



## Sorption of arsenite and arsenate on ferrihydrite: Effect of organic and inorganic ligands

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### ARTICLE INFO

#### Article history:

Received 7 December 2010

Received in revised form 21 February 2011

Accepted 22 February 2011

Available online 2 March 2011

#### Keywords:

Sorption

Ferrihydrite

As(III)

As(V)

Competition

Organic and inorganic ligands

### ABSTRACT

We studied the sorption of As(III) and As(V) onto ferrihydrite as affected by pH, nature and concentration of organic [oxalic (OX), malic (MAL), tartaric (TAR), and citric (CIT) acid] and inorganic [phosphate (PO<sub>4</sub>), sulphate (SO<sub>4</sub>), selenate (SeO<sub>4</sub>) and selenite (SeO<sub>3</sub>)] ligands, and the sequence of anion addition. The sorption capacity of As(III) was greater than that of As(V) in the range of pH 4.0–11.0. The capability of organic and inorganic ligands in preventing As sorption follows the sequence: SeO<sub>4</sub> ≈ SO<sub>4</sub> < OX < MAL ≈ TAR < CIT < SeO<sub>3</sub> ≪ PO<sub>4</sub>. The efficiency of most of the competing ligands in preventing As(III) and As(V) sorption increased by decreasing pH, but PO<sub>4</sub> whose efficiency increased by increasing pH. In acidic systems all the competing ligands inhibited the sorption of As(III) more than As(V), but in alkaline environments As(III) and As(V) seem to be retained with the same strength on the Fe-oxide. Finally, the competing anions prevented As(III) and As(V) sorption more when added before than together or after As(III) or As(V).

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### 1. Introduction

Arsenic (As) is an element ubiquitous in the environment and is extremely toxic for humans, animals and plants [1,2]. Arsenic contamination in water is a worldwide problem, because in drinking water it is rapidly and directly sorbed by humans [1,3–5]. Developing countries are the most severely affected by the arsenic crisis, but the situation is especially alarming in south and southeast Asia [3,6]. The seriousness of this problem has led the World Health Organization to describe it as the greatest mass poisoning in human history. An examined 35 million people in Bangladesh and 6 million in West Bengal are at risk [2,5,7].

In soils high concentrations of As can originate from different sources, as weathering of rocks or minerals with high As contents, biological activities and anthropogenic activities, such as mining smelter, disposal waste and application of As fertilizers and pesticides.

Many inorganic and organo-arsenical forms are present in natural environments, but the most common are arsenite [As(III)] and arsenate [As(V)]. The predominant As speciation is strongly influenced by the redox potential and pH [5,7,8]. Arsenite is 25–60 times more toxic and mobile than As(V), which mainly arise from its state as H<sub>3</sub>AsO<sub>3</sub> at pH < 9.0, as compared to the charged species which predominate in a wide pH range (H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> between 2.5 and 7, HAsO<sub>4</sub><sup>2-</sup> between pH 7.0 and 12.0 [4,5,7,8].

The mobility of As compounds in soil–water–plant systems is affected by sorption/desorption on/from soil components or coprecipitation with metal ions [9–13]. The importance of oxides (mainly Fe-oxides) in controlling the mobility and concentration of As in natural environments is well known [4,5,8,9,12–14]. In particular, As(V) demonstrates a high affinity for most metal hydroxides and clay minerals, whereas As(III) has a strong preference for hydroxides of iron. At circumneutral pH values and higher, As(III) usually adsorbs to a greater extent on ferric hydroxides than As(V) [8,15,16].

Many studies on the structures of As(V) adsorption complexes on various Fe oxyhydroxides have been carried out using X-ray adsorption spectroscopy, whereas very few have been focused on As(III) [4,5,8,13,17–19]. The formation of various inner-sphere complexes has been suggested as the primary mechanism for the sorption of As(V) on iron oxides [13,17]. However, both inner-sphere complexes and outer-sphere complexes have been found in the sorption of As(III) on different iron oxides [13,19]. Ona-Nguema et al. [19] found using EXAFS spectroscopy that As(III) forms bidentate mononuclear edge-sharing and bidentate binuclear corner-sharing on ferrihydrite. A redox reaction between Fe(III)-oxide and As(III) did not occur within 72 h, indicating that the kinetics of the redox reaction between As(III) and Fe(III) is relatively slow [20].

As reported by Inskeep et al. [21] on iron oxides, the sorption capacity of As(III) compares or exceeds that of As(V), the former showing an adsorption envelope centered at pH 8.0, while the latter increases continuously with decreasing pH, but caution should be used in drawing conclusions

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regarding binding strength from the magnitude of retention.

Numerous studies have been carried out on the sorption of As(III) and As(V) onto Fe or Al oxides [4,8,9,22]. The presence of inorganic and organic ligands affects the sorption of As onto soil minerals and soils by competing for available binding sites and/or reducing the surface charge of the sorbents [8,10,12,23–26]. The competition in sorption is affected by the affinity of the competing anions for the surfaces of the sorbents, the nature and surface properties of the minerals and soils, the surface coverage and the reaction time.

Competition between As(V) and phosphate has been widely studied [4,7,8,10–12,27,28] but scant attention has been devoted to compare the effect of different inorganic and organic ligands on the adsorption of As(V) and As(III) onto soil components [24,25,29]. Low molecular mass organic ligands (particularly aliphatic acids, such as acetic, oxalic, tartaric, succinic, malic, and citric acids) are abundant in the rhizosphere, being continuously released by plant roots and microorganisms ([8,30] and references there in). Their presence may affect the mobility of As at soil–root interface.

In order to have useful information on the factors which may influence the mobility and potential toxicity of arsenic in natural environments, we carried out a study on the sorption of As(III) and As(V) onto ferrihydrite as affected by pH, nature and concentration of organic [oxalic (OX), malic (MAL), tartaric (TAR), and citric (CIT) acid] and inorganic [phosphate (PO<sub>4</sub>), sulphate (SO<sub>4</sub>), selenate (SeO<sub>4</sub>) and selenite (SeO<sub>3</sub>)] ligands, surface coverage and the sequence of anion addition.

## 2. Materials and methods

All chemicals were reagent grade and used without further purification. Solutions were prepared with Mill-Q (18 MΩ-cm) water. Plastic volumetric flasks and reaction vessels (polypropylene) were cleaned with HNO<sub>3</sub> 1% and rinsed several times with deionized water before use.

### 2.1. Formation and characterization of ferrihydrite

Ferrihydrite was prepared by precipitating 0.1 mol L<sup>-1</sup> Fe(NO<sub>3</sub>)<sub>3</sub> at pH 5.5 with 0.5 mol L<sup>-1</sup> NaOH at a rate of 0.5 mL min<sup>-1</sup>. The final volume was adjusted to 1 L. After 24 h of aging at 20 °C, the suspension was washed, dialysed with deionized water and freeze-dried. The precipitate was identified by X-ray diffraction (XRD), infrared spectroscopy and electron microscopy.

The X-ray diffraction patterns of randomly oriented sample were obtained using a Rigaku diffractometer with Fe-filtered CoKα radiation generated at 40 kV and 30 mA (Rigaku Co., Tokyo). The infrared spectrum of the sample was obtained using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy analysis. Sample preparation for DRIFT determination was as follows: 0.2 mg of sample was mixed with 200 mg of KBr (Fourier-transform infrared [FT-IR] grade, Aldrich Chemical Co.). The DRIFT spectra were obtained using a PerkinElmer Spectrum One FT-IR Spectrophotometer (PerkinElmer Instruments, Wellesley, MA). The instruments had a spectral resolution of 1 cm<sup>-1</sup>. Finally, for transmission electron microscopic (TEM) examination, one drop of sample suspension before freeze-drying was deposited onto a C-coated Forvar film Cu grid. The TEM micrograph was taken with a Philips CM 120 microscope (Philips, Eindhoven, the Netherlands).

The surface area of ferrihydrite was determined by H<sub>2</sub>O sorption at 20% relative humidity [31] and the point of zero charge (PZC) was determined by laser Doppler velocimetry-photon correlation spectroscopy (Beckham Coulter Electronics, Hialeah, FL)

### 2.2. As(III) and As(V) isotherms

One hundred milligrams of ferrihydrite, in triplicate, was equilibrated at 20 °C with 19.5 mL of 0.02 mol L<sup>-1</sup> KCl at pH 5.0 or 6.0. Suitable amounts of 0.01 mol L<sup>-1</sup> solutions containing K<sub>2</sub>HAsO<sub>4</sub> or K<sub>2</sub>HAsO<sub>3</sub> were added to obtain an initial As(V) or As(III) concentration in the range 5 × 10<sup>-4</sup> to 10<sup>-2</sup> mol L<sup>-1</sup>. The pH of each suspension was maintained constant (5.0 or 6.0) by the addition of 0.1 or 0.01 mol L<sup>-1</sup> HCl or NaOH using a stirred pH-stat apparatus. The final volume was 20 mL and the final solid/solution ratio was 5 g L<sup>-1</sup>. The suspensions were shaken for 24 h in a water bath at 20 °C, centrifuged at 10,000 × g min<sup>-1</sup>, and filtered using membrane filters (0.45 μm). The filtrates were stored at 2 °C until analysis.

The concentrations of As(III) and As(V) in the solutions were determined as described below. Arsenite and As(V) sorption was calculated from the difference between the initial and final As(V) and As(III) concentration in the solutions.

### 2.3. Kinetics of sorption of As(III) and As(V)

The kinetics of As(III) and As(V) by the Fe-oxide was studied by the conventional batch method. One hundred milligram of the sorbent was added to a series of 50-mL flasks (in triplicate), which contained 19.5 mL of 0.02 mol L<sup>-1</sup> KCl. The pH of the suspensions were then adjusted to 6.0 with 0.01 or 0.1 mol L<sup>-1</sup> HCl or KOH. Suitable amounts of 0.01 mol L<sup>-1</sup> solution containing K<sub>2</sub>HAsO<sub>4</sub> or K<sub>2</sub>HAsO<sub>3</sub> (pH 6.0) were added to each flask to obtain a final As(III) and As(V) concentration, respectively of 7 × 10<sup>-3</sup> and 4 × 10<sup>-3</sup> mol L<sup>-1</sup>, corresponding to 1400 [As(III)] and 800 [As(V)] mmol kg<sup>-1</sup> (near to the maximum amount determined by As(III) and As(V) isotherms). The suspensions were shaken in a shaker with a constant-temperature water bath of 20 °C from 0.167 to 48 h. The pH of the suspensions was measured during the reaction period and was kept constant. The suspensions were brought to 20 mL and rapidly filtered through a 0.22 μm filter. The As(III) or As(V) concentration was determined as reported below and the amount sorbed was calculated by taking the difference between the initial and final concentration.

### 2.4. Sorption of As(V) and As(III) as a function of pH

One hundred milligrams of ferrihydrite, in triplicate, was equilibrated at 20 °C with 19.5 mL of 0.02 mol L<sup>-1</sup> KCl at different pH values from 4.0 to 11.0. Predetermined quantities of 0.01 mol L<sup>-1</sup> solutions containing As(III) or As(V), previously adjusted at pH 4.0–11.0, were pipetted into the flasks in order to yield nearly the maximum adsorption of each oxyanion, as previously determined by sorption isotherms. The pH of each suspension was kept constant for 24 h by adding 0.1 or 0.01 mol L<sup>-1</sup> HCl or KOH. The final suspensions (20 mL) were centrifuged at 10,000 × g for 20 min, and filtered through a 0.22-μm filter. Arsenite and As(V) were determined in the supernatants as described below.

### 2.5. Sorption of As(III) and As(V) in the presence of inorganic and organic ligands

Sorption experiments of As(III) and As(V) in the presence of organic (OX, TAR, MAL and CIT) and inorganic (PO<sub>4</sub>, SO<sub>4</sub>, SeO<sub>4</sub>, and SeO<sub>3</sub>) ligands (all the reagents used are K-salts) were carried out at pH 5.0 and 6.0 by adding suitable amounts of As(III) or As(V) (at about 60% surface coverage, as referred to sorption isotherms) together with the competing ligand (As + ligand systems) at initial ligand/As molar ratio (*R*) of 1 and 2. The pH of each suspension (5.0 or 6.0) was kept constant for 24 h by adding 0.1 or 0.01 mol L<sup>-1</sup> HCl or KOH. Some experiments were carried out also at pH 4.0 and 9.0.

**Table 1**  
Isotherm parameters for the sorption of As(III) and As(V) on ferrihydrite at pH 6.0.

	Freundlich model			Langmuir model		
	$K_f$ (mmol kg <sup>-1</sup> )	$n$	$R^2$	$q_m$ (mmol kg <sup>-1</sup> )	$K$	$R^2$
As(III)	1469	4.3	0.98	1337	35.2	0.88
As(V)	752	12.7	0.99	745	70.3	0.98

In order to study the sequence of anion addition on As sorption, experiments were carried out by adding As(III) or As(V) 5 h before the addition of the competing organic or inorganic ligand (As before ligand systems) or by adding the competing ligand 5 h before arsenic (ligand before As systems) at  $R = 1$ , keeping the suspensions to react for 24 h after As addition.

### 2.6. As(V) and As(III) determination

The concentration of As(III) and As(V) in the supernatants was determined by inductively coupled plasma (ICP-AES, Varian, Liberty 150) and Dionex DX-300 Ion Chromatograph (Dionex Co, Sunnyvale, CA), respectively, as described in previous studies [10,11]. The amounts of As(III) and As(V) sorbed was determined by the difference between the quantity of As added initially and that present in the supernatants. The data are the mean of three determinations. The  $\pm$  values in the tables indicate error standard. The intraday repeatability study was carried out by the injection of the same standard solution five consecutive times ( $n = 5$ ) in the same day under the same conditions. The interday precision was carried out for three successive days using the same solution. The relative standard deviation of these measurements was between 2% and 3%.

## 3. Results and discussion

### 3.1. Characterization of the metal oxide

The Fe oxide obtained at pH 5.5 was identified to be ferrihydrite. The X-ray pattern of this sample showed four characteristic broad peaks centered at 0.254, 0.225, 0.198, and 0.148 nm (Fig. 1A). The FT-IR spectrum and TEM indicated that this material was a very poorly crystallized material, with particles less than 100 nm in size, which appear usually aggregated (Fig. 1B and C). The sharp peak at 1384 cm<sup>-1</sup> in the FT-IR spectrum (Fig. 1B) indicates presence of nitrate as impurity. Ferrihydrite showed a surface area of 180 m<sup>2</sup> g<sup>-1</sup> and a PZC of 7.5.

### 3.2. Sorption isotherms of As(III) and As(V)

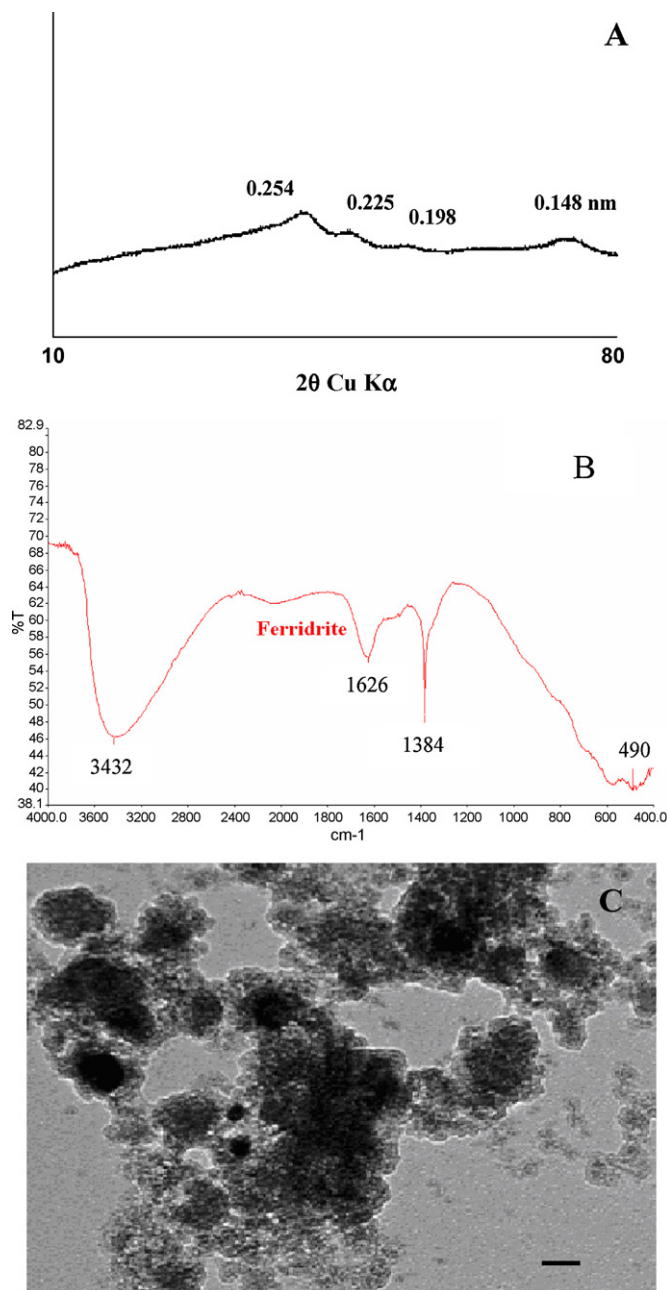
The sorption isotherms of As(III) and As(V) on ferrihydrite at pH 6.0 are depicted in Fig. 2. The sorption data were fitted by Langmuir equation (Eq. (1)) and Freundlich equation (Eq. (2)) as reported below:

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

$$q_e = K_f C_e^{1/n} \quad (2)$$

where  $C_e$  and  $q_e$  are the amount of As(III) or As(V) in the solution (mmol L<sup>-1</sup>) and sorbed on ferrihydrite (mmol kg<sup>-1</sup>), respectively,  $q_m$  and  $K_f$  stand for the maximum amount of As(III) or As(V) that may be sorbed, while  $K$  and  $n$  are the constant related to the sorption energy or sorption intensity.

The sorption data were described better by Freundlich equation than by Langmuir equation (Table 1). The maximum sorption of As(III) and As(V) on ferrihydrite at pH 6.0 as revealed by Freundlich equation was 1469 and 752 mmol kg<sup>-1</sup>, respectively. The  $n$  value

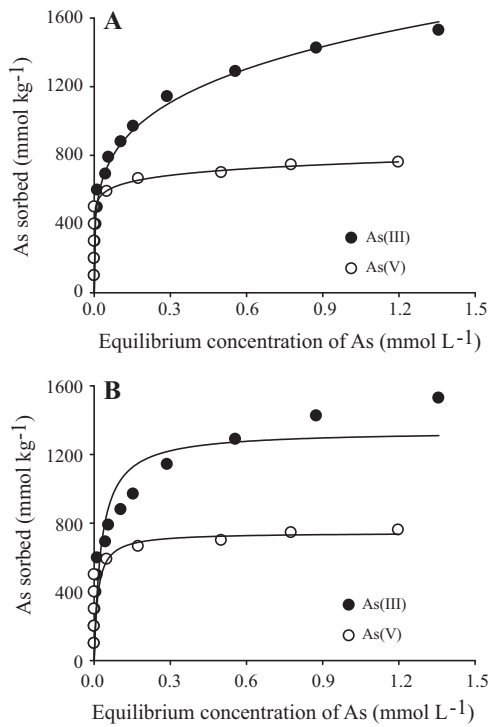


**Fig. 1.** X-ray powder diffractogram (A), FT-IR spectrum (B) and transmission electron micrograph (C) of the iron precipitation product. Bar indicates 100 nm.

from Freundlich fitting and  $K$  value from Langmuir fitting of As(V) were both greater than that of As(III) (Table 1), indicating a greater affinity of ferrihydrite for As(V) than for As(III).

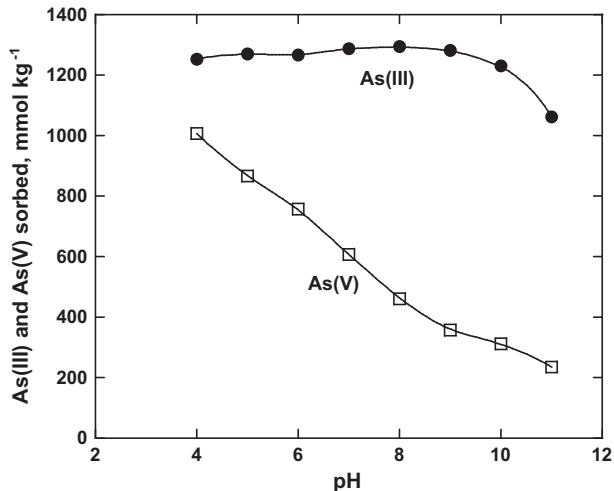
### 3.3. Effect of pH on the sorption of As(III) and As(V)

In the range of pH 4.0–11.0, the sorption capacity of As(III) was always greater than that of As(V) (Fig. 3). The sorption of As(V) onto ferrihydrite was highly pH dependent and decreased by increasing pH from 4.0 to 11.0 from 1000 to 200 mmol kg<sup>-1</sup>, due to the repulsion between the more negative charged As(V) species and the surface sites [9]. In contrast, As(III) sorption was practically constant in the range 4.0–9.0 and, then decreased at pH > 9.0, being As(III) practically uncharged up to pH 9.0. Similar results were found by other researchers [15,21,24,27].

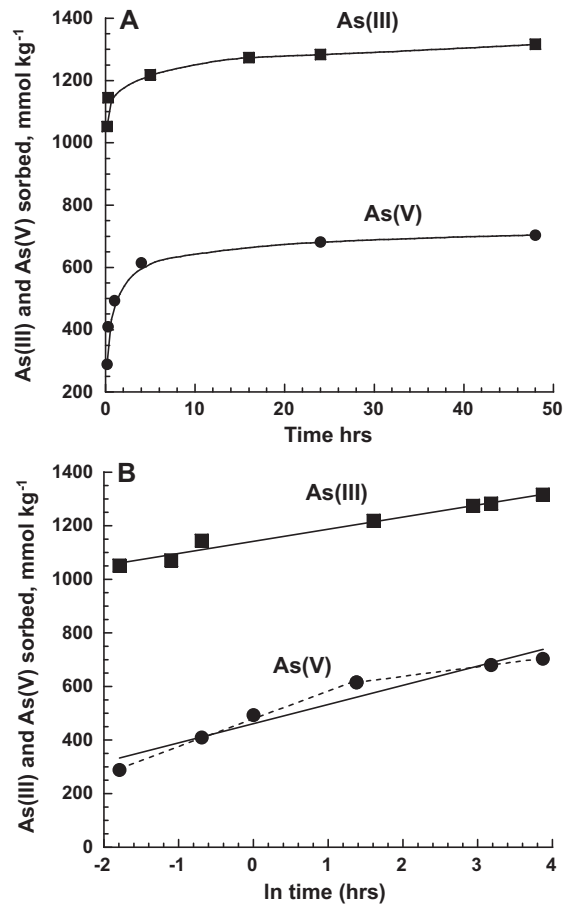


**Fig. 2.** Freundlich (A) and Langmuir (B) fitting for the sorption isotherms of arsenite and arsenate on ferrihydrite at pH 6.0.

Dixit and Hering [15] found that As(V) sorption onto ferrihydrite was more favourable than As(III) at low pH values, but the opposite was true at high pH values. These authors found that with ferrihydrite the crossover pH (i.e. the pH value at which As(III) and As(V) were equally sorbed) was about 6.5 with 50–100 μM total As. Variations in crossover pH values (an increase to higher pH by decreasing As concentration) were found by many authors [9,15,16,32] using ferrihydrite or goethite as sorbents and were attributed to differences in the sorbate and sorbent concentrations. In our study, the lack of a crossover in the range of pH 4.0–11.0 must be attributed to the greater sorbate and sorbent concentration used in comparison to the other studies previously cited. Raven et al. [9] showed that As(III) has a greater sorption capacity on ferrihydrite and goethite than As(V) except at very low solution concentrations.



**Fig. 3.** Effect of pH on the sorption of arsenite and arsenate on ferrihydrite.



**Fig. 4.** Effect of reaction time on the sorption of arsenite and arsenate on ferrihydrite at pH 6.0 at about 100% of surface coverage (A); kinetics of sorption of arsenite and arsenate using the Elovich model (multiple linear segments better describe arsenate sorption, dashed line) (B).

### 3.4. Kinetics of sorption

Fig. 4A shows the effect of reaction time on the sorption of As(III) and As(V) onto ferrihydrite at pH 6.0 and at about 100% of surface coverage. Among the kinetics models tested (first order, parabolic diffusion, pseudo-second-order and Elovich model), the fit for the sorption data was obtained best using the pseudo-second-order (Eq. (3)) and Elovich model (Eq. (4); Table 2) [23], reported below:

$$\frac{t}{q_t} = \frac{1}{(kq_e^2)} + \frac{t}{(q_e)h} = kq_e^2 \quad (3)$$

$$q_t = \left(\frac{1}{\beta}\right) \ln(t) + \left(\frac{1}{\beta}\right) \ln(\alpha\beta) \quad (4)$$

where  $q_t$  and  $q_e$  are the amounts of arsenite or arsenate sorbed at time  $t$  and at equilibrium ( $\text{mmol kg}^{-1}$ ),  $h$  and  $\alpha$  are the initial sorption rate ( $\text{mmol kg}^{-1} \text{h}^{-1}$ ) in pseudo-second-order model and Elovich model, respectively,  $k$  is the rate constant of sorption ( $\text{kg mmol}^{-1} \text{h}^{-1}$ ) in pseudo-second-order model, whereas  $\beta$  is the desorption constant ( $\text{kg mmol}^{-1}$ ) in Elovich model.

In soil chemistry, the Elovich equation has been usually used to describe the kinetics of sorption/desorption of nutrients and pollutants on soils and soil components [23]. Fig. 4B shows the sorption of As(III) and As(V) using the Elovich model. The sorption reactions of As(III) and As(V) can be explained as a biphasic process, the first sorption process occurring during the initial period of 10 min. (0.167 h) and the subsequent sorption occurring during the reaction period of 0.167–48 h. After 0.167 h, 64% of As(III) and 43%

**Table 2**  
Kinetic parameters for the sorption of As(III) and As(V) on ferrihydrite at pH 6.0.

	Pseudo-second-order model				Elovich model		
	$q_e$ (mmol kg <sup>-1</sup> )	$h$ (mmol kg <sup>-1</sup> h <sup>-1</sup> )	$k$	$R^2$	$\alpha$ (mmol kg <sup>-1</sup> h <sup>-1</sup> )	$\beta$ (kg mmol <sup>-1</sup> )	$R^2$
As(III)	1312	6098	0.0035	0.99	$4.0 \times 10^{12}$	0.0221	0.98
As(V)	707	1527	0.0031	0.99	$4.4 \times 10^4$	0.0140	0.97

of As(V), initially added, were sorbed onto the Fe-oxide (Fig. 4B). Multiple linear segments could describe the kinetics process of As(V) (dashed line in Fig. 4B), indicating a possible changeover from some type of sites to others [23]. Multiple linear segments were not observed for As(III), probably being the reaction kinetics particularly fast.

Faster initial sorption rate of As(III) than As(V) was revealed by the fitting with both the models (Table 2). Greater  $k$  value of As(III) than As(V) also indicated that the sorption rate of As(III) in the whole sorption process was higher than that of As(V).

The  $\beta$  value of As(III) was also greater than that of As(V) and may suggest a greater desorption tendency of As(III) than As(V), confirming a greater affinity of ferrihydrite for As(V) than for As(III) (Table 1).

### 3.5. Effect of inorganic and organic ligands on the sorption of As(III) and As(V)

Tables 3 and 4 show the amounts of As(III) sorbed at pH 5.0 (Table 3) and of As(III) and As(V) sorbed at pH 6.0 (Table 4) on ferrihydrite in the absence or presence of inorganic and organic anions added at  $R$  of 1 and 2. Arsenite and As(V) were added at 60% of surface coverage as determined by the sorption isotherms (Fig. 2). Finally, the Tables 5 and 6 show the effect of anion addition on the sorption of As(III) and As(V) onto the Fe-oxide.

The presence of inorganic and organic ligands influenced the sorption of As(III) and As(V) onto ferrihydrite by competing for available binding sites and/or reducing the surface charge of the sorbent [7,8,10,23–26]. The efficiency of each ligand was calculated using the following expression [10]:

Inhibition Efficiency (IE) of a ligand(%)

$$= \left[ 1 - \frac{\text{As sorbed in the presence of a ligand}}{\text{As sorbed when applied alone}} \right] \times 100$$

Our data evidence that the sorption of As(III) and As(V) was affected by the nature and concentration of the anions, pH and sequence of addition of arsenic and competing ligand to the sorbent (Tables 3–6). However, the inorganic and organic ligands showed a tremendous difference in preventing As fixation. Phosphate and SeO<sub>3</sub> were the most efficient, whereas SO<sub>4</sub> and SeO<sub>4</sub> were the

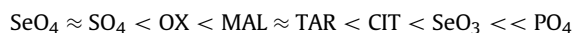
**Table 3**  
Sorption of As(III) onto ferrihydrite at pH 5.0 in the absence and presence of inorganic and organic ligands at initial ligand/As(III) molar ratio ( $R$ ) of 1 and 2; 1000 mmol kg<sup>-1</sup> of As added.

Ligand	As(III) sorbed		As(III) sorbed	
	$R=1$	Efficiency	$R=2$	Efficiency
	mmol kg <sup>-1</sup>	%	mmol kg <sup>-1</sup>	%
No ligand	940.4 ± 16.9	–	940.4 ± 16.9	–
SO <sub>4</sub>	887.1 ± 17.4	5.70 ± 0.1	874.7 ± 20.6	7.0 ± 0.2
SeO <sub>4</sub>	896.1 ± 14.8	4.70 ± 0.1	865.4 ± 22.8	8.0 ± 0.2
SeO <sub>3</sub>	681.1 ± 12.3	27.6 ± 0.9	498.9 ± 14.5	46.9 ± 1.2
PO <sub>4</sub>	534.3 ± 14.2	43.2 ± 1.1	392.5 ± 13.1	58.3 ± 1.4
Ox	831.2 ± 18.2	11.6 ± 0.7	772.2 ± 23.6	17.9 ± 0.4
Mal	708.0 ± 12.6	24.7 ± 0.7	641.8 ± 18.8	31.8 ± 1.3
Tar	692.5 ± 18.4	26.4 ± 1.0	658.3 ± 16.4	30.0 ± 1.0
Cit	680.1 ± 14.8	27.7 ± 1.2	616.9 ± 19.7	34.4 ± 1.5

± Values indicate error standard (SE).

weaker. In fact, at pH 6.0 and  $R=1$  (Table 4), PO<sub>4</sub> prevented As(III) sorption of 48.3%, SeO<sub>3</sub> of 22.3%, whereas SO<sub>4</sub> and SeO<sub>4</sub> had a negligible influence in inhibiting As(III) fixation (<2.5%). By increasing  $R$  to 2 the inhibition increased to 69.3% for PO<sub>4</sub>, 32.5 for SeO<sub>3</sub>, and 3.8 for SeO<sub>4</sub>.

The ability of inorganic and organic anions to inhibit (or retard) As(III) and As(V) sorption onto ferrihydrite was (Tables 3–6):



The data reported in Tables 3–6 clearly evidence that at pH 5.0 and 6.0 all the inorganic and organic ligands used inhibited the sorption of As(III) more than As(V) in spite of greater amounts of the latter were fixed onto the surfaces of ferrihydrite in all the range of pH studied and, particularly, at pH ≥ 6.0 (Fig. 3). At pH 6.0 and at initial ligand/As molar ratio = 2 the efficiency of PO<sub>4</sub> in preventing As(III) sorption was 69.3% versus 57.4% for As(V), that of SeO<sub>3</sub> was 32.5 versus 20.1 and, finally, the efficiency of the organic ligands in preventing As(III) sorption ranged from 11.7% for OX to 21.2% for TAR and 26.5% for CIT, whereas their capacity in inhibiting As(V) was in the range 7.5% for OX to 14.8% for TAR. Usually, at pH 6.0 and both  $R=1$  or 2, PO<sub>4</sub> showed a capacity to prevent As(III) or As(V) fixation more than two times that of SeO<sub>3</sub> and three times that of TAR and MAL.

The efficiency of most of the competing ligands in preventing As(III) sorption increased at pH 5.0 (Table 3), particularly for MAL, TAR, and CIT, but decreased for PO<sub>4</sub>. In previous works [8,10,12,26,29] it has been demonstrated that organic ligands were more effective in preventing As(V) sorption onto soil components in acidic systems, whereas the efficiency of PO<sub>4</sub> in inhibiting As(V) sorption increased by increasing pH (as discussed below).

The efficiency of SO<sub>4</sub> and SeO<sub>4</sub> in preventing As(III) sorption increased at pH 5.0, but these anions still appeared to compete slightly with As(III) and had a negligible effect on As(V) sorption at pH 6.0 (and 4.0, as discussed below), even at SO<sub>4</sub> (or SeO<sub>4</sub>)/As molar ratio of 2 (Tables 3 and 4). These results are not surprising because it is well known that SO<sub>4</sub> and SeO<sub>4</sub> usually form outer-sphere complexes onto the surfaces of variable charge minerals. Some authors [33–35] demonstrated by EXAF that SeO<sub>4</sub> forms a mixture of outer- and inner-sphere surface complexes onto goethite and ferrihydrite, but inner sphere surface complexes decreased by increasing pH from 3.5 to 6.0, whereas SO<sub>4</sub> forms both outer-sphere and inner-sphere surface complexes on goethite at less than pH 6.0, outer-sphere complex at pH > 6.0, but forms predominantly outer-sphere surface complexes on ferrihydrite. Liu et al. [29] demonstrated that SO<sub>4</sub> did not compete efficiently with PO<sub>4</sub> and OX at pH > 5.0, but was able to inhibit PO<sub>4</sub> and OX sorption particularly at pH < 5.0 on goethite. This behaviour was attributed to the possibility of SO<sub>4</sub> to form inner-sphere complexes at low pH values.

We carried out some experiments at pH 4.0 and  $R=1$  and 2, which evidenced that the efficiency of these ligands in preventing As(III) and As(V) sorption increased. Precisely, their inhibition efficiency for As(III) was 6.4% (SO<sub>4</sub>) and 5.8% (SeO<sub>4</sub>) at  $R=1$  and 9.2% (SO<sub>4</sub>) and 7.8% (SeO<sub>4</sub>) at  $R=2$ , whereas their efficiency in preventing As(V) was lower and, precisely, 1.5% (SO<sub>4</sub>) and 2.4% (SeO<sub>4</sub>) at  $R=1$  and 2.5% (SO<sub>4</sub>) and 3.9% (SeO<sub>4</sub>) at  $R=2$ , confirming that these ligands have an almost similar capacity in preventing or retarding

**Table 4**

Sorption of As(III) and As(V) onto ferrihydrite at pH 6.0 in the absence and presence of inorganic and organic ligands at initial ligand/As(III) and As(V) molar ratio (*R*) of 1 and 2. 1000 mmol kg<sup>-1</sup> of As(III) added; 600 mmol kg<sup>-1</sup> of As(V) added n.d. stands for not determined.

Ligand	As(III) sorbed	Efficiency	As(III) sorbed	Efficiency	As(V) sorbed	Efficiency	As(V) sorbed	Efficiency
	<i>R</i> = 1 mmol kg <sup>-1</sup>	%	<i>R</i> = 2 mmol kg <sup>-1</sup>	%	<i>R</i> = 1 mmol kg <sup>-1</sup>	%	<i>R</i> = 2 mmol kg <sup>-1</sup>	%
No ligand	969.1 ± 18.4	–	969.1 ± 18.4	–	600.0	–	600.0	–
SO <sub>4</sub>	954.4 ± 22.3	1.5 ± 0.1	954.4 ± 24.7	1.5 ± 0.1	600.0	0.0	598.8 ± 11.8	0.2
SeO <sub>4</sub>	948.2 ± 19.0	2.2 ± 0.1	932.7 ± 18.6	3.8 ± 0.2	600.0	0.0	594.6 ± 13.5	0.9
SeO <sub>3</sub>	753.1 ± 16.8	22.3 ± 0.9	654.2 ± 17.4	32.5 ± 1.2	485.2 ± 12.8	19.1 ± 0.6	467.5 ± 12.7	20.1 ± 0.9
PO <sub>4</sub>	501.0 ± 14.2	48.3 ± 1.7	297.5 ± 12.0	69.3 ± 2.8	344.8 ± 8.7	41.1 ± 1.2	249.3 ± 14.8	57.4 ± 2.7
Ox	893.4 ± 25.1	7.8 ± 0.4	856.1 ± 33.8	11.7 ± 0.6	568.2 ± 13.9	5.30 ± 0.3	541.7 ± 16.7	7.50 ± 0.3
Mal	839.0 ± 19.7	13.4 ± 0.6	770.2 ± 21.5	20.5 ± 1.0	515.7 ± 15.8	11.9 ± 0.4	501.9 ± 15.8	14.3 ± 0.7
Tar	837.4 ± 14.8	13.6 ± 0.5	763.9 ± 22.5	21.2 ± 0.9	509.1 ± 11.5	13.0 ± 0.5	499.0 ± 12.4	14.8 ± 0.6
Cit	778.4 ± 17.4	19.7 ± 0.9	712.2 ± 23.8	26.5 ± 1.2	n.d.	–	n.d.	–

± Values indicate error standard (SE).

**Table 5**

Sorption of As(III) onto ferrihydrite at pH 6.0 in the absence and presence of inorganic and organic ligands at initial ligand/As(III) molar ratio of 1, when As(III) and a ligand were added together [As(III) + ligand systems], or As(III) was added 5 h before a ligand [As(III) before ligand systems], or when a ligand was added 5 h before As(III) [ligand before As(III) systems] 1000 mmol kg<sup>-1</sup> As added.

Ligand	As(III) sorbed	Efficiency	As(III) sorbed	Efficiency	As(III) sorbed	Efficiency
	As(III) + ligand systems		As(III) before ligand systems		Ligand before As(III) systems	
	mmol kg <sup>-1</sup>	%	mmol kg <sup>-1</sup>	%	mmol kg <sup>-1</sup>	%
No ligand	969.1 ± 18.4	–	969.1 ± 18.4	–	969.1 ± 18.4	–
SO <sub>4</sub>	954.4 ± 22.3	1.5 ± 0.1	959.4 ± 27.2	1.0 ± 0.1	921.6 ± 26.7	4.9 ± 0.2
SeO <sub>4</sub>	948.2 ± 19.0	2.2 ± 0.1	957.5 ± 24.8	1.2 ± 0.1	929.3 ± 24.9	4.1 ± 0.1
SeO <sub>3</sub>	753.1 ± 16.8	22.3 ± 0.9	794.6 ± 20.8	18.0 ± 0.7	594.0 ± 31.9	38.7 ± 1.4
PO <sub>4</sub>	501.0 ± 14.2	48.3 ± 1.7	n.d.	–	n.d.	–
Ox	893.4 ± 25.1	7.8 ± 0.4	917.7 ± 19.8	5.3 ± 0.2	863.5 ± 25.1	10.9 ± 0.5
Mal	839.0 ± 19.7	13.4 ± 0.6	861.5 ± 22.3	11.1 ± 0.5	805.3 ± 17.8	16.9 ± 0.7
Tar	837.4 ± 14.8	13.6 ± 0.5	857.6 ± 31.6	11.5 ± 0.4	789.8 ± 22.0	18.5 ± 0.7
Cit	778.4 ± 17.4	19.7 ± 0.9	816.9 ± 32.7	15.7 ± 0.6	697.5 ± 26.9	28.0 ± 1.1

n.d. stands for not determined; ± values indicate error standard (SE).

As(III) and As(V) sorption. Some experiments carried out using a noncrystalline Al-oxide and mixed Fe–Al oxides (unpublished data) seems to demonstrate that SO<sub>4</sub> inhibit As(III) and As(V) sorption more than SeO<sub>4</sub>. The effect of these ligands in competing with other anions on different sorbents and at different pHs deserves closer attention.

Among the organic ligands used in this work CIT showed a capacity to inhibit As(III) and As(V) sorption greater than MAL, TAR, and OX (in the order cited). Indeed, it is not easy to explain why CIT, MAL and TAR inhibited As sorption more than OX. Dynes and Huang [36] showed that the ability of 12 LMMAOs (including CIT, OX and MAL) to inhibit SeO<sub>3</sub> sorption on poorly crystalline Al hydroxides was usually correlated with the stability constant of the Al–organic solution complexes. The larger the stability constant the more effective the organic ligand was in competing with SeO<sub>3</sub> for

the sorption sites of Al precipitation products. However, some of the organic acids competed less successfully than expected based on their stability constant values. In this work, the stability constants of OX, MAL, TAR and CIT with Fe(III) (1:1) were, respectively, 7.6, 7.1, 7.4 and 11.2, so the weaker efficiency of OX with respect to MAL or TAR cannot be attributed to a lower affinity of this ligand for Fe [37]. A possible explanation is the decrease of the net surface charge after adsorption of polyvalent acids. Jara et al. [38] demonstrated that the PZC of a synthetic allophane coated with iron oxide (5% of Fe<sub>2</sub>O<sub>3</sub>) was 4.82 but shifted to lower pHs when CIT or OX anions were sorbed. In their experiments CIT decreased the PZC more than OX, precisely to 3.57 and 4.05, respectively. Probably, the addition of OX reduced the surface charge of ferrihydrite less than the other organic ligands and, consequently, OX had a lower efficiency in preventing the sorption of As(III) and As(V). Being CIT,

**Table 6**

Sorption of As(V) onto ferrihydrite at pH 6.0 in the absence and presence of inorganic and organic ligands at initial ligand/As(III) molar ratio of 1, when As(V) and a ligand were added together [As(V) + ligand systems], or As(V) was added 5 h before a ligand [As(V) before ligand systems], or when a ligand was added 5 h before As(V) [ligand before As(V) systems] 600 mmol kg<sup>-1</sup> As added.

Ligand	As(V) sorbed	Efficiency	As(V) sorbed	Efficiency	As(V) sorbed	Efficiency
	As(V) + ligand systems		As(V) before ligand systems		Ligand before As(V) systems	
	mmol kg <sup>-1</sup>	%	mmol kg <sup>-1</sup>	%	mmol kg <sup>-1</sup>	%
No ligand	600.0	–	600.0	–	600.0	–
SO <sub>4</sub>	600.0	0	600.0	0	600.0	0
SeO <sub>4</sub>	600.0	0	600.0	0	597.0 ± 12.0	0.5
SeO <sub>3</sub>	485.2 ± 12.8	19.1 ± 0.6	514.8 ± 18.9	14.2 ± 0.6	453.6 ± 20.0	24.4 ± 1.0
PO <sub>4</sub>	344.8 ± 8.7	41.1 ± 1.2	408.0 ± 20.7	32.0 ± 1.3	289.8 ± 11.3	51.7 ± 1.9
Ox	568.2 ± 13.9	5.30 ± 0.3	583.2 ± 22.4	2.8 ± 0.1	553.2 ± 14.7	7.8 ± 0.3
Mal	515.7 ± 15.8	11.9 ± 0.4	561.6 ± 21.8	6.4 ± 0.3	514.2 ± 16.8	14.3 ± 0.5
Tar	509.1 ± 11.5	13.0 ± 0.5	569.4 ± 24.3	5.1 ± 0.2	505.2 ± 13.4	15.8 ± 0.6

± Values indicate error standard (SE).

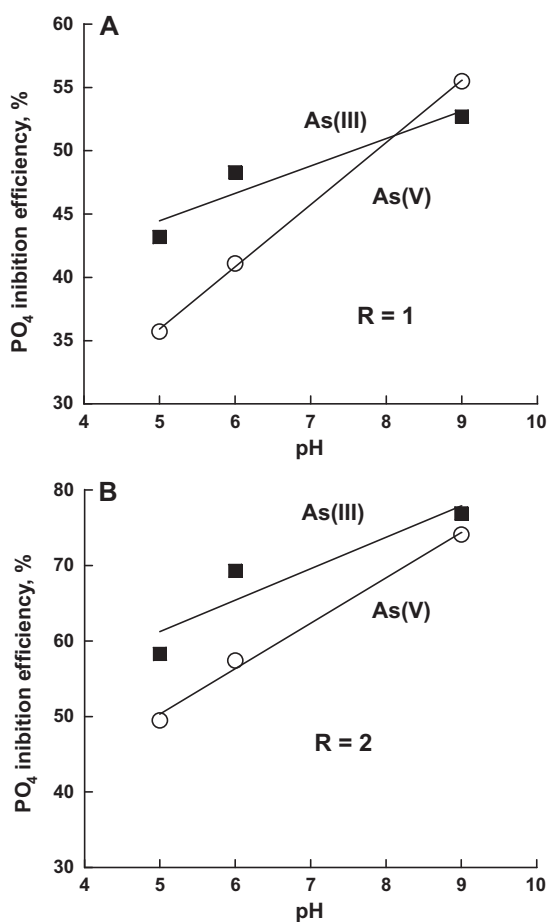


Fig. 5. Efficiency of phosphate in inhibiting arsenite and arsenate sorption onto ferrihydrite at different pH values at  $PO_4/As$  molar ratio  $R$  of 1 and 2. The surface coverage of As was near 100%.

TAR and MAL greater anions than OX a steric effect cannot be ruled out.

Our experiments were carried out in acidic systems. However, because the sorption of As(III) was much greater than that of As(V), particularly in alkaline environments (Fig. 2), it may be possible to hypothesize that at high pH values As(III) may be sorbed more effectively than As(V). For this reason, we have carried out further experiments on the effect of  $PO_4$  at pH 9.0 and at  $R=1$  and 2 on the sorption of As(III) and As(V). We found that the efficiency of  $PO_4$  was practically similar for As(III) and As(V). In fact, at  $R=1$ ,  $PO_4$  reduced As(III) and As(V) sorption of 52.7% and 55.5%, respectively, whereas at  $R=2$  reduced the sorption of As(III) and As(V) of 76.9 and 74.1, respectively. Our experiments seem to demonstrate that at high pH values both As(III) and As(V) are retained with almost the same strength on the surfaces of ferrihydrite, whereas at  $pH < 7.0$ , As(V) is sorbed with a relatively stronger strength than As(III), as depicted in Fig. 5.

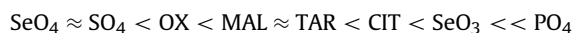
### 3.6. Effect of the sequence of anions addition on As(III) and As(V) sorption

The efficiency of inorganic and organic ligands was also studied at pH 6.0 by differently adding the competitive anions to ferrihydrite. Arsenite or As(V) were added together with the competing ligand (As + ligand systems) (Tables 3–4), 5 h before (As before ligand systems) or after the competing anions (ligand before As systems) (Tables 5 and 6).

The sequence of anions addition strongly affected the sorption of As(III) and As(V). The efficiency of the foreign anions was greater in the ligand before As systems than in the As + ligand and As before ligand systems, in the order listed [10,11]. The efficiency of the inorganic and organic ligands in all the systems was always greater in preventing As(III) than As(V) sorption. By adding each of the competing anions after As(V) (As before ligand systems), their efficiency in inhibiting As(V) sorption was drastically reduced, and precisely, 2.5–1.9 times lower for the organic ligands and about 1.3 times lower for  $SeO_3$  and  $PO_4$ , as referred to the inhibition values ascertained for As + ligand systems, whereas their efficiency in inhibiting As(III) was reduced 1.5–1.2 times by the organic ligands and about 1.2 times lower for  $SeO_3$ . Sulphate and  $SeO_4$  showed at pH 6.0 a very low but clear influence in preventing As(III) sorption, particularly in ligand before As systems (4.9–4.1%; Table 5), whereas for As(V) their influence was always negligible (Table 6).

## 4. Conclusions

The data reported in this work evidence that the sorption of As(III) and As(V) onto ferrihydrite is affected by the nature and concentration of organic and inorganic anions, pH and sequence of addition of As and the competing ligand. The efficiency of the anions studied in preventing As sorption was as follow:



However, whereas  $PO_4$  efficiency increased by increasing pH, the efficiency of the other ligands increased by decreasing pH. Furthermore, in acidic environments all the ligands inhibited the sorption of As(III) more than As(V), in spite of greater amounts of the latter were fixed on ferrihydrite in the range of pH 4.0–11.0. However, in alkaline systems As(III) and As(V) appear to be retained with the same strength.

These findings give important information on the factors which affect As mobility in soil environments, including at the soil–plant interface where low molecular mass organic ligands are continuously released.

## Acknowledgments

This work was supported by the Italian Research Program of National Interest (PRIN) for the financial support of the research (Grant number 2006073324). DiSSPAPA number 240.

## References

- [1] B.K. Mandal, K.T. Suzuki, Arsenic round the world: a review, *Talanta* 58 (2002) 201–235.
- [2] D.J. Vaughan, Arsenic, *Elements* 2 (2006) 71–75.
- [3] M. Berg, H.C. Tran, T.C. Nguyen, H.V. Pham, R. Schertenleib, W. Giger, Arsenic contamination of groundwater and drinking water in Vietnam: a human health threat, *Environ. Sci. Technol.* 35 (2001) 2621–2626.
- [4] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, *Appl. Geochem.* 17 (2002) 517–568.
- [5] W.T. Frankenberger Jr., *Environmental Chemistry of Arsenic*, Marcel Dekker, New York, 2002.
- [6] D. Chakrabarti, M.M. Rahman, K. Paul, U.K. Chowdhury, M.K. Sengupta, D. Lodh, C.R. Charda, K.C. Saha, S.C. Mukherjee, Arsenic calamity in the Indian subcontinent. What lessons have been learned? *Talanta* 58 (2002) 3–22.
- [7] E. Smith, R. Naidu, A.M. Alston, Arsenic in the soil environment: a review, *Adv. Agron.* 64 (1998) 149–195.
- [8] A. Violante, G.S.R. Krishnamurti, M. Pigna, Mobility of trace elements in soil environments, in: A. Violante, P.M. Huang, G.M. Gadd (Eds.), *Biophysico-Chemical Processes of Metals and Metalloids in Soil Environments*, John Wiley & Sons, Hoboken, 2008, pp. 169–213.
- [9] K.P. Raven, A. Jain, R.H. Loeppert, Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes, *Environ. Sci. Technol.* 32 (1998) 344–349.
- [10] A. Violante, M. Pigna, Competitive sorption of arsenate and phosphate on different clay minerals and soils, *Soil Sci. Soc. Am. J.* 66 (2002) 1788–1796.

- [11] A. Violante, S. Del Gaudio, M. Pigna, M. Ricciardella, D. Banerjee, Coprecipitation of arsenate with metal oxides. 2. Nature, mineralogy, and reactivity of iron(III) precipitates, *Environ. Sci. Technol.* 41 (2007) 8275–8280.
- [12] A. Violante, S. Del Gaudio, M. Pigna, M. Pucci, C. Amalfitano, Sorption and desorption of arsenic by soil minerals and soils in the presence of nutrients and organics, in: Q. Huang, A. Violante, P.M. Huang (Eds.), *Soil Mineral–Microbe–Organic Interactions: Theories and Applications*, Springer-Verlag, Berlin, 2008, pp. 39–69.
- [13] S. Goldberg, C.T. Johnston, Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modelling, *J. Colloid Interface Sci.* 234 (2001) 204–216.
- [14] S. Goldberg, Competitive sorption of arsenate and arsenite on oxides and clay minerals, *Soil Sci. Soc. Am. J.* 66 (2002) 413–421.
- [15] S. Dixit, J.G. Hering, Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals; implications for arsenic mobility, *Environ. Sci. Technol.* 37 (2003) 4182–4189.
- [16] B.A. Manning, S.E. Fendorf, S. Goldberg, Surface structures and stability of arsenic (III) on goethite. Spectroscopic evidence for inner-sphere complexes, *Environ. Sci. Technol.* 32 (1998) 2383–2388.
- [17] S. Fendorf, M.J. Eick, P. Grossl, D.L. Sparks, Arsenate and chromate retention mechanisms on goethite. 1. Surface structure, *Environ. Sci. Technol.* 31 (1997) 315–320.
- [18] A. Manceau, The mechanism of anion adsorption on iron oxides: evidence for the bonding of arsenate tetrahedra on free Fe(O, OH)<sub>6</sub> edges, *Geochim. Cosmochim. Acta* 59 (1995) 3647–3653.
- [19] G. Ona-Nguema, G. Morin, F. Juillot, G. Calas, G.E. Brown Jr., EXAFS analysis of arsenite adsorption onto two-line ferrihydrite, hematite, goethite, and lepidocrocite, *Environ. Sci. Technol.* 39 (2005) 9147–9155.
- [20] D.W. Oscarson, P.M. Huang, C. Defosse, A. Herbillon, Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments, *Nature* 291 (1981) 50–51.
- [21] W.P. Inskeep, T.R. McDermott, S. Fendorf, Arsenic (V)/(III) cycling in soils and natural waters: chemical and microbiological processes, in: W.T. Frankenberger Jr (Ed.), *Environmental Chemistry of Arsenic*, Marcel Dekker, New York, 2002, pp. 183–215.
- [22] M.L. Pierce, C.B. Moore, Adsorption of arsenite and arsenate on amorphous iron hydroxide, *Water Res.* 16 (1982) 1247–1253.
- [23] D.L. Sparks, *Environmental Soil Chemistry*, Academic Press, New York, 2002.
- [24] M. Grafe, M.J. Eick, P.R. Grossl, A.M. Saunders, Adsorption of arsenate and arsenite on ferrihydrite in the presence and absence of dissolved organic carbon, *J. Environ. Qual.* 31 (2002) 1115–1123.
- [25] M. Grafe, P.R. Grossl, M.J. Eick, Adsorption of arsenate(V) and arsenite(III) on goethite in the presence and absence of dissolved organic carbon, *Soil Sci. Soc. Am. J.* 65 (2001) 1680–1687.
- [26] A. Violante, S. Del Gaudio, M. Pigna, Adsorption/desorption processes of arsenate in soil environments, in: P.M. Huang, A. Violante, J.-M. Bollag, P. Vityakon (Eds.), *Soil Abiotic and Biotic Interactions and Impact on the Ecosystem and Human Welfare*, Science Publishers, Enfield, NH, 2005, pp. 269–299.
- [27] B.A. Manning, S. Goldberg, Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals, *Soil Sci. Soc. Am. J.* 60 (1996) 121–131.
- [28] A. Jain, R.H. Loeppert, Effect of competing anions on the adsorption of arsenate and arsenite by ferrihydrite, *J. Environ. Qual.* 29 (2000) 1422–1430.
- [29] F. Liu, A. De Cristofaro, A. Violante, Effect of pH phosphate and oxalate on the adsorption/desorption of arsenate on/from goethite, *Soil Sci.* 166 (2001) 197–208.
- [30] P. Hinsinger, F. Courchesne, Biogeochemistry of metals and metalloids at the soil-root interface, in: A. Violante, P.M. Huang, G.M. Gadd (Eds.), *Biophysico-Chemical Processes of Heavy Metals and Metalloids in Soil Environments*, John Wiley & Sons, Hoboken, NJ, 2008, pp. 267–311.
- [31] J.P. Quirk, Significance of surface area calculated from water vapour sorption isotherms by use of the B.E.T. equation, *Soil Sci.* 80 (1955) 423–430.
- [32] X. Sun, H.E. Doner, An investigation of arsenate and arsenite bonding structures on goethite by FTIR, *Soil Sci.* 161 (1996) 865–872.
- [33] D. Peak, E.J. Elzinga, D.L. Sparks, Understanding sulfate adsorption mechanisms of iron (III) oxides and hydroxides: results from ATR-FTIR spectroscopy, in: H.M. Selim, D.L. Sparks (Eds.), *Heavy Metals Release in Soil*, Lewis Publ., Boca Raton, FL, 2001, pp. 167–190.
- [34] D. Peak, D.L. Sparks, Mechanisms of selenate adsorption on iron oxides and hydroxides, *Environ. Sci. Technol.* 36 (2002) 1460–1466.
- [35] P.C. Zhang, D.L. Sparks, Kinetics and mechanisms of sulphate adsorption/desorption on goethite using pressure-jump relaxation, *Soil Sci. Soc. Am. J.* 54 (1990) 1266–1273.
- [36] J.J. Dynes, P.M. Huang, Influence of organic acids on selenite sorption by poorly ordered aluminum hydroxides, *Soil Sci. Soc. Am. J.* 61 (1997) 772–783.
- [37] L.G. Sillen, A.E. Martell, Stability Constants of Metal–Ion Complexes. *Spec. Pub.* 17, in: 485 p, The Chemical Society, London, 1964.
- [38] A. Jara, A. Violante, M. Pigna, M.L. Mora, Mutual interactions of sulfate, oxalate, citrate and/or phosphate on synthetic and natural allophanes, *Soil Sci. Soc. Am. J.* 70 (2006) 337–346.