Arsenic Adsorption from Aqueous Solutions on an Fe(III)-Si Binary Oxide Adsorbent

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This study investigated arsenate and arsenite adsorption on an iron(III) oxide/silica adsorbent that had a Fe/Si molar ratio of 3. Batch experiments were conducted with regard to adsorption kinetics, isotherms, pH effects and interference of phosphate and sulfate on arsenic adsorption. The adsorption of arsenite was faster than that of arsenate. The adsorption kinetics could be well described by the power function equation for both arsenate and arsenite. The arsenate and arsenite adsorption isotherm data were satisfactorily fitted by the Redlich-Peterson, Freundlich-Langmuir and Langmuir models. The equilibrium adsorption capacity for As(III) was larger than that for As(V). This capacity for both As(III) and As(V) increased with temperature, from 11.3 to 14.9 (mg As/g) for As(V) and from 21.1 to 21.5 (mg As/g) for As(III) when the temperature was increased from 20 to 35ºC. The arsenate adsorption was significantly reduced at pH above 7.5, while the arsenite adsorption was almost independent of pH in the range of 3 to 9. The calculated thermodynamic parameters including ΔG^o, ΔH^o and ΔS^o reflected the spontaneous nature of As(V) and As(III) adsorption on this binary oxide adsorbent. The opposite values of ΔH^o indicated that the adsorption of As(V) was exothermic, whereas that of As(III) was endothermic. It was found that the interference of phosphate at pH 7.4 was more significant for arsenate adsorption than for arsenite adsorption. In contrast, sulfate had insignificant interference on arsenic adsorption at the tested sulfate concentration up to 460 mg/L and pH 7.4.

Key words: arsenic adsorption, equilibrium, kinetics, isotherm, hydrous ferric oxide, silica

Introduction

Arsenic is one of the most toxic elements occurring naturally in the environment. In natural water, arsenic is primarily present in inorganic forms and the dominant arsenic species is a function of pH and the redox potential of water. Arsenate—As(V)—is the major arsenic species in surface water and normally exists in four forms in aqueous solutions: H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} over the pH range of 5 to 12. Arsenite—As(III)—is favoured under reducing conditions, and thus is the dominant arsenic in groundwater. As(III) is present mainly as H_3AsO_3 over the pH range of 2 to 9. As(III) is more toxic than As(V) (Ferguson and Davis 1972; Cullen and Reimer 1989; Korte and Fernando 1991).

Arsenic can be removed by adsorption on some metal oxides. Iron(III) oxides are the ones broadly investigated, presumably due to their abundant existence in the natural aquatic system and their larger adsorptive capacity of arsenic. There have been several studies of arsenic adsorption capacities, kinetics and isotherms using single iron(III) oxide in the forms of in situ prepared suspensions and iron oxide-coated sand, mostly amorphous hydrous ferric oxide (FeOOH) or poorly crystalline hydrous ferric oxide (ferrihydrite) (Pierce and Moore 1982; Hsia et al. 1994; Wilkie and Hering 1996; Driehaus et al. 1998; Fuller et al. 1993; Raven et al. 1998; Jain and Loeppert

2000), goethite (α-FeOOH) (Sun and Doner 1998), other crystalline hydrous ferric oxide (Manna et al. 2003) and iron oxide-coated sand (Thirunavukkarasu et al. 2003; Joshi and Chaudhuri 1996). However, most iron(III) oxides are available only as fine powders or are generated in situ as gels or suspensions in an aqueous solution. These forms of iron(III) oxides retain their strong affinities to As(V) and As(III), but are limited to reactor configurations incorporating large sedimentation and filtration units, which cause difficulty in solid/liquid separation (Lo and Chen 1997). Furthermore, iron(III) oxide alone is not suitable as a filter medium due to its low hydraulic conductivity (Theis et al. 1992).

As reported in a prior study (Zeng 2003), a granulated silica-containing iron(III) oxide adsorbent was developed for removal of As(V) and As(III). This adsorbent contained binary oxides, amorphous iron(III) oxide (FeOOH) and silica (SiO_2), in which Fe(III)-Si complexes were possibly formed from simultaneously generated FeOOH sol and silica sol in situ. This granulated binary adsorbent had a capability to remove both As(V) and As(III) with proper physical strength to prevent from disintegrating in water. The adsorption properties of some iron(III) oxide/silica binary solids have been studied by different researchers (Anderson and Benjamin 1990; Meng and Letterman 1993). It was found that the properties of the binary oxides can be different from their component parts and that the adsorption of anions was affected more compared to that of cations. So far there

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has been little study of arsenic adsorption kinetics and equilibrium using an iron(III) oxide/silica binary adsorbent, despite the existence of many such investigations using a single iron(III) oxide. This study was to evaluate the adsorption kinetics, isotherms, pH effects, and thermodynamic parameters on arsenic adsorption using the iron(III) oxide/silica binary adsorbent. In addition, the interference of phosphate and sulfate on adsorption of As(V) and As(III) was examined. Therefore, this study would contribute to the understanding of arsenic adsorption on the iron(III) oxide/silica binary adsorbents.

Materials and Methods

Chemicals

Stock solutions of As(III) and As(V) were prepared in reverse osmosized (RO) and deionized (DI) water using sodium arsenite, $NaAsO_2$ (J.T. Baker, reagent grade) and $Na_2HAsO_4 \cdot 7H_2O$ (BDH, reagent grade), respectively. Arsenic working solutions were freshly prepared by diluting arsenic stock solutions with RO + DI water and standardized by an inductively coupled plasma mass spectrometer with the NIST arsenic standard solution. HNO_3 (0.1–0.5 N) and $NaOH$ (0.1–0.5 N) were used for adjusting the pH of the arsenic solution as necessary. The phosphate (PO_4^{3-}) stock solution (100 mg PO_4^{3-}/L) and the sulfate (SO_4^{2-}) stock solution (5000 mg SO_4^{2-}/L) were prepared separately from di-sodium hydrogen phosphate (Na_2HPO_4) (Fisher, certified A.C.S.) and sodium sulfate (Na_2SO_4) (Fisher, certified A.C.S.). Both solutions were used as the competing ions in some arsenic adsorption experiments.

Preparation of Binary Oxide Adsorbents

Sodium silicate solution (waterglass, Fisher) was premixed with NaOH solution in a stirred tank. The amounts of silicate and NaOH added were determined by the required Fe/Si ratio in the final adsorbents. The silicate/NaOH mixture provided both a source of silica for formation of silica sol and a source of alkali for formation of FeOOH sol. The iron(III) salt solution (1 M $FeCl_3$) was slowly mixed with the above mixture under vigorously stirred conditions to precipitate a gel-like $FeOOH/SiO_2$ suspension, in which Fe(III)-Si complexes were likely formed. The final pH of the formed Fe(III)-Si complex suspension was maintained between 6 and 8 to complete the precipitation reaction and provide a near-neutral pH of the adsorbents. After formation, the suspension was continuously stirred for 2 h, and aged overnight. Then, the suspension was washed and dewatered by filtration or centrifugation. The dewatered solids were granulated to the required size and shape by extrusion or other granulation methods, and finally dried at 120°C for 4 to 6 h. Details of the preparation method and the characteriza-

tion of the adsorbent can be found elsewhere (Zeng 2003). The binary oxide adsorbent used in this study had a Fe/Si molar ratio of 3 (approximately 81.6% FeOOH and 18.4% SiO_2 by weight), which was the optimum Fe/Si molar ratio in the balance of adsorbent strength and arsenic adsorption capacity. This adsorbent also had a specific surface area of 186.1 m^2/g. XRD analysis confirmed that the iron(III) oxide in the adsorbent was in the amorphous form. Before experiments, the adsorbent was ground and sieved through 170 mesh.

Batch Adsorption Procedure

To determine the amount of adsorbed arsenic under the given conditions, approximately 100 mg of adsorbent was weighed and placed in a 250-mL Erlenmeyer flask. One hundred millilitres of arsenic solution (arsenite or arsenate) was added into the flask. The concentration of the arsenic solution ranged from 0.4 to 20 mg/L depending on the type of experiment. Ionic strength was not adjusted during adsorption. The flask was capped and shaken at 180 rpm on an orbital shaker for 24 h to ensure approximate equilibrium. All batch experiments were conducted at room temperature (20–21°C) unless stated otherwise. The pH was manually maintained at a designated value ±0.1 in such a way: pH was initially adjusted to a defined value with 0.01 to 0.05 N HNO_3 and NaOH and then measured and adjusted at an interval of every 1 to 2 h. After 24 h of the reaction period, all samples were filtered through a 0.45-μm membrane filter and the filtrate was analyzed for arsenic. Some samples were also analyzed for dissolved Fe. Blank tests under the same conditions demonstrated no arsenic adsorbed on the wall of the flask during the reaction period. This procedure was used in all adsorption experiments for evaluating isotherms, pH effects, and interferences of competing anions, except for kinetic experiments. The quantity of adsorbed arsenic was calculated by the difference of the initial and residual amounts of arsenic in the solution divided by the weight of the adsorbent. Duplicate experiments demonstrated that results obtained from this adsorption procedure were repeatable and that the experimental error could be controlled within 3%.

Adsorption Kinetics Studies

Arsenic adsorption kinetics was evaluated at 20°C and pH 7.3. The initial As (arsenite or arsenate) solution concentrations of 50 mg As/L (corresponding to 50 mg As/g adsorbent or 61.3 mg As/g FeOOH). The kinetic experiments were conducted in a 1000-mL two-neck distilling flask. The flask was magnetically stirred and partially immersed in water in a plastic tray that was connected to a circulating water bath. With this experimental setup the temperature of the solution inside the flask was well maintained at 20 ± 0.5°C. A combination pH electrode

was inserted into the flask for pH on-line measurement. Two burettes filled separately with 0.1 N HNO_3 and 0.1 N NaOH were set on top of the flask for pH adjustment. Before the start of each kinetic run, 450 mL of RO + DI water and 500 mg of the adsorbent were added to the flask, stirred for 1 h, and pre-adjusted to pH 7.3. Then 50 mL of As stock solution containing 500 mg As/L was added to the flask while pH was maintained at around 7.3. The reaction solution (5–10 mL) was sampled with an air displacement pipettor at different times up to 180 min. The sampled solution was immediately filtered through a 0.45-µm membrane filter, and the filtrate was analyzed for As.

Studies of Adsorption Isotherm and pH Effect

Experiments for studying arsenic adsorption isotherm were conducted at 20°C and pH 6.5 and 9.6 by following the batch adsorption procedure. A series of different initial concentrations of As(V) or As(III) solutions (0–23 mg/L) at pH 6.5 and 9.6 were used. For estimating the thermodynamic parameters of arsenic adsorption, the isotherm experiments were also conducted at 35°C. With a similar procedure, the effects of pH on arsenic adsorption were examined in a series of batch adsorption experiments that used the same initial As concentration (2 mg/L) while maintaining pH at different values between 3 and 10.

Arsenic Adsorption with Competing Anions

The interference of phosphate and sulfate on arsenic adsorption was evaluated in batch experiments, respectively. The experimental method was similar to the batch adsorption method described previously. The difference was that the arsenic working solutions for these competing adsorption experiments were prepared with the separate addition of phosphate and sulfate solutions into the arsenic solution. The initial addition of arsenic was 2 mg/g adsorbent using an arsenic solution in 2 mg As/L and the pH was maintained at approximately 7.4. The concentrations of the competing anions used in the experiments were from 0 to 10 mg/L for phosphate and from 0 to 460 mg/L for sulfate.

Analytical Methods

Arsenic analysis was conducted using a SCIEX Perkin Elmer Elan model 5000 inductively coupled plasma mass spectrometer (ICP-MS). Prior to arsenic analysis, all samples were acidified with concentrated nitric acid (HNO_3) in an amount of 1%, and stored in acid-washed high-density polyethylene containers. The arsenic analyses were conducted within 3 days of the sample collection. The dissolved Fe concentrations in the samples were also analyzed with ICP-MS. Phosphate and sulfate

in solution were determined by ion chromatography with a conductivity detector.

Statistical Analyses

The kinetic and isotherm data were fitted with different models by non-linear regression using the method of least squares. The curve fitting and statistical analyses were performed using SigmaPlot software (SPSS Inc. 2001). The correlation coefficient (R^2) and standard error of estimate (SE) obtained from regression were used for comparing the model applicability.

Results and Discussion

Adsorption Kinetics

The results of the adsorption kinetic experiments for As(V) and As(III) are illustrated in Fig. 1. It was found that the initial adsorption of arsenic was rapid for both As(V) and As(III). However, arsenite adsorption was generally faster than arsenate adsorption in terms of the amount of adsorbed As in a fixed time. Under the present experimental conditions with an initial arsenic loading of 50 mg As/g adsorbent, the percentage adsorption for As(III) was 45.1% while that for As(V) was 27.6% after 3 h of reaction. This is in agreement with the study using ferrihydrite (Raven et al. 1998), where arsenite adsorption was considerably faster than that of arsenate at a higher initial concentration (1000 mg As/g ferrihydrite), although arsenate adsorption was slightly faster than that of arsenite at a lower initial concentration (20 mg As/g ferrihydrite). The slow adsorption kinetics of arsenate on ferrihydrite after an initial rapid adsorption for 5 min was also reported by Fuller et al. (1993). The present kinetic results showed that this binary oxide adsorbent required less contact time for As(III) removal than that for As(V) removal. A similar
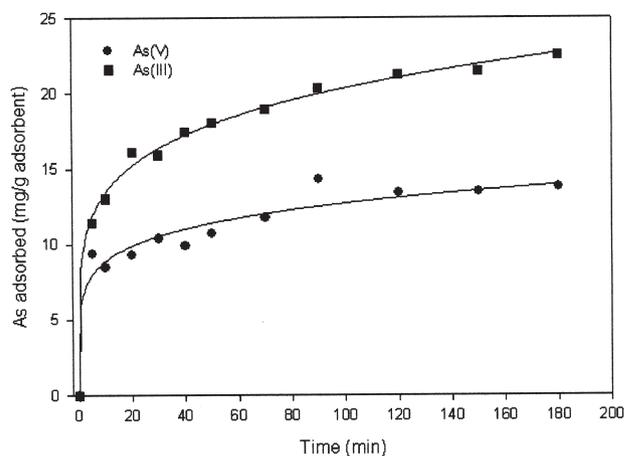
Fig. 1. Kinetics of arsenate and arsenite adsorption with an initial addition of 50 mg As/g adsorbent at 20 ± 0.5°C and pH 7.3 ± 0.1. The fitting curves in this figure were produced by the regressed power function equations.

inference was also drawn by Manna et al. (2003) using crystalline hydrous ferric oxide. These similarities of adsorption kinetics between this binary oxide adsorbent and other single iron(III) oxides are most likely attributed to the fact that the active component in the present binary oxide adsorbent is amorphous hydrous ferric oxide and SiO_2 is virtually inert for arsenic adsorption (Zeng 2003).

Several adsorption kinetic models (power function, simple Elovich, parabolic diffusion [Sparks 1989] and pseudo second-order [Ho 2003] equations) were used to fit the kinetic data by non-linear regression with SigmaPlot software (SPSS Inc. 2001). These model equations and estimated parameters with R^2 and SE are shown in Table 1. Based on R^2 and SE, the kinetics of arsenic adsorption on this Fe(III)-Si binary oxide adsorbent can be best described by the power function equation. Moreover, the kinetic data of As(III) adsorption could also be well fitted by the simple Elovich and pseudo second-order equation with a R^2 value >0.95.

Adsorption Isotherms

The results of isotherm experiments at 20°C are shown in Fig. 2. At pH 6.5, As(V) was adsorbed in larger amounts than As(III) at an As equilibrium concentration approximately smaller than 1.6 mg/L. Above this concentration, As(III) was adsorbed more than As(V). At pH 9.6, As(III) was adsorbed in much larger amounts than As(V). The adsorption of As(V) at pH 9.6 was nearly negligible compared to that at pH 6.5. In contrast, the adsorption of As(III) at pH 6.5 and 9.6 had no significant difference at an As equilibrium concentration approximately up to 0.7 mg/L. Over this concentration, As(III) was adsorbed slightly more at pH 6.5 than at pH 9.6. At an initial loading of 15 mg As/g adsorbent, the adsorption maxima expressed in mg As/g adsorbent was

12.3 for As(V) at pH 6.5, and 12.8 and 12.5 for As(III) at pH 6.5 and 9.6, respectively.

Five isotherms, as described below in equations 1 to 5 (Cooney 1998), were used for fitting the experimental data.

Freundlich equation:	$q = KC^{1/n}$	(1)
Langmuir equation:	$q = bq_mC/(1 + bC)$	(2)
Temkin equation:	$q = A + BlnC$	(3)
Redlich-Peterson equation:	$q = aC/(1 + bC^n)$	(4)
Langmuir-Freundlich equation:	$q = bq_mC^{1/n}/(1 + bC^{1/n})$	(5)

where q is the amount of adsorbed As at equilibrium (mg/g), and C is the As equilibrium concentration in solution (mg/L). The other parameters are different isotherm constants, which can be determined by regression of the experimental data. In practice, the two-parameter equations (Freundlich, Langmuir and Temkin) are more widely used than the three-parameter equations (Redlich-Peterson and Langmuir-Freundlich) due to the inconvenience of evaluating three isotherm parameters. However, a three-parameter equation can often provide a better fit of the isotherm data than a two-parameter one.

The isotherm data from Fig. 2 were fitted to the above five models by non-linear regression with SigmaPlot software (SPSS Inc. 2001). The estimated model parameters with the correlation coefficient (R^2) and the standard error of estimate (SE) for the different models are shown in Table 2. All the model equations were found to be statistically significant at the 95% confidence level. It was found that the three-parameter models (equations 4 and 5) provided better fitting for the isotherm data in terms of R^2 and SE values. The Langmuir equation fitted the data nearly as well as the three-parameter equations, and the Freundlich equation could

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TABLE 1. Estimated kinetic model parameters for arsenic adsorption[a]

	a	*b*	R^2	*SE*
Power function equation (q = a t[b])				
As(V)	6.1914	0.1564	0.952	0.88
As(III)	8.8012	0.1821	0.996	0.43
Simple Elovich equation[b] (q = a + b·lnt)				
As(V)	5.2259	1.6186	0.785	1.02
As(III)	6.1645	3.0907	0.986	0.44
Parabolic diffusion equation (q = at + bt$^{1/2}$)				
As(V)	-0.1184	2.5516	0.824	1.68
As(III)	-0.1835	4.0068	0.929	1.72
Pseudo second-order equation [q = t/(a + bt)]				
As(V)	0.3181	0.0772	0.873	1.43
As(III)	0.2954	0.0465	0.965	1.21

[a]q; adsorbed As (mg/g) at time t (min). The initial As addition was 50 mg As/g adsorbent and pH was maintained at 7.3.
[b]The simple Elovich parameters were estimated without using the origin (q = 0, t = 0).
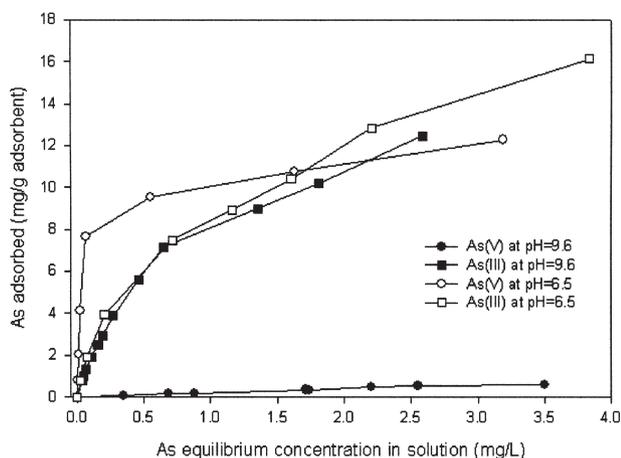
Fig. 2. Adsorption isotherms for arsenate and arsenite at 20°C and pH 6.5 and 9.6.

well fit all adsorption data except for As(V) at pH 6.5. Generally, the applicability of the two-parameter isotherm models for the present data approximately follows the order: Langmuir > Freundlich > Temkin.

In both the Langmuir and Langmuir-Freundlich equations, q_m is the measure of the maximum adsorption capacity. The q_m values for As(V) and As(III) obtained from these two equations were reasonably close except for As(III) at pH 6.5 and 20°C, where q_m was 21.1 (mg/g) from the Langmuir equation but 62.7 (mg/g) from the Langmuir-Freundlich equation. The same exception for As(III) at pH 6.5 and 35°C occurred, where q_m was 21.5 (mg/g) from the Langmuir equation but 74.6 (mg/g) from the Langmuir-Freundlich equation. This exception implies that the Langmuir-Freundlich equation may not be suitable for regression of As(III) adsorption isotherm data from the present adsorbent at a high pH.

Although the fits of the isotherm models are more mathematically meaningful and do not provide any evidence for the actual adsorption mechanisms, the Langmuir constant can be used for calculating the dimensionless separation factor, which is indicative of the isotherm shape that predicts whether an adsorption system is 'favourable' or 'unfavourable.' This separation factor (r) is defined as (Weber and Chakravorti 1974):

$$r = 1/(1 + bC_o) \qquad (6)$$

where b is the Langmuir constant and C_o is the initial solute concentration. With the Langmuir constant in Table 2 and the initial As concentrations of 0.8 to

TABLE 2. Estimated isotherm parameters for arsenic adsorption

	As(V) adsorption		As(III) adsorption	
	pH 6.5	*pH 9.6*	*pH 6.5*	*pH 9.6*
$(q = KC^{1/n})$				
K	9.905	0.209	8.380	7.624
1/n	0.225	0.909	0.498	0.538
R^2	0.928	0.977	0.997	0.986
SE	1.380	0.035	0.346	0.499
$q = q_mbC/(1 + bC)$				
q_m (mg/g)	11.30	3.335	21.14	15.39
b (L/mg)	27.84	0.068	0.713	1.245
R^2	0.982	0.981	0.983	0.993
SE	0.684	0.032	0.781	0.350
$q = A + B \ln C$[a]				
A	10.47	0.254	9.801	8.385
B	1.594	0.248	2.866	2.691
R^2	0.969	0.919	0.921	0.954
SE	0.858	0.061	1.626	0.892
$q = aC/(1 + bC^n)$				
a	408.5	0.206	16.77	25.61
b	37.18	1.934×10^{-8}	7.855	2.124
n	0.935	12.832	0.576	0.784
R^2	0.989	0.993	0.998	0.996
SE	0.606	0.021	0.274	0.287
$q = q_mbC^{1/n}/(1 + bC^{1/n})$				
q_m (mg/g)	11.45	1.054	62.66	18.96
b $(L/mg)^{1/n}$	20.09	0.231	0.158	0.775
1/n	0.910	1.479	0.586	0.843
R^2	0.983	0.988	0.998	0.995
SE	0.743	0.028	0.308	0.318

[a] The Temkin parameters were estimated without using the origin (q = 0, C = 0).

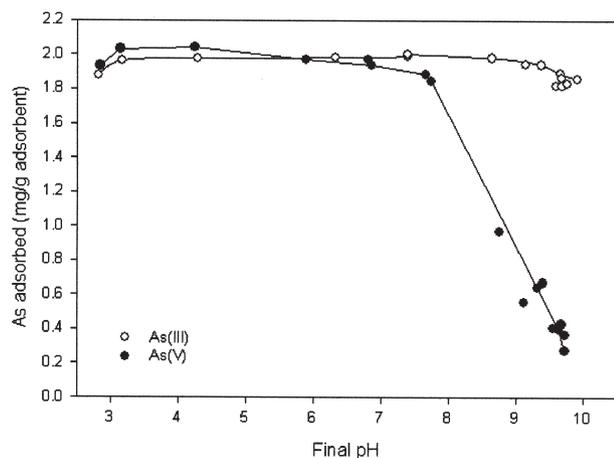20 mg/L, r can be calculated as 0.043 to 0.0018 for As(V) at pH 6.5, 0.95 to 0.42 for As(V) at pH 9.6, 0.64 to 0.066 for As(III) at pH 6.5, and 0.5 to 0.039 for As(III) at pH 9.6. When using the Langmuir-Freundlich equation constants as shown in equation 5, the expression for r can be modified as:

$$r = 1/(1 + bC_o^{1/n}) \qquad (7)$$

where b and 1/n are the Langmuir-Freundlich constants, and C_o is the initial solute concentration. Based on the Langmuir-Freundlich constants in Table 2 and the same As initial concentrations, r can be calculated as 0.058 to 0.0032 for As(V) at pH 6.5, 0.86 to 0.049 for As(V) at pH 9.6, 0.88 to 0.52 for As(III) at pH 6.5, and 0.61 to 0.094 for As(III) at pH 9.6. In either case, the r values for the present experimental data fall between 0 and 1, which is indicative of favourable adsorption of As on the present Fe(III)-Si binary oxide adsorbent. The r values showed that adsorption was more favourable for the higher initial As concentration than for the lower one.
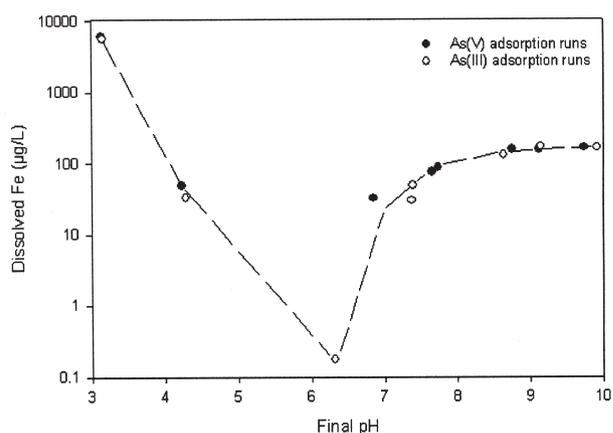
Effect of pH

The pH influence on the arsenic adsorption on this binary oxide adsorbent is shown in Fig. 3. Generally, the percentage arsenic adsorption was greater than 98% throughout the pH range of 3 to 9 for As(III) and 3 to 7 for As(V) with an initial addition of approximately 2 mg As/g adsorbent. Below pH 5.7, As(V) was adsorbed in slightly larger quantities than As(III), whereas As(III) adsorption was significantly greater than As(V) adsorption at pH above 5.7. The As(III) adsorption was clearly less dependent on the pH in the range of 3 to 9, and reached broad maxima from approximately pH 6.5 to 8.6. In contrast, As(V) adsorption decreased with increasing pH, with the maximum adsorption occurring approximately at pH 3.1 to 5. At pH around 3, both As(V) and As(III) adsorptions showed an obvious reduc-

tion, which was likely due to the release of adsorbed arsenic because of the increased solubility of FeOOH at this low pH. The dissolution of FeOOH from the currently used FeOOH/SiO$_2$ binary adsorbent was measured during arsenic adsorption at different pH levels in this study (Fig. 4). It shows that the dissolved Fe was as high as 6000 µg/L at pH about 3, and it dropped to the lowest level of less than 1 µg/L at pH 6.0 to 6.5 and then increased to a level of 100 to 200 µg/L with a further increase of pH.

The observations of the pH effect on the arsenic adsorption using the present Fe(III)-Si binary oxide adsorbent were generally similar to most of those obtained by using the single iron(III) oxides, including ferrihydrite for As(V) and As(III) (Raven et al. 1998; Jain and Loeppert 2000) and hydrous ferric oxide for As(V) (Pierce and Moore 1982; Hsia et al. 1994; Wilkie and Hering 1996). The likely reason is the same as mentioned earlier, that the active component in this binary oxide adsorbent for arsenic adsorption is still an iron(III) oxide. Therefore, the explanations of how pH affects arsenic adsorption on iron(III) oxides can be applied to this binary oxide adsorbent. As reported by Revan et al. (1998), the lower adsorption of As(V) at high pH values was attributable to an increased repulsion between the more negatively charged arsenate species and negatively charged surface sites of iron(III) oxide. Alternatively, this decrease in adsorption of anionic arsenic species like As(V) on FeOOH could be attributed to an increase in competing OH⁻ for adsorption sites with increasing pH (Manna et al. 2003). In contrast, the adsorption of neutral H$_3$AsO$_3$, which is the dominant As(III) species at a wide pH range of 2 to 9, would be less strongly influenced by the anion repulsion forces that would likely play an important role in the adsorption of As(V) species at high pH. In addition, the differing influence of pH on arsenic adsorption on several different mixed oxides was also reported in the

Fig. 3. Effect of pH on arsenate and arsenite adsorption at 20°C with an initial addition of 2.06 mg As/g adsorbent.

Fig. 4. Dissolution of FeOOH from a Fe(III)-Si binary oxide adsorbent as a function of pH during arsenic adsorption at an initial addition of 2.06 mg As/g adsorbent.

literature (Manning and Goldberg 1997; Singh et al. 1988; Yohida et al. 1976). Manning and Goldberg (1997) reported that the maximum adsorption of As(III) on kaolinite, illite and montmorillonite occurred in the pH range of 7.5 to 9.5. Singh et al. (1988) observed the maximum adsorption of As(III) on a hematite ore at pH 7. Yoshida et al. (1976) studied the arsenic adsorption on ferric hydroxide impregnated silica gel particles at pH between 3.4 and 9.8, and observed a maximum adsorption at pH 6 for both As(V) and As(III).

Temperature Effect and Thermodynamic Parameters

The results of arsenic equilibrium adsorption at 20 and 35°C and pH 6.5 are shown in Fig. 5, which were satisfactorily fitted to the Langmuir isotherm model. The adsorption capacities for both As(V) and As(III) were higher at an elevated temperature. However, this increase was more significant for As(V) than for As(III). The arsenic equilibrium adsorption capacity (mg As/g adsorbent) obtained from the Langmuir equation increased from 11.3 to 14.9 for As(V) and from 21.1 to 21.5 for As(III) when temperature was increased from 20 to 35°C. The different extents to which arsenic adsorption capacity increased with temperature might be attributed to the change in surface properties of the adsorbent, solubility of the adsorbate species and endothermic or exothermic nature of the adsorption.

The Langmuir constants can be used for estimation of several process thermodynamic parameters based on the following equations (Gupta 1998):

$$\Delta G° = -RT \ln b \tag{8}$$

$$\ln\left(\frac{b_1}{b_2}\right) = -\frac{\Delta H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{9}$$
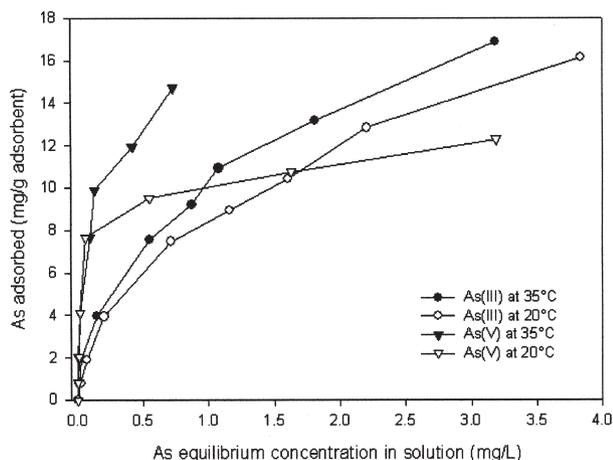
Fig. 5. Adsorption isotherms for arsenate and arsenite at 20 and 35°C and pH 6.5.

$$\Delta G° = \Delta H° - T\Delta S° \tag{10}$$

where b is a Langmuir isotherm constant (L/mol) at temperature T (K), R is an ideal gas constant (8.314 J/mol·K), $\Delta G°$ (J/mol), $\Delta H°$ (J/mol) and $\Delta S°$ (J/mol·K) are the Gibb's free energy, enthalpy and entropy changes, respectively.

The regressed Langmuir constants (with $R^2 \geq 0.98$) and calculated thermodynamic parameters are given in Table 3. The negative $\Delta G°$ values for both As(V) and As(III) confirm the spontaneous nature of the arsenic adsorption process. With the increase of temperature, $\Delta G°$ showed a slight decrease for As(V) and As(III). This indicates that better adsorption was obtained at higher temperature, which is in agreement with the result that the maximum adsorption capacity q_m increased with temperature for As(V) and As(III). The $\Delta H°$ value was negative for As(V) and positive for As(III), respectively, indicating the exothermic nature of As(V) adsorption and the endothermic nature of As(III) adsorption. These opposite thermal natures were also found for As(V) and As(III) adsorption on some mixed oxides such as red mud (Altundoğan et al. 2002), where the adsorption of As(V) was endothermic and the adsorption of As(III) was exothermic. The positive $\Delta S°$ values reflect the affinity of the adsorbent material for As(V) and As(III) and suggest some structural changes in the arsenic species and the adsorbent (Gupta 1998). Furthermore, the positive value of $\Delta S°$ show the increasing randomness at the solid/liquid interface during arsenic adsorption on the adsorbent. However, the exothermic nature of As(V) adsorption indicated by the negative $\Delta H°$ value does not support the result that As(V) adsorption increased with temperature. The temperature effect on the intrinsic kinetics of As(V) adsorption for the present adsorbent is likely to surpass the exothermic effect on the adsorption reaction. The implication of the difference in the thermodynamic parameters between As(V) and As(III) is that the surface adsorption of anionic As(V) species might be different from that of neutral As(III) species on this binary oxide adsorbent.

Interference of Competing Anions

The results of the PO_4^{3-} interference on arsenic adsorption at pH 7.4 are given in Fig. 6. The adsorption of As(V) and As(III) only slightly decreased at the PO_4^{3-} concentration up to 0.91 mg/L. With a further increase in the PO_4^{3-} concentration, arsenic adsorption was greatly reduced. The arsenic removal decreased to 81% for As(V) and 94% for As(III) at the PO_4^{3-} concentration of 9.1 mg/L. These results indicate that the interference of phosphate on arsenic adsorption was more significant for As(V) than for As(III) at a higher PO_4^{3-} concentration. This should be attributed to a well-known fact that the behaviour of arsenate and phosphate in solution is in many aspects very

TABLE 3. Calculated Langmuir constants and thermodynamic parameters at pH 6.5

As species	T (°C)	b (L/µmol)	q_m (mg/g)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/mol·K)
As(V)	20	2.1030	11.29	-35.47	-31.57	0.0133
As(V)	35	1.1103	14.87	-35.67		0.0133
As(III)	20	0.053425	21.14	-26.53	15.54	0.1435
As(III)	35	0.072867	21.52	-28.69		0.1435

similar and they form similar types of surface-complexes (Hiemstra and van Riemsdijk 1999; Hington et al. 1971; Ryden et al. 1987). Jain and Loeppert (2000) confirmed the significant interference of phosphate on As(V) and As(III) adsorption on ferrihydrite. They reported that phosphate and arsenate adsorption followed similar trends with pH, while arsenite and phosphate followed opposite trends with greater phosphate adsorption at low pH and greater arsenite adsorption at high pH.

Similarly, the SO_4^{2-} interference on arsenic adsorption was evaluated. The arsenate and arsenite removal efficiencies showed very small changes and were all greater than 97.5% at the sulfate concentration ranging from 0 to 460 mg/L. The sulfate mass balance for these experiments confirmed that the SO_4^{2-} ion was barely adsorbed on the adsorbent. Although the reduction in arsenic removal efficiency was slightly larger for As(III) than for As(V), the interference of SO_4^{2-} was generally insignificant for arsenic adsorption at the present pH and sulfate concentrations. As reported in the literature (Wilkie and Hering 1996; Hering et al. 1997), significant competitive effects of sulfate were observed for arsenite adsorption on hydrous ferric oxide, and to a lesser extent with arsenate. Jian and Loeppert (2000) reported that the presence of sulfate did not influence arsenate adsorption but resulted in a considerable reduction in arsenite adsorption below pH 7, with the largest reduction at the lowest pH.
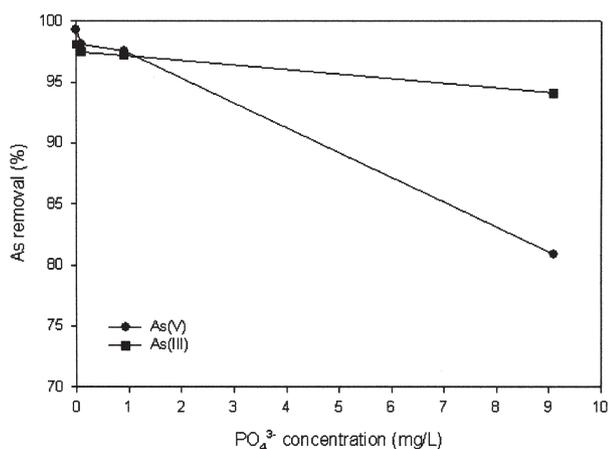

Fig. 6. Effect of phosphate on arsenic adsorption at 20°C and pH 7.4. The initial addition of arsenic was 2 mg/g adsorbent.

Conclusions

Arsenate and arsenite adsorption on an iron(III) oxide/silica binary adsorbent with a Fe/Si molar ratio of 3 was studied in batch experiments. With an initial arsenic loading equivalent to 50 mg/g adsorbent, the arsenite adsorption was faster than the arsenate adsorption, which implies that less contact time would be required for As(III) removal than for As(V) removal. The adsorption kinetics for both As(V) and As(III) at pH 7.3 could be well described by the power function equation.

The As(V) and As(III) adsorption isotherm data were satisfactorily fitted by the Redlich-Peterson, Freundlich-Langmuir and Langmuir isotherm models. The values of the dimensionless separation factor calculated from the Langmuir constants confirmed favourable adsorption of As on this Fe(III)-Si binary oxide adsorbent. The arsenic equilibrium adsorption capacity obtained from the Langmuir equation was larger for As(III) than for As(V). This adsorption capacity for both As(V) and As(III) increased with temperature, from 11.3 to 14.9 (mg As/g) for As(V) and from 21.1 to 21.5 (mg As/g) for As(III) when temperature was increased from 20 to 35°C.

The solution pH had different effects on adsorption of As(V) and As(III). The As(V) adsorption had a maximum adsorption at a pH of approximately 3.1 to 5 and was significantly reduced at a pH above 7.5, while the As(III) adsorption was almost independent of pH in the range of pH 3 to 9.

The thermodynamic parameters including $\Delta G°$, $\Delta H°$ and $\Delta S°$ obtained at pH 6.5 reflected the suitability of arsenic adsorption on this binary oxide adsorbent. $\Delta H°$ was negative for As(V) and positive for As(III), indicating the exothermic nature of As(V) adsorption and the endothermic nature of As(III) adsorption on this binary adsorbent, respectively.

The results of the competitive experiments showed that the adsorption of arsenate and arsenite was only slightly depressed at the PO_4^{3-} concentration up to 0.91 mg/L and pH 7.4. With further increase of the PO_4^{3-} concentration, the reduction of arsenic adsorption increased and was greater for As(V) than for As(III). In contrast, the interference of SO_4^{2-} on As(III) and As(V) adsorption was generally insignificant at the tested pH 7.4 and sulfate concentration of 0 to 460 mg/L. The arsenic adsorption behaviours of this binary oxide

adsorbent were basically similar to those of a single iron(III) oxide.

References

Anderson P, Benjamin MM. 1990. Surface and bulk characteristics of binary oxide suspensions. Environ. Sci. Tech. **24(5)**:692–698.

Altundoğan HS, Altundoğan S, Tümen F, Bildik M. 2002. Arsenic adsorption from aqueous solutions by activated red mud. Waste Manage. **22**:357–363.

Cooney DO. 1998. Adsorption design for wastewater treatment. Lewis Publishers, Boca Raton, Fla.

Cullen WR, Reimer KJ. 1989. Arsenic speciation in the environment. Chem. Rev. **89**:713–764.

Driehaus W, Jekel M, Hildebrandt U. 1998. Granular ferric hydroxide – a new adsorbent for the removal of arsenic from natural water. J. Water SRT–Aqua **47(1)**:30–35.

Ferguson JF, Davis J. 1972. A review of the arsenic cycle in natural waters. Water Res. **6**:1259–1274.

Fuller CC, Davis JA, Waychunas GA. 1993. Surface chemistry of ferrihydrite: Part 2. Kinetics of arsenate adsorption and coprecipitation. Geochimica et Cosmochimica Acta **57**:2217–2282.

Gupta VK. 1998. Equilibrium uptake, sorption dynamics, process development, and column operations for the removal of copper and nickel from aqueous solution and wastewater using activated slag, a low-cost adsorbent. Ind. Eng. Chem. Res. **37**:192–202.

Hering JG, Chen P-Y, Wilkie JA, Elimelech M. 1997. Arsenic removal from drinking water during coagulation. J. Environ. Eng. **8**:800–807.

Hiemstra T, van Riemsdijk WH. 1999. Surface structural ion adsorption modeling of competitive binding of oxyanions by metal (hydr)oxide. J. Colloid Inter. Sci. **210**:182–193.

Hington FJ, Posner AM, Quirk JP. 1971. Competitive adsorption of negatively charged ligands on oxide surface. Discuss. Faraday Soc. **52**:334–342.

Ho Y-S. 2003. Removal of copper ions from aqueous solution by tree fern. Water Res. **37**:2323–2330.

Hsia TH, Lo SL, Lin CF. 1994. Characterization of arsenate adsorption on hydrous iron oxide using chemical and physical methods. Colloids Surf. A **85**:1–7.

Jain A, Loeppert RH. 2000. Effect of competing anions on the adsorption of arsenate and arsenite by ferrihydrite. J. Environ. Qual. **29**:1422–1430.

Joshi A, Chaudhuri M. 1996. Removal of arsenic from

groundwater by iron oxide coated sand. J. Environ. Eng. **122(8)**:769–771.

Korte NE, Fernando Q. 1991. A review of arsenic (III) in groundwater. Crit. Rev. Environ. Control **21(1)**:1–39.

Lo S-L, Chen T-Y. 1997. Adsorption of Se(IV) and Se(VI) on an iron-coated sand from water. Chemosphere **35(5)**:919–930.

Manna BR, Dey S, Debnath S, Ghosh UC. 2003. Removal of arsenic from groundwater using crystalline hydrous ferric oxide (CHFO). Water Qual. Res. J. Canada **38(1)**:193–210.

Manning BA, Goldberg A. 1997. Adsorption and stability of arsenic(III) at the clay mineral-water interface. Environ. Sci. Tech. **31(7)**:2005–2011.

Meng X, Letterman RD. 1993. Effect of component oxide interaction on the adsorption properties of mixed oxides. Environ. Sci. Tech. **27(5)**:970–975.

Pierce ML, Moore CB. 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. Water Res. **16**:1247–1253.

Raven KP, Jain A, Loeppert RH. 1998. Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes. Environ. Sci. Tech. **32**:344–349.

Ryden JC, Syers JK, Tillman RW. 1987. Inorganic anion sorption and interactions with phosphate sorption by hydrous ferric oxide gel. J. Soil Sci. **38**:211–217.

Singh DB, Prasad G, Rupainwar DC, Singh VN. 1988. As(III) removal from aqueous solution by adsorption. Water Air Soil Pollut. **42**:373–386.

Sparks DL. 1989. Kinetics of soil chemical processes. Academic Press, Inc., New York.

SPSS Inc. 2001. SigmaPlot 2001 user's guide. Chicago, Ill.

Sun X, Doner HE. 1998. Adsorption and oxidation of arsenite on goethite. Soil Science **163(4)**:278–287.

Theis TL, Iyer R, Ellis SK. 1992. Evaluating a new granular iron oxide for removing lead from drinking water. J. AWWA **84**:101–105.

Thirunavukkarasu OS, Viraraghavan T, Subramanian KS. 2003. Arsenic removal from drinking water using iron oxide-coated sand. Water Air Soil Pollut. **142**:95–111.

Weber TW, Chakravorti RK. 1974. Pore and solid diffusion models for fixed bed adsorbents. J. Am. Inst. Chem. Eng. **20**:228–238.

Wilkie JA, Hering JG. 1996. Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbates/adsorbent ratio and co-occurring solutes. Colloids Surf. A **107**:97–110.

Yohida I, Kobayashi H, Uena K. 1976. Selective adsorption of arsenic ions on silica gel impregnated with ferric hydroxide. Anal. Lett. **9(12)**:1125–1133.

Zeng L. 2003. A method for preparing silica-containing iron(III) oxide adsorbents for arsenic removal. Water Res. **37(18)**:4351–4358.