High Efficiency Stabilization of Lead in Contaminated Soil by Thermal-organic Acid Activated Phosphate Rock

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Abstract

Phosphate rock powder (PR) has been shown to possess the potential to stabilize lead (Pb) in soil. Most of the phosphorus (P) minerals in the world are low-grade ores, which makes it difficult to achieve the expected stabilization effect on heavy metals. This study compared the changes in the phase composition and structure of PR and three kinds of activated phosphate rock powder (APR) (organic acid activated PR, thermal activated PR, and thermal-acid activated PR), and used APR for the stabilization of Pb-contaminated soil. PR/APR was characterized by different methods. The stabilization effectiveness of APR on Pb-contaminated soil was evaluated by toxicity leaching procedure, the Pb products adsorbed on APR and stabilization mechanism of APR on Pb were analyzed. The results showed that the crystallinity of fluorapatite phase decreased after all the activation treatments. The APR showed decreased crystallinity and 3.4-fold increase in specific surface area, and a 53.07% and 49.32% increase in soluble P content in oxalic acid activated PR and citric acid activated PR, respectively, when compared with those of PR. These changes improved the stabilization effect of APR on Pb-contaminated soil, and the stabilization effectiveness was as follows: thermal-acid activated PR > organic acid activated PR > thermal activated PR. In particular, oxalic acid-600°C activated PR showed the best effect, presenting 94.0%-99.8% reduction in Pb leaching concentration following addition of 2%-10% modifier. Product characterization after Pb adsorption on APR showed that Pb was adsorbed onto APR by forming pyromorphite precipitation with APR.

Highlights

1. Surface area of PRO-600 was 3.4-fold higher than that of PR.
2. Structure of APR changed from agglomerated crystal to a porous structure.
3. Thermal-acid activated PR exhibited better Pb stability than the other two APRs.
4. Leaching concentration of Pb decreased by 99.8% when 10% PRO-600 was added.
5. Pb was adsorbed on APR mainly by forming pyromorphite precipitation with APR.

Introduction

With rapid urbanization and industrialization, heavy metals contamination of soil has attracted worldwide attention (Yubo et al. 2020). With the development of cities, industries, and agriculture, soil contamination is becoming an increasingly serious issue. The increase in the contents of heavy metals, especially lead (Pb), in soil poses a significant threat to the environment and human health (Park et al. 2011). Many industries, including metal processing, mining, electroplating, and battery recycling, can cause Pb pollution, among which Pb-acid battery recycling plants are one of the major sources of Pb pollution, accounting for more than 80% of global Pb usage (Chowdhury et al. 2021, Gottesfeld et al. 2018, Silvano et al. 2012). Previous studies have shown that the Pb content in the soil of Pb-acid battery plants could be as high as 10%-30%, which poses a high risk owing to the high bioavailable Pb content (Zhang et al. 2015). As Pb is highly toxic and nondegradable, its accumulation in soil and transport

through the soil matrix can cause potential hazard to plant growth and human health (Su et al. 2015). Therefore, effective strategies are required to remediate Pb-polluted soil.

Extensive research on remediation technology of soil Pb contamination has been conducted around the world, and remediation techniques such as physical remediation (thermal desorption technology, vitrification technology, etc.), chemical remediation (stabilization remediation technology, electric remediation, etc.), and bioremediation (including microbial remediation, phytoremediation, animal remediation) have been developed. Among them, chemical stabilization has been reported to exhibit advantages such as rapid effect, economic and environment friendly approach, and wide application scope, making this technique more suitable for remediation of large areas of heavy metals contaminated soil (Awa & Hadibarata 2020, Kumpiene et al. 2008, Silvano et al. 2012, Yao et al. 2012).

Pb-contaminated soil remediation technology based on phosphorous (P)-containing minerals has been widely studied all over the world. P-containing materials, such as phosphate rock (PR) and hydroxyapatite, can induce the formation of lead phosphate, thereby stabilizing Pb in the soil (Xu et al. 2019). The main benefits of this approach are low cost of P-containing minerals, stability of the products, and possibility of long-term remediation (Jiang et al. 2012). PR is a direct, economical, and lasting source of P (Li et al. 2020), and there are abundant reserves of P minerals around the world. In 2015, the world's P reserves reached 49.75 billion tons, with China ranking second in the world with 13 billion tons of P reserves (Xu et al. 2017). However, most of these resources are low grade ores from which high concentrations of phosphate are difficult to obtain (Xu et al. 2019); hence, direct remediation of heavy metals contamination using PR may be difficult to achieve the desired effect.

Activation of PR can promote the release of P from PR and stimulate phytoavailability of P in PR-treated soil (Zhu et al. 2015), thus driving the stabilization of Pb in contaminated soil. While current research on PR activation is mainly focused on single treatment method, such as acid activation (Huang et al. 2019, Su et al. 2015), biological activation (Abbasi & Manzoor 2018, Xu et al. 2019), etc., the combined use of multiple activation methods to activate PR has not been widely investigated, and its remediation effect, application scope, and mechanism on Pb-contaminated soil are not yet clear. Besides, application of thermal treatment, which is a common activation method, to activate PR has not yet been reported. Therefore, the objectives of the present study were to (1) prepare organic acid activated PR, thermal activated PR, and thermal-acid activated PR, (2) discuss the possible stabilization mechanism by analyzing the physical structure and chemical composition of the activated PR (APR), (3) evaluate the stabilization effect of APR on Pb-contaminated soil in a Pb-acid battery plant site through toxicity characteristic leaching procedure (TCLP) method, and (4) provide theoretical basis and technical support for the application of modified PR in remediation of heavy metals contaminated soil.

Materials And Methods

2.1 Materials

Soil samples were collected from a Pb-acid battery plant site in Jilin Province, China (128.93° N, 43.11° E), and then dried, crushed, and passed through a 2-mm sieve. The initial pH of the soil samples was 7.61, Pb concentration in the soil samples was 2,861 mg/kg, and TCLP-leached concentration of Pb was 7.17 mg/L.

PR used in this study was obtained from Zhongxiang Wangji Phosphate Fertilizer Plant, Hubei Province, China. X-ray fluorescence (XRF) of the PR showed that the main inorganic components of PR were CaO and P₂O₅ (40.49% and 20.09%, respectively), along with trace amounts of Mg, Si, F, Al, and S. All the experimental reagents were purchased from China National Pharmaceutical Group Corporation, and were of analytical grade.

2.2 Preparation of APR

2.2.1 Organic acid activation of PR

For obtaining oxalic acid activated PR (PRO) and citric acid activated PR (PRC), 100 g of PR were added to two beakers and respectively mixed with 0.5 mol/L oxalic acid solution and 0.5 mol/L citric acid. Subsequently, the beakers were left at room temperature for 7 days, dried at 60°C in an oven (Zhang et al. 2018), and the dried PRO and PRC were ground.

2.2.2 Thermal activation of PR

To obtain activated PR at 200°C (PR200), 400°C (PR400), and 600°C (PR600), 100 g of PR were heated in muffle furnace at 200°C, 400°C, and 600°C for 2 h, respectively, and cooled.

2.2.3 Thermal-acid activation of PR

For thermal-acid activation of PR, 100 g of PR200, PR400, and PR600 were respectively mixed with 1 L of 0.5 mol/L oxalic acid solution or 1 L of 0.5 mol/L citric acid solution, left at room temperature for 7 days, and then dried at 60°C in an oven. Subsequently, the dried thermal-acid activated PR were ground to obtain oxalic acid-200°C activated PR (PRO-200), oxalic acid-400°C activated PR (PRO-400), oxalic acid-600°C activated PR (PRO-600), citric acid-200°C activated PR (PRC-200), citric acid-400°C activated PR (PRC-400), and citric acid-600°C activated PR (PRC-600).

2.3 Stabilization of Pb-contaminated soil

In a beaker containing 30 g of dried and sieved soil samples, PR/APR were added at the ratios of 2%, 5%, 7%, and 10% soil dry weight, respectively. Then, deionized water was added to the mixtures at a water:solid ratio (W/S) of 30% and thoroughly mixed, and the mixtures were placed at room temperature

in a dark environment for 7–10 days. Subsequently, the Pb leaching concentration and pH of the soil were determined. The experiments were performed in triplicate.

2.4 Testing methods

The crystal morphology of PR, APR, and APR-adsorbed Pb product was determined using an X-ray diffraction (XRD) meter (D8 Advance, Bruker-AXS, Billerica, MA, USA) at 40 kV and 40 mA with CuK α radiation, scanning range of 10–85° in 2 θ , and scanning rate of 1°/min. The data obtained were analyzed using Jade 6.5 software. The elements in PR and APR were determined by XRF analyzer (ARL 9900, Thermo Fisher Scientific, Waltham, MA, USA) at 60 kV. LiF200, LiF220, Ge111, and AX03 were selected as the spectroscopic crystals. The morphology of PR, APR, and APR-adsorbed Pb product was observed using scanning electron microscope (SEM; S-4800, Hitachi, Tokyo, Japan) at 15 kV low accelerating voltage. The specific surface areas of PR and APR were detected by automatic specific surface area analyzer (QuadraSorb SI, Quantachrome, Boynton Beach, LA, USA). The surface functional groups of APR-adsorbed Pb product were examined by Fourier transform infrared spectrometer (FT-IR; VERTEX 70V, Bruker, Billerica, MA, USA). The pH of the sample was determined using a pH meter (Delta320, Mettler-Toledo, Columbus, OH, USA). The leaching concentration of Pb in soil was measured by TCLP (USEPA 2014) and inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500, Santa Clara, CA, USA).

Results And Discussion

3.1 XRD analysis of PR and APR

3.1.1 Organic acid activation of PR

The change in the diffraction peak in the XRD patterns can reflect the crystal structure of PR, with sharp diffraction peaks indicating good crystallinity and passivation of diffraction peaks denoting the existence of organic matter (Feng et al. 2008). The XRD patterns of PR and two kinds of organic acid activated PR are shown in Fig. 1. It can be clearly noted from the figure that the main components of PR were fluorapatite (Ca₅(PO₄)₃F) and dolomite (CaMg(CO₃)₂). After activation with oxalic acid, the peak intensity of fluorapatite weakened and the peak shape widened, indicating that the crystallinity of fluorapatite decreased. Likewise, the peak intensity of dolomite was significantly weakened and the peak of calcium oxalate appeared, demonstrating that fluorapatite and dolomite dissolved to release Ca²⁺ and combined with C₂O₄²⁻ in oxalic acid to form calcium oxalate monohydrate. This result is consistent with the findings of Jiang et al. (Jiang et al. 2012) and Zhang et al. (Zhang et al. 2018). The peak intensity of fluorapatite in PRC decreased, but was higher than that in PRO. Furthermore, the dolomite peak disappeared and hydroxyapatite peak appeared, suggesting that fluorapatite and dolomite dissolved in citric acid to release Ca²⁺ and P elements.

Analysis of the elements content in PR and organic acid activated PR (Table 1) revealed that the Ca contents in PRO and PRC decreased from 50.33% to 39.73% and 33.11%, respectively, and the P contents decreased from 8.80% to 4.13% and 4.46%, respectively, which proved that the mineral components containing Ca and P in PR reacted and released active Ca and P ions. In addition, 53.07% and 49.32% of P in PR was dissolved after oxalic acid activation and citric acid activation, respectively, indicating that organic acid activation may increase the release of P in PR, and that oxalic acid had stronger ability to release P in PR than citric acid. Similarly, Huang et al. (Huang et al. 2019) and Mendes et al. (Mendes et al. 2020) also reported that organic acids can promote the release of P from PR and increase its available P content. Furthermore, Mendes et al. (Mendes et al. 2020) suggested that the higher PR activation efficiency of oxalic acid was mainly owing to the interaction of two adjacent carboxylic groups in oxalic acid, which reduced the value of its dissociation constant ($pK_{a1}=1.25$) to lower than that of citric acid ($pK_{a1}=3.13$). As a result, oxalic acid was much more acidic than citric acid, with stronger ability to release P from PR.

3.1.2 Thermal activation of PR

The XRD patterns and main fluorapatite peaks of PR and the three kinds of thermal activated PR are shown in Fig. 2. It can be seen from the figure that thermal activation only changed the intensity and shape of the diffraction peaks in various phases of PR, and there was no evident formation of new substance in the activation process. The intensity and shape of the fluorapatite peak changed after thermal treatment, and the peak intensity weakened and peak shape widened with the increasing treatment temperature.

With thermal activation, the specific surface area of PR increased in proportion to the treatment temperature, and PR200, PR400, PR600 presented 5.52%, 6.36% and 43.22% higher specific surface area, respectively, when compared with PR. Thus, thermal activation of PR predominantly removed the impurities and internal moisture, changed the crystal structure, and increased the specific surface area, resulting in an improvement in surface adsorption of Pb, which was more conducive to Pb adsorption and stability.

3.1.3 Thermal-acid activation of PR

Figure 2 shows the XRD patterns and main fluorapatite peaks of thermal-acid activated PR. The peak intensity of fluorapatite in thermal-acid activated PR was significantly weakened and the peak shape was broadened, when compared with that in organic acid activated PR and thermal activated PR. The peak intensity of fluorapatite in the PRO series was lower than that in the PRC series, and weakened with the increasing treatment temperature. Besides, the fluorapatite peak shape widened with the increasing treatment temperature. These findings are consistent with the results of organic acid activation of PR and thermal activation of PR. It must be noted that the effect of organic acid activation of PR on reduction of fluorapatite peak intensity was stronger than that of thermal activation of PR.

3.2 SEM analysis of PR and APR

The results of the present study revealed that oxalic acid exhibited stronger ability to release P than citric acid, and thus, the activation effect of PRO was better among the three thermal treatments and the specific surface area of PR600 was significantly increased. In the thermal-acid activation of PR, the effects of acid and thermal conditions on PR were consistent with those observed following acid or thermal activation of PR. Therefore, PR, PR600, PRO, and PRO-600 were selected for SEM analysis (Fig. 3). The PR presented a compact structure, good crystallinity, and large particle size. After activation, the APR exhibited loose structure, low crystallinity, smaller particle size, and porous structure, which increased its specific surface area. It has been reported that the increase in the specific surface area of PR is owing to surface precipitation and erosion by organic acid during the activation process (Chen et al. 2015, Liu 2020). As a result, the pore and micropore structure of APR was increased, which was conducive to physical adsorption of Pb on PR and enhanced Pb adsorption and stability (Tansel et al. 2006).

3.3 Stabilization of Pb in soil by PR and APR

The leached Pb concentrations in soil treated with PR and different kinds of APR are shown in Fig. 4. When compared with PR, APR exerted a more obvious stabilization effect on Pb-contaminated soil, with thermal-acid activated PR exhibiting the best effect. The stabilization effectiveness of different kinds of APR was as follows: thermal-acid activated PR > organic acid activated PR > thermal activated PR. With the addition of 2%-10% activator, the stabilization effect of PRO was better than that of PRC, and the soil Pb leaching concentration decreased by 87.1%-99.1% and 29.7%-78.7%, respectively. The stabilization effect of PR on Pb-contaminated soil was directly proportional to the thermal treatment temperature (200°C-600°C), and the Pb leaching concentration in soil treated with PR600 decreased by 52.9%-86.8%. PRO-600 exhibited the best stabilization effect, reducing Pb leaching concentration in soil by 94.0%-99.8%.

The pH of the treated soil increased from 7.61 to 7.96-8.87, which may be owing to the addition of excessive PR/APR. It is presumed that PR addition to the Pb solution results in pyromorphite precipitation, releasing H^+ that could dissolve phosphate in the solution, which in turn could consume H^+ . Therefore, the pH of the solution first decreased and then increased. When this dissolution-precipitation reaction reached an equilibrium, the change in the pH of the solution theoretically became zero. However, under practical conditions, excessive amounts of P-containing substances are often added, resulting in an increase in soil pH after the equilibrium reaction (Chen et al. 2010, Ma et al. 1993). Alternatively, the change in soil pH may also be related to the content of available Ca and Mg in PR/APR. Previous studies have shown that the contents of exchangeable Ca and Mg in soil presented a significant positive correlation with soil pH (Yong et al. 2011), which may be one of the reasons for the increase in soil pH with the addition of PR/APR observed in the present study. Soil pH can affect the forms of Pb that occur in soil. When the soil pH is low, a competitive relationship exists between H^+ and heavy metal ions, which

leads to the inhibition of heavy metal adsorption. However, when the soil pH is high, such adsorption competition is weakened and heavy metal ions are more stable, and thus Pb^{2+} in the soil can easily form hydroxide or carbonate precipitation/co-precipitation (Hamid et al. 2018). Chuan et al. (Chuan et al. 1996) found that the content of available Pb in soil was very low under alkaline conditions (pH = 8), and Houben et al. (Houben et al. 2012) showed that the bioavailability of Pb in soil decreased with the increase in alkalinity. Therefore, it can be concluded that APR enhanced the stability of soil Pb by increasing the soil pH.

Recent studies have suggested that P-containing materials reduced the availability of Pb in soil mainly by varying the soil pH, adsorption, and precipitation. PR treated with acids can combine in the form of H_2PO_4^- with Pb in the soil to form stable pyromorphite (Arnich et al. 2003, Chaturvedi et al. 2007, Cheyns et al. 2012), and can improve soil pH, weaken the adsorption competition between H^+ and Pb^{2+} , promote Pb^{2+} to precipitate, and reduce the mobility of Pb in soil (Huang et al. 2019). Therefore, the stability of Pb in soil increases with the increasing amount of P released by the dissolution of PR in organic acids. As the P release ability of PRO was stronger than that of PRC because oxalic acid could more effectively promote the dissolution of PR and release P, the stabilization effect of PRO on soil Pb was stronger than that of PRC. The Pb leaching concentration in soil decreased after treatment with thermal activated PR, and the stabilization effect of APR on Pb in soil improved with the increasing temperature of thermal activation. This effect may be owing to the change in the structure of PR following high temperature treatment, which increased the specific surface area of PR and promoted adsorption of Pb in soil by PR. The specific surface area of PR significantly increased with the increasing the thermal activation temperature. Thus, PR600 exhibited the most significant stabilization effect. Furthermore, thermal-acid activation of PR showed significantly improved stabilization effect on soil Pb owing to the combined influences of organic acid activation and thermal activation. Thus, the stabilization effectiveness of APR was as follows: thermal-acid activated PR > organic acid activated PR > thermal activated PR.

3.4 Characterization of APR-adsorbed Pb

To further verify the above-mentioned results, Pb^{2+} adsorption on PRO-600 (which presented maximum beneficial characteristics) was examined by adding $\text{Pb}(\text{NO}_3)_2$ (analytical reagent) solution to PRO-600 at a dry weight basis of 600 mg/g, and characterizing and analyzing the reaction products. The XRD patterns before and after the reaction of PRO-600 with Pb are shown in Fig. 5. Pyromorphite $[\text{Pb}_5(\text{PO}_4)_3\text{Cl}]$ was detected in the products after the reaction of PRO-600 with Pb, and the peak intensity of fluorapatite weakened or even disappeared because PO_4^{3-} in PRO-600 first reacted with Pb in aqueous solution and then gradually formed $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ with the increase in pH, resulting in Pb immobilization. This further verified the hypothesis of dissolution-precipitation reaction between APR and Pb. Ma (1996) (Ma 1996) analyzed the products of hydroxyapatite adsorbed by Pb and found that P-Pb precipitation can occur at both high and low concentration of dissolved Pb.

The SEM/EDS analysis results of PRC-600 before and after Pb^{2+} adsorption and the mapping diagrams of typical elements are shown in Fig. 6. The SEM images revealed that PRO-600 had rougher surface and more pores. However, after adsorption of Pb, the pores were reduced and the surface was covered with irregular particles. It must be noted that pore plugging may be detrimental to secondary adsorption. The main elements in the product after adsorption were Ca, O, Mg, P, etc. and the proportion of Pb was increased, when compared with those before adsorption, which may be owing to the formation of P-Pb compounds after Pb adsorption. Combined with the XRD results, it can be inferred that the abovementioned product was $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$. As shown in the mapping diagram in Fig. 6, Ca and Mg in the product formed after the reaction between PRC-600 and Pb^{2+} were more loosely distributed than those before the reaction, and Pb elements appeared after the reaction, thus indicating that the cations in PRO-600 were replaced by Pb resulting in Pb adsorption.

FT-IR spectroscopy was employed to analyze the changes in the functional groups before and after the reaction between PRC-600 and Pb (Fig. 7). The FT-IR peak at 1313 cm^{-1} corresponded to the stretching peak of metal carboxylate; the characteristic peak at 1616 cm^{-1} conformed to the bending vibration mode, and the five peaks between 3000 cm^{-1} and 3500 cm^{-1} were consistent with the asymmetric and symmetric stretching peaks of water molecules coordinated with calcium oxalate (Ali et al. 2008). After the adsorption of Pb, the O-C-O bending vibration peak at 519 cm^{-1} shifted and the intensity of the calcium oxalate absorption peak (1313 cm^{-1}) weakened, implying that the oxygen-containing active groups in PRO-600 participated in the reaction when the material adsorbed Pb and calcium oxalate was consumed during the adsorption process. In addition, the absorption peaks of H_2PO_4^- at 889 cm^{-1} and 958 cm^{-1} disappeared, suggesting that phosphate played an important role in the process of Pb adsorption by PRO-600. Thus, the results of XRD, SEM-EDS-mapping, and FTIR characterization of the reaction product of PRO-600 and Pb revealed that Pb^{2+} was adsorbed on APR mainly through solution-precipitation reaction to form pyromorphite.

Conclusion

In this study, PR was used as a raw material to examine the effectiveness of different activation methods such as organic acid activation, thermal activation, and thermal-acid activation, and the stabilization effect of APR on Pb-contaminated soil was analyzed. The results indicated that organic acid activation, thermal activation, and thermal-acid activation decreased the crystallinity of PR and increased the specific surface area of PR by making its structure porous. Oxalic acid presented better activation effect than citric acid, and no evident formation of new substance was noted in the process of thermal activation of PR. The high temperature treatment altered the crystal structure of PR, making it conducive to Pb adsorption, which enhanced Pb adsorption and stability, and the activation effect improved with the increasing treatment temperature (200°C - 600°C). All the three treatments enhanced the stabilization effect of PR on Pb in soil and their effectiveness was as follows: thermal-acid activated PR > organic acid activated PR > thermal activated PR. PRO-600 exhibited the best stabilization effect, reducing Pb leaching concentration in soil by 94.0%-99.8% with the addition of 2%-10% modifier. Characterization of the

product obtained after Pb adsorption on PRO-600 revealed that Pb was adsorbed on APR via pyromorphite precipitation. These results suggested that thermal-acid activated PR was a more efficient stabilization material for treating Pb-contaminated soil.

Declarations

Availability of data and materials The data and materials used or analyzed during the current study are available from the corresponding author on reasonable request.

Author Contribution Ziwen Song: Conceptualization, Experiments, Data methodology, Writing - original draft. Zhuo Zhang: Conceptualization, Methodology, Writing - review & editing. Canyu Luo: Experiments, Data analysis. Likun Yang: Experiments, Data recording. Jin Wu: Data analysis.

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Competing interests The authors declare no competing interests.

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Tables

Table 1 Elements content and pH of PR and organic acid activated PR

Element	Ca (%)	P (%)	Mg (%)	Si (%)	F (%)	pH
Sample						
PR	50.33	8.80	4.64	1.09	1.15	9.53
PRO	39.73	4.13	3.33	0.72	0.28	4.71
PRC	33.11	4.46	4.36	0.66	0.35	3.37

Figures

Figure 1

XRD patterns of PR and organic acid activated PR.

Figure 2

XRD patterns and main fluorapatite peaks of thermal activated PR and thermal-acid activated PR.

Figure 3

SEM analysis of PR before and after activation (a. PR, b. PR600, c. PRO, d. PRO-600).

Figure 4

Leached Pb concentrations in soil treated with PR and different kinds of activated PR (a. PR, PR200, PR400, PR600; b. PRC, PRC-200, PRC-400, PRC-600; c. PRO, PRO-200, PRO-400, PRO-600) under the condition of various dry weight ratios. Error bars represent standard deviation (SD) ($n = 3$).

Figure 5

XRD patterns of PRO-600 after adsorption of Pb^{2+} .

Figure 6

SEM-EDS-mapping images of PRO-600 after adsorption of Pb²⁺.

Figure 7

FT-IR spectra of PRO-600 after adsorption of Pb²⁺.

Supplementary Files

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