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Phase migration and transformation of uranium in mineralized immobilization by wasted bio-hydroxyapatite

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ABSTRACT

In this work, phase migration and transformation of uranium were investigated to understand the mechanism of uranium immobilization on bio-hydroxyapatite (Bio-HAP_{600}), in which waste fish bone was successfully converted into a novel Bio-HAP_{600} by calcination at 600 °C. The physicochemical properties of Bio-HAP_{600} were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and Fourier Transform Infrared Spectrometer (FTIR) analyses. Sorption behaviors were investigated by batch experiments in comparison with commercial nano HAP. Phase transformation and fate of uranium during sorption process were investigated by SEM mapping and XRD analysis. Results showed that sorption equilibrium of Bio-HAP_{600} was achieved within 10 min. The maximum uranium sorption capacity of 384.6 mg/g was comparable to commercial available Nano-HAP. Chemical mineralization played a dominant role in the retention of uranium on Bio-HAP. Sorption of U (VI) was highly dependent on the content of P, Ca and O. Formation of nano flake crystal of autunite ($Ca(UO_2)_2(PO_4)_2(H_2O)_6$) was ascribed as the transformation and fate of uranium mineralization, contributing to the favorable immobilization of uranium. The results indicate that calcination of fish bone leading to Bio-HAP can be a feasible way to produce efficient uranium adsorbent for immobilizing uranium through forming nano flake crystals of autunite.

1. Introduction

Activities associated with nuclear industry and uranium-mining produced numerous uranium contamination. Because of the high mobility and inevitable environmental risks, immobilization and retardation of uranium in the form of UO_2^{2+} has attracted substantial attention (Nekhunguni et al., 2017a).

Attempts had been made hitherto to address the above issues, such as reduction fixation through zero valent iron (Durazzo et al., 2017; Guo et al., 2017; Kong et al., 2016), ion exchange (Othman et al., 2017; Wang et al., 2017), coagulation precipitation (Singh et al., 2017), sorption (Humelnicu et al., 2010), electrodeposition (Lu et al., 2017), microorganism biosorption (Marsili et al., 2005, 2007), and so on. Nevertheless, reducing U(VI) into U(IV) precipitant show the possibility of being oxidized to U(VI) after being exposed to the air, which has the risk of secondary pollution due to the release of immobilized uranium (Farrell et al., 1999). Ion exchange resin is widely concerned for immobilizing U(VI), the immobilized efficiency is determined by exchange capacity (Bendiaf et al., 2017). Adsorption/sorption was also concerned since sorption process was widely regarded as one of the most efficient processes in environmental pollution remediation (Nekhunguni et al., 2017b). The key issue of sorption process is to concern the efficient, cost effective and environmental friendly materials.

To enhance the removing efficiency of uranium, modifying the surface characteristics of the materials by grafting functional groups was paid more attention (Anirudhan et al., 2009; Chen et al., 2016; Li et al., 2017a). Carboxyl, hydroxyl, amino and phosphoryl groups played important role in immobilizing uranium from

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aqueous solution by complexation. Phosphoryl, as an excellent ligand with lone electron pairs, could form stable complexes with many metal ions by producing strong complexation (Roden, 2007; Saxena and D'Souza, 2006). Especially, the phosphoryl group has strong complexation with uranyl ions because numerous electronic space orbits of U^{6+} make it become a good coordination with the centrosome, complex ability of phosphate ligand (Chen et al., 1999). Besides the artificial grafted functional materials, exploring phosphate minerals for immobilizing uranium has attracted interesting of researchers since the formed uranium solids has low solubility. Formation of uranyl phosphates could be observed in natural ores as well as contaminated sediments. Thus, immobilization of uranium by phosphate derived materials is prospective in future. However, the natural phosphate mineral is nonrenewable, the natural raw phosphate minerals were limited by their low sorption capacities (Chen et al., 2017).

Hydroxyapatite($Ca_{10}(PO_4)_6(OH)_2$, HAP) crystal was found in deposits of bone tissues and teeth as the main component of inorganic phase (Sadat-Shojai et al., 2013a), while a lot of fish bones were discharged in Guangzhou City because it is famous for aquatic food. In the past, these fish bones were discharged as kitchen waste, further disposal processes were required. Due to the viewpoint of sustainable development, conversion of wasted fish bone into HAP by calcination was attempted in recent years (Chakraborty and Roychowdhury, 2013; Goto and Sasaki, 2014; Venkatesan et al., 2015). Works concerned to the immobilization of uranium on recycled HAP could be considered to comply with the principle of environmental development and cleaner production process. The migration and transformation of uranium immobilized on HAP should be clearly investigated to understand the immobilization mechanism. The objective of this work was to investigate the immobilization behavior as well as migration and transformation of uranium onto grass carp bone derived HAP, which addressed the issues of uranium decontamination and waste reutilization, complying with the viewpoints of sustainable development and cleaner production process. Herein, the uranium immobilization behaviors were investigated by batch sorption experiments in comparison with commercial Nano-HAP. The immobilization mechanism and phase transformation were understood by phase and morphology transformation in assist of SEM mapping and XRD analysis.

2. Materials and methods

2.1. Materials

Freshwater grass carp bones were collected from a Chinese restaurant, and washed by deionized water at room temperature roughly for removing other residuals. Subsequently, the pretreated bones were vacuum-dried at 105 °C for 24 h to get rid of free water. The collected bones were stored by freezing at −4 °C for further process. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were analytical grade and purchased from Guangzhou Chemical Reagent Factory, China. All solutions were prepared with double deionized water. Stock solution of U (VI) (1000 mg/L) was prepared by dissolving appropriate amount of uranyl nitrate ($UO_2(NO3)_2 \cdot 6H_2O$) (GR), further adjusting the pH in solution to 3.

2.2. Preparation of Bio-HAP

Dried bones were calcined in muffle furnace at determined temperatures ranged from 200 to 900 °C for 3 h. Finally, the calcinated samples were smashed and sieved through 100–150 meshes. The prepared hydroxyapatite samples were named as Bio-HAP_T, where the letter "T" represented the calcined temperature.

2.3. Batch sorption experiments

Sorption experiments were conducted in a series of Erlenmeyer flasks. In each test, 0.1 g Bio-HAP_T was poured into 40 mL uranium solution to assure an adsorbent dosage of 0.25 g/L. The mixture was agitated in a digital thermostatic water bath oscillator (SHA-82A) at 303.15 k, where pH value was adjusted to 3.0 with 0.1 M HNO_3 and 0.1 M NaOH. And residual U (VI) in solution was measured by a UV-Fluorescence uranium analyzer at the certain time intervals after withdrawing the suspended particles. Specifically, the sorption amount (Q_t, mg/g) of U (VI) at t time could be calculated using Eq. (1):

$$Q_t = \frac{(C_0 - C_t)V}{m_p} \quad (1)$$

where C_0 and C_t are the residual concentration of U(VI) at initial and t time (min), respectively; m_p is the mass of the added adsorbent (g) and V represents the volume of the reaction solution (L).

2.4. Characterization and analytical methods

Surface texture and morphology of the solid phase transformation were examined by SEM (JEOLJSM-7001F, Japan). XRD analysis was collected with Cu Kα irradiation at 40 kV and 30 mA in the range of 5–80° using PANalytical PW3040/60 (Holland). Microtopography and microcomponent were conducted by SEM mapping (S-520/ISIS-300, Hitachi/Oxford, Japan) equipped with mapping analysis. Elemental analysis was investigated using an energy dispersive spectrometer (EDS, X-Max^N, Oxford, Japan). Thermogravimetric (TG) analysis of the Bio-HAP precursor was performed using Thermal analyzer (STA449F3, Netzsch, Germany). Functional groups were investigated using FTIR analysis (Bruker Tensor27, Germany). Specific surface area (S_{BET}) was determined by an auto-sorption system analyzer (ASAP, 2020, Micromeritics Instrument Corp) and calculated by Brunauer-Emmet-Teller equation.

The residual uranium concentration in aqueous was determined by using a WGJ-III UV-Fluorescence uranium analyzer (Hangzhou Daji Photoelectric Instrument Co. Ltd). For each measurement, 5 mL uranium-bearing sample was transferred into the test cell firstly. 500 μL fluorescence-enhancing agents (BRIUG 201), which can complex with the free UO_2^{2+} in the mixed solution systems to generate a high fluorescent intensity, were added into the sample cell mentioned above. After that, about 5 μL uranium standard solution in a concentration of 1 μg/mL was injected into the above solution by microsyringe. The absorbance was obtained, and the residual concentration was calculated from the previously standard calibration curves.

3. Results and discussion

3.1. Characterization of bio-hydroxyapatite

SEM is widely used for surface micro-morphology studies. As Goto and Sasaki (2014) previously reported, there was about 30–40% mass loss of fish bone, which resulted from the decomposition of organic compounds such as protein and fat during high-temperature calcined process. Hence, fish bone in this work was calcinated at diverse calcination temperatures firstly. Fig. 1 presented the micro-morphology of fish bone in the absence of calcination and incinerated at temperatures of 300 °C, 500 °C, 600 °C, 700 °C, and a contrastive commercial hydroxyapatite. Clearly, morphologies of these samples were highly temperature dependent. For the bones without calcination, visible bone fiber texture can be observed in Fig. 1a. When the calcination temperature