Antimonate and antimonite adsorption by a polyvinyl alcohol-stabilized granular adsorbent containing nanoscale zero-valent iron

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HIGHLIGHTS

- For stability and functional excellence, nanoscale Fe^0 was stabilized by PVA.
- PVA–Fe^0 composites were fabricated into granules to use as adsorbents for Sb removal.
- Sb(III) and Sb(V) adsorption on the granules was systematically evaluated.
- Sb(III)/Sb(V) were chemically bound onto magnetite, the active phase on granules.

ARTICLE INFO

ABSTRACT

Nanoscale zero-valent iron (Fe^0) has attracted increasing attention for hazardous ion removal. In this study, nanoscale Fe^0 was stabilized by polyvinyl alcohol (PVA) and fabricated to granules for stability and functional excellence. Then Sb(III) and Sb(V) removal from water was evaluated. The effects of contact time, initial Sb(III) and Sb(V) concentrations, pH and co-existing anions on the Sb removal efficiency were systematically investigated. Antimony adsorption was rapid and followed a pseudo-second rate law. The maximum adsorption capacity of granular PVA–Fe^0 was 6.99 and 1.65 mg/g for Sb(III) and Sb(V), respectively. High concentration levels of co-existing anions inhibited antimony removal, but little inhibition would be expected at their natural environmental concentrations in water. The antimony uptake mechanism by PVA–Fe^0 was investigated using XRD, XPS and FTIR characterizations. Fe^0 was present in an acetalized PVA matrix before adsorption. It had been converted into magnetite (Fe_3O_4) after Sb(III) and Sb(V) adsorption. FTIR analyses confirmed the presence of active magnetite and magnetite's chemical binding to Sb(III) and Sb(V) after adsorption. The convenient handling properties combined with the good efficiency of PVA–Fe^0 granules suggests they are promising adsorbents for antimony removal from contaminated water.

1. Introduction

Antimony (Sb) is the ninth most mined metal for industrial uses worldwide [1]. It is used in a variety of industrial products including flame retardants, manufacture of semiconductors, catalysts for plastics synthesis, and alloys for ammunition [2]. Antimony and its compounds are classified as priority pollutants by the USEPA and the EU, based on its health effects [3,4].

Sb and arsenic (As) are both metalloids belonging to Group 15 of the periodic table. Arsenic pollution has created great concern and was intensively investigated because of its wide distribution and health risks. In contrast, antimony pollution is less studied, partially because global Sb production and its resulting pollution are concentrated in just a few countries [3]. However, world Sb production is considerably larger than that of As. The 2012 estimated Sb output was 180,000 metric tons compared to 44,000 metric tons for As, and also Sb mining and consumption are continuously increasing [5]. The 2012 estimated Sb mine output increased 1.3-fold over that in 2007 [5]. China, Bolivia, Russia, South Africa, and Tajikistan are major producers and suppliers of the global market. China has produced more than 75% of world Sb consumption. Most large mines are located in Hunan, Guangxi, and Yunnan Provinces in China [6].

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Antimony occurrences in aquatic environment result from rock weathering, soil runoff and anthropogenic activities. Typical dissolved antimony concentrations in unpolluted waters are less than 1 µg/L. Serious pollution is mostly caused by antimony mining and smelting industries [3,7]. High dissolved Sb concentrations in water ranging from 4.58 mg/L to 29.4 mg/L were reported in mining areas in China [7].

Considering its potential health risk, the WHO set a guideline of 20 µg/L for the maximum Sb concentration in drinking water, while the USEPA and the Ministry of Health of China set stricter maximum contaminant levels (MCL) of 6 µg/L and 5 µg/L, respectively.

For the challenges of antimony mitigation and removal from water, coagulation/flocculation, adsorption and membrane filtration have been investigated for the removal of Sb from water [8–10]. When initial Sb is high, coagulation/flocculation cannot subsequently meet the strict regulations for Sb in effluent [8]. High selectivity for Sb removal by membrane filtration in a desalination process could not be expected. However, adsorption is considered to be simple, compact, easy to operate and efficient to mitigate Sb below the regulation levels. Several kinds of adsorbents including hydrated ferric oxides [11], akaganeite [12], goethite [13], manganite [14], Fe–Mn bimetal oxides [4], Fe–Zr bimetal oxides [15], kaolinite [16], montmorillonite, bentonite [10] graphene [17], etc., have been investigated for Sb removal from water.

Zero valent iron (Fe^0) has drawn increasing attention as an effective remediation medium for many contaminants in the past two decades [18–20]. Fe^0 nanoparticle technologies are considered promising to provide cost-effective solutions for challenging environmental cleanup problems [21,22] was well as for antimony removal from water. However, Fe^0 nanoparticles generally exhibit high agglomeration, lack of stability and low reducing specificity in water. In addition, environmental, health and safety issues also exist [23]. Surface stabilizers like PVA [24], chitosan (CS) [25], alginate [26], activated carbon [27], porous carbonate media [28], polyelectrolytes [29] and other approaches may solve those problems.

In this study, iron nanoparticles were stabilized using polyvinyl alcohol (PVA–Fe^0) and then granulated to serve as a new adsorbent. The ability to simultaneously remove antimonite and antimonate from water was evaluated versus contact time, initial concentration, solution pH, and coexisting anions. In addition, the antimony removal mechanism by the granular adsorbent was investigated using a combination of XRD, XPS and FT-IR observations.

2. Materials and methods

2.1. Materials

Analytical grade reagents $FeSO_4 \cdot 7H_2O$, $NaBH_4$, $K(SbO)C_4H_4O_6 \cdot 0.5H_2O$, $K_2H_2Sb_2O_7 \cdot 4H_2O$, $Na_2HAsO_4 \cdot 12H_2O$, Na_3PO_4, Na_4SiO_4, Na_2SO_4, $NaNO_3$, $NaCl$ and liquid paraffin were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. PVA-124 (Mw = 100,000–110,000, alcoholysis degree = 98–99%) is from Kuraray, Japan. $K_2H_2Sb_2O_7 \cdot 4H_2O$ (0.2085 g) and $K(SbO)C_4H_4O_6 \cdot 0.5H_2O$ (0.2743 g) were dissolved in 1 L deionized water, respectively, to make 100 mg/L Sb(III) and Sb(V) stock solutions. In addition, 10 mg/L of Sb(III) and Sb(V) standard solutions were bought from National Research Center for Certified Reference Materials, China, for HG-AFS testing. Common anion solutions were prepared using their salts.

2.2. Adsorbent preparation and characterization

Granular acetalized polyvinylalcohol–Fe^0 was prepared following a procedure modified from that reported by Bai et al. [24].

PVA-124 (Mw = 100,000–110,000, alcoholysis degree = 98–99%) (4 g) was dissolved into 80 mL of boiling deionized water for 1 h. During this period, deionized water was continuously added to keep the volume constant. The resulting solution was then cooled and kept at 30 °C. $FeSO_4 \cdot 4H_2O$ (2.5 g) was added and fully dissolved. Liquid paraffin (80 mL) was then added and the mixture was immediately stirred at 400–500 rpm for 30 min at ambient temperature to gradually form small granules. Then, 1 mL of 1 M HCl and 2 mL of glutaric dialdehyde (50%) were added to the contents and stirring was continued at 500 rpm for 2 h. The resulting granules were washed three times with petroleum ether. Then an ethanol solution (100 mL) containing 1.5 g $NaBH_4$ was added and mixed with the granules for 3 h. The granules were washed by deionized water three times. Washing with water could cause immediate formation of iron oxide films in place of zero valent iron outside the granules. The final products were vacuum-dried and all adsorption experiments were carried out on freshly made granules.

The granules' sizes were measured using Image-Pro Plus 5.0 software (Media Cybernetic, USA). The crush strength was determined using a crushing strength tester (KY-20, Jiangyan Keyuan Corp., China), which exerted a steadily increasing force on a granule until it was crushed, with a sensor recording the force (expressed as crushing strength) at the point of failure. The reported result is an average of 50 granules. The XRD patterns of the granular adsorbent were obtained on an X'Pert PRO MPD diffractometer (PANalytical, the Netherlands). The specific surface areas and pore volumes of the adsorbent were determined by BET N_2 adsorption–desorption analysis using a Micromeritics ASAP2000 surface area analyzer (Norcross, USA). The porosity and pore size distributions were determined using a mercury intrusion method employing a Poremaster 60 GT porosimeter (Quantachrome, USA). The bulk density was calculated by weighing a measured volume of granular specimens. The surface morphology was determined by a S-4500 (Hitachi, Japan) FE-SEM.

2.3. Batch adsorption experiment

A predetermined amount of Sb(III) and Sb(V) stock solution and deionized water were added into a series of 2000-mL glass conical flasks to give a total volume of 1500 mL in each. Then, the granular adsorbents were added at a dose of 2 g/L. The pH of the mixtures was adjusted and maintained at 7.0 ± 0.2 throughout the experiment. The mixtures were stirred at 160 rpm, and maintained at 25 ± 1 °C. Approximately 4-mL aliquots were taken from the suspension at predetermined intervals. These samples were immediately filtered through a 0.45-µm membrane, and then residual antimony in solution was analyzed. The adsorption isotherms for Sb(III) and Sb(V) on PVA–Fe^0 granules under 15 °C, 25 °C and 35 °C were determined using initial Sb(III) and Sb(V) concentrations from 0 to 20 mg/L, respectively, adsorbent doses of 2 g/L and at a pH of 7.0 ± 0.2. The effect of solution pH on antimony removal was analyzed in 250-mL glass bottles containing 100 mL of solution with pre-selected concentrations and sorbent doses of 2 g/L. The pH was adjusted and maintained at a specified value in the range 3–11. Temperature was maintained at 25 ± 1 °C. After shaking for 48 h, the residual antimony in solution was analyzed.

The effects of common anions (Cl^-, SO_4^{2-}, NO_3^-, SiO_4^{4-} and PO_4^{3-}) on Sb(III) and Sb(V) removal were evaluated. Solutions of the common anions were respectively spiked in 1-, 10- and 100-fold concentrations greater than the 5 mg/L level of Sb(III) or Sb(V). The PVA–Fe^0 granule dose was 2 g/L. The pH was maintained at 7.0 ± 0.2 and the temperature was controlled at 25 ± 1 °C.