



Remediation of lead-contaminated sediment by biochar-supported nano-chlorapatite: Accompanied with the change of available phosphorus and organic matters

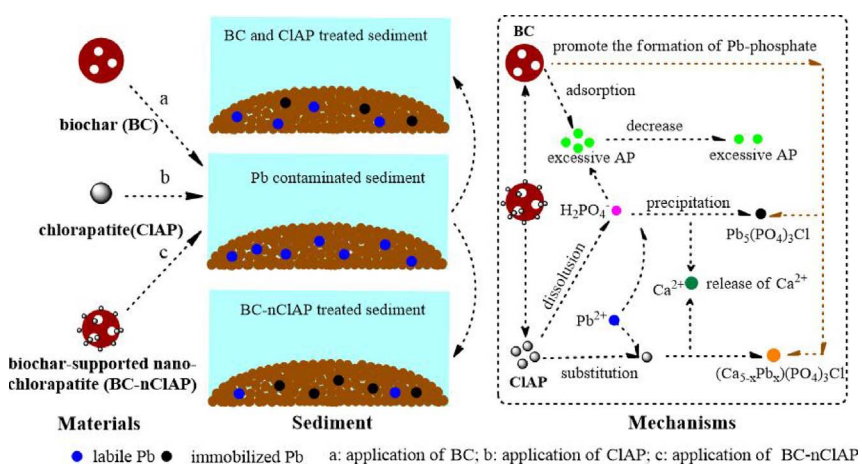
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GRAPHICAL ABSTRACT



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ABSTRACT

Some rivers in China have been seriously contaminated due to the discharge of lead (Pb) smelting wastewater. In this study, biochar-supported nano-chlorapatite (BC-nClAP) was synthesized to immobilize Pb in contaminated sediment. The remediation effect of BC-nClAP on Pb-contaminated sediment was evaluated through batch experiments and the materials were characterized by x-ray diffraction, scanning electron microscope, Brunner-Emmet-Teller and electronic differential system. It was found that BC-nClAP can transform Pb effectively from labile fraction into stable fraction with a maximum transformation efficiency increasing to 94.1% after 30 days of treatment, and the stabilization efficiency of toxicity characteristic leaching procedure reached 100% only after 16 days of treatment. The content of available phosphorus (AP) in the sediments treated by BC-nClAP was much less than that treated by nClAP, which indicated a lower risk of eutrophication and suggested the dissolution-precipitation mechanism involved in Pb immobilization. BC-nClAP presented the best immobilization

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efficiency of Pb and the content of organic matters in BC-nCIAP treated samples increased the most, thus the OM might play an important role during the Pb immobilization.

1. Introduction

The contamination of heavy metals has attracted more and more attentions around the world due to its high toxicity to organisms in recent years [1,2]. Toxic metals' contamination has been proved to be an increasingly global problem and is considered to pose a serious threat to environment [3,4]. Because heavy metals cannot be degraded via microbial or chemical processes, they would persist in environment for a long time and bioaccumulate in human body by food chain, posing a potential toxicity to human, such as bone aching, cancer and other seriously diseases [5–7].

When heavy metals were discharged to rivers, sediments might be the final destination of them [8,9]. Lead (Pb) contaminated sediments is becoming increasingly common due to the wide application of Pb in electroplating, metallurgy, and agriculture [10]. Pb is one of the hazardous environmental contaminants in China, even in the world [11,12]. The most rivers' sediments in China have been contaminated by heavy metals, especially Pb-contamination [13]. Consequently, there is an imperative need to remediate Pb-contaminated sediments [14,15]. Pb in sediments can form several speciations when it entered into the sediment [16,17]. They were divided into four speciations according to BCR (European Community Bureau of Reference) sequential extraction procedure: acid soluble/exchangeable fraction (F-exc), reducible fraction (F-red), oxidizable fraction (F-oxi), and residual fraction (F-res), and the stability of them are in order of F-res > F-oxi > F-red > F-exc [18–21].

In recent years, remediation for Pb-contaminated sediments with phosphate-based remediation has drawn a great attention [22]. Phosphate-based materials were proven to be an effective and inexpensive method for *in situ* remediation in previous study [23]. Phosphate-based remediation has an excellent ability in the immobilization of Pb(II), Cd(II), Zn(II), and Cu(II), especially the Pb(II), which can cooperate well with phosphate by the formation of phosphate-Pb compounds presented as pyromorphite ($Pb_5(PO_4)_3X$, X = F, Cl, Br, OH) [24,25]. Among these researches, chlorapatite (CIAP) has been recognized as an ideal

phosphate materials to immobilize Pb in sediments [26]. The main mechanisms of Pb immobilization by CIAP in sediments including dissolution-precipitation, adsorption and rhizosphere effect [27]. However, negative effects followed by the application of CIAP in the sediment environment cannot be neglected, for example, it may bring excess phosphorus into the environment, causing eutrophication [28].

Sodium dodecyl sulfate modified nano-chlorapatite and rhamnolipid stabilized nano-chlorapatite have been synthesized in our previous study and both of them presented well stabilization efficiency for Pb. However, both of them could not control the available phosphorus effectively and the eutrophication risk has not been solved [18,29]. Considerable research interest has been focused on synthesis of biochar-based nanocomposites to remove contaminants in environment, such as MgO-biochar nanocomposites [30], graphene-coated biochar [31] and carbon nanotube (CNT)-coated biochar [32]. However, most of these biochar-supported nanocomposites were used to remove water contamination. As we all know, biochar (BC) had a remarkable adsorption capacity for contaminant due to its large specific surface area, porous structure and active functional groups [33,34]. In this paper, biochar-supported nano-chlorapatite (BC-nCIAP) was first synthesized to immobilize Pb in contaminated sediments and we estimate that it may exert both the advantage of biochar and CIAP since: (1) the pore property of biochar might present improvement effect and it may absorb excessive phosphorus released by chlorapatite to prevent secondary contamination; (2) the surface functional groups of biochar may reduce the agglomeration of CIAP to achieve better remediation efficiency [35,36].

Consequently, this study aims to: (1) synthesize BC-nCIAP and characterize the BC-nCIAP by scanning electron microscope (SEM), Brunner-Emmet-Teller (BET), x-ray diffraction (XRD), and electronic differential system (EDS); (2) detect the chemical speciation of Pb and the leachable Pb fraction to investigate the Pb immobilization effect of BC-nCIAP on the contaminated sediments; (3) test the content of the available phosphates (AP), organic matters (OM) and some other index to analyze the possible interaction mechanisms between the materials

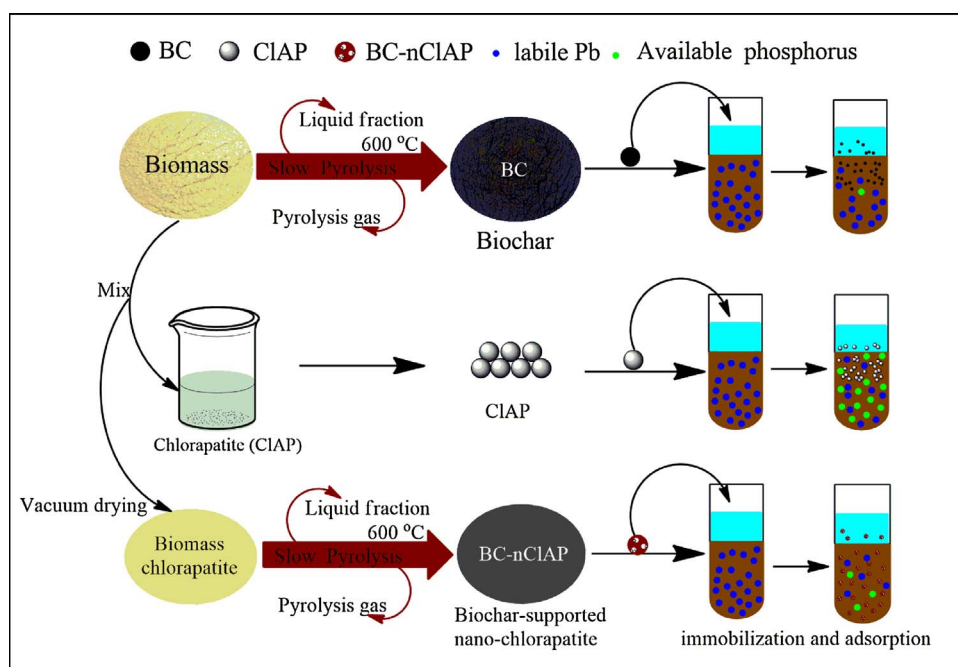


Fig. 1. Schematics of the preparation of biochar (BC), chlorapatite (CIAP) and biochar-supported nano-chlorapatite (BC-nCIAP) and their application for immobilization of Pb with the adsorption of available phosphorus.

and sediments.

2. Materials and methods

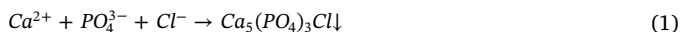
The bamboo sawdust, calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 99%), sodium phosphate tribasic dodecahydrate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, 98%) and the rest of the main chemicals using in this experiment were purchased from JingKang Scientific Ltd (Changsha, China). The experiments were conducted in triplicate and the results were expressed as mean \pm standard deviation.

2.1. Synthesis of materials

Three kinds of materials were synthesized respectively in this experiment: BC, CIAP and BC-nCIAP, the synthesis procedures were presented in below.

Synthesis of BC: BC was derived by pyrolyzing bamboo sawdust with nitrogen-filled environment. The cleaned and dried bamboo sawdust was ground into powder and passed through a 100 mesh sieve and then placed in a tube furnace for further pyrolysis. Pyrolysis process was operated by raising the temperature to 600 °C at a rate of 7 °C/min and then maintained for 2 h under the protection of nitrogen. Finally, the tube was cooled to room temperature and collected. The BC was obtained.

CIAP was synthesized as follows: Firstly, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ were dissolved into the deionized water (resistivity of 18.2 M Ω cm) to achieve the solutions of 0.268 mol/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.160 mol/L $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, respectively. 25 mL of 0.268 mol/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ were added into 50 mL deionized water and 25 mL of 0.160 mol/L $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ were added into the mixture solution dropwise by the acid burette at a steady speed of 5–8 drops per minute under constantly stirring at 1000 r/min for 24 h. After, the pH of the suspension was adjusted to 6.0 with diluted HCl. The CIAP was obtained. In this experiment, mechanism for the generation of $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ (CIAP) was shown in the following equation:



BC-nCIAP was synthesized on the basis of prepared BC and CIAP in the above. A given mass of bamboo sawdust prepared above were added into the CIAP suspensions with constantly stirring for 24 h. Then these suspensions were centrifuged at 5000 r/min for 20 min and then dried at 60 °C for 12 h. The calcination process of BC-nCIAP was totally the same as BC. Finally, the materials were ground into powder to pass through a 100 mesh sieve and put into self-styled bag in the dryer for later use. Fig. 1 showed the schematics of the preparation of BC, CIAP and BC-nCIAP and their application for immobilization of Pb.

2.2. Characterization of materials

The specific surface area of BC-nCIAP was measured by nitrogen adsorption isotherm using a Brunauer-Emmett-Teller surface analyzer (BET, NOVA 1000 e, Quantachrome Instruments). Scanning electron microscopy (SEM, JSM-6700F) was used to observe the surface morphology of BC and BC-nCIAP. Minerals in BC-nCIAP, CIAP and BC were analyzed by using a X-ray diffractometer (XRD-6100, SHIMADZU) and the data was collected over the 2θ range from 10° to 80° using Cu $K\alpha$ radiation. Surface elemental analysis was conducted with electronic differential system (EDS, EDAX GENESIS).

2.3. Sample collection and preparation

The sediment samples of this experiment were collected from Xiawangang River in Hunan province in southern China. All the sediment samples were natural withered for 5–7 d and then ground into powder to through 100 mesh sieve. After sifting, all the sediments

samples were stored in a dryer under the condition of 4 °C before being used. Some properties of this sediment and the national standard concentrations of heavy metals in sediment samples in China are listed in Table S1 (Supplementary Material). The concentration of Pb in sediment samples was 589.7 ± 13.2 mg/kg which approximately more than 1.5 times of the national standard (350 mg/kg), so the sediment of this river is showing a big threat to the environment and organisms.

2.4. Sediment remediation experiment

The remediation experiments were performed with 0.5 g of sediments in the centrifuge tube. 0.3 g BC and BC-nCIAP were added into the sediments in the centrifuge tubes, respectively, and then 5 mL deionized water were added into the centrifuge tube to achieve a suspension-to-sediment ratio of 10:1 (mL/g). By contrast, 5 mL of CIAP were also added into centrifuge tube to achieve a suspension-to-sediment ratio of 10:1 (mL/g). For the measurement of available phosphorus, the amount of sediments, materials and chemical reagent were all five-fold of other experimental indexes. Then all the samples were placed in a shaker to react for 1, 5, 10, 16, 23 and 30 days under 25 °C. After the remediation, the samples were taken out from the shaker and centrifuged at 4000 r/min for 20 min, and the supernatant and sediment were separated and stored respectively for the further measurement.

2.5. BCR sequential extraction procedure and toxicity characteristic leaching procedure (TCLP)

50 mL centrifuge tube which contains 0.5 g treated sediment was used for the analysis of the heavy metal speciation and TCLP. The BCR (European Community Bureau of Reference) sequential extraction procedure according to previous papers was conducted with some modifications following the steps shown in Supplementary Material [37,38]. The TCLP experiment was conducted according to method mentioned in Xenidis et al [39]. Details about the procedures here used are given in the Supplementary Material.

The supernatants collected from the experiment of BCR and TCLP were all filtrated through the 0.45 μm membrane filter and stored at 4 °C before being measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, OPTIMA8000, PerkinElmer, U.S.A.).

2.6. Available phosphorus (AP) and organic matter (OM)

50 mL centrifuge tube which contains 2.5 g treated sediment was used for the analysis of AP and 0.5 g for OM. The molybdenum-antimony anti-spectrophotometric method was used in this experiment to evaluate the AP level in the sediment [40]. And in order to determine the OM level of the sediment, the potassium dichromate volumetric method-the dilution heating method was used in the experiment [18]. Details about the procedures here used are also given in the Supplementary Material.

2.7. Cation exchange capacity (CEC) and hydrogen ion concentration (pH)

50 mL centrifuge tube which contains 0.5 g treated sediment was used for the analysis of CEC and pH. Details about the methods and discussions are given in the Supplementary Material [41].

3. Results and discussions

3.1. Characterization of materials

The morphology of BC and BC-nCIAP were measured by SEM. The red circle represented the megascopic location of the low multiple SEM image. The SEM image of BC showed in Fig. 2a indicated that BC possessed some porous structure which was conducive to the adsorption

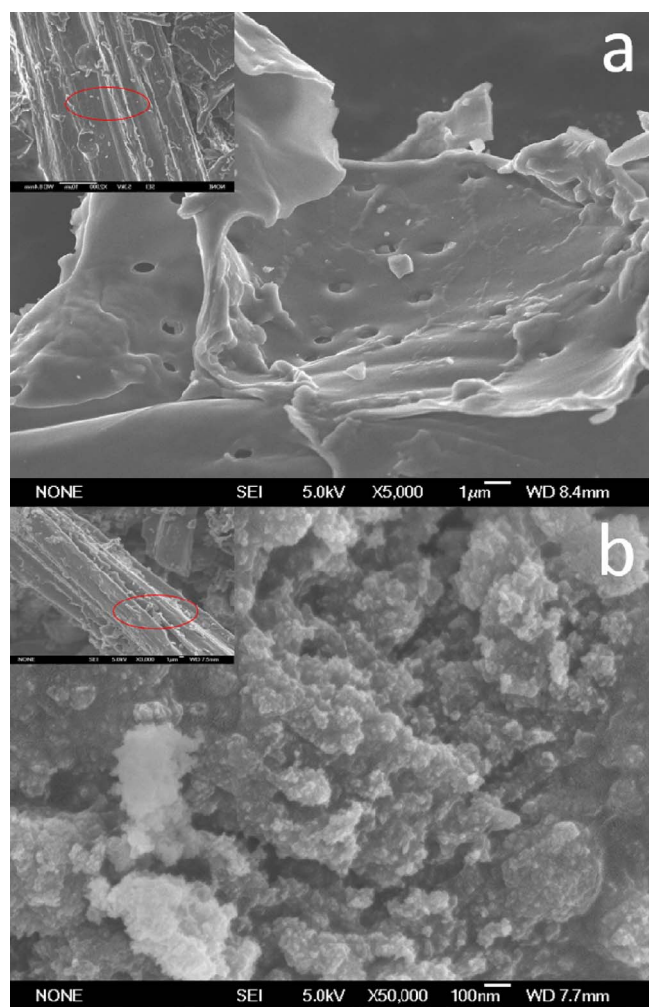


Fig. 2. SEM images of bamboo sawdust biochar (BC) produced through pyrolysis at 600 °C (a) and biochar-supported nano-chlorapatite (BC-nClAP) (b), respectively.

of heavy metals [42]. Little white particles on the surface of plain biochar can be observed, which might be some organic matter particles or some carbonates, metasilicates and sulfates exist in biochar after pyrolysis (Fig. 2a and Fig. S1). The SEM image of BC-nClAP showed plenty of white particles which indicated that the ClAP was dispersed on the surface or within the pores of the BC (Fig. 2b). Some obvious peaks appeared in the EDS spectrum of BC-nClAP were determined to be C, O, Na, S, P, Cl and Ca, well demonstrating that the white particles (Fig. 2b) in SEM image of BC-nClAP were the ClAP that dispersed on the surface or within the pores of BC and the ClAP was synthesized successfully with the support of biochar (Fig. 3). The specific surface of BC and BC-nClAP were determined by BET analyzer. The BET surface area of the BC was 396.050 m²/g while the BET surface area of BC-n ClAP was 306.188 m²/g. In combination with the SEM results showed in Fig. 2, it can be found that BC possessed some porous structure which may result in a larger specific surface area. However, due to the ClAP dispersed on the surface or within the pores of the BC, the specific surface area of BC-nClAP was smaller than BC.

The XRD pattern of ClAP was similar to BC-nClAP (Fig. 4). The ClAP and BC-nClAP appeared similar characteristic peaks. Furthermore, the intensity of the main characteristic peak (Ca₅(PO₄)₃Cl) of BC-nClAP was weaker than ClAP. It indicated that the chlorapatite was dispersed within the pores of BC in BC-nClAP particles.

3.2. Effects of nanoparticle treatment on Pb immobilization in sediment

3.2.1. Chemical speciation of Pb

The percentage of chemical speciation distribution of Pb which measured by BCR procedure in BC (M1), ClAP (M2) and BC-nClAP (M3) treated sediment were presented in Fig. 5. In the original sediment, the mainly speciation of Pb was F-oxi which was approximately 60.5% while the percentage of F-exc, F-red and F-res were about 8.2%, 11.1% and 20.2%, respectively. The percentage of F-res was increased while the percentage of F-exc and F-red were decreased with the rising of remediation time (Fig. 5). However, the percentage of F-oxi displayed an irregular change compared with other three speciations. From Fig. 5a, we found that the percentage of F-exc and F-red in BC and BC-nClAP treated sediment were all obvious decreased to a low level at the remediation time of 30 days. So it can be easily found that the BC and BC-nClAP were more effective to transform the F-exc and F-red of Pb compared with the ClAP (Fig. 5b). And it can be easily found that BC can promote the transformation of Pb from F-exc, F-red to F-oxi while it did not possess a good efficiency to transfer Pb from F-oxi to F-res (Fig. 5a). The BC-nClAP possessed a higher efficiency than others which can promote the transformation of F-exc, F-red and F-oxi to F-res (Fig. 5).

Previous study has pointed out that the Pb might be immobilized into chlor-pyromorphite by precipitation effect, which was a mineral structure substance with a low K_{sp} (10^{-84.4}); for ClAP and BC-nClAP, which contained phosphate (PO₄³⁻), the immobilization of Pb may be induced by the effect of PO₄³⁻ and it has been proved that phosphate has a brilliant efficiency for *in situ* remediation of Pb contaminated sediment [23]. However, the main reaction of BC to contaminants is adsorption due to its large specific surface area, porous structure and active functional groups, so it only has higher transformation efficiency than ClAP in F-exc and F-red. Due to the combined action of biochar and phosphate, BC-nClAP achieved better remediation efficiency than BC and ClAP.

From Fig. 5, it was demonstrated that the percentage of F-res increased from 20.2% to 40.1% in BC treated sediment and from 22.1% to 42.3% in ClAP treated sediment, but increasing from 29.2% to 94.1% in BC-nClAP treated sediment during 1d to 30d. The remediation efficiency of BC-nClAP was twice than the single use of BC or ClAP which indicated that BC-nClAP possessed best efficiency on Pb immobilization. Based on the ClAP remediation mechanism, the addition of biochar brought an unexpected remediation effects. For BC-nClAP, compared with pristine biochar (BC), after the introduction of chlorapatite, the amount of oxygen-containing functional groups (such as carboxylate, -COOH; and hydroxyl, -OH) may increase on the surface of the biochar. The improvement of functional groups may provide more available bonding sites for heavy metals. And these functional groups

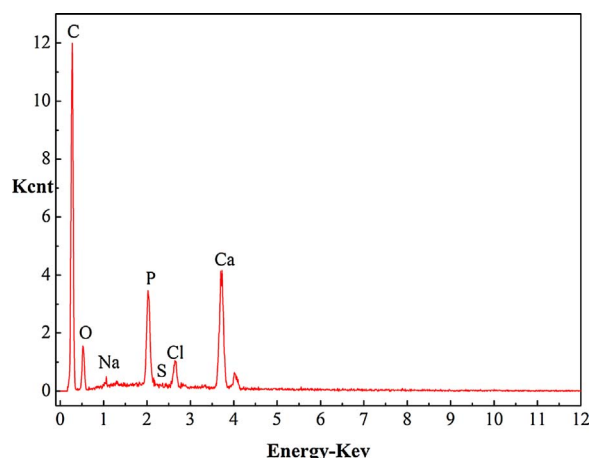


Fig. 3. EDS spectrum of the BC-nClAP.

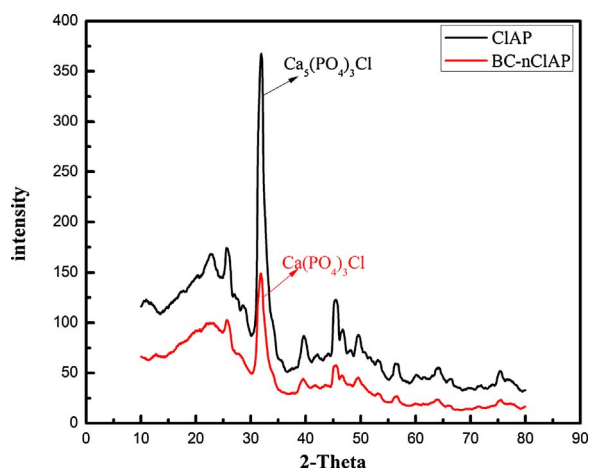


Fig. 4. XRD patterns of the CIAP and BC-nCIAP, the main characteristic peak is $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$.

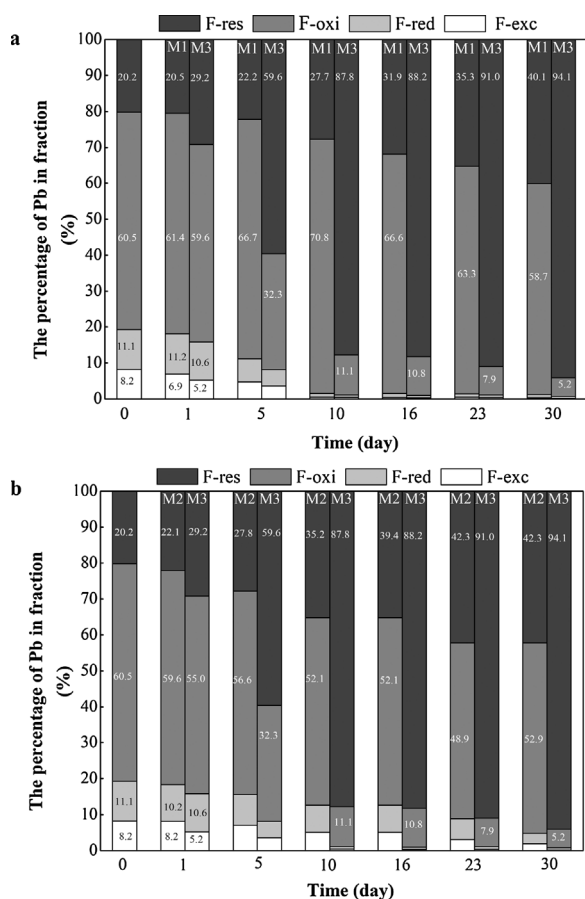


Fig. 5. The percentage of each chemical speciation (F-exc, F-red, F-oxi and F-res) of Pb in BC (M1), BC-nCIAP (M3) (a) and CIAP (M2), BC-nCIAP (M3) (b) treated sediment during 30 days. Day 0 represents the level of untreated sediment.

might strengthen the interactions between biochar and heavy metals by forming surface complexes, cation-p bonding, electrostatic attraction and ion-exchange, which contribute to the higher remediation efficiency of Pb [43].

According to the previous researches, they have pointed out that biochar can promote precipitation of Pb to $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ and $\beta\text{-Pb}_9(\text{PO}_4)_6$ under the conditions of rich phosphates and carbonates, respectively [44]; at the same time, phosphate ions carried by BC-nCIAP can directly absorb heavy metal ions in sediments by precipitation, so the combination of BC and CIAP obtained a better remediation

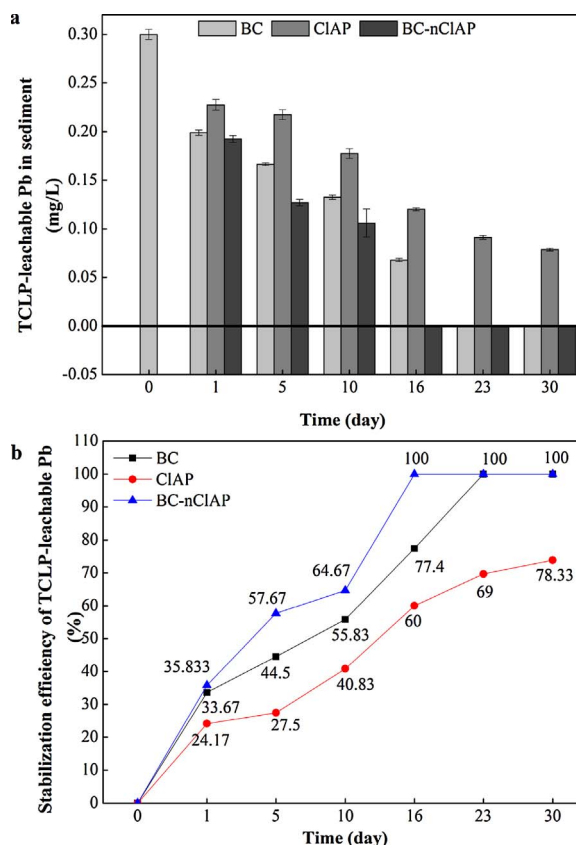


Fig. 6. The TCLP-leachable Pb fraction in BC, CIAP and BC-nCIAP treated sediment (a) and the stabilization efficiency of TCLP-leachable Pb in BC, CIAP and BC-nCIAP treated sediment (b) during 30 days of treatment, respectively. The error bars represent the standard deviation of the means (n = 3) and day 0 represents the level of untreated sediment.

efficiency. In a conclusion, the application of BC-nCIAP can promote the precipitation of Pb and improve the immobilization efficiency of Pb.

3.2.2. TCLP leachability of Pb

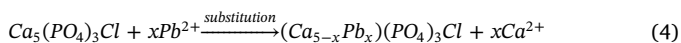
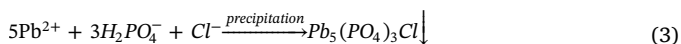
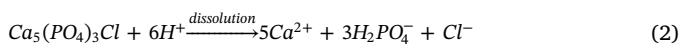
The TCLP method was used to evaluate whether contaminated soils or solid wastes are to be classified as hazardous wastes [45,46]. In this paper, it was used to assess the leaching toxicity of Pb in sediment. As we can see, Fig. 6a and b showed the change of TCLP-leachable Pb and its stabilization efficiency in the BC, CIAP and BC-nCIAP treated sediment samples, respectively.

The critical value of TCLP-leachable Pb concentrations for all the firing range soils in the United States Environmental Protection Agency (USEPA) hazardous waste was 5 mg/L [39]. Although we can see (Fig. 6a) that the TCLP-leachable Pb in the original sediment was 0.30 mg/L, which was lower than USEPA's critical value (5 mg/L), it still had potential threat to the organisms. The TCLP-leachable Pb concentrations were sharply reduced from 0.30 mg/L to 0 mg/L in the BC and BC-nCIAP treated sediments (Fig. 6a). It was found that the stabilization efficiency of TCLP-leachable Pb have reached to 100% when they were treated for 16 days in BC-nCIAP treated samples and 23 days in BC treated samples. However, the TCLP-leachable Pb of CIAP treated samples was only reduced to 78.33% after 30 days of treatment in Fig. 6b. Thus it can be seen that the time-dependent effect appeared in Fig. 5 could also be found in the change of TCLP-leachable Pb in Fig. 6. BC-nCIAP not only showed a better Pb-immobilization ability than BC and CIAP, but also presented a higher stabilization efficiency of TCLP-leachable Pb than BC and CIAP.

The BC showed the higher stabilization efficiency of TCLP-leachable Pb than CIAP (Fig. 6b). It was due to the properties of BC which had large specific surface area, porous structure and active functional

groups, and also can promote the formation of insoluble phosphate-Pb compounds (Section 3.2.1). Consequently, BC-nClAP existed both the properties of BC and ClAP, thus resulted in the highest stabilization efficiency of TCLP-leachable Pb. When the labile fraction of Pb reached the phosphate, it can be transformed into strongly bound phosphate-Pb fraction (pyromorphite) [47].

According to the record of a lot of papers, some direct evidence for pyromorphite formation in phosphate remediation soils have detected [26,48]. The mechanisms are showed in the below equations:



The equations above were not only the mechanism of the decrease of TCLP-leachable Pb but also the increase of F-res mentioned in Section 3.2.1 [49,50]. The dissolution of $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ and the precipitation of $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ which were the main mechanism for Pb immobilization in sediment were shown in Eq. (2) and (3). And the Eq. (4) showed another mechanism for the $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ formation [50]. It was the substitution (ion exchange) effect that the Pb (II) is substituted for Ca (II) in the chlorapatite structure, then the $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ is formed. Therefore, because of the combination action of biochar and phosphate (ClAP), BC-nClAP achieved a high efficiency for the change of TCLP-leachable Pb and chemical speciation of Pb.

3.3. Change of available phosphorus (AP)

Based on existing research, using phosphate materials to immobilize heavy metals have achieved a well effect, but it also led to a potential threaten to environment such as eutrophication [51].

Previous studies reported that high addition of the phosphate may induce a high concentration of excessive phosphorus [18]. The contents of AP in the BC, ClAP and BC-nClAP treated samples were presented in Fig. 7. We observed that the contents of AP in the BC, ClAP and BC-nClAP treated samples were decreased in the order of: ClAP > BC-nClAP > BC. More effective groups (PO_4^{3-}) can be released to immobilize Pb in the sediment with the increasing addition of ClAP. As shown in Fig. 7, the content of AP was increased before 16 days after the addition of ClAP, which can be explained primarily by the dissolution mechanism of $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ (Eq. (2)); then the content of AP presented a decrease tendency after 16 days which can be connected to the increase of F4 (Fig. 5, mentioned in Section 3.2.1) because of the precipitation of $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ (Eq. (3) and (4)). So the content of AP might be related to the Pb immobilization process in treated sediment samples.

However, it can also be observed from Fig. 7 that the content of AP in BC-nClAP treated samples was obviously lower than ClAP treated samples which seemed that the ClAP with the high content of AP can afford more PO_4^{3-} to immobilize Pb. Nevertheless, it has been confirmed from Figs. 5 and 6 that the BC-nClAP showed a higher efficiency in immobilizing Pb and reducing the TCLP-leachable Pb in the sediment than ClAP. The reason of the result can be explained by follows: firstly, the biochar in BC-nClAP can reduce the agglomeration of ClAP and improve the dispersity in the sediment. So BC-nClAP can be delivered more easily to the contaminated sediment to afford PO_4^{3-} for the Pb immobilization, some of PO_4^{3-} were transformed into phosphate-Pb compounds [36,52]; secondly, the phosphorus which released by ClAP was not all used to afford effective groups such as PO_4^{3-} to immobilize Pb, some of which cannot be used effectively and turned into excessive phosphorus. As we all know, biochar presented strong adsorption properties for variety of contaminants and both available phosphorus and Pb in our study can be adsorbed by it (Fig. 5 and 8). Therefore, in consideration of the limited adsorption sites on biochar, there might be a competitive adsorption between phosphorus and Pb on BC-nClAP.

However, according to the BCR results of BC and BC-nClAP treated samples, the biochar adsorbed Pb and phosphorus could react with each other to form a more stable fraction (F-res) of Pb with the introduction of chlorapatite even there is a competitive adsorption between them. Biochar has a larger surface area and rich functional groups which can afford adsorption sites for phosphate ions reacting physical deposition on the surface of biochar [51,53]. Therefore, due to the characteristics of biochar, BC-nClAP not only have a high efficiency for Pb immobilization but also accelerated the depletion of AP. Thus the BC-nClAP may be a desirable remediation material since it has a higher efficiency for Pb immobilization than ClAP and it can also enhance the effectiveness of PO_4^{3-} by accelerating the depletion of AP. The phosphate applications may result in eutrophication, but the application of BC-nClAP would not bring the same problems.

3.4. Change of organic matter (OM)

The OM is one of the most significant scavengers for metals in sediments [54]. A number of researches have certified that OM content can not only control the binding of heavy metals to sediments but also reduce bioavailability and toxicity of heavy metals [55–57]. Previous researches reported biochar can increase CEC, pH and OM in soils [41], but in our study the CEC and pH were not changed obviously (Fig. S2 and Fig. S3) while OM was greatly affected by the addition of amendments (Fig. 8). As we can see in Fig. 8, the original content of OM was 58.94 g/kg and the content of OM was increased with the addition of BC, ClAP, and BC-nClAP. An interesting phenomenon can be found that the comparison of the content of OM in treated samples was increased with the order as: BC-nClAP > ClAP > BC. In addition, there was almost no obvious regularity between identical materials in the remediation time.

It has been found that a series of low-molecular-weight organic acids, including formic, citric, acetic, oxalic, and malic acids, can be discovered in soils due to the decomposition of organic matter and microbial metabolites [58]. Previous studies pointed out that organic acids can promote the release of phosphate from low and medium reactive phosphate rock [59].

As shown in Fig. 8, the content of OM in BC-nClAP treated samples was more than other two materials which may connect to the immobilization of Pb and the reduction of the TCLP-leachable Pb (mentioned in Sections 3.2.1 and 3.2.2). BC-nClAP also had a higher efficiency in Pb immobilization and TCLP-leachable Pb reduction than BC and ClAP. The reason might be concluded by the change of OM: Based on researches above, organic matters can be supposed that the organic acids can induce the release of phosphate from phosphate materials and then promote the immobilization of Pb through precipitation in contaminated sediments. BC-nClAP had plenty of OM which can bring

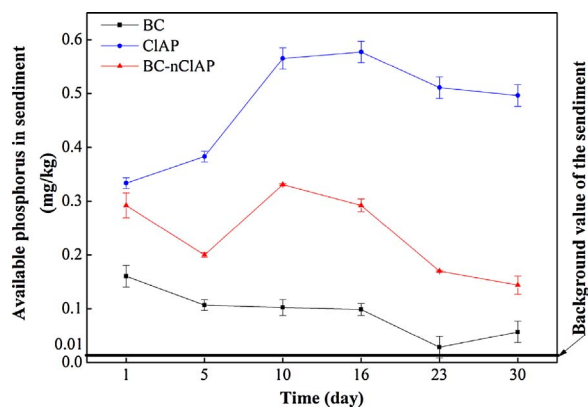


Fig. 7. Available phosphorus in BC, ClAP and BC-nClAP treated sediment during 30 days of treatment, respectively. The error bars represent the standard deviation of the means ($n = 3$) and the line of the background value represents the level of untreated sediment.

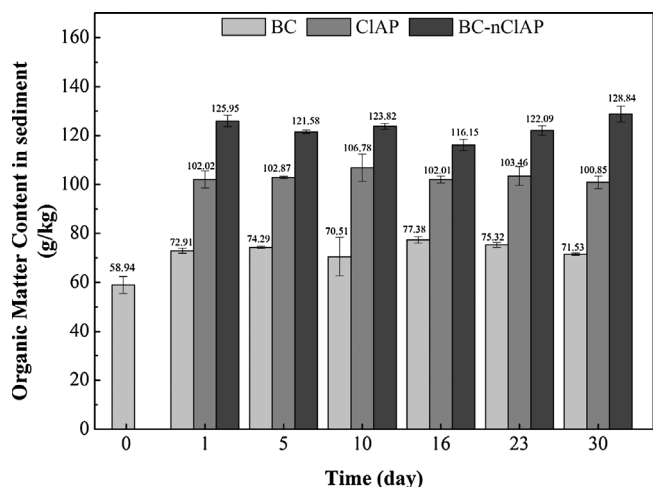


Fig. 8. The change of organic matter in BC, CIAP and BC-nCIAP treated sediment during 30 days of treatment, respectively. The error bars represent the standard deviation of the means ($n = 3$) and day 0 represents the level of untreated sediment.

plenty of organic acids to promote the dissolution of phosphate to sediments to immobilize Pb due to plenty of OM in biochar. So the BC-nCIAP can achieve a better effect on immobilizing Pb and reducing the toxicity of Pb.

Consequently, the result demonstrated that the immobilization efficiency of Pb in the sediment was increased and the toxicity of TCLP-leachable Pb was decreased with the increasing contents of OM, which was consistent with our findings in Sections 3.2.1 and 3.2.2. It was to say that the organic acids which decomposed by OM may also be an important mechanism involved in the Pb immobilization in the sediment and it is worth exploring in the further.

4. Conclusions

In this present study, BC-nCIAP, a novel class of composite materials was synthesized to immobilize Pb in contaminated sediment in Xiawangang River. The materials were characterized by SEM, BET, XRD and EDS, which demonstrated that CIAP was dispersed on the surface or within pores of biochar. These results confirmed BC-nCIAP was successfully synthesized. Meanwhile, the experiments showed that BC, CIAP, and BC-nCIAP all can transfer Pb from labile fraction to stable fraction in contaminated sediment during 30 days remediation and reduced the mobility and biotoxicity of Pb in sediment. With the supported of biochar, BC-nCIAP can not only perform better in Pb immobilization and TCLP-leachable Pb reduction than CIAP, but also decrease the content of excessive AP into the sediment when compared with CIAP. Thus it can immensely reduce the eutrophication risk which may induce by the application of phosphate materials. The dissolution-precipitation mechanism in Pb immobilization was involved with the increase of AP in BC, CIAP and BC-nCIAP treated sediment samples. In addition, the OM in BC-nCIAP treated sediments was more than two other materials and it demonstrated that the addition of biochar in CIAP brought a lot of organic matters. The organic acids decomposed by organic matters might play an important role in mechanism of Pb immobilization in sediment. Therefore, the application of BC-nCIAP was more feasible for Pb immobilization in contaminated sediment. Biochar-supported nanocomposites have become an important process for expanding the environmental applications of biochar and nanotechnology. We should get insight into choosing appropriate feedstocks with suitable composition and optimizing production conditions to produce more biochar-supported nanocomposites with higher immobilization ability for heavy metals and more other specific contaminants.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jhazmat.2018.01.024>.

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