Synthesis of graphene oxide/schwertmannite nanocomposites and their application in Sb(V) adsorption from water

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HIGHLIGHTS

- Graphene oxide and schwertmannite were combined into nanocomposites.
- A synergistic effect on Sb(V) uptake was observed for the composite adsorbent.
- The schwertmannite component is the main active phase in the composite for Sb(V) uptake.
- The surface groups of graphene oxide also contributed to Sb(V) adsorption.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:

Received 4 November 2014

Received in revised form 17 January 2015

Accepted 19 January 2015

Available online 28 January 2015

Keywords:

Adsorption
Antimony removal
Schwertmannite
Graphene oxide
Composites

ABSTRACT

Schwertmannite was incorporated onto graphene oxide to form nanocomposites (GO–SCH) to serve as an adsorbent for Sb(V) removal. A synergistic effect on Sb(V) uptake was observed for the composite adsorbent. A maximum Sb(V) adsorption capacity of 158.6 mg Sb(V)/g of GO–SCH at an equilibrium Sb(V) concentration of 8.0 mg/L at pH 7.0 was obtained. This capacity is superior to either GO or SCH alone. The effect of contact time, solution pH and co-existing competitive anions on Sb(V) uptake by GO–SCH was evaluated. External mass transfer governed the Sb(V) uptake kinetics within 1 h. After 1 h, intraparticle diffusion gradually became predominant. Common co-existing anions at their natural environmental concentrations had little effect on the performance of GO–SCH. Sb(V) in spiked tap water (100 µg/L), simulated river water (6400 µg/L), and acid mine drainage (50,000 µg/L) was adsorbed by GO–SCH to well below the regulation levels for these waters. XRD and SEM analyses showed that SCH was well incorporated among GO platelets and highly dispersed on the GO carrier's surface. FTIR and Raman spectra showed that both SCH and GO surfaces in the composites contribute to Sb(V) removal and SCH was the main active phase. This was also confirmed by XPS Fe 2p spectra. Sb 3d_{3/2} XPS spectra indicated that no surface precipitation or reduction of Sb(V) to Sb(III) occurred. Deconvolution of C 1s XPS spectra and Boehm titration indicated the surface carboxyl, lactonic and phenolic hydroxyl groups of GO also contribute to Sb(V) removal. The outstanding Sb(V) uptake ability of GO–SCH suggests it is a promising adsorbent for antimony removal from contaminated water.

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1. Introduction

Antimony is an emerging pollutant and increasing concerns about its effects in aquatic and soil environments are being raised because of its wide application. Antimony (Sb) is widely used in flame retardants, glass decolorizers, additives in glassware, catalysts in plastics, pigments in paints, and alloys in ammunition [1,2].

Large amounts of Sb have been released into the aquatic environment from Sb mining, processing, its many applications and final disposal. Antimony exists mainly as inorganic Sb(V) and Sb(III) in water. The deprotonated form of antimonous acid, $\text{Sb}(\text{OH})_6^-$, is the dominant Sb(V) species over most environmentally relevant pH values (pH 3–10) in oxygenated water, while Sb(III) is present in the ambient aquatic environment as uncharged antimonous acid $\text{Sb}(\text{OH})_3$ [3]. In unpolluted fresh water, typical concentrations of dissolved antimony are less than $1 \mu\text{g/L}$ [1]. However, in contaminated areas the concentrations of Sb can reach up to 4.58–29.4 mg/L [2], several thousand times more than its natural levels.

Antimony compounds may inhibit the repair of DNA damage in hamster cells and human hematopoietic cells [4,5]. It is suspected to induce cancer and this risk is under further investigation [6]. Antimony and its compounds are regulated as priority pollutants by the United States Environmental Protection Agency and the European Union [1]. Many countries and agencies have set rigorous regulations (maximum contaminant levels, limits or guidelines, etc.) for antimony in drinking water. Such limits include: USEPA, 0.006 mg/L; WHO, 0.020 mg/L; China, 0.005 mg/L; EU, 0.005 mg/L, etc. [7].

The worsening contamination, related health risks, and rigorous Sb regulations in water have led to urgent demands for antimony pollution control and mitigation. Several methods to remediate antimony from water have been reported, including adsorption [8], coagulation [7], coagulation combined with membrane filtration [9], ion exchange [10], and electrochemical deposition [11], etc. Up to now adsorption has been and still is the most often investigated and used method. Adsorption is simple, cheap, easy to operate, takes little space, and effectively meets the rigorous concentration regulations for the effluent [12]. Improving this technique focuses on the discovery of novel and high performance adsorbents.

Graphene, a two-dimensional carbon nanomaterial that is the fundamental building block of graphite, provides a large surface area, excellent electrical, thermal and mechanical properties [13]. Graphene oxide (GO), which is an oxidized form of graphene, contains epoxy, hydroxyl, keto, and carboxyl reactive oxygen functional groups. It serves as a suitable adsorbent for the sequestration and removal of pollutants from water. Graphene, graphene oxide and their functionalized preparations exhibit exciting adsorption abilities for removing hazardous anions, heavy metals, including Sb(III), Cr(VI), Cu(II), Pb(II), Hg(II), Cd(II), Ni(II), and cationic dyes such as methylene blue (MB) and safranin T (ST) from contaminated water [14–17]. Incorporating active components with GO to synthesize new nanocomposites with high adsorption abilities for hazardous anion removal has drawn wide attention [8,18]. Schwertmannite is a poorly crystalline Fe(III)-oxyhydroxy sulfate mineral with a variable composition, typically represented as $\text{Fe}_8\text{O}_8(\text{OH})_{8-2x}(\text{SO}_4)_x$ (where x falls within 1–1.75). It naturally occurs in acid mine drainage and is known to be an effective scavenger of arsenate, phosphate and some heavy metals. Synthesized schwertmannite has also been demonstrated to be effective in arsenate and phosphate removal [19,20]. Considering the chemical similarity of As, P and Sb, assembling schwertmannite with GO could generate a promising adsorbent for Sb removal.

In the present study, schwertmannite-loaded graphene oxide was synthesized as an adsorbent for Sb(V) removal from water.

The main objectives of this research were (1) to compare the Sb(V) uptake abilities of schwertmannite-graphene composites (GO-SCH) to those of schwertmannite used alone and graphene used alone, (2) to investigate the adsorption kinetics and equilibrium of Sb(V) on GO-SCH the effect of co-existing anions, and the regeneration and reuse of magnetically amended GO-SCH, and finally (3) to investigate Sb(V) adsorption mechanism on GO-SCH using multiple techniques, including FTIR, Raman, XPS and Boehm titration.

2. Materials and methods

2.1. Materials

All chemicals were analytical grade except for reagent grade KBH_4 and HCl, which were used for Sb analysis. Sb(V) 10 mg/L standard solutions were bought from National Research Center for Certified Reference Materials, China. Graphite was purchased from Sinopharm Chemical Reagent Beijing Co., and Ltd. Sb(V) stock solutions were prepared by dissolving potassium antimonate in deionized water. Solutions containing Sb(V) were freshly prepared by diluting the stock solution with distilled water. Co-existing anion solutions were prepared using their salts.

2.2. Preparation of graphene oxide/schwertmannite nanocomposites

Graphene oxide was prepared using the modified Hummers method reported by Marcano et al. [21]. Graphite (1 g) was added into 50 mL mixed acid solution (80% H_2SO_4 + 20% H_3PO_4). After the mixture was bathed in ice water for 30 min, ground KMnO_4 fine powder (6 g) was slowly added into the mixture to avoid any violent or explosive reactions. The temperature of the mixture was kept below 10°C in ice-bath while adding KMnO_4 . A dark green suspension formed. The suspended material was bathed in water at $35\text{--}40^\circ\text{C}$ until the mixture became pasty. Deionized water, 50 mL, was slowly added into the mixture to dilute the paste, then the temperature was raised to 95°C for 30 min. The reaction was ended by adding 200 mL deionized water and 20 mL 30% H_2O_2 into the mixture at room temperature. The color of the mixture changed from dark brown to yellow and precipitates formed. Then the precipitates were rinsed with 5% HCl and centrifuged, and further washed by deionized water until the supernatant reached

Fig. 1. XRD patterns of graphene/schwertmannite nanocomposites (GO-SCH), graphene (GO) and schwertmannite (SCH) along.

Fig. 2. TEM images of (a) GO (b) SCH and (c) GO-SCH and (d) SEM images of GO-SCH composites.

pH = 6. After filtration and drying under vacuum, the gray powder was collected.

A schwertmannite (SCH) sample was prepared using a wet chemical process [22]. After 2 L of distilled water had been heated to 60 °C, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10.8 g) and Na_2SO_4 (3 g) were added and vigorously stirred and heated at 60 °C for another 12 min. Then the mixture was cooled to room temperature. The suspension was dialyzed for 3 d and centrifuged to separate the paste. Then the paste was finally freeze dried.

The graphene oxide/schwertmannite composites (GO-SCH) were prepared by a co-precipitation method. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.4 g) and Na_2SO_4 (1.5 g) were added into GO dispersion (1 g/L) at 60 °C. The mixture was kept at 60 °C and vigorously stirred for 12 min. Then the mixture was cooled to room temperature and centrifuged at 5000 rpm for 15 min. The centrifuged solid was dried at 60 °C under vacuum for 24 h. The product was collected for further use.

2.3. Adsorbents characterization

The XRD patterns of the adsorbents were obtained on an X'Pert PRO MPD diffractometer (PANalytical, the Netherlands) with a $\text{Cu K}\alpha$ source ($k = 1.54178 \text{ \AA}$). Samples were scanned at a speed of $2^\circ/\text{min}$ from 3° to 70° , at 40 kV and 40 mA. The specific surface areas and pore volumes of the samples were determined by BET N_2 adsorption-desorption analysis using a Micromeritics ASAP2000 surface area analyzer (Norcross, USA). The surface morphology was determined by using a H800 high resolution transmission

electron microscope (Hitachi, Japan), and an XL30S FEG scanning electron microscope (FEI, the Netherlands). X-ray fluorescence (XRF) spectrometry measurements were performed on a S4 explorer X-ray spectrometer (Bruker-AXS, Germany). FTIR spectra were recorded on a Vector 22 spectrophotometer (Bruker, German) at a resolution of 2 cm^{-1} , working in the transmission mode. Raman spectra were collected using a 950 FT-Raman spectrometer (Thermo Nicolet, USA) at a resolution of 2 cm^{-1} . Laser excitations were achieved at 532 nm. Zeta potentials (ζ) were measured in the pH range 3–10.5 using a Zetasizer Nano Z analyzer (Malvern, UK). XPS spectra were measured on a PHI Quantera spectrometer (U.S.A). An Al $K\alpha$ anode radiation source was used as the excitation source. Curve fittings of the C 1s spectra were performed using a Gaussian-Lorentzian peak shape after performing a Shirley background correction using the XPSpeak software 4.1 by Raymond W.M. Kwok (The Chinese University of Hong Kong, China). The amounts surface carboxyl, lactonic and phenolic hydroxyl groups were determined employing the Boehm titration procedure [23].

2.4. Batch adsorption experiments

A Sb(V) stock solution and deionized water were added into a series of 2000 mL glass conical flasks to give a total volume of 1000 mL in each. Then, 0.3 g/L adsorbent dose were added. The pH of each mixture was adjusted and maintained at 7.0 ± 0.2 throughout the experiments. The mixtures were stirred at 150 rpm, and maintained at $25 \pm 1^\circ \text{C}$. Approximately 4 mL aliquots were taken from the suspension at predetermined intervals. These

Fig. 3. Effect of contact time on Sb(V) adsorption onto GO-SCH, SCH and GO adsorbents. Initial Sb(V) concentration, 20 mg/L; adsorbent dose 0.3 g/L; total solution volumes, 1000 mL; pH, 7.0 ± 0.2 and temperature, 25 ± 1 °C. (a) Fitting with pseudo-first and pseudo-second order models and (b) fitting with the Weber-Morris intraparticle model [24].

Table 1
Kinetics constants for Sb(V) adsorption on the GO, SCH and the GO-SCH adsorbents.

Adsorbent	Pseudo-first-order model			Pseudo-second-order model		
	k_1 (1/h)	q_e (mg/g)	R^2	k_1 (1/h)	q_e (mg/g)	R^2
GO	4.976	60.0	0.987	0.070	62.2	0.965
SCH	5.502	32.5	0.965	0.129	34.3	0.991
GO-SCH	3.634	4.9	0.709	0.290	5.6	0.821

aliquots were immediately filtered through a 0.22 μm membrane, and then the residual Sb in each solution was analyzed. Sb(V) adsorption isotherms on the adsorbents were obtained experimentally at 25 °C. Isotherm experiments on GO-SCH were also carried out at 15 °C and 35 °C, respectively. Initial Sb(V) concentrations from 0 to 60 mg/L, respectively, were used on an adsorbent dose of 0.3 g/L at a pH of 7.0 ± 0.2 . The effect of solution pH on antimony removal was analyzed in 100 mL glass bottles containing 50 mL of Sb solution with pre-selected concentrations and an adsorbent dose of 0.3 g/L. The pH was adjusted and maintained at a specified value in the range 3–10.5. After shaking for 24 h at 25 ± 1 °C, the residual antimony in solution was analyzed.

Table 2

External mass transfer diffusion coefficients of Sb(V) uptake by GO, SCH and GO-SCH.

	$[d(C_t - C_0)/dt]^*$	m (g)	S (m^2/g)	k_L (m/s)
GO	0.94	0.3	459.89	1.4×10^{-5}
SCH	0.51	0.3	130.94	2.6×10^{-5}
GO-SCH	0.42	0.3	62.21	4.5×10^{-5}

* These values were determined using the Eq. (3) by using the data points of $t = 0$ h and $t = 0.5$ h.

The effects of co-existing anions (SO_4^{2-} , NO_3^- , Cl^- , HCO_3^- , PO_4^{3-} and SiO_4^{4-}) on Sb(V) adsorption were investigated when considering their typical concentration ranges in natural groundwater [25]. Sb(V), 20 mg/L, was spiked with (100, 300 and 500 mg/L) sulfate, (10, 30 and 60 mg/L) nitrate, (100, 300 and 500 mg/L) chloride, (50, 100 and 200 mg/L) bicarbonate, (2, 5 and 10 mg/L) phosphate and (6, 9 and 12 mg/L) silicate, respectively, to make three solutions, each with a total volume of 100 mL at pH 7.0 ± 0.1 . The suspensions were agitated at 160 rpm for 24 h at 25 ± 1 °C.

2.5. Magnetic modification, separation and recycling

GO-SCH was magnetically amended using a reported procedure which is detailed in [Supplementary material \(S1\)](#) [25]. After magnetic modification, the adsorbent was evaluated in a batch mode. Sb(V) adsorption was first performed from 50 mL solutions with an Sb(V) concentration of 10 mg/L, an adsorbent dose of 0.3 g/L, and a pH of 7.0 ± 0.2 . After a 10 h adsorption period, GO-SCH was then collected by magnetic separation. The desorption experiments were performed by shaking the Sb-loaded adsorbent in 100 mL 0.1 M HCl and 0.1 M EDTA mixed solutions for a period of 8 h at 25 ± 1 °C. Then the adsorbent was washed with deionized water and used in the next reuse-regeneration cycle.

2.6. Analytical methods

The residual Sb(V) concentrations were analyzed by a hydride generation-atom fluorescence spectrometer (HG-AFS, AF-9600, Beijing Kechuang Haiguang Instrument Corporation, China) using published methods [26]. The detection line for Sb(V) is 1 $\mu\text{g/L}$.

3. Results and discussion

3.1. Adsorbent characterization

The XRD patterns of GO, SCH and GO-SCH are shown in [Fig. 1](#). The graphene oxide is characterized by a typical peak at 11.5° . This peak differs from the characteristic peak at 20.1° of graphene (G). This change indicates the presence of oxygen-containing surface groups in GO. The schwertmannite sample is confirmed by peaks at 26.3° , 35.1° , 55.3° and 63.7° (according to PDF 47-1775). In the GO-SCH composites, the typical peaks of both GO and SCH appeared but they were weakened. The attenuation of GO's characteristic peak at 11.5° in the GO-SCH composites may due either to the stacking of graphene oxide layers or to the incorporating of schwertmannite nanoparticles into the composites [27]. The diminished SCH peaks demonstrate the schwertmannite nanoparticles were dispersed on the GO carrier's surface and do not aggregate into well-formed crystal sizes that are large enough to give strong sharp XRD peaks. This agrees with the presence of mostly nanosized, more amorphous particles. In all, it indicates SCH and GO have well been integrated into nanocomposites.

HR-TEM images of GO, SCH and GO-SCH are shown in [Fig. 2\(a\)–\(c\)](#). GO was observed as fairly flat sheets and the schwertmannite

Fig. 4. Adsorption isotherms of Sb(V) onto GO-SCH, SCH and GO adsorbents. Initial Sb(V) concentrations, 0–60 mg/L; adsorbent dose, 0.3 g/L; total solution volumes, 50 mL; pH, 7.0 ± 0.2 ; temperature, 25 ± 1 °C, and shaking time, 24 h.

particles as aggregates. In GO-SCH, schwertmannite nanoparticle clusters were randomly dispersed and decorated on the GO sheets. The SEM image of GO-SCH is shown in Fig. 2(d). The GO was found to have aggregated schwertmannite ~50 nm diameter nanoparticles associated and adhered to the GO sheets. Both TEM and SEM images of a GO-SCH sample that had adsorbent Sb(V) from a 30 mg/L Sb(V) solution were presented in [Supplementary material \(Fig. S1\(a\) and \(b\)\)](#). There is no difference between the SEM and TEM images before and after Sb(V) adsorption. This indicates that the interaction with Sb(V) in solution does not measurably change the surface morphology of GO-SCH. XRF elemental analysis of the GO-SCH sample, before and after adsorption from a 30 mg/L Sb(V) solution at pH = 7.0 ± 0.2 are given in [Table S1 in the Supplementary material](#). The surface Sb(V) contents obviously raised from 0% to 13.0% and S dropped from 6.2% to 2.6%.

N₂ adsorption-desorption analyses show that the specific BET surface areas of GO, SCH and GO-SCH were 459.9 m²/g, 130.9 m²/g and 287.6 m²/g, respectively.

The pH_{pzc} values of GO, SCH and GO-SCH were determined and shown in Fig. S2. Incorporating both GO (pH_{pzc} = 2.1) and SCH (pH_{pzc} = 5.1) into a composite increased the pH_{pzc} to 6.8 for GO-SCH, which is favorable for anion adsorption.

3.2. Sorption studies

3.2.1. Adsorption kinetics

Adsorption kinetic parameters are critical for designing adsorption units and optimizing operation conditions. First, kinetics are necessary data. Second, such data is used to make decisions about what kind of and which specific adsorbent will be selected for use. The third, it is important because kinetic properties control the cycle time of a fixed bed adsorption process. Fast kinetics implies

Fig. 5. Effect of pH on Sb(V) adsorption onto GO-SCH, SCH and GO adsorbents. Initial Sb(V) concentration, 40 mg/L; adsorbent dose, 0.3 g/L; total solution volumes, 50 mL; pH range, 3–10.5; temperature, 25 ± 1 °C, and shaking time, 24 h.

a sharp breakthrough curve, while slow kinetics leads to a distended breakthrough curve [28].

The Sb(V) uptake kinetics of GO-SCH, SCH and GO are shown in Fig. 3(a) and (b). The kinetics of Sb(V) adsorption by GO-SCH was initially rapid within the first 3 h. Then Sb(V) uptake gradually reached equilibrium within 24 h, showing a plateau with 95% of Sb(V) removed. The Lagergren pseudo-first-order [29] and Ho's pseudo-second-order models [30,31] were used to fit the experimental data and the kinetic parameters obtained are summarized in Table 1. The mathematical representations of the two models are given in Eqs. (1) and (2), respectively:

$$q_t = q_e(1 - e^{-k_1 t}) \quad \text{Pseudo-first-order nonlinear form} \quad (1)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad \text{Pseudo-second-order nonlinear form} \quad (2)$$

Here q_e and q_t are the amount of adsorbed Sb(V) at equilibrium. At any time t (mg/g adsorbent), k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the equilibrium rate constants for pseudo first- and second-order sorption, respectively, and t is the exposure time (min).

In general, slightly higher correlation coefficients were observed for the pseudo-second-order model than for the pseudo-first-order equation (Table 1) in most cases for the all adsorbents. But this treatment does not clearly distinguish the adsorbing process.

To further understand the kinetics process, both external mass transfer and intraparticle diffusion processes of Sb(V) uptake by GO-SCH were investigated. External mass transfer can be described by Eq. (3):

$$\left[\frac{d(C_t/C_0)}{dt} \right]_{t=0} = \frac{-mSk_L}{V} \quad (3)$$

Table 3

A performance comparison between the GO-SCH adsorbent and various adsorbents for antimony(V) removal from water.

Adsorbents	Concentration range (mg/L)	pH	Dose (g/L)	Adsorption capacity (mg/g)	Reference
Present study	0–55 (initial concentration)	3–10.5	0.3	158.6	–
Nanoscale zero-valent iron	0–20 (initial concentration)	4–10	2	1.65	[32]
α-FeOOH	–	2–12	25	48.7	[33]
Fungi aerobic granules of Fe(III)-treated	20–100 (initial concentration)	2–11.5	1	111	[34]
Kaolinite	1 (initial concentration)	6	25	12	[35]
Bentonite	0.05–4 (initial concentration)	6	25	36	[26]
Activated alumina	5–75 (initial concentration)	2–11	1	38	[36]
Iron–zirconium bimetal oxide	0–25 (initial concentration)	3–11	0.2	51	[31]

Fig. 6. Effect of co-existing anions on Sb(V) adsorption onto (a) GO-SCH, (b) SCH and (c) GO adsorbents. Initial Sb(V) concentrations, 20.0 mg/L; total solution volumes, 100 mL; temperature, 25 ± 1 °C; contact time, 24 h; adsorbent dosage, 0.3 g/L (The dashed lines correspond to the removal efficiencies of the adsorbent without the co-existing anions present).

In Eq. (3) C_t and C_0 are the concentrations of Sb(V) in aqueous solution (mg/L) and the initial concentration of Sb(V) in aqueous solution (mg/L); t is the adsorption time (s), m is the mass of

Fig. 7. Re-adsorption ability of GO-SCH after magnetic separation followed by regeneration. Initial Sb(V) concentration = 10 mg/L; adsorbent dose = 0.3 g/L; shaking time = 10 h; pH = 7.0 ± 0.2 , and temperature = 25 ± 1 °C. The used adsorbent was regenerated in a 0.1 M HCl and 0.1 M EDTA mixed solution for 8 h. (Dash line corresponding to the capacity of the fresh adsorbent).

adsorbent (g), S is the external surface area per mass of adsorbent (cm^2/g), V is the solution volume (mL), and k_L is the external mass transfer coefficient in liquid phase (cm/s). Values of k_L were estimated by using the first two data points of the concentration decay curve and are summarized in Table 2. GO-SCH has a larger k_L value than GO and SCH alone. This means a higher intrinsic diffusion potential exists which drives solutes across the boundary layer surrounding the GO-SCH adsorbent particles in comparison with either GO or SCH.

Intraparticle diffusion is described by the Weber–Morris intraparticle model [24]. Its mathematical representation is usually given as Eq. (4):

$$q_t = k_p t^{0.5} \quad (4)$$

Here q_t is the amount of adsorbed antimony at time t (mg/g adsorbent), k_p (h^{-1}) is the equilibrium rate constant for intraparticle diffusion, and t is the exposure time (h). The intraparticle coefficients determined for the three segments are listed in Table S2.

In Fig. 3(b), three linear regions were clearly observed over the full time range. This result indicates that three steps govern adsorption rather than one. The first linear portion of the plot (about within 1 h) had a steeper q_t versus $t^{0.5}$ slope, which is associated with external mass transfer (Table 2). The second linear portion had a lower q_t versus $t^{0.5}$ slope. This region represents a gradual adsorption stage where either intraparticle or pore diffusion is rate-limiting. The third linear portion is the final equilibrium stage where intraparticle diffusion starts to slow down due to the extremely low solute concentration in solution [31].

3.2.2. Adsorption isotherms

The adsorption isotherms of the three types adsorbents were shown in Fig. 4. GO-SCH has a much higher capacity than either SCH or GO alone, following a capacity order of GO-SCH $\gg$ SCH > GO. A synergistic effect was observed for a combination of graphene oxide and schwertmannite nanocomponents. GO-SCH showed an inspiring maximum adsorption capacity around 158.6 mg/g Sb(V) at an equilibrium concentration of 8.0 mg/L at pH 7.0. The synergistic effect could originate from a better dispersion of schwertmannite nanoparticles on GO surface than that in SCH alone. In addition, surface functions including carboxyl, lactonic and phenolic hydroxyl groups on GO also contribute to the significant enhancement of Sb(V) uptake ability as shown in

Fig. 8. Removal of Sb(V) from spiked tap water, simulated river water and simulated acid mine drainage by the GO-SCH adsorbent. Shaking time, 0–72 h; temperature, 25 ± 1 °C. (a) Initial Sb(V) concentrations 100 µg/L; pH, 5.0; adsorbent dose, 0.3 g/L, (b) Initial Sb(V) concentrations 6400 µg/L; pH, 5.0; adsorbent dose, 0.3 g/L, (c) Initial Sb(V) concentrations 50,000 µg/L; pH, 3.5; adsorbent dose, 3 g/L.

Sections 3.3.2 and 3.3.3. Langmuir and Freundlich isotherm models were applied and the parameters obtained are reported in Table S3. The Langmuir fits are better, giving higher correlation coefficients (R^2) than the Freundlich model, favoring monolayer adsorption. The effect of temperature on Sb(V) uptake showed that the Sb(V) adsorption on GO-SCH is an endothermic process and the adsorption capacity increased with increasing temperature (Fig. S3). More discussion is supplied in Supplementary materials (S2). These parameters could be used to evaluate and compare the uptake abilities of various adsorbents and for adsorption unit design in the future. In addition, the adsorption capacity of GO-SCH in the present study was compared with other reported adsorbent Sb(V) uptake values (Table 3) and found to be superior to many reported adsorbents.

3.2.3. Effect of pH on adsorption

The effect of pH on Sb(V) adsorption by the three adsorbents is shown in Fig. 5. The Sb(V) uptake on GO-SCH was approximately constant in the pH range of 3.0–5.0 and then slightly dropped in the pH range from pH 5.0 to 9.5. Sb(V) adsorption on SCH remains almost constant between pH 3.0 and 6.0 and slightly decreased from pH 6.0 to 9.5. A continuous adsorption decrease was observed for GO from pH 3.0 to 9.5. The drop in Sb(V) adsorption capacity vs. pH for GO-SCH and SCH is due to the changes of pH-dependent electrostatic forces existing between the sorbent surface and antimonite anions. $\text{Sb}(\text{OH})_5(\text{aq})$ and $\text{Sb}(\text{OH})_6^-$ co-exist when pH is below 5.0. The negatively charged $\text{Sb}(\text{OH})_6^-$ becomes totally dominant as solution pH increases from 3.0 to 5.0, while the positive

surface charges of GO-SCH and SCH gradually drop, as indicated by the decrease of their Zeta potential values from pH 3.0 to 9.5 (Fig. S2). This results in reductions in the electrostatic attractive forces between $\text{Sb}(\text{OH})_6^-$ and the adsorbents' surface. This is further reflected by the drops of Sb(V) removal as pH increases. In addition, the relatively higher surface potential of GO-SCH versus that of SCH also contributes to the higher GO-SCH adsorption capacity versus that of SCH at each given pH condition.

3.2.4. Effect of co-existing anions

In practice, natural water contains multiple anions. The effect of co-existing anions (Cl^- , SO_4^{2-} , NO_3^- , SiO_4^{4-} , HCO_3^- , PO_4^{3-} , etc.) on Sb(V) adsorption by GO, SCH and GO-SCH is illustrated in Fig. 6(a)–(c). The Sb(V) adsorption performance of GO-SCH was nearly constant with added NO_3^- and PO_4^{3-} present in concentrations up to 200 mg/L. With Cl^- concentrations up to 200 mg/L, only a very small inhibition effect was observed. SiO_4^{4-} at 200 mg/L showed a medium inhibition effect with 75% of GO-SCH's adsorption capacity for Sb(V) retained. At 200 mg/L, HCO_3^- showed the most obvious inhibition effect with 58% of GO-SCH's adsorption capacity retained. Sb(V) adsorption by SCH exhibited only a tiny inhibition from SO_4^{2-} , NO_3^- and PO_4^{3-} concentrations as high as 200 mg/L. Cl^- caused only slight inhibition, SiO_4^{4-} a medium inhibition and HCO_3^- exhibited an obvious inhibitory effect at high concentrations (200 mg/L). GO experienced only small inhibitions of Sb(V) adsorption with all six anions. Even the largest inhibition effect by 200 mg/L of SiO_4^{4-} , reduced the adsorption capacity of GO by only 20%.

The inhibition effect of these six anions on GO-SCH and SCH followed a similar order, but the extent of inhibition on GO-SCH is weaker than on SCH. With each co-existing anion at the same concentration, the retained adsorption capacities followed the order GO-SCH > SCH > GO. We infer that SCH is the main active component with a high adsorption ability. GO also contributes to adsorption performance while serving as a carrier for SCH nanoparticles in the composites. In addition, a synergistic effect between SCH and GO exists in the composites.

3.2.5. Regeneration and reuse

The regeneration and recycling behavior of GO-SCH were evaluated through 5 regeneration cycles are presented in Fig. 7. The capacities of reused GO-SCH remained intact for the first two cycles and later slightly dropped after the 5th cycle. In a practical treatment process, the influent concentration of Sb(V) is usually much lower than that which was used to evaluate and obtain the maximum adsorption capacity. Obviously, these results justify that GO-SCH is a promising future adsorbent when it is magnetically amended and reused.

3.2.6. Treatment of spiked tap water, simulated river water and acid mine drainage

Sb may occur in contaminated tap water, river water and acid mine drainage. Tap water always has complex anion and cation components. River water and mine drainage contain multiple heavy metals and dissolved humic acids and the latter always lowers pH. Sb(V) removal from all three waters are shown in Fig. 8. Antimony levels in spiked tap water (100 µg/L), simulated river water (6400 µg/L) and acid mine drainage (50,000 µg/L) as summarized in Table S4, were lowered to well below their regulation level of 5 µg/L, 100 µg/L and 1000 µg/L [37–39], respectively, with dosages of 0.3 g/L, 0.3 g/L and 3 g/L in less than 10 h. GO-SCH was shown to be effective in such cases, especially in an emergency for Sb contaminants mitigation from these sources.

Fig. 9. (a) FTIR and (b) Raman spectra of GO, SCH and GO-SCH before adsorption, and GO-SCH after adsorption of Sb(V) from a 30 mg/L Sb(V) aqueous solution.

3.3. Adsorption mechanisms

3.3.1. FTIR and Raman spectra

The FTIR and Raman spectra of GO, SCH, and GO-SCH after Sb(V) adsorption are shown in Fig. 9(a) and (b), respectively. The broad IR peaks around 3400 cm^{-1} and 1621 cm^{-1} observed for all the samples were the OH bond stretching modes of free water (surface adsorbed water). Peaks at 1725 , 1621 , 1385 , 1226 and 1071 cm^{-1} of GO are attributed, respectively, to carbonyl (C=O) and aromatic (C=C) stretching, aliphatic CH_3 and CH_2 angle bending, and both aromatic and aliphatic C–O stretching modes [18]. Peaks at 1122 cm^{-1} and the shoulder at 1049 cm^{-1} for the SCH sample are the triply degenerate ν_3 bands of SO_4 , and 980 cm^{-1} is the ν_1 symmetric stretching of SO_4 [40]. For the GO-SCH sample before Sb(V) adsorption, the peak observed at 980 cm^{-1} is due to the ν_1 symmetric stretching vibration of SO_4 from the SCH component. The peaks at 1071 cm^{-1} and 1150 cm^{-1} were assigned to the stretching bands of C–O–H and C–O groups from GO, respectively. The appearance of both SCH and GO peaks confirmed that the nanocomposites were composed of GO and SCH. The Fe–O vibration (ca. at 700 and $410\text{--}490\text{ cm}^{-1}$) in both SCH and the composites was not observed due to the low sensitivity of the IR. After Sb(V) adsorption, the intensities of IR band (980 cm^{-1}) of SO_4 and bands associated with C–O–H and C–O groups (1071 cm^{-1} and 1150 cm^{-1} , respectively) all decreased. This resulted from exchange of SO_4 with adsorbed Sb(V) [31] and the reaction between GO surface groups with Sb(V).

The Raman spectrum of GO contained two characteristic bands, the G band at 1588 cm^{-1} and the D band at 1352 cm^{-1} . The redshift of the G band from its usually observed 1575 cm^{-1} position indicated the presence of isolated double bonds that resonate at a low frequency. The intensity ratio of the G to D bands, 0.84, showed an oxidized graphene structure and the presence of defects

caused by oxidation in the samples [41]. The G and D bands of graphene were observed in all the GO-SCH composites with some extent of frequency shift. The other bands at 271 cm^{-1} and 207 cm^{-1} , 376 cm^{-1} and 579 cm^{-1} are ascribed to Fe–O vibrations of schwertmannite and its phase-transformed product, magnetite, respectively [42]. After Sb(V) adsorption, the stretching vibration of Sb–O at 623 cm^{-1} was observed [43]. In addition, the bands at 1103 cm^{-1} and 439 cm^{-1} are C_{2v} symmetric modes of SO_4 , and 1006 cm^{-1} is assigned to the asymmetric mode of SO_4 [44].

3.3.2. XPS analysis

The O 1s, Fe 2p and C 1s XPS spectra of GO-SCH both before and after adsorption of Sb(V) from a 30 mg/L aqueous solution are shown in Fig. 10(a)–(d), respectively. The appearance of a Sb $3d_{3/2}$ peak (540.2 eV) in the O 1s + Sb 3d spectra of GO-SCH after Sb(V) adsorption confirmed that Sb(V) was chemically bound to the adsorbent. The Sb $3d_{3/2}$ peak (540.2 eV) due to Sb(V) bonded to GO-SCH was positively shifted from the corresponding Sb $3d_{3/2}$ peak (540.6 eV) of Sb(V). This confirms that the detected antimony species was chemically distinct from the adsorbate. Therefore, surface precipitation of Sb(V) had not occurred. In addition, the Sb $3d_{3/2}$ binding energy of Sb(V) adsorbed sample is higher than the 539.7 eV binding energy for Sb(III) oxide [45], indicating that no Sb(V) reduction occurred at the surface. The Fe $2p_{3/2}$ and Fe $2p_{1/2}$ peak intensities slightly weakened after Sb(V) adsorption but no shifting of the binding energy was observed.

Deconvolution of the C 1s peak (Table S5) shows the presence of four types of carbon bonds, the C–C bonds in nonoxygenated rings (C–C, 284.6 eV), the C–O bonds in hydroxyl and epoxy (C–OH, 286.9 eV), C=O bonds in carbonyl (C=O, 287.7 eV) and C=O bonds in carboxyl (O=C–OH, 288.8 eV) [46,47]. The fractions of carbon present in C–OH, C=O and O=C–OH groups decreased from 16.8%, 20.2% and 8.1% before adsorption to 16.4%, 19.8%, and 7.3%

Fig. 10. XPS spectra of (a) O 1s + Sb 3d, (b) Fe 2p, (c) and (d) C 1s for the GO-SCH adsorbent both before and after Sb(V) adsorption.

Table 4

Oxygen-containing surface functional groups on GO-SCH determined by Boehm titration.

	Before 30 mg/L Sb(V) adsorption (mmol/g)	After 30 mg/L Sb(V) adsorption (mmol/g)
Carboxyl	2.33	0.80
Lactonic	1.30	0.86
Phenolic hydroxyl	0.19	0.17

after given above Sb(V) adsorption. This firmly indicated that the surface groups in GO also involved in Sb(V) adsorption as well as serving as a SCH carrier.

3.3.3. GO surface group analysis by Boehm titration

The carboxyl, lactonic and phenolic hydroxyl surface functional groups of GO-SCH were titrated using the Boehm titration method and the results are shown in Table 4. The amounts of carboxyl, lactonic and phenolic hydroxyl groups decreased from 2.33 mmol/g, 1.30 mmol/g and 0.19 mmol/g to 0.80 mmol/g, 0.86 mmol/g and 0.17 mmol/g, respectively. This confirmed that these functional groups participated in the interaction between Sb(V) and GO and contributed to Sb(V) removal. These results compliment the results from deconvolution of the C 1s spectra.

The overall findings can now be summarized. TEM and SEM images show that SCH disperses better on GO than that in SCH alone. XRF characterization confirmed that Sb(V) was adsorbed on GO-SCH. The decreases of the Fe—O Raman band intensity, SO₄ and carbon surface groups IR band intensities, together with the changes of Fe 2p and C 1s XPS spectra, all demonstrate the

interaction of Sb(V) with Fe—O surface sites and carbon surface groups, and confirm the contribution of SO₄ exchange with Sb(V) anions. When combined with the Sb(V) adsorption capacity advantage of SCH versus GO from the isotherm data, it is clear that SCH in the composite adsorbent was the main active phase. GO also contributes to the Sb(V) uptake ability.

4. Conclusions

GO-SCH nanocomposites were successfully synthesized and applied to the efficient Sb(V) removal from water. A synergistic effect on the Sb(V) uptake ability was observed when graphene oxide and schwertmannite nanocomponents incorporated into nanocomposites. A maximum Sb(V) adsorption capacity of 158.6 mg/g Sb(V) was obtained at an equilibrium concentration of 8.0 mg/L at pH 7.0. This capacity is superior to many reported adsorbents. External mass transfer is predominant for GO-SCH within the first hour with a coefficient of 3.863 m²/h. After that, intraparticle diffusion gradually governs the process. GO-SCH could be effectively used for treatment of spiked tap water (100 µg/L), simulated river water (6400 µg/L) and acid mine drainage (50,000 µg/L). The GO-SCH exposure decreased the Sb(V) concentrations to well below their corresponding regulated levels for these three waters. A magnetic-hybrid composite was recycled through five magnetic separation, regeneration and reuse cycles with little loss of Sb(V) capacity. FTIR, Raman and TEM analyses showed that GO and SCH were well incorporated into nanocomposites. SCH was the main active adsorbing phase in the composites, which their XPS Fe 2p spectra confirmed. XPS Sb 3d spectra

showed no surface precipitation or reduction of Sb(V) occurred. C 1s deconvolution and Boehm titration indicated that surface carboxyl, lactonic and phenolic hydroxyl groups also contribute Sb(V) removal.

Acknowledgement

This work was supported by the Fundamental Research Funds for the Central Universities (TD-JC-2013-3).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2015.01.071>.

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