



## Enhanced arsenate removal performance of nanostructured goethite with high content of surface hydroxyl groups



Pei-Yun Wu, Yong Jia<sup>\*</sup>, Yin-Ping Jiang, Qun-Ying Zhang, Shuang-Sheng Zhou, Fang Fang, Dai-Yin Peng

Institute of Pharmaceutical Chemistry, Department of Pharmacy, Anhui University of Chinese Medicine, Anhui Academy of Chinese Medicine, Hefei 230031, China

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### ABSTRACT

Goethite ( $\alpha$ -FeOOH) with high content of surface hydroxyl groups was synthesized by using a simple sodium dodecyl sulfate (SDS) assisted solution method. The presence of SDS can increase the surface area and the contents of surface hydroxyl groups. The adsorption properties towards arsenate (As(V)) ions were investigated, including adsorption kinetics, adsorption isotherm, influences of pH and coexisting anions, and regeneration of the adsorbent. The maximal adsorption capacity was  $60.6 \text{ mg g}^{-1}$  at pH 7.0, which is about three times larger than the ones synthesized in pure water, and also is favorable compared to those reported in the literature using other adsorbents. The coexisting of phosphate and carbonate inhibited the As(V) removal especially at high concentrations. The as-prepared  $\alpha$ -FeOOH could be readily regenerated using NaOH solution and be repeatedly used in the field of water purification. In addition, the removal mechanism was revealed by X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy and the zeta potential study. The point of zero charge ( $\text{pH}_{\text{PZC}}$ ) of the  $\alpha$ -FeOOH is 6.35. At high solution pH, the ion-exchange between the surface hydroxyl groups and As(V) ions dominates in the adsorption of As(V). Around the  $\text{pH}_{\text{PZC}}$ , the hydrogen bonding also contributes to the As(V) removal. When the solution pH is lower than  $\text{pH}_{\text{PZC}}$ , the electrostatic attraction plays key roles in As(V) removal.

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### Introduction

Recently, the removal of arsenic from water has attracted great attention owing to its toxicity to human health [1]. Adsorption method has been proven to be a promising technology for water treatment because of its low cost and easy-to-operate. Nano metal oxides were very important adsorbents because of their remarkable advantages such as easy preparation and high efficient [2]. Among the metal oxides, iron oxides have attracted great interests owing to their effective, low cost, natural abundance and environmental safety [3–6]. The removal efficiency of the metal oxide adsorbents was greatly depended on their surface structures, because the removal mechanism was mainly the ion-exchange process based on the surface active groups, the electrostatic attraction and the hydrogen bonding between the surface active groups and the toxic arsenic ions in water. Besides the carbonate-like species [6,7] and sulfate ions [8], the surface hydroxyl groups are the widely reported ion-exchange groups. Thus, iron

oxyhydroxides, such as  $\alpha$ -FeOOH,  $\beta$ -FeOOH and  $\gamma$ -FeOOH have attracted great attention owing to their abundant hydroxyl groups, low cost and environmental safety [9–14]. Among them, owing to its easy preparation, good thermal stability and adsorption properties,  $\alpha$ -FeOOH presents an important potential application. However, the hydroxyl groups of  $\alpha$ -FeOOH can be divided into buck hydroxyl groups and surface hydroxyl groups [6,15–18]. The structural hydroxyl groups have almost no contributions to arsenic removal because the adsorption process can only take place on the surface of it [16–18]. So, the preparation of  $\alpha$ -FeOOH with large surface area will be in favor of the exposure of the hydroxyl groups on the surface, and for the improvement of the adsorption properties. Furthermore, it is also desirable to develop simple preparation method to increase the content of the surface hydroxyl groups. In addition, the complex synthesis method and high reaction temperature will increase the cost of the preparation as well as the water treatment.

Up to now, several methods have been reported for the synthesis of  $\alpha$ -FeOOH, such as hydrothermal route [6,10,19,20], reflux method [11,21], gas–liquid diffusion technique [22], hydrolysis combined with aging at high temperature [16,23], and directly room temperature hydrolysis method [9,24]. Among

<sup>\*</sup> Corresponding author. Tel.: +86 551 65169222; fax: +86 551 65169223.

E-mail address: [yjiaahedu@163.com](mailto:yjiaahedu@163.com) (Y. Jia).

them, the directly room temperature hydrolysis is the most simple and low cost method. However, the obtained  $\alpha$ -FeOOH synthesized in pure water by using this method were aggregated seriously [9,24], which was not in favor of the removal of toxic anions. In our previous work [9], we found that the presence of cetyltrimethylammonium bromide can slow down the growth rate of the products, avoid the congregation of the nanorods and increase the size of the products. More importantly, the content of the surface hydroxyl groups were increased which resulted in an enhanced adsorption properties towards toxic As(V) ions. However, the surface area was decreased compared with the ones synthesized in pure water, which was not in favor of the improvement of the adsorption properties. In addition, Lakshmipathiraj et al. reported the synthesis of  $\alpha$ -FeOOH by oxidation of ferrous carbonate precipitated from the double decomposition of ferrous sulfate doped with sodium dodecyl sulfate (SDS). But the influence of the SDS amount on the structure of the final products was not clear [25]. Herein, we report the synthesis of  $\alpha$ -FeOOH via directly oxidation of ferrous sulfate using SDS as surfactant. With the presence of SDS, the size of the nanorods was decreased to less than 100 nm, and the surface area of the products was  $293.2 \text{ m}^2 \text{ g}^{-1}$ . More importantly, the contents of the surface hydroxyl groups were increased greatly compared with the products synthesized in pure water. As a result, the obtained  $\alpha$ -FeOOH presents an excellent removal properties towards As(V) ions, which were attributed to the high content of the surface hydroxyl groups. The results bring forward an effective way to synthesis of  $\alpha$ -FeOOH adsorbent with high contents of surface hydroxyl groups, high surface area, and improved adsorption properties.

## Experimental

### Materials

All chemicals used were analytical grade and were purchased from Shanghai Chemical Reagents Company and used without further purification. The As(V) stock solution was prepared with de-ionized water using  $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$ . As(V) working solutions were freshly prepared by diluting As(V) stock solution with de-ionized water. The concentrations of arsenic species were given as elemental arsenic concentration in this work.

### Synthesis of $\alpha$ -FeOOH

In a typical synthesis protocol, 5.56 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was dissolved in 100 mL of SDS solution with a concentration of  $0.1 \text{ mol L}^{-1}$ . Then, 3.28 g of anhydrous  $\text{CH}_3\text{COONa}$  was added. The above solution was stirred vigorously for 3 h in air at room temperature. The final brown products were centrifuged and washed with de-ionized water and absolute ethanol several times, and then dried in an oven at  $60^\circ\text{C}$ . To study the roles of SDS, the control experiment without using SDS was performed in pure water at room temperature.

### Characterization

The as-prepared products were characterized by field emission scanning electron microscopy (SEM, FEI Sirion 200 FEG, operated at 10 kV), transmission electron microscopy (TEM, JEOL-2010, operated at 200 kV), X-ray diffraction (XRD, X'Pert ProMPD, Cu-K $\alpha$  radiation, wavelength  $1.5418 \text{ \AA}$ ), thermal gravimetric analysis (TGA, Pyris 1, heating rate  $10^\circ \text{ min}^{-1}$  in flow air), Fourier transform infrared spectroscopy (FTIR, Nicolet Analytical Instruments, NEXUS-870) and X-ray photoelectron spectroscopy (XPS, VG ESCALAB MKII spectrometer, Mg KR X-ray source, 1253.6 eV,

120 W) analyses. Nitrogen adsorption–desorption measurements for the products were performed using a Micromeritics ASAP 2020 M + C instrument with a degassing temperature of  $80^\circ\text{C}$ , and using Brunauer–Emmett–Teller (BET) calculations for surface area and Barret–Joyner–Halender (BJH) calculations for pore size distribution. Zetasizer Nano Series model ZEN 3600 (Malvern, UK) was employed to measure the isoelectric points of  $\alpha$ -FeOOH. These measurements were performed in 1 mM KCl.

### Batch adsorption and desorption experiments

Batch adsorption experiments were conducted to obtain the adsorption isotherm of the As(V) ions. The experiments were carried out in 20 mL glass vessel containing 10 mL of As(V) solution and 10 mg of adsorbent, and then the flask was shaken at 150 rpm in a shaker at  $25^\circ\text{C}$  for 12 h. The pH of the solutions was adjusted every 4 h with  $0.1 \text{ mol L}^{-1}$  HCl or/and NaOH solution to around  $\text{pH } 7.0 \pm 0.1$  during shaking process. After the adsorption, the adsorbent was separated from the solution by centrifugation, and the residual As(V) concentration in solution was determined by using an inductively coupled plasma atomic emission spectrometer (Jarrell–Ash model ICAP 9000). The residual adsorbents were centrifuged and soaked into  $1.0 \text{ mol L}^{-1}$  of NaOH solution for 12 h. Then, the solution was filtered, and the adsorbents were rinsed with de-ionized water until the filtrate was neutral. The obtained adsorbents were dried in the oven at  $60^\circ\text{C}$ . The method of testing the adsorption capability of the regenerated adsorbents was the same as the adsorption experiments above.

To explore the competitive effects of various coexisting ions (chloride ions, sulfate, nitrate, bicarbonate, carbonate and phosphate) on the removal of As(V) ions, 10 mL of  $20.82 \text{ mg L}^{-1}$  As(V) solutions, each containing three concentration levels ( $0.1$ ,  $1.0$  and  $10 \text{ mmol L}^{-1}$ ) of the coexisting ions and 10 mg of the adsorbent were shaken for 12 h at  $25^\circ\text{C}$ . The solution pH was adjusted to  $7.0 \pm 0.1$  by adding  $0.1 \text{ mol L}^{-1}$  HCl or/and NaOH solution. After the adsorption reached equilibrium, the adsorbent was separated from the solution by centrifugation, and the residual As(V) concentration in solution was analyzed to determine the As(V) concentrations.

Kinetics study experiment was carried out by adding 100 mg of  $\alpha$ -FeOOH into 150 mL glass vessels, containing 100 mL of  $5.21 \text{ mg L}^{-1}$  As(V) solution. The solution pH was adjusted to  $7.0 \pm 0.1$  by adding  $0.1 \text{ mol L}^{-1}$  HCl or/and NaOH solution. The suspension was placed into an air incubator at an agitation speed of  $150 \text{ rpm min}^{-1}$ . About 6 mL suspension was sampled using a pipette at different time intervals. After that the sample was centrifuged and analyzed to determine the As(V) concentrations. All samples used in our analysis were analyzed within 24 h after collection.

## Results and discussion

### Structure of $\alpha$ -FeOOH

The as-prepared product was characterized by XRD, and the results are shown in Fig. 1a. All diffraction peaks can be indexed to orthorhombic phase  $\alpha$ -FeOOH (JCPDS 81-0464). No other diffraction peaks were observed compared with the standard card shown in Fig. 1a. At the same time, the wide diffraction peaks suggests that poor crystalline quality of  $\alpha$ -FeOOH was obtained. The thermal stability of the obtained  $\alpha$ -FeOOH was also studied, and the results are shown in Fig. 1b. From the TGA and DTG curves, the first 9.83 wt % weigh loss bellow  $110.1^\circ\text{C}$  should be attributed to the detachment of the physically adsorbed water, which was much higher than the previous reported  $\alpha$ -FeOOH [9,19]. Furthermore, in the range of  $110.1$ – $500^\circ\text{C}$ , the total 11.27 wt% weight loss can be attributed to the hydrogen bonded water and the dehydration of

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