



# Adsorption and heterogeneous oxidation of arsenite on modified granular natural siderite: Characterization and behaviors



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## ABSTRACT

Although natural siderite has been investigated to remove both As(III) and As(V), it has relatively low adsorption rate and capacity. It is crucial to enhance its adsorption characteristics for As removal prior to being used in practical application. Modified granular natural siderite (MGNS) was fabricated through addition of organic binder, extrusion granulation and calcination, and evaluated for adsorption characteristics by means of batch and column tests. Results showed that MGNS had higher adsorption rate and capacity for As(III) in comparison with natural siderite. Arsenic(III) adsorption achieved equilibrium at 24 h, with adsorption capacity of 9.43 mg/g estimated from Langmuir isotherm at 25 °C. Column tests showed that there was less difference in total As loads in MGNS-packed filters for As(III)-spiked deionized water, As(III)-spiked tap water, and real-world high-As groundwater. The coexistence of anions had no significant effect on As adsorption in both batch and column experiments. Results of XRD, SEM and BET analysis indicated that MGNS, as an Fe(II)/(III) hybrid system, had a much larger specific surface area relative to the pristine natural siderite due to massive spherical aggregates attaching to the siderite matrix. XANES spectra showed that As(V) was the major species in the adsorbent after As(III) adsorption. Its proportion in total As slightly increased with the increase in contact time. Adsorption and heterogeneous oxidation of As(III) were believed to be the main mechanisms of As(III) removal by MGNS. This study suggested that MGNS is a potential adsorbent for effectively removing As from As-contaminated groundwater in filter application.

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## 1. Introduction

Due to its high toxicity and carcinogenicity, increasing attention has been focused on drinking water As in the last decades. Arsenic poisoning episodes have been reported all over the world. Most are the results of exposure to high As drinking water, especially groundwater, which has affected over 100 million people worldwide, including America, Argentina, Bangladesh, Chile, China, Hungary, India, Mexico, Romania, and Vietnam (Viraraghavan et al., 1999; Nordstrom, 2002; Smedley and Kinniburgh, 2002; Tchounwou et al., 2003; Hughes et al., 2011; Guo et al., 2014). Considering its potential health risk, the World Health Organization, 1996 has set a recommendation guideline limit of 10 µg/L for As in drinking water. It is notable that the new standard for drinking water has been executed after risk assessment in China since 2007

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(Ministry of Health of PR China, 2006; Liu et al., 2009). The maximum contaminant level (MCL) of As in drinking water has been reduced from 50 µg/L to 10 µg/L in urban areas, although 50 µg/L is still adopted in rural areas. Overall, it is an emerging issue to improve novel treatment technologies and to develop new materials for As removal from As-contaminated drinking water.

Although As is mostly found in inorganic form as oxyanions of trivalent As(III) or pentavalent As(V) in natural waters, As-enriched groundwater was generally dominated by As(III), up to 96%, in the form of the uncharged As(III) species H<sub>3</sub>AsO<sub>3</sub> at neutral pH (Smedley and Kinniburgh, 2002; Berg et al., 2007; Guo et al., 2008). Thus, As(III) is more difficult to be removed from water by means of adsorption and coprecipitation due to the lack of electrostatic attraction, in comparison with As(V) (Mohan and Pittman, 2007). In recent years, Fe-based sorbents have been developed and shown good adsorption behaviors for As removal. Some synthetic materials, containing Fe-(oxyhydr)oxides, such as granular ferric hydroxide (GFH) and Bayoxide E33 (Thirunavukkarasu et al., 2003a; Mohan and Pittman, 2007), have been used for As removal in practice as commercial adsorbents. However, the synthesized adsorbents would induce a significant hydraulic

obstruction during water treatment processes, and are usually more expensive than naturally occurring Fe minerals, such as magnetite, goethite, hematite and siderite, which have already been studied for As removal (Ohe et al., 2005; Giménez et al., 2007; Guo et al., 2007a,b; Jönsson and Sherman, 2008).

Previous studies have shown that siderite, both natural and synthetic, efficiently removed aqueous As species, including both As(III) and As(V) (Guo et al., 2007a,b, 2010, 2011). Guo et al. (2007a) reported that As adsorption on natural siderite with the particle size of 0.10–0.25 mm achieved equilibrium at a contact time of 3 days, and the estimated maximum adsorption capacities were 1.04 and 0.52 mg/g for As(III) and As(V), respectively. In contrast, due to the small size and the great reactivity of the adsorbents, As adsorption on ferrous carbonate, synthesized by mixing Fe(II) with  $\text{HCO}_3^-$ , reached equilibrium at only 3 h, with the estimated adsorption capacities for As(III) and As(V) being up to 10 mg/g (Guo et al., 2010, 2011). However, the complex preparation processes, high cost and low hydraulic conductivity of the synthetic siderite limited its application in rural areas. To overcome these limitations, the natural siderite with the fine grain size of <0.10 mm, simultaneously generated in the process of mineral crushing, was a good alternative as a principal component. However, there is no information on As removal by using the fine grain size of natural siderite. In addition, it was recently observed that the bi-mineral coexistence during partial mineral transformation from siderite to goethite greatly enhanced As adsorption capacity of synthetic siderite under oxic conditions (Guo et al., 2013), which provides the preliminary idea for modification of natural siderite in enhancing As adsorption (Zhao and Guo, 2014).

This study was carried out to investigate the possibility of using the fine grain size of natural siderite as the major components in fabricating modified granular natural siderite (MGNS) for As(III) removal. The modified granular adsorbents were synthesized by addition of organic binder, extrusion granulation, and calcination, which greatly improved the adsorption capacity of the material. The adsorbent was evaluated for adsorption characteristics in terms of batch and column tests. Effects of contact time, reaction temperature, solution pH, background electrolytes and coexisting anions on As(III) removal were intensively investigated in batch tests. Arsenic-spiked water and real-world high As groundwater were used to assess the performance of MGNS-packed columns in removing As. Additionally, removal mechanisms were expounded by means of BET surface area measurement, XRD, scanning electron microscopy, and X-ray adsorption spectroscopy.

## 2. Materials and methods

All reagents used were of analytical grade. The As(III) stock solution was prepared with deionized (DI) water using sodium arsenite ( $\text{NaAsO}_2$ , Fluka Chemical). Diverse As(III) solutions were freshly prepared by diluting As(III) stock solution with DI water.

### 2.1. Preparation of MGNS adsorbent

Natural siderite was obtained from a mineral company in Guizhou Province, China. Prior to experiments, the siderite was sieved with a 150-mesh sieve to get the fine grain size particles, which were used for adsorbent synthesis. Polyanionic cellulose (PAC) (Luzhou North Chemical Industries Co., Ltd., China) was used as the binder. The mixture with solid–liquid ratio of 5 g siderite to 1 mL DI water (containing 2% PAC) was adequately stirred and then extruded into strip-like adsorbent with a diameter of about 1.5 mm under a pressure of about 5.5 MPa. These strips were modified in a muffle furnace at 50–600 °C for 0.5–4.0 h. The maximum As removal efficiency was observed for the modified siderite being

calculated at 350 °C for about 2 h. Finally, the calcinated strips were manually cut into particles with length of 1–2 mm, which were assigned as MGNS and used in both batch and column experiments. The average crushing strength reached up to 50 N per single particle.

### 2.2. Batch experiments

Batch tests were carried out at a fixed dose of 10 g/L, with 0.5 g adsorbent in 50 mL solution in 100 mL high density polyethylene (HDPE) bottles under oxic conditions. These bottles were placed in a shaking water bath with a temperature controller, at a shaking rate of 150 rpm.

Adsorption isotherm studies were performed with As(III)-spiked DI water by varying initial As(III) concentrations (1–100 mg/L) at different temperatures (i.e., 25, 35, and 45 °C) with contact time of 48 h. Other batch experiments were carried out with initial As(III) concentration of 5 mg/L at 25 °C with contact time of 48 h. Adsorption kinetic studies were conducted with contact time from 0.5 to 96 h using As(III)-spiked DI water and natural high-As groundwater obtained from the Hetao basin, Inner Mongolia. Chemical compositions of natural high-As groundwater are shown in Table 1, indicating that it was of Na– $\text{HCO}_3$ –Cl type. Effect of initial solution pH on As(III) adsorption was investigated in As(III)-spiked DI water with initial pH between 2 and 10, which were adjusted by using 0.05 M (mol/L) HCl and 0.01 M NaOH. Effect of background electrolytes was tested using As(III)-spiked DI water with sodium chloride and sodium bicarbonate concentrations between 1 and 100 mM. In addition, effect of co-existing anions was studied using As(III)-spiked DI water containing individual anions with 0.5, 1, 2, 5, 10 and 20 mg/L of N as  $\text{NO}_3^-$ , or S as  $\text{SO}_4^{2-}$ , or Si as  $\text{SiO}_3^{2-}$ , or P as  $\text{PO}_4^{3-}$ . It is worth noting that all batch experiments were conducted in duplicate and reported as a mean value.

### 2.3. Column experiments

Plexiglass columns, with an inner diameter of 30 mm, a height of 150 mm and a working volume of about 100 mL, were used in the column study as fixed-bed up-flow reactors.

Arsenic(III)-spiked DI water, As(III)-spiked tap water, and real-world high-As groundwater, were used as influent, and pumped through the MGNS-packed column filters at an up-flow rate of 1.8 mL/min with a peristaltic pump (BT100-1F, Longerpump) under oxic conditions. Quartz sand with grain size of 0.5–1.0 mm was packed at the bottom of the column (10 mm height), and the MGNS in the upper (115 mm height, about 118 g weight), presenting the mean bed porosity of 0.55. The empty bed contact time (EBCT) was about 45 min. In order to evaluate the feasibility of MGNS in practical application, four columns were setup to treat different types of high-As water. Column A was used for treating 1.0 mg/L As(III)-spiked tap water, column B for 1.0 mg/L As(III)-spiked DI water, column C for 2.0 mg/L As(III)-spiked DI water, and column D for real-world high-As groundwater. Chemical compositions of tap water and real-world high-As groundwater are shown in Table 1. Effluent solutions from the column filters were collected at regular intervals and analyzed for residual As concentration.

### 2.4. Analytical methods

Solution pH was monitored by a standard pH meter (PB-10, Sartorius). Dissolved Fe and As concentrations were analyzed by ICP-MS (7500C, Agilent). Multi-element standard solutions (GBW 081532 and GBW 081533) from National Institute of Metrology (China) were tested every 5 samples for quality control. The relative standard deviation (RDS) was less than  $\pm 2\%$ , with the

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