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Competitive sorption of arsenic and antimony onto synthetic ferrous sulfide

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Abstract

Purpose The competitive sorption of arsenite, As(III), and antimonite, Sb(III) on mackinawite (FeS) was investigated, so as to better understand the influence between As(III) and Sb(III) in anaerobic water, soil, or sediment systems rich in FeS.

Methods FeS was synthesized and As(III) and Sb(III) were simultaneously or sequentially added into the FeS suspensions, so as to simulate the competitive sorption of As(III) and Sb(III) on the surface of FeS particles when As(III) and Sb(III) were parallelly sorbed or As(III) sorption was priorly aged.

Results It was found that As(III) uptake by FeS could be significantly inhibited by Sb(III) at pH 7.0. When As(III) (initial concentration: 1 mg L^{-1}) and Sb(III) were simultaneously added into FeS suspensions at pH 7.0, the presence of Sb(III) reduced the As(III) uptake by FeS from 51.8% (no Sb(III) added) to 22.7% (1 mg L^{-1} Sb(III) added) and to 6.9% (5 mg L^{-1} Sb(III) added), respectively. In contrast, As(III) uptake by FeS was only slightly inhibited at pH 5.5 and not inhibited at pH 9.0. It was postulated that the competitive sorption of As(III) and Sb(III) was primarily associated with the binding of As(III) and Sb(III) to FeS at the sulfur sites and the different chalcophility of Sb(III) and As(III) led to the significant replacement of As(III) by Sb(III) at pH 7.0. It was also found that aging of As(III) sorption significantly reduced the amount of As(III) that was outcompeted by Sb(III).

Conclusion This study revealed the competitive sorption of As(III) and Sb(III) on FeS particles, and implicated the importance of competitive sorption in evaluating the mobilization or immobilization of arsenic or antimony in iron- and sulfur-rich anaerobic lake sediments or soils.

Keywords FeS · Arsenic · Antimony · Competitive sorption

1 Introduction

Arsenic (As) and antimony (Sb) are toxic metalloids of global concern (Amarasiriwardena and Wu 2011; Kulp et al. 2014). In environmental systems, both As and Sb predominantly exist as oxyanions, such as $H_2AsO_4^-$, $HAsO_4^{2-}$ (As(V)) and $Sb(OH)_6^-$ (Sb(V)) in relatively oxic environments or H_3AsO_3 (As(III)) and $Sb(OH)_3$ (Sb(III)) in anoxic environments (Filella et al. 2002; Wilson et al. 2010). Because As and Sb usually exhibit similar geochemical behavior (Wilson et al. 2010), co-existence of As and Sb contamination could be found in surface water and sediment systems (Mok and Wai 1990; Casiot et al. 2007; Fawcett et al. 2015).

The mobility of metal(loid)s in the environment has been recognized to be highly related to iron minerals. On the surface of ferric (hydr)oxides minerals, the sorption of As and Sb affected by co-existing anions has been widely

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Highlights

- As(III) sorption on FeS was inhibited by Sb(III).
- The competitive sorption of As(III) and Sb(III) was strongest at neutral pH.
- Aging of As(III) sorption weakened the competitive effect of Sb(III).

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investigated. For example, PO_4^{3-} is a well-known anion that significantly affects the sorption of As(V) and Sb(V) on iron (hydr)oxides (Griggs et al. 2011; Marzi et al. 2022). Sulfate, Cl^-, HCO_3^-, and NO_3^- generally have minor influence on the sorption of As and Sb on iron oxides (Biswas et al. 2009; Luther et al. 2012), whereas silicate can decrease the As(V) sorption obviously and the inhibitory effect of silicate on As(V) sorption is stronger than that of PO_4^{3-} (Ciardelli et al. 2008; Zhang et al. 2009). Kolbe et al. (2011) investigated the competitive behavior of As(V), Sb(V), and PO_4^{3-} on akaganeite, and proposed that the affinity of these ions to akaganeite follows an order of PO_4^{3-} > As(V) > Sb(V). Qi and Pichler (2016) investigated the competitive sorption of Sb(III) and Sb(V) on ferrihydrite, and reported that Sb(V) sorption could be inhibited by Sb(III) whereas Sb(III) sorption was not affected by Sb(V). Qi and Pichler (2017) investigated the competitive sorption of As(III), As(V), Sb(III), and Sb(V) onto ferrihydrite and pointed out that Sb(III) can inhibit As(III) sorption.

In anaerobic environments, amorphous FeS is typically the initial iron sulfide phase to form (Wolthers et al. 2003; Burton et al. 2011, 2019) and is an important iron mineral. The naturally formed FeS can serve as a major sink of metal(loid)s in sediment and significantly affect the mobility of metal(loid)s (Wolthers et al. 2003, 2005; Han et al. 2011a). The competitive sorption between As, Sb and anions on FeS can differ significantly from that on oxidizing minerals. Niazi and Burton (2016) investigated the competition between As and PO_4^{3-} on nanoparticulate FeS and reported that PO_4^{3-} did not significantly affect the sorption of either As(V) or As(III) to nanoparticulate FeS. They concluded that the mechanism for As uptake on FeS would be specific to As, thereby preventing any competitive effect of co-existing PO_4^{3-}. Han et al. (2013) reported that arsenite retention by nanoparticulate FeS was not significantly affected by dissolved silica, and proposed that the insignificant impact of dissolved silica on As retention was possibly related to the As-S solid phase associations. Han et al. (2020) reported that PO_4^{3-} has a negligible effect on the arsenic release in the FeS-dominant environment. Based on theoretic calculation, they proposed a binding strength (on FeS) order of: As(V) > PO_4^{3-} > As(III).

Previous studies have demonstrated that, under reducing conditions, both As and Sb can be largely sorbed by FeS (Wolthers et al. 2005; Han et al. 2011a, 2018; Li et al. 2021). Therefore, competitive sorption between As and Sb oxyanions on the surface of FeS might be expected. Although this competition might significantly affect the mobility of As and Sb in anoxic waters, soils or sediments, it has not been well addressed so far. In this work, we investigated the competitive sorption of As(III) and Sb(III) on the surface of FeS particles. Nanoparticulate FeS was synthesized and two types of experiments were conducted. In one experiment As(III) and Sb(III) were added simultaneously, whereas in the other one Sb(III) was added after 24 h aging of As(III) sorption on FeS. The objective of this study was to simulate the competitive behavior of As(III) and Sb(III) on FeS and to elucidate the mobility on As and Sb in anoxic environments.

2 Methods and materials

2.1 Materials

Deionized water (DW) (resistivity: 18.2 MΩ·cm) was prepared with a Milli-Q system (Millipore, Bedford, MA, USA). Deoxygenated deionized water (DDW) was prepared by sparging DW with high-purity N_2 (99.99%). Sodium (meta)arsenite ($NaAsO_2$, ≥ 99.0 purity) was purchased from Sigma Inc. (Mississauga, ON, Canada). Potassium antimonyl tartrate (PAT) sesquihydrate (> 99% purity) was purchased from Acros Organics Inc. (New Jersey, USA). This antimony reagent was used here because of it high solubility that was required in the sorption experiments. Ferrous sulfate heptahydrate ($FeSO_4·7H_2O$), sodium sulfide nonahydrate ($Na_2S·9H_2O$), sodium chloride (NaCl), and other chemicals were of analytical grade. All solutions were prepared with DDW. Stock solutions of As(III) (500 mg L^{-1}), Sb(III) (500 mg L^{-1}), S(-II) (6.4 g L^{-1}, 0.2 M), and Fe(II) (11.2 g L^{-1}, 0.2 M) were prepared by dissolving sodium (meta)arsenite, potassium antimonyl tartrate sesquihydrate, sodium sulfide nonahydrate, and ferrous sulfate heptahydrate in DDW, respectively.

2.2 Synthesis of FeS and sorption experiments

The synthesis of FeS and the interaction of As(III) or Sb(III) with FeS were conducted in an anaerobic chamber (Model 855-ACB, Plas-Labs, Co., USA) at an atmospheric composition of 95% Ar/5% H_2. The residual oxygen inside the chamber was removed by Pd catalysts, resulting in an oxygen concentration below 1 ppm.

For the synthesis of FeS, 0.2 M $FeSO_4$ solution and 0.2 M Na_2S solution (V:V = 1:1) were mixed thoroughly and black FeS precipitates were quickly formed. The characteristics of FeS synthesized by the reaction of Fe(II) with S(-II) were previously reported by Ma et al. (2020) and Li et al. (2021). Overall, the synthesized FeS was amorphous and appeared as clusters of nanoparticles because FeS particles tended to agglomerate rapidly.

The freshly precipitated FeS was aged for 3 h before it was used for the experiments on the interaction of As(III) and/or Sb(III) with FeS. For all the experiments, the initial FeS content was 44 mg L^{-1}. Sodium chloride was added to obtain 0.1 M (5.85 g L^{-1}) NaCl as a background ionic medium. Experiments were conducted in polyethylene vials.

The vials were sealed well and removed from the anaerobic chamber. Then, the vials were placed on a shaker to mix the suspensions thoroughly.

Equilibrium experiments on the competitive sorption of As(III) and Sb(III) on FeS was conducted by simultaneous addition of As(III) and Sb(III) into the FeS suspensions. Stock solutions of As(III) or Sb(III) were added into the FeS suspensions to obtain preset initial As(III) or Sb(III) concentrations. The initial As(III) concentrations were set to 0, 0.3, 0.6, and 1 mg L^{-1}, and the initial Sb(III) concentrations were set to 0, 0.5, 1, and 5 mg L^{-1}. The pH of the solution was adjusted to 5.5, 7.0, and 9.0 by addition of 0.1 M HCl and 0.1 M NaOH solution. The Eh of the solution was also measured. The initial volume of the solution was adjusted to 50 mL through the addition of DDW. The reaction mixture was sampled at the end (24 h) of experiments.

Moreover, kinetic sorption experiments were conducted at pH 7.0 to check the effect of aging of As(III) sorption on the competition between As(III) and Sb(III). In the sequential kinetic experiment, As(III) stock solution was firstly added and the initial As(III) concentration was set to 1 mg L^{-1}. After 24 h aging of As(III) sorption on FeS, Sb(III) stock solution was added and the initial Sb(III) concentration was set to 5 mg L^{-1}, and then the experiment was conducted for another 24 h (total reaction time: 48 h). The reaction mixture was sampled at 0.5, 1, 2, 4, 8, 12, 24, 24.5, 25, 26, 28, 36, 48 h. In the simultaneous kinetic experiment (for contrast), As(III) and Sb(III) stock solutions were simultaneously added into the FeS suspensions. The initial As(III) and Sb(III) concentrations were set to 1 and 5 mg L^{-1}, respectively. The reaction was run for 24 h, and the reaction mixture was sampled at 0.5, 1, 2, 4, 8, 12, 24 h. Each kinetic experiment was carried out in duplicate.

After sample collection, the solution sample was immediately filtered using a cellulose membrane (0.22 μm pore size) for determination of the concentrations of dissolved As(III), Sb(III), and Fe(II).

2.3 Analyses

The pH of the solution was measured with a Denver UB-7 pH-meter, and the Eh was measured with a redox potential meter (TOA-DKK, Japan). The concentration of Fe(II) was measured by a 1,10-phenanthroline spectrophotometric method (APHA 1998). The precision of the measurement of Fe(II) in the solution was better than 3%. The concentration of As(III) and Sb(III) was determined by hydride generation-atomic fluorescence spectrometry (HG-AFS) (AFS-2202E, Haiguang Instruments Corp., Beijing, China). Regarding the HG-AFS determination, the detection limit for As(III) and Sb(III) was 0.03 μg L^{-1} and 0.05 μg L^{-1}, respectively.

3 Results and discussion

3.1 Simultaneous sorption of As(III) and Sb(III) in equilibrium experiments

For the mixture of FeS (44 mg L^{-1}) and As(III) or/and Sb(III) at pH 5.5, 7.0, and 9.0, the Eh was -112.2 ± 8.1, -201.4 ± 7.8, and -304.4 ± 10.3 mV, respectively. The Eh values of the reaction mixture varied with pH. The addition of As(III) or/and Sb(III) did not influence the Eh value significantly.

The result of the uptake of As(III) and Sb(III) by FeS when As(III) and Sb(III) were added simultaneously was shown in Fig. 1. Generally, the uptake of As(III) or Sb(III) was dependent on pH. When sole As(III) was added in the FeS suspensions (Fig. 1a, c, e, Sb(III) = 0 mg L^{-1}), the residual $As(III)_{aq}$ concentration in the treatment with each initial As(III) concentration (0.3, 0.6, and 1 mg L^{-1}) increased with increasing pH, indicating a higher uptake of As(III) by FeS at lower pH. A similar trend was observed for the uptake of Sb(III) by FeS when sole Sb(III) was added in the FeS suspensions (Fig. 1b, d, f, As(III) = 0 mg L^{-1}). Similar pH dependence of the uptake of As(III) or Sb(III) by FeS has also been reported in previous studies (Han et al. 2011a, 2018; Niazi and Burton 2016; Li et al. 2021). Han et al. (2018) pointed out that the pH dependence of As(III) and Sb(III) sorption on FeS followed a typical anion sorption pattern of higher removal with lower pH. However, the influence of pH on the uptake of As(III) differed from that of Sb(III). For example, when 1 mg L^{-1} As(III) or Sb(III) was solely added, the residual $As(III)_{aq}$ concentration was 1.9, 482, and 841 μg L^{-1} while the residual $Sb(III)_{aq}$ concentration was 7.9, 84, and 295 μg L^{-1} in the treatments at pH 5.5, 7.0, and 9.0. It should be noted that, compared to the residual $Sb(III)_{aq}$ concentration, the residual $As(III)_{aq}$ concentration was lower in the treatment at pH 5.5 but was higher in the treatments at pHs 7.0 and 9.0. This indicated that the uptake of As(III) by FeS was higher than that of Sb(III) at pH 5.5 but was lower than that of Sb(III) at pHs 7.0 and 9.0.

When As(III) and Sb(III) were simultaneously added in the FeS suspensions, competitive sorption of As(III) and Sb(III) on FeS occurred and was significantly dependent on pH. At pH 5.5, both $As(III)_{aq}$ and $Sb(III)_{aq}$ concentrations were low (Fig. 1a), indicating a high uptake of As(III) and Sb(III) on FeS. In the case of 0.3 mg L^{-1} initial As(III), the $As(III)_{aq}$ concentration did not show a clear trend because it was at a very low level (from bdl to 0.3 μg L^{-1}). In the case of 0.6 and 1 mg L^{-1} initial As(III), however, the $As(III)_{aq}$ concentration generally increased when the initial Sb(III) concentration increased from 0 to 5 mg L^{-1}, indicating that As(III) uptake at pH 5.5 was slightly inhibited by Sb(III).

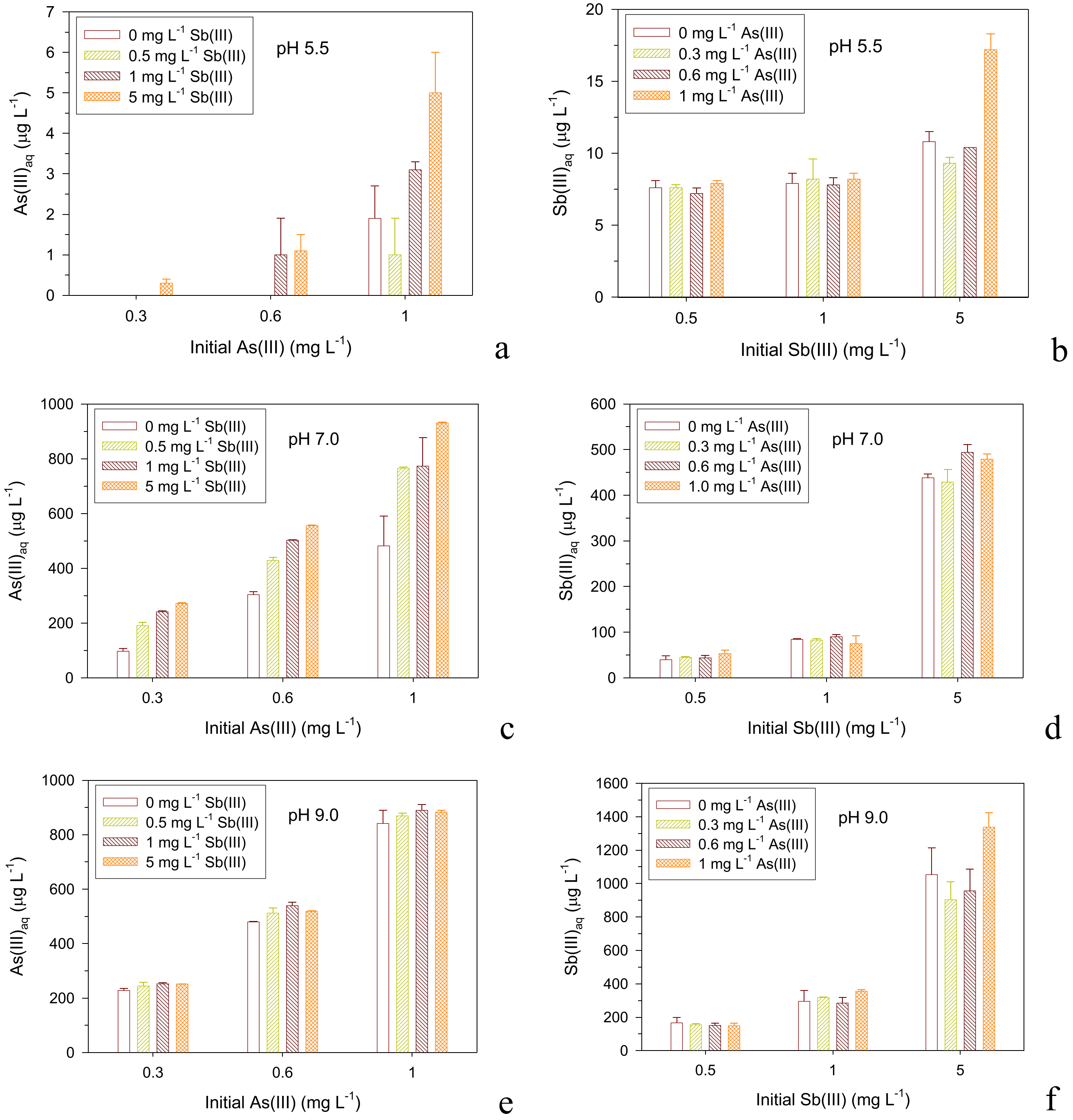

Fig. 1 Residual $As(III)_{aq}$ and $Sb(III)_{aq}$ concentrations in the treatments in which As(III) and Sb(III) were simultaneously added (FeS: 44 mg L^{-1}; reaction time: 24 h)

This trend was more obvious in the pH 7.0 treatment. At pH 7.0, the $As(III)_{aq}$ concentration increased significantly with the increase of initial Sb(III) (Fig. 1c). For example, in the case of 1 mg L^{-1} initial As(III), the $As(III)_{aq}$ concentration was 482 μg L^{-1} when Sb(III) was absent and was up to 773 or 931 μg L^{-1} when 1 or 5 mg L^{-1} Sb(III) was simultaneously added. This means that the simultaneous addition of 1 or 5 mg L^{-1} Sb(III) reduced the As(III) uptake from 51.8% to 22.7% or to 6.9%, respectively. This result indicated that As(III) sorption at pH 7.0 was notably inhibited by Sb(III). The stronger sorption of Sb(III) than As(III) was consistent with the above-mentioned lower removal of As(III) than that of Sb(III) at pH 7.0. At pH 9.0, the residual $As(III)_{aq}$ was generally constant when the initial

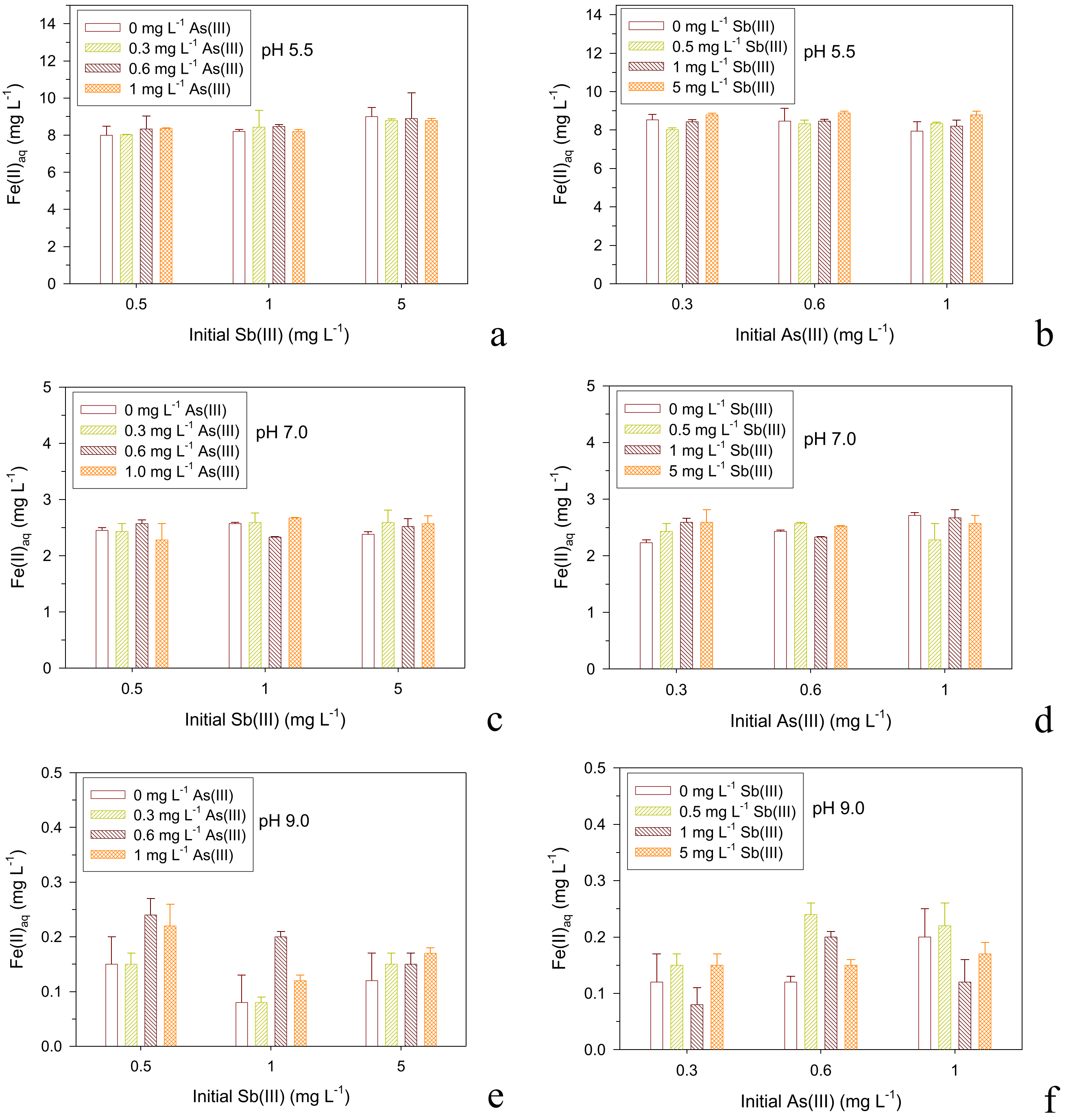

Fig. 2 Fe(II)$_{aq}$ concentrations in the treatments in which As(III) and Sb(III) were simultaneously added (FeS: 44 mg L^{-1}; reaction time: 24 h)

Sb(III) increased from 0 to 5 mg L^{-1} (Fig. 1e), indicating that the addition of Sb(III) did not affect As(III) sorption at pH 9.0. Regarding the uptake of Sb(III) affected by As(III), it can be seen that the residual Sb(III)$_{aq}$ concentration in the treatments at pHs 5.5, 7.0, and 9.0 was relatively constant regardless of the initial As(III) concentration (Fig. 1b, d, f). This result indicates that the uptake of Sb(III) was not affected by As(III).

The Fe(II)$_{aq}$ concentration in the treatments were shown in Fig. 2. In the treatments at pH 5.5, 7.0, and 9.0, the Fe(II)$_{aq}$ concentration was ca. 8.2, 2.4, and 0.1 mg L^{-1}, corresponding to a FeS solubility of 29.3%, 8.6%, and 0.4%, respectively. It can be seen that the Fe(II)$_{aq}$ concentration was notably higher in the treatments at lower pH. Similarly, the higher solubility of FeS at lower pH has also been reported in previous studies (Wolthers et al. 2005; Han et al.

2018; Li et al. 2021). As previously reported by Morse et al. (1987), FeS can dissolve to some extent under acidic or neutral conditions through the following reaction but hardly dissolve under alkaline conditions.

$$FeS_{(s)} + H^+ \rightleftharpoons Fe^{2+} + HS^- \quad (1)$$

In this reaction, a high concentration of protons (at low pH) can outcompete Fe(II) and result in the release of Fe(II) from solid phase (FeS) into aqueous phase.

The $Fe(II)_{aq}$ concentration in FeS suspensions could also be related to the presence of metal(loid)s. It was previously reported that addition of Sb(III) in the FeS suspension could enhance the release of Fe(II) from FeS at acidic pH (Li et al. 2021). Additionally, enhanced dissolution of Fe(II) from FeS with increasing As(III) concentrations could be observed under oxic conditions but could not be observed in anoxic conditions (An et al. 2017). In the present study, however, the $Fe(II)_{aq}$ concentration in the treatment at pH of 5.5 or 7.0 was basically constant (approximately 8 mg L^{-1} at pH 5.5 and 2.5 mg L^{-1} at pH 7.0) although the initial Sb(III) or As(III) concentrations varied (Fig. 2). This indicates that the influence of As(III) or Sb(III) on the $Fe(II)_{aq}$ concentration was weak. This result could be attributed to the low initial concentrations of As(III) (0 to 1 mg L^{-1}) or Sb(III) (0 to 5 mg L^{-1}) compared to the initial FeS content (44 mg L^{-1}). By contrast, the initial Sb(III) concentration in the study of Li et al. (2021) was at a high level of 20 mg L^{-1}. The possible reactions between As(III)/Sb(III) and FeS can be described as follows (Han et al. 2018; Li et al. 2021).

$$3\ FeS_{(s)} + 2\ H_3AsO_3 + 6\ H^+ \rightarrow 3\ Fe^{2+} + As_2S3_{(s)} + 6\ H_2O \quad (2)$$

$$3\ FeS_{(s)} + 2\ Sb(OH)_3 + 6\ H^+ \rightarrow 3\ Fe^{2+} + Sb_2S_{3(s)} + 6\ H_2O \quad (3)$$

A contrast of the solubility products of Sb_2S_3 (log K_{sp} = -92.8, Mane and Lokhande 2003), As_2S_3 (Log K_{sp} = -11.9, Eary 1992) and crystalline FeS (log K_{sp} = -27.39, Jong and Parry 2003) and nanoparticle FeS (log K_{sp} = -3.5, Rickard 2006) indicates that both As(III) and Sb(III) has a potential to compete with Fe(II) to be bound to the sulfide, resulting in the release of Fe(II). However, this competition will be weak when the concentration of As(III) or Sb(III) is low. This explains the basically constant $Fe(II)_{aq}$ concentration in the treatments.

3.2 Sequential sorption of As(III) and Sb(III) in kinetic experiments

Since strong competitive sorption between As(III) and Sb(III) on FeS occurred at pH 7.0, two kinetic experiments with sequential and simultaneous addition of As(III) and Sb(III) were carried out at pH 7.0, so as to understand the effect of aging of As(III) sorption on the competitive sorption of As(III) and Sb(III) on FeS.

In the kinetic experiment of sequential system, Sb(III) was added 24 h after As(III) addition. The temporal variation of $As(III)_{aq}$ concentration in the sequential and simultaneous systems is shown in Fig. 3a. Before 24 h, the $As(III)_{aq}$ concentration in the simultaneous system (in the presence of Sb(III)) was much higher than that in the sequential system. The higher $As(III)_{aq}$ concentration in the simultaneous system was consistent with the above-mentioned inhibition of As(III) sorption by Sb(III) at pH 7.0 (Fig. 1c). In the sequential system, the $As(III)_{aq}$ increased after Sb(III) addition at 24 h (Fig. 3a). The $As(III)_{aq}$ concentration was 615 µg L^{-1} at 24 h and then increased to 679 µg L^{-1} at 48 h. This indicated that some As(III) previously sorbed on FeS was gradually outcompeted by Sb(III). However, the $As(III)_{aq}$ concentration after 24 h was still markedly lower than that in the simultaneous system. This means that, compared to

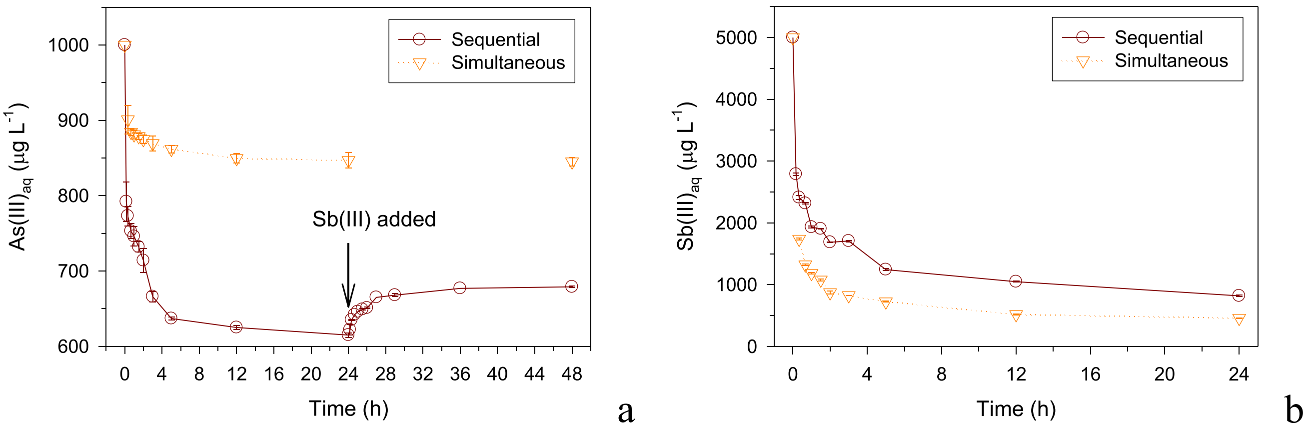

Fig. 3 Kinetic variation of $As(III)_{aq}$ and $Sb(III)_{aq}$ concentrations in the sequential and simultaneous treatments

the simultaneous system, a fraction of As(III) that was previously immobilized in the sequential system could no longer be released by the competition of Sb(III).

The temporal variation of Sb(III)$_{aq}$ concentration in the kinetic experiments of sequential and simultaneous systems is shown in Fig. 3b. For the simultaneous system, the variation of Sb(III)$_{aq}$ concentration from 0 to 24 h was shown. For the sequential system, the variation of Sb(III)$_{aq}$ concentration from 0 to 24 h in Fig. 3b corresponded to that from 24 (addition of Sb(III)) to 48 h in Fig. 3a. In the case Sb(III) was added 24 h later than As(III) in the sequential system, the residual Sb(III)$_{aq}$ concentration was higher compared to the simultaneous system, indicating that the 24 h aging of As(III) sorption in the sequential system inhibited the sorption of Sb(III) to some extent. This is in striking contrast to the above-mentioned result that the simultaneous addition of As(III) did not inhibit the sorption of Sb(III). It showed that the 24 h aging of As(III) sorption led to stronger immobilization of As(III) on FeS.

3.3 Interactions between As(III), Sb(III), and FeS in the reaction mixture

The behavior of As and Sb are thought to be highly related to the speciation of arsenite and antimonite in the system. Arsenite has pK_a1 of 9.22, pK_a2 of 12.13, and pK_a3 of 13.4 (Wilson et al. 2010), so As(III) in water exists predominantly as H_3AsO_3 below pH 9.22. Antimonite has pKa of 11.9 (Wilson et al. 2010), and the speciation of Sb(III) in water is dominated by $Sb(OH)_3$ between pH 2.0 and 12.0 (Krupka and Serne 2002; Cui et al. 2017). Therefore, in the pH range of 5.5 to 9.0, the dominant species of As(III) and Sb(III) in As(III)/Sb(III)-water system should be H_3AsO_3 and $Sb(OH)_3$, respectively. In the FeS-As(III)/Sb(III)-H_2O system, the speciation of As(III) and Sb(III) can be largely influenced by pH and the possible presence of aqueous S(-II). Because pH affects the dissolution of FeS and accordingly the generation of aqueous S(-II), H_3AsO_3 and $Sb(OH)_3$ are likely to transform to sulfide precipitates or sulfidic complexes when pH is in an appropriate range (Filella et al. 2002; Wilson et al. 2010).

Under acidic and neutral conditions, precipitation as sulfides of As and Sb have been reported to be important in the interaction of As(III) or Sb(III) with FeS. When reacted with FeS at pH 5.5–6.5, As(III) could coprecipitate as poorly crystalline As_2S_3 at the surfaces of FeS before the solution is saturated with respect to amorphous As_2S_3 (Farquhar et al. 2002; Wolthers et al. 2005). At pH 5, As(III) formed As_2S_3 (orpiment) in a FeS-coated sand system, but formed As_2S_3 and AsS (realgar) in a nano-particulate FeS system (Han et al. 2011a, b, 2018). Similar to As_2S_3, amorphous phase of Sb_2S_3 was observed in the interaction of Sb(III) with FeS at acidic or neutral pH in the study of Han et al. (2018) and in two studies carried out in our laboratory (Li et al. 2021; Wang et al. 2022). Besides, Kirsch et al. (2008) reported the existence of SbS_3-like species on the surface of FeS. According to a thermodynamic simulation, Gallegos et al. (2008) and Han et al. (2011b) predicted the formation of amorphous As_2S_3 and AsS in the Fe-As-S-H_2O system. Therefore, it is postulated that precipitation as sulfides of As and Sb was significant to the uptake of As(III) and Sb(III) by FeS in the treatments at pH 5.5 and 7.0. Particularly, the lower concentration of As(III)$_{aq}$ than that of Sb(III)$_{aq}$ (Fig. 1a, b) in the treatment of sole As(III) or Sb(III) at pH 5.5 probably helped to support the hypothesis of AsS formation, because if AsS did not exist, the lower solubility of Sb_2S_3 (log $K_s = -92.8$, Mane and Lokhande 2003) than that of As_2S_3 (log $K_s = -11.9$, Eary 1992) should have resulted in a lower concentration of Sb(III)$_{aq}$ than that of As(III)$_{aq}$.

From acidic to basic pH range, the removal mechanism of As(III) or Sb(III) in the FeS-As(III)/Sb(III)-H_2O system reflects a transition from sulfide precipitation to sorption of H_3AsO_3 and $Sb(OH)_3$ surface complexes (Gallegos et al. 2007; Han et al. 2018). This means a decline of the precipitation as sulfides of As and Sb as pH increases. The binding of ions to metal sulfide is related to the functional group developed on the surface of solid. A metal sulfide in aqueous solution is expected to develop a thiol group (≡S-H) and a metal hydroxide group (≡Me-OH). Presence of sulfidic sulfur in a metal sulfide suspension may result in the conversion of a ≡Me-OH group to a ≡Me-S-H group (Bebie et al. 1998). At acidic and neutral pH FeS is partially soluble to form aqueous SH^-, so the conversion of ≡Fe-OH group to ≡Fe-S-H group can be important. However, at alkaline pH FeS dissolution is negligible, so the ≡Fe-S-H groups on FeS at pH 9.0 were proposed to be less significant than the ≡FeOH groups and most As(III) and Sb(III) would be bound to FeS at ≡FeOH sites. Because both As and Sb are chalcophile and ≡S-H groups are important on FeS at acid or neutral pH, the binding of As(III) and Sb(III) to ≡S-H groups on FeS at pH 7.0 is suggested to be important in addition to the precipitation of As(III) and Sb(III) sulfides. Consistently, Farquhar et al. (2002) and Vega et al. (2017) suggested that As(III) was sorbed on sulfur sites of FeS probably as a sorbed complex. Similar with As(III), Sb(III) also form complexes on FeS, and the major Sb(III) binding on FeS has been reported to be on sulfur instead of iron (Han et al. 2018).

The competition of As(III) and Sb(III) on FeS at pH 7.0 is suggested to be highly related to the surface complexes of As(III) and Sb(III) on FeS. As inferred by the much lower solubility of Sb_2S_3 than that of As_2S_3, it is thought that Sb(III) has a higher affinity to ≡S-H group than As(III). Consequently, As(III) bound to ≡S-H groups of FeS is suggested to be very sensitive to be replaced by Sb(III). The replacement reaction of As(III) by Sb(III) on the sulfur sites

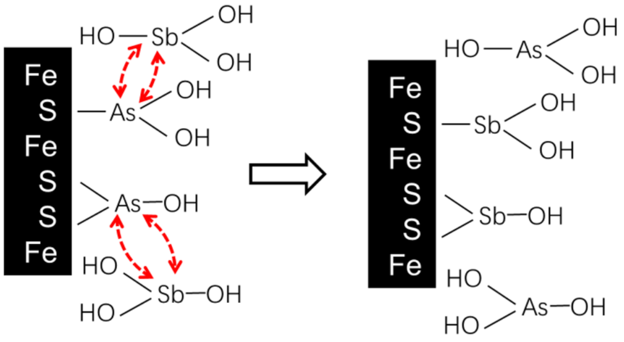

Fig. 4 Proposed reaction for the competition of As(III) and Sb(III) on the surface of FeS at pH 7.0

of FeS particles is described in Fig. 4. This replacement was important at neutral pH as reflected by the significant amount of soluble As(III) in the treatment at pH 7.0 (Fig. 1c). In contrast, the competition between As(III) and Sb(III) at pH 5.5 was relatively weak (Fig. 1a, b), possibly because As(III) and Sb(III) were mostly present as arsenic sulfides and antimony sulfides on the surface of FeS at acidic pH and only a small amount of As(III) and Sb(III) were bound to ≡SH groups. The sulfide precipitates of As and Sb were highly stable under acidic conditions (Krupp 1988; Wilkin and Ford 2002; Rodriguez-Freire et al. 2014; Olsen et al. 2018), resulting in a very low mobility of As(III) or Sb(III). For example, As_2S_3 is very stable at low pH, and the binding of As(III) with sulfide at low pH is reported to be sufficiently strong that even 6 M HCl will not keep spiked As(III) in the dissolved fraction (Wilkin and Ford 2002).

In FeS-As(III)/Sb(III)-H_2O system, As(III) and Sb(III) are also likely to form thiolated species. The formation of thiolated species of As(III) or Sb(III) is quite dependent on pH. Increase in pH will facilitate the thiolation of As(III) by $S(-II)_{aq}$ (Wilkin and Ford 2002).

$$As_2S_{3\,(s)} + H_2S_{\,(aq)} = 2\,AsS_2^- + 2\,H^+ \tag{4}$$

The $S(-II)_{aq}$ in this reaction can originate from the partial dissolution of FeS (reaction (1)). The dissolution of Sb_2S_3 in sulfidic system is similar with that of As_2S_3 (Dubey and Ghosh 1962). In the treatment at pH 5.5, the formation of thioarsenite and thioantimonite was considered unfavorable because a low pH could significantly enhance the stability of As_2S_3 and Sb_2S_3 (Krupp 1988; Wilkin and Ford 2002; Rodriguez-Freire et al. 2014; Olsen et al. 2018). At pH 7.0, a partial dissolution of FeS occurred as reflected by the aqueous Fe(II) in solution (Fig. 2c, d) and the stability of As_2S_3 and Sb_2S_3 decreased relative to that at pH 5.5. As a result, thioarsenite and thioantimonite species were possibly formed to some extent at pH 7.0. Consistent with this, Gallegos et al. (2007) previously reported that in the interaction of As(III) with FeS at pH 7.0, a fraction of As(III) could form (thio)arsenite. Vega et al. (2017) also proposed the presence of thioarsenic species in the As(III)-FeS system at a similar pH value of 7.5. In the treatment at pH 9.0, because the release of aqueous S(-II) could be limited due to the high stability of FeS (Fig. 2e, f), the formation of thioarsenite and thioantimonite species was postulated to be limited. Thioarsenic species have been reported to have a lower affinity to FeS compared to arsenite (Couture et al. 2013). However, no comparison between the affinity of thioarsenic species and that of thioantimony species to FeS has been reported so far, making it impossible to further discuss on the significance of thiolated species of As(III) and Sb(III) to the competitive sorption of As(III) and Sb(III) on FeS.

In the kinetic experiment of the sequential system, the stronger immobilization of As(III) after 24 h aging (Fig. 3a) may be associated with time-dependent change of As(III) binding on FeS that may affect the binding strength. Ion exchange is an important reaction that could result in stronger immobilization of metal(loid) on FeS. Balsley et al. (1996) investigated the retention of iodide by HgS and Cu_2S and suggested that iodide sorption apparently occurs by exchange of hydroxyls attached to Hg and Cu sites. Regarding Pb and Cd interactions with FeS, Coles et al. (2000) suggested that Pb and Cd displaced some Fe(II) from FeS through ion exchange and form (Pb,Fe)S and (Cd,Fe)S on the surface of FeS. Similarly in the reaction of Hg(II) with FeS, formation of HgS was observed (Jeong et al. 2007). It is postulated here ion exchange possibly occurred on FeS during the aging of As(III) sorption and subsequently increased the affinity of As(III) on FeS. For example, when As(III) formed surface complexes on FeS, ion exchange between As(III) and Fe(II) could occur afterwards and possibly result in higher affinity of As(III) on the surface of FeS.

3.4 Implications for the behavior of metalloids in some anaerobic environments

Concomitant serious contamination of As and Sb in sediments of mining area has been reported (Ashley et al. 2003; Casiot et al. 2007). In anaerobic sediment environments characterized by a high flux of organic matter, the transformation of iron oxides into iron sulfides is common (Emiroglu et al. 2004). Therefore, in some sediments, high concentrations of Sb and As may be accompanied by the presence of particulate FeS. Previous work suggests that nanoparticulate FeS may play a major role in removing As from sediment porewater (Niazi and Burton 2016). However, the presence of other metal(loid)s such as Sb can make this process more complicated. The present work clearly shows that when As(III) was freshly sorbed onto FeS at neutral pH, the presence of Sb(III) largely inhibited the sorption of As(III) and accordingly resulted in the high mobilization of As. However, when the sorption of As(III) on FeS was aged for a period, the competition of Sb(III) was significantly mitigated. Conversely, at neutral pH, the aged sorption of As(III) inhibited the sorption of Sb(III) to some extent while the freshly sorbed As(III) did not take effect.

It is suggested that in anaerobic environments such as anaerobic sediments or soils, the presence of Sb may seriously affect the mobility of As through the competition for sorption sites on FeS. Besides, some other metal(loid)s are also potential competing sorbate in the natural environments, and the properties of these sorbates must be considered in evaluating their effect on the behavior of As or Sb.

4 Conclusions

Coexisting As and Sb contamination can be found in anaerobic environments (*e.g.* lake sediment) rich in iron and sulfur. Our study demonstrated that competitive sorption of As(III) and Sb(III) occurred on the surface of FeS particles. This competition was proved to be strong at pH 7.0. When As(III) and Sb(III) were simultaneously added into the FeS suspensions at pH 7.0, As(III) sorption was highly inhibited by Sb(III) and consequently most As(III) was present in the dissolved fraction. When As(III) sorption on FeS was aged for a period of 24 h prior to the addition of Sb(III), however, the inhibitive effect of Sb(III) on As(III) sorption was significantly weakened. The competitive sorption of As(III) and Sb(III) was postulated to be primarily associated with the binding of As(III) and Sb(III) to FeS at the sulfur sites. Sb(III) has a higher chalcophility than As(III), so As(III) bound to FeS at the sulfur sites can be partially outcompeted by Sb(III).

The results of this study suggested the importance of competitive sorption of As and Sb on FeS in evaluating the mobility of As or Sb in iron- and sulfur-rich anaerobic sediments or soils.

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Data availability All data are included in the article.

Declarations

Competing interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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