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Enhanced oxidative and adsorptive capability towards antimony by copper-doping into magnetite magnetic particles†

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This study compared the removal capability and mechanisms involved in the removal of aqueous Sb by non-doped and Cu-doped Fe₃O₄ (magnetite). After doping Cu into Fe₃O₄, it exhibited a smaller particle size with slightly declined saturation magnetization, and enhanced antimony adsorptive capability. Non-doped Fe₃O₄ showed a maximum adsorption capacity ($Q_{\max}$) of 34.46 mg Sb(III) g⁻¹ and 7.07 mg Sb(V) g⁻¹ at pH 7.0. The doping of Cu improved the Sb adsorption with a $Q_{\max}$ of 43.55 mg Sb(III) g⁻¹ and 30.92 mg Sb(V) g⁻¹ accordingly. The co-existing sulfate and carbonate had a negligible effect on Sb removal; however, phosphate at 10 mM decreased the Sb(III) and Sb(V) removal by 50.1% and 18.2% for Fe₃O₄ and by 14.1% and 58.6% for Cu-doped Fe₃O₄. As for Cu-doped Fe₃O₄, the results indicated that the Sb(III) oxidation on ≡Cu^{II}-O sites was much more significant than that on ≡Fe^{III}-O sites and the dissolution oxygen amount did not affect this process. Upon the electron transfer from Sb(III) to Cu(II), the formed Cu(I) and Sb(V) tends to release into the solution and the Cu(I) disproportionates to give Cu(II) ions and a precipitate of Cu(0) thereafter. The magnetic Cu-doped Fe₃O₄ shows good removal efficiency towards both Sb(III) and Sb(V) and is a potential adsorbent for Sb removal in practice.

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1. Introduction

In 2014, approximately 160 000 tons of antimony (Sb) was mined and used to produce various industrial products such as flame-retardants and ammunitions globally.¹ Although background Sb concentrations in natural water and soils are normally low, the anthropogenic activities contribute to the significantly elevated Sb concentrations in the environment.² Sb exists in several oxidation states of -III, 0, +III, +V, and among which antimonate [Sb(V)] usually exists in aerobic waters, whereas antimonite [Sb(III)] is mainly found in anaerobic conditions on account of chemical and microbial processes.³ Long-term exposure to Sb contaminated drinking water creates great risks towards human health. The United States Environmental Protection Agency (USEPA) classifies antimony as the priority pollutant, and the maximum contaminant level (MCL) in drinking water is 6 µg L⁻¹. The more strict MCLs of 2 and 5 µg L⁻¹ have been issued in Japan and China.⁴ The development of highly-efficient and cost-effective method for Sb removal from drinking water is practically valuable.

So far, many techniques such as coagulation and flocculation,⁵ reverse osmosis,⁶ electrochemical process,⁷ and adsorption^{8,9} have been proposed for Sb removal. Among these methods, adsorption is advantageous with high efficiency, low-cost, and low maintenance requirement. It is widely considered as one of the best available technologies for medium- and small-scale systems.¹⁰ Conventional adsorbents such as activated carbon,¹¹ aluminum-based adsorbent,¹² and iron-based adsorbent¹³ have been developed for Sb adsorption. However, their adsorptive capacity is not as high as expected, and the high operating costs of solid-liquid separation process which hinders their large-scale applications.

Recently, magnetic particles, as a new kind of adsorbent attracted worldwide attention due to their exhibited excellent adsorption performance and low-cost magnetic solid-liquid separation in the water purification.^{14,15} Over the past decade, the novel magnetic adsorbents, *e.g.* MnO₂ modified graphene oxide nanocomposite,¹⁶ γ-Fe₂O₃,⁵ magnetite (Fe₃O₄),⁶ and nano-scale zero-valent iron (nZVI),¹⁷ have been developed for removal of various pollutants from water. Pure Fe₃O₄ shows excellent magnetic properties; however, its adsorption efficiency towards Sb is relatively low.^{18,19} The doping of transition metal elements like zinc,²⁰ cobalt,²¹ copper,²² manganese²³ into Fe₃O₄ increases its surface sites available for adsorption, and the adsorption capability may be improved accordingly.²⁴ For example, the doping of copper (Cu) into Fe₃O₄ increases the adsorption sites and improved its adsorption towards arsenic.²⁵ Furthermore,

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Wang *et al.* found that As(III) was efficiently oxidized to As(V) by O₂ on Fe₃O₄:Cu particles, and the Cu(II)/(I) couple was proposed to play a dominant role.²⁶ Unfortunately, there is lack of direct evidence that Cu-doped Fe₃O₄ owes enhanced catalytic effect on adsorption or oxidation of Sb. From the thermodynamics point-of-view, Cu-doped Fe₃O₄ may also act as an electronic mediation center to accelerate the oxidation of aqueous Sb(III). This effect may play an important role with respect to the adsorption of reductive species. However, previous studies have rarely focused on application of Cu-doped Fe₃O₄ for removal of Sb(III) and Sb(V) from drinking water.

In the present work, we prepared two magnetic samples of non-doped Fe₃O₄ and Cu-doped Fe₃O₄ by solvothermal method, and compared their magnetic properties and surface characters. The adsorptive behaviors of non-doped Fe₃O₄ and Cu-doped Fe₃O₄ towards Sb(III) and Sb(V) as well as the effects of pH, ionic strength, and coexisting anions on adsorption were investigated in batch experiments. Furthermore, the species transformation of Sb and Cu during adsorption of Sb(III) onto Cu-doped Fe₃O₄ in N₂- or O₂-purging systems were analyzed, and the mechanisms and possible pathways involve in were proposed accordingly.

2. Experimental

2.1 Chemicals

All of the chemical reagents used in this study, including iron(III) chloride hexahydrate (FeCl₃·6H₂O), copper(II) chloride dehydrate (CuCl₂·2H₂O), ethylene glycol (C₂H₆O₂), sodium acetate (C₂H₃NaO₂), polyethylene glycol (H(OCH₂CH₂)_n OH), unless otherwise noted, were analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd, China.

The Sb(III) and Sb(V) stock solutions (100 mg L⁻¹) were prepared by dissolving the antimony potassium tartrate (C₄H₄KO₇Sb·0.5H₂O) and potassium pyroantimonate (KSb(OH)₆) (Sigma-Aldrich Co. Ltd, USA) with ultrapure water (Millipore, 18.2 MΩ·cm resistivity), respectively.

2.2 Adsorbents preparation

According to a modified version of the procedure of Deng,²⁷ the non-doped Fe₃O₄ and Cu-doped Fe₃O₄ magnetic nanoparticles were prepared by solvothermal method. Briefly, while preparing Cu-doped Fe₃O₄, an amount of 1.08 g FeCl₃·6H₂O and 1.71 g CuCl₂·2H₂O were dissolved in 80 mL ethylene glycol, and the solution was stirred at room temperature for 30 min to yield a clear solution of a dark olive color. Then 7.2 g CH₃COONa and 2.0 g polyethylene glycol were added into the above solution with stirring in a 70 °C water-bath. After being stirred for 30 min, the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed and heated at 200 °C for 12 h. After cooling to room temperature naturally, the formed products were collected by magnetic separation and then washed several times with ethanol and deoxygenated water. After being dried at 65 °C for 12 h in vacuum, the synthesized composites were crushed and stored under N₂ atmosphere. And the preparation of non-doped Fe₃O₄ sample followed similar procedures except that no CuCl₂·2H₂O was added.

2.3 Characterization of Cu-doped Fe₃O₄ and non-doped Fe₃O₄ magnetic particle

The specific surface area (*S*_{BET}) of samples were calculated by applying the multipoint Brunauer Emmett and Teller (BET) equation on the nitrogen adsorption data collected on an ASAP 2020 surface area analyzer (Micromeritics, USA). Prior to BET analysis, all samples were degassed under vacuum at 150 °C for 4 h. X-ray diffraction (XRD) patterns were recorded on an X'Pert PRO MPD X-ray diffractometer (PANalytical B.V., The Netherlands) equipped with Cu Kα radiation. All diffraction patterns then analyzed using PANalytical X'Pert HighScore Plus 2.0 software packages and the peaks were matched using ICDD PDF-4+ 2004 database. The surface-sensitive analyses were performed with an X-ray photoelectron spectrometer (XPS) (Kratos, U.K) using a monochromatic Al-Kα anode radiation source. The XPS results were fitted Gaussian–Lorentzian peak functions on a Shirley background using a nonlinear least squares curve fitting program (XPS Peak) and corrected using the C 1s level at 284.8 eV. The surface morphologies of non-doped Fe₃O₄ and Cu-doped Fe₃O₄ were observed under the transmission electron microscope type H-7500 (Hitachi, Japan). The samples were injected into a flow cell of Zetasizer 2000 (Malvern, U.K.) and the particle electrophoretic mobility was measured to calculate the zeta potential. The Fourier transform infrared spectroscopy (FT-IR) spectra of original adsorbents and those with adsorbed Sb were collected at a range of 400–4000 cm⁻¹ using a TENSOR 27 spectrometer (Bruker, Germany) by the KBr (1 : 100 ratio) pellet method. The room temperature (300 K) magnetic susceptibility and *M*–*H* hysteresis loop of samples were investigated with Physical Property Measurement System (PPMS) equipped with a Vibrating Sample Magnetometer (VSM) (Quantum, USA).

2.4 Batch adsorption experiments

2.4.1 Adsorption kinetics. Batch adsorption kinetics experiments were conducted in 1 liter beaker with mechanical stirring (150 rev min⁻¹) at 25 ± 1 °C. For each experiment, 0.18 g non-doped Fe₃O₄/Cu-doped Fe₃O₄ was added to 900 mL solutions with the initial concentration of Sb(III) and Sb(V) were 50 mg L⁻¹. The potassium nitrate (KNO₃) as the background electrolyte was added to get the ionic strength (IS) of 0.1 M. The pH was adjusted during adsorption using 0.1 M NaOH and 0.1 M HNO₃ to achieve pH variation in the range of 7.0 ± 0.2. Approximately 4 mL aliquots were taken at predetermined reaction time and the samples were immediately filtered through 0.45 μm membrane and kept at 4 ± 0.5 °C for further analysis. Finally, the adsorbents were collected by filtration, rinsed by deionized water, and freeze-dried for the further characterization.

To confirm the lower concentration antimony removal, a sorption study with 0.2 g L⁻¹ adsorbent was conducted using initial Sb concentrations of 50 μg L⁻¹. Other adsorption experimental procedures were the same as above.

2.4.2 Adsorption isotherms. Adsorption isotherms experiments were conducted in a 250 mL capped flask with continuous rotary shaking (150 rev min⁻¹) by a thermostatic

reciprocating shaker at 25 ± 1 °C. For each experiment, 0.02 g of adsorbent was added to 100 mL solutions with different initial antimony concentrations (in the range from 5 to 100 mg L⁻¹) and shake for 12 h. After adsorption, the suspensions were filtered through 0.45 µm membrane filters for further analysis.

2.4.3 Effects of pH and ionic strength. While investigating the effects of pH on Sb sorption, the initial pH was adjusted to be in the range from 3.0 to 7.0 and 3.0 to 10.0 for the Sb(III) and Sb(V) adsorption systems, respectively. It was noted that Sb(III) tends to precipitate in the form of Sb₂O₃ at pH > 7.0.¹⁷ The solution pH was adjusted at different intervals during adsorption to avoid significant pH variation. While investigating the effects of IS on aqueous Sb adsorption, the KNO₃ was added to obtain desired IS of 0.01 M and 0.1 M. The suspensions were filtered through 0.45 µm membrane after 12 h reaction, and the concentrations of Sb, Fe, and Cu in the supernatant were analyzed thereafter.

2.4.4 Effect of co-existing anions. The carbonate, sulfate, and phosphate widely exist in natural waters. To investigate their effects on antimony adsorption, batch experiments as noted above were preceded except that these anions (CO₃²⁻, SO₄²⁻, and PO₄³⁻) at 1 and 10 mM were added prior to the addition of adsorbents. The adsorbent dose was 0.2 g L⁻¹. The pH was maintained at 7.0 ± 0.2 and the temperature was controlled at 25 ± 1 °C.

2.4.5 Species transformation in adsorption process. The Sb(III) solutions at 50 mg L⁻¹ were respectively purged with high purity N₂ and O₂ for 30 min and the dissolved oxygen (DO) of each sample was verified by a 550A meter (YSI, USA) before and after adsorption process. To avoid possible nitrate oxidation, KNO₃ was not added and pH was adjusted to 7.0 ± 0.2 and 11.0 ± 0.2 by using 0.1 M NaOH and 0.1 M HCl.²⁸ Dose of 0.2 g L⁻¹ non-doped Fe₃O₄ or Cu-doped Fe₃O₄ were added to the oxygen-free (N₂ purged, DO < 0.1 mg L⁻¹) and oxygen-enriched (O₂ purged, DO > 15.0 mg L⁻¹) solution. Then all the flasks were carefully sealed to avoid air intrusion. Samples were shaken by a thermostatic reciprocating shaker (150 rev min⁻¹, 25 ± 1 °C). The control experiments followed similar procedures except that no non-doped Fe₃O₄ or Cu-doped Fe₃O₄ was added for determining aqueous antimony species transformation. After 12 h adsorption, about 5 mL suspension was collected and filtered through 0.45 µm membrane filters to analyze the aqueous Sb(III)/(V). The analysis of aqueous copper species transformation followed similar procedures except using the Sb(III), Sb(V) and non-adsorbate solution as comparisons.

2.5 Analytical methods

The concentrations of total Sb, Cu, and Fe in aqueous samples acidified with HNO₃ (1% v/v) were determined by the Agilent 710 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Agilent Co., USA). The AF-630A hydride generation atomic fluorescence spectrometer (HG-AFS) (Beifen-Ruili, China) was employed to analyze the valence state of aqueous Sb.²⁹ The concentrations of aqueous Cu^I were spectrophotometrically determined using a modified bathocuproine method.^{30,31} The reactions between Cu(I) and bathocuproine

contributed to the formation of Cu(I)-bathocuproine complex. This complex may be quantitatively measured at 484 nm with a T6 spectrophotometer (Persee, China) against a blank solution in a 10 cm cell. The concentration of Cu^{II} was calculated by subtracting Cu^I from the total dissolved copper.

3. Results and discussions

3.1 Characterization of Fe₃O₄ and Cu-doped Fe₃O₄ microspheres

The dominant reactions involved in the preparation of Cu-doped Fe₃O₄ and non-doped Fe₃O₄ are as follows:

Here, ethylene glycol acts as the reductant and surfactant for the synthesis of monodispersed particles.³²

Finally, these iron(III) and copper(II)/iron(II) hydroxides react to form magnetite structures:

Chemical composition analysis revealed that the molar ratio of Cu to Fe on the Cu-doped Fe₃O₄ surface was 1 : 2.32 (Table S1†), and this was close to that of the precursors, *i.e.*, 1 : 2. The chemical formula of non-doped Fe₃O₄ and Cu-doped Fe₃O₄ may be expressed as Fe_{3.15}O₄ and Cu_{0.72}Fe_{1.66}O₄. The XRD patterns of the non-doped Fe₃O₄ and Cu-doped Fe₃O₄ adsorbents are illustrated in Fig. 1(a). As indicated from the XRD patterns, all the peaks in both non-doped and Cu-doped Fe₃O₄ can be assigned to the inverse cubic spinel structure, and the crystal structure of the Cu-doped is inferred to be similar to that of Fe₃O₄. The peaks of non-doped Fe₃O₄ are observed at $2\theta = 30.05^\circ$, 35.30° , 42.93° , 56.93° , and 62.49° , and these peaks respectively represent the Bragg reflections from the (220), (311), (400), (511), and (440) planes (as identified by ICDD card 01-086-1356). It is noted that a weak peak of residual FeCl₃ (2θ at 33.42°) can also be observed (ICDD card 00-001-1059). The XRD patterns of the Cu-doped Fe₃O₄ were indexed as CuFe₂O₄ (ICDD card 01-077-0427), and the newly-appeared peak at 43.36° was attributed to Cu⁰ (ICDD card 03-065-9026) and those at 36.49° and 42.42° could match the Cu^I₂O card (ICDD card 01-077-0199). This indicated the partial reduction of Cu^{II} to Cu⁰/Cu^I during the synthesis of Cu-doped Fe₃O₄. Additionally, the peaks of Cu 2p in the XPS data indicated that there had two or three copper species (Cu⁰/Cu^I and Cu^{II}) in the Cu-doped Fe₃O₄ sample (Fig. S1†). Moreover, several XRD peaks were observed to gradually shift to higher diffraction angles after Cu-doping. This may be attributed to the slight change in the lattice constant after the substitution of Fe²⁺/Fe³⁺ ions by copper ions with different ionic radius.^{26,33}

The doping of Cu into Fe₃O₄ also showed effects on the binding energy (BE) of elemental Fe [Fig. 1(b)]. The levels of Fe

Fig. 1 (a) XRD patterns and (b) XPS results of Fe 2p core level photoelectron spectra of non-doped Fe_3O_4 and Cu-doped Fe_3O_4 .

$2p_{3/2}$ and Fe $2p_{1/2}$ were determined to be 710.01 and 723.51 eV for Fe_3O_4 , and these results are in accordance with previous study.³⁴ After Cu doping, the peaks of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ shift to higher binding energy of 710.15 and 723.85 eV. The higher binding energy was relative to higher positive oxidation state, owing to the extra coulombic interaction between the photo-emitted electron and the ion core. It is reported that the divalent iron (Fe^{II}) within Fe_3O_4 may be partly or fully replaced by other divalent ions such as Cu^{II} .^{33,35} The shift of Fe 2p XPS peaks revealed the substitution of the Fe^{II} sites (octahedral or tetrahedral) by Cu^{II} , and the ratio of elemental Fe with higher oxidation state (Fe^{III}) was increased thereafter.

The BET surface areas (S_{BET}) of samples calculated from nitrogen adsorption and desorption isotherm plot [Fig. 2(a)]. The Cu-doped Fe_3O_4 sample showed higher S_{BET} of $67.20 \text{ m}^2 \text{ g}^{-1}$ than non-doped Fe_3O_4 ($S_{\text{BET}} = 9.66 \text{ m}^2 \text{ g}^{-1}$). According to the IUPAC classification, all the samples exhibit type-IV isotherms with a very narrow hysteresis loop in the relative pressure (P/P_0) range of 0.4–1.0, which exhibits a typical less-pore structure.³⁶ The increased surface area also is seen in the representative TEM images [Fig. 2(b)]. The standard deviation of particle size

Fig. 2 (a) N_2 adsorption (solid symbols) and desorption (open symbols) isotherm of Fe_3O_4 and Cu-doped Fe_3O_4 at 77 K (b) TEM images and size distribution of non-doped Fe_3O_4 and Cu-doped Fe_3O_4 with Gaussian fitting.

was found to be 528.9 nm for Fe_3O_4 and 44.5 nm for Cu-doped Fe_3O_4 . Additionally, the non-doped Fe_3O_4 were spherical with narrow size distributions, whereas the Cu-doped Fe_3O_4 showed much smaller size with roughen edges. In a typical solvothermal process, the diameters of the ferrite microspheres are influenced by reaction time, the species types, and concentrations of raw materials,²⁷ which is suitable for adsorbent optimization. The co-precipitation method may also synthesize the Fe_3O_4 and Cu-doped Fe_3O_4 and their particle diameter was reported to be 14.49 and 11.78 nm, respectively.²⁵ The obtained materials in this study exhibited larger particle size and were easier to be removed by magnetic separation [eqn (S1)†].³⁷ The doping of Cu into Fe_3O_4 decreased the particle size, increased surface area, and may provide more active sites available for adsorption as compared to Fe_3O_4 .

The magnetic particles with higher saturation magnetization are more susceptible to magnetic field, and can be easier separated by magnetic separation. The magnetic properties of

Fig. 3 Magnetization curve of (1) non-doped Fe_3O_4 and (2) Cu-doped Fe_3O_4 .

the non-doped Fe_3O_4 and Cu-doped Fe_3O_4 particles were compared by the magnetization curves measured by VSM at 300 K (Fig. 3). The magnetic saturation value (M_s) of the Cu-doped Fe_3O_4 was determined to be 43.1 emu g^{-1} , whereas that of the Fe_3O_4 was observed to be 67.1 emu g^{-1} . The decreased M_s might be attributed to Cu^{2+} substituting the iron cations (Fe^{2+} or Fe^{3+}) from the lattice, and this effect resulted in disordered structure and decreased magnetic properties accordingly.³⁸ Generally, the obtained Cu-doped Fe_3O_4 showed relatively high M_s as compared with other magnetic adsorbents [e.g. MnFe_2O_4 (35.2 emu g^{-1}),³⁹ Ascorbic acid coated Fe_3O_4 (40.0 emu g^{-1}),⁴⁰ magnesium ferrite (32.9 emu g^{-1})⁴¹], and the Cu-doped Fe_3O_4 is viewed as a promising magnetic adsorbent which could be separated by a magnetic field easily.

3.2 Adsorptive behaviors of Fe_3O_4 and Cu-doped Fe_3O_4 towards Sb(III) and Sb(V)

3.2.1 Adsorption kinetics. The effect of contact time on the Sb adsorption was examined to determine the time required for reaching adsorption equilibrium. Fig. 4 illustrates the adsorption density (q_t) of Sb(III) and Sb(V) onto these two microspheres with prolonged contact time (t). Three adsorption kinetic models,^{42,43} Pseudo-first-order eqn (4), Pseudo-second-order eqn (5), and Elovich model eqn (6), were used to fit the experimental data and the obtained kinetic parameters are summarized in Table 1.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (5)$$

$$q_t = k_3 \ln(t) + C \quad (6)$$

where q_e and q_t (mg g^{-1}) are the amounts of solute sorbed on the surface of the sorbent at equilibrium and at time t (min),

respectively. The k_1 , k_2 , and k_3 are the rate constants of the Pseudo-first-order, Pseudo-second-order, and Elovich equations, respectively.

It was observed that Cu-doped Fe_3O_4 had higher adsorption density and velocity towards Sb(III) and Sb(V) than Fe_3O_4 , and the adsorption process could be divided into three stages. In the initial rapid adsorption stage (0–1 h), Cu-doped Fe_3O_4 contributed to the q_t of 77.9% and 94.2% to the equilibrium sorption capacity (q_e) of Sb(V) and Sb(III) , respectively. In the second stage (1–6 h), the intra-particle diffusion dominated in the adsorption of Sb, and the adsorption rate slowed down greatly. The 6 h contact time could achieve over 93% of the q_e for all samples. In the third stage (6–12 h), the q_t of both Sb(III) and Sb(V) showed little variation, and the contact time of 12 h was sufficient to approach the equilibrium.

As indicated from R^2 values (Table 1), Pseudo-first-order equation model was best fitted to describe the adsorption of Sb(III) onto Fe_3O_4 and that of Sb(V) onto Cu-doped Fe_3O_4 . Comparatively, Elovich equation fitted best for the adsorption of Sb(V) onto Fe_3O_4 and that of Sb(III) onto Cu-doped Fe_3O_4 . Elovich model is relative to the adsorption on highly-heterogeneous surfaces with the dominant mechanisms of surface chemisorption.⁴⁴

In natural condition, antimony concentration usually presents less than $50 \mu\text{g L}^{-1}$ in freshwater systems.⁴⁵ It is necessary to treat antimony-contaminated water and control the antimony concentration to permissible limits, which are $10 \mu\text{g L}^{-1}$ and $6 \mu\text{g L}^{-1}$ in the World Health Organization (WHO) and US EPA guidelines,^{46,47} respectively. As shown in Fig. S2(a),† the initial Sb(III) concentration was about $50.0 \mu\text{g L}^{-1}$ and the equilibrium adsorption capacity, whatever non-doped or Cu-doped Fe_3O_4 , was achieved within 4 h. Furthermore, the removal rate was over 90%, and the residual antimony concentration was lower than the guidelines of WHO and US EPA. However, we found that Sb(V) was more difficult to be removed using the same procedure [Fig. S2(b)†]. The non-doped Fe_3O_4 removed the aqueous Sb(V) from $50.0 \mu\text{g L}^{-1}$ to $12.87 \mu\text{g L}^{-1}$, which exceeded the WHO and EPA drinking water guideline. Similar to the high Sb concentration study's findings, the Cu-doped Fe_3O_4 showed more Sb(V) adsorption capacity than non-doped Fe_3O_4 . The residual Sb concentration was detected only $4.47 \mu\text{g L}^{-1}$ after treated with Cu-doped Fe_3O_4 . Sb(V) is the principal form of antimony in the aqueous environments,⁴⁸ as compared to Sb(III) . Therefore, high adsorption capacity of Sb(V) is more meaningful to practical application.

Additionally, it was observed that Sb(III) easily adsorbed onto these two adsorbents than Sb(V) and the obtained $q_{e,\text{Sb(III)}}$ values were twice or more to those of $q_{e,\text{Sb(V)}}$. This trend is contrary to that of As(III) which is more difficult to be removed than As(V) by adsorption process.²⁶ The reduction of Sb(V) to Sb(III) is inferred to improve Sb removal; unfortunately, it was rather difficult to achieve on the basis of thermodynamic considerations and operational requirements. The development of novel adsorbents with high capability towards Sb(V) is of crucial importance, and the Cu-doping greatly improves the adsorption capability of Fe_3O_4 towards Sb(V) which is practically valuable.

Fig. 4 Adsorption kinetics of (a) Sb(III) and (b) Sb(V) on Fe_3O_4 and Cu-doped Fe_3O_4 ($[\text{Sb(III)}]_0 = [\text{Sb(V)}]_0 = 50 \text{ mg L}^{-1}$, adsorbents doses = 0.2 g L^{-1} , $\text{pH} = 7.0$).

3.2.2 Adsorption isotherms. Fig. 5 illustrates the adsorption isotherms of Sb(III) and Sb(V) onto these two adsorbents, and the fitted constants by Langmuir eqn (7), Freundlich eqn (8), Langmuir 2-surface eqn (9) and Sips isotherm eqn (10) that are presented in Table 2.

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (7)$$

$$q_e = K_F (C_e)^{1/n} \quad (8)$$

$$q_e = \frac{q_{m1} b_1 C_e}{1 + b_1 C_e} + \frac{q_{m2} b_2 C_e}{1 + b_2 C_e} \quad (9)$$

$$q_e = \frac{q_m (b_3 C_e)^\beta}{1 + (b_3 C_e)^\beta} \quad (10)$$

where, q_e is the amount of antimony adsorbed on the solid phase (mg g^{-1}), C_e is the equilibrium antimony concentration in the solution (mg L^{-1}), q_m is the monolayer adsorption capacity of the sorbent (mg g^{-1}), and K_L and b_3 are the Langmuir adsorption constant (L mg^{-1}) related with the free energy of adsorption. K_F is a constant relating the adsorption capacity and $1/n$ is an empirical parameter relating the adsorption intensity. In eqn (9), q_{m1} and q_{m2} represent as monolayer adsorption capacity of two different active sites respectively and b_1 , b_2 as the adsorption/desorption equilibrium constant related to the bonding energy.

Langmuir and Langmuir 2-surface isotherms assume monolayer adsorption onto surfaces with finite adsorption sites and no transmigration of adsorbate in the plane of surfaces. Comparatively, Freundlich isotherm assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as the function of surface coverage.⁴⁹ The Sips isotherm is the combination of Langmuir and Freundlich isotherms and assumes that the distribution of binding affinities of the adsorption sites with the adsorbate can be described by a Gaussian-like distribution expression.⁵⁰ In eqn (10), q_m (mg g^{-1}) and b_3 (L mg^{-1}) have the same meaning as q_m and K_L in Langmuir model, whereas the exponent β introduced from Freundlich model indicates the heterogeneity of the adsorption sites. The applicability of these isotherms was compared by the R^2 coefficients.

Results in Fig. 5 and Table 2 indicated that these four models could well describe the adsorption of Sb(III) and Sb(V) onto these two adsorbents with R^2 ranging from 0.799 to 0.987. The obtained q_m values from the Langmuir isotherm of Sb(III) and Sb(V) on Cu-doped Fe_3O_4 was 1.41 and 4.87 times to those on Fe_3O_4 surfaces. Comparatively, Cu-doped Fe_3O_4 could provide more active sites available to capture antimony than Fe_3O_4 . Table 2 indicated that the Sips isotherm was best to describe the adsorption of Sb(III) and Sb(V) onto Fe_3O_4 and that of Sb(III) onto Cu-doped Fe_3O_4 . The adsorption of Sb(V) onto Cu-doped Fe_3O_4 could be best described by the Langmuir 2-surface model which

Table 1 Adsorption kinetics constants for the adsorption of Sb(III) and Sb(V) onto Fe_3O_4 and Cu-doped Fe_3O_4

Condition		Pseudo-first-order equation			Pseudo-second-order equation			Elovich equation		
		q_e (mg g^{-1})	K_1	R^2	q_e (mg g^{-1})	K_2	R^2	C	K_3	R^2
Sb(III)	Fe_3O_4	32.84	0.03	0.964	37.13	0.001	0.924	-4.72	7.17	0.862
	Cu-doped Fe_3O_4	38.89	0.17	0.890	41.95	0.006	0.959	20.10	4.29	0.987
Sb(V)	Fe_3O_4	4.14	0.07	0.818	4.56	0.018	0.883	0.45	0.74	0.920
	Cu-doped Fe_3O_4	22.99	0.04	0.980	25.65	0.002	0.976	-2.92	4.97	0.950

Fig. 5 Adsorption isotherms of (a) Sb(III) and (b) Sb(V) on Fe_3O_4 and Cu-doped Fe_3O_4 ($[\text{Sb(III)}]_0 = [\text{Sb(V)}]_0 = 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 \text{ mg L}^{-1}$, adsorbents doses = 0.2 g L^{-1} , pH = 7.0).

Table 2 The fitted parameters for the adsorption of Sb(III) and Sb(V) on Fe_3O_4 and Cu-doped Fe_3O_4

Condition		Langmuir			Freundlich			Sips		Langmuir 2-surface		
		$q_{\text{max}} (\text{mg g}^{-1})$	K_L	R^2	n	K_F	R^2	q	R^2	q_{m1}	q_{m2}	R^2
Sb(III)	Fe_3O_4	30.92	0.378	0.975	6.061	15.19	0.975	35.8	0.987	19.6	13.7	0.987
	Cu-doped Fe_3O_4	43.55	1.78	0.926	12.69	31.40	0.853	42.6	0.958	23.2	20.2	0.932
Sb(V)	Fe_3O_4	7.068	0.116	0.832	4.01	2.183	0.799	6.94	0.847	3.53	3.53	0.847
	Cu-doped Fe_3O_4	34.46	0.089	0.925	3.266	8.206	0.976	36.75	0.95	34.43	10.05	0.982

is often used to describe the heterogeneous surfaces with different bonding energies. The surface sites on Cu-doped Fe_3O_4 surfaces may include two different sites of Cu–O (cupric oxide) and Fe–O (iron oxide), and the adsorption capability of strong and weak adsorption sites were determined to be 34.43 and 10.05 mg g^{-1} respectively.

Comparatively, Cu-doped Fe_3O_4 showed higher adsorption capacity towards Sb(III) and Sb(V) than the non-doped Fe_3O_4 , and this may be mainly attributed to its low particle diameter, high surface area, and more and powerful adsorption site. Table 3 further compares the adsorption capacity of these two adsorbents with other reported adsorbents. Cu-doped Fe_3O_4 may not be the best adsorbent to adsorb Sb; however, its magnetic character with relatively high adsorption density enables it as a promising alternative adsorbent for Sb removal.

3.2.3 Effects of solution pH and ionic strength. Solution pH has influence on adsorbent surface charge and Sb species distribution, and affects the adsorption processes thereafter. The species distribution of Sb(III) and Sb(V) over a wide pH range from 2.0 to 12.0, as indicated from Visual MINTEQ software modeling, are illustrated in Fig. S3,† and Sb(OH)_3 and Sb(OH)_6^- were the dominant species of Sb(III) and Sb(V) at pH 7.0.⁵⁹ Fig. S4† illustrates the adsorption of Sb(III) and Sb(V) onto Fe_3O_4 and Cu-doped Fe_3O_4 in wide pH ranges at IS of 0.01 and 0.1 M KNO_3 . The elevated pH benefited the adsorption of Sb(III), whereas inhibited that of Sb(V) onto both Fe_3O_4 and Cu-doped

Fe_3O_4 . The adsorption density of Sb(III) increased from 3.32 mg g^{-1} to 36.01 mg g^{-1} for Fe_3O_4 and from 40.92 mg g^{-1} to 51.58 mg g^{-1} for Cu-doped Fe_3O_4 with elevated pH from 3.0 to 7.0 [Fig. S4(a)†]. Comparatively, the adsorption of Sb(V) showed opposite trends and decreased from 33.75 mg g^{-1} to 9.52 mg g^{-1} for Fe_3O_4 and from 81.79 mg g^{-1} to 20.27 mg g^{-1} for Cu-doped Fe_3O_4 with elevated pH from 3.0 to 10.0 [Fig. S4(b)†]. A similar phenomenon of pH effects is observed in the case of adsorption of Sb(III) and Sb(V) onto nano-size zero-valent iron (nZVI)⁶⁰ and ferric manganese binary oxide (FMBO).⁶¹ The promoted Sb(V) adsorption at elevated pH could be attributed to the formation of inner-sphere complex on the surfaces of Fe_3O_4 and Cu-doped Fe_3O_4 .¹⁰ Furthermore with elevated IS_{KNO_3} from 0.01 to 0.1 M, the adsorption of Sb(III) and Sb(V) was slightly affected in wide pH range, and this supported the involvement of inner-sphere complex in adsorption. Ackermann *et al.*⁶² also confirmed the formation of inner-sphere complex on Fe oxide surfaces by extended X-ray adsorption fine structure (EXAFS) analysis.

The zeta potential in the various solution pH is presented in Fig. 6 for Fe_3O_4 and Cu-doped Fe_3O_4 . The zeta potential of Fe_3O_4 decreased from 25.1 to -42.5 mV and that of Cu-doped Fe_3O_4 from 3.23 to -22.5 mV with elevated pH from 3.0 to 10.0, and their pH_{pzc} (pH at which the surface is zero-charged) were both near to 4.5. The more negatively-charged surfaces increased the repulsive forces and inhibited the adsorption of anionic

Table 3 Comparison of Sb(III) and Sb(V) sorption capacity with different sorbents

Adsorbents	Sorption capacity (mg g ⁻¹)		Initial Sb concentrations (mg L ⁻¹)	Adsorbent doses (mg L ⁻¹)	pH	Reference
	Sb(III)	Sb(V)				
Cyanobacteria	4.9	—	10	0.04–1.0	4	51
Graphene oxide	36.5	—	10	600	7	52
MWCNTs	0.4	—	4	200	7	53
Zeolite-supported magnetite	—	19	100	500	3	54
Zn-Fe-LDH	—	100	50	200	7	55
QFGO	2.9–6.1	—	10	20 000	—	56
Diatomite	35.2	—	10–400	4000	6	57
ZCN	70.8	57.2	10–500	1000	7	58
Fe ₃ O ₄	30.92	7.07	50	200	7	This study
Cu-doped Fe ₃ O ₄	43.55	34.46	50	200	7	

Sb(OH)₆⁻, which was thermodynamically stable in pH 4.0–10.0 [Fig. S3(b)†]. Comparatively, the negative surface at higher pH showed less effect on the adsorption of non-ionic Sb(OH)₃, and the observed pH-dependent adsorption of Sb(III) may be attributed to the involvement of different mechanisms besides electrostatic attraction. Fig. 6 also compares the zeta potential of these adsorbents before and after sorbing Sb(III) and Sb(V). The adsorption of Sb(III) decreased zeta potential more significantly than that of Sb(V), and this indicated the strong interaction between Sb(III) and the surfaces of both adsorbents. The significant pH_{pzc} shift inferred the involvement of specific adsorption in Sb adsorption besides electrostatic interaction.⁶³

3.2.4 Effect of co-existing anions. In natural water systems, the widely presented anions may occupy the sorption sites and inhibit the removal of antimony. The co-existing species, *i.e.*, PO₄³⁻, SO₄²⁻, and CO₃²⁻, inhibited the adsorption of Sb(III) and Sb(V) onto Fe₃O₄ and Cu-doped Fe₃O₄ in the order of PO₄³⁻ > SO₄²⁻ > CO₃²⁻ (Fig. S6†). The carbonate and sulfate at concentrations of above 10 mM, which may be their maximum concentrations in natural waters, showed limited effects on antimony adsorption. Comparatively, phosphate at the same level showed more significant inhibition and its adverse effect

on the adsorption has been widely reported.^{64,65} Phosphate, arsenate, and antimonate are oxyacids of main V group elements with similar chemical structure, and they preferred to occupy the same sorbing sites. Quantitatively, phosphate at extremely high concentration of 10 mM decreased the Sb(III) and Sb(V) removal by 50.1% and 18.2% for Fe₃O₄ and by 14.1% and 58.6% for Cu-doped Fe₃O₄. In considering that phosphate concentrations in most natural waters are below 1 mM, and the inhibitive effect on Sb adsorption may be ignored accordingly.

3.3 Proposed mechanism of Sb(III) and Sb(V) adsorption

To investigate the mechanisms involved in the adsorption of antimony, the XPS spectra of the Fe₃O₄ and Cu-doped Fe₃O₄ after adsorbing Sb(III)/Sb(V) at pH 7.0 were collected and the O 1s and Sb 3d spectra are illustrated in Fig. 7.

The spectra of Sb 3d_{3/2} did not overlap with O 1s and was used for peak fitting herein. The binding energy of Sb 3d_{5/2} peak is set by the Sb 3d_{3/2} peak according to the spin-orbit splitting ($\Delta = 9.39$ eV).

The adsorption of either Sb(III) or Sb(V) contributed to the appearance of new Sb 3d_{3/2} peaks with the binding energy of 540.0 eV and 540.3 eV in the spectra of Fe₃O₄ and Cu-doped Fe₃O₄, respectively. Interestingly, the Sb 3d_{3/2} showed the same binding energy in regardless of the initial Sb species of either Sb(III) or Sb(V). The binding energy of Sb 3d_{3/2} in Sb₂O₃ and Sb₂O₅ was reported to be 539.6 and 540.2 eV, respectively.⁶⁶ The dominant Sb species on the surfaces of both adsorbents was determined to be Sb(V) and the oxidation of Sb(III) to Sb(V) was inferred to involve in the adsorption of Sb(III) on both adsorbents. The slight difference in the BE (0.3 eV) of Sb 3d_{3/2} between these two adsorbents may be attributed to the different bonding state of antimony on their surfaces. The heterogeneous oxidation of Sb(III) on the surfaces of metal oxides has been reported in literature: Leuz *et al.* reported that the adsorbed Sb(III) may be oxidized by aqueous oxygen and goethite acts as a catalyst to enhance Sb(III) oxidation.⁶⁷ Wang *et al.* also reported that As(III) is efficiently oxidized to As(V) by O₂ on Cu-doped Fe₃O₄ surfaces.²⁶ The elements with high valence, *e.g.* Mn^{IV}, Fe^{III}, are good electron acceptors and may participate in the oxidation of Sb(III) to Sb(V).^{61,68} Moreover,

Fig. 6 The variation of the zeta potential of (a) Cu-doped Fe₃O₄ and (b) Fe₃O₄ before and after the adsorption of Sb(III) and Sb(V).

Fig. 7 O 1s and Sb 3d XPS spectra of [(a) Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4 + \text{Sb(III)}$, (c) $\text{Fe}_3\text{O}_4 + \text{Sb(V)}$, (d) Cu-doped Fe_3O_4 , (e) Cu-doped $\text{Fe}_3\text{O}_4 + \text{Sb(III)}$, (f) Cu-doped $\text{Fe}_3\text{O}_4 + \text{Sb(V)}$].

Cu^{II} has strong oxidant capacities and its compounds are commonly used as oxidation agents.^{69–71} So the question is: what role does copper play within Sb(III) oxidation process, catalyst or oxidant?

To further confirm the oxidation of Sb(III) by Cu-doped Fe_3O_4 , the species distribution and transformation of Sb after adsorption was quantitatively analyzed in aerobic (O_2 -purging) and anaerobic (N_2 -purging) systems. After the adsorption of Sb(III) on these two adsorbents at pH 7.0, the concentrations of aqueous Sb(III) [$\text{Sb(III)}_{\text{aqueous}}$] and Sb(V) [$\text{Sb(V)}_{\text{aqueous}}$] are illustrated in Fig. 8(a). In the presence of Fe_3O_4 , the oxidation of Sb(III) was rather slight and the ratios of Sb(V) to total Sb was below 10% in solution. Comparatively, the oxidation of Sb(III) was significant in the presence of Cu-doped Fe_3O_4 , and Sb(V) was the dominant species with the ratios of over 50% either in bulk solution and on Cu-doped Fe_3O_4 surface. Additionally, the oxidation of Sb(III) occurred in both N_2 - and O_2 -purging systems and the ratios of aqueous Sb(V) to total Sb were observed to be 62.3% and 58.9%, respectively. In the absence of Cu-doped Fe_3O_4 , the oxidation of Sb(III) can barely be achieved in either N_2 - or O_2 -purging systems. These results indicate the significance of Cu-doped Fe_3O_4 on Sb(III) oxidation. Our results are in agreement with the literature that ambient O_2 was unlikely to be a significant oxidant in oxidation of Sb(III) to Sb(V).⁷² Moreover, higher pH value was found to greatly enhance oxidation process by Cu-doped Fe_3O_4 . Almost all aqueous Sb(III) can be oxidized to Sb(V) in presence of Cu-doped Fe_3O_4 at pH 11.0; however, very little Sb(III) could be oxidized using non-doped Fe_3O_4 .

On the other hand, the Cu $2p_{2/3}$ peak at 942.3 eV disappeared after the adsorption of Sb(III) (Fig. S1†), and this supported the reduction of Cu(II) to that with lower chemical valence, *i.e.*, Cu^0 , Cu^{I} . Furthermore, the thermodynamic calculation also indicated that Sb(III) may be oxidized to Sb(V) by Cu^{II} , and the possible chemical reactions eqn (11) and (12) are given as follows:

Fig. 8 (a) Species distribution of antimony in solution involved in the adsorption of Sb(III) onto Fe_3O_4 and Cu-doped Fe_3O_4 at different pH (b) species distribution of copper in solution adsorption involved in the adsorption of Sb(III) and Sb(V) onto Cu-doped Fe_3O_4 .

It was noted that CuFe_2O_4 was viewed as the dominant constituent of Cu-doped Fe_3O_4 and $\text{Sb}(\text{OH})_3$ as the main Sb(III) species at pH 7.0 (Fig. S3†). The higher equilibrium constant (K) is relative to stronger intensity toward the products. The two copper species of Cu^{I} and Cu^0 may be produced; however, Cu^{I} may be the dominant product as indicated from the K values.

To further illustrate the possible oxidation and reduction reactions involve in, the concentrations of aqueous copper(I)/(II) before and after the adsorption of Sb(III) and Sb(V) onto Cu-doped Fe_3O_4 were quantitatively analyzed [Fig. 8(b)]. It was observed that the concentrations of aqueous copper in the control experiments were extremely low to be below 0.4 mg L^{-1} .

Fig. 9 Proposed mechanisms for the adsorption of Sb(III) and Sb(V) onto Fe₃O₄ and Cu-doped Fe₃O₄.

The adsorption of Sb(V) slightly decreases the concentrations to as low as 0.15 mg L⁻¹. Comparatively, in Sb(III) adsorption systems the concentrations of dissolve Cu (total of Cu^I and Cu^{II}) increased significantly to 1.3 and 2.1 mg L⁻¹ in O₂- and N₂-purging systems, owing to the heterogeneous electron transfer from Sb(III) to Cu-doped Fe₃O₄ surface. However, the leaching copper into the aqueous phase could exceed the drinking water limit of 2.0 mg L⁻¹ and we need to remove Cu after Sb removal.⁴⁶ Fortunately, there are cheap and reliable methods that could also be used to remove Cu from water *e.g.* chemical precipitation,⁷³ sorption,⁷⁴ and ultrafiltration.⁷⁵

After the oxidation of Sb(III), the aqueous Sb(V) concentrations increased, owing to the release of the formed Sb(V) and Cu(I) from Cu-doped Fe₃O₄ surface to solution. And then, copper(I) ions in solution disproportionate to give copper(II) ions and a precipitate of copper. As some of the Sb(III) oxidation by O₂ in oxygen-rich conditions, the Cu-doped Fe₃O₄ can release less copper than in oxygen-deficiency conditions.

On the basis of these results, the possible mechanisms involved in the adsorption and oxidation of Sb(III) and the release of Sb(V) on the surfaces of Fe₃O₄ and Cu-doped Fe₃O₄ were proposed and illustrated in Fig. 9:

As for the “iron-based pathway” (for Fe₃O₄ and Cu-doped Fe₃O₄), the adsorption of Sb(III)/Sb(V) included following major reactions:

- Surface dissolution, hydrolysis, and the formation of surface hydroxyl groups;
- Adsorption of Sb(III)/Sb(V) onto ≡Fe^{III}-O sites;

(III) Electron transfer from Sb(III) to Fe(III) and heterogeneous oxidation of Sb(III) (slight);

(IV) Electron transfer from Fe(II) to Fe(III/II).

As for the “copper-based pathway” (for Cu-doped Fe₃O₄ only), the adsorption of Sb(III) mainly included the following reactions:

(I) Surface dissolution and hydrolysis and the formation of surface hydroxyl groups;

(II) Adsorption of Sb(III)/Sb(V) onto ≡Cu^{II}-O sites;

(III) Electron transfer from Sb(III) to Cu(II) and heterogeneous oxidation of Sb(III) (significant);

(IV) Release of Cu(I) and Sb(V) into solution;

(V) Cu(I) disproportionate to give copper(II) ions and a precipitate of copper.

4. Conclusions

The doping of Cu into Fe₃O₄ by solvothermal method improves the adsorption capability towards Sb(III) and Sb(V) as compared to the non-doped Fe₃O₄. The maximum adsorption capacity of Cu-doped Fe₃O₄ is determined to be 43.55 mg g⁻¹ for Sb(III) and 34.46 mg g⁻¹ for Sb(V) at pH 7.0. The elevated pH is beneficial to the adsorption of Sb(III), whereas inhibitive to that of Sb(V). The co-existing PO₄³⁻ shows adverse effect on Sb removal; however, the inhibiting extent at 1 mM is relatively low. Cu doping shows little effect on the crystalline of Fe₃O₄ but remarkably increases the *S*_{BET} from 9.66 to 67.20 m² g⁻¹, and this effect plays an important role in the enhanced Sb removal. Additionally, Cu-

doping greatly increases the oxidative ability towards Sb(III) and enables the heterogeneous electron transfer from Sb(III) to Cu(II). The electron transfer from Sb(III) to Fe(III) on $\equiv\text{Fe}^{\text{III}}\text{-O}$ sites might occur; however, the extent is rather weak. The formed Sb(V) and Cu(I) tends to release from adsorbents surfaces partially, and Cu(I) may disproportionate to give copper(II) ions and a precipitate of copper. Cu-doped Fe_3O_4 shows good magnetic character and high adsorption capacity, and may be promising to remove antimony from the contaminated water.

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