Comparative removal of As(V) and Sb(V) from aqueous solution by sulfide-modified α-FeOOH

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Highlights

- Sulfide-modified $\alpha$-FeOOH was synthesized for As(V) and Sb(V) removal.
- As(V)/Sb(V) adsorption capacity and affinity were remarkably improved.
- Enhanced removal was maintained at pH range from 2 to 11.
- Reduction of As(V) to As(III) followed by adsorption was identified.
- Removal was not affected by the presence of coexisting anions.

Graphical abstract

Sulfide-modified $\alpha$-FeOOH
Abstract

Efficient elimination of As(V) and Sb(V) from wastewater streams has long been a major challenge. Herein, sulfide-modified α-FeOOH adsorbent was fabricated via a simple sulfidation reaction for removing As(V) and Sb(V) from aqueous media. Compared with the pristine α-FeOOH, sulfide-modified α-FeOOH increased the adsorption of As(V) from 153.8 to 384.6 mg/g, and Sb(V) adsorption from 277.8 to 1111.1 mg/g. The enhanced adsorption of both As(V) and Sb(V) was maintained at the pH range from 2 to 11, and was not interfered by various coexisting anions such as Cl⁻, SO₄²⁻, NO₃⁻, SiO₃²⁻ and PO₄³⁻. The adsorption affinity increased from 0.0047 to 0.0915 and 0.0053 to 0.4091 for As(V) and Sb(V), respectively. X-ray photoelectron spectroscopic investigation demonstrated a reductive conversion of As(V) to As(III) during the adsorption process with sulfide-modified α-FeOOH, but with no obvious variation of Sb(V) speciation. While the removal mechanism for As(V) was reduction followed by adsorption via hydroxyl groups, mainly surface complexation was involved in the removal of Sb(V). This study presented a simple strategy to enhance the adsorption capacity and adsorption affinity of α-FeOOH toward As(V)/Sb(V) via sulfide-modification.

Keywords: Adsorption affinity and capacity; Arsenic and antimony; Iron-based adsorbents; Metalloid speciation; Sulfide-modification; Wastewater treatment.

Capsule: Sulfide-modified α-FeOOH remediates both low and high arsenic/antimony
levels under varying pH and competitive anions – conditions common in wastewater.
1. Introduction

Severe pollution of arsenic (As) and antimony (Sb) in natural water has triggered ever-increasing worldwide concerns, owing to the grave threats of these elements to human health (Fendorf et al., 2010; Herath et al., 2017). Anthropogenic factors such as mining activities, coal burning, and industrial consumption of As- and Sb-containing materials are primarily responsible for the build-up of these elements in the soil and water systems (Fawcett et al., 2015; Wei et al., 2015). Long term exposure to elevated concentrations of As and Sb could damage tissues and organs in human, and may even lead to cancer (Zhang et al., 2020; Smith et al., 2018; Winship, 1987; Herath et al., 2017). In view of the significant menaces of As and Sb on human health, the maximum contamination levels (MCLs) in drinking water for As (10.0 μg/L) and Sb (5.0 μg/L) were regulated by the US Environmental Protection Agency (USEPA) and World Health Organization (WHO) (Yamamura et al., 2003; Wang et al., 2018b). Furthermore, As and Sb exhibit homologous chemical and toxicological features, and these two metals often co-exist in many contaminated sites (Ungureanu et al., 2015). Therefore, effective technologies are needed to eliminate As and Sb from contaminated water and soil.

Various methods have been utilized to scavenge As and Sb from wastewater, such as adsorption (Lin et al., 2019; Mukhopadhyay et al., 2019), electrocoagulation (Cao et al., 2017), membrane filtration (Bolisetty et al., 2017), coprecipitation (Yuan et al., 2019), and ion exchange (Lee et al., 2017). Adsorption was considered as the most widely adopted methods by the virtue of its high removal efficiency, easy operation,
and low cost. Numerous adsorbents have been employed to purge As and Sb in contaminated water, including biochar (Niazi et al., 2018; Han et al., 2017), metal oxides (Qiu et al., 2019; Wang et al., 2016), metal-organic frameworks (Liu et al., 2018a), graphene oxide (Yang et al., 2015) and clay minerals (Mukhopadhyay et al., 2017; 2019; Sarkar et al., 2013). Among the adsorbents, iron materials were considered to be the most potential ones for As and Sb removal, owing to merits such as abundant source, low cost, excellent reactivity, and environmental friendliness (Wei et al., 2019; Zhang et al., 2017; Wang et al., 2018a). Nevertheless, the adsorption affinity and capacity of iron oxy-hydroxides toward As and Sb could be relatively weak, which might hinder the practical utilization of iron-based adsorbents for wastewater treatment. When seeking or designing materials with high adsorption affinity and capacity toward As and Sb, it is worth to pay attention that the toxicity of As and Sb to human mainly owes to the puissant affinity between As/Sb and sulfhydryl groups in proteins (Lin et al., 1999; Ning and Xiao, 2007). Furthermore, As and Sb are both sulfophilic elements, mainly exist in the form of sulfide deposits in the nature. The dominant As minerals are orpiment (As$_2$S$_3$), realgar (As$_4$S$_4$) and arsenopyrite (FeAsS) (Bowell et al., 2014). Similarly, antimony trisulfide (Sb$_2$S$_3$) is the main sulfide mineral in the case of Sb (Okkenhaug et al., 2011). In marine systems, aquifers, and river and lake sediments, sulfate reducing bacteria mediate sulfate reduction resulting in the formation of soluble sulfide, and it further reacts with As or Sb to form orpiment (As$_2$S$_3$), realgar (As$_4$S$_4$), arsenopyrite (FeAsS), or stibnite (Sb$_2$S$_3$) (Pope et al., 2004; O’Day et al., 2004). Accordingly, sulfur act an vital role on the cycling of As and Sb in the environment,
and from this perspective, designing sulfur-based materials could be a promising strategy for enhanced removal of As and Sb from aqueous media.

Goethite ($\alpha$-FeOOH) is a ubiquitous iron oxyhydroxide found in sediments, rocks and soils, and thermodynamically highly stable in nature (Oganessian et al., 2017). $\alpha$-FeOOH has previously been utilized for scavenging As and Sb from contaminated water (Zhang et al., 2017; Xi et al., 2013). In anoxic conditions of a subsurface environment, S(-II) originating from microbial sulfate reduction could transform iron oxyhydroxides into iron sulfide or polysulfide. Inspired from the natural iron oxyhydroxide transformation process induced by S(-II), we put forward a novel sulfide-modification of $\alpha$-FeOOH for enhancing the adsorption of As(V) and Sb(V) from wastewater. To the best of our knowledge, only limited number of studies have focused on sulfide-modified $\alpha$-FeOOH as the adsorbent for scavenging As(V), and no study investigated the comparative removal of As(V) and Sb(V) from polluted water (Hao et al., 2018).

The objectives of this work are to: (1) fabricate a collection of sulfide-modified $\alpha$-FeOOH materials with various S/Fe ratios, (2) investigate the structural and morphological information of sulfide-modified $\alpha$-FeOOH via scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), (3) explore the adsorption features of As(V) and Sb(V) on sulfide-modified $\alpha$-FeOOH via performing pH, kinetics, isotherm, coexisting anions experiments, and (4) propose the possible mechanisms of As(V)/Sb(V) adsorption on the sulfide-modified $\alpha$-FeOOH.
2. Materials and methods

2.1 Reagents

Sodium hydroxide (NaOH), hydrochloric acid (HCl), iron(III) nitrate nonahydrate (Fe(NO$_3$)$_3$$\cdot$9H$_2$O), sodium arsenate (Na$_3$AsO$_4$$\cdot$12H$_2$O), potassium antimonate hydrated (KSb(OH)$_6$), sodium hyposulfite (Na$_2$S$_2$O$_4$), sodium chloride (NaCl), sodium sulphate (Na$_2$SO$_4$), sodium nitrate (NaNO$_3$), sodium silicate (Na$_2$SiO$_3$), and sodium dihydrogen phosphate (NaH$_2$PO$_4$) were all of analytical grade, and obtained from Sinopharm Chemical Reagent Co. Ltd, China. KSb(OH)$_6$ and Na$_3$AsO$_4$$\cdot$12H$_2$O were dissolved in ultrapure water to prepare the Sb(V) and As(V) stock solutions, respectively. The As(V) and Sb(V) working solutions were obtained through diluting the stock solutions. In all the batch experiments, a background electrolyte concentration was maintained by 0.1 M KNO$_3$.

2.2 Synthesis of $\alpha$-FeOOH

A hydrothermal method was employed to synthesize $\alpha$-FeOOH (Padhi and Parida, 2014). Briefly, certain amount of Fe(NO$_3$)$_3$$\cdot$9H$_2$O was dissolved in ultrapure water under vigorous stirring, subsequently the solution pH was adjusted to 12 via NaOH addition, and further stirred for 30 min. Then, the reddish-brown mixture was transferred into a 100 mL Teflon-lined autoclave for hydrothermal reaction for 24 h at 180°C. After reaction, the autoclave was cooled down, and the obtained yellow product was repeatedly washed with ultrapure water until the supernatant pH was neutral. Then,
the product was separated by centrifugation (6000 rpm for 5 min), and dried at 60°C for 48 h.

2.3 Synthesis of sulfide-modified α-FeOOH

The sulfide-modified α-FeOOH was fabricated by using dithionite as the sulfidation reagent (Kim et al., 2011). Typically, certain amount of α-FeOOH was suspended in de-oxygenated ultrapure water (in 250 mL three-neck flask), and ultrasonicated for 30 min. Then, 1 mol/L Na₂S₂O₄ solution was freshly prepared by dissolving Na₂S₂O₄ in de-oxygenated ultrapure water. Under nitrogen atmosphere, certain volume of fresh Na₂S₂O₄ solution with different S/Fe ratios (S/Fe= 0.1, 0.3, 0.5, 0.8, 1.0) were drop-wise added to the α-FeOOH suspension, sealed the bottle, and agitated for another 48 h. The obtained precipitate was washed by de-oxygenated ultrapure water for several times, and separated by centrifugation. The product was finally dried in a vacuum oven. The step-wise synthesis procedure is shown schematically in Supplementary Information (SI; Fig. S1).

2.4 Adsorbent characterization

The crystal composition of sulfide-modified α-FeOOH was characterized by XRD (D8 Advance, Bruker, Germany) performed with Cu Kα radiation (λ = 1.5418 Å) at the 2θ range of 10° to 80°. FTIR spectra of the adsorbents were collected by an IR Prestige-21 spectrometer (Shimadzu, Japan) at the wavelength scope of 4000 – 400 cm⁻¹ via KBr pellet method. To investigate the surface chemical composition and elemental valence
states in the adsorbents, XPS investigation was conducted on a PHI Quantera II ESCA system (Ulvac-Phi, Japan) with a monochromatic Al Kα radiation at 1486.8 eV. The binding energy of the data was calibrated to the C1s peak at 284.8 eV. The surface morphology of the adsorbents was observed by SEM associated with energy dispersion spectrometer (EDS) (Quanta 250FEG, FEI, USA). Certain amount of adsorbent was dispersed in water at pH range of 2 to 11, and the solution pH was preserved at the desired value and adjusted every 6 h. Then, the zeta potential values of the adsorbents were measured by a zetasizer (ZetaPALS, Brookhaven, USA).

2.5 Batch experiments

Batch adsorption experiments were performed to investigate the effect of contact time, initial adsorbate concentration, initial pH and coexisting anions on the adsorption behavior of As(V) and Sb(V) by sulfide-modified α-FeOOH. A 100 mL conical bottle containing 50 mL As(V) or Sb(V) solution was adopted for all the batch adsorption experiments implemented in duplicate. The fabricated adsorbents were added at a dosage of 0.5 g/L, and a background ionic strength was maintained by 0.1 M KNO₃. The conical bottles were sealed, and shaken on an oscillator at 200 rpm for 24 h at 25°C. After adsorption, supernatants were filtered through 0.22 μm membrane filter for determining the residual aqueous concentration of As(V) or Sb(V). Furthermore, adsorbents after adsorption were collected by centrifugation, washed and dried at vacuum, and used for the characterization studies. The adsorption capacity (mg/g) of As(V) and Sb(V) on the adsorbents was obtained using Eq. 1:

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  

(1)
where, $q_e$ (mg/g) represents the equilibrium adsorption capacity; $C_0$ and $C_e$ (mg/L) represent the supernatant concentrations of adsorbate at the initial and equilibrium times, respectively; $V$ (L) is the adsorbate volume; and $m$ (g) is the mass of the adsorbent.

To examine the influence of pH on adsorption, the solution pH was varied from 2 to 11 adjusted via adding 1 M HNO$_3$ or NaOH solutions. The solution pH was preserved at the desired value and adjusted every 6 h to avoid any change of the solution pH. Apart from the initial pH effect, a constant pH value of 3 was adopted for all other experiments. To explore the time-dependent adsorption behavior, adsorbent (0.5 g/L) was transferred to an initial As(V) or Sb(V) concentration of 300 mg/L or 500 mg/L (50 mL), respectively. Aliquots of suspension was sampled at different time intervals to determine the residual As(V) and Sb(V) concentration. Adsorption isotherm investigations were performed at the initial concentration varying from 50 to 500 mg/L.

Effects of commonly coexisting anions in wastewater on adsorption performance of As(V) and Sb(V) were explored by conducting the adsorption tests with 200 mg As or Sb/L in 500 mg/L sodium salt solutions of various anions (NaCl, Na$_2$SO$_4$, NaNO$_3$, Na$_2$SiO$_3$, NaH$_2$PO$_4$).

2.6 Analysis of As and Sb

Inductively coupled plasma-optical emission spectrometer (ICP-OES) (7000DV, Perkin Elmer, USA) was used to measure the concentrations of As and Sb in the aliquots. Samples were diluted where needed, acidified with 1% HNO$_3$, and analyzed within 48 h. The displayed data in this study were the average values of duplicate experiments.
3. Results and discussion

3.1 Characterization of sulfide-modified α-FeOOH

The pure α-FeOOH exhibited a uniform acicular morphology (Fig. 1a). The sulfide-modification significantly changed the appearance of α-FeOOH. When the S/Fe mole ratio increased from 0 to 0.3, the sulfide-modification of α-FeOOH caused a variation of particle length (Fig. 1a-c), but the sulfide-modified α-FeOOH still kept the acicular morphology (Fig. 1b and c). When controlling the S/Fe mole ratio from 0.5 to 1.0, the acicular morphology was significantly destroyed, which was followed by the formation of larger aggregates (Fig. 1d-f). Due to the increase of S/Fe mole ratio, the acicular shape became shorter, and even was damaged to form large sized rough and irregular particles.

The functional groups of sulfide-modified α-FeOOH with different S/Fe mole ratios was obtained by FTIR (Fig. 2a). The band at 3111 cm$^{-1}$ represented the stretching vibration of O-H (Liu et al., 2017), which reflected the non-stoichiometric hydroxyl groups of α-FeOOH. The intensity of O-H band was weakened along with the increasing S/Fe mole ratio, revealing a reduction of hydroxyl groups on sulfide-modified α-FeOOH. This might be attributed to the partial transformation of α-FeOOH to sulfur-bearing iron minerals. The bands at 790 and 890 cm$^{-1}$ were ascribed to the Fe-O-H bending vibrations of α-FeOOH (Rahimi et al., 2015; Liu et al., 2018b). The Fe-O-H bands also exhibited an attenuating trend with the increase of S/Fe mole ratio. Meanwhile, the band at 609 cm$^{-1}$ was attributed to the Fe-O stretching of α-FeOOH.
(Wei et al., 2017). After sulfide-modification, a new band located at 1134 cm$^{-1}$ was observed, which could relate to the superficial oxidation of FeS$_2$ (Jiang et al., 2015). No significant stretching frequency concerning FeS was detected (Gong et al., 2014).

The crystal phases of the sulfide-modified α-FeOOH were identified by XRD (Fig. 2b). The pure α-FeOOH exhibited a space group symmetry of Pbnm ($Z = 4$) with the lattice parameters of $a = 4.55979$ Å, $b = 9.951$ Å, and $c = 3.0178$ Å (Yang et al., 2006). The diffraction peaks of pure α-FeOOH (JCPDS No. 29-0713) at 2θ values 17.80º, 21.22º, 26.32º, 33.24º, 34.70º, 36.65º, 41.19º, 53.24º and 59.02º were indexed as the Bragg reflections of (020), (110), (120), (130), (021), (111), (140), (221), and (151) crystal planes, respectively. The diffraction peaks of the main crystal planes of α-FeOOH were still detected after sulfidation (Fig. 2b), indicating that the sulfide-modification did not destroy the original crystal structure of α-FeOOH. However, the intensity of the diffraction peaks was abated with the increase of S/Fe mole ratio, which was similar with other modified α-FeOOH (Liu et al., 2018c). When the S/Fe ratio was higher than 0.3, a new reflection located at $2\theta = 32.7^\circ$ could be indexed to plane (2 1 1) of FeS (JCPDS No. 76-0964).

XPS spectra were collected to further investigate the surface composition of the sulfide-modified α-FeOOH materials. The two main peaks of Fe 2p spectrum at the binding energy (BE) of $\sim$725.1 eV and $\sim$711.1 eV (Fig. 3a-d) represented Fe 2p$_{1/2}$ and Fe 2p$_{3/2}$, respectively (Zhang et al., 2019). The fitted Fe 2p spectra in Fig. 3a and b showed the features of Fe(III). With further increase of the S/Fe ratio, the binding energies at 710.1 eV, 724.3 eV, and 710.2 eV (Fig. 3c and d) could be assigned to Fe(II)
species existing on the surface (Tang et al., 2017; Wan et al., 2014). The observed signals of Fe(II) species indicated the reduction transformation of Fe(III) to Fe(II) in α-FeOOH by sulfide (Wan et al., 2014). Meanwhile, the reduced concentration of O$^{2-}$ in O1s spectra (Fig. 3e-h) could be assigned to the partial replacement of Fe-O groups by Fe(II)-S groups. The abundance of sulfur species was enhanced with the gradual rise of S/Fe molar ratio, which was previously observed for sulfide-modified zero valent iron (S-ZVI) (Xu et al., 2019). Additionally, disulfide (S$_2^{2-}$) (BE $\sim$ 66.6 eV), polysulfide (S$_n^{2-}$) (BE $\sim$ 167.7 and 166.6 eV), and sulfite (SO$_3^{2-}$) (BE $\sim$ 169.4 and 168.2 eV) species on the sulfide-modified α-FeOOH surface (Fig. 3i-k) were confirmed (Mangayayam et al., 2019). Therefore, the XPS results suggested that sulfide was binding with Fe(II) which originated from the reduction of Fe(III) in α-FeOOH. The sulfur species of S$_2^{2-}$, S$_n^{2-}$ and SO$_3^{2-}$ were generated from the hydrolysis of Na$_2$S$_2$O$_4$ (Eq. 2-6).

\[
\begin{align*}
2\text{S}_2\text{O}_4^{2-} + \text{H}_2\text{O} & \rightarrow \text{S}_2\text{O}_3^{2-} + 2\text{SO}_3^{2-} + 2\text{H}^+ \quad \text{(2)} \\
\text{S}_2\text{O}_4^{2-} + \text{S}_2\text{O}_3^{2-} + 2\text{H}_2\text{O} + \text{H}^+ & \rightarrow 3\text{HSO}_3^- + \text{H}_2\text{S} \quad \text{(3)} \\
\text{H}_2\text{S} & \rightarrow \text{S}^{2-} + 2\text{H}^+ \quad \text{(4)} \\
\text{S}_2\text{O}_3^{2-} & \rightarrow \text{SO}_3^{2-} + \text{S} \quad \text{(5)} \\
\text{S}^{2-} + \text{S} + \text{FeOOH} & \rightarrow \text{FeS}_2 + \text{H}_2\text{O} \quad \text{(6)}
\end{align*}
\]

Surface charge of an adsorbent is a key property that influences the adsorption of metal(loid) ions through electrostatic attraction. An adsorbent with low point of zero charge (pH$_{pzc}$) favors the removal of cationic heavy metals (e.g., Cu, Cd, Pb, Ni). For oxyanions of heavy metal(loid)s such as As, Sb and Se, a high pH$_{pzc}$ would result in
greater adsorption via electrostatic attraction. The zeta potential values of α-FeOOH and sulfide-modified α-FeOOH suspensions were determined at the pH range of 2 to 11 (Fig. 4). The pristine α-FeOOH exhibited a $\text{pH}_{\text{pzc}}$ of 6.69. The $\text{pH}_{\text{pzc}}$ value of sulfide-modified α-FeOOH significantly increased from 6.69 to 7.40, 7.64, 10.29, 10.39 and 10.43 when the S/Fe ratio increased to 0.1, 0.3, 0.5, 0.8 and 1.0, respectively. Similar phenomenon was found in other thiol-functionalized or sulfide modified iron materials (Ma et al., 2018; Ji et al., 2019). A positively charged surface of sulfide-modified α-FeOOH was exhibited at pH =10 when the S/Fe ratio was greater than 0.3 (Fig. 4).

Therefore, adsorbents with an increased positive surface charge were resulted following the sulfide-modification, which was a merit of the sulfide-modified α-FeOOH favoring the adsorption of metal(loids) like As(V) and Sb(V).

3.2 Effect of pH on adsorption

Metal(loid) adsorption by adsorbents might highly rely on the solution pH which could affect the surface charge of the adsorbents, and the existing metal(loid) species (Prabhu et al., 2019; Wang et al., 2016). The influence of pH on the removal of As(V) and Sb(V) was tested in the pH range of 2.0 to 11.0. The adsorption capacities of sulfide-modified α-FeOOH were higher than the pristine α-FeOOH in the entire pH range (2.0 to 11.0) (Fig. 5). The adsorption of As(V)/Sb(V) was pH dependent, and the adsorption capacities gradually decreased with the increase of pH from 2.0 to 11.0. Similar tendency was observed for oxyanion adsorption on Ce(III)–doped Fe$_3$O$_4$ (Qi et al., 2017), La-doped magnetic biochar (Wang et al., 2018b), FeOOH nanoparticles (Zhang...
et al., 2017), and Fe-Ti-Mn composite oxide (Zhang et al., 2019d). The gradual drop of adsorption capacity with an increase of solution pH could be ascribed to the conversion of surface charge from positive to negative values (Fig. 4) together with the varied inorganic As(V)/Sb(V) species (Fig. S2). The forms of As(V) likely were H$_2$AsO$_4^-$, HAsO$_4^{2-}$ and AsO$_4^{3-}$ when pH varied from 2.0 to 11.0 (Fig. S2). The hydrolysis of H$_3$AsO$_4$ and Sb(OH)$_5$ generated anionic species of the elements (H$_2$AsO$_4^-$, HAsO$_4^{2-}$, AsO$_4^{3-}$ and Sb(OH)$_6^-$) with the increase of pH value. These anions might compete with OH$^-$ ions for the adsorption sites at high solution pH (Liu et al., 2016a). Furthermore, the Coulombic repulsion between As(V) or Sb(V) oxyanions and the declining surface positive charge of sulfide-modified α-FeOOH could be accountable for the decreased adsorption of As(V)/Sb(V) at high solution pH.

3.3 Adsorption kinetics

The influence of reaction time on the adsorption behavior of As(V) and Sb(V) by the sulfide-modified α-FeOOH was illustrated (Fig. S3). Adsorption reactions of As(V) and Sb(V) by the sulfide-modified α-FeOOH was rapid within the first 100 min, and more than 80% of the equilibrium adsorption was achieved during this time (Fig. S3a and d). Subsequently, a slower adsorption rate occurred until the equilibrium was reached. This kind of adsorption pattern occurred mainly due to the abundance of adsorption sites at the beginning of the reaction, and as time went on, the active sites were occupied by oxyanions, which then brought about the low adsorption rate toward the end of the reaction. To further investigate the adsorption kinetics process,
the pseudo-first order and pseudo-second order were adopted to fit the experiment

data. A higher coefficient of determination ($R^2$) (Table 1; Fig. S3b, c, e and f)

indicated that the pseudo-second order model adequately described the As(V)/Sb(V)

adsorption behaviors on the adsorbent. It was inferred that the adsorption of As(V)

and Sb(V) on sulfide-modified α-FeOOH was controlled by chemical reactions

(Zhang et al., 2013). With an increase of the S/Fe ratio in the adsorbents, the

equilibrium adsorption capacity toward As(V) and Sb(V) increased from 70.92 to

285.7 mg/g, and 131.6 to 1000 mg/g, respectively (Table 1). To investigate the effect

of the materials on solution pH, the adsorbents were dispersed in ultrapure water with

a solid/liquid ratio at 0.025 g/50 mL. After shaking for 24 h, the final pH was

determined. The pH values were 7.20, 6.91, 6.58, 6.03, 5.87 and 5.72 for materials

with S/Fe ratio of 0, 0.1, 0.3, 0.5, 0.8 and 1.0, respectively. The final pH values were

further checked at the end of kinetic experiments at initial pH = 3 and adsorbent

dosage = 0.5 g/L. The solution pH did not change notably (Table S1).

3.4 Adsorption isotherm

The As(V) and Sb(V) adsorption amounts of the sulfide-modified α-FeOOH were

estimated via isotherm studies (Fig. S4a and d). The Langmuir and Freundlich model

(SI Text) fitting results are shown in Table 2, and Fig. S4b, c, e and f. The Langmuir

model was more appropriate (with greater $R^2$ value) than the Freundlich model to

explain the As(V) and Sb(V) sorption properties on sulfide-modified α-FeOOH. It

could be inferred that a homogeneous adsorption occurred on the surface of the
adsorbents. Based on the model fitting results (Table 2), the calculated maximum adsorption capacities ($q_{\text{max}}$) were 153.8 – 384.6 mg/g, and 277.8 – 1111.1 mg/g for As(V) and Sb(V), respectively. The $q_{\text{max}}$ values thus endowed the sulfide-modified $\alpha$-FeOOH adsorbents with outstanding potentials for practical remediation of As(V) and Sb(V) in contaminated water with notably better performance than previously published adsorbents (Table S2). The significant enhancement of the adsorption capacity on the sulfide-modified $\alpha$-FeOOH might be owing to the strong affinity between sulfur and As(V)/Sb(V). The enhancement for Sb(V) was more remarkable than As(V), and the adsorption capacity of the sulfide-modified $\alpha$-FeOOH at S/Fe=1.0 was 3.99 and 2.5 times higher for As(V) and Sb(V), respectively, than the pristine $\alpha$-FeOOH.

The $q_{\text{max}}$ and Langmuir constant b are two important parameters reflecting the adsorption capacity and adsorption affinity, respectively. Large $q_{\text{max}}$ value is beneficial for remediating high adsorbate concentration (e.g., industrial wastewater), whereas large b value is important for low adsorbate concentration needing remediation (e.g., groundwater and drinking water). At low adsorbate concentration, a small $q_{\text{max}}$ value with large b value could gain higher $q_e$ than the situation of large $q_{\text{max}}$ and small b values (Cao et al., 2012). As presented in Table 2, the $q_{\text{max}}$ and b values for As(V)/Sb(V) adsorption were increased with increasing S/Fe ratio in the adsorbents. The enhancement of $q_{\text{max}}$ and b values for Sb(V) was more remarkable than As(V). The overall results thus indicated that sulfide-modification could dramatically increase the adsorption capacity and affinity of As(V) and Sb(V) on the
modified adsorbents, which is beneficial for the practical remediation of As(V) and Sb(V) in polluted water at different contamination levels.

3.5 Effect of coexisting anions

A great deal of anions can co-occur with As(V) or Sb(V) in wastewater environment, which might interfere with the elimination of As(V) or Sb(V) by adsorbents. The co-existing anions including Cl\(^-\), SO\(_4\)\(^{2-}\), NO\(_3\)-, and SiO\(_3\)\(^{2-}\) in this study displayed a marginal influence on As(V)/Sb(V) adsorption by sulfide-modified \(\alpha\)-FeOOH (Fig. 6). However, PO\(_4\)\(^{3-}\) exhibited a significant hindrance on As(V)/Sb(V) removal, indicating that PO\(_4\)\(^{3-}\) possessed a strong competition for active adsorption sites on the surface of sulfide-modified \(\alpha\)-FeOOH. The elements P, As and Sb belong to the same VA group in the periodic table. The similar atomic structure and hydrolysis behavior of PO\(_4\)\(^{3-}\) and As(V) or Sb(V) (Zhang et al., 2019c) could cause the strong competition during the adsorption process, thereby impacting the As(V)/Sb(V) adsorption capacity of the adsorbent in the presence of PO\(_4\)\(^{3-}\).

3.6 Adsorption mechanisms

To reveal the role of sulfide-modification on As(V) or Sb(V) sorption by sulfide-modified \(\alpha\)-FeOOH, the surface chemical environments of the sulfide-modified \(\alpha\)-FeOOH before and after As(V)/Sb(V) adsorption were further studied by XPS. The high resolution As3d spectra of As(V)-adsorbed \(\alpha\)-FeOOH and sulfide-modification \(\alpha\)-FeOOH were shown in Fig. 7a. Compared to the As3d spectra of As(V)-adsorbed \(\alpha\)-
FeOOH (BE \sim 45.9 eV), a combined spectra showing both As(V) 3d and As(III) 3d peaks was observed for As-adsorbed sulfide-modified \( \alpha \)-FeOOH. Specifically, the BE of 45.7 eV, 46.2 eV and 45.9 eV could be assigned to As(V), and 45.1 eV, 45.4 eV and 45.2 eV could be assigned to As(III) for the S/Fe ratio of 0.3, 0.5, 1.0, respectively (Wu et al., 2018; Penke et al., 2019; Zhou et al., 2020). The sulfide-modified \( \alpha \)-FeOOH thus exhibited a reductive transformation of As(V) to As(III) with the raise of S/Fe ratios, where the percentage of As(III) was 40.46, 55.11, and 70.70% of the total As for the S/Fe ratio of 0.3, 0.5 and 1.0, respectively. The reduction of As(V) by sulfide-modified \( \alpha \)-FeOOH could be attributed to the introduced sulfur species (\( S_2^{2-} \), \( S_n^{2-} \) and \( SO_3^{2-} \)). Therefore, As(V) was partially reduced to As(III), which likely contributed to the enhanced removal of As(V) by the sulfide-modified \( \alpha \)-FeOOH. This phenomenon was also observed in the case of As(V) removal using FeS adsorbent (Liu et al., 2016b). However, the BE of Sb3d spectra (Fig. 7b) after Sb(V) adsorption on \( \alpha \)-FeOOH and sulfide-modified \( \alpha \)-FeOOH showed no significant variation. Specifically, the BE of Sb3d were 540.0, 540.2, 540.4, and 540.2 eV for different S/Fe ratios, assigning all the peaks to Sb(V) only (He et al., 2019; Liu et al., 2019). Therefore, no reduction of Sb(V) occurred on the surface of sulfide-modified \( \alpha \)-FeOOH. Similar phenomenon was reported during the removal of Sb(V) by FeS\(_2/\alpha\)-Fe\(_2\)O\(_3\) (He et al., 2019). The sulfide-modified \( \alpha \)-FeOOH in this study exhibited chemical constituents of FeS\(_2/\alpha\)-FeOOH (as depicted by the XPS and FTIR results), which is similar to previously reported FeS\(_2/\alpha\)-Fe\(_2\)O\(_3\) adsorbents (He et al., 2019). It could be speculated that the \( \equiv\text{Fe-OH} \) and \( \equiv\text{S-H} \) were both responsible for the removal of Sb(V) by sulfide-modified \( \alpha \)-FeOOH.
The morphology of sulfide-modified α-FeOOH after As(V) and Sb(V) adsorption are shown in Fig. S5-S8. When the S/Fe ratio was less than 0.3, there was no obvious variation in the needle-like particles after reacting with As(V) (Fig. S5b, e and h) and Sb(V) (Fig. S7b, e and h), as compared with original adsorbents (Fig. 1). However, when the S/Fe ratio was higher than 0.3, the morphology of the adsorbents was dramatically altered after interacting with As(V) (Fig. S6) and Sb(V) (Fig. S8), and irregular small particles were formed. The peaks of As or Sb were observed in corresponding EDS spectra after removed by sulfide-modified α-FeOOH (Fig. S5-S8). Furthermore, the intensity of As and Sb peaks in the respective EDS spectrum became stronger along the raise of S/Fe ratio, indicating that the sulfide-modification improved the adsorption capacity of α-FeOOH toward As(V) and Sb(V).

To explain the role of Fe and S on the elimination of As(V)/Sb(V) by sulfide-modified α-FeOOH, variations of Fe and S species after the adsorption process were also studied by XPS. The Fe2p and S2p spectra of sulfide-modified α-FeOOH (S/Fe=1.0) pre- and post-adsorption of As(V) and Sb(V) are shown in Fig. S9. The peaks at 710.0 and 724.2 eV were assigned to Fe$^{2+}$ signals (Wan et al., 2014), and these two peaks shifted to 711.3 and 725.3 eV, and 710.8 and 724.8 eV after the sorption of As(V) and Sb(V), respectively (Fig. S9a), implying that Fe$^{2+}$ was partially oxidized to Fe$^{3+}$. Therefore, the ≡Fe-OH functional groups likely contributed to the sorption of As(V) and Sb(V). The S2p spectra also exhibited a significant variation after As(V) and Sb(V) adsorption (Fig. S9b). The S species in the original sulfide-modified α-FeOOH were S$_2^{2-}$, S$_n^{2-}$ and SO$_3^{2-}$, but the S$^{2-}$ species disappeared after the adsorption, leaving behind
only SO$_3^{2-}$ and S$_n^{2-}$. These results indicated that S species were oxidized, and participated in the reduction of As(V). The $\equiv$S-H functional groups were likely involved in the removal of Sb(V) (He et al., 2019).

Based on the discussion above, the conceived adsorption mechanisms between sulfide-modified $\alpha$-FeOOH and As(V)/Sb(V) could be summarized as the following:

(1) The adsorption kinetics for sulfide-modified $\alpha$-FeOOH toward As(V)/Sb(V) were well expressed by the pseudo second order, demonstrating that the adsorption process of As(V) and Sb(V) on sulfide-modified $\alpha$-FeOOH was controlled by a chemical reaction mechanism.

(2) The XPS results suggested that the abundant S species on sulfide-modified $\alpha$-FeOOH converted As(V) to As(III); the $\equiv$S-H functional groups were involved in the adsorption of Sb(V).

(3) The pH effect on adsorption indicated that electrostatic attraction also contributed to the As(V)/Sb(V) removal process. The sulfide-modified $\alpha$-FeOOH held more positive surface charges than $\alpha$-FeOOH, which was in favor of As(V)/Sb(V) removal. The sulfide-modified $\alpha$-FeOOH exhibited the crystal phase of $\alpha$-FeOOH, and contained abundant surface hydroxyl groups (as confirmed by XPS and FTIR). Therefore, the As(V/III) and Sb(V) were adsorbed through surface complexation reactions too via the $\equiv$Fe-OH groups.

4. Conclusions

In this work, a novel sulfide-modified $\alpha$-FeOOH was synthesized, and utilized
for As(V) and Sb(V) removal from aqueous solutions. The sulfide-modification exhibited significant effect on the morphology, crystal phases, surface composition, and surface charge of the α-FeOOH, consequently influenced the As(V)/Sb(V) adsorption performance. The sulfide-modified α-FeOOH increased the adsorption capacities of As(V) and Sb(V), but it was more notable for Sb(V). The adsorption affinity of sulfide-modified α-FeOOH toward As(V) and Sb(V) were also increased with increasing S/Fe ratio in the adsorbents. The kinetic and isotherm investigations implied that chemisorption and monolayer adsorption controlled the removal of As(V) and Sb(V) by the sulfide-modified α-FeOOH. The sulfide-modified α-FeOOH possessed a reducibility effect toward As(V), but not toward Sb(V). Overall, this study put forward a strategy to increase the adsorption affinity and capacity of As(V) and Sb(V) on α-FeOOH via sulfide modification. The sulfide-modified α-FeOOH thus exhibited promising implications for the remediation of As(V) and Sb(V) in aqueous media containing both high and low adsorbate concentrations.

Acknowledgements

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Declaration of interest
The authors declare no competing financial interests for this study.

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stability of Fe(III)-As(V) co-precipitate in the presence of ascorbic acid: Effect of pH and Fe/As molar ratio. Chemosphere 218, 670-679.


highly efficient arsenic removal: Preparation and performance evaluation.


**Figure captions**

Fig. 1. SEM images of (a) α-FeOOH, and sulfide modified α-FeOOH samples at S/Fe mole ratios of (b) 0.1, (c) 0.3, (d) 0.5, (e) 0.8, (f) 1.0.

Fig. 2. FTIR spectra (a), and XRD patterns (b) of α-FeOOH and sulfide-modified α-FeOOH materials at S/Fe mole ratios of 0.1, 0.3, 0.5, 0.8 and 1.0.

Fig. 3. High resolution XPS spectra of iron (Fe 2p) (a-d), oxygen (O 1s) (e-h), and sulfur (S 2p) (i-k) for sulfide-modified α-FeOOH materials synthesized at various S/Fe ratios.

Fig. 4. pH versus zeta potential curves of α-FeOOH and sulfide-modified α-FeOOH materials synthesized at various S/Fe mole ratios.

Fig. 5. Effect of pH on (a) As(V) and (b) Sb(V) adsorption by α-FeOOH and sulfide-modified α-FeOOH materials synthesized at various S/Fe mole ratios.

Fig. 6. Effect of co-existing anions on (a) As(V) and (b) Sb(V) adsorption by α-FeOOH and sulfide-modified α-FeOOH materials synthesized at various S/Fe mole ratios.

Fig. 7. High-resolution XPS spectra of (a) As 3d, and (b) Sb 3d following adsorption of As(V) and Sb(V) on α-FeOOH and sulfide-modified α-FeOOH materials synthesized at various S/Fe mole ratios.
Table 1. Pseudo-first order and pseudo-second order kinetic model parameters for As(V) and Sb(V) adsorption on $\alpha$-FeOOH and sulfide modified $\alpha$-FeOOH.

Table 2. Langmuir and Freundlich isotherm model parameters for the adsorption of As(V) and Sb(V) on $\alpha$-FeOOH and sulfide modified $\alpha$-FeOOH.
Figures

Fig. 1.
Fig. 2.
Fig. 3.
Fig. 4.
Fig. 5.
Fig. 6.
Fig. 7.
Table 1. Pseudo-first order and pseudo-second order kinetic model parameters for As(V) and Sb(V) adsorption on α-FeOOH and sulfide modified α-FeOOH.

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<th>Pseudo-second order model</th>
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<td>$q_{e,cal}$ (mg/g)</td>
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Table 2. Langmuir and Freundlich isotherm model parameters for the adsorption of As(V) and Sb(V) on α-FeOOH and sulfide modified α-FeOOH.

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<th>Freundlich model</th>
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<td>$q_{\text{max}}$ (mg/g)</td>
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<td>S/Fe=1.0</td>
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Supplementary Information for:

**Comparative removal of As(V) and Sb(V) from aqueous solution by sulfide-modified α-FeOOH**

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1. SI Texts

Modeling of adsorption data

Adsorption kinetics

Kinetic investigation is crucial for understanding the adsorption mechanism as well as the equilibrium time. The pseudo-first order and pseudo-second order (Ho, 2006; Yue et al., 2018) models were adopted to probe the kinetic results. The linear equations were expressed as:

Pseudo-first-order: \[ \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \]  
\[ \text{(SEq.1)} \]

Pseudo-second-order: \[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  
\[ \text{(SEq.2)} \]

Where, \( q_e \) (mg/g) and \( q_t \) (mg/g) represent the adsorption capacity of As(V) or Sb(V) at equilibrium and time \( t \) (min), \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g/(mg min)) are the corresponding rate constants.

Adsorption isotherms

Adsorption isotherms were used to explore the adsorption characteristics such as the maximum adsorption as well as the adsorbate distribution between the liquid and solid phases. The Langmuir and Freundlich isotherm (Lee et al., 2018; Najib and Christodoulatos, 2019) models were utilized for analyzing the adsorption isotherm data. The equations were expressed as:

Langmuir isotherms model: \[ \frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{b q_{\text{max}}} \]  
\[ \text{(SEq.3)} \]

Freundlich isotherms model: \[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  
\[ \text{(SEq.4)} \]

Where, \( C_e \) (mg/L) and \( q_e \) (mg/g) are the equilibrium concentration and equilibrium adsorption capacity for As(V) or Sb(V), \( q_{\text{max}} \) (mg/g) is the predicted maximum adsorption capacity of
sulfide-modified α-FeOOH, $b$ (L/mg) is the Langmuir constant concerning the adsorption affinity and the energy of adsorption, $K_F$ (mg/g (1/mg$^{1/n}$)) is the Freundlich constant concerning the capacity of adsorbent, $n$ is the Freundlich exponential constant concerning the favorability of the adsorption process.

2. SI Figures

Fig. S1. Schematic for the synthesis steps of sulfide-modified α-FeOOH.
Fig. S2. As(V) and Sb(V) species distribution at different solution pH values.
Fig. S3. Time dependence of As(V) and Sb(V) adsorption on α-FeOOH and sulfide-modified α-FeOOH materials synthesized at various S/Fe mole ratios; (a–c) effect of contact time, pseudo-first order kinetic plot, and pseudo-second order kinetic plot for As(V) adsorption, respectively; (d–f) effect of contact time, pseudo-first order kinetic plot, and pseudo-second order kinetic plot for Sb(V) adsorption, respectively.
Fig. S4. Concentration dependence of As(V) and Sb(V) adsorption on α-FeOOH and sulfide-modified α-FeOOH materials synthesized at various S/Fe mole ratios; (a–c) adsorption isotherm, Langmuir plot, and Freundlich plot for As(V) adsorption, respectively; (d–f) adsorption isotherm, Langmuir plot, and Freundlich plot for Sb(V) adsorption, respectively.
Fig. S5. SEM images and EDS spectra of adsorbents after As(V) adsorption; (a-c) S/Fe=0, (d-f) S/Fe=0.1, and (g-i) S/Fe=0.3.
Fig. S6. SEM images and EDS spectra of adsorbents after As(V) adsorption; (a-c) S/Fe=0.5, (d-f) S/Fe=0.8, and (g-i) S1.0.
Fig. S7. SEM images and EDS spectra of adsorbents after Sb(V) adsorption: (a-c) S/Fe=0, (d-f) S/Fe=0.1, and (g-i) S/Fe=0.3.
Fig. S8. SEM images and EDS spectra of adsorbents after Sb(V) adsorption: (a-c) S/Fe=0.5, (d-f) S/Fe=0.8, and (g-i) S1.0.
Fig. S9. High-resolution XPS spectra of Fe 2p and S 2p of sulfide-modified α-FeOOH (S/Fe=1.0).
3. SI Table

Table S1. Effect of sulfide modified α-FeOOH (0.5 g/L) on the solution pH during the adsorption of As(V) and Sb(V) (500 mg/L)

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<th>S/Fe ratio</th>
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<td>4</td>
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</tr>
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Table S2. Comparison of maximum adsorption capacities ($q_{\text{max}}$) for As(V) and Sb(V) on various adsorbents

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<th>Adsorbates</th>
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<th>Adsorbents</th>
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<th>References</th>
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<td></td>
<td>5.0</td>
<td>Fe@MesoPS</td>
<td>140-190</td>
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<td>RGO/Mn₃O₄</td>
<td>105.5</td>
<td>Zou et al., 2016</td>
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<td>1111.1</td>
<td>Present study</td>
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### 4. SI References


