Qi, Pengfei ; Pichler, Thomas

Competitive adsorption of As(III), As(V), Sb(III) and Sb(V) onto ferrihydrite in multi-component systems: Implications for mobility and distribution

Journal Article as: peer-reviewed accepted version (Postprint)

DOI of this document*(secondary publication): https://doi.org/10.26092/elib/3181

Publication date of this document: 01/08/2024

* for better findability or for reliable citation

Recommended Citation (primary publication/Version of Record) incl. DOI:

Qi, Pengfei ; Pichler, Thomas. 2017. Competitive adsorption of As(III), As(V), Sb(III) and Sb(V) onto ferrihydrite in multi-component systems: Implications for mobility and distribution. In: Journal of Hazardous Materials, vol. 330, pp. 142-148. © Elsevier. DOI: 10.1016/j.jhazmat.2017.02.016.

Competitive adsorption of As(III), As(V), Sb(III) and Sb(V) onto ferrihydrite in multi-component systems: Implications for mobility and distribution

Pengfei Qi[a,b,*], Thomas Pichler[b]

[a] College of Materials and Engineering, Qingdao University, Qingdao, China
[b] Geochemistry & Hydrogeology, Department of Geosciences, University of Bremen, Klagenfurter Straße, 28359 Bremen, Germany

HIGHLIGHTS

- Sb(III) had a stronger inhibitory influence on As(III) adsorption than Sb(V) did.
- Sb(V) adsorption was more negatively affected by As(V) than As(III).
- The affinity order of As(III), As(V), Sb(III) and Sb(V) in quaternary systems was dependent on pH.
- Competitive adsorption mainly occur between As(III) and Sb(III), or take place between As(V) and Sb(V).

Keywords:
Competitive adsorption
As(III, V)
Sb(III, V)
Multi-component
Ferrihydrite

---

[*] Corresponding author at: Geochemistry & Hydrogeology, Department of Geosciences, University of Bremen, Klagenfurter Straße, 28359 Bremen, Germany.
E-mail address: pengfei@uni-bremen.de (P. Qi).

1. Introduction

Environmental contamination by coexisting toxic elements, such as arsenic (As) and antimony (Sb), has received substantial attention because of a higher risk to human health and ecological safety. High levels of co-occurring As and Sb in waters and soils around old mining and smelting areas have been reported in many areas [1–4]. Arsenic and Sb are metalloids of the fifth main group of the periodic table sharing the same electron configuration in their outer shell (s^2p^3). They both occur in the same range of oxidation states (−3 to +5), which are mostly found in inorganic forms either as trivalent (As(III)) and (Sb(III)) species under anoxic conditions or as pentavalent (As(V) and Sb(V)) species under oxic conditions in aquatic environment. Since As and Sb are expected to share numerous similarities in chemical properties and toxicity, it is more difficult to assess and remediate the contamination of coexisting As and Sb species.

Both As and Sb can be adsorbed strongly onto hydrous ferric oxide (HFO), such as goethite, ferrihydrite and akaganeite [5–8]. They appear to exhibit a similar adsorption behavior. For example, both the adsorption of As(V) and Sb(V) was found to be dependent on pH with increased adsorption under acidic pH conditions [9,10], while the adsorption of As(III) and Sb(III) was reported as being less pH dependent [11,12]. The coexistence of other potential adsorbates could have similar influences on adsorption behavior of As and Sb. For example, sulfate (SO_4^{2-}), carbonate (HCO_3^-) and nitrate (NO_3^-) have minor influence on the individual adsorption of As and Sb, while phosphate (PO_4^-) is a well-known competitor for the adsorption of both As(V) and Sb(V) [13–16]. Moreover, As and Sb could share a similar adsorption mechanism through the formation of inner-sphere complexes [17–19]. Thus it is crucial to evaluate the simultaneous adsorption behavior of As and Sb, particularly when both compete for the surface sites. So far, few studies have been reported concerning the simultaneous removal of As and Sb. It was observed that Sb(V) adsorption was disturbed by As(V) onto akaganeite, while conversely, the addition of Sb(V) did not have any influence on the adsorption of As(V) [7]. Xu et al. [20] reported that the presence of As(III) affected Sb(V) adsorption on activated alumina slightly, while the coexistence of As(V) substantially suppressed Sb(V) adsorption. Unfortunately there has been no study focusing on the competitive adsorption of As(III,V) and Sb(III,V) in quaternary aqueous solutions, i.e., when all four possible species are present at the same time. However, around Sb mining areas the four possible redox species could occur together in waters and soils. Among the different types of hydrous ferric oxides (HFO), ferrihydrite is one of the predominant adsorbents for potentially toxic contaminants because of its large surface area and reactivity. It can be a low-cost adsorbent material for water treatment [21] and is commonly found in aquatic systems, soils and sediments. Due to its known affinity to both As and Sb, ferrihydrite should play an important role for the immobilization if both elements are present at the same time, thus it is worthy to explore the competitive/simultaneous adsorption behavior of As and Sb species.

The main objectives of this study were to compare the competitive interactions and simultaneous adsorption behavior of As(III, V) and Sb(III, V) onto ferrihydrite (1) in binary systems by varying the solution pH, (2) in ternary systems under the presence of interfering ions of NO_3^-, PO_4^{3-} and SO_4^{2-} and (3) in quaternary systems at varying pH.

2. Experimental section

2.1. Materials

All reagents used were of analytical grade. Stock Sb(III, V) and As(V) solutions were prepared by dissolving potassium antimonyl tartrate trihydrate ($C_8H_4K_2O_{12}Sb_2 \cdot 3H_2O$, Sigma-Aldrich), potassium hexahydroxoantimonate (H_6KO_6Sb, Fluka) and sodium arsenate $Na_2HAsO_4 \cdot 7H_2O$ (Sigma-Aldrich) in deionized distilled (DDI) water, respectively. Another stock solution of As(III) was prepared by dissolving As_2O_3 (Sigma-Aldrich) in a 4% NaOH solution. All working As and Sb solutions were freshly prepared each time, and the ionic strength was maintained at 0.01 M NaCl.

Ferrihydrite was prepared following an established method [12] by drop wise adding a 1 molar solution of KOH (Sigma-Aldrich, Germany) to 500 mL of a 0.2 molar $Fe(NO_3)_3 \cdot 9H_2O$ (Alfa Aesar, Germany). The suspension was kept under constant stirring until the pH increased to 7.4 ± 0.1. The precipitated material was washed with DDI water, freeze-dried, ground and stored in polyethylene bags in the refrigerator. X-ray diffraction analysis of the material confirmed two-line ferrihydrite [12]. The surface area of freeze-dried ferrihydrite was determined by the method of BET (Brunauer-Emmett-Teller) and found to be $120\,m^2/g$.

2.2. Competitive adsorption experiment setup

Adsorption experiments were conducted to study competitive interactions of either As and either Sb species in various binary systems over a wide range of pH, where 25 mg ferrihydrite was suspended in 40 mL of a solution containing one As and one Sb species. The concentration of each species in the binary experiments was 40 mg/L. The pHs of the suspensions were adjusted to 3.5, 4.5, 5.5, 6.5, 7.5 and 8.5 using 0.1 M HCl or NaOH. The tubes were capped tightly and shaken in a Rotoshake (RS12/RS18) at 20 rpm. Kinetics experiments were carried out and 24 h reaction time was adequate to reach equilibrium. After a reaction period of 24 h, the solution was filtered through a 0.45 μm membrane, and the total concentrations of As and Sb in the binary system were determined respectively.

The simultaneous adsorption experiments of As(III, V) and Sb(III, V) onto ferrihydrite were performed to study the affinity order over a wide range of pH in quaternary systems. Triplicate 40 mL solutions containing equal concentrations of the four species were prepared in 50 mL plastic tubes with an adsorbent concentration of 0.3125 g/L. The pH range in this experiment was identical as in the binary systems. Simultaneous adsorption isotherms experiments were conducted at pH 5 at room temperature around 20 °C under quaternary conditions. The experiments were initiated by suspending a fixed amount of ferrihydrite (12.5 mg) in 40 mL mixture solutions having different initial concentrations (4–25 mg/L for each species). The simultaneous speciation of As and Sb redox couples in the supernatant was determined after 24 h.

To study the influence of common interfering ions such as phosphate (PO_4^{3-}), sulfate (SO_4^{2-}) and nitrate (NO_3^-) on the simultaneous adsorption of (As(III) and Sb(III)) or (As(V) and Sb(V)), solutions containing equal concentrations of either As and Sb species with increasing concentration of one oxyanion were prepared at the adsorbent dosage of 0.625 g/L and at pH 6. The concentration ratios of the interfering ions to objective ions were 0, 0.5, 1, 2 and 2.5, where the concentrations of objective ions were kept constant. The total concentrations of As and Sb in the supernatant were determined after 24 h.

2.3. Analytical methods

The total concentrations of As and Sb were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using an Optima 7300 instrument (Perkin Elmer). The speciation analysis of As(III, V) and Sb(III, V) was conducted using double-focusing sector field-inductively coupled plasma-mass spectrometry (SF-ICP-MS) coupled to high performance liquid chromatography (HPLC) (Thermo Scientific Element 2 and Thermo

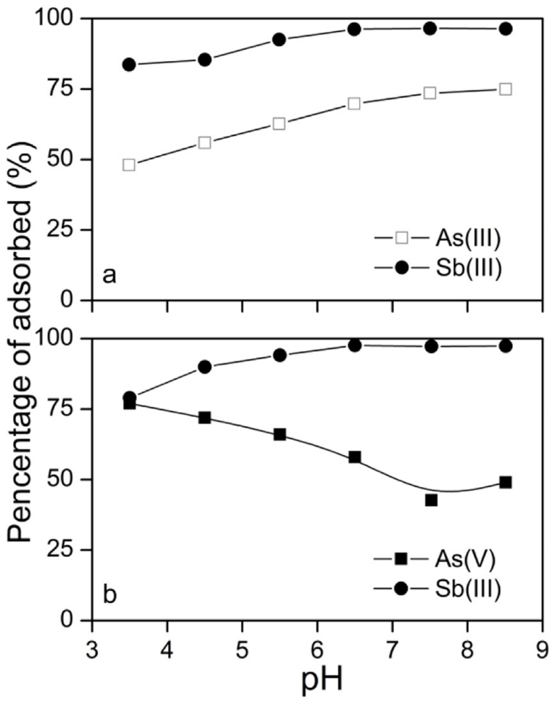

Fig. 1. Adsorption envelopes of As and Sb as a function of pH in the binary systems of As(III)/Sb(III) and As(V)/Sb(III) (initial concentration: 40 mg/L; pH: 3.5–8.5; adsorbent dosage: 0.625 g/L).

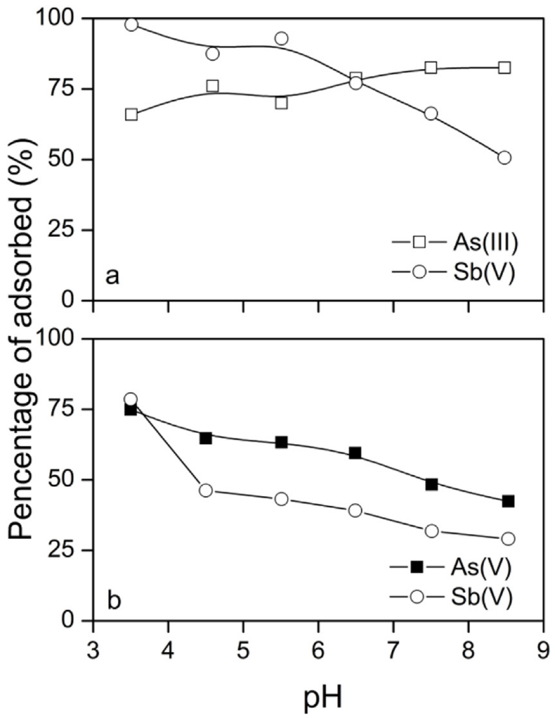

Fig. 2. Adsorption envelopes of As and Sb as a function of pH in the binary systems of As(III)/Sb(V) and As(V)/Sb(V) (initial concentration: 40 mg/L; pH: 3.5–8.5; adsorbent dosage: 0.625 g/L).

Scientific Accela 1250 Pump and an Hamilton PRP-X100) following Wu et al. [22]. The detection limits for As(III, V) and Sb(III, V) were 0.02 µg/L, 0.06 µg/L, 0.2 µg/L and 0.02 µg/L, respectively. After determination of the speciation by SF-ICP-MS, the samples were checked by hydride generation atomic fluorescence spectroscopy (HG-AFS) on a PSA 10.055 Millennium Excalibur system for speciation analysis and by ICP-OES for total concentrations. To assure precision and accuracy during all analytical procedure replicates, a certified reference material (NIST 1643e) was used and the analytical uncertainty was less than 4%. The deviation between the sum of As and Sb species, determined by SF-ICP-MS, and the total As and Sb concentrations, determined by ICP-OES or AFS was less than 10%.

3. Results

3.1. Competitive adsorption in binary systems

In Fig. 1 the simultaneous adsorption behavior of As and Sb as a function of pH is shown in the binary systems of As(III)/Sb(III) and As(V)/Sb(III). The adsorption envelopes of Sb(III) in the presence of As(III) and As(V) were similar indicating that the two As species had the same (little) effect on Sb(III) adsorption, although it seemed that at low pH, As(V) somewhat interfered with the adsorption of Sb(III). At a pH of 3.5 approximately 5% more Sb(III) were adsorbed in the presence of As(III) than in the presence of As(V), while starting at a pH of 4.5 the effect of both As species on Sb(III) adsorption was more or less identical. The adsorption percentage of As(III) increased with increasing pH from approximately 50% to 75% (Fig. 1a), while at the same time the adsorption percentage of As(V) decreased from 75% to less than 50% (Fig. 1b). The adsorption of Sb(III) was more complete than that of either As species and the percentage of adsorbed Sb(III) was close to 100% starting at pH 6.

Fig. 2 shows the adsorption behavior of As and Sb in the binary systems of As(III)/Sb(V) and As(V)/Sb(V). The adsorption envelopes of Sb(V) in the presence of As(III) and As(V) were different indicating that the two As species had a different effect on Sb(V) adsorption. At low pH As(III) had an insignificant effect on Sb(V) adsorption (Fig. 2a), while in the presence of As(V) approximately 25% less Sb(V) were adsorbed across the pH range than in the presence of As(III) (Fig. 2b). This suggests that the presence of As(V) could decrease Sb(V) adsorption to a greater extent than As(III) does. The adsorption of As(III) was less efficient in the presence of Sb(III) than that in the presence of Sb(V) (Figs. 1a and 2a). For example, at pH 3.5 and 8.5, 66% and 82.5% of As(III) were adsorbed in the presence of Sb(V), respectively, but only 48% and 75% of As(III) were adsorbed in the presence of Sb(III). In contrast to As(III), As(V) adsorption in the As(V)/Sb(III) system did not change considerably compared to that in the As(V)/Sb(V) system (Figs. 1b and 2b), indicating that the effect of the two Sb species on the adsorption of As(V) was almost similar.

3.2. Simultaneous adsorption in quaternary systems

The simultaneous adsorption behavior of As(III), As(V), Sb(III) and Sb(V) onto ferrihydrite under quaternary conditions (i.e., all four species were present at the same time) is shown in Fig. 3. Regardless of pH Sb(III) was always adsorbed stronger than the other three species. More than 90% of Sb(III) were removed starting at a pH of more than 6. In general the adsorption behavior seemed identical to that in the binary systems, where the adsorption of Sb(III) and As(III) increased with increasing pH, while the adsorption of As(V) and Sb(V) decreased with increasing pH. At a pH less than 4, As(III) showed the lowest affinity compared to the other three species. However, the adsorption percentages of As(III), As(V) and Sb(V) were more or less identical at a pH of 4.5. The adsorption of As(III) exceeded both As(V) and Sb(V) adsorption at a pH above 5, while As(V) showed slightly stronger adsorption than Sb(V) at a pH above 5. The affinity for adsorption onto ferrihydrite was in the order of Sb(III) > As(V) ≈ Sb(V) > As(III) at a pH of below 4 and in the order of Sb(III) > As(III) > As(V) > Sb(V) at a pH of above 5. The

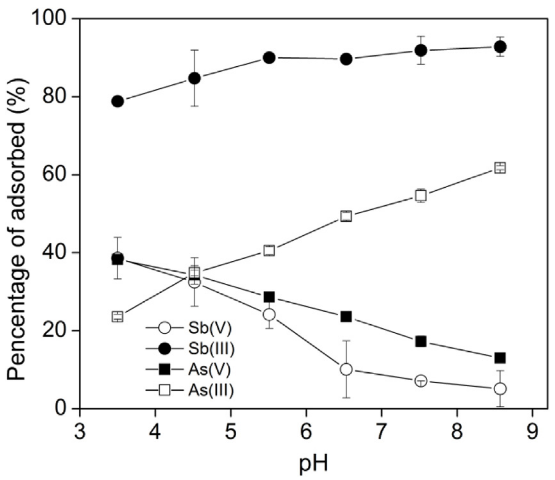

Fig. 3. Simultaneous adsorption envelopes of As(III), As(V), Sb(III) and Sb(V) as a function of pH in the quaternary systems (initial concentration: 20 mg/L; pH: 3.5–8.5; adsorbent dosage: 0.3125 g/L).

adsorption efficiency under quaternary conditions was less for all species compared to that under binary conditions (Fig. 3). At low pH As(III) was affected the most, while at higher pH As(V) and Sb(V) adsorption diminished more. The adsorption of Sb(III) was affected the least and the strongest affected was Sb(V).

3.3. *Simultaneous adsorption isotherm studies*

Fig. 4 shows the simultaneous adsorption experimental results in quaternary system and the non-linear adsorption isotherm fittings for the experimental data. Sb(III) showed the strongest adsorption ability independent of initial concentrations. As(III) displayed a slightly stronger adsorption affinity than As(V) and Sb(V) with increasing initial concentrations. Although Sb(III) showed the strongest adsorption affinity but did not reach saturation since there was no development of a plateau in its adsorption envelope. This was in contrast to As(III), As(V) and Sb(V), which almost reached an adsorption maximum. Thus only As(III), As(V) and Sb(V) were fitted with the adsorption isotherm models. Two widely used isotherms are the Langmuir and Freundlich isotherms [23]. The Langmuir isotherm theory assumes that the adsorption takes place on the specific homogeneous sites of the adsorbent [24]:

$$C^* = \frac{\alpha\beta C}{1 * \alpha C} \tag{2}$$

where α is an adsorption constant related to binding energy (L/mg) and β is the maximum adsorption capacity (mg/kg) and C is the concentration of solute in equilibrium with the mass of solute adsorbed onto the solid phase. The Freundlich model on the other hand assumes heterogeneous adsorption on the surface sites with different energies [25]. The equation is:

$$C^* = KC^n \tag{3}$$

where K and n are constants.

The Freundlich model was preferred for adsorption of As(III) and As(V) in the quaternary systems, as indicated by the correlation coefficient. However the Langmuir model better described the adsorption of Sb(V). Since Sb(V) adsorption was negatively affected by the presence of As(V), this suggests that the adsorption sites were not specific for Sb(V). The Freundlich model assumes that the surface sites are heterogeneous and multilayered. Conversely speaking, this is in agreement with the observed competition between As and Sb on the surface sites.

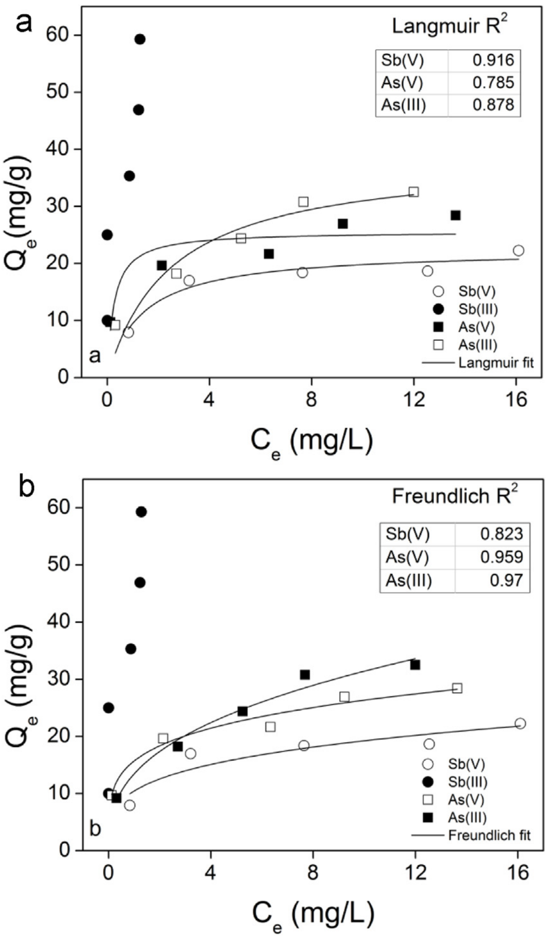

Fig. 4. Adsorption isotherms for simultaneous adsorption of As(III), As(V), Sb(III) and Sb(V) onto ferrihydrite under quaternary conditions at pH 5. The symbols show the experimental results and the solid lines represent the non-linear fitting for: (a) Langmuir adsorption and (b) Freundlich adsorption models.

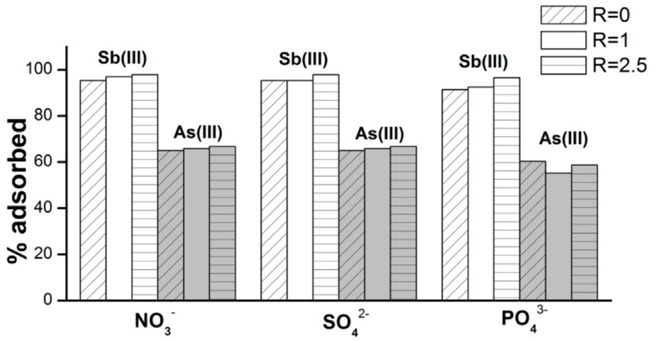

Fig. 5. The simultaneous adsorption behavior of As(III) and Sb(III) under the presence of increasing amounts of oxyanions (SO_4^{2-}, PO_4^{3-}, NO_3^-) in the ternary systems (initial concentration: 40 mg/L; pH: 6; concentration ratios of competing ions with objective ions R = 0, 1 and 2.5).

3.4. *Effect of interferences in ternary systems*

The influences of the oxyanions NO_3^-, PO_4^{3-} and SO_4^{2-} on the simultaneous adsorption of As(III) and Sb(III) are presented in Fig. 5, showing that none of the three oxyanions had a distinct influence on the simultaneous adsorption behavior of the two trivalent species. At pH 6 both As(III) and Sb(III) were adsorbed in the same proportions as in the binary systems without interfering oxyanions (Fig. 1), moreover, their adsorption envelopes remained more or

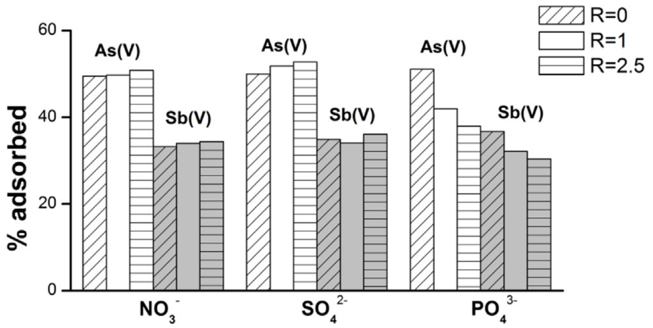

Fig. 6. The simultaneous adsorption behavior of As(V) and Sb(V) under the presence of increasing amounts of oxyanions (SO_4^{2-}, PO_4^{3-}, NO_3^-) in the ternary systems (initial concentration: 40 mg/L; pH: 6; concentration ratios of competing ions with objective ions R = 0, 1 and 2.5).

less constant across the range of NO_3^-, PO_4^{3-} and SO_4^{2-} concentrations studied. The adsorption of Sb(III) was always more complete than that of As(III), indicating that the three oxyanions are no competition for the surface sites under ternary conditions nor do they affect the order of adsorption affinity of As(III) and Sb(III).

Fig. 6 showed the simultaneous adsorption behavior of As(V) and Sb(V) in the presence of coexisting ions of NO_3^-, PO_4^{3-} and SO_4^{2-}. The adsorption envelopes of As(V) and Sb(V) in the presence of NO_3^- were similar to that in the presence of SO_4^{2-}, but a difference was discovered in the presence of PO_4^{3-}. The adsorption of As(V) decreased noticeably with increasing of PO_4^{3-} concentration, while the adsorption of Sb(V) also decreased, but to a lesser extent (Fig. 6).

4. Discussion

4.1. Competitive interactions between As and Sb

In the binary and ternary systems Sb(III) was more strongly adsorbed by ferrihydrite than As(III) (Fig. 1a and Fig. 5), as well as in the quaternary systems (Fig. 3). The removal of Sb(III) being preferred to As(III) was reported previously [26,27]. The relatively stronger adsorption of Sb(III) compared to As(III) could be attributed that Sb(III) is a stronger Lewis base than As(III) [28], having a higher pK_a value (pK_{a1} (H_3AsO_3) = 9.22; pK_a ($Sb(OH)_3$) = 11.9). The iron hydroxides are frequently amphoteric, and if considering the surface sites of ferrihydrite as Lewis acids, the interaction between Sb(III) and the surface sites would be stronger than for As(III). Moreover, the adsorption of As(III) was weaker in the presence of Sb(III) compared to its adsorption in the presence of Sb(V) (Figs. 1a and 2a), suggesting that Sb(III) is a stronger competitor for As(III) adsorption by ferrihydrite than Sb(V). It is ascribed that As(III) and Sb(III) have similar atomic structures and species distribution [29].

As(V) was adsorbed more effectively than Sb(V) onto ferrihydrite in the binary systems except at the low pH of 3.5 (Fig. 2b). This was also confirmed under ternary conditions in the presence of interfering oxyanions (Fig. 6). Under quaternary conditions, As(V) showed slightly higher adhesion ability than Sb(V) from pH more than 5 (Fig. 3). Firstly, as reviewed by Wilson et al. [29], the observed successive deprotonation of arsenic acid (H_3AsO_4) (pK_1 = 2.2; pK_2 = 6.97) caused the As(V) complex to reach a higher negative charge, in contrast to the single deprotonation of antimonic acid (H_3SbO_4) (pK_a = 2.72), i.e., $HAsO_4^{2-}$ vs. $H_2SbO_4^-$. A more positive charge could be required from the surface adsorption sites to offset and balance the more negatively charged As(V). Secondly, the coordination of Sb(V) with oxygen is octahedral and has a larger spatial structure (radius ratio: Sb(V)/O = 0.51) than that of As(V) species (radius ratio: As(V)/O = 0.4) [30], which could lead to a weaker adsorption of Sb(V) than As(V). Thirdly, in the presence of ferrihydrite Sb(III) is easier oxidized to Sb(V) than As(III) to As(V). The stronger Sb(III) oxidation might be prone to lead to more formed Sb(V) retaining in the aqueous phase if there are insufficient adsorption sites. Due to the stronger competition between As(V) and Sb(V), Sb(V) adsorption in the presence of As(V) was less effective than that in the presence of As(III) (Fig. 2).

The coexisting ion of PO_4^{3-} appeared to have no influence on the adsorption of Sb(III) and As(III). However, the adsorption of As(V) and Sb(V) was impeded, and PO_4^{3-} had a stronger negative influence on As(V) adsorption than on Sb(V) adsorption under ternary conditions (Fig. 6). Similar results were reported that the adsorption of Sb(V) was disturbed to a higher extent by As(V) than by PO_4^{3-} onto akaganeite, and As(V) adsorption was only disturbed by PO_4^{3-} [7]. The stronger competition between As(V) and PO_4^{3-} could be ascribed to the fact that the structures of As(V) and PO_4^{3-} are analogous with tetrahedral linkages and similar pK_a values, while Sb(V) is octahedral coordinated to 6 oxygen atoms [7,31].

Looking at the adsorption envelopes in the binary systems it becomes clear that the presence of Sb(III) had a more inhibitory effect on As(III) adsorption, and the presence of As(V) had a stronger negative influence on Sb(V) adsorption. It suggests that the competition mainly occurs between Sb(III) and As(III) or between Sb(V) and As(V) under binary conditions. Similarly, As(III) adsorption on activated alumina decreased with increasing Sb(III) at both low and high initial concentrations [32]. Another study also concluded that the coexisting As(V) substantially suppressed Sb(V) adsorption on activated alumina [20]. But taken together our previous and current results, as shown in Fig. 6, not merely Sb(III) but also As(V) had a significant negative influence on As(III) adsorption particularly at low pH, which could cause the lowest adsorption efficiency for As(III) at a pH of 3.5 in the quaternary system. In addtiion, both the presence of Sb(III) and As(V) significantly reduced the adsorption efficiency of Sb(V) under binary conditions (Fig. 7). Under quaternary conditions Sb(III) showed a distinctly stronger affinity onto ferrihydrite than any of the other three species (Fig. 3). However, only Sb(III) envelopes under quaternary conditions (less adsorption sites available) was more or less identical to those in the binary systems (Fig. 7), clearly demonstrating that Sb(III) easily outcompetes the other species. Thus, based on observations of the competitive interaction between As and Sb made in our present and previous studies, it is indicated that Sb(III) and As(V) are strongly adsorbed on ferrihydrite through specific interaction. Since both species can strongly bind with the hydroxyl functional groups on the ferrihydrite surface via specific interaction, they have the competitive edge compared to other species. Whereas a combination of outer- and inner-sphere complexes seemed to be the case for As(III) and Sb(V) adsorption, indicating that at least a fraction of the adsorbates are non-specifically and thus weakly bonded to the surface of ferrihydrite by simple electrostatics interaction. This would be in agreement with our results that both the presence of As(V) and Sb(III) have significant adverse effects on the adsorption of As(III) and Sb(V). Evidence of a combination of outer- and inner-sphere complexes had also been reported for Sb(V) adsorption on iron modified aerobic granules [33] and for As(III) adsorption on iron oxides [34]. An inner-sphere formation of bidentate mononuclear edge-sharing between Sb(III) and HFO was reported by using extended X-ray absorption fine structure (EXAFS) [11]. More spectroscopy evidence are requisite to explore the competitive adsorption mechanism of As(III,V) and Sb(III,V) on mineral phase.

4.2. Implications of competition

Knowledge about the competitive/simultaneous removal of individual adsorbates in a multi-component system where sev-

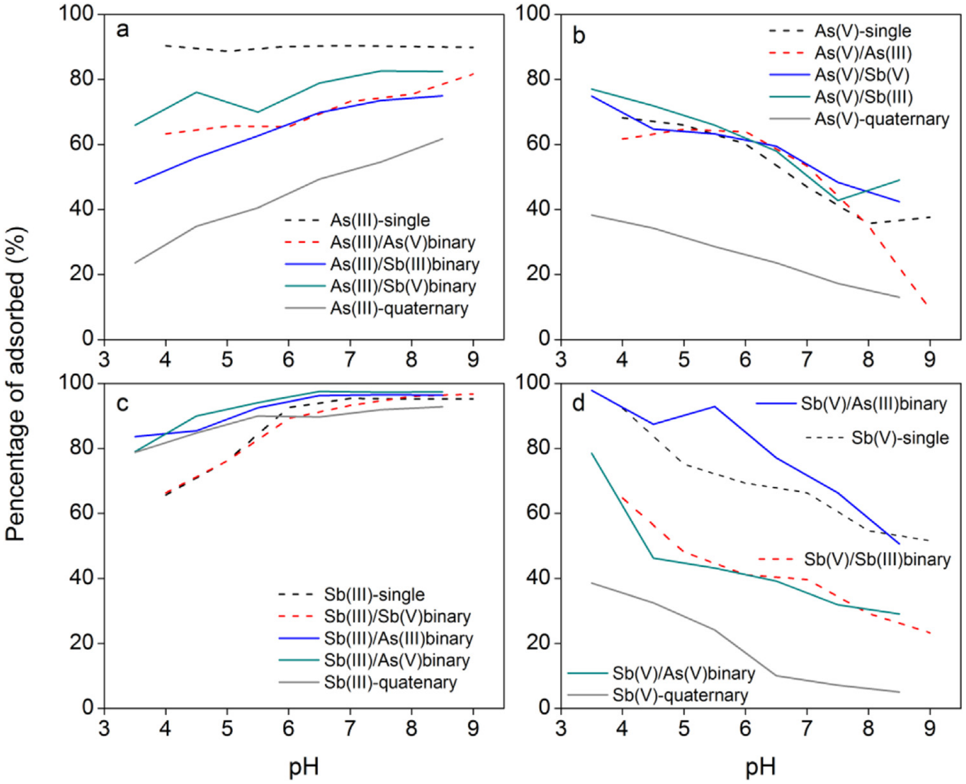

Fig. 7. Overview of the adsorption envelopes for each species of As(III) (a), As(V) (b), Sb(III) (c) and Sb(V) (d) in single, various binary and quaternary systems.

eral adsorbates compete for the same adsorption sites is crucial to understand their fate, mobility and transport in the environment. For example, the competition for adsorption sites most likely contributed to the observed distribution of As and Sb species and the evident discrepancies of their geochemical behavior in mine waters [35]. The much stronger adsorption of As(III) than As(V) may also explain the unusual species distribution in natural aqueous systems [36]. According to the results of our study, in the presence of iron hydrous oxides and under redox conditions, which would allow the presence of the four redox species, Sb(V) could be the most dominant species in solution since it was outcompeted by the other adsorbates and had the lowest adsorption capacity. The presence or absence of Sb(III) would have a tremendous impact on the mobility of As(III), As(V) and Sb(V) since Sb(III) is preferentially adsorbed. The mobility of As(III) is particularly enhanced at low pH (Fig. 3).

Under quaternary conditions, since As(III) adsorption was affected strongest at low pH and both As(V) and Sb(V) adsorption diminished at higher pH, ferrihydrite could have the highest efficiency for the simultaneous removal of As and Sb from aqueous media around neutral pH values. With increasing pH As(III) was adsorbed stronger than As(V) and Sb(V). Thus increasing pH in an environmental system, such as mine water, has the advantage that the trivalent species are preferentially removed from an aqueous phase. Moreover, given that both Sb(III) and As(III) are approximately ten times more toxic than Sb(V) and As(V), this behavior may reduce toxicological risks especially in areas contaminated by co-existing As(III), As(V), Sb(III) and Sb(V).

5. Conclusions

Our study demonstrated that ferrihydrite is a potential effective adsorbent for the simultaneous removal of As(III), As(V), Sb(III) and Sb(V) in multi-component systems. The four possible redox species did compete for the available surface sites. Both the adsorption of As(III) and Sb(V) onto ferrihydrite was obviously reduced as a result of the addition of Sb(III) and As(V), but on the other hand the presence of As(III) and Sb(V) did not play any significant role in the adsorption of Sb(III) and As(V). The adsorption affinities of As and Sb in the quaternary systems were related to pH, which was in the order of Sb(III) > As(V) ≈ Sb(V) > As(III) at a pH of below 4 and Sb(III) > As(III) > As(V) > Sb(V) at a pH of above 5. The simultaneous isotherm adsorption in quaternary systems were well described by the Freundlich model, suggesting the heterogeneous nature of the surface sites for As and Sb adsorption onto ferrihydrite. An improved understanding of the simultaneous/competitive adsorption of the four possible redox species also contribute to a better understanding of their mobility and transport in the environment. Sb(V) could be the dominant species in the presence of iron hydrous oxides and redox conditions since Sb(V) was significantly affected and had the lowest adsorption capacity.

Acknowledgements

We acknowledge Laura Knigge for her help on measuring the samples by ICP-OES. We also thank Debo Wu for his help measuring the samples by ICP-MS, and Britta Hinz for English editing. PQ thanks the China Scholarship Council (CSC) and University of Bremen for financial support. TP acknowledges support by the German Research Foundation (DFG) INST 144/288-1.

References

[1] E. Hiller, B. Lalinská, M. Chovan, Ľ. Jurkovič, T. Klimko, M. Jankulár, R. Hovorič, P. Šottník, R. Fľaková, Z. Ženišová, Arsenic and antimony contamination of waters, stream sediments and soils in the vicinity of abandoned antimony mines in the Western Carpathians, Slovakia, Appl. Geochem. 27 (2012) 598–614.

[2] M. He, X. Wang, F. Wu, Z. Fu, Antimony pollution in China, Sci. Total Environ. 421 (2012) 41–50.

[3] F. Wu, Z. Fu, B. Liu, C. Mo, B. Chen, W. Corns, H. Liao, Health risk associated with dietary co-exposure to high levels of antimony and arsenic in the world's largest antimony mine area, Sci. Total Environ. 409 (2011) 3344–3351.

[4] Y. Serfor-Armah, B. Nyarko, S. Dampare, D. Adomako, Levels of arsenic and antimony in water and sediment from Prestea, a gold mining town in Ghana and its environs, Water Air Soil Pollut. 175 (2006) 181–192.

[5] A.-K. Leuz, H. Mönch, C.A. Johnson, Sorption of Sb(III) and Sb(V) to goethite: influence on Sb(III) oxidation and mobilization, Environ. Sci. Technol. 40 (2006) 7277–7282.

[6] P. Qi, T. Pichler, Sequential and simultaneous adsorption of Sb(III) and Sb(V) on ferrihydrite: implications for oxidation and competition, Chemosphere 145 (2016) 55–60.

[7] F. Kolbe, H. Weiss, P. Morgenstern, R. Wennrich, W. Lorenz, K. Schurk, H. Stanjek, B. Daus, Sorption of aqueous antimony and arsenic species onto akaganeite, J. Colloid Interface Sci. 357 (2011) 460–465.

[8] J. Zhu, M. Pigna, V. Cozzolino, A.G. Caporale, A. Violante, Sorption of arsenite and arsenate on ferrihydrite: effect of organic and inorganic ligands, J. Hazard. Mater. 189 (2011) 564–571.

[9] K.A. McComb, D. Craw, A.J. McQuillan, ATR-IR spectroscopic study of antimonate adsorption to iron oxide, Langmuir 23 (2007) 12125–12130.

[10] J. Xi, M. He, C. Lin, Adsorption of antimony(V) on kaolinite as a function of pH, ionic strength and humic acid, Environ. Earth Sci. 60 (2010) 715–722.

[11] X. Guo, Z. Wu, M. He, X. Meng, X. Jin, N. Qiu, J. Zhang, Adsorption of antimony onto iron oxyhydroxides: adsorption behavior and surface structure, J. Hazard. Mater. 276 (2014) 339–345.

[12] P. Qi, T. Pichler, Closer look at As(III) and As(V) adsorption onto ferrihydrite under competitive conditions, Langmuir 30 (2014) 11110–11116.

[13] S. Luther, N. Borgfeld, J. Kim, J. Parsons, Removal of arsenic from aqueous solution: a study of the effects of pH and interfering ions using iron oxide nanomaterials, Microchem. J. 101 (2012) 30–36.

[14] B.K. Biswas, J.-i. Inoue, H. Kawakita, K. Ohto, K. Inoue, Effective removal and recovery of antimony using metal-loaded saponified orange waste, J. Hazard. Mater. 172 (2009) 721–728.

[15] Z. He, R. Liu, H. Liu, J. Qu, Adsorption of Sb(III) and Sb(V) on freshly prepared ferric hydroxide (FeOxHy), Environ. Eng. Sci. 32 (2015) 95–102.

[16] G. Zhang, H. Liu, R. Liu, J. Qu, Adsorption behavior and mechanism of arsenate at Fe–Mn binary oxide/water interface, J. Hazard. Mater. 168 (2009) 820–825.

[17] M. Vithanage, A.U. Rajapaksha, X. Dou, N.S. Bolan, J.E. Yang, Y.S. Ok, Surface complexation modeling and spectroscopic evidence of antimony adsorption on iron-oxide-rich red earth soils, J. Colloid Interface Sci. 406 (2013) 217–224.

[18] V.K. Mittal, S. Bera, S. Narasimhan, S. Velmurugan, Adsorption behavior of antimony(III) oxyanions on magnetite surface in aqueous organic acid environment, Appl. Surf. Sci. 266 (2013) 272–279.

[19] X. Sun, H.E. Doner, An investigation of arsenate and arsenite bonding structures on goethite by FTIR, Soil Sci. 161 (1996) 865–872.

[20] Y.H. Xu, A. Ohki, S. Maeda, Adsorption and removal of antimony from aqueous solution by an activated alumina, Toxicol. Environ. Chem. 80 (2001) 133–144.

[21] X. Meng, G.P. Korfiatis, C. Christodoulatos, S. Bang, Treatment of arsenic in Bangladesh well water using a household co-precipitation and filtration system, Water Res. 35 (2001) 2805–2810.

[22] D. Wu, T. Pichler, Simultaneous speciation analysis of As, Sb and Se redox couples by SF-ICP-MS coupled to HPLC, Anal. Methods 6 (2014) 5112–5119.

[23] C. Travis, E.L. Etnier, A survey of sorption relationships for reactive solutes in soil, J. Environ. Qual. 10 (1981) 8–17.

[24] S. Kundu, A.K. Gupta, Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization, Chem. Eng. J. 122 (2006) 93–106.

[25] A. Sarı, Ö.D. Uluozlü, M. Tüzen, Equilibrium, thermodynamic and kinetic investigations on biosorption of arsenic from aqueous solution by algae (Maugeotia genuflexa) biomass, Chem. Eng. J. 167 (2011) 155–161.

[26] C. Shan, Z. Ma, M. Tong, Efficient removal of trace antimony(III) through adsorption by hematite modified magnetic nanoparticles, J. Hazard. Mater. 268 (2014) 229–236.

[27] X. Guo, Z. Wu, M. He, Removal of antimony(V) and antimony(III) from drinking water by coagulation–flocculation–sedimentation (CFS), Water Res. 43 (2009) 4327–4335.

[28] A. Leuz, H. Mönch, C.A. Johnson, Sorption of Sb(III) and Sb(V) to goethite: influence on Sb(III) oxidation and mobilization, Environ. Sci. Technol. 2006 (2006) 7277–7282.

[29] S.C. Wilson, P.V. Lockwood, P.M. Ashley, M. Tighe, The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: a critical review, Environ. Pollut. 158 (2010) 1169–1181.

[30] L. Pauling, The formulas of antimonic acid and the antimonates, J. Am. Chem. Soc. 55 (1933) 1895–1900.

[31] A.C. Scheinost, A. Rossberg, D. Vantelon, I. Xifra, R. Kretzschmar, A.-K. Leuz, H. Funke, C.A. Johnson, Quantitative antimony speciation in shooting-range soils by EXAFS spectroscopy, Geochim. Cosmochim. Acta 70 (2006) 3299–3312.

[32] F. Bullough, D.J. Weiss, W.E. Dubbin, B.J. Coles, J. Barrott, A.K. SenGupta, Evidence of competitive adsorption of Sb(III) and As(III) on activated alumina, Ind. Eng. Chem. Res. 49 (2010) 2521–2524.

[33] L. Wang, C.-L. Wan, Y. Zhang, D.-J. Lee, X. Liu, X. -f. Chen, J.-H. Tay, Mechanism of enhanced Sb(V) removal from aqueous solution using chemically modified aerobic granules, J. Hazard. Mater. 284 (2015) 43–49.

[34] S. Goldberg, C.T. Johnston, Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling, J. Colloid Interface Sci. 234 (2001) 204–216.

[35] S.E. Fawcett, H.E. Jamieson, D.K. Nordstrom, R.B. McCleskey, Arsenic and antimony geochemistry of mine wastes, associated waters and sediments at the Giant Mine, Yellowknife, Northwest Territories, Canada, Appl. Geochem. 62 (2015) 3–17.

[36] R.E. Price, J.P. Amend, T. Pichler, Enhanced geochemical gradients in a marine shallow-water hydrothermal system: unusual arsenic speciation in horizontal and vertical pore water profiles, Appl. Geochem. 22 (2007) 2595–2605.