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ORIGINAL PAPER

Application of a high-surface-area schwertmannite in the removal of arsenate and arsenite

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Abstract Schwertmannite is a poorly crystalline Fe(III) hydroxide, which always shows high sorption capacities to pollutants. In this study, schwertmannite synthesized from the Fe^{3+} hydrolyzation method showed a hedgehog-like shape, with a specific surface area of 325.5 $m^2\ g^{-1}$, which was much higher than that of the sphere-like schwertmannite synthesized from the Fe^{2+} oxidation method, with a specific surface area of 48.2 $m^2\ g^{-1}$. The former was then used to evaluate its sorption performance to As(V) and As(III). Sorption of As(V) and As(III) could reach equilibrium in 200 min, and the maximum sorption capacities of As(V) and As(III) were 182.86 and 45.50 mg g^{-1} at pH 3.0, respectively, and 143.25 and 217.85 mg g^{-1} at pH 7.0, respectively. Sorption capacity was dependent on pH and more As(V) adsorbed on schwertmannite at lower pH, while As(III) sorption increased with the increase of pH. Our results also indicated that the presence of sulfate reduced the sorption of As(V) from 85.4 to 67.6 mg g^{-1} as sulfate concentration increased from 0.2 to 6 g L^{-1}, while such an effect was not apparent in As(III) sorption. Nitrate and chloride did not show significant interference on the sorption of both As(V) and As(III). Schwertmannite showed better repeated uses in the removal of As(V) and As(III) after seven repeated using cycles with removal percentages of 95.3 % at pH 3.0 and 63.9 % at pH 7.0 to As(V), and 31.0 % at pH 3.0 and 81.6 % at pH 7.0 to As(III).

Keywords Arsenite · Arsenate · Iron (hydr)oxide · Schwertmannite · Sorption

Introduction

Arsenic is a toxic contaminant in aqueous environment, and it is always originated from the weathering of arsenic-bearing sulfide minerals such as pyrite and arsenopyrite as well as through a range of anthropogenic activities (Smedley and Kinniburgh 2002; Appleyard et al. 2006). With the extensive use of arsenic-containing fertilizers, fossil fuels and pesticides, arsenic may accumulate in water resources (Mandal and Suzuki 2002). Long-term drinking water with arsenic will cause skin, lung and kidney cancer as well as diseases such as neurological disorders and muscular weakness (Jain and Ali 2000). With the serious toxicity of arsenic, the WHO regulated the discharged guideline of arsenic to 10 μg L^{-1} (WHO 1993). In oxygen-rich aqueous environments, arsenate [As(V)] primarily exists as $H_2AsO_4^-$ and $HAsO_4^{2-}$ as the pK_a values of the arsenate acid are p$K_{a1} = 2.1$, p$K_{a2} = 6.7$ and p$K_{a3} = 11.2$, while arsenite [As(III)] mainly exists as H_3AsO_3 with the p$K_{a1} = 9.1$, p$K_{a2} = 12.1$ and p$K_{a3} = 13.4$ (Mohan and Pittman 2007).

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Sorption is a promising method for the treatment of arsenic-containing wastewater, and traditional sorbents such as activated carbon, red mud, blast furnace slag, clay minerals, zeolites and some iron oxides are widely used so far. However, activated carbon is expensive and is required in large amounts to purify wastewater, while low-cost sorbents usually show a low sorption capacity and a low selectivity to arsenic. In addition, the treatment of these sorbents after use may also cause secondary pollution to the environment. In the recent years, iron oxides, such as ferrihydrite, magnetite, goethite, hematite and schwertmannite, have been reported to play important roles in the sink of arsenic in natural environments because of their great abundance and high affinities to arsenic (Pedersen et al. 2006). Sorption of arsenic on iron oxides always depends on specific surface areas. Micron-size goethite had a sorption capacity of 12.5 mg g^{-1} to As(V) (Ladeira and Ciminelli 2004) and 6.74 mg g^{-1} to As(III) (Dixit and Hering 2003), while nanoparticles of ferrihydrite and akaganeite had a sorption capacity of 111.02 and 141.3 mg g^{-1} to As(V), respectively (Raven et al. 1998; Solozhenkin et al. 2003). Magnetite with the size of 12 nm had removal percentages of 98.4 % to As(V) and 99.2 % to As(III) in the solution of initial arsenic concentrations of 500 µg L^{-1}, while the 300 nm magnetite only showed removal percentages of 29.2 and 24.9 %, respectively (Yavuz et al. 2006). Sorption of both As(V) and As(III) was significantly affected by pH, with more sorption of As(V) at lower pH and more sorption of As(III) at higher pH (Guo and Chen 2005). Considering the low binding affinity of As(III) relative to As(V) with iron oxides (Gupta et al. 2012), oxidation of As(III) to As(V) by oxidants such as MnO_x and H_2O_2 followed by the subsequent sorption of As(V) on iron oxides seemed to be an effective way for the removal of As(III) (Yamani et al. 2012). Previous studies showed that Fe–Mn binary oxide could have a removal percentage of 89 % to As(III) (Zhang et al. 2007). Guo et al. (2008) also found that 0.5 mol L^{-1} H_2O_2 could cause an increase of 15 % in the removal of As(III) by hematite.

Schwertmannite always forms in acidic (pH 3–4) and sulfate-rich aqueous environment. It is a poorly crystalline Fe(III)-hydroxide typically represented as $Fe_8O_8(OH)_{8-2x}(SO_4)_x$, ($1 \leq x \leq 1.75$) (Bigham et al. 1996). Its unit cell always consists of 8 $FeO_3(OH)_3$ octahedra forming double chains, which are shared over edges and run parallel to the *b* axis (Regenspurg and Peiffer 2005). Sulfate bounds to schwertmannite into the structure (tunnel sulfate) or adsorbs to the surface with a ratio of 3:1 (Bigham et al. 1990). The sorption mechanism of arsenic on schwertmannite involves ligand exchange with surface-adsorbed or structural SO_4^{2-} (Fukushi et al. 2004). Schwertmannite has shown good sorption capacities to As(III) and As(V). It had sorption capacities of 113.9 mg g^{-1} to As(III) at pH 7.5 (Liao et al. 2011), while 20 mg g^{-1} to As(III) at pH 3.0 (Paikaray et al. 2011). As(V) could reach a sorption capacity of 80.9 mg g^{-1} on schwertmannite at pH 4.0 (Fukushi et al. 2003b).

Although sorption mechanism of arsenic on schwertmannite was clearly known and the transformation of schwertmannite to the more stable iron oxides was also investigated (Davidson et al. 2008; Collins et al. 2010), the potential of using this environmental-friendly sorbent in the removal of arsenic wastewater is still not discussed. In this study, two synthetic methods will be used in order to obtain schwertmannite with the large specific surface area. Sorption capacities of this iron oxide to As(III) and As(V) will then be investigated at different pHs or in the presence of different co-existing anions. In addition, the stability of schwertmannite and its using cycles in the repeated treatment of arsenic wastewater will also be explored to test its applicability as an effective arsenic sorbent. The present study was conducted in School of Chemical Engineering and Technology, Tianjin University, Tianjin, PR China, and was carried out from December 2011 to June 2012.

Materials and methods

Chemicals

All laboratory glassware was repeatedly rinsed with deionized water before use. All reagents were of analytical grade, and all solutions were prepared with deionized water.

Synthesis of schwertmannite

Two pathways to prepare schwertmannite were developed. In the Fe^{2+} oxidation method (Regenspurg et al. 2004), 16.45 g $FeSO_4{\cdot}7H_2O$ was dissolved in 1 L deionized water and reacted with 5.3 mL 30 % H_2O_2. The solution became dark red, and a red-orange material precipitated immediately with the final pH of 2.5 after 24 h. The solid was then centrifuged, washed three times and freeze-dried before use. The deionized water was also replaced with diluted H_2SO_4 solution with the initial pH of 3.0, and the speed of adding H_2O_2 was changed from pouring 5.3 mL to drop-wise addition at the speed of 1 mL per minute. In the Fe^{3+} hydrolyzation method (Kumpulainen et al. 2008), 500 mL pre-heated deionized water was mixed with 2.6 g $Fe_2(SO_4)_3$ in a round-bottomed flask with a mechanical stirrer. The flask was placed in a water bath at 85 °C for 1 h. The solid was then centrifuged, washed three times and freeze-dried before use.

Sorption kinetics of As(V) and As(III) on schwertmannite

Sorption kinetics was designed as described previously (Ren et al. 2012). Schwertmannite 1 g L^{-1} was equilibrated in 0.1 mol L^{-1} of 150 mL NaCl solution for 2 h. NaCl solution was used to provide a stable background of ionic strength (Burton et al. 2009). After that, As(V) or As(III) was added in the system with the initial concentration of 100 mg L^{-1}. pH of the suspension was adjusted to 3.0 only by HCl or NaOH to avoid the interferences from other anions such as sulfate and nitrate. Samples were then placed on a shaker at 140 rpm and room temperature (25 °C). During the experiments, 1.2 mL sample was taken out regularly (every half an hour at first and per hour at last) and centrifuged at 12,000 rpm for 5 min. The supernatant was used to determine the concentration of As(V) or As(III).

Equilibrium sorption of schwertmannite to As(V) and As(III)

Equilibrium sorption experiments were also designed as mentioned previously (Liao et al. 2011). Series of As(V) or As(III) were added into the equilibrated schwertmannite suspension in 0.1 mol L^{-1} of 30 mL NaCl solution with the sorbent concentration of 1 g L^{-1}. The pH was then readjusted to 3.0 or 7.0, and reaction time was controlled at 300 min to ensure the sorption equilibrium. The presence of anions such as sulfate, nitrate and chloride on the sorption of As(V) and As(III) by schwertmannite was also investigated with the initial concentration of As(V) or As(III) of 100 mg L^{-1}. In order to investigate the using cycles of this sorbent in the repeated removal of arsenic contaminated water, a semi-continuous sorption was designed. Schwertmannite 5 g L^{-1} was added in 0.1 mol L^{-1} of 30 mL NaCl solution with 100 mg L^{-1} As(V) or As(III) at pH 3.0 or 7.0. After reaching equilibrium, the samples were centrifuged and the supernatant was used to determine the concentration of As(V) or As(III). The precipitate was subsequently dispersed into the freshly prepared arsenic solution again and repeatedly used in the following removal of arsenic. The initial concentrations of As(V) or As(III) were also controlled at 100 mg L^{-1}. Samples were then placed on a shaker at 140 rpm and 25 °C. After 300 min, 1.2 mL of sample was taken out and centrifuged at 12,000 rpm for 5 min, and then the supernatant was used to determine the concentration of As(V) or As(III).

Analytical methods and characterization

The concentration of As(V) and As(III) was determined by the colorimetric method (Dhar et al. 2004). The color reagent was mixed by ascorbic acid (9.74 wt%), ammonium molybdate (3 wt%), potassium antimonyl tartrate (0.56 wt%) and sulfuric acid (22.44 wt%) with the volume ratios of 2:6:1:5. All samples were acidified by 1 % HCl, and then, 5.5 mL sample was mixed thoroughly with 0.5 mL color reagent for the determination of As(V). As to total As determination, 0.5 mL 0.1 M KIO_3 was added into the sample for 10 min to completely oxidize As(III) to As(V). The color reagent was then added to determine total As in the sample. Absorbance was measured at the wavelength of 880 nm. As(III) concentration was obtained by the subtraction of total As and As(V) concentrations. In our previous study, detection limits for As(V) and total As were found to be 0.005 and 0.022 mg L^{-1}, respectively (Han et al. 2011).

The molecular formula of schwertmannite could be expressed as $Fe_8O_8(OH)_{8-2x}(SO_4)_x$ $(1 \leq x \leq 1.75)$ as mentioned above, and "x" could be determined by the ratio of Fe:S (Bigham et al. 1996). Fe was determined by ICP-AES (ICP, Varian 715 s) and $BaCl_2$ turbidimetrical method was used for SO_4^{2-} determination (Rodier 1975; Wang et al. 2013). Schwertmannite morphology before and after the treatment of arsenic was characterized by a high-resolution analytical transmission electron microscopy (TEM, JEM-2100F, JEOL). Specific surface area of schwertmannite was determined by a volumetric adsorption analyzer (BET, Tristar 3000, Micromeritics). The crystalline structure of schwertmannite was characterized by X-ray diffraction (XRD, D/Max-2500, Rigaku) using an X-ray diffractometer fitted with a Cu X-ray source. Samples were scanned from $2\theta = 10°–90°$ with a $2\theta = 0.02°$ step size.

Results and discussion

Characterization of synthesized schwertmannite

The crystalline structures of schwertmannite synthesized through different methods were investigated by XRD (Fig. 1a). Abbreviations of schwertmannite synthesized through various methods were as follows: Fe^{2+} oxidation method with a low speed of H_2O_2 addition in deionized water (Sch-1), Fe^{2+} oxidation method with a high speed of H_2O_2 addition in deionized water (Sch-2), Fe^{2+} oxidation method with a low speed of H_2O_2 addition in H_2SO_4 solution (Sch-3), Fe^{2+} oxidation method with a high speed of H_2O_2 addition in H_2SO_4 solution (Sch-4) and Fe^{3+} hydrolyzation method (Sch-5). All samples showed the same characteristic peaks at $2\theta = 26°, 35°$ and $61°$, which were the characteristic peaks of schwertmannite (Regenspurg et al. 2004).

XRD results of Sch-1, 2, 3 and 4 showed that changes in pH and Fe^{2+} oxidation rate did not cause significant differences in crystalline structure in the Fe^{2+} oxidation

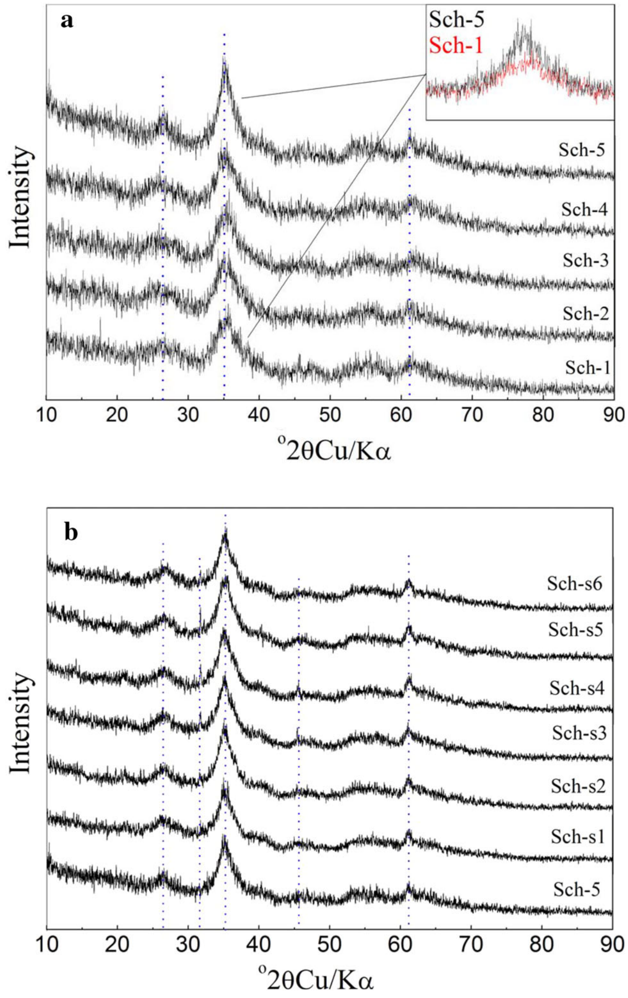


Fig. 1 **a** XRD analysis of schwertmannite synthesized under different conditions. Fe^{2+} oxidation method with a low speed of H_2O_2 addition in deionized water (*Sch-1*), Fe^{2+} oxidation method with a high speed of H_2O_2 addition in deionized water (*Sch-2*), Fe^{2+} oxidation method with a low speed of H_2O_2 addition in H_2SO_4 solution (*Sch-3*), Fe^{2+} oxidation method with a high speed of H_2O_2 addition in H_2SO_4 solution (*Sch-4*) and Fe^{3+} hydrolyzation method (*Sch-5*). **b** The XRD pattern of schwertmannite after the sorption in the presence of As(III), As(V), sulfate or nitrate. The presence of 100 mg L^{-1} As(V) (*Sch-s1*), 100 mg L^{-1} As(III) (*Sch-s2*), 100 mg L^{-1} As(V) and 1,000 mg L^{-1} NO^{3-} (*Sch-s3*), 100 mg L^{-1} As(III) and 1,000 mg L^{-1} NO^{3-} (*Sch-s4*), 100 mg L^{-1} As(V) and 1,000 mg L^{-1} SO_4^{2-} (*Sch-s5*),100 mg L^{-1} As(III) and 1,000 mg L^{-1} SO_4^{2-} (*Sch-s6*) and initial schwertmannite (*Sch-5*)

method (Fig. 1a). Sch-1 was therefore chosen as a representative schwertmannite and used to make a comparison with Sch-5 in the following characterizations. Compared to Sch-1, 2, 3 and 4, the peaks of Sch-5 were sharper, indicating that Sch-5 had a more orderly crystalline structure.

TEM results showed differences in the morphology and particle size between "Sch-1" and "Sch-5" (Fig. 2). Sch-1 showed a sphere shape with a diameter of 500 nm, while Sch-5 had a hedgehog-like shape with a diameter of 100 nm round core and acicular shell of 100 nm average lengths. The specific surface area of Sch-1 and Sch-5 was 48.18 $m^2\ g^{-1}$ and 325.52 $m^2\ g^{-1}$, respectively. The specific surface area for schwertmannite was always in the range of 100–300 $m^2\ g^{-1}$ in natural environment (Carlson et al. 2002), while previous studies have suggested the specific surface area of schwertmannite 42.9 $m^2\ g^{-1}$ (Jönsson et al. 2005) and 55 $m^2\ g^{-1}$ (Webster et al. 1998). Considering the larger specific surface area and the better crystalline structure of Sch-5, it was then used to evaluate its sorption performance to As(V) and As(III). The different morphology and crystalline structure of schwertmannite between the two synthetic methods might be caused by the growing rate of iron oxides from ions (Tresintsi et al. 2012). In natural environment, schwertmannite showed the hedgehog-like morphology during the gradually growing process (Bigham et al. 1994). Another widely used method for schwertmannite synthesis that lasted for a month also showed similar hedgehog-like morphology (Schwertmann and Cornell 2008). The rapid oxidation and hydrolyzation process of Fe(II) by H_2O_2 in the Fe^{2+} oxidation method caused the aggregation of the freshly formed schwertmannite units and resulted in a sphere shape with a larger diameter than that of the hedgehog-like schwertmannite (Fernandez-Martinez et al. 2010).

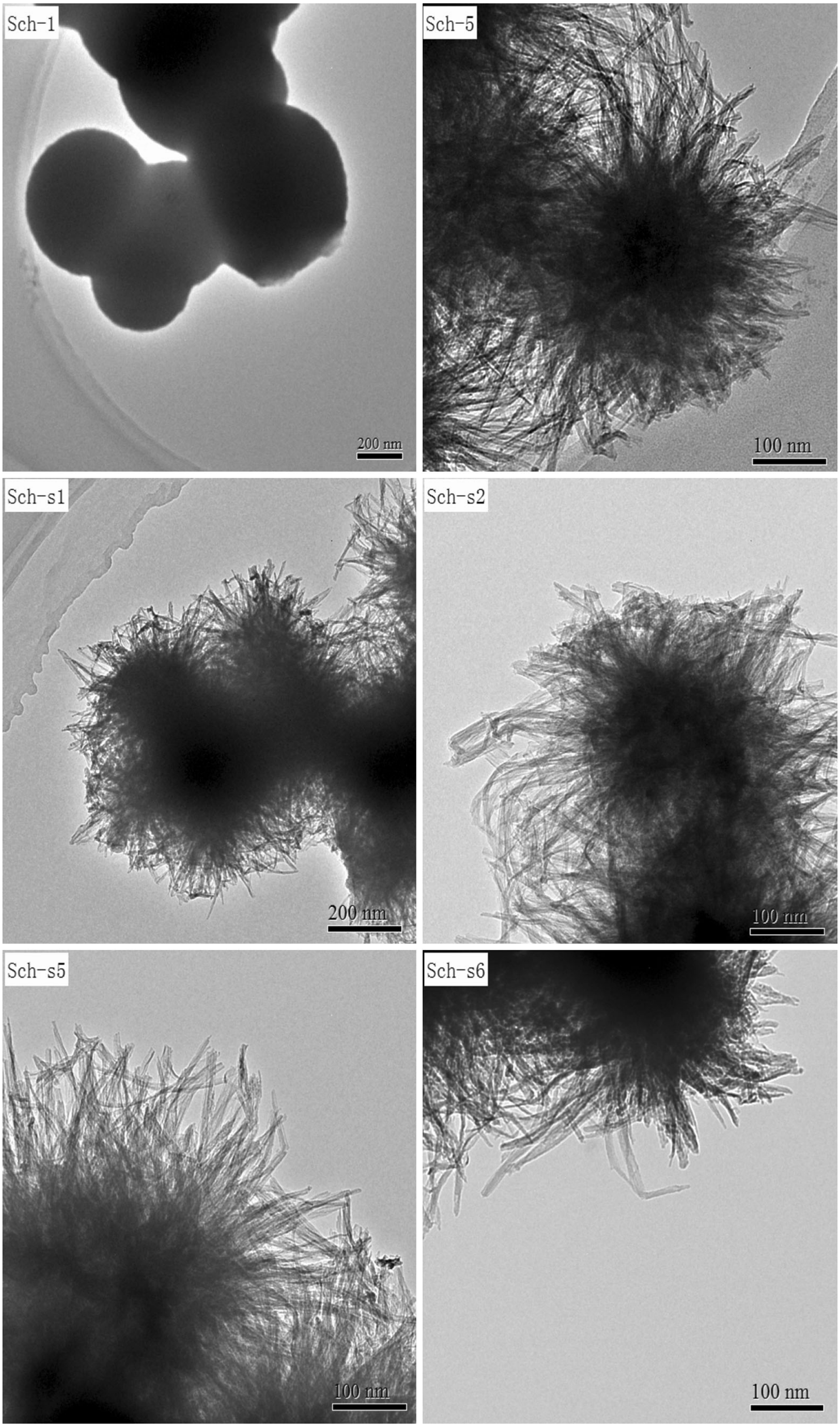
Fig. 2 TEM images in this study. **Sch-1** The analysis of schwertmannite synthesized by the Fe^{2+} oxidation method and **Sch-5** schwertmannite synthesized by the Fe^{3+} hydrolyzation method. **Sch-s1**, **Sch-s2**, **Sch-s5** and **Sch-s6** followed the meanings of symbols in Fig. 1 ▶

The molecular formula of schwertmannite was commonly accepted as $Fe_8O_8(OH)_{8-2x}(SO_4)_x$ $(1 \leq x \leq 1.75)$ (Bigham et al., 1996). In our study, the molecular formula of Sch-1 and Sch-5 was $Fe_8O_8(OH)_{4.16}(SO_4)_{1.92}$ and $Fe_8O_8(OH)_{4.5}(SO_4)_{1.75}$, respectively. The synthesized schwertmannite always had the molecular formula of $Fe_8O_8(OH)_{3.90\pm0.30}\ (SO_4)_{2.05\pm0.15}$ by the Fe^{2+} oxidation method (Burton et al. 2008), while a formula of $Fe_8O_8(OH)_{4.47}(SO_4)_{1.65}$ by the Fe^{3+} hydrolyzation method was reported in a previous study (Kumpulainen et al. 2008).

Sorption of As(V) and As(III) on schwertmannite

Kinetics of As(V) and As(III) sorption on schwertmannite showed that both sorption of As(V) and As(III) could reach equilibrium in 200 min at pH 3.0, and schwertmannite adsorbed more As(V) (87.3 mg g^{-1}) than As(III) (29.6 mg g^{-1}) under the experimental conditions (Fig. 3).

Sorption capacities of As(V) and As(III) were also evaluated under different arsenic concentrations and pH values. Equilibrium isotherm showed that the sorption


Sch-1
200 nm
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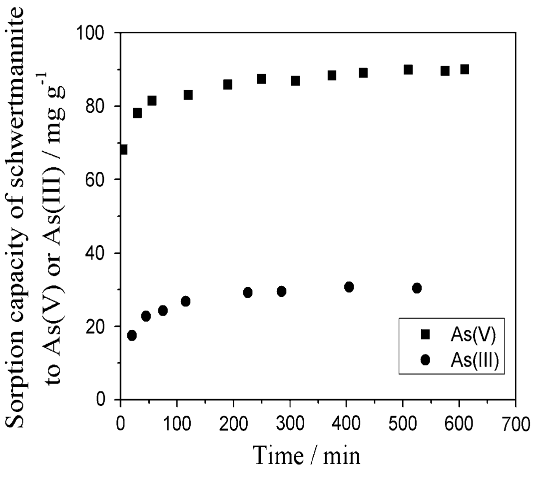

Fig. 3 Sorption kinetics of As(V) and As(III) on schwertmannite at pH 3.0 under the conditions of schwertmannite of 1 g L^{-1} and arsenic of 100 mg L^{-1}

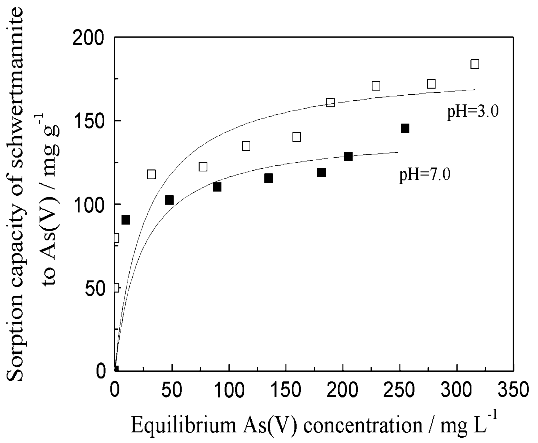

Fig. 4 Sorption capacity of As(V) on schwertmannite at pH 3.0 and 7.0 with schwertmannite concentration of 1 g L^{-1}; the lines represent simulation results by Langmuir isotherm

Table 1 Sorption capacity of schwertmannite to As(V) or As(III) under pH 3 and 7

As species	Q_{max} (mg g^{-1})	K	R^2
As(V), pH 3	182.86	0.037	0.940
As(V), pH 7	143.25	0.043	0.968
As(III), pH 3	45.50	0.034	0.984
As(III), pH 7	217.85	0.025	0.964

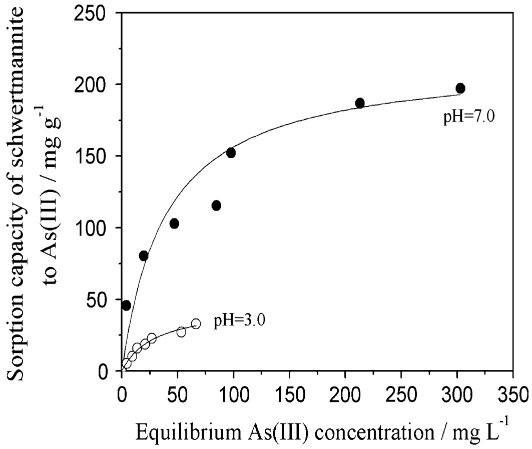

Fig. 5 Sorption capacity of As(III) on schwertmannite at pH 3.0 and 7.0 with schwertmannite concentration of 1 g L^{-1}; the lines represent simulation results by Langmuir isotherm

capacity increased rapidly at low As(V) and As(III) concentrations and began to level off at high concentrations, indicating saturation of the sorption sites on schwertmannite. The sorption capacity of As(V) and As(III) on schwertmannite could be well described by the Langmuir model. The maximum sorption capacities of As(V) were 182.86 and 143.25 mg g^{-1} at pH 3.0 and pH 7.0, respectively, and it was obvious that sorption of As(V) was more favorable at lower pH (Fig. 4; Table 1). Sorption of As(III) was contrary to that of As(V), and more As(III) could be removed under higher pH, with 45.50 and 217.85 mg g^{-1} to As(III) at pH 3.0 and pH 7.0, respectively (Fig. 5; Table 1). This suggested that schwertmannite had a larger sorption capacity than the conventional sorbents. Activated carbon sorbents showed arsenic sorption capacities of 29.9 mg g^{-1} to As(III) and 30.48 mg g^{-1} to As(V) (Pattanayak et al. 2000). Goethite, ferrihydrite and akaganeite showed sorption capacities of 12.5, 111.02 and 141.3 mg g^{-1} to As(V), respectively, which were all less than that of schwertmannite (Raven et al. 1998; Solozhenkin et al. 2003; Ladeira and Ciminelli 2004). The higher sorption capacity of schwertmannite than that of the conventional sorbents and other iron oxides suggested that schwertmannite could be used as an efficient sorbent for the removal of As(V) and As(III).

In order to further determine the effect of pH on the removal of arsenic, pH range from 2.0 to 11.0 was selected in the sorption process. Figure 6 further confirmed that lower pH was in favor of As(V) sorption, while more As(III) was adsorbed on schwertmannite at higher pH. Schwertmannite had a stable sorption capacity of As(V) 87.3 mg g^{-1} from pH 3.0 to 7.0, while it decreased significantly from pH 7.0 to 11.0 with a result of As(V) 73.0 mg g^{-1} at pH 11.0. Sorption of As(III) was different from As(V), which increased with the increase in pH. The sorption capacity of As(III) increased from 7.4 mg g^{-1} at pH 2.0 to 88.0 mg g^{-1} at pH 11.0.

The effect of pH on the sorption of arsenic on schwertmannite could be attributed to the speciation of arsenic, the surface charge of schwertmannite in aquatic environment and the sorption mechanism. As(V) exists as H_3AsO_4

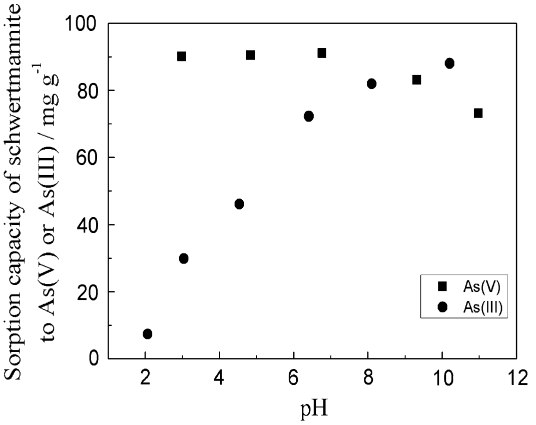

Fig. 6 Effect of pH on the sorption of As(V) and As(III) on schwertmannite under the conditions of schwertmannite of 1 g L^{-1} and arsenic of 100 mg L^{-1}

and $H_2AsO_4^-$ at $pH < 3$; as $H_2AsO_4^-$ at $4 < pH < 5.5$; and as $HAsO_4^{2-}$ and AsO_4^{3-} when $pH > 7$ (Fig. 7). It could be deduced that the positively charged schwertmannite [the point of zero charge (pH_{pzc}) of schwertmannite was 7.2 (Jönsson et al. 2005)] could easily adsorb $H_2AsO_4^-$ at low pH, while having a low sorption capacity of $HAsO_4^{2-}$ and AsO_4^{3-} at high pH. The effect of pH on the sorption of As(V) to goethite, hematite and magnetite also showed similar tendency with steady sorption capacity under acid condition and significant decrease under alkalic condition (Mamindy-Pajany et al. 2011).

The sorption behavior of As(III) was inverse to that of As(V). As(III) primarily exists as H_3AsO_3 when $pH < 7$ and exists as H_3AsO_3 and $H_2AsO_3^-$ when $pH > 7$. The abundant positive charge on schwertmannite under acidic condition had little effect on the sorption of the neutral H_3AsO_3. In addition to electronic attraction, ligand exchange also played important roles in the sorption of As(III) on schwertmannite. Sulfate adsorbed or incorporated into the structure of schwertmannite could exchange with arsenate and arsenite in solution (Fukushi et al. 2004; Liao et al. 2011). As the proton could stabilize the sulfate in schwertmannite (Burton et al. 2009), the high pH favored the ligand exchange between arsenite and sulfate. That was the reason why sorption of H_3AsO_3 increased with the increase of pH. Kersten and Vlasova (2009) also found that sorption capacity of As(III) on goethite increased with pH and reached the maximum value at pH 9.0, followed by a decrease when $pH > 9$.

The effect of ligand exchange also contributed to the sorption of As(V) at high pH. With the decrease in positive charges on schwertmannite as pH increased from 3.0 to 6.8, no significant difference was found in the sorption capacities of As(V). It could be attributed to the increase in the ligand exchange between As(V) and sulfate at high pH. Although further increase of pH (from 6.8 to 11.0) could increase the ligand exchange between As(V) and sulfate, sorption of As(V) decreased due to the electronic repulsion between negative charges on schwertmannite and $HAsO_4^{2-}/AsO_4^{3-}$ under alkalic conditions.

The presence of sulfate significantly decreased the sorption capacity of As(V) with a decrease of 19.5 mg g^{-1} from sulfate concentration of 0.2–6 g L^{-1}, while such an effect was not significant in As(III) sorption process. Nitrate and chloride did not show significant interference on the sorption of As(V) or As(III) on schwertmannite (Fig. 8). Previous studies showed that sulfate could cause a decrease of 5 % in As(V) sorption on hematite (Youngran et al. 2007). Chloride could cause As(V) sorption decrease in 24, 10 and 8 % on magnetite, hematite, and goethite, respectively (Mamindy-Pajany et al. 2011). These coexisting anions did not have significant effects on the

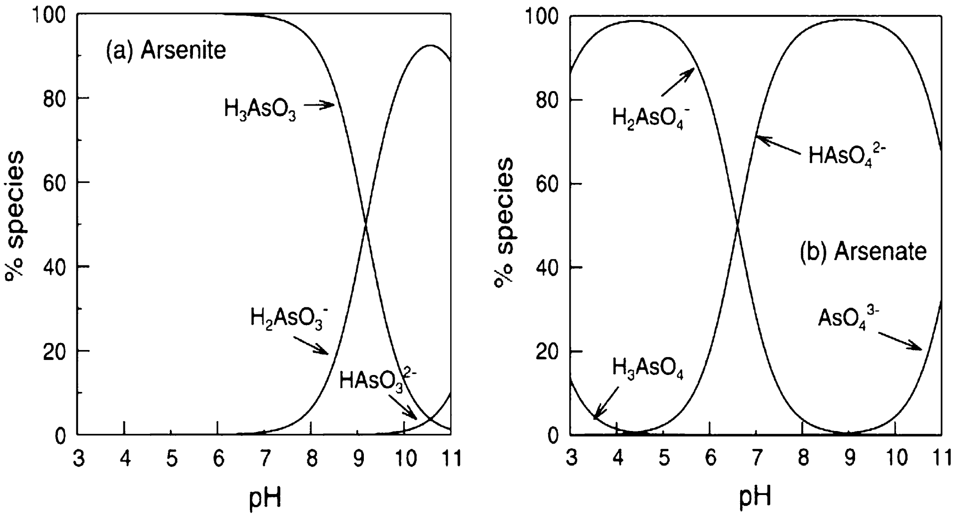

Fig. 7 Speciation of As(V) and As(III) under different pH conditions (Smedley and Kinniburgh 2002)

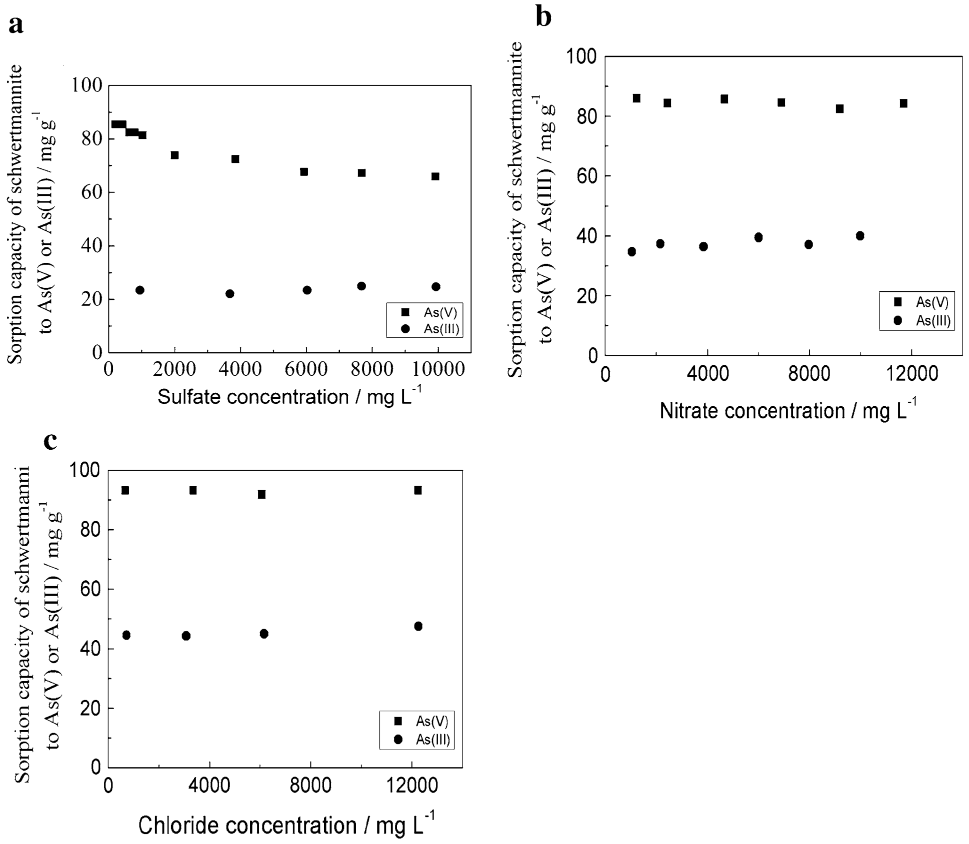

Fig. 8 Effect of co-existing anions on the sorption of As(V) and As(III) on schwertmannite at pH 3.0 under the conditions of schwertmannite of 1 g L^{-1} and As of 100 mg L^{-1}. **a**, **b** and **c** The effects of SO_4^{2-}, NO^{3-}, and Cl^{-}, respectively

sorption capacities to As(V) and As(III), and schwertmannite synthesized in our study might be used in arsenic-polluted wastewater with high ionic strength.

Characterization of schwertmannite after sorption of As(V) or As(III)

The structure and morphology of schwertmannite after As(V) or As(III) sorption with co-existing anions were investigated by XRD and TEM. In the presence of 100 mg L^{-1} As(V) (Sch-s1); 100 mg L^{-1} As(III) (Sch-s2); 100 mg L^{-1} As(V) and 1,000 mg L^{-1} NO^{3-} (Sch-s3); 100 mg L^{-1} As(III) and 1,000 mg L^{-1} NO^{3-} (Sch-s4); 100 mg L^{-1} As(V) and 1,000 mg L^{-1} SO_4^{2-} (Sch-s5); and 100 mg L^{-1} As(III) and 1,000 mg L^{-1} SO_4^{2-} (Sch-s6), XRD analysis indicated that no significant change was found in schwertmannite crystalline structure, and TEM images also showed no morphological change in schwertmannite (Fig. 1b, 2 Sch-s1, Sch-s2, Sch-s5 and Sch-s6). The little peaks appeared at $2\theta = 32°$ and 45° were the peaks of background NaCl in the sorption system. From the contrast of schwertmannite in the presence of different anions (Sch-s1 to Sch-s6) with the initial schwertmannite (Sch-5), differences could be found at positions of $2\theta = 27°$, 35° and 62° (Fig. 1b). The three sharper peaks of Sch-s1 to Sch-s6 indicated that As(V) and As(III) could improve the regularity and ordering of schwertmannite (Fukushi et al. 2003a). Schwertmannite is a metastable mineral and previous studies showed that arsenic could retard the slow transformation of schwertmannite to goethite under oxidizing conditions (Acero et al. 2006; Burton et al. 2010). However, 99 % of the adsorbed arsenic remained in the solid phase throughout the entire aging and transform process (Acero et al. 2006), which suggested the possibility of applying this kind of iron hydroxide as a stable sorbent for the removal of arsenic in wastewater with no secondary pollution even it was transformed to other iron oxides.

Aftertreatment of the arsenic-adsorbed schwertmannite

Results from repeated use of schwertmannite in arsenic removal showed that schwertmannite could adsorb arsenic sufficiently at specific pH condition (Fig. 9). The results showed that 5 g L^{-1} schwertmannite could adsorb 120 mg g^{-1} As(V) with no arsenic left in the solution at pH 3.0 during the six-cycles sorption and 99.32 mg g^{-1} As(III) at pH 7.0 in the five-cycles sorption. Sorption of As(V) decreased 4.7 % in the seventh cycle at pH 3.0, while 7.3 and 36.2 % decrease in the sixth and seventh cycles at pH 7.0, respectively. Sorption of As(III) showed a more stable sorption property at pH 7.0 than As(V), which decreased 3.4, 4.5 and 18.4 % in the fifth to seventh cycles,

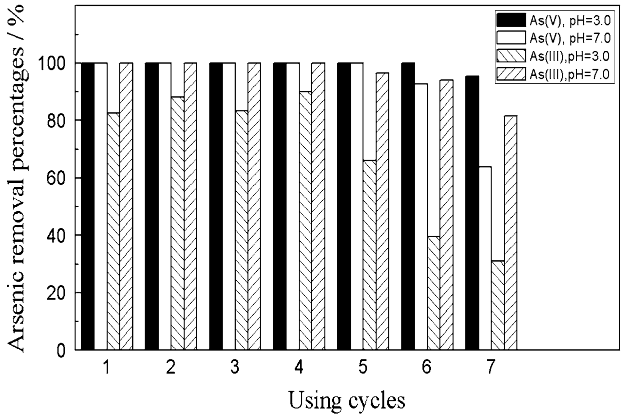

Fig. 9 Continuous sorption of As(V) and As(III) on schwertmannite at pH 3.0 and pH 7.0 with schwertmannite concentration of 5 g L^{-1} and As concentration of 100 mg L^{-1} in each using cycle

respectively. Although the sorption of As(III) at pH 3.0 was lower than 7.0, it could still keep a stable sorption capacity during the four-cycles sorption which showed a good using cycles property. The results indicated that schwertmannite could be a reusable sorbent.

How to treat the sorbents after losing sorption capacity to contaminants is a big problem in the scale-up of sorption process. Considering the easy dissolution of the arsenic-loaded schwertmannite by acids, it was reasonable to use this kind of environmental-friendly sorbent to concentrate diluted-arsenic from arsenic-containment water. Schwertmannite after seven-cycles' use in this study was dissolved in 25 mL 65 % HNO_3, and the concentration of arsenic in the solution reached As(V) of 720 mg L^{-1} or As(III) of 596 mg L^{-1}. In this case, both Fe(III) and concentrated arsenic could be effectively recovered for further purification with no secondary pollution produced.

Conclusion

In this study, we developed a high-surface-area schwertmannite which showed higher sorption capacities to As(V) and As(III) than that of most of adsorbents in previous studies. Besides, the adsorption of arsenic could stabilize the structure of schwertmannite, which was a significant difference with common adsorbents that could avoid the release of the adsorbed arsenic. The present study revealed that schwertmannite synthesized from Fe^{3+} hydrolyzation method had a large specific surface area of 325.5 m^2 g^{-1} and showed a maximum sorption capacity to As(V) of 182.86 mg g^{-1} at pH 3.0 and As(III) of 217.85 mg g^{-1} at pH 7.0. The pH-dependent sorption of As(V) remained stable with a capacity of 87.3 mg g^{-1} from pH 3.0 to 7.0 and decreased significantly from pH 7.0 to 11.0, with a result of 73.0 mg g^{-1} at pH 11.0. The sorption behavior of As(III) was contrary to that of As(V), which increased with the increase of pH with sorption capacities of 7.4 and 88.0 mg g^{-1} at pH 2.0 and 11.0, respectively. Co-existing sulfate could decrease the sorption of As(V) but not As(III), while no obvious effects were detected for As(V) and As(III) sorption by nitrate and chloride. XRD and TEM analyses also showed no significant change on the crystalline structure or morphology of schwertmannite after the sorption of As(V) and As(III). Schwertmannite showed a better performance in the repeated removal of As(V) than that of As(III). The diluted-arsenic-contaminated wastewater could be effectively recovered by dissolving the arsenic-containing iron oxides by acids, which indicated that schwertmannite could be used as a stable, reusable and environmental-friendly sorbent in the removal of As(V) and As(III).

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