Poorly crystalline hydroxyapatite: A novel adsorbent for enhanced fulvic acid removal from aqueous solution

Wei Wei [a,b,c], Lei Yang [a], Wenhui Zhong [a], Jing Cui [a], Zhenggui Wei [a,b,c,*]

[a] Department of Environmental Science and Engineering, Nanjing Normal University, Nanjing 210023, China
[b] Jiangsu Provincial Key Laboratory of Materials Cycling and Pollution Control, Nanjing Normal University, Nanjing 210023, China
[c] Jiangsu Center for Collaborative Innovation in Geographical Information Resource Development and Application, Nanjing Normal University, Nanjing 210023, China

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ABSTRACT

In this study, poorly crystalline hydroxyapatite (HAP) was developed as an efficient adsorbent for the removal of fulvic acid (FA) from aqueous solution. Surface functionality, crystallinity, and morphology of the synthetic adsorbent were studied by Fourier-transformation infrared (FT-IR) spectroscopy, powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). The effects of various parameters such as crystallinity of adsorbent, contact time, adsorbent dosage, pH, initial adsorbate concentration, temperature, ionic strength and the presence of alkaline earth metal ions on FA adsorption were investigated. Results indicated that the nanosized HAP calcined at lower temperature was poorly crystalline ($X_c = 0.23$) and had better adsorption capacity for FA than those ($X_c = 0.52, 0.86$) calcined at higher temperature. FA removal was increased with increases of adsorbent dosage, temperature, ionic strength and the presence of alkali earth metal ions, but decreased as the pH increased. Kinetic studies showed that pseudo-second-order kinetic model better described the adsorption process. Equilibrium data were best described by Sips models, and the estimated maximum adsorption capacity of poorly crystalline HAP was 90.20 mg/g at 318 K, displaying higher efficiency for FA removal than previously reported adsorbents. FT-IR results revealed that FA adsorption over the adsorbent could be attributed to the surface complexation between the oxygen atom of functional groups of FA and calcium ions of HAP. Regeneration studies indicated that HAP could be recyclable for a long term. Findings of the present work highlight the potential for using poorly crystalline HAP nanoparticles as an effective and recyclable adsorbent for FA removal from aqueous solution.

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1. Introduction

Natural organic matter (NOM) is a mixture of chemically complex polyelectrolytes with varying molecular weights, produced mainly from the decomposition of plant and animal residues [1]. Humic substances (HS) such as humic acid (HA) and fulvic acid (FA) comprise the greatest proportion of NOM, about 70% of which in water is FA [2–5]. The presence of excessive FA in drinking water production can cause serious environmental and health problems. For instance, FA and other HS not only cause color, odor and taste problems but also lead to biological instability of drinking water in distribution system [6,7]. Furthermore, the presence of dissolved macromolecular organic matter like FA and HA may reduce the effectiveness of the water treatment processes [6]. More seriously, FA has been shown to be especially reactive with a variety of disinfectants used for the purification of drinking water forming disinfection by-products (DBPs) such as trihalomethanes (THMs), which are known or suspected human carcinogens [8–10]. Therefore, it is of great importance to remove FA from drinking water.

Various methods such as coagulation/flocculation [11], membrane filtration [12], ion exchange [13], advanced oxidation [14], and adsorption [15], have been developed to remove FA from drinking water. Among them, adsorption is considered as an effective process due to its simplicity of design, ease of operation and high efficiency. Until now, numerous adsorbents, such as activated carbon [15–17], modified vermiculite [18], tobermorite [19], gibbsite and imogolite [5], modified zeolite [6], goethite [9,20], green algae [21], *Bacillus subtilis* and activated sludge [22], chitosan hydrogel beads [23], Mg/Al layered double hydroxides [24], SiO2 particles [25], and carbon nanotubes [26–28] have been reported for FA

removal. However, there are several problems associated with their use, for example, high cost, low adsorption capacity, or narrow available pH range. So, it is very necessary and significant to explore new adsorbents with low cost, high adsorption capacity, and wide applicability to remove FA from water.

Recently, nanosized materials represent a promising application in a variety of fields due to their high surface area, reactivity and their ability to become dispersed in aqueous solution [29]. Nanosized materials usually display higher surface area and adsorption ability than the traditional materials. In these regards, nanosized materials are one of the most promising candidates for adsorbents to remove FA, HA and other pollutants from aqueous solution. For instance, nanoporous carbon materials [30], nanoscale zero-valent iron [31], iron oxide magnetic nanoparticles [32], Mg/Al layered double hydroxides-Fe$_3$O$_4$ nanocomposites [33], and magnetic chitosan nanoparticle [34] have been applied for effective removal of HA from aqueous solution. However, only a few studies have been conducted to investigate the removal of FA using nanosized materials [25–28].

Nanosized hydroxyapatite [Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, HAP] exhibits excellent biocompatibility and adsorption properties, and has been considered as an environmental benign functional material [35]. HAP has attracted a great deal of attention due to its high capacity for the removal of pollutants, low water solubility, high stability under reducing and oxidizing conditions, availability and low cost [36]. It has been widely used as adsorbent for the adsorption and separation of biomolecules [37–39], and for the removal of various pollutants from contaminated soil and water [40–42]. The environmental risk of nanosized HAP itself can be neglected because it has displayed good cytocompatibility [43]. Moreover, nanosized HAP has also been used for the adsorption of oxalic acid, fluoride, and nitrobenzene in our previous work [29,37,40]. However, little knowledge is available about the adsorption behaviors and influencing factors of FA onto nanosized HAP, and information concerning the interaction mechanisms of FA with poorly crystalline HAP is even more deficient.

In this study, the poorly crystalline nanosized HAP was synthesized and used as a novel adsorbent for the removal of FA from aqueous solution. The nanosized HAP was characterized by Fourier-transformation infrared (FT-IR) spectroscopy, powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). The adsorption of FA on nanosized HAP as a function of adsorbent crystallinity, contact time, adsorbent dosage, pH, initial adsorbate concentration, temperature, ionic strength and the presence of alkaline earth metal ions was investigated by using batch experiments. The possible mechanisms for FA adsorption onto nanosized HAP were proposed.

2. Materials and methods

2.1. Reagents and chemicals

For the preparation of nanosized HAP, Ca(NO$_3$)$_2$·4H$_2$O, NH$_4$H$_2$PO$_4$, and NH$_3$·H$_2$O were purchased from Shanghai Guoyao Chemical Co. Ltd. (China). FA was obtained as a commercial reagent-grade solid from Sigma (USA), and used without any further purification. All the other chemicals used were of analytical grade. Deionized water was used throughout the study.

2.2. Preparation and characterization of adsorbent

The nanosized HAP adsorbent was prepared by a chemical precipitation method as described in our previous paper [44]. However, a brief description is given below. Ca(NO$_3$)$_2$·4H$_2$O was dissolved in distilled water to form 0.5 mol/L solution, into which

NH$_4$H$_2$PO$_4$ was added with a Ca/P molar ratio of 1.667, during the addition, the pH of the suspension was maintained at 11.0 using ammonia solution. After the complete addition, the suspension was further stirred for 24 h and centrifuged at 4000 rpm for 10 min. Then the precipitated HAP was washed with deionized water till the pH turned to 7.0. The resultant powders were dried at 80 °C for 24 h, and then calcined at 100 (noted HAP-100), 400 (noted HAP-400) and 800 °C (noted HAP-800) for 2 h, respectively. The final products calcined at different temperatures were used as the adsorbents for FA.

The phase purity and crystallinity of the prepared HAP were determined by powder X-ray diffraction (XRD) using Cu Kα (λ = 1.5405 Å) radiation on a Rigaku D/max-IIIB X-ray powder diffractometer. The HAP samples before and after the adsorption of FA were analyzed by Fourier transform infrared (FT-IR) spectroscopy (Tensor 27, Bruker, Germany) as KBr pellets to confirm the phase formation. The morphology and size of the synthetic nanosized HAP were characterized by a Hitachi Model H-7650 transmission electron microscope (TEM). The specific surface area of nanosized HAP was determined by nitrogen adsorption at 77 K (Micromeritics ASAP 2010). Surface area was calculated from adsorption data using BET equation. And batch equilibration technique was applied to determine pH$_{PZC}$ (point of zero charge) of nanosized HAP.

2.3. Adsorption experiments

All adsorption experiments were conducted in triplicates and the results were reported as average. Adsorption experiments were conducted at various contact time, pH values, initial FA concentrations and temperatures in batch mode. When the effect of pH was investigated, the solution pH was adjusted using 0.1 mol/L HNO$_3$ or NaOH solutions. Adsorption experiments were conducted in conical flasks containing 100 mL of FA solution and 0.2 g of nanosized HAP at specified temperature. The flasks were shaken on a shaker equipped with thermostat at 200 rpm. The remaining concentration of FA was no longer changed with contact time when the adsorption process reached equilibrium, after which the solutions were filtered and the residual FA in the supernatant was then determined using a UV-2450 spectrophotometer (Shimadzu, Japan) at λ = 254 nm.

The removal efficiency of FA was calculated from the equation below:

$$\%\text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

The adsorption capacity of FA was calculated from the following mass balance equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where q_e (mg/g) is the equilibrium adsorption capacity; C_0 and C_e (mg/L) are the initial and equilibrium concentrations of FA in solution; V (L) is the volume of aqueous solution containing FA; and m (g) is the weight of adsorbent.

2.4. Desorption and regeneration

To determine the desorption behavior of FA loaded nanosized HAP, sodium hydroxide was used as the desorbing agent. Typically, 0.2 g nanosized HAP was added to 250 mL flask receiving 100 mL of 50 mg/L FA solution at pH 7.0, and the mixture was shaken in thermostatic shaker for 15 h. After achieving the adsorption equilibrium, FA loaded nanosized HAP was centrifuged and the residual FA concentration was detected spectrometrically. FA loaded nanosized HAP was redispensed in 2 mol/L NaOH solution and shaken