Effect of competing solutes on arsenic(V) adsorption using iron and aluminum oxides

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Abstract

The study focused on the effect of several typical competing solutes on removal of arsenic with Fe_2O_3 and Al_2O_3. The test results indicate that chloride, nitrate and sulfate did not have detectable effects, and that selenium(IV) (Se(IV)) and vanadium(V) (V(V)) showed slight effects on the adsorption of As(V) with Fe_2O_3. The results also showed that adsorption of As(V) on Al_2O_3 was not affected by chloride and nitrate anions, but slightly by Se(IV) and V(V) ions. Unlike the adsorption of As(V) with Fe_2O_3, that with Fe_2O_3 was affected by the presence of sulfate in water solutions. Both phosphate and silica have significant adverse effects on the adsorption of As(V) adsorption with Fe_2O_3 and Al_2O_3. Compared to the other tested anions, phosphate anion was found to be the most prominent solute affecting the As(V) adsorption with Fe_2O_3 and Al_2O_3. In general, Fe_2O_3 has a better performance than Al_2O_3 in removal of As(V) within a water environment where multi competing solutes are present.

Key words: adsorption; arsenic; iron oxide; aluminum oxide; sulfate; selenium(IV); vanadium(V); phosphate; silica

Introduction

Arsenic (As) is well known as a useful compound in industrial applications such as smelting, agricultural pesticides and insecticides (LANL, 2004). However, As has also been considered as a strong poisonous chemical due to its odorless and nearly tasteless nature (Buchanan, 1962; Ferguson and Gavis, 1972). Even small amounts of arsenic in drinking water can have adverse effects on human health. Known consequences include cardiovascular diseases, conjunctivitis, and skin cancer (Tseng *et al*., 1968; Klaassen, 1996; Zhang *et al*., 2004; Safiullah *et al*., 2004; Yean *et al*., 2005; Zhang and Stanforth, 2005). Of organic and inorganic arsenic, inorganic arsenic commonly exists in two valence states, As(III) and As(V), in groundwater or surface water (Ferguson and Gavis, 1972; Reynolds *et al*., 1999). Inorganic arsenic also has adverse effects on human health. As(III) effects on human health are more adverse than those of As(V); however, it is easy to transform As(III) easily to As(V) in oxygenated environments (Brookins, 1988). In addition, the efficiency of removal of As(V) by mineral oxides is found to be greater than that of As(III). Therefore, the preoxidation of As(III) to As(V) by using oxidizing agents including oxygen and ozone, prior to adsorption is recommended (Oscarson *et al*., 1983; Frank and Clifford, 1986).

Due to the serious effects of arsenic on people's health,

World Health Organization (WHO) recommended 10 μg/L as the guideline value for arsenic in drinking water in 2001 (WHO, 2001) and the U.S. Environmental Protection Agency (USEPA) also promulgated 10 μg/L as its new arsenic standard for drinking water (USEPA, 2001a). Therefore, development of various arsenic removal technologies is important. Metal oxides have been studied by many researchers as one of the most promising arsenic removal technologies. These materials include amorphous ferric hydroxide (Pierce and Moore, 1982), granular ferric hydroxide (GFH) (Thirunavukkarasu *et al*., 2003), amorphous aluminum oxide (Anderson *et al*., 1976), and activated alumina (Rosenblum and Clifford, 1983). Our previous research has shown that Fe_2O_3 and Al_2O_3 are good adsorption media (Jeong *et al*., 2005) for As(V) without the presence of competing solutes. It was observed that their arsenate adsorption capacities varied with the pH values of As(V) solutions, and the highest adsorption of As(V) on both Fe_2O_3 and Al_2O_3 was observed at pH 6.

However, some soluble solutes in water are often present in groundwater and surface water (Meng *et al*., 2002; Roberts *et al*., 2004; Hug *et al*., 2005). Welch *et al*. (1998) reported that the phosphate (as P) in the shallow groundwater from the southern Carson Desert in the United States is higher than 4 mg/L. Many studies have indicated that the competing solutes affect the removal of As(V) by adsorbents. The presence of phosphate resulted in a severe reduction in arsenate adsorption by ferrihy-

drite (Jain and Loeppert, 2000), goethite (α-FeOOH) and gibbsite (γ-Al(OH)$_3$) (Manning and Goldberg, 1996b), kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), montmorillonite ((Na, Ca)(Al, Mg)$_6$(Si$_4$O$_{10}$)$_3$(OH)$_6$-nH$_2$O), and illite ((K, H$_3$O)(Al, Mg, Fe)$_2$(Si, Al)$_4$O$_{10}$(OH)$_2$, (H$_2$O)) (Manning and Goldberg, 1996a). The high concentration of sulfate reduced the removal of arsenate on alumina and hydrous ferric oxide, although the competing effect of sulfate anions was of a lower degree than that of phosphate anions (Wilkie and Hering, 1996; Xu *et al*., 1988). Meng *et al*. (2000) showed that the removal of As(V) by coprecipitation and adsorption with ferric chloride was moderately affected due to the presence of silicate. Lee *et al*. (2004) discovered that 35.5 mg/L of silica and 13 μg/L of V(V) in groundwater had an unfavorable impact on As(V) adsorption using GFH. Davis and Misra (1997) found that Se(IV) could be a competing solute in the adsorption of As(V) onto aluminum-based oxides.

This research studied the competitive effect of co-occurring solutes on the adsorption of As(V) with Fe$_2$O$_3$ and Al$_2$O$_3$, including chloride, nitrate, sulfate, phosphate, silicate, Se(IV) and V(V). It is expected that the research will provide more information for actually applying Fe$_2$O$_3$ and Al$_2$O$_3$ in the removal of As(V) in water treatment industry.

1 Materials and methods

1.1 Preparation of adsorbents and solutions

Iron oxide (Fe$_2$O$_3$-PVS; physical vapor synthesis, Bailey-PVS, USA) and aluminum oxide (Al$_2$O$_3$-ALO101, Praxair, USA), as mentioned in a previous paper (Jeong *et al*., 2005), were used in our experiments for studying the competing effects of solutes on the adsorption of As(V). These oxides, Fe$_2$O$_3$ and Al$_2$O$_3$, are nonporous adsorbents with low specific surface areas (5.05 and 0.55 m^2/g) and were used in our experiments without further purification.

Chemicals including NaCl, NaNO$_3$, Na$_2$SO$_4$, Na$_2$HPO$_4$, Na$_2$SiO$_3$·9H$_2$O, and V$_2$O$_5$ were reagent grade materials from Fisher Chemicals (USA). Sodium arsenate (Na$_2$HAsO$_4$·7H$_2$O) and sodium selenite (Na$_2$SeO$_3$) were purchased from Matheson Coleman and Bell (Norwood, Ohio, USA) and from Sigma-Aldrich (USA), respectively. Stock solutions of arsenate (HAsO$_4$$^{2-}$, 10 mg/L), chloride (Cl$^-$, 1 g/L), sulfate (SO$_4$$^{2-}$, 1 g/L), nitrate as nitrogen (NO$_3$$^-$-N, 1 g/L), phosphate (HPO$_4$$^{2-}$, 1 g/L), silica (SiO$_3$$^{2-}$, 1 g/L), vanadium as vanadate (V^{5+}, 5 mg/L), and selenium as selenite ion (SeO$_3$$^{2-}$, 5 mg/L) were prepared by dissolving the respective chemicals in deionized water. All of these solutions, with the exception of the silica solution, were further diluted to suitable concentrations on the day of use. Silica stock solution was prepared every week and rapidly mixed with arsenate-contaminated water to maintain the main silicate species found in natural aquatic systems (monomeric H$_4$SiO$_4$); the quick dilution was used to avoid the formation of silicate polymers (Stumm and Morgan, 1996; Roberts *et al*., 2004).

1.2 Batch experiment

Batch experiments were performed in a jar tester (PB-700TM, Phipps & Bird, USA) having six jars each of 2 L volume and six two-paddle stirrers to study the effect of competing ions on the adsorption of As(V) by Fe$_2$O$_3$ and Al$_2$O$_3$. The tested initial As(V) concentration was 200 μg/L (2.67×10^{-6} mol/L), and the dosages of Fe$_2$O$_3$ and Al$_2$O$_3$ varied in the ranges of 0.05–1 g/L and 0.5–6 g/L, respectively. Each of the competing solutes was separately added into water samples. Amounts of solutes added in the water samples were based on the typical concentrations of solutes in the natural water bodies (Meng *et al*., 2002; US EPA, 2001b; APHA, 1999; Heinz Center, 2000). Generally, the concentrations of sulfate and chloride were much higher than those of nitrate and silica in the water. The concentrations of phosphate, V(V) and Se(IV) were usually lower than 1 mg/L in ground or surface water. The pH values of the test solutions were adjusted to 6 ± 0.1 using either diluted 0.1 mol/L hydrochloric acid (HCl) or 0.1 mol/L sodium hydroxide (NaOH) solutions before adsorption. No buffer was used to keep the pH value of each tested As(V) solution as a constant during each adsorption process because it is impractical to control pH by using a buffer in the real water treatment industry. To avoid the interference of other ions, all glassware was cleaned by soaking in 0.1 mol/L HNO$_3$ and 0.5 mol/L HCl and rinsed four times with deionized water. In order to avoid the effect of silica of glass beakers, polyethylene beakers were used in the experiments by following standard jar test methods (APHA, 1999). No competing anions on the walls of jars were detected through blank experiments. At room temperature (25±0.5°C), As(V) adsorption onto Fe$_2$O$_3$ and Al$_2$O$_3$ with competing solutes was conducted with a stirring rate of 130±5 RPM for 1 h and 2 h, respectively. To analyze the concentrations of As(V) in water after adsorption, supernatant of water samples was collected from the jar using a 10-ml disposable syringe. The samples were filtered through 0.45 μm syringe filters (Millipore Millex) and analyzed for the concentrations of arsenic and competing anions. The As(V) adsorption uptakes were the difference between the initial and the equilibrium concentrations of As(V) in water. The experiments were performed in triplicate and the mean values were accepted.

1.3 Analytical methods of arsenate and solutes

Arsenate (As(V)), vanadium (V(V)), and selenium (Se(IV)) concentrations in all the samples were measured by inductively coupled plasma-mass spectrometry (ICP-MS, 4500 Series, Hewlett Packard (HP)) following Standard Methods (APHA, 1999). Because high concentrations of chloride interfere in measuring As(V), the interference correction equation provided by HP was applied to identify and measure arsenic concentrations. The analysis of phosphate (HPO$_4$$^{2-}$ as total P) was also performed using ICP-MS (Dixit and Hering, 2003). The detection limits of ICP-MS were 0.1 μg/L for arsenic, and 1 μg/L for phosphate, V(V), and Se(IV), respectively. The measurements were considered as reasonable data in cases

of less than 10% relative standard deviation (RSD) for 0–50 μg/L solute concentrations and the RSD was ±5% in the range of 50–600 μg/L solute concentrations.

The analyses of anions, including nitrate (NO_3^--N), sulfate (SO_4^{2-}), and chloride (Cl^-), were conducted in our laboratory using an ion chromatograph (IC-DX-120, Dionex) equipped with a Dionex Ion Pac As14 (4 mm × 250 mm) column and conductivity detection. The eluent solution used for ion chromatography (IC) was $Na_2CO_3/NaHCO_3$ (3.5 mmol/L:1 mmol/L). The molybdosilicate method was used for detecting silica concentrations (APHA, 1999). The concentration of silica was analyzed using a UV visible spectrophotometer (DMS 100, Varian) with a 1-cm light path at a 410-nm wavelength. The detection limit for silica was 1 mg/L. The digestion with $NaHCO_3$ was not used for checking the existence of molybdate-unreactive silica. Prior to each analysis, standard solutions of each solute were prepared by diluting stock solutions of each solute solution with deionized water.

2 Results and discussion

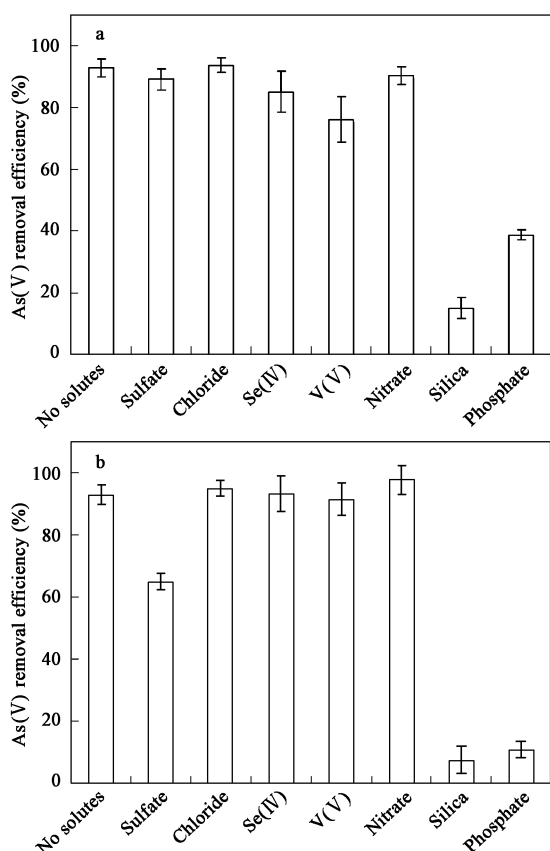Fig.1 shows the As(V) removal efficiencies of 0.5 g/L of Fe_2O_3 and 4 g/L of Al_2O_3 with the presence of high concentrations of competing solutes including sulfate (SO_4^{2-}), chloride (Cl^-), nitrate (NO_3^--N), vanadium (V), selenium (IV), silica (SiO_3^{2-}), and phosphate (HPO_4^{2-}) when the initial As(V) concentrations and pH of water solutions were 200 μg/L and 6±0.1, respectively. Fig.1a shows that when the dosage of Fe_2O_3 is 0.5 g/L, chloride, nitrate, and sulfate solutes hardly affected the As(V) removal efficiencies, while V(V) and Se(IV) slightly affected the As(V) adsorption and silica and phosphate ions significantly decreased As(V) removal efficiencies. Fig.1b shows that at 4 g/L dosage of Al_2O_3, chloride, nitrate, V(V), and Se(IV) solutes have little effect on the As(V) removal efficiencies; sulfate ions moderately reduced As(V) removal efficiencies; silica and phosphate ions significantly decreased As(V) removal efficiencies.

2.1 Chloride and nitrate

As shown in Figs.1a and 1b, the adsorption of As(V) on Fe_2O_3 and Al_2O_3 was found to be independent of the concentration of chloride and nitrate at pH 6. We observed that the concentrations of these ions remained the same after adsorption processes. This finding is consistent with that reported by Xu *et al.* (2002) when they used aluminum-loaded shirasu-zeolite for removal of As(V). This observation can be attributed to the fact that complexes of chloride and nitrate with Fe_2O_3 or Al_2O_3 are much weaker than those between arsenate and Fe_2O_3 or Al_2O_3.
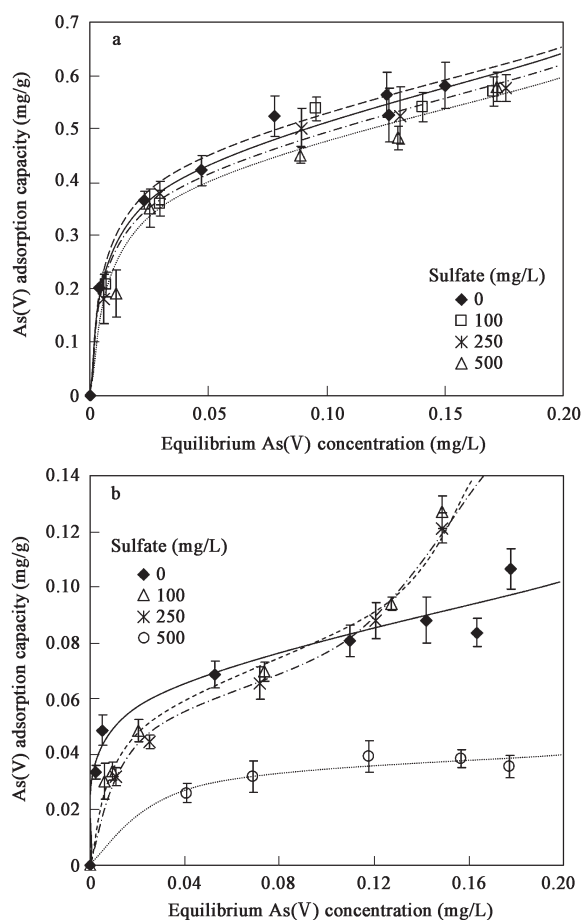

Fig. 1 Effects of various competing solutes on As(V) removal efficiency using Fe_2O_3 (a) and Al_2O_3 (b). Initial As(V) concentration 200 μg/L; sulfate and chloride 500 mg/L for each; Se(IV) and V(V) 100 μg/L for each; nitrate 20 mg/L; silica 10 mg/L; phosphate 1000 μg/L; pH 6±0.1. Dosage, 0.5 g/L (a); 4.0 g/L (b).

Fig. 2 Adsorption isotherm of As(V) by Fe_2O_3 (a) and Al_2O_3 (b) with the presence of sulfate. Initial As(V) concentration 200 μg/L; pH 6±0.1.
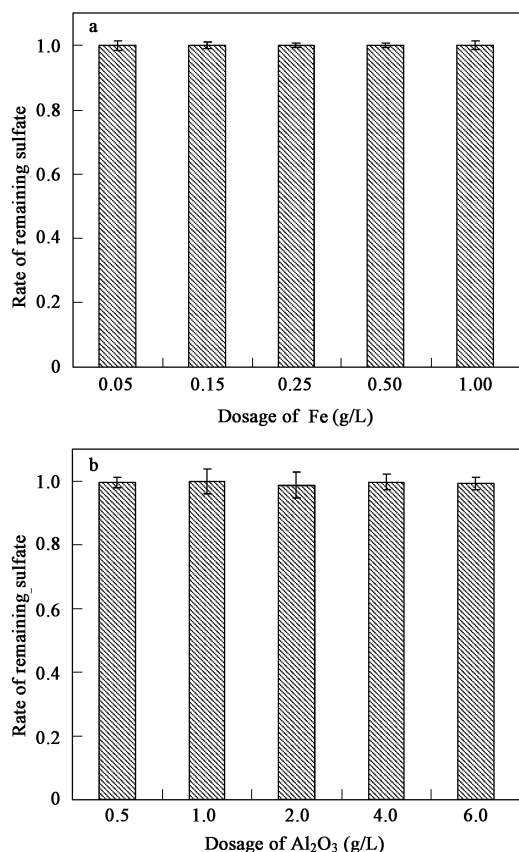
Fig. 3 Comparison of remaining sulfate concentrations after As(V) adsorption with various dosages of Fe_2O_3 (a) and Al_2O_3 (b). Initial sulfate concentration 250 mg/L; pH 6±0.1.

2.2 Sulfate

The As(V) adsorption isotherm curves for Fe_2O_3 and Al_2O_3 within different sulfate environments are shown in Fig.2. Fig.2a demonstrates that the As(V) adsorption isotherm curves were hardly affected by lower concentrations of sulfate; however, the isotherms showed moderate decreasing trends with the increasing of sulfate concentrations, especially at concentrations greater than 250 mg/L. This result is supported by other studies. Meng *et al.* (2000) reported that sulfate with concentrations up to 300 mg/L had no apparent effect on the removal of As(V) with ferric chloride at a pH value of 6.8. They attributed the phenomenon to the fact that the binding affinity between sulfate and ferric hydroxide was much weaker than that between As(V) and ferric hydroxide. Zeng (2004) revealed that the interference of 460 mg/L of sulfate ions on arsenate adsorption with an iron(III)-silica based binary oxide adsorbent was insignificant. Xu *et al.* (1988) stated that sulfate with a high concentration slightly reduced the removal of arsenate with alumina. As presented in Fig.2b, the adsorption of As(V) on Al_2O_3 with a heterogeneous surface (Jeong *et al.*, 2005) is affected by sulfate whose concentrations are relatively higher the initial As(V) concentration. The similar phenomenon was also observed by others such as Balistrieri and Chao (1990).

As shown in Fig.3, the concentration of sulfate after As(V) adsorption on Al_2O_3 remained unchanged from its initial concentration, which is different from those reported
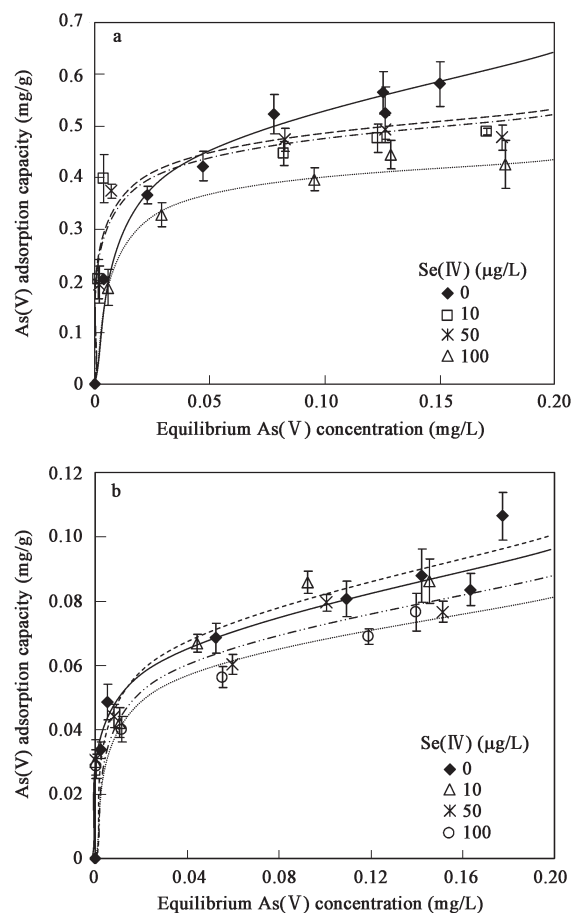

Fig. 4 Adsorption isotherm of As(V) by Fe_2O_3 (a) and Al_2O_3 (b) with the different concentration of Se(IV). Initial As(V) concentration 200 μg/L; pH 6±0.1.

by Wijnja and Schulthess (2000) from their As(V) adsorption tests. They observed through Raman and attenuated total reflectance-Fourier transformed infrared (ATR-FTIR) that both inner- and outer-sphere surface complexes of sulfate ions occur on goethite and aluminum hydroxide surfaces without arsenate anions. By comparing the spectral intensities of sulfate anions on goethite and aluminum oxide, they further revealed that complexation of sulfate anions with aluminum oxide is weaker than that with Fe oxide. Thus, we conclude that the interactions of sulfate ions with surfaces of Fe_2O_3 and Al_2O_3 is weaker those goethite and aluminum hydroxide.

2.3 Selenium

The effects of Se(IV) on As(V) adsorption with Fe_2O_3 and Al_2O_3 are shown in Fig.4. Figs. 4a and 4b show that Se(IV) has larger effect on the adsorption of As(V) with Fe_2O_3 than with Al_2O_3. In addition, as shown in Fig.5, the concentration of Se(IV) after adsorption decreases rapidly with increasing of Fe_2O_3 dosage, while it does slowly with increasing Al_2O_3 dosage. When the initial Se(V) concentration was 50 μg/L, 95% of Se(IV) was adsorbed on the surface of 0.5 g/L Fe_2O_3 added while only 10% of Se(IV) was removed by 0.5 g/L of Al_2O_3.

Our result with Se(IV) is supported by the study of Peak and Sparks (2002). According to Peak and Sparks
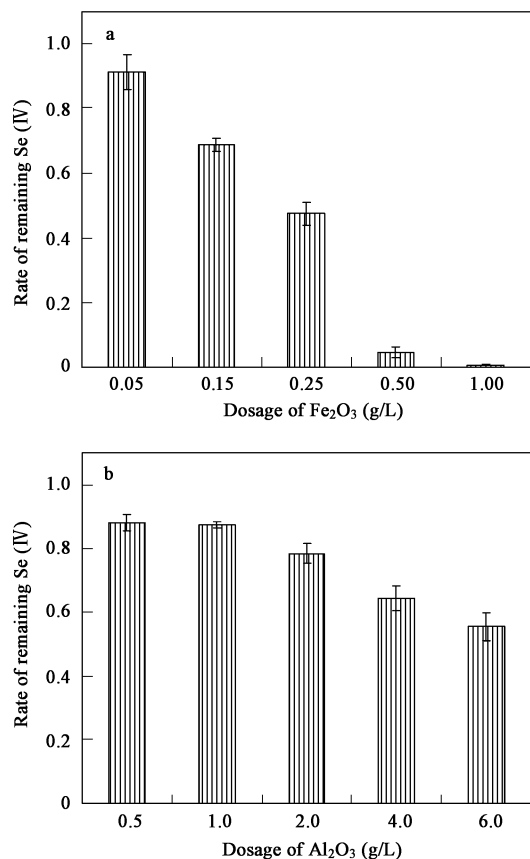
Fig. 5 Comparison of remaining Se(IV) concentrations after As(V) adsorption with various dosages of Fe_2O_3 (a) and Al_2O_3 (b). Initial Se(IV) concentration 50 μg/L; pH 6±0.1.

Fig. 6 Adsorption isotherm of As(V) by Fe_2O_3 (a) and Al_2O_3 (b) with different concentrations of V(V). Initial As(V) concentration 200 μg/L; pH 6±0.1.

(2002), selenate ions form inner-sphere and/or outer-sphere surface complexes on surface of iron oxides and hydroxides such as hematite, goethite and hydrous ferric oxide (HFO) under certain pH and ionic strength. Wijnja and Schulthess (2000), using ATR-FTIR spectroscopy, reported that selenate (SeO_4^{2-}) ions are adsorbed on goethite and aluminum oxide and that complexation of selenate with iron oxide is stronger than that with aluminum oxide. These results indicate that the binding affinity of As(V) with Fe_2O_3 and Al_2O_3 is stronger than that of selenite, and the complexation of selenite with Fe_2O_3 is stronger than that with Al_2O_3.

2.4 Vanadium

As shown on Fig.6, V(V) slightly affects the As(V) adsorption capacity of Fe_2O_3 but has little effect on that of Al_2O_3. The As(V) adsorption capacity of Fe_2O_3 did not change in the presence of 10 μg/L V(V). Similar results were observed with Al_2O_3 in the presence of 50 μg/L V(V). In high V(V) concentration range (> 50 μg/L), however, the adsorption isotherm curve of As(V) on Fe_2O_3 showed a gradual decrease. It was found that the isotherm curves eventually reach a saturation plateau with the increase of the concentration of V(V) as observed by Lee *et al.* (2004).

Fig.7 indicates that the remaining V(V) concentrations of As(V) solutions decreased significantly with the increasing of dosage of Fe_2O_3. When the initial V(V)
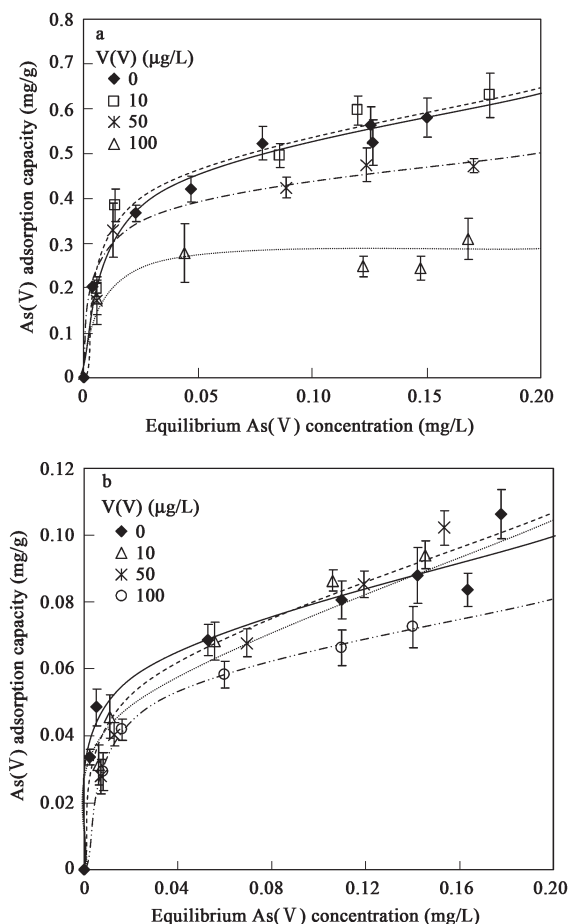
concentration was a 50 μg/L, Fe_2O_3 and Al_2O_3 adsorb 90% and 10% of V(V), respectively, under the given adsorption conditions. The difference was consistent with the findings of Shieh and Duedall (1988). Golob *et al.* (1971) reported that vanadium (V) can only poorly be absorbed on activated aluminum oxide. Several investigators discovered that in dilute solutions the principal species of V(V) are mononuclear vanadate oxyanions ($VO_2(OH)^{2-}$ and $VO_3(OH)^{2-}$), which are similar to the behavior of phosphate anions (Wanty and Goldhaber, 1992; Wehrli and Stumm, 1989), and that vanadate oxyanions can adsorb onto the surface of negatively charged iron oxide or clay mineral such as goethite (α-FeOOH) (Cruywagen and Heyns, 1991; Sigg and Stumm, 1980; Peacock and Sherman, 2004) through ligand exchanges. Based on the characteristics of V(V), we can assume that V(V) competes with As(V) for adsorption on the active sites of Fe_2O_3 but the interaction of As(V) with the surface of Fe_2O_3 is still stronger than that of V(V).

2.5 Phosphate

Depending on the pH value, phosphates can present in any of the following four forms in dilute aqueous solution: phosphate ion (PO_4^{3-}), hydrogen phosphate ion (HPO_4^{2-}), dihydrogen phosphate ion (H_2PO^{4-}), or aqueous phosphoric acid ($H_3PO_4(aq)$). PO_4^{3-} ions are more
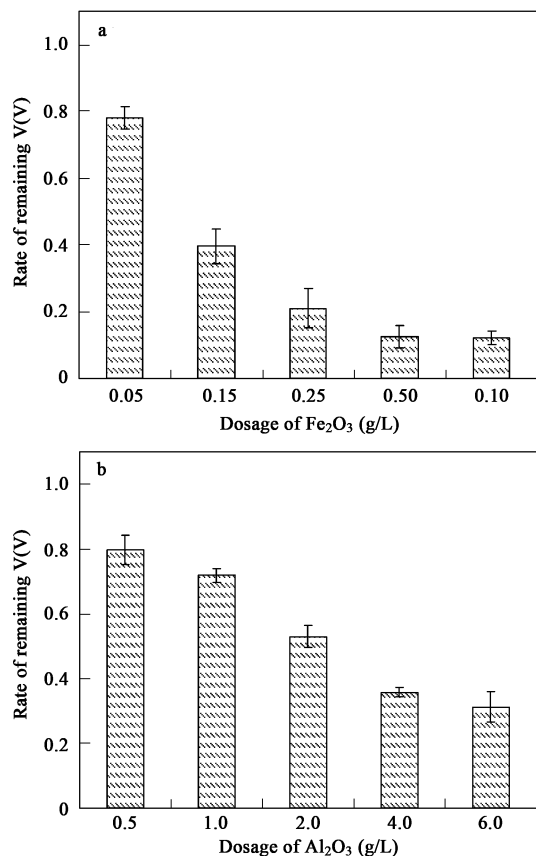
Fig. 7 Comparison of remaining V(V) concentrations after As(V) adsorption with various dosages of Fe_2O_3 (a) andAl_2O_3 (b). Initial V(V) concentration 50 μg/L; pH 6±0.1.

Fig. 8 Adsorption isotherm of As(V) by Fe_2O_3 (a) and Al_2O_3 (b) with different concentrations of phosphate. Initial As(V) concentration 200 μg/L; pH 6±0.1.

prevalent in strong basic conditions, HPO_4^{2-} ions more likely appear in weak basic conditions. $H_2PO_4^-$ ions and aqueous H_3PO_4 predominate in weak and strong acid conditions, respectively (Wikipedia, 2005).

Fig.8 shows that the increase of phosphate concentration can sharply decrease the As(V) adsorption capacity of Fe_2O_3 and Al_2O_3 even though the trend in low phosphate concentration range is not obvious. The adsorption of As(V) with Al_2O_3 is affected by phosphate to a higher degree than with Fe_2O_3. To achieve the same As(V) adsorption with Al_2O_3 as with Fe_2O_3, higher dosages of Al_2O_3 are required. These results are consistent with several researchers' findings (Meng *et al*., 2002; Manning and Goldberg, 1996b; Xu *et al*., 2002). For example, Meng *et al*. (2002) reported that the addition of phosphate (HPO_4^{2-}) to water solutions significantly affect the removal of As(V) on iron hydroxides in a over 0.25 mg/L concentration range.

Fig.9 shows that phosphate anions compete with arsenate ions and adsorb onto Fe_2O_3 and Al_2O_3 in the water. The remaining concentration of phosphate after adsorption decreased significantly with the increase of dosages of Fe_2O_3 and moderately with increase of dosages of Al_2O_3. At initial concentration of 500 μg/L phosphate, 1 g/L of Fe_2O_3 can remove 78% of phosphate, while same dosage of Al_2O_3 adsorbs only 25% of the phosphate anion. This result seems reasonable considering the fact that it is consistent with other researchers' results (Nooney *et al*.,
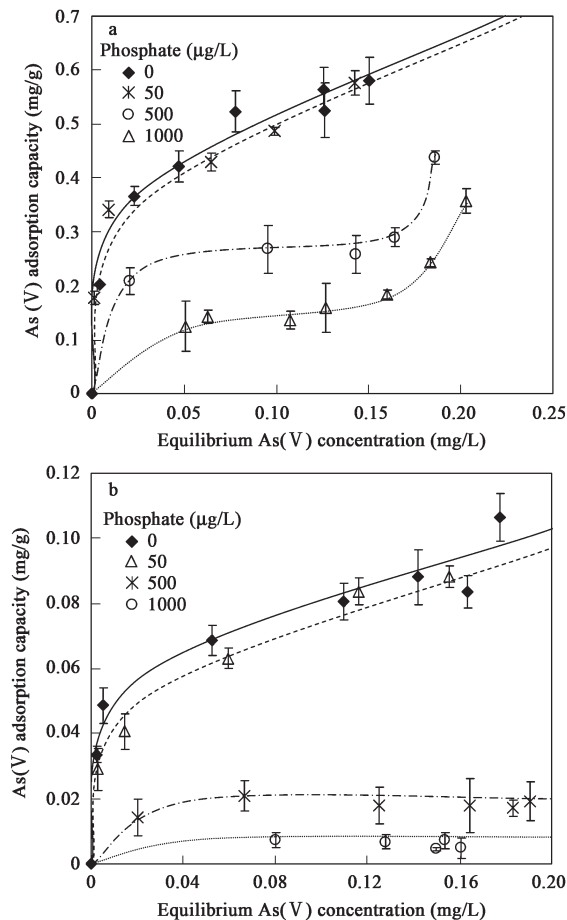
1996). Madrid *et al*. (1974) indicated that phosphate ions can easily adsorb onto three kinds of iron oxides (goethite, lipidocrocite, and hematite) at pH 3.2 to 9.6 and they found that the reactions fit well to both Langmuir and Freundlich isotherms. Nooney *et al*. (1996) also found that phosphate uptake was rapid on a thin Fe_2O_3 film of adsorbent in 10 min of exposure time. Javid *et al*. (2004) reported that gibbsite (γ-Al_2O_3) was an effective anion exchange material for phosphate anions at a low pH and that phosphate uptake on γ-Al_2O_3 results from electrostatic interactions (ion exchange) rather than nonelectrostatic adsorption.

Phosphate is very adsorptive on the surfaces of iron and aluminum oxides and has significant effects on the adsorption of arsenic even in low concentration range because of the structural resemblances between arsenic and phosphate ions (Pierce, 1981; Wasay *et al*., 1996; El Khatib and Balba, 2004). In other words, phosphate can compete with arsenate for binding sites on Fe_2O_3 and Al_2O_3 due to the similarity of their structure. But the complexes of As(V) with Fe_2O_3 and Al_2O_3 should be stronger than those of phosphate according to the findings of Meng *et al*. (2002), which suggest that the constant of binding affinity value of As(V) is seven times greater than that of phosphate on iron hydroxides.
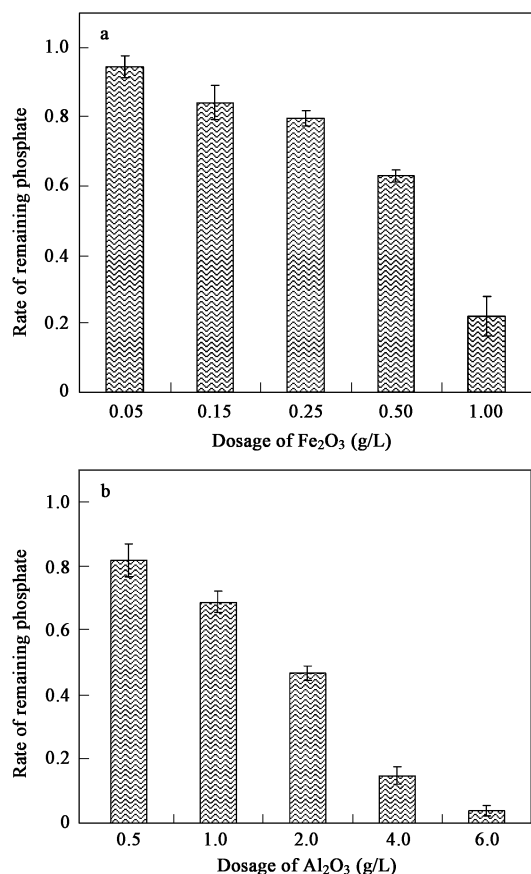
Fig. 9 Comparison of remaining phosphate concentrations after As(V) adsorption with various dosages of Fe_2O_3 (a) and Al_2O_3 (b). Initial phosphate concentration 500 μg/L; pH 6±0.1.

2.6 Silica

The average silica concentration in surface and groundwater is about 14 mg/L (APHA, 1999), therefore, understanding the effect of silica on As(V) adsorption using Fe_2O_3 and Al_2O_3 is important. The changes of As(V) adsorption capacities of Fe_2O_3 and Al_2O_3 with the concentration of silica are shown in Fig.10. The As(V) adsorption isotherms of Fe_2O_3 and Al_2O_3 show significant decreasing trends when silica concentrations increase. The adsorption of As(V) on Fe_2O_3 at the concentration of 1 mg/L silica increases slightly while that on Al_2O_3 increases are relatively large. We assume that silica with a low concentration may have an enhancing effect on the adsorption of As(V) because of favorable electrostatic effects at the surface of Fe_2O_3 and Al_2O_3 (Wilkie and Hering, 1996). The adsorption of As(V) decreased significantly when silica concentrations increased from 5 to 10 mg/L. The silica solute has higher adverse effects on Al_2O_3 than on Fe_2O_3. These results match those observed by others. Meng et al. (2000) reported that with 10 mg/L silicate the removal of As(V) with ferric chloride dropped approximately by 45%, and the As(V) adsorption capacity reduced from 0.96 to 0.27 mg/g Fe. In addition, they suggested that the As(V) adsorption reduction resulted from the strong association of silicate with ferric hydroxide, which reduced the surface sites available for As(V) and increased electrostatic repulsion between As(V) and the negatively charged surface
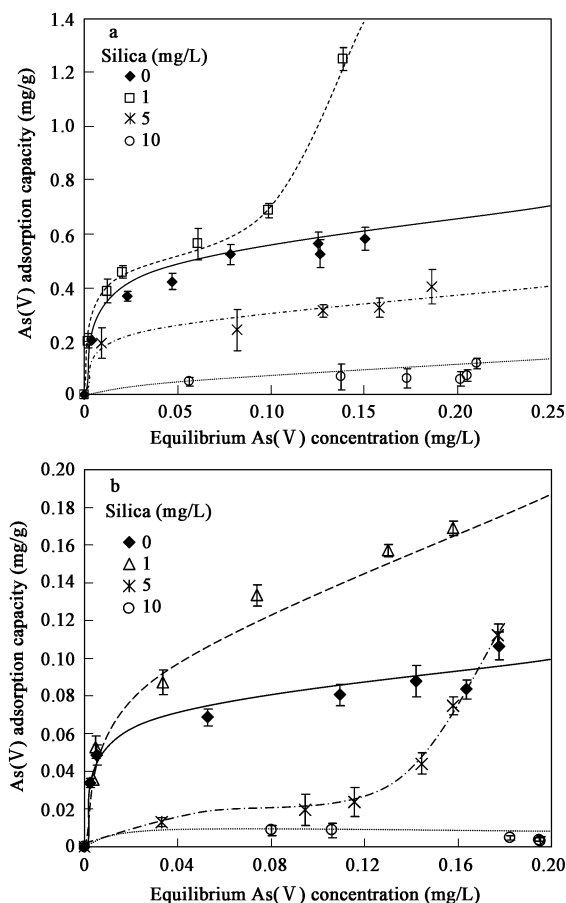

Fig. 10 Adsorption isotherm of As(V) by Fe_2O_3 (a) and Al_2O_3 (b) with different concentrations of silica. Initial As(V) concentration 200 μg/L; pH 6±0.1.

sites. Meng et al. (2002) also showed that the adsorption of As(V) on iron hydroxides did not change considerably when the SiO_2 concentrations are lower than 1.4 mg/L because the binding constant of silicate was 800 times lower than that of As(V), but it was obviously affected from 99% to 85% when silica concentrations are higher than 1.5 mg/L. Singh et al. (2005) found that the dissolved silicate competes with As(V) in the ferrihydrite-based As(V) coprecipitation and adsorption removal processes, and they proposed that the effect of silicate is to cause a combination of complexation reactions between Fe(III), Si(IV), and As(V) species, and competition between As(V) and Si(IV) for adsorption sites on ferrihydrite.

2.7 Comparison of As(V) adsorption parameters of Fe_2O_3 and Al_2O_3 with the existence of various competing solutes

Table 1 shows the As(V) adsorption parameters of the Langmuir isotherm of Fe_2O_3 and Al_2O_3 within the environment of the studied competing solutes including sulfate, Se(IV), V(V), phosphate, and silica. Under the given test conditions lists in Table 1, the maximum As(V) adsorption capacity (q_{max}) and regression coefficient (R^2) of Langmuir isotherm plot in the absence of competing solutes were observed to be 0.616 mg/g and 0.93 when Fe_2O_3 was used, and 0.098 mg/g and 0.94 when Al_2O_3 was used. In

Table 1 Langmuir adsorption isotherm parameters of As(V) on Fe_2O_3 and Al_2O_3 in the presence of competing solutes

Adsorbents	200 μg/L of As(V) competing solutes	As(V) adsorption parameter		
		*b (L/mg)	*q_{max} (mg/g)	*R^2
Fe_2O_3	No solutes	60.53	0.616	0.93
	Sulfate 250 mg/L	81.33	0.572	0.96
	Selenium(IV) 50 μg/L	32.84	0.503	0.95
	Vanadium(V) 50 μg/L	91.49	0.521	0.96
	Phosphate 500 μg/L	82.56	0.327	0.59
	Silica 5 mg/L	145.58	0.327	0.74
Al_2O_3	No solutes	44.56	0.098	0.94
	Sulfate 250 mg/L	50.31	0.087	0.96
	Selenium(IV) 50 μg/L	7.06	0.076	0.87
	Vanadium(V) 50 μg/L	55.19	0.098	0.89
	Phosphate 500 μg/L	154.98	0.019	0.61
	Silica 5 mg/L	11.86	0.045	0.82

Conditions: initial As(V) concentration 200 μg/L, pH 6±0.1. *b and q_{max} are the two parameters in Langmuir adsorption isothermal equation shown as: $\frac{1}{q_e} = \frac{1}{q_{max}bC_e} + \frac{1}{q_{max}}$, where b is a constant, q_{max} represents the maximum adsorption capacity of the adsorbent; R^2 is the regression coefficient of $1/q_e - 1/C_e$ plot.

the presence of phosphate at 500 μg/L concentration, the adsorption capacity (q_{max}) and the regression coefficient (R^2) of Langmuir isotherm plot were reduced to 0.327 mg/g and 0.59 when Fe_2O_3 was used, and 0.019 mg/g and 0.61 when Al_2O_3 was used. Addition of 5 mg/L silica to arsenic solution reduced the values of q_{max} and R^2, respectively, to 0.327 mg/g and 0.74 when Fe_2O_3 was used, and respectively, to 0.045 mg/g and 0.82 when Al_2O_3 was used. Considering the adsorption bond strength, b, selenite ion bonds on Fe_2O_3 and Al_2O_3 were much weaker than those of the other competing solutes. Silica ion bonds are stronger than the others on Fe_2O_3, while phosphate ion bonds are much stronger than the others on Al_2O_3. These results show that effects of competing solutes including phosphate and silica on adsorption of arsenic with Fe_2O_3 are less significant than with Al_2O_3.

Therefore, based on the lower concentration level of phosphate compared with other competing solutes, and the values of the adsorption capacity and regression coefficient (R^2) of Langmuir isotherm plots discussed above, phosphate anions are found to be the most prominent solute competing against As(V) for adsorption on Fe_2O_3 and Al_2O_3. With the values of adsorption capacity and dosages considered, Fe_2O_3 is found to be a better adsorbent than Al_2O_3 for removing As(V) in the presence of competing solutes in water.

3 Conclusions

Different competing solutes have different effects on the adsorption of As(V) with Fe_2O_3 and Al_2O_3. Chloride and nitrate anions do not show notable effects on the adsorption of As(V) with Fe_2O_3 and Al_2O_3. Sulfate anions have moderate adverse effects on the adsorption of As(V) with Al_2O_3 while they do not have considerable effects on the adsorption of As(V) with Fe_2O_3. The stronger complexes formed between Se(IV) and V(V) with Fe_2O_3 than with Al_2O_3 make the adsorption of As(V) with Fe_2O_3 more significantly affected than with Al_2O_3. The most significant interference with the removal of As(V) by Fe_2O_3 and Al_2O_3 occurs in the presence of phosphate and silica solutes. Generally speaking, Fe_2O_3 has a better performance than Al_2O_3 in adsorbing As(V) when the studied competing ions exist in As(V) solutions although both materials can reduce the level of As(V) in water to the level lower than that required by WHO and USEPA.

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