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Mechanism of lead immobilization by oxalic acid-activated phosphate rocks

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Abstract
Lead (Pb) chemical fixation is an important environmental aspect for human health. Phosphate rocks (PRs) were utilized as an adsorbent to remove Pb from aqueous solution. Raw PRs and oxalic acid-activated PRs (APRs) were used to investigate the effect of chemical modification on the Pb-binding capacity in the pH range 2.0–5.0. The Pb adsorption rate of all treatments above pH 3.0 reached 90%. The Pb binding on PRs and APRs was pH-independent, except at pH 2.0 in activated treatments. The X-ray diffraction analysis confirmed that the raw PRs formed cerussite after reacting with the Pb solution, whereas the APRs formed pyromorphite. The Fourier Transform Infrared spectroscopy analysis indicated that carbonate (CO\(_3^{2-}\)) in raw PRs and phosphate (PO\(_4^{3-}\)) groups in APRs played an important role in the Pb-binding process. After adsorption, anomalous block-shaped particles were observed by scanning electron microscopy with energy dispersive spectroscopy. The X-ray photoelectron spectroscopy data further indicated that both chemical and physical reactions occurred during the adsorption process according to the binding energy. Because of lower solubility of pyromorphite compared to cerussite, the APRs are more effective in immobilizing Pb than that of PRs.

Key words: Pb; activated phosphate rocks; oxalic acid; immobilization
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Introduction
Human exposure to contaminated environment includes leaching of metals from the soil into water and consumption of edible plants grown in the contaminated environment (Madrid et al., 2006). In addition, soil and dust ingestion by humans, especially children, is of health concern (Chaney and Ryan, 1994). Therefore, implementing remediation practices to reduce metal availability is necessary to protect human health.

Lead (Pb) contamination is of great environmental concern due to its impact on human health. Pb, which can be released into the environment via numerous routes, has no known physiological function for plants or humans and even the smallest quantities can have adverse effects on organisms (Fisher et al., 2006). Anthropogenic activities primarily associated with industrial processes (manufacturing and disposal of domestic and industrial waste materials) are the major source of Pb contamination in environment (Adriano, 2001).

Chemical immobilization of Pb using phosphate addition is a widely-accepted technique to immobilize Pb from aqueous solution and contaminated soils (Miretzky and Fernandez-Cirelli, 2008). Pb phosphates have low solubility; they are several orders of magnitude less soluble than the analogous carbonates and sulphates (Nriagu, 1984).

Sparingly-soluble newly-formed lead-phosphate phases similar to chloropyromorphite (Pb\(_5\)(PO\(_4\))\(_5\)Cl) can control availability and mobility of Pb in the environment, and consequently reduce human exposure if soils are the main contamination pathway (Bosso et al., 2008). Pb immobilization by reaction with phosphates was tested in batch experiments, either in laboratory or the field, and most reports showed decreased Pb bioavailability (Hettiarachchi and Pierzynski, 2004). The stability of products, the low cost of phosphate materials and the possibility of applying them in situ for the long-term remediation have been suggested as the main benefits of this approach.

The resources reserve of the earth’s phosphorus ore is abundant, but some low-grade ores have poor effectiveness when applied directly, and need to be activated by converting the phosphorus into the available forms for plant use. Hence, most of the phosphorus ore is not fully utilized in the phosphate fertilizer industry. China has the second-largest phosphate rock reserve in the world, but most of it is the low-grade (P\(_2\)O\(_5\) < 23%) and refractory ore (Zhang et al., 2008).

Under certain conditions, some plant roots can secrete a relatively large amount of low-molecular-weight organic acids (LMWOAs) and some macromolecular compounds to promote dissolution of phosphate (Jemo et al., 2006; Kohler et al., 2007). In addition, LMWOAs were found in the secretion of phosphorus-solubilizing bacteria (Oualhmane et al., 2009). The main LMWOAs in soil that incid...
been detected are citric, oxalic, malic, tartaric acid, etc (Kpomblekou and Tabatabai, 2003). Most of them play an important role in mineral weathering and soil formation, rhizosphere change and nutrient cycling (Ström et al., 2005).

A direct application of the mid- or low-grade phosphate rocks (PRs) as an amendment to contaminated environments to immobilize heavy metals is a practical and feasible method (Cao et al., 2002). There were lots of studies about the utilization of the PRs to immobilize Pb in contaminated environment, while the research about the oxalic acid-activated PRs was barely reported. The present study investigated the Pb immobilization with four raw PRs and oxalic acid-activated PRs (APRs), with elucidation of a Pb-removal mechanism using the X-ray diffraction (XRD), scanning electron microscopy with energy dispersive spectroscopy (SEM with EDS), Fourier Transform Infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) analyses. The goal of this research was to determine the mechanism of Pb immobilization by application of PRs especially APRs and provide further information on the appropriate utilization of PR resources.

1 Materials and methods

1.1 Materials

The PRs used were purchased from Baokang, Nanzhang and Zhongxiang Counties of Hubei Province and Kaiyang City of Guizhou Province (hereafter named BPR, NPR, ZPR and KPR, respectively). All PRs are deposit types. After activation by oxalic acid, the PRs were defined as ABPR, ANPR, AZPR and AKPR, respectively. The PRs were crushed to pass through a 0.149 mm sieve. Their basic properties are presented in Table 1. A stock solution of Pb(NO$_3$)$_2$ (200 mg Pb/L) was prepared by dissolving Pb(NO$_3$)$_2$ in deionized water. The pH of treatment solutions was adjusted to desired values with 0.1 mol/L HCl or NaOH solution. All the chemicals were of analytical grade.

1.2 Sample treatment

Oxalic acid was chosen as the activating agent. The four raw PRs were mixed with 0.5 mol/L oxalic acid at a liquid-solid ratio of 10:1 and equilibrated at (28±1)°C for 6 days. Each raw and activated PRs samples of 0.5 g was weighed into the 100 mL centrifuge tubes. Subsequently, 50 mL Pb$_2$O$_5$ solution of 200 mg Pb/L at different pHs (i.e., pH 2.0, 3.0, 4.0 and 5.0) was added into each tube. After reacting with Pb solution, the adsorption experiment was conducted under the reaction temperature 25°C at 220 r/min and shaking for 24 h. The supernatants collected after shaking, centrifuging and filtering of the suspensions were used for Pb and Pb determination, whereas the residue was dried in an oven at 50°C for further analysis. The experiments were performed in triplicate.

1.3 Analysis

The Pb concentration in the supernatant was determined by flame atomic absorption spectrometry (FAAS-240, Varian Australia Pty Ltd., Australia). PRs were digested with heated nitric acid at a ratio of 1:1 (W/V). The available P was extracted by 2% (W/W) citric acid. The total and available P was determined by vanadium-molybdate-yellow colorimetry (Nanjing Agricultural University, 1992). The determination of iron, aluminum, calcium and magnesium oxides was according to the national standard method GB/T 1871-1995, i.e., after PRs dissolution in aqua regia, iron oxide and alumina of PRs were determined by spectrophotometry, calcium oxide by volumetric method, and magnesium oxide by FAAS. The content of CO$_2$ was analyzed by a thermogravimetric analyzer DSC200PC/PG209C (NETZSCH-Gerätebau GmbH, Germany). Statistical analysis was performed by Excel, Origin and SAS software.

Residues were subjected to X-ray diffraction (XRD), scanning electron microscope with X-ray energy dispersive spectroscopy (SEM with EDS), Fourier Transform Infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The XRD analysis was performed with Cu Kα radiation on a D8 Bruker Advance X-ray diffractometer (Bruker, Germany). The instrument was operated at 35 kV and 30 mA. A step size of 0.05° of 2θ and a scan time of 5 s at each step were used in the step scan mode. Samples were analyzed over a 20 range of 5°–70°. Crystallographic identification of the synthesized phases was accomplished by comparing the experimental XRD patterns to standards compiled by the Joint Committee on Powder Diffraction and Standards, which were card #01-087-2029 for fluorapatite, #01-089-3935 for calcite, #00-021-0838 for calcium oxalate crystals, #00-005-0417 for cerussite, and #01-089-4338 for pyromorphite. SEM with EDS observations for the residue were recorded on a Quanta 600 FE SEM with EDS analysis (The Dutch Philips FEI Company, Holland). FT-IR spectra were recorded on a FT-IR System 2000 and Spectrum 100 infrared spectrometers (Perkin-Elmer, USA). The FT-IR spectra of the adsorbents were recorded in the range of 650–4000 cm$^{-1}$ to obtain information regarding stretching and bending vibrations of the functional groups that were involved in the adsorption of metal ions.

<table>
<thead>
<tr>
<th>PRs</th>
<th>Total</th>
<th>Available</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>Al$_2$O$_3$</th>
<th>MgO</th>
<th>Pb</th>
<th>CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P$_2$O$_5$ (W/W, %)</td>
<td>P$_2$O$_5$ (W/W, %)</td>
<td>W/W, %)</td>
<td>(W/W, %)</td>
<td>(W/W, %)</td>
<td>(W/W, %)</td>
<td>(mg/kg)</td>
<td>(W/W, %)</td>
</tr>
<tr>
<td>BPR</td>
<td>26.1</td>
<td>2.24</td>
<td>45.4</td>
<td>3.50</td>
<td>0.042</td>
<td>6.44</td>
<td>9.16</td>
<td>10.8</td>
</tr>
<tr>
<td>ZPR</td>
<td>23.2</td>
<td>2.61</td>
<td>38.1</td>
<td>38.5</td>
<td>0.109</td>
<td>1.46</td>
<td>18.9</td>
<td>16.1</td>
</tr>
<tr>
<td>NPR</td>
<td>24.2</td>
<td>2.90</td>
<td>40.5</td>
<td>35.1</td>
<td>0.103</td>
<td>4.64</td>
<td>45.1</td>
<td>17.8</td>
</tr>
<tr>
<td>KPR</td>
<td>35.6</td>
<td>7.22</td>
<td>52.0</td>
<td>0.21</td>
<td>0.200</td>
<td>0.30</td>
<td>ND</td>
<td>30.7</td>
</tr>
</tbody>
</table>

PRs: phosphate rocks; ND: not determined; ZPR: Zhongxiang PR; BPR: Baokang PR; NPR: Nanzhang PR; KPR: Kaiyang PR.
X-ray photoelectron spectroscopy (XPS) was performed by VG MULTILAB2000 (Thermo Electron Corporation, USA). Peaks were identified by comparing the previously reported data and online XPS database provided by National Institute of Standard and Technology (Cao et al., 2004).

2 Results and discussion

2.1 Pb adsorption by PRs and APRs at different pHs

Figure 1 shows the effect of pH on the Pb adsorption by four raw PRs and APRs from aqueous solutions. The Pb adsorption capacity by all samples changed little between pH 2.0 and 5.0, except AZPR and AKPR for which the minimum adsorption capacity of 16.1 and 16.2 mg Pb/g was observed at pH 2.0. It is probably due to that in AZPR and AKPR treatments much H⁺ compete for adsorption sites with Pb²⁺ ions since the final pH of the supernatants were 2.27 and 2.26 after reaction with Pb solution. The Pb adsorption rate of all treatments above pH 3.0 reached 90% and it change little from pH 3.0 to 5.0. Thus, the tested PRs were effectively in adsorbing Pb regardless of whether the PRs were activated or not between pH 3.0 and 5.0. The pH of aqueous solution is known as the most important variable governing heavy metal adsorption onto adsorbents (Lalhruaitluanga et al., 2010), whereas the Pb binding on PRs and APRs nearly was pH-independent, except at pH 2.0 in activated treatments. Experiments were not carried out with the pH above 5.0 because Pb⁺⁺ precipitation appeared at higher pH values. This phenomenon was consistent with the results of Alhakawati and Banks (2004).

2.2 P concentration and pH in supernatant after Pb adsorption reaction

As shown in Fig. 2, with the increase of initial pH, the final P concentrations in supernatant decreased for the four APR treatments, ranging from 713 to 686 mg/L, 458 to 376 mg/L, 395 to 308 mg/L and 378 to 300 mg/L, respectively, while there was no P observed in supernatant in the four raw PRs treatments.

Solution pH had little effect on Pb immobilization. Only at pH 2.0, the Pb removal from solution by AZPR and AKPR was not as good as in other treatments, suggesting that some oxalic acid was left after activation. The primary mechanism of Pb immobilization was via dissolution of PRs and formation of a fluoropyromorphite-like mineral (Li, 2001). Therefore, the P from dissolution of PRs, and the Pb in solution would likely convert to fluoropyromorphite and other Pb-minerals after 24 hr. Although some P was left in solution after Pb removal by PRs, especially after reaction with APR, P is a nutrient that can be immobilized by soil and taken up by plants. Thereby, it is unlikely that these small concentrations of soluble P would lead to an environmental problem.

Based on the theory of dissolution kinetics and ion adsorption dynamics, the bond strength of oxide on whose surface the protons can combine with ions can be weakened, leading to separation of metal ions from the oxide and promotion of mineral dissolution in acidic solution (Li, 2001; Sparks, 1989). In this reaction system, the protons were consumed in the mineral dissolution at low pH, and then supernatant pH was increased. At the initial pH 4.0, the dissolution rate of PRs decreased. When the dissolution rate is slower than the adsorption rate during the reaction process with the increasing initial pH, the reaction is dominated by adsorption.

The reaction of Pb with PRs was controlled by diffusion, adsorption and exchange when the solution pH was above 3.0. Because protons were consumed in the mineral dissolution at initial pH 2.0 and 3.0, the supernatant pH after reaction reached the maximum at the initial solution pH 3.0 for all raw PR treatments reacting with Pb (Fig. 3). However, a similar phenomenon did not occur for the Pb reaction with APR, which was possibly due to a complex buffering system $H_2C_2O_4^{-}-HC_2O_4^{-}$ and $HC_2O_4^{-}-C_2O_4^{2-}$ in the reaction that increased the buffer capacity between pH 2.0–4.0 more than the $H_2PO_4^{-}-HPO_4^{2-}$ buffering system in the APR reaction with Pb could do.

The effectiveness of PRs in adsorbing Pb was enhanced by increasing solution pH at the same initial Pb con-
centrations, except in the APRs treatments. According to the previous studies, the higher the solubility of apatite, the more the reducing in Pb concentration because the main function of apatite, in this case, was to supply P to precipitate Pb (Ma et al., 1995; Cao et al., 2009). In the APRs treatments, although the P concentration in the low-pH filtrate was relatively high, it was not effective in reducing Pb concentrations in solution due to the residual oxalic acid that can decrease solution pH.

2.3 X-ray diffraction analysis of PR/APR and Pb reaction products

The XRD patterns of all as-prepared powders were obtained, but only a portion is shown in Fig. 4.

Clearly defined fluorapatite peaks (d: 0.2800, 0.2772, 0.2702 nm) could be observed in all samples. After treatment with oxalic acid, the crystallinity of the fluorapatite phase gradually decreased as manifested by broadening peak width and decreasing peak intensity. The gradual decrease of crystallinity is an indication of increasing P release from fluorapatite. Calcite (d: 0.3062, 0.2248 nm) was also observed in the tested PRs.

The formation of weddellite (d: 0.2744, 0.6190, 0.3350 nm) or whewellite (d: 0.5950, 0.3652, 0.2357 nm) was observed in all samples after treatment with oxalic acid due to $\text{C}_2\text{O}_4^{2-}$ in solution combining with $\text{Ca}^{2+}$ liberated by dissolving raw PRs and other carbonates; in contrast, only the peaks of whewellite appeared in ABPR and ABPR+Pb.

The presence of cerussite (d: 0.3593, 0.3498, 0.2487 nm) was detected in all raw PRs reacting with the Pb solution (Fig. 4), whereas the peaks of pyromorphite (d: 0.2966, 0.2885 nm) were observed in all APRs (Fig. 4). It is important to consider a far lower $K_{\text{sp}}$ of $\text{PbCO}_3$ (7.4×10^{-14}) than $\text{CaCO}_3$ (2.8×10^{-9}). The Pb$^{2+}$ ions in the reaction with raw PR can combine with $\text{CO}_3^{2-}$ in calcite according to theory of precipitation-dissolution equilibrium, but not with fluorapatites which have the mean $K_{\text{sp}}$ values of 10^{8.57} (10^{5.52}–10^{10.1}) (Zhu et al., 2009).

The Pb$^{2+}$ ions can interact with $\text{PO}_4^{3-}$ from APR first, and then pyromorphite is formed with increasing pH.

Both ABPR and ABPR+Pb have peaks of pyromorphite. The peak intensity in ABPR+Pb increased because there was more Pb$^{2+}$ reacting with $\text{PO}_4^{3-}$, favoring the formation of pyromorphite. However, the appearance of pyromorphite in ABPR might be questionable due to some overlapping between peaks of calcium oxalate and pyromorphite.

2.4 XPS analysis of PR/APR and Pb reaction products

The samples of BPR and ABPR after reaction with the Pb solution at initial pH 5.0 were chosen for XPS analysis because of the high Pb removal rate. XPS surface analysis (Table 2) confirmed that both chemical and physical reactions occurred during the adsorption process according to the binding energy (BE), whereas precipitation mechanisms predominated for the retention of Pb on PRs. The Pb removal was more efficient with ABPR than BPR by comparing the end BE of Pb$_{ab}$ and the change of atomic percentage shown in Table 2. Also, the symmetry of carbon element gained by XPS showed that only one carbon formed in the sample of BPR+Pb. The same phenomenon was not obvious for ABPR reacting with Pb, probably because Cu$_2$C$_2$O$_4$ coexisted with calcite formed in the reaction between oxalic acid and BPR.

2.5 SEM with EDS analysis of PR/APR and Pb reaction products

The SEM micrographs and elemental spectra of selected particles obtained by EDS analysis of raw PR, APR, PR+Pb and APR+Pb are illustrated in Fig. 5. The tested sample of raw BPR powders contained large agglomerate crystals containing a significant amount of Ca, P, O, F and C, with a low Mg content, which indicated the existence of fluorapatite (Fig. 5a). After BPR was treated with oxalic acid, the original cluster crystal structures were changed to amorphous (Fig. 5b).

The components of particles analyzed on ABPR did...
Fig. 5  SEM with EDS analysis of BPR, ABPR, BPR+Pb and ABPR+Pb reaction. Experimental condition: initial Pb concentration of 200 mg Pb/L, pH 5.0. (a) BPR; (b) ABPR; (c) BPR+Pb; (d) ABPR+Pb.

Table 2  XPS parameters of BPR and ABPR reacting with Pb

<table>
<thead>
<tr>
<th>PR</th>
<th>Atomic orbit</th>
<th>Start BE (eV)</th>
<th>Peak BE (eV)</th>
<th>End BE (eV)</th>
<th>FWHM (eV)</th>
<th>At. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPR</td>
<td>C1s</td>
<td>291.17</td>
<td>284.62</td>
<td>281.7</td>
<td>2.05</td>
<td>27.13</td>
</tr>
<tr>
<td></td>
<td>O1s</td>
<td>534.5</td>
<td>531.05</td>
<td>527.95</td>
<td>2.22</td>
<td>61.89</td>
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<tr>
<td></td>
<td>P2p</td>
<td>135.5</td>
<td>132.95</td>
<td>130.6</td>
<td>2.03</td>
<td>8.35</td>
</tr>
<tr>
<td></td>
<td>Pb4f</td>
<td>146</td>
<td>138.35</td>
<td>135.05</td>
<td>1.96</td>
<td>8.63</td>
</tr>
<tr>
<td>ABPR</td>
<td>C1s</td>
<td>290.8</td>
<td>287.91</td>
<td>281.9</td>
<td>2.52</td>
<td>15.25</td>
</tr>
<tr>
<td></td>
<td>C1sAl 30</td>
<td>290.8</td>
<td>284.63</td>
<td>281.9</td>
<td>2.55</td>
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<tr>
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<td>P2p</td>
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<td>133.26</td>
<td>130.3</td>
<td>2.05</td>
<td>8.24</td>
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<td>138.58</td>
<td>135.55</td>
<td>2.05</td>
<td>3.11</td>
</tr>
</tbody>
</table>

BE: binding energy; FWHM: full width at half maximum; At.: atomic percentage.

not change obviously in comparison with the raw BPR. A mass was formed after raw BPR reacted with the Pb solution (Fig. 5c), containing Pb, Ca, C and O, with low Cu. After the oxalic acid-treated BPR reacted with the Pb solution, anomalous block shaped particles and elements Pb, Ca, P, Cl, O, F, low Si, Mg, C and Cl were observed.
(Fig. 5d). The bulks seen in Fig. 5d were likely the crystals of pyromorphite as suggested by XRD, with the same phenomenon occurring in other three PRs (images not presented). These observations were consistent with the dissolution-precipitation mechanisms for Pb immobilization by apatite proposed by other researchers (Chen et al., 2010; Singh et al., 2006; Van Cappellen and Berner, 1991). The SEM images with EDS analyses were in agreement with the results of XRD measurements.

2.6 FT-IR analysis of PR/APR and Pb reaction products

The FT-IR spectra of the reaction of raw PRs and APRs with the Pb solution were examined to determine possible interactions between the function groups and Pb (Fig. 6). Figure 6a depicts the FT-IR of the BPR samples before and after reaction with Pb. The peaks at 1450, 1453, 1428 and 1426 cm$^{-1}$ are attributed to the anti-symmetrical, elastic, vibrating absorption $v_3$ patterns of CO$_{3}^{2-}$, and 880 cm$^{-1}$ is the elastic, vibrating $v_2$ absorption pattern of CO$_{3}^{2-}$ in BPR and BPR+Pb. The changes of raw BPR prior to and after reaction with Pb in the FT-IR spectra (Fig. 6a) showed that the main characteristic bands of crystals conformed to the characteristic peaks of calcite crystals (Shahwan et al., 2005).

The peaks at 1092, 1093, 1042 and 1046 cm$^{-1}$ are due to the anti-symmetrical, elastic, vibrating $v_3$ absorption patterns of PO$_{4}^{3-}$, and 965 cm$^{-1}$ is the symmetrical, elastic, vibrating $v_1$ absorption pattern of PO$_{4}^{3-}$ in two samples, all of which indicated the presence of fluorapatite with phosphate groups (Wu and Liao, 2005; Śliosarczyk et al., 2005; Bhadang and Gross, 2004). The FT-IR peaks at 1313 cm$^{-1}$ are due to the metal-carboxylate stretch (Fig. 6b). The characteristic peaks at 1612 and 1606 cm$^{-1}$ correspond to the bending modes, whereas the peaks between 3000 and 3500 cm$^{-1}$ correspond to the asymmetric and symmetric stretch of the water molecules coordinated with the calcium oxalate molecules (Mohamed et al., 2008). The peaks at 884, 885, 671 and 669 cm$^{-1}$ also coincide with the reported vibrational modes of pure calcium oxalate monohydrate crystals (Ouyang et al., 2006). These peaks were in good agreement with the archived data for CaC$_2$O$_4$·H$_2$O crystals reported by Shen et al. (2007).

After PR was activated by oxalic acid, the absorption patterns of CO$_{3}^{2-}$ disappeared, peak intensity of PO$_{4}^{3-}$ decreased greatly, and corresponding characteristic absorption patterns of CaO$_{4}^{2-}$ began to appear. The relevant explanation for a shift in the spectra, reduction and disappearance of the peaks involves an effect of chemical pretreatment on metal adsorption by the functional groups.

The FT-IR analysis of the as-prepared powders was in a good agreement with the results of the XRD, XPS and SEM with EDS analyses.

3 Conclusions

The tested PRs were effective in adsorbing Pb (200 mg Pb/L) between pH 3.0–5.0 regardless of whether the PRs were activated or not. Solution pH had little effect on Pb adsorption, even though dissolved P concentration increased with a drop in solution pH.

Raw PRs formed cerussite after reacting with the Pb solution, whereas the APRs formed pyromorphite as confirmed by XRD. The FT-IR analysis indicated that carbonate (CO$_{3}^{2-}$) in raw PRs and phosphate (PO$_{4}^{3-}$) in APRs played an important role in binding Pb. It is suggested to use APR as an adsorbent to remove Pb from aqueous solution because of the low solubility of pyromorphite

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