Characterization of aqueous lead removal by phosphatic clay:
Equilibrium and kinetic studies

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Abstract

Immobilization of heavy metals from contaminated environments is an emerging field of interest from both resource conservation and environmental remediation points of view. This study investigated the feasibility of using phosphatic clay, a waste by-product of the phosphate mining industry, as an effective sorbent for Pb from aqueous effluents. The major parameters controlling aqueous Pb removal, viz. initial metal ion concentrations, solution pH, sorbent amounts, ionic strength and presence of both inorganic and organic ligands were evaluated using batch experiments. Results demonstrated that aqueous Pb removal efficiency of phosphatic clay is controlled mainly by dissolution of phosphatic clay associated fluoroapatite \([\text{Ca}_{10}(\text{PO}_4)_{6}\text{CaCO}_3(\text{F,Cl,OH})_2]\), followed by subsequent precipitation of geochemically stable pyromorphite \([\text{Pb}_{10}(\text{PO}_4)_{6}(\text{F,Cl,OH})_2]\), which was confirmed by both X-ray diffraction (XRD) and scanning electron microscopic (SEM) analysis. Lead removal efficiency of phosphatic clay increased with increasing pH, sorbent amount and decreasing ionic strength. It also depends on the nature of complexing ligands. Formation of insoluble calcium oxalate and lead oxalate in the presence of oxalic acid explained high uptake of Pb by phosphatic clay from aqueous solution. However, Pb sorption kinetics onto phosphatic clay were biphasic, with initially fast reactions followed by slow and continuous Pb removal reactions. The slow reactions may include surface sorption, co-precipitation and diffusion. The exceptional capability of phosphatic clay to remove aqueous Pb demonstrated its potential as a cost effective way to remediate Pb-contaminated water, soils and sediments.

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1. Introduction

Recently, more research efforts have been focused on the beneficial utilization of industrial waste by-products as a cost effective sorbent material in order to minimize their processing cost and solve their disposal problems in an environmentally sustainable way. Phosphatic clay is a major waste by-product of phosphate strip mining, particularly in Florida, USA. Normally, for each tonnes of phosphate produced, 1 tonne each of sand and phosphatic clay is also produced. Phosphatic clay has a characteristically high content of natural apatite (~24–32% of dry weight), which is too fine-grained to recover during processing. In addition to apatite, phosphatic clay consists of aluminosilicate minerals, smectite, kaolinite, illite, attapulgite and palygorskite with lesser amount of several other minerals [1,2]. The favorable phosphatic clay characteristics such as neutral pH, high cation exchange capacity (CEC), presence of natural apatite and smectite suggests that it could be a cost effective sorbent for the removal of aqueous heavy metals from contaminated water as well as for in situ stabilization of heavy metal contaminated soils and sediments [3,6]. Application of phosphatic clay could also have the secondary benefits of improving soil fertility, soil structure and moisture-holding capacity particularly when added to sandy soils [7].

Lead contamination has been identified as a worldwide problem due to its long-term and widespread use. Lead enters the environment as a result of both natural process and anthropogenic activities. Natural processes include pedogenic mineral breakdown and translocation of products, as well as sedimentation from dust storms, volcanic eruptions and forest fires. Anthropogenic activities of lead contamination include mining and smelting operations, battery recycling, combustion of leaded gasoline, salvage yards, urban and industrial wastes, continuous use of fertilizers, pesticides and use of Pb bullets [8–10].
In situ reduction in Pb bioavailability is a promising remediation approach that has the potential to remove metals from solutions and/or stabilize these metals in contaminated soils and sediments [3]. However, converting Pb to a less bioavailable form is not always straightforward. Some forms of Pb that are sparingly soluble in the existing soil environment can be highly soluble after ingestion. For example, cerussite (PbCO₃) has been identified as a major Pb mineral phase in many contaminated soils, particularly from battery recycling sites [11,12]. Lime had been applied to a number of sites to neutralize soil acidity resulting from co-disposal of acidic solutions along with battery debris, which promoted the formation of carbonate containing Pb compounds such as cerussite and hydro-cerussite Pb₅(CO₃)₂(OH)₂. Effective in situ Pb immobilization using phosphorous amendments requires enhanced solubility of these existing Pb minerals by inducing acidic conditions to promote pyromorphite formation, in which Pb is much more strongly bound and less bioavailable compared to cerussite [13]. However, these acidic conditions may further enhance the mobility of other heavy metals such as Cd, Cu, Ni and Zn that are present in contaminated soils and may increase the risk of their leaching to the groundwater.

In natural environments, sorbents are complex mixtures of a variety of minerals, which compete for the uptake of metals. The effects of various factors such as pH, ionic strength and nature of ligands influencing Pb sorption have been studied using both pure minerals such as goethite [9,14], silicate clay minerals [15–19] and soils [20,21]. In the past, several studies explored the feasibility of using apatite as a potential reactive media to remediate heavy metal contaminated soils, sediments, mining wastes and contaminated surface and groundwater [4–6]. However, Pb sorption onto phosphatic clay is a more complex process compared to other minerals. In case of phosphatic clay, precipitation and surface sorption reactions may occur simultaneously due to presence of both apatite and clay minerals [22].

Metal sorption depends on pH because of resulting changes in metal species and surface charge of adsorbing media. Mineral surfaces become more negatively charged with increasing pH and surface groups that have lost protons may be able to sorb cations more readily (and anions less readily) from solutions. Generally, studies related to the effects of ionic strength on Pb sorption were largely limited to pure mineral systems. In such systems, the decrease in Pb sorption with increasing ionic strength is attributed to competition between Pb and other cations for available sorption sites in the background electrolyte solution. Different concentrations of natural and synthetic ligands are present in soils, sediments and aquatic systems. The most common inorganic ligands found in soils and sediments are Cl⁻, PO₄³⁻, OH⁻, NO₃⁻, CO₃²⁻ and SO₄²⁻ [23]. On the other hand, simple aliphatic organic acids with one or three carboxyl group such as oxalic acid and citric acid occur frequently in soil and subsurface environment from biological activities [24,25]. They alter chemical process in soils through complexation reaction with metal ions in soil solution and ligand exchange reaction at soil surfaces. It becomes very important to take it into account for developing a suitable remediation strategy.

Some naturally occurring clay minerals may serve as cost effective sorbents for the removal of heavy metals, metalloids and radionuclides from contaminated water. Although, their observed sorption capacity is relatively low compared to the synthetic sorbents, still these materials may provide an inexpensive substitute for the treatment of contaminated industrial, mine surface water and groundwater. The exceptional characteristics of phosphatic clay suggest its beneficial utilization as a cost effective reactive media for immobilizing Pb and several other heavy metals (e.g. Cd, Ni, Zn and U) from contaminated surface water and groundwater using permeable reactive barrier. The main objectives of this investigation were to compare quantitatively the effects of concentrations, pH, ionic strength and inorganic and organic ligands on the aqueous Pb removal efficiency of phosphatic clay as well as to investigate in detail its Pb removal kinetics.

2. Materials and methods

2.1. Phosphatic clay and reagents

The phosphatic clay used in this study was obtained from PCS Phosphate Mining Company, White Springs, FL, USA. Sample preparation included air-drying, crushing by mortar and pestle, and pass through a 60-mesh sieve. Sample characterization included surface area measurement, mineralogical analysis and total elemental analysis. The measured surface area of the phosphatic clay was 33.65 ± 1.19 m²/g determined by single point Brunauer, Emmett and Teller (BET) N₂ sorption procedure. Selected element concentrations of the phosphatic clay sample are shown in Table 1. Phosphatic clay mineralogy was determined both prior to and after various aqueous metal/ligand-treatments using X-ray diffraction (XRD) in conjunction with standard cation-saturation procedures for identification of expandable phyllosilicates [26]. X-ray diffraction analyses were conducted on a computer-controlled X-ray diffractometer equipped with stepping motor and graphite crystal monochromator. Scans were conducted from 2 to 60° at a rate of 2° θ per minute. Particle morphology of phosphatic clay was assessed by scanning electron microscopy (SEM) and elemental spectra for individual particles were obtained using energy-dispersive X-ray spectroscopy (EDS) during SEM observations.

Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage by weight (DW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>47.5 ± 2.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.3 ± 0.8</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.54 ± 0.5</td>
</tr>
<tr>
<td>MgO</td>
<td>1.59 ± 0.2</td>
</tr>
<tr>
<td>CaO</td>
<td>18.0 ± 2.3</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>12.0 ± 1.1</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>5.3 ± 0.6</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>28.8 ± 1.9</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>84.0 ± 3.2</td>
</tr>
</tbody>
</table>

*Trace metal concentration (mg kg⁻¹).*
Deionized water from a Barnstead Nano-Pure system was used in rinsing and preparation of samples. Labware used for each experiment was cleaned in phosphate free detergent first, then acid-washed, and finally rinsed with deionized water. Lead stock solution of 5180 mg L\(^{-1}\) (25 mM) was prepared from its nitrate salt. All chemicals used were analytical reagent grade. In this study, both kinetic and sorption experiments were conducted at room temperature and under aerobic conditions.

2.2. Kinetics experiment

In order to gain insight into the overall Pb removal behavior of phosphatic clay, kinetic experiments were conducted using batch tests. A total of 0.5 g phosphatic clay powder was weighed into 250 mL polycarbonate bottles and pre-equilibrated with 150 mL of 0.05 M KNO\(_3\) as a background electrolyte solution. Concentrated Pb solution was added to each bottle to provide an initial Pb concentration of \(\sim\) 50 mg L\(^{-1}\). Bottles containing these slurries were shaken on a reciprocating shaker (\(\sim\) 30 rpm) for >120 h at room temperature (25 ± 3 °C). Periodically, 8 mL slurry samples were taken from each bottle using plastic syringes and filtered immediately through 0.22 μm syringe filters. Metal concentrations in the filtrate were analyzed using either a flame atomic absorption spectrometer (Perkin-Elmer model 3030) or an atomic absorption spectrophotometer equipped with graphite furnace (Perkin-Elmer model SAMMA 6000), depending on metal concentrations. The detection limits were defined by 3σ (where σ is the standard deviation) of five blanks, observed Pb detection limits were 105 and 0.8 μg L\(^{-1}\) for flame atomic absorption and graphite furnace, respectively. These Pb standards (Fisher Scientific) were prepared in ~2% of nitric acid. Total phosphorus concentrations were determined by a spec-trophotometer using the molybdenum blue/ascorbic acid method [27]. Solution pH was determined using a Fisher Scientific Accumet model 20 pH/conductivity meter.

2.3. Lead sorption experiments

All metal sorption experiments were performed in batch mode. A 30 mL aliquot of 0.05 M KNO\(_3\) background electrolyte solution containing a known amount of Pb concentration ranging from 0 to 200 mg L\(^{-1}\) was equilibrated with 0.05 and 0.10 g of phosphatic clay powder in 40 mL polycarbonate centrifuge tubes. The slurries were shaken on a reciprocating shaker operated at 30 ± 1 rpm at room temperature of 25 ± 3 °C for 24 h. No pH control was imposed during sorption. The supernatant and solid residues were separated by centrifugation (Beckman J2-21) at 10,000 rpm for 20 min.

The solid residues (after interaction with the highest Pb concentration during the sorption experiment) were analyzed for determination of new solid phase minerals using XRD and SEM. Filtrates were analyzed for pH, Ca, P and Pb as described in the previous sections. The amount of sorbed metal was calculated as the difference between the amount added initially and that remaining in solution after equilibration.

The effect of pH on the Pb removal efficiency of phosphatic clay at three different concentrations of background electrolyte KNO\(_3\) was performed in this study. A 0.1 g of phosphatic clay was equilibrated with 30 mL of 0.001, 0.05 and 0.1 M KNO\(_3\) solutions and adjusting their initial pH to different levels ranging from pH 2 to 8. The slurries were shaken on a reciprocating shaker operated at 30 ± 1 rpm at room temperature of 25 ± 3 °C for 24 h. During this period slurry pH was readjusted to target pH levels manually. After stable pH levels were obtained, Pb concentration was raised equivalent to 100 mg Pb L\(^{-1}\) by adding concentrated Pb stock solution. After addition of the Pb stock solution, the rest of experimental procedure including shaking centrifugation and metal analysis remained similar to the previous sorption experiment.

Another series of experiments were performed to evaluate the effects of both inorganic and organic ligands on Pb sorption by phosphatic clay as a function of increasing ionic strengths. Prior to addition of ligands and Pb ions to phosphatic clay slurries, pH was adjusted to 6.5 and 4.5 by addition of 0.1 M HNO\(_3\)/KOH and maintained for 6–8 h by using auto titrator (Metrohm Dossimat Model 686). However, in case of inorganic ligands, different amounts of either 2.5 M KNO\(_3\) or KCl solution were added to 30 mL slurry samples in 40 mL polycarbonate centrifuge tubes containing the same metal concentrations. For organic ligands, variable ionic strengths were obtained by adding different amount of 2.5 M KNO\(_3\) solution to samples containing the concentrations of Pb along with dissolved organic carbon (DOC–Aldrich Chemicals) added as humic acid, oxalic acid and citric acid. Shaking, centrifugation and metal analysis were performed as described previously. The DOC in supernatant was determined by using a total organic carbon auto-analyzer (TOC–5050A, Shimadzu).

3. Results and discussion

3.1. Phosphatic clay characterization

Both elemental and mineralogical characterization of phosphatic clay confirmed its typical composition. Apatite, phyllosilicates (smectite, polygorskite and kaolinite) and calcite were also identified through mineralogical analysis (Fig. 1). Relatively high concentrations of Al, Si, Ca and P in phosphatic clay reflected the presence of apatite and phyllosilicate as its major constituents (Table 1). Quartz was also present in trace amounts. The major components of phosphatic clay that possess a potential to adsorb Pb are apatite and 2:1 clay minerals such as smectite [3,14]. Background trace metal contents in the phosphatic clay were negligible compared to the amount of sorbate added during the series of sorption experiments.

3.2. Lead removal kinetics

Lead removal kinetics for phosphatic clay could be influenced by the dissolution of its mineral components, because these may possess high potential to interact with aqueous Pb during the sorption experiment. Initially, we evaluated phosphatic clay dissolution in 0.05 mol L\(^{-1}\) KNO\(_3\) background electrolyte concentration in the absence of Pb at the same liquid:solid ratio (L/S) of 300, as a function of increasing reaction time. After
Fig. 1. X-ray diffraction patterns of phosphatic clay without and after its interaction with 200 mg L\(^{-1}\) Pb-solution. Mineral abbreviations: Sm, smectite; Pg, polygorskite; Ka, kaolinite; Qt, quartz; Py, pyromorphite and Ap, apatite.

45 h of dissolution, Ca concentration (15 ± 0.2 mg L\(^{-1}\)) changed substantially, but PO\(_4\) concentration and pH still increased continuously at a very slow rate (Fig. 2A).

Changes occurring in solution chemistry during Pb interactions with phosphatic clay were monitored for an initial concentration of ~50 mg L\(^{-1}\) for Pb as a function of its increasing reaction time (Fig. 2B). Initially, the equilibrium pH decreased sharply and then it increased slowly with increasing reaction time. The initial sharp decrease in solution pH may be combined hydroxylapatite dissolution/Pb-hydroxylapatite precipitation reaction rather than the dissolution or dissociation of CO\(_2\) or release of protons via surface exchange between Pb\(^{2+}\) and H\(^+\) [6]. The gradual increase in solution pH reflected slow dissolution of phosphatic clay driven by low P concentrations in solution. With ~50 mg L\(^{-1}\) Pb in the initial solution, pH dipped more than one unit in the first 5 min. Dissolution of phosphatic clay components such as apatite and carbonate slowed down the decrease in solution pH due to Pb\(^{2+}\) uptake by the phosphatic clay, leading to depletion of protons and hence rise in solution pH.

Batch sorption kinetic experiment revealed that Pb sorption behavior involved fast and slow sorption reactions (Fig. 2B). Within the first 10 min, >78% of the Pb was removed. Following the initial fast reaction, the sorption reaction continued for ~120 h. After 30 h, only a small amount of additional Pb removal occurred. The observed sharp decrease in solution pH corresponded well to the sharp decrease in aqueous Pb concentrations during the initial reaction of aqueous Pb with phosphatic clay.

The two-stage time dependent Pb removal behavior is similar to the results observed for pure minerals obtained by other researchers [28]. Fast reactions are most likely the result of initial precipitation of Pb and P as a pyromorphite during aqueous Pb interaction with phosphatic clay. In addition to this, chemical reactions with surface sites on phosphatic clay are also readily accessible to metal ions. Benjamin and Leckie [29] also observed that sorption of Cd, Pb and Zn metals on amorphous iron oxyhydroxide was initially fast followed by much slower second step. The slow reaction can be explained by diffusion to internal site, surface precipitation or sorption to available sorption sites that have slow reaction rate due to their low affinity [30]. In all cases, total P concentration reduced to below its detection limit (~equivalent to P concentration in the blank) due to the formation of geochemically stable Pb-phosphate and the limited solubility of apatite associated with phosphatic clay. Since phosphatic clay is a mixture of several minerals containing several different types of sorption sites, it is most likely that multiple slow reaction mechanisms were responsible for the slow-phase Pb sorption onto phosphatic clay.

3.3. Lead isotherms

The amount of Pb removed per unit weight of phosphatic clay plotted as a function of equilibrium Pb concentration for two different amounts of phosphatic clay is shown in Fig. 3. These isotherms represent the typical sorption behavior of phosphatic clay as a function of increasing initial Pb concentration after 24 h equilibration. For initial Pb concentration below 15 mg L\(^{-1}\) the
Fig. 3. Langmuir sorption isotherms of Pb$^{2+}$ onto phosphatic clay (A) and their linear fittings (B) after the transformation by the Langmuir Eq. (1). The data are from 24 h sorption experiment.

The Pb sorption data have been analyzed using the Langmuir model to evaluate the mechanistic parameters directly associated with the sorption process. The linear form of Langmuir equation is represented by

$$\frac{C}{m} = \frac{C}{M} + \frac{1}{bM}$$ (1)

where $C$ is the equilibrium concentration of adsorbate ions (mg L$^{-1}$), $m$ the amount of metals adsorbed (mg g$^{-1}$), $M$ and $b$ are Langmuir constants related to maximum sorption capacity and energy of sorption, respectively. The sorption data were fitted to a linear form of the Langmuir equation and are plotted in Fig. 3B. The fit of the data to Langmuir isotherm is generally good with some deviations at higher concentrations. These deviations from the Langmuir equation in our study suggest the possibility of other mechanisms in addition to precipitation and coprecipitation taking place simultaneously [33]. In addition to apatite, presence of several other clay minerals such as smectite and kaolinite in phosphatic clay increased its sorption capacity for Pb [22].

X-ray diffraction analysis of phosphatic clay after its interaction with aqueous Pb solutions at the highest concentration (∼200 mg L$^{-1}$) confirmed the formation of pyromorphite as evidenced by its diffraction peaks at 2.92 Å (Fig. 1). Microscopic analysis reveals an amorphous to cluster of lath-like lead phosphate crystals (Fig. 4A). The presence of pyromorphite is also suggested by EDS (Fig. 4B).
The sharp increase in Pb sorption with small changes in pH is similar to the observation published earlier for the sorption of hydrolysable metal ions [15,29]. Several models have been suggested to explain the metal sorption mechanisms involving metal ions: the metal hydrolysis model, metal proton exchange model [36] and pH dependent ion exchange model based on electrostatic potential on plane of sorption and surface charge density. The following equations show the hydrolysis of metal ions resulting in the formation of metal hydroxyl species [36]:

\[
M^{2+} + H_2O \rightarrow MOH^+ + H^+
\]  
(2)

\[
MOH^+ + \text{Phosphatic clay}^- \leftrightarrow MOH - \text{Phosphatic clay}
\]  
(3)

Using speciation calculation, it has been observed that the concentration of PbOH\(^+\) is relatively negligible relative to Pb\(^2+\) over the studied pH ranges. For the metal hydroxyl species to be adsorbed on the phosphatic clay, it must possess exceptional affinity for the phosphatic clay surface that will drive the metal hydrolysis reaction (Eq. (3)) to the right, maintaining Le Chatelier’s principal of equilibrium. Tiller et al. [37] also concluded that sorption is controlled by metal ions hydrolysis.

3.5. Effects of ionic strength

In order to explain the effects of ionic strength at fixed pH values, we also studied aqueous Pb removal by phosphatic clay at a given initial concentration of \(~104\) mg \(L^{-1}\) where ionic strength varied from 0.005 to 0.1 M KNO\(_3\) or KCl at pH 4.5 and 6.5, respectively. Observed aqueous Pb removal decreased with increasing ionic strength of background electrolyte solution, but magnitudes of these effects decreased with increasing pH, indicating Pb sorption remained important retention mechanism. A strong dependence on ionic strength is typical for an outer-sphere complex, whereas insensitivity of ionic strength is an indication for inner surface complexation. Phosphatic clay also possessed high cation exchange capacity (\(~26.9\) cmol kg\(^{-1}\)). In the presence of high ionic strength background electrolyte solution (0.1 M KNO\(_3\)), there was probably competition between Pb and other cations for available sorption sites on phosphatic clay, causing reduced uptake of Pb [38,39].

The increasing electrolyte concentration may also affect the sorption of Pb ions on phosphatic clay through increased competition of ions from supporting background electrolyte on the permanent negatively charged substrate surface [20]. These observed effects of ionic strength on metal sorption have been attributed mainly to (i) change in the activity of free Pb\(^{2+}\) and PbOH\(^+\) due to ion pair formation and effect of ionic strength on pH, (ii) competition for the available sorption sites on clay surfaces [40] and (iii) changes in the electrostatic potential in plane of sorption [41].

3.6. Effects of ligands

3.6.1. Inorganic ligands

Sorption experiments using KCl and KNO\(_3\) as background electrolyte solution as a function of their increasing ionic strength produced similar trends for Pb sorption on phosphatic
clay at pH 4.5 and 6.5, respectively (Fig. 6). At the same ionic strength of background electrolyte, observed Pb removal differed between NO$_3^-$ and Cl$^-$ anions. The nature of ligand could play a significant role for Pb sorption to phosphatic clay. For example, the presence NO$_3^-$ ions reduced Pb removal significantly compared to Cl$^-$ ions at the same ionic strength. This could be explained by the formation of geochemically stable chloro-pyromorphite in presence of Pb$^{2+}$, PO$_4^{3-}$ and Cl$^-$ ions with its low solubility, resulting in the reduction of ionic concentration (free Cl$^-$ concentration). On the other hand, formation of hydroxyl-pyromorphite took place in the presence of NO$_3^-$ ions without major change in its ionic concentration therefore most of NO$_3^-$ ions remained free in the solution. Studying the effects of NO$_3^-$, Cl$^-$, SO$_4^{2-}$ and CO$_3^{2-}$ on Pb$^{2+}$ immobilization by hydroxyapatite, Ma et al. [42] observed a greater decrease in Cl$^-$ compared to NO$_3^-$ ions in solution. Overall, Cl$^-$ ions remained more effective than NO$_3^-$ in reducing aqueous Pb concentrations due to formation of sparingly soluble chloro-pyromorphite precipitation in the presence of Cl$^-$ ions. The more effective behavior of chloride (compared to that of nitrate) in restricting Pb aqueous solubility may simply arise from the precipitation of PbCl$_2$, a sparingly soluble salt.

### 3.6.2. Organic ligands

Simultaneous removal of Pb$^{2+}$ and dissolved carbon per unit mass of phosphatic clay as a function of increasing ionic strength at fixed pH of 6.5 and 4.5 are shown in Figs. 7 and 8, respectively. In these experiments, assuming surface area of 34.5 m$^2$ g$^{-1}$, complete monolayer coverage of surface would have resulted in loss of $\sim$30–40 mg L$^{-1}$ of dissolved carbon from solution, which is approximately equalent to the measured DOC concentrations for the studied organic acids. It also showed that the increasing ionic strength resulted in a simultaneous decrease in both amounts of sorbed Pb and soluble carbon and the observed trend remained similar at both pH. These results showed that Pb binding to phosphatic clay surface is influenced to a significant extent by the presence of dissolved organic ligands. Complexation reactions generally include metal–ligand ion pair, soluble metal–ligand complexation and chelations. These organic ligands may form complexes with Pb, inhibiting it from precipitating with available P in solution. Therefore, competition between dissolved organic matter and Pb for sorption thus appears to be a potentially important process in natural water, suggesting that presence of organic ligands may reduce Pb removal efficiency of phosphatic clay.

Among the organic ligands studied, oxalic acid possessed exceptional capability to form insoluble precipitates of calcium and lead oxalate resulting in reduced cation competition for the available sorption sites on phosphatic clay. X-ray diffraction analysis of phosphatic clay also confirmed the formation of Pb/Ca oxalate in the presence of oxalic acid (data not shown). This could explain the greater sorption of Pb onto phosphatic clay in the presence of oxalic acid. On the other hand, citric acid formed more soluble solid phases with Ca and Pb compared to oxalic acid. Presence of citric acid inhibited precipitation.
of geochemically stable pyromorphite, resulting in the reduced aqueous Pb removal by phosphatic clay.

4. Conclusions

The effects of initial metal ion concentrations, sorbent amounts, solution pH, ionic strength and presence of both inorganic and organic ligands on the removal of aqueous Pb by phosphatic clay as well as its Pb removal kinetics were investigated by using a series of batch experiments. The sorption data suggests that solution pH was the most important parameter in controlling Pb sorption onto phosphatic clay. As expected, the amount of Pb uptake at equilibrium increased with increasing sorbent amount, pH, decreasing ionic strength and also depended on the nature of complexing ligands. Our results suggested that the interaction between phosphatic clay and aqueous Pb in solution was controlled mainly by the dissolution of phosphatic clay components (such as fluoroapatite), followed by precipitation of pyromorphite-like mineral as confirmed by XRD and SEM analysis. It can be concluded that Pb sorption kinetics were biphasic, initially rapid reaction followed by slow continuous sorption reaction most likely resulting from precipitation, followed by ion exchange, complexation and slow diffusion. These results imply that phosphatic clay could be a cost effective option for the remediation of metal contaminated soils and sediments as well as aqueous effluents.

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References


