

Competitive Adsorption of As(III) and As(V) by Ferrihydrite: Equilibrium, Kinetics, and Surface Complexation

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Abstract The competitive/simultaneous adsorption of arsenite (As(III)) and arsenate (As(V)) onto ferrihydrite is one of main processes controlling the distribution of arsenic under oxidizing conditions in the natural environment. Adsorption reactions of As(III) and As(V) with ferrihydrite were investigated by employing a combination of batch adsorption experiments and Fourier transform infrared (FTIR) spectroscopy measurements in single and binary systems, i.e., both As species were present at the same time. Isotherm studies showed that the adsorption of As(III) in the binary system was less than that in single system, indicating that As(V) hindered As(III) adsorption. The presence of As(III) had almost no impact on As(V) adsorption at pH 5 in the binary systems. Freundlich model described the equilibrium data well ($R^2 > 0.94$), and the adsorption affinity onto ferrihydrite was in the following order: As(III)-single > As(III)-binary > As(V)-single > As(V)-binary. Kinetic data of As(III) and As(V) from single and binary systems were both well described by pseudo-second-order equation ($R^2 > 0.98$). FTIR showed that after adsorbing of either As species, a new peak occurred at 826 cm^{-1} due to the formation of Fe-O-As bonds, indicating that competition between As(III) and As(V) could take place on the surface sites as a result of the formation of a similar surface complexes.

Keywords Competitive adsorption · As(III) and As(V) · Ferrihydrite · Equilibrium and kinetics

1 Introduction

Arsenic (As) is a contaminant that occurs naturally in many regions of the world. It is one of public concerns due to its toxic properties, which is harmful to public health (Mandal and Suzuki 2002; Villaescusa and Bollinger 2008). In aquatic environments arsenate (As(V)) and arsenite (As(III)) are the dominant inorganic species under oxidizing and reducing conditions, respectively, and their distribution generally depends on pH and redox potentials (Oremland and Stolz 2003; Price et al. 2007, 2013a, b; Smedley and Kinniburgh 2002). Under a wide range of environmental conditions, As(V) occurs as the negatively charged HAsO_4^{2-} complex, while As(III) occurs as the neutrally charged H_3AsO_3^0 complex. The adsorption of As onto solid particles in aquifer matrices plays an important role in controlling its retention and mobility in the environment (Stollenwerk 2003). Adsorption by hydrous ferric oxides (HFOs), which are common minerals, is believed to be one of the main processes controlling the distribution of As species under oxidizing conditions in natural systems (Maji et al. 2012; Pichler et al. 1999; Waychunas et al. 1993). Contaminated water often contains both As redox species, which brings importance to the study of simultaneous adsorption of As(III) and As(V) in binary systems. We previously presented new information about the competitive adsorption of As(III) and As(V) onto ferrihydrite as a function of parameters such as pHs, adsorbent

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dosages, concentration of coexisting As species, and order of addition (Qi and Pichler 2014). However, to our knowledge, there has not yet been a report to probe the mechanism of competitive adsorption of As(III) and As(V) onto ferrihydrite by a combination of batch adsorption experiments and spectroscopy measurements.

Adsorption equilibrium and dynamics are important for describing the adsorption process, and numerous papers have been reported to study the adsorption kinetics and isotherms of As in single systems (Banerjee et al. 2008; Kundu and Gupta 2006a; Maji et al. 2011, 2013a, b; Raven et al. 1998; Smith and Naidu 2009). Few studies have considered the adsorption kinetics and isotherms of As(III) and As(V) under competitive conditions. For example, Maiti et al. (2012) studied competitive adsorption kinetics of As(III) and As(V) on treated laterite. Fourier transfer infrared (FTIR) spectroscopy has been widely used as a direct approach to study the mechanism of As adsorption onto iron oxides. For example, Goldberg and Johnston (2001) found that As(V) formed inner-sphere and As(III) formed both inner and outer-sphere complexes on amorphous iron oxides using both FTIR and Raman spectroscopies. However, most spectroscopy studies were based on batch experiments of each individual As redox species, and there is no spectroscopy data available for the competitive adsorption of As(III) and As(V) on ferrihydrite.

In this study, we present new data about the competitive adsorption of As(III) and As(V) onto ferrihydrite through applicable isotherm and kinetic models both in single and binary systems. This study also provides an insight into the mechanism of competitive adsorption of the two As redox species by a combination of batch adsorption experiments and FTIR spectroscopy measurements.

2 Materials and Methods

2.1 Materials and Reagents

All of the chemicals used in the experiments were of analytical grade and used without further purification. Distilled deionized (DDI) water was used to prepare the standard solutions and dilute the samples. $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma-Aldrich, Spain) was dissolved in DDI water to obtain a primary stock solution of 1000 mg/L As(V). Another stock solution of 1000 mg/L

As(III) was prepared by dissolving As_2O_3 (Sigma-Aldrich, Spain) in a 4 % NaOH solution. All of the working As solutions were prepared by diluting the stock solutions with DDI water each time.

Ferrihydrite was synthesized by following the method used in our previous study (Qi and Pichler 2014), which consisted of adding a 1 M solution of KOH (Sigma-Aldrich, Germany) to 500 mL of a 0.2 M of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Alfa Aesar, Germany) at a constant rate, until the pH increased to 7.4 ± 0.1 until precipitation of ferrihydrite commenced. The ferrihydrite was identified as two-line ferrihydrite by X-ray diffraction analysis (XRD). The surface area of the freeze-dried ferrihydrite was $120 \text{ m}^2/\text{g}$ determined with the Brunauer-Emmett-Teller (BET) method.

2.2 Adsorption Experiments

All of the adsorption experiments were conducted with a background electrolyte of 0.01 M NaCl at room temperature around 20 °C. Possible oxidation of As(III) during the experiments was monitored following Qi and Pichler (2014), and oxidation was not observed (Qi and Pichler 2014). Kinetic experiments were undertaken in single and binary systems at pH 5 and pH 9. Exactly 50 mg of ferrihydrite was added to a series of 50-mL polythene vials and suspended in a solution containing either As(III), As(V), or a mixture of both species. Initial concentrations of As(III) and As(V) in each systems were identical (50 mg/L). The vials were capped and shaken in a Rotoshake (RS12/RS8) at 20 rpm, and the samples were taken at regular time intervals (0.083, 0.25, 0.42, 0.67, 1, 2, 4, and 24 h). After shaking, the suspensions were immediately filtered using 0.25- μm syringe filters and stored at 4 °C until determination of total As or As speciation.

Single and competitive adsorption isotherm experiments were performed at pH 5 at room temperature. For single systems, the experiments were initiated by suspending 50 mg of ferrihydrite in a solution containing either As(III) or As(V) with an initial concentration of 10, 25, 40, 50, 60, 80, 100, and 125 mg/L. For binary systems, the same dosage of ferrihydrite was suspended in a solution containing a mixture of As(III) and As(III), where each of the two species had the same initial concentration as in single systems. The pH of the suspensions was adjusted to 5 by HCl or NaOH, and the tubes were sealed and shaken continuously in a shaker for 24 h after which they were filtered and analyzed. The suspensions were filtered using syringe filters, and the

supernatant was analyzed for total As or As speciation. Adsorption capacities were calculated according to the following equation:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where Q_e (mg/g) is the equilibrium adsorption capacity; C_0 and C_e are the initial and equilibrium concentrations (mg/L), respectively; V is the volume of adsorption solution (L); and m is the mass of ferrihydrite (g).

2.3 Analytical Methods

Total concentrations of As were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using an Optima 7300 instrument (Perkin Elmer). The detection limit of As was 0.02 mg/L, and the analytical error was better than $\pm 2\%$. Concentrations of As speciation were analyzed by hydride generation-atomic fluorescence spectroscopy (HG-AFS) on a PSA 10.055 Millennium Excalibur system coupled to a liquid chromatography (LC) system. The detection limits were 0.17 $\mu\text{g/L}$ for As(III) and 0.38 $\mu\text{g/L}$ for As(V) (Wu and Pichler 2014).

2.4 Adsorption Models

2.4.1 Adsorption Isotherms

The Langmuir and Freundlich isotherm equations, probably the most common isotherm models, were used to describe the equilibrium characteristics of the adsorption experiments. The Langmuir isotherm theory assumes that the adsorption takes place on specific homogeneous sites of the adsorbent, which indicates that once an adsorbate molecule occupies a site, no further adsorption can take place at that site (Kundu and Gupta 2006b). The model is defined as:

$$q_e = \frac{bC_e q_m}{1 + bC_e} \quad (2)$$

where q_m and b can be determined from the intercept and slope of the equation; C_e is the equilibrium metal concentration (mg/L); q_e is the adsorption capacity at equilibrium (mg/g); q_m is the Langmuir adsorption capacity (mg/g); and b is the Langmuir constant (L/mg).

The Freundlich model assumes heterogeneous sorption on the surface sites with different energies (Sari et al. 2011) and is defined as:

$$q_e = K_f C_e^{1/n} \quad (3)$$

The magnitude of the value of $1/n$ generally ranges from 0 to 1 as a measure of adsorption intensity, where K_f is the constant representing the adsorption capacity.

2.4.2 Adsorption Kinetic Models

The adsorption kinetics data were assessed using first- and pseudo-second-order models, which are given by the following two equations:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where q_t and q_e represent the amount of As adsorbed at any time t and at equilibrium time, respectively; k_1 represents the first-order model adsorption rate constant (h^{-1}); and k_2 is the rate constant of sorption of pseudo-second-order model ($\text{g mg}^{-1} \text{h}^{-1}$).

2.5 FTIR Investigation

The Fourier transform infrared (FTIR) spectroscopy spectrograms of ferrihydrite before and after adsorption of As(III) and As(V) under single and binary conditions were obtained using transmission mode (Thermo-Nicolet Avatar 370 FTIR), with a wave number ranging from 400 to 4000 cm^{-1} . The samples were ground and pressed into disks mixing with dried spectral grade potassium bromide (KBr). All FTIR measurements were conducted at room temperature.

3 Results and Discussion

3.1 Single Adsorption Isotherms

Isotherm studies were performed by varying the adsorbate concentrations with a fixed adsorbent dosage. The adsorption isotherm experimental data of As(V) and As(III) under single and competitive conditions are shown in Fig. 1 as well as the non-linear fits of the isotherm models. Both the adsorption of As(III) and As(V) increased with growing initial concentrations. As(V) reached a sorption maximum

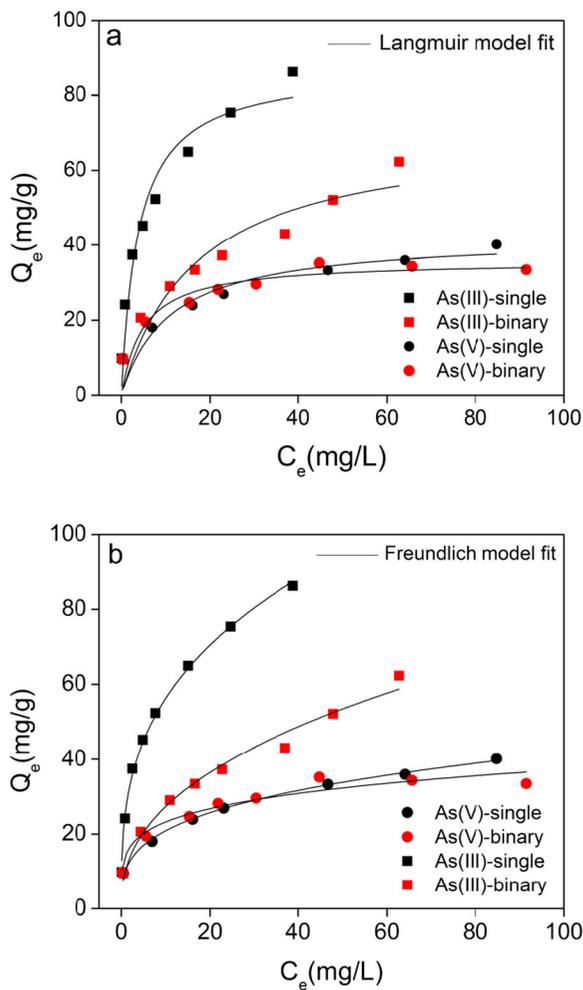


Fig. 1 Adsorption isotherms of As(III) and As(V) on ferrihydrite in single and binary systems at pH 5. The *symbols* show the experimental results, and the *solid lines* represent the non-linear fitting of **a** Langmuir adsorption and **b** Freundlich adsorption models

and achieved equilibrium at an initial As(V) concentration of 80 mg/L, whereas the adsorption of As(III) increased continuously and there was no evidence for a plateau in its adsorption isotherm. This indicates that adsorption of As(III) did not attain equilibrium in the range of concentrations studied. Moreover, As(III) was more favorably adsorbed onto ferrihydrite than As(V) particularly at high initial As concentrations, which is consistent with previous observations (Qi and Pichler 2014; Raven et al. 1998). According to electrostatic attraction, it is generally predicted that the negatively charged As(V) species should be more strongly adsorbed by iron hydroxides than the non-charged As(III) species. However, the prediction is contrary to some reported experimental results (Qi and Pichler

2014; Raven et al. 1998). The higher adsorption of As(III) onto ferrihydrite could possibly be caused by surface ligand bonding (Jain et al. 1999) or by forming of ferric arsenite on the surface sites.

The non-linear fitting parameters for the Langmuir and Freundlich models are shown in Table 1. As indicated by the value of R^2 , the Freundlich model effectively described the experimental data for both the adsorption of As(III) and As(V) in the single component systems. The constant value of K_f for As(III) was higher than for As(V), which indicated that As(III) had a significantly higher affinity for surface sites onto ferrihydrite than As(V). The better fit of the Freundlich model to our data suggests that the adsorption of As(III) and As(V) onto ferrihydrite was more likely related to multi-layer adsorption, and the surface sites were heterogeneous for As(III) and As(V) with the distribution of different adsorption energies.

3.2 Competitive Adsorption Isotherms

Under binary conditions, As(III) was more strongly adsorbed on the surface sites than As(V) at high initial adsorbate concentrations, just as observed in single systems. Moreover, the presence of As(III) seemed to have no pronounced inhibitory effect on As(V) adsorption, while As(III) adsorption was sensitive to the coexistence of As(V). The amount of adsorbed As(III) decreased in the presence of As(V) from 86 to 62 mg/g at an initial concentration of 125 mg/L, resulting in an inhibitory effect of approximately 38 %. The results of the competitive isotherm experiments demonstrated that the presence of As(III) had an insignificant influence on the adsorption of As(V), while As(III) adsorption was negatively affected by As(V) at low pH. This could be due to the fact that As(V) was strongly adsorbed on surface sites at low pH

Table 1 Comparisons of Langmuir and Freundlich isotherm model parameters for As(III) and As(V) adsorption on ferrihydrite in single and binary systems

Ion	System	Langmuir			Freundlich		
		b (L/mg)	q_m (mg/g)	R^2	K_f	n	R^2
As(V)	Single	0.09	42.39	0.873	10.5	3.34	0.997
As(V)	Binary	0.2	35.85	0.803	14.5	4.88	0.996
As(III)	Single	0.26	87.43	0.937	26.63	3.07	0.943
As(III)	Binary	0.06	71	0.892	10.51	2.41	0.978

values via coulombic force and Lewis acid-base interactions (Banerjee et al. 2008). Furthermore, the amount of adsorbed As(V) increased with growing initial concentration and then reached a plateau just as observed in the single system, while As(III) adsorption seemed to increase continuously and did not reach equilibrium.

The experimental data of the competitive adsorption experiments showed an excellent fit to the Freundlich isotherm model. A higher value of the exponent $1/n$ or K_f led to a higher affinity and greater heterogeneity of the adsorbent sites (Wu et al. 2013). As shown in Table 1, the value of K_f of As(III) obtained under binary conditions decreased remarkably compared to that obtained under single conditions, which indicates that the presence of As(V) has a negative effect on As(III) adsorption. The value of K_f of As(V) in the presence of As(III) was higher than in the single system, which implies that the addition of As(III) had no inhibitory influence on As(V) adsorption at pH 5. The surface sites on ferrihydrite for As were deemed heterogeneous, and the adsorption affinity decreased in the following order: As(III)-single > As(III)-binary > As(V)-single > As(V)-binary.

3.3 Adsorption Kinetics

The adsorption kinetic curves of As(III) and As(V) in the single and binary systems are shown in Fig. 2. The adsorption for both As(III) and As(V) was initially rapid, followed by a slower phase until gradually approached equilibrium. But some differences were found in their adsorption behavior. For example, As(III) adsorption in the single solute system occurred rapidly with over 80 % of removal after 2 h at a pH of 5, whereas the rate of As(V) adsorption was slower than that of As(III) with approximately 70 % of removal in the same time span. The rate of As(III) adsorption was independent on the solution pH, and the As(V) adsorption rates decreased with increasing pH. Similarly, Raven et al. (1998) reported that As(III) was faster adsorbed onto ferrihydrite than As(V) at relatively high initial As concentrations, and the rate of As(V) adsorption was dependent on the solution pH and was faster at low As concentrations. Zhang et al. (2007) observed that As(III) adsorption was particularly fast during the first hour, in which nearly 80 % of the As(III) was removed from solution. The adsorption of As(V) on two-line ferrihydrite increased rapidly during the first 2 h but then reached a plateau (Frau et al. 2010), which could be attributed the higher affinity of As(III) relative to As(V).

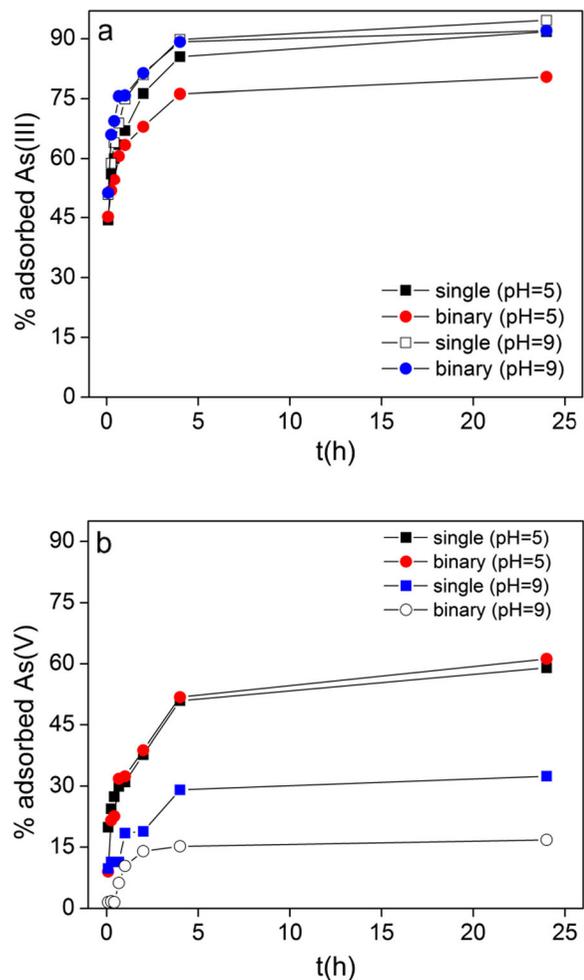


Fig. 2 Time of **a** As(III) and **b** As(V) adsorption onto ferrihydrite in single and binary systems, respectively (pHs 5 and 9; initial As concentration 50 mg/L)

As(III) adsorption in single and binary systems followed an identical pattern at pH 9. It indicates that the presence of As(V) had an insignificant influence on the adsorption rate of As(III) at higher pH values. However, the amount of adsorbed As(III) in the binary systems was less than what was observed in the single system at pH 5 at the same time intervals. For example, 68 % of As(III) was removed in the binary system, while approximately 76 % of As(III) was removed in the single system within the first 2 h. Approximately 80 and 91 % of As(III) adsorption were completed after 24 h in the binary and single systems, respectively.

It seemed that the presence of As(III) did not significantly affect the As(V) adsorption kinetics at pH 5, which is similar to the observations obtained from the isotherm studies. But As(V) adsorption was slowed and decreased in the presence of As(III) at pH 9. It could be ascribed that

As(III) is more strongly adsorbed at higher pH values and thus outcompeted As(V). A previous study reported similar results that As(V) adsorption in the presence of a non-competitor anion such as chloride was rapid but was three times slower in the presence of a stronger competitor anion such as phosphate (Frau et al. 2010).

The adsorption kinetics experimental data was analyzed by two kinetics models using linear methods, pseudo-first-order and pseudo-second-order models, as shown in Figs. 3 and 4. The adsorption rate constants and other parameters obtained from the two kinetic models are listed in Table 2. Since As(V) adsorption dramatically decreased at higher pH values, the experimental data of As(V) which were obtained at pH 9 were omitted from the model. The adsorption kinetics of As(III) and As(V) in single and binary systems were all correlated with a pseudo-second-

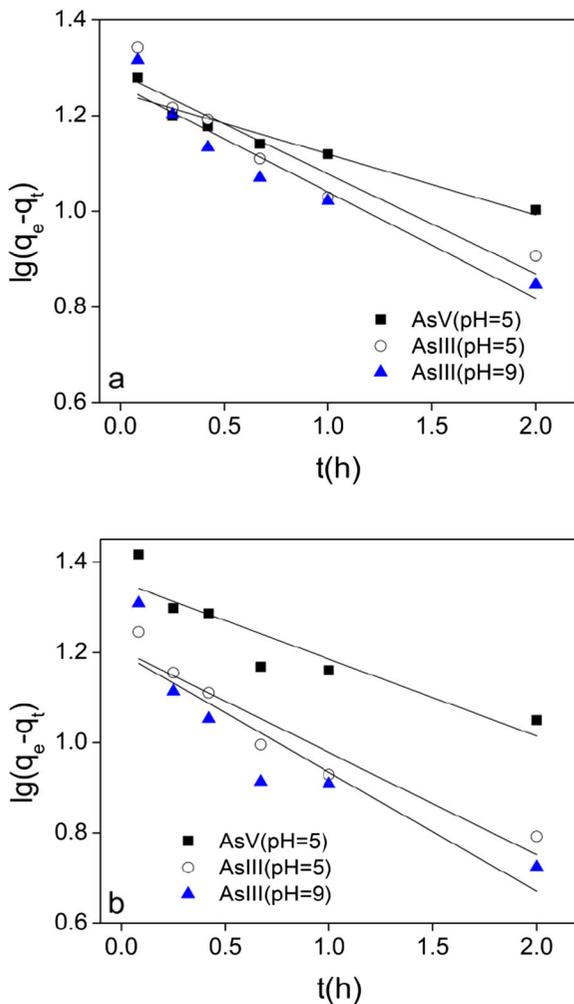


Fig. 3 Pseudo-first-order kinetic plots of As(III) and As(V) at different pH values in a single and b binary systems

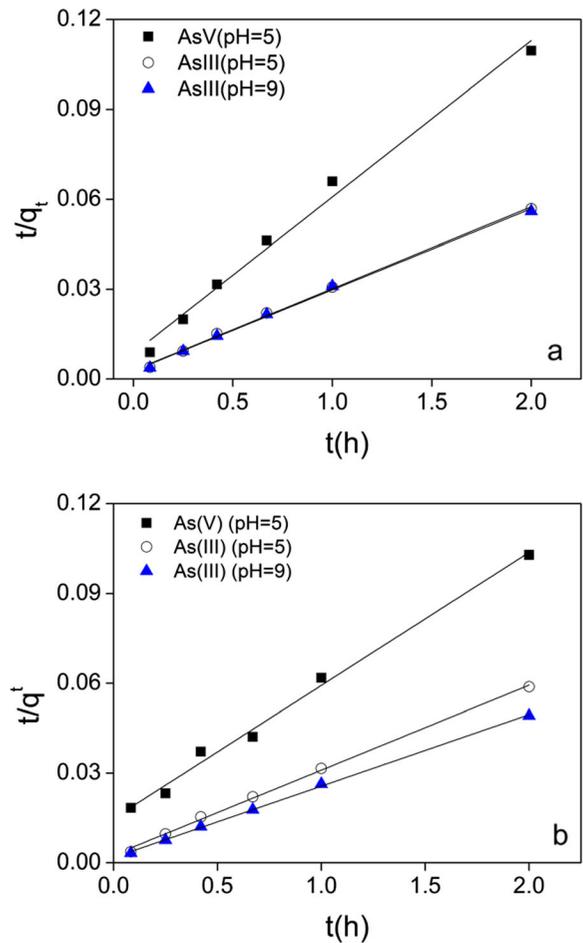


Fig. 4 Pseudo-second-order kinetic plots of As(III) and As(V) at different pH values in a single and b binary systems

Table 2 Kinetics parameters obtained from pseudo-first-order model and pseudo-second-order model

Adsorbate	pH	Single systems			Binary systems		
		k_2	q_e	R^2	k_2	q_e	R^2
Pseudo-first-order model							
As(V)	5	0.67	17.78	0.915	0.96	22.91	0.805
As(III)	5	1.11	19.50	0.885	0.86	19.95	0.90
As(III)	9	1.17	18.20	0.907	1.40	15.85	0.788
Pseudo-second-order model							
As(V)	5	0.31	19.23	0.987	0.13	22.73	0.991
As(III)	5	0.26	37.04	0.997	0.30	35.71	0.997
As(III)	9	0.27	36.95	0.997	0.29	43.48	0.999

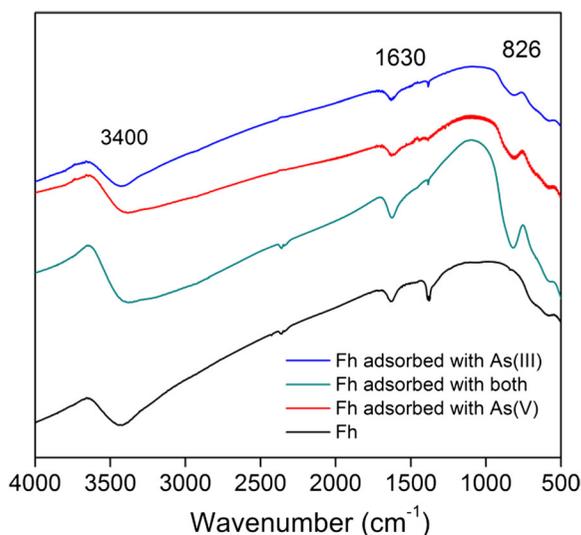


Fig. 5 Comparisons of FTIR spectra of ferrihydrite (Fh) before and after adsorbing either of the two As species or both at pH 5 and at an initial As concentration of 80 mg/L

order model with high correlation coefficients (R^2). This suggests that the two As redox species are adsorbed onto ferrihydrite by a rate-determining mechanism under both single and binary conditions. The adsorption of both As(III) and As(V) was initially fast but then slowed down, probably due to an insufficient amount of adsorption sites. The small change in the value of k_2 for As(III) either alone or in the presence of As(V) indicates that As(V) had an insignificant influence on the As(III) adsorption rate. The lower value of k_2 for As(V) in the binary system suggests that the presence of As(III) negatively affects the rate of As(V) adsorption. It seems that the influence on the adsorption rate by competition is somehow contrary to the observed for the amount of As adsorbed at equilibrium. Furthermore, according to the adsorption isotherm data, the ferrihydrite adsorption sites were not saturated for As(III), and thus the value of q_e calculated from the pseudo-second-order equation cannot be considered accurate. Consequently, although the second-order equation provides a good description for the data, some deviations could exist for our results. For example, the value of q_e calculated for As(III) in the binary system should be similar to that calculated in the single system at pH 9.

3.4 FTIR Spectra Analysis

To obtain further insights into the adsorption mechanisms of As(III) and As(V) under competitive conditions, FTIR spectroscopy was used to probe the nature of the interaction between the adsorbed As redox species and ferrihydrite. Figure 5 shows the FTIR spectra of dried ferrihydrite before and after the adsorption under both single and binary conditions at a pH of 5. The peak near 3400 cm^{-1} observed for all samples could be ascribed to OH stretching, while the peak at about 1630 cm^{-1} could be assigned to deformation and vibration of the H-O-H band for water molecules, indicating the presence of physisorbed water on ferrihydrite (Ren et al. 2011; Zhang et al. 2009). The spectra of ferrihydrite after the individual adsorption of As(III) and As(V), and simultaneous adsorption of both species had a similar shape and similar band positions (Fig. 5), suggesting that both As redox species could share a similar adsorption mechanism. After the adsorption experiments, a new peak appeared in the ferrihydrite spectra at around 826 cm^{-1} . The appearance of this peak can be assigned to the occurrence of Fe-O-As bonds, which is an indication of the possible formation of inner-sphere bonds. This implies that both the adsorption of As(III) and As(V) can be achieved through inner-sphere surface complexes with the formation of Fe-O-As bands. This is in good agreement with previous spectroscopic studies about As(V) adsorption onto ferrihydrite, which also reported that at about 830 cm^{-1} , the observed band was attributed the stretching vibration of As-O coordinated with an Fe atom (Gao et al. 2013; Jia et al. 2007). Seemingly, the competition between the two species takes place on the surface sites of ferrihydrite (as illustrated in Fig. 6). The presence of As(V) had a significant negative influence on the adsorption of As(III) at pH 5 in the binary systems, indicating that a fraction of As(III) species could not combine with the surface functional group strongly and directly. Inner-sphere complexes are in general more stable than outer-sphere complexes (Bradl 2004) and not easy to be substituted by other metal ions. Thus the competitive adsorption experimental results imply that As(V) could be strongly adsorbed onto ferrihydrite by inner-sphere complexes. As(III) could be weakly bonded on the surface sites by a combination of inner-sphere and outer-sphere



Fig. 6 A schematic of the mechanism depicting the competition between As(III) and As(V) for ferrihydrite surface sites

complexes since As(III) adsorption was negatively affected by the presence of As(V), although the FTIR spectra did not provide direct evidence for the formation of mixed inner- and outer-sphere complexes. Nevertheless, additional spectroscopic techniques are required to explore the surface properties of ferrihydrite following the simultaneous adsorption of both As species.

4 Conclusions

In this paper, the nature of the competitive adsorption of As(III) and As(V) on ferrihydrite was studied by using a combination of batch adsorption experiments and spectroscopy measurements. The isotherm studies showed that As(III) adsorption onto ferrihydrite was largely impeded by the presence of As(V) particularly at pH 5 under binary conditions, whereas the presence of As(III) had an insignificant influence on As(V) adsorption. Non-linear regression analysis was carried out to determine the best model for the equilibrium adsorption data under single and binary conditions. The adsorption under both conditions was well described by the Freundlich model, indicating that the adsorption sites on ferrihydrite for As are heterogeneous. The kinetics of As(III) and As(V) adsorption followed a pseudo-second-order model, suggesting that adsorption of both As(III) and As(V) was controlled by a rate-determining mechanism. The FTIR spectroscopy analysis offered direct evidence that both of the two As redox species could compete for ferrihydrite surface sites in binary systems, since they share a similar adsorption mechanism through the formation of Fe-O-As bonds.

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References

- Banerjee, K., Amy, G. L., Prevost, M., Nour, S., Jekel, M., Gallagher, P. M., & Blumenschein, C. D. (2008). Kinetic and thermodynamic aspects of adsorption of arsenic onto granular ferric hydroxide (GFH). *Water Research*, *42*, 3371–3378.
- Bradl, H. B. (2004). Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloid and Interface Science*, *277*, 1–18.
- Frau, F., Addari, D., Atzei, D., Biddau, R., Cidu, R., & Rossi, A. (2010). Influence of major anions on As (V) adsorption by synthetic 2-line ferrihydrite. Kinetic investigation and XPS study of the competitive effect of bicarbonate. *Water, Air, and Soil Pollution*, *205*, 25–41.
- Gao, X., Root, R. A., Farrell, J., Ela, W., & Chorover, J. (2013). Effect of silicic acid on arsenate and arsenite retention mechanisms on 6-L ferrihydrite: a spectroscopic and batch adsorption approach. *Applied Geochemistry*, *38*, 110–120.
- Goldberg, S., & Johnston, C. T. (2001). Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling. *Journal of Colloid and Interface Science*, *234*, 204–216.
- Jain, A., Raven, K. P., & Loeppert, R. H. (1999). Response to comment on “Arsenite and arsenate adsorption on ferrihydrite: surface charge reduction and net OH-release stoichiometry”. *Environmental Science and Technology*, *33*, 3696.
- Jia, Y., Xu, L., Wang, X., & Demopoulos, G. P. (2007). Infrared spectroscopic and X-ray diffraction characterization of the nature of adsorbed arsenate on ferrihydrite. *Geochimica et Cosmochimica Acta*, *71*, 1643–1654.
- Kundu, S., & Gupta, A. (2006a). Adsorptive removal of As (III) from aqueous solution using iron oxide coated cement (IOCC): evaluation of kinetic, equilibrium and thermodynamic models. *Separation and Purification Technology*, *51*, 165–172.
- Kundu, S., & Gupta, A. K. (2006b). Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization. *Chemical Engineering Journal*, *122*, 93–106.
- Maiti, A., Basu, J. K., & De, S. (2012). Experimental and kinetic modeling of As(V) and As(III) adsorption on treated laterite using synthetic and contaminated groundwater: effects of phosphate, silicate and carbonate ions. *Chemical Engineering Journal*, *191*, 1–12.
- Maji, S. K., Kao, Y. H., & Liu, C. W. (2011). Arsenic removal from real arsenic-bearing groundwater by adsorption on iron-oxide-coated natural rock (IOCNR). *Desalination*, *280*, 72.
- Maji, S. K., Kao, Y. H., Wang, C. J., Lu, G. S., Wu, J. J., & Liu, C. W. (2012). Fixed bed adsorption of As(III) on iron-oxide-coated natural rock (IOCNR) and application to real arsenic-bearing groundwater. *Chemical Engineering Journal*, *203*, 285–293.
- Maji, S. K., Wang, S. W., & Liu, C. W. (2013a). Arsenate removal from aqueous media on iron-oxide-coated natural rock (IOCNR): a comprehensive batch study. *Desalination and Water Treatment*, *51*, 7775–7790.
- Maji, S. K., Kao, Y. H., Liao, P. Y., Lin, Y. J., & Liu, C. W. (2013b). Implementation of the adsorbent iron-oxide-coated natural rock (IOCNR) on synthetic As(III) and on real arsenic-bearing sample with filter. *Applied Surface Science*, *284*, 40–48.
- Mandal, B. K., & Suzuki, K. T. (2002). Arsenic round the world a review. *Talanta*, *58*, 201–235.
- Oremland, R. S., & Stolz, J. F. (2003). The ecology of arsenic. *Science*, *300*, 939–944.
- Pichler, T., Veizer, J., & Hall, G. E. (1999). The chemical composition of shallow-water hydrothermal fluids in Tutum Bay,

- Ambitle Island, Papua New Guinea and their effect on ambient seawater. *Marine Chemistry*, 64, 229–252.
- Price, R. E., Amend, J. P., & Pichler, T. (2007). Enhanced geochemical gradients in a marine shallow-water hydrothermal system: unusual arsenic speciation in horizontal and vertical pore water profiles. *Applied Geochemistry*, 22, 2595–2605.
- Price, R. E., London, J., Wallschläger, D., Ruiz-Chancho, M. J., & Pichler, T. (2013a). Enhanced bioaccumulation and biotransformation of As in coral reef organisms surrounding a marine shallow-water hydrothermal vent system. *Chemical Geology*, 348, 48–55.
- Price, R. E., Savov, I., Planer-Friedrich, B., Bühring, S. I., Amend, J., & Pichler, T. (2013b). Processes influencing extreme As enrichment in shallow-sea hydrothermal fluids of Milos Island, Greece. *Chemical Geology*, 348, 15–26.
- Qi, P., & Pichler, T. (2014). Closer look at As(III) and As(V) adsorption onto ferrihydrite under competitive conditions. *Langmuir*, 30, 11110–11116.
- Raven, K. P., Jain, A., & Loeppert, R. H. (1998). Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes. *Environmental Science and Technology*, 32, 344–349.
- Ren, Z., Zhang, G., & Chen, J. P. (2011). Adsorptive removal of arsenic from water by an iron–zirconium binary oxide adsorbent. *Journal of Colloid and Interface Science*, 358, 230–237.
- Sari, A., Uluozlü, Ö. D., & Tüzen, M. (2011). Equilibrium, thermodynamic and kinetic investigations on biosorption of arsenic from aqueous solution by algae (*Maugeotia genulflexa*) biomass. *Chemical Engineering Journal*, 167, 155–161.
- Smedley, P. L., & Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, 17, 517–568.
- Smith, E., & Naidu, R. (2009). Chemistry of inorganic arsenic in soils: kinetics of arsenic adsorption-desorption. *Environmental Geochemistry and Health*, 31, 49–59.
- Stollenwerk, K. G. (2003). Geochemical processes controlling transport of arsenic in groundwater: a review of adsorption. In *Arsenic in ground water* (pp. 67–100).
- Villaescusa, I., & Bollinger, J.-C. (2008). Arsenic in drinking water: sources, occurrence and health effects (a review). *Reviews in Environmental Science and Bio/Technology*, 7, 307–323.
- Waychunas, G. A., Rea, B. A., Fuller, C. C., & Davis, J. A. (1993). Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. *Geochimica et Cosmochimica Acta*, 57, 2251–2269.
- Wu, D., & Pichler, T. (2014). Simultaneous speciation analysis of As, Sb and Se redox couples by SF-ICP-MS coupled to HPLC. *Analytical Methods*, 6, 5112–5119.
- Wu, Y., Wen, Y., Zhou, J., Cao, J., Jin, Y., & Wu, Y. (2013). Comparative and competitive adsorption of Cr(VI), As(III), and Ni(II) onto coconut charcoal. *Environmental Science and Pollution Research*, 20, 2210–2219.
- Zhang, G., Qu, J., Liu, H., Liu, R., & Wu, R. (2007). Preparation and evaluation of a novel Fe-Mn binary oxide adsorbent for effective arsenite removal. *Water Research*, 41, 1921–1928.
- Zhang, G., Liu, H., Liu, R., & Qu, J. (2009). Adsorption behavior and mechanism of arsenate at Fe–Mn binary oxide/water interface. *Journal of Hazardous Materials*, 168, 820–825.