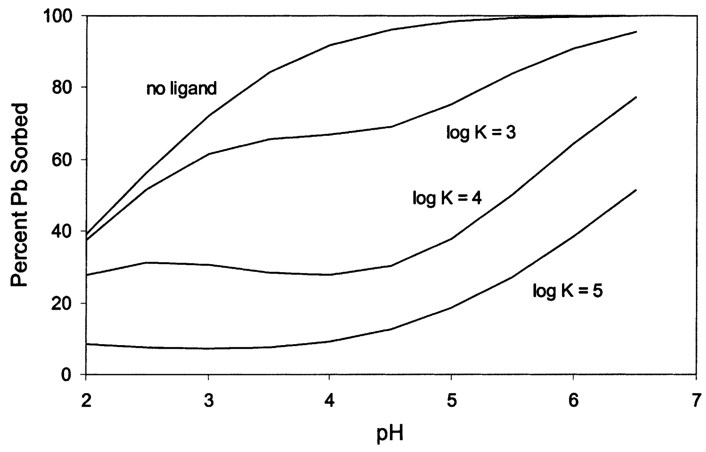

Fig. 8. Model predictions of effect of $\log K$ formation constant for Pb-ligand complex on Pb removal for soil 1.

particles and resin. It was found that performance was inhibited significantly when the resin was held in the cell compared to being mixed in the soil slurry. Although the cause of differences was not established, hypotheses related to insufficient mixing or clogging were not supported by the data. While additional work is needed to understand the reasons for performance differences, this work clearly showed that mixing the resins with soil slurry was needed for good performance.

At the field scale, the resin-in-pulp approach has been used, but simpler and less labor intensive recovery methods would be advantageous. Development of resins that were slightly buoyant may be desirable so that after reaction of a mixed soil/resin slurry the soil could be allowed to settle and the resin float to the surface under quiescent conditions. Alternatively, resin imbedded in a continuous membrane has been proposed [16].

5. Conclusions

This experimental and modeling study has compared the relative effectiveness of soluble and immobilized acetate for removal of Pb from field soils. It is shown that when mixed in the soil slurry, the cation exchange resin was much more effective in removing Pb from two contaminated soils than soluble acetate. An additional significant benefit of using resin in a soil slurry is that aqueous phase Pb concentrations are very low.

Modeling predictions of the resin/soil slurry were based on independent experiments of Pb partitioning to the soil (in the absence of the resin) and to the resin (in the absence of soil) were in good agreement with experimental data, suggesting that performance prediction of alternative resins may be possible if the resin affinity for aqueous phase metal species is known. Through model simulations, it is shown that the poor performance of soluble acetate compared to the resin is due, in part, to adsorption of complexed Pb, but more importantly that the resin has a very strong affinity for Pb (formation constant $\log K$ from 4 to 5 needed for complexing ligand to match resin performance).

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