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# Synthesis and evaluation of a new class of stabilized nano-chlorapatite for Pb immobilization in sediment



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#### h i g h l i g h t s

#### g r a p h i c a l a b s t r a c t

- SDS-nClAP was synthesized using SDS within 40.4 nm.
- The SDS-nClAP could effectively transform Pb labile Pb to stable fraction with a maximum increase of 38.3%.
- The SDS-nClAP could reduce the TCLP-leachable Pb from 0.30 to 0 mg/L after 45-d treatment.
- Dissolution-precipitation process may be the main mechanism.



a.b: natural processes: a<sub>1</sub>: remediation effect of SDS-nClAP: b<sub>1</sub>: remediation effect of ClAP

## a r t i c l e i n f o

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### A B S T R A C T

During the past years, efforts have been made to deal with the Pb contaminated sediment in Xiawangang River in Hunan province, China, but it remains a serious problem since the smelting pollutants were accumulated. According to previous studies, phosphate showed an effective ability to transfer labile Pb to pyromorphite  $(Pb_5(PO_4)_3X, X=F, Cl, Br, OH)$  but its application was limited by its solubility and deliverability. Hence a new class of nano-chlorapatite was synthesized by using sodium dodecyl sulfate (SDS) as a stabilizer and characterized by TEM, FESEM, DLS, FTIR, and EDAX. Results demonstrated thatthe SDS stabilized nano-chlorapatite (SDS-nClAP) was in spherical or spheroidal shape with a hydrodynamic diameter of 40.4 nm. Experimental data suggested that SDS-nClAP was effective in transforming labile Pb to stable fraction with a maximum increase of 38.3%, also the reduction of TCLP-leachable Pb from 0.30 to 0 mg/L after 45-d treatment. The increase of available phosphorus in both SDS-nClAP and ClAP treated sediment samples verified dissolution-precipitation mechanism involved in Pb immobilization. Additionally, the increment of organic matter in 10:1 treated samples was approximately 5-fold than that in 2:1 treated samples, which revealed that the micro-organisms may play an important role in it. © 2016 Elsevier B.V. All rights reserved.

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#### **1. Introduction**

It is well-known that sediment plays an important role in the transportation and chemical-speciation-transformation of heavy metals since it is the largest container and sources of metals in the aquatic ecosystem [\[1,2\].](#page--1-0) The sediment from lakes, harbors or rivers which located in the industrial areas, especially the metal smelter, received the most of industrial wastewater containing lots of heavy metals, leading to seriously heavy metal pollution in sediment [\[3\].](#page--1-0) Once the heavy metals are exposed to the organisms, the detrimental effects to the plants, microbes, animals and humans should not be neglected  $[4-12]$ . Thus it is necessary to find an effective method to remedy the polluted sediment  $[13-15]$ . Accordingly, the main factor we need to take into consideration is the chemical speciation of heavy metals which greatly associates with the transportation and mobilization of the heavy metals in sediment [\[16\]](#page--1-0) while the total content of heavy metals in sediment could not give any effective information about the physical and chemical behaviors of the heavy metals in most cases [\[3\].](#page--1-0) BCR (European Community Bureau of Reference) sequential extraction method divides the heavy metal into four speciations: acid soluble/exchangeable fraction (F1) and reducible fraction (F2), both of which can be easily leached into environment and result in a direct damage to the organisms [\[2\];](#page--1-0) oxidizable fraction (F3), which can be transformed into F1 and F2 with the change of redox potential and pH, showing a potential eco-toxicity to the organisms  $[17]$ ; the last is the residual fraction (F4) which is universally accepted as the most stable fraction and almost unreactive under a wide range of natural conditions [1,18]

Different approaches used in dealing with contaminated sediments can be divided into ex situ and in situ methods in general which mostly depend on the characteristics of sediments [\[19\].](#page--1-0) Phosphate amendments have been widely recognized as a lowcost, effective and non-disruptive in situ remediation method for heavy metal polluted solid wastes. And the phosphate has a perfect immobilized efficiency in Cu(II), Zn(II), and Cd(II), especially the Pb(II), which can be transferred to the most strongly bound Pb fraction presented as pyromorphite  $(Pb_5(PO_4)_3X, X=F, Cl, Br, OH)$ with the remediation of phosphates [\[20–23\].](#page--1-0) In previous studies, particulate phosphate and soluble phosphate salts were commonly used in metal immobilization  $[24]$ . The soluble phosphate salts can dissolve easily in sediment-solution with a high mobility and they could supply more effective phosphorus (P) for metal immobilization [\[25\],](#page--1-0) but it may greatly increase the environmental risk of eutrophication by releasing excessive P. On the other hand, even the fine-ground particulate phosphates are hardly delivered to the contaminated zone in sediment due to its large size and lower solubility, which is unfavourable for the in situ remediation [\[22\].](#page--1-0) Thus it is urgent to investigate a new class of phosphate for the sediment remediation.

Based on the previous studies of Liu and Zhao [\[24,26,27\],](#page--1-0) a new class of nano-chlorapatite was synthesized in this study by using sodiumdodecyl sulfate (SDS, an anionic surfactant with the formula  $CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>OSO<sub>3</sub>Na$ ) as a stabilizer and characterized by dynamic light scattering (DLS), transmission electron microscopy (TEM), field emission scanning electron microscope (FESEM), fourier transform infrared spectrometry (FTIR) and energy dispersive X-ray (EDAX). In order to investigate the Pb immobilization effect of the synthesized nano-chlorapatite on the polluted sediment, the leachable Pb fraction and the chemical speciation of Pb were detected in the experiment. Moreover, the available phosphates and organic matter were also observed in this research for analyzing the possible interaction mechanisms between the nano-particles and the sediment [\[28–30\].](#page--1-0)

#### **2. Materials and methods**

All the chemicals used in this experiment were of analytical or higher grade. All the containers and equipments were washed extensively with ultrapure water from an Ultra-pure Water System and all the solutions were prepared with the ultrapure water. The experiment was conducted in triplicate and the results were expressed as mean  $\pm$  standard deviation.

#### 2.1. Synthesis and characterization of SDS-nClAP

SDS stabilized chlorapatite nanoparticles (SDS-nClAP) was synthesized in this study by following the steps below: Firstly, dissolved the SDS, CaCl<sub>2</sub> $\cdot$ 2H<sub>2</sub>O and Na<sub>3</sub>PO<sub>4</sub> $\cdot$ 12H<sub>2</sub>O into the ultrapure water to achieve the solutions of  $1\%$  (w/w) SDS, 26.8 mM Ca<sup>2+</sup> and 16 mM  $PO<sub>4</sub><sup>3-</sup>$ , respectively. Then under the constantly mixing (magnetic stirrer with a Teflon-coated stir bar) at 1000 r/min, 12.5 mL of 26.8 mM Ca<sup>2+</sup> were added into 25 mL 1% (w/w) SDS solution using an acid burette at a steady speed of 5 ∼ 8 drops per minute. After stiring for 12 h, another 12.5 mL of 16.0 mM  $PO<sub>4</sub>$ <sup>3–</sup> were added into the mixture dropwise by the acid burette (5 ∼ 8 drops per minute) with constantly mixing at 1500 r/min. To give a visually comparison between the chlorapatite particles (ClAP) and SDS-nClAP, a ClAP suspension start with 25 mL ultrapure water instead of 25 mL 1% (w/w) SDS solution was prepared with other conditions unchanged. For the completely formation of the SDSnClAP, the mixture was continued stirred for 12 h at 1500 r/min after the titration reached the end. Then an amount of 50 mM HCl were used to make the final pH of the two suspensions to 6.0. The details were summarized in laboratory flowchart shown in [Fig.](#page--1-0) 1. The molar ratio of Ca<sup>2+</sup> to PO<sub>4</sub><sup>3–</sup> was chosen according to the chemical formula of ClAP represented as  $Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl$ , which generated through the following equation [\[24\]:](#page--1-0)

$$
5Ca^{2+} + 3PO_4^{3-} + Cl^- \to Ca_5(PO_4)_3Cl \downarrow
$$
 (1)

The hydrodynamic diameters of synthesized SDS-nClAP were characterized by DLS. The TEM samples were prepared by placing a drop of the SDS-nClAP suspension on a carbon-coated copper grid and dried at 28 $\degree$ C for 24 h, then the TEM images were taken by a JEM-3010 (JEOL, Japan) at 120 kV to observe the cross section structure of the material. For analyzing the surface morphology, the freeze-dried material was placed on a piece of double coated carbon conductive tape and sprayed by gold for several seconds, then FESEM was conducted by a JSM-6700 (JEOL, Japan) along with an EDAX attachment. The functional groups on the surface of SDSnClAP were analyzed by the KBr pellet method using a Shimadzu FTIR spectrophotometer (IRAffinity-1) at spectral range varying from 4000 to 400 cm<sup>-1</sup>.

#### 2.2. Sample collection and preparation

The sediment samples were collected from Xiawangang River in Zhuzhou, Hunan province in China. All the sediment samples were tiled on a cardboard, dry naturally for  $5 \sim 7$  d and then sieved through a 2 mm nylon sieve to remove the coarse debris. After this, the dried sediment was placed in a mortar, ground by a pestle then sieved to <150  $\mu$ m. All the samples were stored at 4 °C and keep dry before being used. Some properties of the sediment and the concentrations of heavy metals in sediment samples along with the national standard of heavy metals in China are listed in [Table](#page--1-0) 1. The Pb concentration in sediment samples (589.7  $\pm$  13.2 mg/kg) was more than 1.5 times of the national standard (350 mg/kg), showing a big threat to the organisms.

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