

# **Adsorption behavior of arsenic and antimony onto ferrihydrite under competitive conditions**

Dissertation

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# Table of Contents

<b>Abstract .....</b>	<b>VII</b>
<b>Kurzfassung .....</b>	<b>IX</b>
<b>1. Introduction .....</b>	<b>1</b>
1.1 Speciation, toxicity, sources and distribution .....	2
1.1.1 As speciation .....	2
1.1.2 Sb speciation.....	3
1.1.3 Toxicity .....	4
1.1.4 Sources and distribution in the environment .....	4
1.2 Remediation of As and Sb.....	5
1.2.1 Adsorption behavior of As.....	6
1.2.2 Adsorption behavior of Sb .....	7
1.2.3 Redox process of Sb(III) accompanied with adsorption .....	8
1.3 Adsorption mechanism.....	9
1.4 Simultaneous removal of As and Sb.....	10
<b>2. Scopes and objectives.....</b>	<b>13</b>
<b>3. Closer look at As(III) and As(V) adsorption onto ferrihydrite under competitive conditions.....</b>	<b>17</b>
Abstract.....	18
3.1 Introduction .....	20
3.2 Materials and methods .....	22
3.3 Results .....	25
3.4 Discussion.....	31
3.5 Conclusions.....	35
<b>4. Closer look at As(III) and As(V) adsorption onto ferrihydrite under competitive conditions: isotherms and kinetics .....</b>	<b>37</b>
Abstract.....	38

4.1 Introduction .....	39
4.2 Materials and methods .....	40
4.3 Results and discussion.....	44
4.4 Conclusions.....	52
<b>5. Sequential and simultaneous adsorption of Sb(III) and Sb(V) on ferrihydrite: Implications for oxidation and competition .....</b>	<b>53</b>
Abstract.....	54
5.1 Introduction .....	55
5.2 Experimental section.....	56
5.3 Results .....	58
5.4 Discussion.....	64
5.5 Conclusions.....	68
5.6 Supplementary Information .....	69
<b>6. Simultaneous adsorption of As(III), As(V), Sb(III) and Sb(V) in aqueous media by ferrihydrite.....</b>	<b>71</b>
Abstract.....	72
6.1 Introduction .....	73
6.2 Experimental section.....	74
6.3 Results .....	76
6.4 Discussion.....	81
6.5 Conclusions.....	87
<b>7. Conclusions and outlooks .....</b>	<b>89</b>
7.1 Conclusions.....	89
7.2 Outlook.....	91
<b>Acknowledgement .....</b>	<b>93</b>
<b>References .....</b>	<b>95</b>
<b>Appendix .....</b>	<b>109</b>

## **Abstract**

Arsenic (As) and antimony (Sb) are naturally toxic elements widely distributed in a multiple of fields of the environment. They are generally considered to share numerous similarities in chemical properties, adsorption and redox behavior, toxicity and mobility. Elevated concentrations of As and Sb are released into the environment, but very little is known about their simultaneous adsorption behavior in the system containing more than one redox species. First, the competitive interactions between arsenite (As(III)) and arsenate (As(V)) onto ferrihydrite were investigated as a function of initial pH, adsorbent dosage, concentration of coexisting ligands and the order of addition. It was further studied by applying applicable adsorption isotherms and kinetic models. Second, the adsorption and oxidation of Sb(III) at varying Fe/Sb ratios and pH values was evaluated. The simultaneous adsorption of Sb(III) and Sb(V) was also studied. Finally, the simultaneous adsorption behavior of As(III), As(V), Sb(III) and Sb(V) was investigated in multi-component systems.

The pH generally had a great impact on As adsorption under both single ion and competitive conditions. However, the presence of As(V) in solution was the controlling factor on As(III) adsorption and As(III) more or less outcompeted As(V) across the pH scale from 4 to 10. As(III) and As(V) was adsorbed almost equally up to a pH of 5 at an adsorbent dosage of 0.5 g/L and up to a pH of 6 at an adsorbent dosage of 1 g/L in binary systems. This was contrary to the theoretical prediction that As(V) should adsorb stronger than As(III) at pH values below the point of zero charge (pzc) of ferrihydrite of about 7 to 8. At low pH As(V) impedes the adsorption of As(III), but to a lesser degree than As(III) impedes As(V) adsorption at a pH above 6. The order of addition of the two As reox species also had significant effects on their competitive adsorption behavior.

Both the adsorption of As(III) and As(V) under single and competitive conditions can be successfully described by the Freundlich isotherm model. The adsorption affinity onto ferrihydrite was ordered as follows: As(III)-single > As(III)-binary > As(V)-single > As(V)-binary. The adsorption kinetics for both As(III) and As(V) comply with the

## ABSTRACT

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pseudo-second order kinetics model. Moreover, the isotherm and kinetic competitive studies showed that As(V) significantly impeded the adsorption of As(III), whereas the presence of As(III) had an insignificant effect on the adsorption of As(V) at pH 5. The FTIR spectra provided the evidence that both As(III) and As(V) could be adsorbed onto ferrihydrite through inner-sphere surface complexes by the formation of Fe-O-As bonds.

The simultaneous adsorption and oxidation of Sb(III) was confirmed by the appearance of Sb(V) in the solution at varying Fe/Sb ratios (500, 100 and 8) and varying pH values (3.8, 7 and 9). This newly formed Sb(V) was subsequently removed from solution at a Fe/Sb ratio of 500 or at a pH of 3.8. However, Sb(V) were almost remained alone in the liquid phase at the end of experiments at lower Fe/Sb ratios and higher pH, indicating that competition could take place between the newly formed Sb(V) and Sb(III), and Sb(III) outcompeted Sb(V). This was independently confirmed by simultaneous adsorption experiments of Sb(III) and Sb(V) in binary systems. Under such conditions, the presence of Sb(V) had no influence on the adsorption of Sb(III) while Sb(V) adsorption was significantly inhibited by Sb(III) at a wide pH range (4 to 10).

The simultaneous adsorption behavior of As(III), As(V), Sb(III) and Sb(V) were evaluated in multi-component (binary, ternary, quaternary) systems. The presence of Sb(III) had a stronger inhibitory effect on As(III) adsorption than Sb(V), and the presence of As(V) had a stronger inhibitory effect on Sb(V) adsorption than As(III). The adsorption behavior of the four redox species under quaternary conditions was pH dependent. Sb(III) always showed the strongest affinity on ferrihydrite. The Freundlich model provided a good fit for the simultaneous adsorption data under quaternary conditions. The major anions of  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  did not compete for the adsorption of As(III) and Sb(III) in ternary systems. The presence of  $\text{PO}_4^{3-}$  had a negative influence on the adsorption of As(V) and Sb(V) in ternary systems, while both  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  had no distinct effect on the adsorption of As(V) and Sb(V). This study indicates that Sb(III) and As(V) could be strongly adsorbed on ferrihydrite mainly by inner-sphere complexes, while a combination of outer- and inner-sphere complexes could be involved for the adsorption of Sb(V) and As(III).

## Kurzfassung

Arsen (As) und Antimon (Sb) sind natürlich auftretende, toxische Elemente, die in vielen Bereichen in der Umwelt weit verbreitet sind. Grundsätzlich haben sie viele Ähnlichkeiten bezüglich ihrer chemischen Eigenschaften, des Adsorptions- und Redoxverhaltens, der Toxizität sowie der Mobilität. Erhöhte Konzentrationen von As und Sb treten durch Freisetzung in der Umwelt auf, allerdings ist bisher wenig bekannt über ihr gleichzeitiges Adsorptionsverhalten in Systemen mit mehr als einer Redoxspezies. Als erstes wurde das konkurrierende Verhalten von Arsenit (As(III)) und Arsenat (As(V)) an Ferrihydrit als Funktion des ursprünglichen pH-Wertes, der Menge des Adsorbenten, der Konzentration nebeneinander bestehender Liganden und der Reihenfolge der Zugabe untersucht. Weiterhin wurden Adsorptionsisothermen und die Kinetik aus Batchversuchen betrachtet. Zusätzlich wurde die gleichzeitige Adsorption und Oxidation von Sb(III) bei verschiedenen Fe/Sb Verhältnissen und pH-Werten bestimmt. Ebenfalls wurde die zeitgleiche Adsorption von Sb(III) und Sb(V) analysiert. Schließlich folgte die Untersuchung des Verhaltens simultaner Adsorption von As(III), As(V), Sb(III) und Sb(V) in Mehrstoffsystemen.

Allgemein hatte der pH-Wert großen Einfluss auf die Adsorption von As, als alleiniges Ion, wie auch unter konkurrierenden Bedingungen. Jedoch war der Gehalt von As(V) in der Lösung der bestimmende Faktor für das Adsorptionsverhalten und As(III) hat As(V) über eine pH-Wert Skala von 4 bis 10 mehr oder weniger verdrängt. As (III) und As(V) wurden in einem Zweistoffsysteem bis zu einem pH-Wert von 5 bei einer Sorbentenmenge von 0,5 g/L und bis zu einem pH-Wert von 6 bei einer Konzentration des Sorbenten von 1 g/L fast gleichwertig adsorbiert. Dies stand im Widerspruch zur theoretischen Vorhersage, wonach As(V) bei pH-Werten unterhalb des Ladungsnnullpunktes von Ferrihydrit von 7 bis 8 stärker adsorbiert werden sollte als As(III). Bei geringen pH-Werten hemmt As(V) die Adsorption von As(III), allerdings in geringerem Maße als As(III) die Adsorption von As(V) bei pH-Werten über 6 einschränkt. Die Zugabe von Anionen hatte ebenfalls einen signifikanten Einfluss auf ihr konkurrierendes Adsorptionsverhalten.

Die Adsorption von As(III) und As(V) kann unter getrennten wie konkurrierenden Bedingungen mit der Freundlich Isotherme passend beschrieben werden. Der Adsorptionsgrad an Ferrihydrit hatte die Reihenfolge: As(III)-einzeln > As(III)-Zweistoffsyste m > As(V)-einzeln > As(V)-Zweistoffsyste m. Die Adsorptionskinetik von As(III) und As(V) entspricht dem Modell der Kinetik pseudo-2. Ordnung. Zudem zeigten die Untersuchungen der Isothermen und der Kinetik unter konkurrierenden Bedingungen, dass As(V) die Adsorption von As(III) signifikant hemmt, während in Gegenwart von As(III) einen insignifikanten Einfluss auf die Adsorption von As(V) bei pH-Wert 5 hatte. Die Analyse des FTIR-Spektrometers lieferte den Beweis, dass sowohl As(III) als auch As(V) in innersphärischen Oberflächenkomplexen über Fe-O-As-Bindungen an Ferrihydrit adsorbieren können.

Die zeitgleich Adsorption und Oxidation von Sb(III) wurde durch das Vorkommen von Sb(V) in der Lösung bei unterschiedlichen Fe/Sb Verhältnissen (500, 100 und 8) und variierenden pH-Werten (3.8; 7 und 9) bestätigt. Das neu gebildete Sb(V) wurde schließlich bei einem Fe/Sb Verhältnis von 500 oder bei pH-Wert 3,8 aus der Lösung entfernt. Dennoch verblieb am Ende der Experimente bei geringeren Fe/Sb Verhältnissen und höheren pH-Werten Sb(V) fast alleine in der flüssigen Phase, was auf ein Konkurrenzverhalten zwischen Sb(III) und dem neu gebildeten Sb(V) hinweist, wobei Sb(III) das Sb(V) verdrängt. Dies wurde unabhängig durch gleichzeitige Adsorptionsversuche von Sb(III) und Sb(V) in Zweistoffsyste men bestätigt. Unter diesen Bedingungen hatte die Gegenwart von Sb(V) keinen Einfluss auf die Adsorption von Sb(III), während die Adsorption von Sb(V) durch Sb(III) bei pH-Werten zwischen 4 und 10 signifikant gehemmt wurde.

Das zeitgleiche Adsorptionsverhalten von As(III), As(V), Sb(III) und Sb(V) wurde in Zweistoff-, Dreistoff- und Vierstoffsyste men ausgewertet. Die Gegenwart von Sb(III) hatte einen stärkeren hemmenden Einfluss auf die Adsorption von As(III) als Sb(V). Die Anwesenheit von As(V) hatte einen stärkeren hemmenden Einfluss auf die Adsorption von Sb(V) als As(III). Das Adsorptionsverhalten der vier Redoxspezies im Vierstoffsyste m war pH abhängig. Sb(III) zeigte stets die größte Affinität an Ferrihydrit. Das Freundlich Modell zeigte X

eine gute Anpassung der Daten aus der gleichzeitigen Adsorption im Vierstoffsystem. Die Hauptanionen  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  und  $\text{SO}_4^{2-}$  hatten keine Auswirkungen auf die Adsorption von Sb(III) und As(III) im Dreistoffsystem. Die Anwesenheit von  $\text{PO}_4^{3-}$  hatte einen negativen Einfluss auf die Adsorption von Sb(V) und As(V) im Dreistoffsystem, während  $\text{NO}_3^-$  und  $\text{SO}_4^{2-}$  keine bedeutenden Auswirkungen auf die Adsorption von Sb(V) und As(V) zeigten. Die Untersuchungen geben Hinweise darauf, dass Sb(III) und As(V) überwiegend durch innersphärische Komplexe stark an Ferrihydrit adsorbieren, während bei der Adsorption von Sb(V) und As(III) sowohl außer- als auch innersphärische Komplexe beteiligt sind.

## KURZFASSUNG

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## 1. Introduction

Arsenic (As) is the 20th most abundant element in the Earth's crust, 14th in seawater, and 12th in the human body (Eisler, 1988). It is widely dispersed in nature and used commercially as pesticides, wood preservation, semiconductors and manufacturing. It is a well-known toxic element in nature and gains high concerns for decades. The As contamination issues were reported for many regions and countries, such as India, Bangladesh, Vietnam, Canada and China (Berg et al., 2001; Das et al., 1996; Mandai et al., 1999; Nickson et al., 1998; Rodríguez-Lado et al., 2013; Sun, 2004; Wang and Mulligan, 2006). Since 1958, the World Health Organization (WHO) had a public position on As in drinking water and since 1993 it established the maximum contaminant level of As in drinking water as 10.0 µg/L (Yamamura et al., 2003). The toxicity and health hazards of As have been reported for decades (e.g. Abernathy et al., 1999; Choong et al., 2007; Jain and Ali, 2000).

Antimony (Sb) is a natural occurring element and situated fourth in the Group V of the periodic table exactly beneath As. It is widely dispersed in the lithosphere and often present together with As. Sb is used in a variety of industrial products in high quantities. However, unlike As, Sb first attracted public attention in the mid-1990 (Filella et al., 2009). In contrast to As, less information is available on Sb. Previous studies have confirmed that Sb has harmful effects on human health and well-being (e.g. Cooper and Harrison, 2009; Sundar and Chakravarty, 2010). In 1993, the WHO set a guideline of Sb in drinking water as a permissible level as 5.0 µg/L (WHO, 2004).

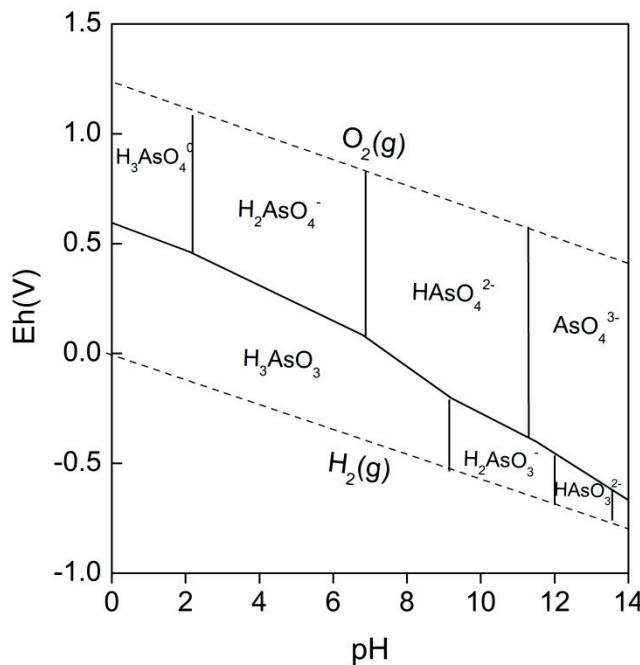
As and Sb are widely dispersed and typically coexist in the environment. However, the simultaneous adsorption of As and Sb has been hardly investigated. Considering that they are generally recognized to have some similarities in the chemical properties, the simultaneous adsorption behavior of As and Sb should need comprehensive investigations when they both compete on surface sites. It is also important to understand the geochemical behavior of As and Sb in the environment.

## 1.1 Speciation, toxicity, sources and distribution

### 1.1.1 As speciation

The chemical properties, toxicity, mobility and transport of As and Sb in the environment are strongly dependent on their oxidation states. The system pH and redox potential (Eh) are the most important factors that control the distribution of oxidation states (Becking et al., 1960).

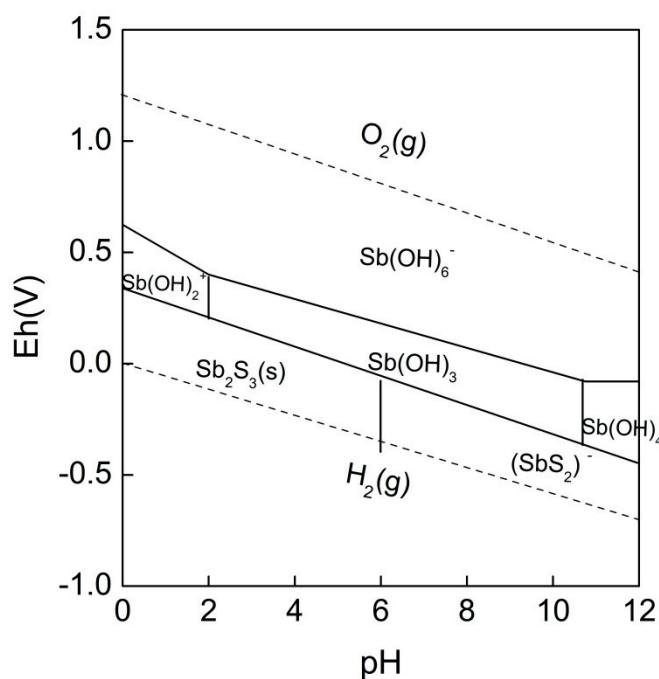
Arsenic is stable in four oxidation states (-III, 0, III, V), but mostly found in the inorganic forms as trivalent arsenite ( $\text{As(III)}$ ) and pentavalent arsenate ( $\text{As(V)}$ ) in aquatic systems. Figure 1 shows the Eh-pH diagram of As. Under oxidizing and aerated conditions, the negatively charged anions of  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$  and  $\text{AsO}_4^{3-}$  ( $\text{p}K_1=2.20$ ;  $\text{p}K_2=6.97$  and  $\text{p}K_3=11.53$ ) are the principal As(V) species. Under reducing conditions, trivalent As is stable as a neural form of  $\text{H}_3\text{AsO}_3$  in the pH range of 0 to 9.



**Figure 1.** Eh-pH diagram for aqueous arsenic species at 25°C and 1 bar total pressure in the  $\text{As}-\text{O}_2-\text{H}_2\text{O}$  system (modified from Smedley and Kinniburgh (2002))

### 1.1.2 Sb speciation

Antimony also exists essentially in four oxidation states, like As, which exists mainly as two species in most natural systems, trivalent antimonite ( $\text{Sb(III)}$ ) and pentavalent antimonate ( $\text{Sb(V)}$ ). The Eh-pH diagram of Sb is shown in Figure 2. These two inorganic forms of Sb are subjected to hydrolysis in aquatic systems by forming hydroxide species. For example,  $\text{Sb(OH)}_6^-$  is the only major form of  $\text{Sb(V)}$  over a wide range of pH, which is different with  $\text{As(V)}$  having the successive deprotonation steps over a similar range of pH. The dominant  $\text{Sb(III)}$  species is the uncharged pyramidal antimonous acid  $\text{Sb(OH)}_3$  in a wide pH range from 2 to 11, and exists as  $\text{Sb(OH)}_2^+$  in acidic media and as  $\text{Sb(OH)}_4^-$  in basic media. Under reducing conditions with the presence of sulfur,  $\text{Sb}_2\text{S}_3$  (stibnite) is formed at low to intermediately pH values and  $\text{SbS}_2^-$  is formed at higher pH values. The stability and structure of aqueous complexes formed by  $\text{Sb(III)}$  and  $\text{Sb(V)}$  with simple organic ligands were determined (Tella and Pokrovski, 2008; Tella and Pokrovski, 2009), which showed that stable complexes could be formed between  $\text{Sb(OH)}_3$  and oxalic, citric and lactic acids.



**Figure 2.** Eh-pH diagram of Sb in the Sb-S-H<sub>2</sub>O system (modified from Filella et al. (2002a))

### 1.1.3 Toxicity

Arsenic has been known to be toxic to both plants and animals for years. It is suspected to be a carcinogen for humans, which mostly affects the lungs and skin (e.g. Hughes, 2002; Shannon and Strayer, 1989). The chronic As toxicity on human is mostly caused by the intake of contaminated drinking water and food (Ratnaike, 2003). The toxicity of As is highly associated with its oxidation state. Generally, the inorganic As species are more toxic than their organic forms, and As(III) is usually more toxic than As(V). The inorganic As(III) compounds are approximately 60–80 times more toxic to humans than As(V) compounds (Villaescusa and Bollinger, 2008). Thus, it becomes necessary to determine As speciation in the analysis of samples.

Antimony and its compounds are gaining increasing environmental concern due to their more toxic behavior to plants and animals than expected. Sb(III) oxides had been shown to cause lung cancer in rats (Gebel, 1997). Both chronic exposure and long-term inhalation of Sb have undoubtedly harmful effects to eyes, skin and lungs (Cooper and Harrison, 2009). The accumulation of Sb in crops is a potential threat to human health and well-being. Similar to As, the trivalent Sb compounds are also generally more toxic than the pentavalent ones (Winship, 1986).

### 1.1.4 Sources and distribution in the environment

Both As and Sb occur naturally in the environment at trace levels. Arsenic is a component for more than 245 minerals (Mandal and Suzuki, 2002), which are generally found in metal ore deposits. Surface and ground waters near former mining or smelting sites often contain elevated levels of As and Sb. The major natural source of As is the weathering of rocks, and another major source is the deposition of As from the atmosphere (Tamaki and Frankenberger Jr, 1992). Anthropogenic activities such as combustion of fossil fuels, smelter operations and the application of agriculture products also contribute to the elevated As in the environment. In general, As is widely spread in many areas of the environment, including soils, sediments, waters, air and living organisms.

## INTRODUCTION

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Antimony is less common in nature than As. The abundance of Sb in the Earth's crust is approximately 0.2 mg/kg (Anderson, 2012) while As is present in the Earth's crust at an average of 2 to 5 mg/kg (Tamaki and Frankenberger Jr, 1992). It is observed that more than 100 natural minerals contain Sb. Similar to As, Sb can be found in natural waters, sediments and soils, and in atmosphere as a result of natural processes and human activities (Filella et al., 2002b). It was reported that the Sb smelting and mining processes resulted in a serious Sb contamination by releasing a large quantity of Sb into the environment (He et al., 2012; Wilson et al., 2004).

### 1.2 Remediation of As and Sb

The contamination of As and Sb in natural waters is a serious and worldwide problem and has become an challenge for scientists. A variety of technologies have been used and proposed to remove the two toxic elements from aqueous media, including adsorption, oxidation/precipitation, conventional co-precipitation, coagulation/flocculation, ion-exchange, membrane separation, electrochemical methods and other techniques like using household co-precipitation and filtration processes (e.g. Giles et al., 2011; Hering et al., 1997; Kameda et al., 2014; Kang et al., 2000; Melitas et al., 2002; Meng et al., 2001; Richmond et al., 2004; Song et al., 2014; Song et al., 2006; Wu et al., 2010; Zhu et al., 2011b). Among these methods, adsorption is considered as one of the most feasible methods for removing metalloids from water/wastewater in terms of the simplicity of operation, cost effectiveness and the regeneration capability (e.g. Ali and Gupta, 2006; Mohan and Pittman, 2007; Ungureanu et al., 2015). Numerous adsorbents were used for the removal of As and Sb, for example, natural and synthetic iron oxides (Dixit and Hering, 2003; Müller et al., 2010; Streat et al., 2008), aluminum oxides (Ilgen and Trainor, 2011; Jeong et al., 2007; Xu et al., 2001), titanium dioxide (Dutta et al., 2004; Jegadeesan et al., 2010), manganese oxides (Bajpai and Chaudhuri, 1999; Wang et al., 2012), activated carbon (Chen et al., 2007; Navarro and Alguacil, 2002), red mud (Altundoğan et al., 2000), resins (Balaji et al., 2005; Riveros, 2010),

clay minerals and sands (Lin and Puls, 2000; Maji et al., 2008; Manning and Goldberg, 1997; Rakshit et al., 2015).

### 1.2.1 Adsorption behavior of As

The distribution of the surface charge of most minerals is related to pH, which is positively charged when  $\text{pH} < \text{pzc}$  (point of zero charge) and negatively charged when  $\text{pH} > \text{pzc}$ . The existed species of As are also strongly affected by pH. A majority of studies reported about the effect of pH on the adsorption behavior of As. For example, it was widely observed that As(V) adsorption was at a maximum at acidic pH values and rapidly decreased in basic media onto siderite, hematite, goethite, magnetite and ferrihydrite (e.g. Guo et al., 2007; Mamindy-Pajany et al., 2009; Mamindy-Pajany et al., 2011; Raven et al., 1998). As(III) adsorption behavior exhibited less pH dependence on the surface sites of ferrihydrite (Raven et al., 1998; Swedlund and Webster, 1999; Wilkie and Hering, 1996; Zhu et al., 2011b). It was reported that both the adsorption of As(III) and As(V) decreased with the increase of solution pH on a novel Fe-Mn binary oxide (Zhang et al., 2007).

The effects of the competing ions such as phosphate, sulfate, carbonate and silicate on the adsorption behavior of As are important because As hardly exists alone in aqueous systems. The presence of tetrahedral anions, such as phosphate and silicate, were reported to significantly suppress the adsorption of As(V) on the surface sites of zero-valent iron (Su and Puls, 2001), natural iron ores (Zhang et al., 2004), goethite (Liu et al., 2001), iron hydroxides (Meng et al., 2002) and Fe–Mn binary oxides (Zhang et al., 2009). Other ions such as chloride, nitrate, sulfate and carbonate have an insignificant and negligible influence on both the adsorption of As(III) and As(V) (Kundu and Gupta, 2006a; Meng et al., 2000).

Based on the adsorption theory of electrostatic attraction, the negatively As(V) species should be more strongly adsorbed than the neutral As(III) species onto hydrous ferric oxide. There is however discrepancy between the theoretical considerations and the experimental observations in the previous studies. Raven et al. (1998) concluded that As(V) adsorption on ferrihydrite was faster at low As concentrations and pH, but As(III) was retained in much

## INTRODUCTION

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larger amounts than As(V) at high initial concentrations. Another study conducted by Zhu et al. (2011a) presented similar observations that the adsorption capacity of As(III) was greater than As(V) in the pH range of 4 to 11 on ferrihydrite. Therefore, the initial concentrations of adsorbates have a major influence on the adsorption behavior of As, which is also affected by the oxidation states of species and adsorbent dosages.

Lots of previous studies have been involved in the study of the adsorption behavior of As in single systems. So far, less information is available on the competitive adsorption of As(III) and As(V). Jain and Loeppert (2000) studied the competitive adsorption of As(III) and As(V) onto ferrihydrite and the competitive interactions were highly dependent on pH and initial As concentrations. The presence of As(V) had a more pronounced effect on As(III) adsorption at low initial concentrations than vice versa, and As(V) had no influence on As(III) adsorption but As(III) substantially reduced As(V) adsorption at high initial concentration. Maiti et al. (2012) evaluated the adsorption capacity of single As species and a mixture of As(III) and As(V) on treated laterite. The competitive adsorption kinetics revealed that the adsorption of As(V) was not competitive with As(III) but the adsorption of As(III) was slightly affected by As(V). Goldberg (2002) reported that the presence of equimolar As(III) had no competitive effect on As(V) adsorption on amorphous Al and Fe oxides and clays, but the adsorption of As(III) was slightly affected by As(V) on kaolinite and illite. Hsu et al. (2008) observed that the total As removal efficiencies by reclaimed iron-oxide coated sands were in the order of As(V) > As(V)+As(III) > As(III) at the same initial solution pH and adsorbent dosage, and the results demonstrated that a weak chemical interaction or competition took place between As(III) and As(V).

### **1.2.2 Adsorption behavior of Sb**

The adsorption behavior of Sb was studied on different types of iron oxides, for example, on goethite (Leuz et al., 2006b), hematite (Shan et al., 2014) and magnetite (Mittal et al., 2013). It was observed that the factor of pH had an evident influence on the adsorption behavior of Sb. The adsorption of Sb(V) was favored at acidic pH while the adsorption of Sb(III) was

## INTRODUCTION

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constant over a broad range of pH on iron hydroxides (Guo et al., 2014; Leuz et al., 2006b). It was also reported that Sb(III) adsorption was independent on pH and ionic strength on the red earth soil with rich iron oxides while the highest Sb(V) adsorption occurred at lowest pH and affected by the ionic strength (Vithanage et al., 2013). Shan et al. (2014) pointed out that the removal of trace Sb(III) by hematite modified magnetic nanoparticles was not obviously affected by the solution pH, the ionic strength and the coexisting anions (chloride, nitrate, sulfate, silicate and phosphate). Zhao et al. (2014) evaluated Sb(III) and Sb(V) removal by zero-valent iron nanoparticles coated with PVA. The maximum adsorption capacity of both Sb(III) and Sb(V) was obtained at pH less than 5, but as pH increased Sb(III) adsorption dropped slightly while Sb(V) adsorption dropped significantly. The coexistence of oxyanions also could affect the removal efficiency of Sb. It was reported that the presence of nitrate, sulfate and phosphate had a slight effect on the adsorption of Sb(III), but sulfate, phosphate and carbonate inhibited the adsorption of Sb(V) (He et al., 2015; Wu et al., 2010; Xi et al., 2011). It was observed that the presence of phosphate significantly decreased Sb(III) adsorption on goethite and the presence of nitrate and sulfate had no effect on the adsorption of Sb(III) (Xi et al., 2013). However, to the best of my knowledge, there were no reports about the competitive adsorption of Sb(III) and Sb(V) in previous studies.

### **1.2.3 Redox process of Sb(III) accompanied with adsorption**

The mobility and the fate of Sb could be strongly influenced by both adsorption and redox processes. In contrast to Sb(V) as a stabilized oxidation state in the environment, Sb(III) can be oxidized in the presence of hydrogen peroxide, hydroxyl radical ( $\cdot\text{OH}$ ), iodate, and co-oxidants of iron and oxygen (Leuz et al., 2006a; Leuz and Johnson, 2005; Quentel et al., 2004). The previous studies reported the simultaneous adsorption and oxidation of Sb(III) such as on goethite (Fan et al., 2014; Leuz et al., 2006b), amorphous Fe and Mn oxyhydroxides (Belzile et al., 2001). Fan et al. (2014) reported that Sb(III) can be adsorbed and oxidized by goethite with the irradiated light and the solution pH had a great impact on its oxidation. However, the fate and mobility of the formed Sb(V) during the process of Sb(III)

adsorption are still controversial. A recent study by Kong et al. (2015) reported that the oxidation of Sb(III) occurred in both solution and on pyrite surfaces in oxic conditions and the oxidation efficiency of Sb(III) increased with the increase of pH. Another study pointed out that the oxidation of Sb(III) by manganite took place rapidly as well as the formation of soluble Sb(V) in a few minutes. The XANES analyses also showed that Sb(V) was the dominant species adsorbed on manganite (Wang et al., 2012), which is in agreement with the observations obtained from other studies (Guo et al., 2014; Xi et al., 2013). The complexation with EDTA could prevent and decrease the rate of the oxidation of Sb(III) to Sb(V) at a regular time interval, which can be used to preserve the inorganic Sb species (Daus and Wennrich, 2014; Ilgen et al., 2014; Wu and Pichler, 2015). A review summarized by Filella et al. (2009) reported that the oxidation of Sb(III) could be prevented by the addition of other organic acids such as lactic, ascorbic, citric, tartaric acids. Thus, in order to better understand the fate and mobility of the newly formed Sb(V), it is more significant to determine the Sb speciation in the supernatant of Sb(III) adsorption.

### 1.3 Adsorption mechanism

Spectroscopy methods are extensively used to study the adsorption mechanisms of ions on surfaces, including Fourier transform infrared (FTIR), extended X-ray absorption fine structure spectroscopy (EXAFS), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. The formation of inner-sphere complexes between As and the surface sites was identified by the spectroscopic studies, such as on manganite (Liu et al., 2015), goethite (Sun and Doner, 1996), ferrihydrite and crystalline FeOOH (Waychunas et al., 1993), aluminum and iron oxides (Arai et al., 2001; Goldberg and Johnston, 2001). Spectroscopy techniques are also used to determine the adsorption mechanism of Sb, which was mainly adsorbed in an inner-sphere mode on the surface sites of iron oxides (McComb et al., 2007; Mitsunobu et al., 2010; Vithanage et al., 2013), aluminum oxides (Ilgen and Trainor, 2011), Fe-modified aerobic granules (Wang et al., 2015). Thus due to both As and Sb could share

similar adsorption mechanisms, the study of the simultaneous/competitive adsorption of As and Sb is more meaningful.

The adsorption mechanisms of As and Sb were also assessed by the modeling approaches such as surface complexation modeling (Goldberg and Johnston, 2001; Guo et al., 2014; Han et al., 2010; Jang et al., 2003; Kanematsu et al., 2013; Vithanage et al., 2013). However, most of the modeling approaches were based on batch experiments in single species systems. The potential for predicting the competitive adsorption mechanism of As and Sb using modeling methods needs further studies.

### 1.4 Simultaneous removal of As and Sb

Local soils and waters around old mining and smelting areas are generally found to have high concentrations of As and Sb. For example, it was reported that a dietary of co-exposure of high levels of As and Sb had health risks to residents in the world's largest Sb mining area (Xikuangshan, China) (Wu et al., 2011). Elevated concentrations of As and Sb were detected in ground water and surface water in the close vicinity of abandoned Sb mines, reaching up to 2150 µg/L As and 9300 µg/L Sb (Hiller et al., 2012). The contamination of the coexistence of As and Sb was also reported in Corsica (Migon and Mori, 1999) and Ghana (Serfor-Armah et al., 2006). However, the simultaneous removal of As and Sb has attained relatively little attention. Sazakli et al. (2015) reported that granular ferric oxide exhibited a high efficiency for the simultaneous removal of As and Sb from drinking water. The presence of As did not substantially affect the removal of Sb and vice versa. Lu et al. (2015) synthesized a ferric-based layered double hydroxide (Zn-Fe-LDH), which showed a high efficiency for the simultaneous removal of As(V) and Sb(V) from aqueous solutions. Kolbe et al. (2011) compared the sorption behavior of the inorganic As and Sb species on akaganeite. The addition of Sb(V) did not influence the adsorption of As(V) while the adsorption of Sb(V) adsorption was reduced due to the presence of As(V). A recent study reported that the

## INTRODUCTION

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different adsorption affinity of As(V) and Sb(V) in soils was related to their distinct structures, and Sb(V) was more mobile than As(V) in soils (Dousova et al., 2015).

Both As and Sb mainly exist in two oxidation states (+3 and +5) in the aquatic environment. They are often found to combine with Fe-rich phases involving both amorphous and crystalline iron oxides in nature. The four possible redox species could be present together. They could compete on the surface sites of the minerals. However, there has been no study about the simultaneous removal of As(III), As(V), Sb(III) and Sb(V) from the same system. Thus, the simultaneous removal involving the four redox species is necessary.

Ferrihydrite, which is also known as hydrous ferric oxide (HFO), is one of the most predominant adsorbents for toxic contaminants because of its large surface area and high reactivity. It is designated as “2-line” and “6-line” ferrihydrite according to the number of peaks in X-ray diffraction patterns (Michel et al., 2007). It is commonly found in aquatic systems, soils and sediments. In this research, ferrihydrite was selected as an adsorbent for exploring the simultaneous adsorption properties and competitive interactions of As and Sb. Meanwhile, the study of the competitive/simultaneous adsorption of As and Sb onto ferrihydrite is also important for understanding their geochemical behavior, distribution, accumulation and transport in the natural environment.

## INTRODUCTION

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## 2. Scopes and objectives

This study mainly focused on investigating the adsorption properties and behavior of As and Sb under competitive conditions. So far, most studies have been involved in the adsorption of As and Sb individually. However, there are a lot similarities between As and Sb, and they are often detected to be present together in nature. Thus it is more meaningful to study the simultaneous adsorption behavior of As and Sb in multi-component systems. This study also contributes to better understand the fate, mobility and transport of As and Sb in the environment. This project mainly involved:

- 1) Batch experiments were carried out to investigate the competitive interactions between As(III) and As(V) on ferrihydrite by varying pH, adsorbent dosage, concentration ratios and the order of additions. The adsorption kinetic and isotherm studies of As(III) and As(V) were also conducted in single and binary systems. The competitive adsorption mechanism of As(III) and As(V) was explored.
- 2) Sequential and simultaneous adsorption experiments of Sb(III) and Sb(V) were conducted. Sb speciation analysis in aqueous phase was determined during single Sb(III) adsorption experiments in order to explore the properties of simultaneous oxidation and adsorption of Sb(III).
- 3) The simultaneous adsorption behavior of As(III), As(V), Sb(III) and Sb(V) on ferrihydrite was evaluated in multi-component systems. The effect of anions of  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  on the simultaneous adsorption of As(III) and Sb(III), or As(V) and Sb(V), were studied. The competitive interactions of the four redox species were discussed.

Specifically, four papers are presented in this thesis. The first paper “Closers look at As(III) and As(V) adsorption onto ferrihydrite under competitive conditions” (Chapter 3), which was published in Langmuir, gives an overview about the adsorption behavior of As(III) and As(V) in single and binary systems. The main objective in this study was to investigate the competitive interactions of As(III) and As(V) on ferrihydrite as a function of pH, adsorbent

## SCOPES AND OBJECTIVES

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dosage, concentration of coexisting ligands and the order of addition. It was observed that As(III) more or less outcompeted As(V) across the pH scale from 4 to 10. It also gave a closer look on the mobility and transport of As species in the environment.

Chapter 4 with the title of “Closer look at As(III) and As(V) adsorption onto ferrihydrite under competitive conditions: isotherms and kinetics” was a subsequent study of the competitive adsorption of As(III) and As(V) through applicable isotherm and kinetic models. Furthermore, the competitive adsorption mechanism of the two As redox species was discussed using the spectroscopy method of FTIR.

Chapter 5 is about “Sequential and simultaneous adsorption of Sb(III) and Sb(V) on ferrihydrite: Implications for oxidation and competition”, which is published in “Chemosphere”. It presents the simultaneous adsorption and oxidation of Sb(III) onto ferrihydrite as well as the simultaneous adsorption of Sb(III) and Sb(V) as a function of pH. Sb is gaining environmental concern because of its more toxic properties than expected. However, less is known about Sb compared to As. The simultaneous adsorption and oxidation of Sb(III) was confirmed by the appearance of Sb(V) in the solution at varying Fe/Sb ratios and pH values. It was found that the presence of Sb(V) had no impact on Sb(III) adsorption while Sb(V) adsorption was negatively affected by Sb(III) over a wide pH range.

In the environment As could occur along with Sb and both of which are toxic. But the simultaneous adsorption and competitive interactions of As and Sb have been hardly studied. Thus the last study about “Simultaneous adsorption of As(III), As(V), Sb(III) and Sb(V) in aqueous media by ferrihydrite” is shown in Chapter 6. In this study, the simultaneous adsorption behavior involving the four redox species were evaluated on ferrihydrite as a function of pH in multi-component (binary, ternary, quaternary) systems. The effect of interfering ions ( $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) were also evaluated. This study showed that both the adsorption of As(III) and Sb(V) was reduced by the presence of Sb(III) and As(V), but As(III) and Sb(V) did not play any significant role in the adsorption of Sb(III) and As(V).

My contributions to each chapter are listed as follows:

**Chapter 3: “Closer look at As(III) and As(V) adsorption onto ferrihydrite under competitive conditions”**

- Literature study
- Participated in experimental design
- Did experiments and measured samples by HG-AFS
- Data interpretation
- Wrote the first draft of the published paper

**Chapter 4: “Closer look at As(III) and As(V) adsorption onto ferrihydrite under competitive conditions: isotherms and kinetics”**

- Participated in experimental design
- Did adsorption experiments
- Sample analysis by HG-AFS
- Wrote the first draft of the manuscript

**Chapter 5: “Sequential and simultaneous adsorption of Sb(III) and Sb(V) on ferrihydrite: Implications for oxidation and competition”**

- Literature study
- Major participant in experimental design
- Did experiments
- Measured samples by HG-AFS
- Wrote the first draft of the published paper

**Chapter 6: “Simultaneous adsorption of As(III), As(V), Sb(III) and Sb(V) in aqueous media by ferrihydrite”**

- Did adsorption experiments
- Sample analysis by HG-AFS
- Data interpretation
- Wrote the first draft of the manuscript

## **SCOPES AND OBJECTIVES**

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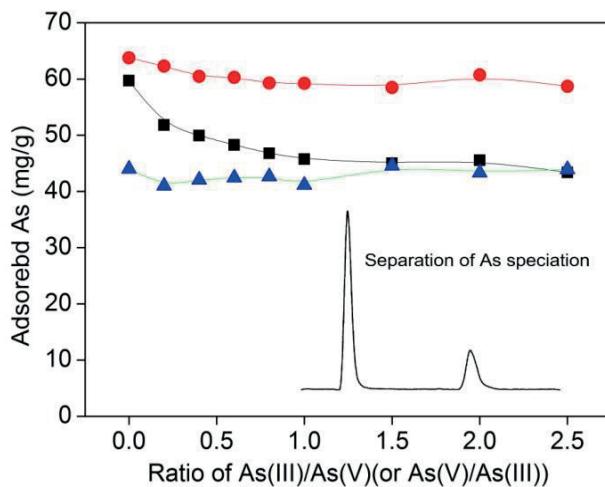
### **3. Closer look at As(III) and As(V) adsorption onto ferrihydrite under competitive conditions**

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**TOC graphic****Abstract**

Batch experiments were conducted in order to investigate the competitive interaction of arsenite (As(III)) and arsenate (As(V)) onto ferrihydrite as a function of initial pH, adsorbent dosage, concentration of coexisting ligands, and order of addition. The pH generally had a great impact on adsorption under both single ion and competitive conditions. However, the amount of As(V) in solution was the controlling factor of adsorption behavior, and As(III) more or less outcompeted As(V) across the pH scale from 4 to 10. Under competitive conditions, i.e., both species were present at the same time, As(III) and As(V) was adsorbed almost equally up to a pH of 5 at an adsorbent dosage of 0.5 g/L and up to a pH of 6 at an adsorbent dosage of 1 g/L. This was contrary to the theoretical prediction that As(V) should adsorb more strongly than As(III) at pH values below the point of zero charge (pzc) of ferrihydrite of about 7 to 8. At low pH, As(V) impedes the adsorption of As(III) but to lesser degree than As(III) impedes As(V) adsorption at a pH above 6. The effect of As(III) on the adsorption of As(V) increased with an increase in pH, and the adsorption of As(V) was almost absent at pH 9 at an adsorbent dosage of 1 g/L and at pH 8 at an adsorbent dosage of 0.5 g/L. In the range of ferrihydrite dosages from 0.2 to 1.6 g/L, As(III) was adsorbed preferentially over As(V) under the availability of less adsorbent. The order of anion addition also had significant effects on 18

their competitive adsorption behavior: the first species was always more favored to compete for the adsorbing sites than when the two species were added to the suspensions simultaneously.

### **3.1 Introduction**

Arsenic (As), a natural metalloid, is present in virtually every part of the environment, including atmosphere, soil, rocks, water and food, which can have an impact on human health, something that has been recognized as a global problem (Bissen and Frimmel, 2003; Jones, 2007; Smedley and Kinniburgh, 2002). Trivalent As (As(III)) and pentavalent As (As(V)) are regularly detected in groundwater, and both species are known to exist. Exposure to inorganic arsenic (As(III) or As(V)) affecting the lungs, skin, liver, kidney and blood vessels was recognized to be a risk for human, As(V) and more toxic As(III) must be removed from drinking water when concentrations are above of what is considered safe for human consumption (Ahmed et al., 2006; Basu et al., 2014). Among a number of techniques, such as chemical precipitation, ion exchange, filtration and reverse osmosis, adsorption is considered as an inexpensive, simple, safe, and versatile method for the removal of As (Gallegos-Garcia et al., 2012). In nature, adsorption onto the mineral ferrihydrite seems to be the main mechanism to control the fate and transport of As (Pichler et al., 1999b). Thus, numerous studies quantified As(V) and As(III) adsorption behavior on iron oxides and hydroxides, such as ferrihydrite, goethite and hematite (Dixit and Hering, 2003; Maiti et al., 2008; Pierce and Moore, 1982; Raven et al., 1998). Up to a pH of about 7 to 8 the surface of ferrihydrite is mainly positively charged and theoretically the adsorption of the As(V) oxyanion,  $\text{HAsO}_4^{2-}$  should be favored over that of the neutrally charged As(III) complex,  $\text{H}_3\text{AsO}_3$ . There is however discrepancy between theoretical considerations and experimental observations. Several studies concluded that As(V) adsorption is pH dependent whereas As(III) adsorption is less affected by pH (Jeong et al., 2007; Kundu and Gupta, 2006a; Maiti et al., 2008; Manning et al., 1998). It was pointed out that sorption of As(V) onto HFO and goethite was more favorable than that of As(III) below pH 5 to 6 (Dixit and Hering, 2003). Jain and Loepert (2000) observed As(V) was better adsorbed than As(III) on ferrihydrite at low pH and at low initial concentration, while the opposite occurred at high initial arsenic concentration. Raven et al. (1998) reported that As(V) adsorption was greater than As(III)

adsorption at a lower pH whereas As(III) adsorption was greater at a higher pH or at high arsenic concentrations.

As(V) mainly formed inner-sphere complexes on hydrous ferric oxide (HFO), whereas As(III) was retained by a combination of inner and outer-sphere surface complexes (Goldberg and Johnston, 2001; Ona-Nguema et al., 2005; Waychunas et al., 1993).

The presence of competing anions, such as sulfate, bicarbonate, silicate, selenium and antimony, significantly affects As adsorption (Bullough et al., 2010; Jeong et al., 2007; Manning and Goldberg, 1996). For example, phosphate is a major competitor for both As(V) and As(III) (Stachowicz et al., 2008). Similarly, the presence of As(III) might influence the adsorption of As(V) and vice versa. Most research into As adsorption involved only single-component adsorption of either As(III) or As(V). Only a few studies concerning the competitive adsorption of As(III) and As(V) exist. Jain and Loeppert (2000) also found that in the dual anion system at equimolar As concentrations of  $\leq 156 \text{ mg}\cdot\text{L}^{-1}$  each, As(V) influenced the retention of As(III) in the pH range of 4 to 10 more pronouncedly than As(III) influenced the retention of As(V). Goldberg (2002) reported that the presence of As(III) had no competitive effect on As(V) adsorption, and the influence of As(III) adsorption on As(V) was minor and apparent only for kaolinite and illite.

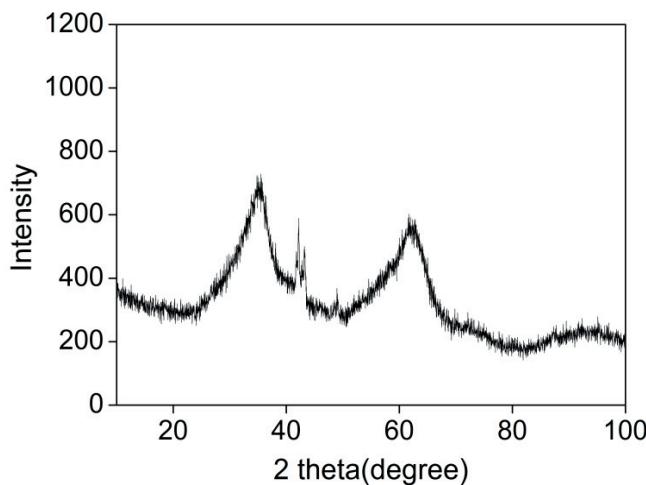
To understand better the competition between As(III) and As(V) for adsorption sites on ferrihydrite, a set of experiments were carried out for the individual species, i.e. either As(III) or As(V) was present and both species were present at the same time. The objectives of this work were to evaluate (1) the individual and competitive adsorption of As(V) and As(III) within a wide range of pH (4 to 10) at different adsorbent dosages; (2) the competition as a function of adsorbent dosages; (3) the effect of increasing concentrations of As(III) on the removal of As(V) and vice versa; and (4) the order of species addition on competitive adsorption.

## **3.2 Materials and methods**

### **3.2.1 Materials**

Distilled de-ionized water (DDI) with a resistivity better than  $18 \text{ M}\Omega\cdot\text{cm}$  was used to prepare all of the solutions. Stock solutions of As(V) and As(III) (1000 mg/L) were prepared by dissolving of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (Sigma-Aldrich, Spain) and  $\text{As}_2\text{O}_3$  (Sigma-Aldrich, Spain) in the DDI water and 4% NaOH solution, respectively. To maintain a relatively constant ionic strength, all working As solutions were freshly prepared with a background electrolyte concentration of 0.01 M NaCl. Other reagents used, such as HCl, NaOH, and NaCl, were at least analytical grade.

Ferrihydrite was synthesized according to the method of Schwertmann and Cornell (2008) by adding dropwise and under constant stirring a 1 molar solution of KOH (Sigma-Aldrich, Germany) to 500 mL of 0.2 molar  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Alfa Aesar, Germany) until the pH increased to  $7.4 \pm 0.1$  and ferrihydrite started to precipitate. The precipitate was then 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 (Figure 1), and the surface area of freeze-dried ferrihydrite was  $120 \text{ m}^2/\text{g}$ , as analyzed by the BET (Brunauer-Emmett-Teller) method. The discrepancy between this value and the theoretically possible value may due to the aggregation the nano particles (Schwertmann and Cornell, 2008).



**Figure 1.** X-ray diffraction pattern of the synthesized ferrihydrite.

### 3.2.2 Experimental procedure

The experiments of As(III) and As(V) adsorption were carried out in 50 mL polyethylene vials. A solution of As(III) or As(V) of known concentrations or their mixture in equal concentration was pipetted into vials in contact with 0.5 g/L or 1 g/L adsorbent (molar ratio of Fe/As corresponding to 8.48 or 16.96). The vials were capped and shaken in a Rotoshake (RS12/RS8) at 20 rpm at room temperature for 24 h. Kinetics experiments were carried out and 24 hour reaction time was adequate to reach equilibrium. The pH of the suspension was adjusted using HCl or NaOH at the beginning, and once the experiment approached equilibrium, the final pH was measured to assess the change in pH during the experiment. The suspensions were filtered with a syringe filter with a pore size of 0.45  $\mu\text{m}$ , and the supernatant was then analyzed for total As or As speciation. Arsenic speciation was measured, and As(V) was undetectable in the supernatant of As(III) adsorption. In addition, dissolved iron was negligible, indicating that the oxidation of As(III) did not occur. Similarly, previous studies also reported that no oxidation occurred within 72 hours (Oscarson et al., 1981) and Manning et al. (1998) found no heterogeneous oxidation of As(III) to As(V) on goethite using spectroscopy (XANES). In addition, Zhao et al. (2011) showed that As(III) oxidation on ferrhydrite did not occur at low Fe/As ratios. The oxidation of dissolved As(III) to

As(V) by atmospheric oxygen is unlikely because the reaction vessels were capped, oxygen diffusion was slow and the As concentrations were sufficiently high (Johnson and Pilson, 1975). Therefore, oxidation and reduction of As is not an disturbing factor in our competitive adsorption experiments.

To study the effect of the adsorbent dosage on adsorption, a series of 50 mL As solutions containing As(III), As(V) or a mixture of both species were equilibrated with increasing amounts of adsorbent (0.2 to 1.6 g/L) for 24 h in a shaker at pH 6.

To investigate the competitive effect of As(III) on the adsorption of As(V) at pH 4 and vice versa at pH 4 and 9, the competition during adsorption was evaluated by varying the individual concentrations of As(V) and As(III). A mixture of As solution, with the concentration ratios of As(III)/As(V) (or As(V)/As(III)) from 0 to 2.5, was brought in contact with 1 g/L adsorbent, and the residual arsenic species were determined after 24 h.

Experiments with simultaneous and sequential addition of As(V) and As(III) were carried out for a series of initial As concentrations. During the simultaneous addition experiments, a mixture of both species with equal concentrations was brought into contact with 25 mg of ferrihydrite at the same time. The mixture was then shaken for 48 h. During the sequential addition experiments, As(III) was first added to 25 mg ferrihydrite and then shaken for 24 h. The same concentration of As(V) was then added after 24 h and shaken for an additional 24 h. In another experiments the order was reversed, i.e., As(V) was added first and shaken for 24 h, and then As(III) was added and shaken for another 24 h. The supernatants of all experiments were analyzed for As speciation.

### **3.2.3 Analytical methods**

As species were separated by liquid chromatography (LC) using Hamiltion PRP-X100 column, and the concentrations were determined by hydride generation atomic fluorescence spectroscopy (HG-AFS) on a PSAnalytical Millennium System, which was directly coupled to the LC system. The detection limit for As(III) and As(V) of this method are 0.17 µg/L and 0.38 µg/L (Gomez-Ariza et al., 1998; Wu and Pichler, 2014), respectively, with a precision of ± 2%.

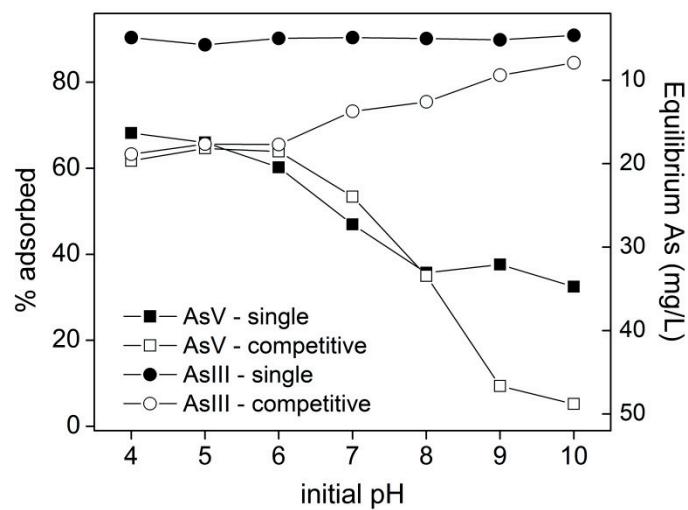
The flow rate was 1.5 mL/min, and a 20 mM phosphate buffer ( $\text{H}_6\text{NO}_4\text{P}$ , Fluka, India) was used as the mobile phase. The pH of the mobile was adjusted to 6 with ammonia. A detailed description of the analytical procedures can be found elsewhere (Price et al., 2007).

The total As concentration was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) on an Optima 7300 DV instrument. On the basis of at least three repeat measurements, the analytical precision was estimated to be between 2 and 3 % and the detection limit was 0.02 mg/L.

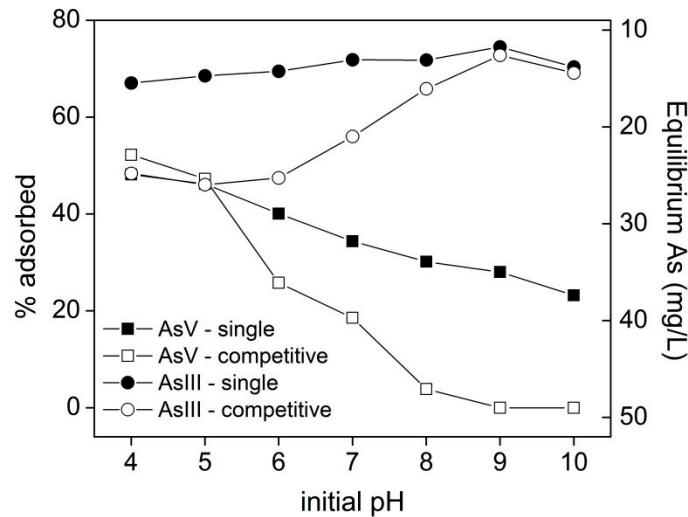
### **3.3 Results**

#### **3.3.1 Effect of initial pH**

Figures 2 and 3 show the relationship between the initial solution pH and the percentage of As adsorbed under single and competitive conditions at different ferrihydrite dosages. The As(V) adsorption efficiency is clearly dependent on pH, with a higher adsorption capacity at lower pH, decreasing with increasing pH. A different trend was observed for As(III) adsorption, which was more or less constant over a wide pH range. The shapes of the As(V) adsorption edges in the presence of As(III) were similar to those observed without As(III), and the influence of As(III) on As(V) adsorption was negligible under acidic conditions. Competition between the two species was demonstrated by the change in adsorption behavior relative to the availability of adsorption sites. In Figure 2 at a ferrihydrite dosage of 1 g/L, As(V) adsorption remained relatively constant until a pH of 6, while at a ferrihydrite dosage of 0.5 g/L, adsorption decreased at pH greater than 5. The presence of As(V) always had an inhibitory impact on the adsorption of As(III) over a wide pH range (4 - 10) at each ferrihydrite dosage studied. The inhibitory effect on As(III) adsorption by As(V) was stronger at low pH than at high pH. The quantities of As(III) adsorbed decreased under competitive conditions compared with those adsorbed when As(III) was added alone. For example, at a ferrihydrite dosage of 1 g/L and at pH 4, 90.4 % of As(III) was adsorbed in the single species system but only 63.3 % As(III) was adsorbed in the presence of As(V).



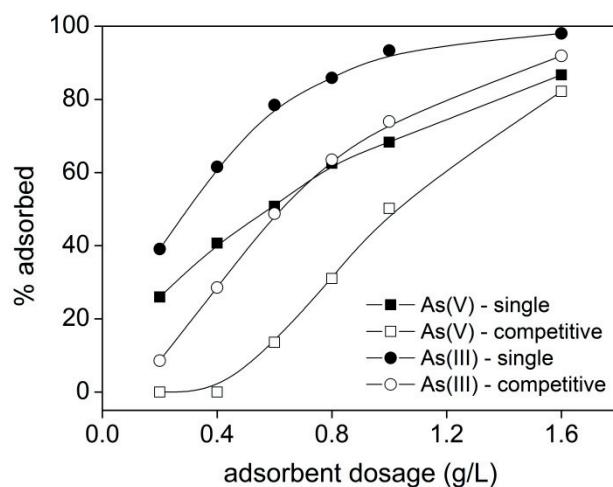
**Figure 2.** Percent adsorption of As(III) and As(V) onto ferrihydrite as a function of initial pH in single and competitive adsorption experiments (single adsorption, concentration of each As species, 50 mg/L; competitive adsorption, As(III) and As(V), 50 mg/L each; initial pH range from 4 to 10; adsorbent dosage, 1 g/L).



**Figure 3.** Percent adsorption of As(III) and As(V) onto ferrihydrite as a function of initial pH in single and competitive adsorption experiments (single adsorption, concentration of each As species, 50 mg/L; competitive adsorption, As(III) and As(V), 50 mg/L each; initial pH range from 4 to 10; adsorbent dosage, 0.5 g/L).

### 3.3.2 Effect of adsorbent dosage

The adsorption capacity can be affected by the quantity of adsorbent, particularly under competitive conditions. The dependence of As adsorption on the adsorbent dosage from 0.2 to 1.6 g/L is shown in Figure 4 as the removal of the two As species from solution, i.e. adsorption, increased with increasing ferrihydrite dosages. Compared to the adsorption of a single species, at the ferrihydrite dosage less than 0.4 g/L, less As(III) was adsorbed under competitive conditions, whereas As(V) adsorption was negligible. Both As(III) and As(V) uptake under competitive conditions was lower than their respective adsorption during single-species experiments; i.e., the individual adsorption percentages of As(V) and As(III) were 68.3 %, and 93.4 % at a ferrihydrite dosage of 1 g/L, while their adsorption percentages under competitive conditions were 50.2 and 73.9 %, respectively. Competition was weaker with increasing ferrihydrite dosages; i.e., the inhibitory extent on As(III) adsorption by As(V) was around 26 versus 6.25 % at a ferrihydrite dosage of 0.8 versus 1.6 g/L. This suggests that the competition increases with a decreasing number of adsorption sites and could be considered for site heterogeneity on the surface of ferrihydrite.

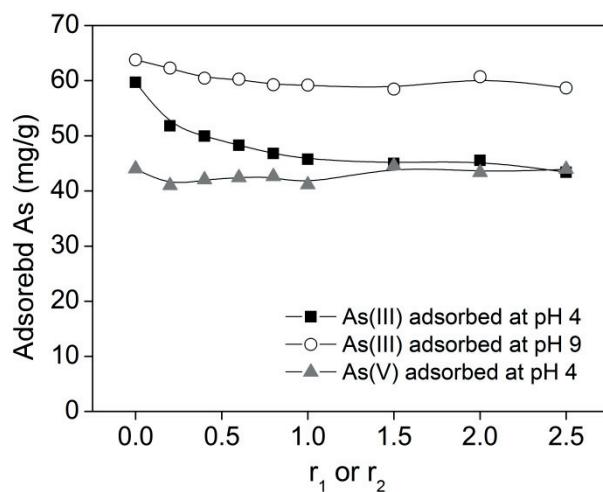


**Figure 4.** Effect of adsorbent dosage on the removal of As(V) and As(III) in single and competitive adsorption experiments (single adsorption, concentration of each As species, 50 mg/L; competitive adsorption, As(III) and As(V), 50 mg/L each; pH value, 6; adsorbent dosage, 0.2 to 1.6 g/L).

### 3.3.3 Effect of increasing concentrations of As (III) (or As(V)) on adsorption of As(V) (or As(III))

Figure 5 presents the amount of As(III) adsorbed on ferrihydrite at pH 4 and 9 in the presence of increasing concentrations of As(V). The adsorption of As(V) at low pH 4 under the condition of increasing concentration of As(III) is shown in Figure 5. The initial concentration ratio of competing and objective ions ( $\text{As(V)}/\text{As(III)} = r_1$  or  $\text{As(III)}/\text{As(V)} = r_2$ ) ranged from 0 to 2.5.

The amount of As(III) adsorption decreased gradually with an increase in  $r_1$  from 0 to 2.5 at both pH values, i.e., from 59.7 to 43.4 mg/g at pH 4 and from 63.8 to 58.7 mg/g at pH 9. The decline of As(III) adsorption was larger under acidic conditions than under alkaline conditions. The adsorption envelope stayed the same up to an  $r_1$  of 1.5. Comparatively, the quantities of As(V) adsorbed remained practically constant at pH 4 for  $r_2$  ranging from 0 to 2.5. Therefore, adsorption of As(III) was disturbed in the presence of As(V) and decreases as the abundance of As(V) increases. The adsorption of As(V) was irrespective of the presence of increasing concentrations of As(III).

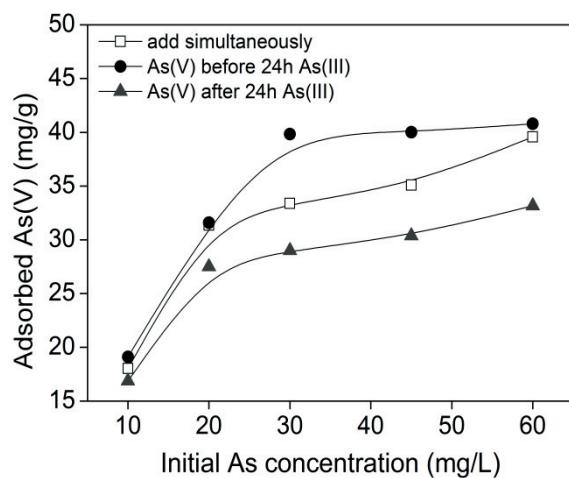


**Figure 5.** As(III) adsorption behavior under increasing concentrations of As(V) ( $\text{As(V)}/\text{As(III)}$  concentration ratio  $r_1 = 0$  to 2.5; pH values, 4 or 9), and As(V) adsorption behavior under increasing concentrations of As(III) ( $\text{As(III)}/\text{As(V)}$  concentration ratio  $r_2 = 0$  to 2.5; pH value, 4)

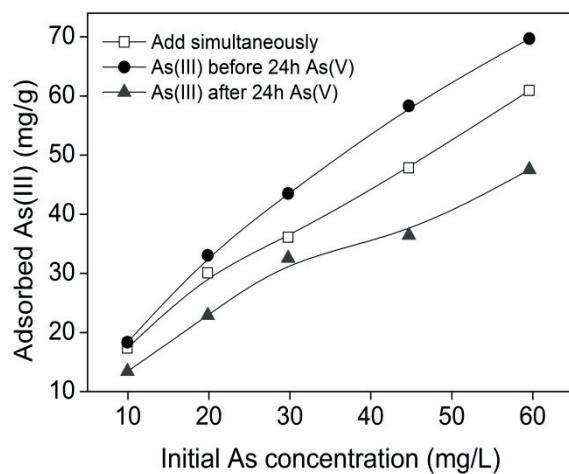
### **3.3.4 Influence of the order of addition**

The competitive adsorption experiments with As(III) and As(V) added simultaneously and sequentially were conducted at pH 5. Figures 6 and 7 show the amounts of As(V) and As(III) adsorbed at different initial As concentrations when: the competing species were added (a) at the same time, (b) 24 h before, and (c) 24 h later. The results show that the order of addition had a significant influence on the amount of either As(III) or As(V) adsorbed in the experiments with both species present at the same time. The overall amount of arsenic adsorbed increased with the initial As concentrations.

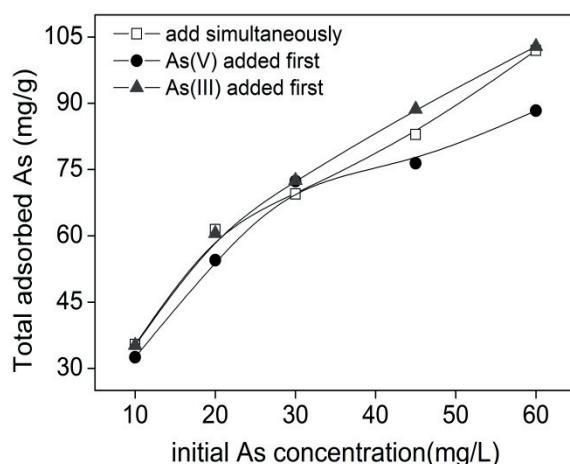
Most arsenic was adsorbed when the main species were added to ferrihydrite 24 h prior, while the smallest amount of arsenic was adsorbed when the competing species were added 24 h prior (Figures 6 and 7). The amount of arsenic adsorbed was between these two values, when both the main and competing species were added at the same time. In other words, when As(III) and As(V) were added simultaneously, the ability of As(V) preventing the adsorption of As(III) was slightly greater than that in the As(V) before As(III) systems whereas lower than those in the As(III) before As(V) systems. However, compared to the order of addition affected either As(III) or As(V) adsorbed, it did not have a considerable influence on the total amounts of As(III) and As(V) adsorbed (Figure 8). It is evident that the first As species was always more favored to compete for the adsorption sites than when the species were added simultaneously. This is particularly true once the conditions get more and more competitive.



**Figure 6.** Adsorption behavior of As(V) under competitive conditions as a function of exposure order (pH value, 5; adsorbent dosage, 0.5 g/L; As(V) added 24 h before As(III); As(III) added 24 h before As(V); and the two species added simultaneously)



**Figure 7.** Adsorption behavior of As(III) under competitive conditions as a function of exposure order (pH value, 5; adsorbent dosage, 0.5 g/L; As(III) added 24 h before As(V); As(V) added 24 h before As(III); and the two species added simultaneously)



**Figure 8.** The total amounts of As(V) and As(III) adsorbed onto ferrihydrite under competitive conditions as a function of exposure order (pH value, 5; adsorbent dosage, 0.5 g/L; As(III) added 24 h before As(V); As(V) added 24 h before As(III); and the two species added simultaneously)

### 3.4 Discussion

#### 3.4.1 Arsenic adsorption behavior under varying pH

The solution pH is an important control for the distribution of the As species, which in turn highly affects the adsorption. The adsorption of As(V) was favored at low pH and decreased considerably with increasing pH, while the pH had a minor influence on As(III) adsorption, which corresponds to their adsorption behavior under competitive conditions (Figures 2 and 3). The dependence of As(V) adsorption on pH may be caused by (1) electrostatic attraction and (2) the formation of inner-sphere complexes by ligand exchange (Goldberg and Johnston, 2001). Specific adsorption may occur between uncharged species  $\text{H}_3\text{AsO}_3^0$  and HFO (Bowell, 1994; Pierce and Moore, 1982). It was reported that the mechanism of adsorption of As(III) may be a complexation reaction rather than a surface potential (Pokhrel and Viraraghavan, 2008). Contrary to theoretical considerations, As(III) showed a higher affinity than As(V) even at low pH in our single adsorption experiments. A study conducted by Chakravarty et al. (2002) showed that ferruginous manganese ore was an efficient adsorbent for both arsenic species but showed a higher adsorption for As(III). Similar findings were observed by others

who reported that As(III) was adsorbed more strongly than As(V) on ferrihydrite at high As concentrations of  $13.3 \text{ mol}_{\text{As}} \text{ kg}_{\text{fer}}^{-1}$  and  $3.47 \text{ mol}_{\text{As}} \text{ kg}_{\text{fer}}^{-1}$  (Jain and Loeppert, 2000; Raven et al., 1998). At low As concentrations, the adsorption of As(III) was approximately equal to that of As(V). In this study, the As(III) adsorption was already stronger at lower As concentrations of  $0.67 \text{ mol}_{\text{As}} \text{ kg}_{\text{fer}}^{-1}$  than those reported by Raven et al. (1998), which should be caused by a lower surface area of the ferrihydrite used in this study of  $120 \text{ m}^3/\text{g}$ , and hence less adsorption sites. The effect is identical to that of increasing the As concentration in solution. The final pH of As(V) adsorption drifted 1 to 2 units to higher pH comparing to initial pH.  $\text{HAsO}_4^{2-}$  are the predominant dissolved species in the pH range of 3 to 6, and the adsorption of As(V) is supported by the existence of  $\text{H}^+$ . No addition of  $\text{H}^+$  may contribute to the lower adsorption of As(V). The pH variation during the adsorption should attract attention in case it is useful in explaining the adsorption mechanism which is still unknown.

### **3.4.2 Competitive interaction between As(III) and As(V)**

Under competitive adsorption conditions, As(III) and As(V) were adsorbed in almost equal amounts up to a pH of 5 at a adsorbent dosage of 0.5 g/L and up to a pH of 6 at an adsorbent dosage of 1 g/L (Figures 2 and 3). This finding was contrary to the common belief that As(V) is more strongly adsorbed than As(III) at a pH below its point of zero charge (approximately 7 to 8). At the same time, As(V) affects the adsorption of As(III) but to a lesser degree: as the pH increases, As(III) is more strongly adsorbed (Figures 2 and 3). This is even more pronounced as adsorption conditions get more competitive: the ferrihydrite dosage decreases to 0.5 g/L (Figure 3), which demonstrates the greater affinity of As(III) for ferrihydrite across the whole pH spectrum studied.

The potential of As(III) to outcompete As(V) under competitive conditions is further demonstrated in Figures 4 and 5. Compared to As(V), As(III) was adsorbed preferentially at lower ferrihydrite dosages at a pH below the PZC during competitive adsorption, which is in agreement with the result that As(III) generally showed a higher affinity for adsorption onto ferrihydrite than did As(V). Only when there was virtually no more competition with abundant

adsorption sites for both species at a high ferrihydrite dosage was As(V) adsorbed almost as much as As(III) (Figure 4). These findings are consistent with studies that reported that adsorption of As(V) on goethite and ferrihydrite can be lessened by the presence of As(III) at high pH values, while the adsorption of As(III) was influenced by As(V) at a wide range of pH (Jain and Loeppert, 2000; Kanematsu et al., 2013).

The inhibitory effect on the adsorption of As(III) by As(V) was stronger at low pH, the value of which ranged from the  $pK_1$  to  $pK_2$  of As acid approximately ( $H_3AsO_5$ ;  $pK_1=2.3$ ;  $pK_2=6.8$ ). This may be ascribed to the fact that As(V) was more strongly retained on ferrihydrite by electrostatic attraction in this pH range, while As(III) may be loosely bound on the surface sites and can be partially replaced by As(V). It was reported that As(III) was less strongly adsorbed than As(V) on goethite (Stachowicz et al., 2008). As pointed out by Jain et al. (1999) the uncharged As(III) species would likely be less retained on the surface of ferrihydrite than the negatively charged As(V) species. Another explanation according to Arai et al. (2001) is that As(V) forms inner-sphere complexes regardless of pH and ionic strength and that As(III) forms inner-sphere complexes at low pH but together with out-sphere complexes with increasing pH. The inner-sphere complex of As(V) may affect the formation of inner-sphere As(III) complexes on ferrihydrite at low pH.

### **3.4.3 Mechanism of arsenic adsorption under competitive conditions**

Anions could be adsorbed on the adsorbents through nonspecific and/or specific adsorption. It has been shown that the electrostatic interaction, surface complexation and specific adsorption are the main adsorption mechanisms for the adsorption of arsenic on iron oxides(Guo et al., 2007). During competitive adsorption with sufficient As(III) and As(V) present in solution, both As(III) and As(V) were adsorbed onto ferrihydrite (Figure 3). We found that As(III) continued to be strongly adsorbed when the adsorption sites were not available for excess As(V) at high pH. Moreover, the total amount of As(III) and As(V) adsorbed in the competitive adsorption experiments was significantly larger than either As species adsorbed but lower than the sum total of each As species adsorbed when added

alone. The oxide surface contains adsorption sites which are accessible for both species where competitive adsorption could take place and adsorption site which are species-exclusive (Hingston et al., 1971). It is pointed out that the iron oxides have two types of surface sites, one of which is accessible to both As(V) and phosphate and one type for phosphate only (Zeng et al., 2007). The competitive adsorption between As(III) and As(V) may take place only for sites accessible to both species.

The sequence of contact with ferrihydrite had a significant effect on the adsorption of either arsenic species (Figures 6 and 7). If added in sequence, either As(III) first or As(V) first, the species which was added first can occupy the adsorption sites more successfully. During simultaneous addition, the two species may be expected to compete for some sites directly. While during sequential addition, the first species must be desorbed before the second ion can be adsorbed. Previous studies also reported the order of anions addition affected the adsorption of phosphate and As(V) on the surfaces of goethite (Hongshao and Stanforth, 2001; Liu et al., 2001). The results may indicate that only a small fraction of the arsenic adsorbed is desorbed and replaced by the competing ions added later. It is evidence that both As(III) and As(V) adsorption is dominated by forming stable surface complexes (inner-sphere complexes) on HFO.

#### **3.4.4 Implication for As(III) and As(V) mobility in the environment**

The relative affinity for the adsorption of As(III) and As(V) onto ferrhydrite depends on the pH of the solution, the adsorbent dosage, and competing ions. In single systems, As(III) was adsorbed more favorable than was As(V) over the studied pH ranges. However, As(V) was adsorbed to a similar extent as As(III) at low pH under competitive conditions (Figure 2 and 3). The presence of As(V) would decrease the affinity of As(III) on the surface of HFO.

These results have some implications for the mobility of As in the environment. The general recognition that As(III) is more soluble and mobile than As(V), due to As(III) weakly adsorbed on iron oxides, is one-sided and oversimplified. The greater affinity of As(III) for adsorption onto ferrihydrite suggests that the existence of iron hydroxides in the soil must exert an

inhibitory effect on its mobility. In the aquatic system, As(V) may compete for the surface sites of HFO, and thus some As(III) may desorb. Thus the presence of As(V) would enhance the mobility of As(III), and As(III) may be slightly more agile than As(V) under acid aquatic conditions.

### **3.5 Conclusions**

The dependence of As(V) adsorption on pH and the independence of As(III) adsorption with respect of pH were observed in both single and competitive adsorption experiments. Contrary to the theoretical prediction that As(V) should adsorb more strongly than As(III) at pH values below the point of zero charge (pzc) of ferrihydrite of about 7 to 8, As(III) more or less outcompeted As(V) across the pH scale from 4 to 10. At low pH, As(V) impedes the adsorption of As(III) but to a lesser degree than As(III) impedes As(V) adsorption already at a pH above 6, which is below the PZC of ferrihydrite. The effect of As(III) on the adsorption of As(V) increased with an increase in pH, and adsorption of As(V) was almost absent at a pH of 8 to 9. The decrease of adsorbed As(III) was higher at low pH ranging from  $pK_1$  to  $pK_2$  for arsenate acid and lower with increasing pH. The decrease in adsorbed As(III) also depended on the concentrations of coexisting As(V). The order of species addition had a significant effect on their competitive adsorption because each arsenic species could occupy the adsorption sites successfully when in contact with ferrihydrite first.

The results confirm that there was competition during the simultaneous adsorption of As(III) and As(V). It is inferred that the competition is limited on some adsorption sites which are common for both As(V) and As(III). Ferrihydrite displays an inhibitory effect on As(III) mobility in the environment, although the presence of As(V) enhances the mobility of As(III) and As(III) may be slightly more mobile than As(V) under acidic conditions.

### **Acknowledgements**

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**4. Closer look at As(III) and As(V) adsorption onto ferrihydrite under competitive conditions: isotherms and kinetics**

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## **Abstract**

Single and competitive adsorption properties of As(III) and As(V) onto ferrihydrite were investigated by applying batch adsorption isotherms and kinetic studies. Both isotherm and kinetic competitive studies showed that the presence of As(V) significantly inhibited the adsorption of As(III), whereas the presence of As(III) had an insignificant impact on As(V) adsorption at pH 5. Equilibrium isotherm models were employed to describe the adsorption of As(III) and As(V) under single and competitive conditions, both of which can be successfully described by the Freundlich isotherm model. The adsorption affinity onto ferrihydrite was ordered as follows: As(III)-single > As(III)-binary > As(V)-single > As(V)-binary. The adsorption kinetics of As(III) and As(V) were both well described by pseudo-second order kinetics model. The Fourier transfer infrared spectroscopy (FTIR) provided the evidence that both As(III) and As(V) could be adsorbed onto ferrihydrite through inner-sphere surface complexes with the formation of As-O-Fe bonds.

#### **4.1 Introduction**

Arsenic (As) is a contaminant that occurs naturally in water in many regions of the world and is of significant 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, redox conditions and biological activity (Oremland and Stolz, 2003; Price et al., 2007; Price et al., 2013a; Price et al., 2013b; Smedley and Kinniburgh, 2002). The adsorption of As onto solid particles in soils and aquifer matrices plays an important role in controlling its retention and mobility in the environment (Stollenwerk, 2003). Hydrous ferric oxides (HFO), which are common minerals in such environments are believed to be one of the most important adsorbents for As in surface water and groundwater systems, given its reactivity and large specific surface area (Pichler et al., 1999b; Waychunas et al., 1993). Because As(III) and As(V) behave different during adsorption and could occur together in aquatic systems, it is important to understand how the two species interfere with each other and to better understand their transport and fate in aquatic systems. We previously presented new information about the competitive interaction of As(III) and As(V) during adsorption by the ferrihydrite, a common HFO, as a function of parameters, such as pHs, adsorbent dosages, concentration of coexisting As species and order of addition (Qi and Pichler, 2014). However, to our knowledge it seems that there is no report to probe the mechanism of competitive adsorption of As(III) and As(V) onto ferrihydrite combined batch adsorption methods and spectroscopy methods.

Adsorption equilibrium and dynamics are important for describing the adsorption processes and numerous studies have been conducted regarding the As adsorption isotherms and the kinetics in single systems, i.e., only one As species present at a given time. For example, Raven et al. (1998) observed that only a few hours were needed to reach adsorption equilibrium for both As(III) and As(V) adsorption on ferrihydrite. Smith and Naidu (2009) reported that As(V) adsorption kinetics were initially fast during the first 15 min and then

continued at a slower rate. Linear regression analysis showed that As(III) adsorption on iron oxide coated with cement followed the Langmuir isotherm but fit the Freundlich isotherm best according to error analysis (Kundu and Gupta, 2006a). As(V) exhibited higher removal rates than As(III) at low pH on granular ferric hydroxide, and thermodynamic studies showed that both As(III) and As(V) adsorption were endothermic and spontaneous (Banerjee et al., 2008). A few studies have considered the adsorption kinetics and isotherms of As(III) and As(V) under competitive conditions. For example, Maiti et al. (2012) reported the competitive adsorption kinetics of As and indicated that As(V) adsorption was not affected by As(III) on treated laterite but As(III) adsorption was slightly impeded by the presence of As(V). Fourier transfer infrared spectroscopy (FTIR) has been widely used as a kind of direct approach to study the mechanism of As adsorption on 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 of the spectroscopy studies are based on the batch experiments of each As redox species, and there is no spectroscopy data available about 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 methods and FTIR spectroscopy.

## **4.2 Materials and methods**

### **4.2.1 Materials and reagents**

All of the chemicals used in these experiments were of analytical grade, and used without further purification. Distilled deionized water (DDI) 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  $\text{As}_2\text{O}_3$  (Sigma-Aldrich, Spain) in 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  $7.4 \pm 0.1$  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.

#### **4.2.2 Adsorption experiments**

All of the experiments were conducted with a background electrolyte of 0.01 M NaCl at room temperature. The kinetic experiments were undertaken in single and binary systems at pH 5 and 9, respectively. Exactly 50 mg of ferrihydrite were 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. The initial concentrations of As(III) and As(V) in each systems were identical (50 mg/L). The tubes were capped and shaken for 0.083, 0.25, 0.42, 0.67, 1, 2, 4 and 24 h. The suspensions were immediately filtered with  $0.25 \mu\text{m}$  syringe filters and stored at  $4^\circ\text{C}$  until determination of total As or As speciation.

Single and competitive adsorption isotherms 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(V), 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 filter, and the supernatant were analyzed for total As or As speciation. The 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 and  $m$  is the mass of ferrihydrite.

#### **4.2.3 Analytical methods**

The 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. The 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 for As(III) and As(V) were 0.17 µg/L and 0.38 µg/L (Wu and Pichler, 2014), respectively.

#### **4.2.4 Adsorption models**

##### **4.2.4.1 Adsorption Isotherms**

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

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

where  $q_m$  and  $K_L$  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  $K_L$  is the Langmuir constant (L/mg).

The Freundlich model assumes heterogeneous sorption on the surface sites with different energies (Sarı 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.

#### **4.2.4.2 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, and  $k_1$  represents the first-order model adsorption rate constant ( $\text{h}^{-1}$ ) and  $k_2$  is the rate constant of sorption of pseudo-second-order model ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{h}^{-1}$ ).

#### **4.2.5 FTIR investigation**

The Fourier transfer infrared spectroscopy (FTIR) spectrograms of the dried ferrihydrite before and after the adsorption of As(III), As(V) and both of the two species were obtained using transmission mode (Thermo-Nicolet Avatar 370 FTIR), with a wave number range of 400 to 4000  $\text{cm}^{-1}$ . The samples were ground and pressed into disks mixing with dried spectral grade potassium bromide (KBr). All FTIR measurements were conducted at room temperature.

## **4.3 Results and discussion**

### **4.3.1 Single adsorption isotherms**

The As(V) and As(III) adsorption isotherms onto ferrihydrite under single and competitive conditions are shown in Figure 1. Both the adsorption of As(III) and As(V) increased with the increasing initial concentrations. As(V) reached a sorption maximum 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 the adsorption of As(III) did not attain equilibrium in the range of concentrations studied. Moreover, As(III) was more favorably adsorbed on ferrihydrite over As(V), particularly at high initial As concentrations, which was consistent with the previous observations (Qi and Pichler, 2014; Raven et al., 1998).

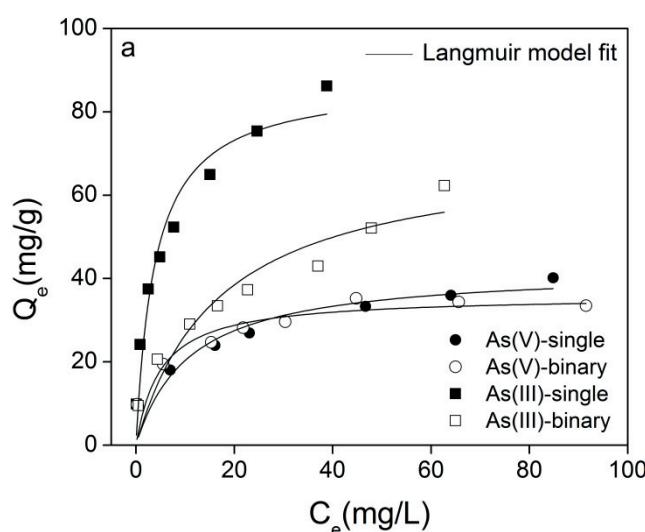
The non-linear fitting parameters for the Langmuir and Freundlich models are shown in Table 1. As indicated by the value of  $R^2$ , the Freundlich model effectively described the experimental data for both the adsorption of As(III) and As(V) in single component systems. The constant value of  $K_f$  for As(III) was higher than that of As(V), which indicated that As(III) had a significantly higher affinity than As(V) for adsorption onto ferrihydrite. 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.

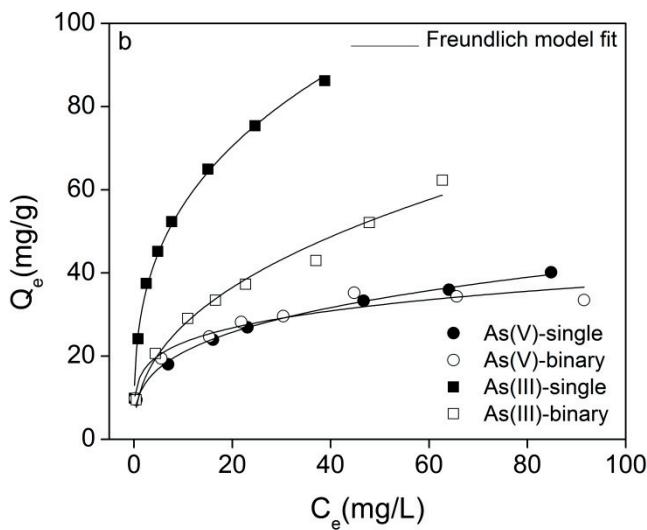
### **4.3.2 Competitive adsorption isotherms**

Figure 1 shows the competitive adsorption isotherms in the binary systems. There, As(III) was more strongly adsorbed on ferrihydrite than As(V) at high initial 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) compared to that in the single systems. For example, the uptake of As(III) decreased from 86 mg/g in the single system to 62 mg/g in the binary system at an initial concentration of 125

mg/L, and the inhibitory extent on As(III) by As(V) was approximately 38 %. The results from 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 credited to the fact that As(V) is strongly adsorbed on surface sites at low pH values via Coulombic force and Lewis acid-base interactions (Banerjee et al., 2008). Furthermore, the amount of adsorbed As(V) increased as the initial concentration increased 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 in the binary system decreased remarkably compared to that obtained in the single systems, 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 that 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 are heterogeneous, and the affinity decreased as follows: As(III)-single > As(III)-binary > As(V)-single > As(V)-binary.





**Figure 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

**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		
		$K_L$	$q_m$	$R^2$	$K_f$	$n$	$R^2$
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

#### 4.3.3 Adsorption kinetics

The adsorption kinetic curves of As(III) and As(V) in the single and binary systems are shown in Figure 2. The adsorption of As(III) and As(V) on ferrihydrite was initially rapid but then slowed down. 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

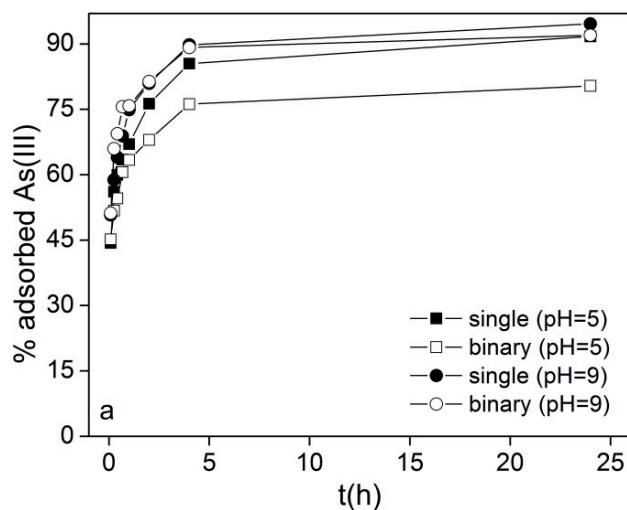
approximately 70 % of removal in the same time span. The rates of As(III) adsorption were independent on the solution pH, and the As(V) adsorption rates decreased as the pH increased, which is consistent with the effect of pH on the removal of As(III) and As(V). Similarly, Raven et al. (1998) reported that As(III) was adsorbed onto ferrihydrite faster 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 2-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).

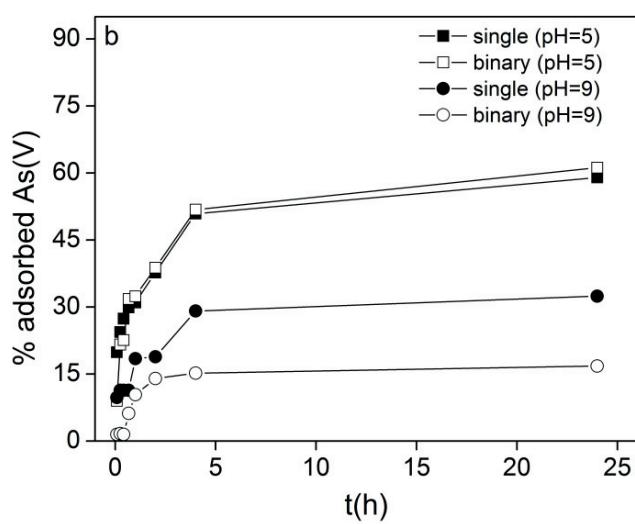
As(III) adsorption in single and binary systems followed an identical pattern at pH 9. It indicates that the presence of As(V) had an insignificant influence on the adsorption rate of As(III) at higher pH values. However, the amount of adsorbed As(III) in the binary systems was less compared to that 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 hours 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 and thus outcompeted As(V) on the surface sites at higher pH values. Frau et al. (2010) reported 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 strong competitor anion such as phosphate.

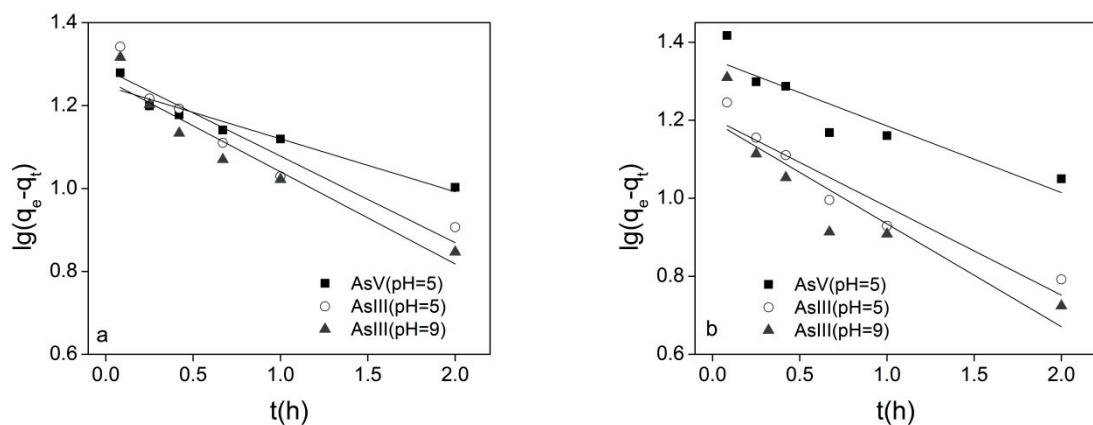
The kinetic adsorption data was analyzed by two kinetic models using linear methods, as shown in Figures 3 and 4. As(III) and As(V) adsorption kinetics were both correlated with a pseudo-second order model (Figure 4). Since As(V) adsorption dramatically decreased at

higher pH values, the experimental data which were obtained at pH 9 were omitted from the model. The adsorption rate constants and other parameters obtained from the pseudo-second order model are listed in Table 2. The results suggest that the adsorption of As(III) and As(V) are rate-determining steps under both single and competitive conditions. 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) should have 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 in contrary to that observed for the amount of adsorbed As at equilibrium. Furthermore, because the ferrihydrite adsorption sites were not saturated for As(III) according to the adsorption isotherm data, the value of  $q_e$  calculated from the pseudo-second order equation cannot be considered quite accurate. Consequently, although the second-order equation provides a good description for the data, a deviation existed for some of the results. For example, the value of  $q_e$  calculated for As(III) in the binary system should be similar to that calculated from single system at pH 9.

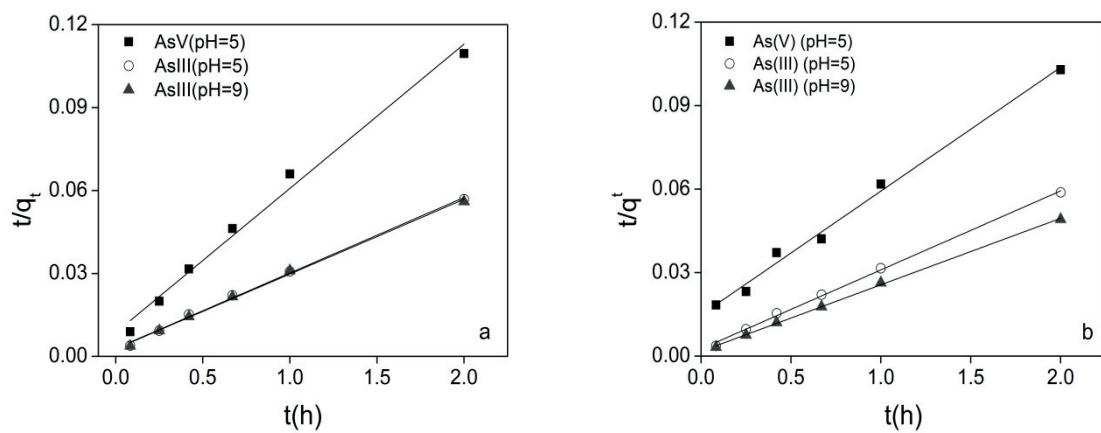




**Figure 2.** Time of (a) As(III) and (b) As(V) adsorption onto ferrihydrite in single and binary systems respectively (pH: 5 and 9; initial As concentration: 50 mg/L)



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



**Figure 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

Pseudo-first-order model							
adsorbate	pH	Single systems			Binary systems		
		$k_2$	$q_e$	$R^2$	$k_2$	$q_e$	$R^2$
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

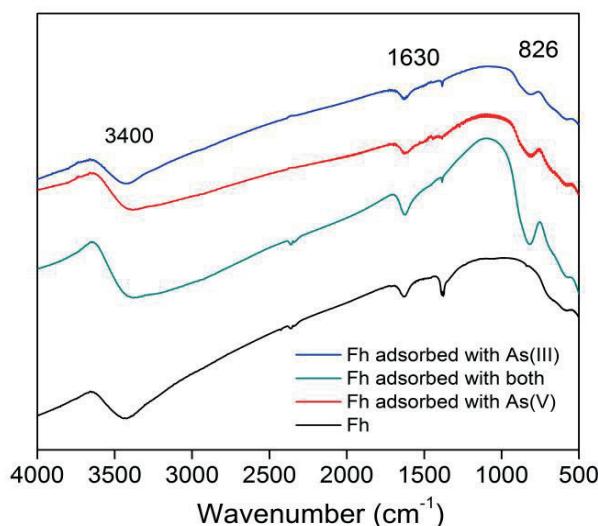
  

Pseudo-second-order model							
adsorbate	pH	Single systems			Binary systems		
		$k_2$	$q_e$	$R^2$	$k_2$	$q_e$	$R^2$
As(V)	5	0.31	19.23	0.987	0.13	22.73	0.991
As(III)	5	0.26	37.04	0.997	0.30	35.71	0.997
As(III)	9	0.27	36.95	0.997	0.29	43.48	0.999

#### 4.3.4 FTIR spectra analysis

To elucidate the competitive adsorption mechanism of As(III) and As(V) onto ferrihydrite, FTIR spectroscopy was used to probe the nature of the interactions between As redox species and ferrihydrite. Figure 5 shows the FTIR spectra of dried ferrihydrite before and after

the adsorption under single and binary conditions at a pH of 5. The peak near  $3400\text{ cm}^{-1}$  observed for all samples could be ascribed to OH stretching, while the peak at about  $1630\text{ cm}^{-1}$  could be assigned to the 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 the ferrihydrite after adsorption had a similar shape and had similar band positions. The appearance of the new peak at  $826\text{ cm}^{-1}$ , which was not present before adsorption but observed for all ferrihydrite samples after adsorption, could be assigned to Fe-O-As bonds and thus be evidence for the formation of inner sphere bonds. This is consistent with the observations reported by Jia et al. (2007), indicating that both the adsorption of As(III) and As(V) can be achieved through inner-sphere surface complexes by the formation of As-O-Fe bands. Thus the competition between As(III) and As(V) should occur on the surface sites of ferrihydrite. However, the presence of As(V) had an inhibitory impact on the adsorption of As(III) at low pH, suggesting that As(III) could be weakly bonded on the surface sites not only by inner-sphere complexes, but by a combination of inner-sphere and outer-sphere complexes.



**Figure 5.** FTIR spectra of ferrihydrite 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.

#### **4.4 Conclusions**

Both adsorption isotherm and kinetics studies showed As(III) adsorption onto ferrihydrite was largely impeded by the presence of As(V), particularly at low pH, whereas the presence of As(III) had an insignificant influence on As(V) adsorption at pH 5. The good fit of the adsorption data to the Freundlich model indicates 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, indicating that adsorption was a rate-determining step. The FTIR spectral analysis implies that inner-sphere complexes could be formed during both As(III) and As(V) adsorption, thus they can compete for the surface sites on ferrihydrite.

#### **Acknowledgement**

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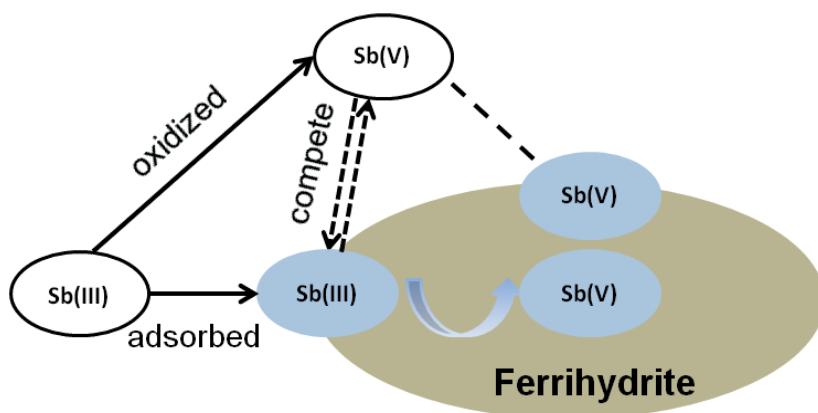
## **5. Sequential and simultaneous adsorption of Sb(III) and Sb(V) on ferrihydrite: Implications for oxidation and competition**

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**Graphical abstract****Abstract**

Antimony (Sb) is a naturally occurring element of growing environmental concern whose toxicity, adsorption behavior and other chemical properties are similar to that of arsenic (As). However, less is known about Sb compared to As. Individual and simultaneous adsorption experiments with Sb(III) and Sb(V) were conducted in batch mode with focus on the Sb speciation of the remaining liquid phase during individual Sb(III) adsorption experiments. The simultaneous adsorption and oxidation of Sb(III) was confirmed by the appearance of Sb(V) in the solution at varying Fe/Sb ratios (500, 100 and 8) and varying pH values (3.8, 7 and 9). This newly formed Sb(V) was subsequently removed from solution at a Fe/Sb ratio of 500 or at a pH of 3.8. However, more or less only Sb(V) was observed in the liquid phase at the end of the experiments at lower Fe/Sb ratios and higher pH, indicating that competition took place between the newly formed Sb(V) and Sb(III), and that Sb(III) outcompeted Sb(V). This was independently confirmed by simultaneous adsorption experiments of Sb(III) and Sb(V) in binary systems. Under such conditions, the presence of Sb(V) had no influence on the adsorption of Sb(III) while Sb(V) adsorption was significantly inhibited by Sb(III) over a wide pH range (4 to 10). Thus, in the presence of ferrihydrite and under redox conditions, which allow the presence of both Sb species, Sb(V) should be the dominant species in aquatic environments, since Sb(III) is adsorbed preferentially and at the same time oxidized to Sb(V).

**Keywords:** Antimony(III,V); Ferrihydrite; Adsorption; Oxidation; Competition

## 5.1 Introduction

Antimony (Sb) is a naturally occurring element of growing environmental concern. Large quantities of Sb have been released into the environment as a result of both natural and anthropogenic processes such as rock weathering, soil runoff, Sb mining and smelting (Filella et al., 2002b; Filella et al., 2007). Inorganic Sb exists primarily as the pentavalent species (Sb(V)) in oxic systems and as the trivalent species (Sb(III)) in anoxic systems (Vink, 1996). Its toxicity, adsorption behavior and other chemical properties are similar to that of arsenic (As) (Gebel, 1997; Wilson et al., 2010). However, due to a lower abundance in the environment and the relatively low solubility of most Sb compounds, it is less studied compared to As.

The mobility of Sb is susceptible to redox changes, such as oxidation of Sb(III) to Sb(V) which can be effectively initiated in aerated Fe(III)-H<sub>2</sub>SO<sub>4</sub> solutions, by H<sub>2</sub>O<sub>2</sub>, and by manganese and iron oxyhydroxides (Asta et al., 2012; Belzile et al., 2001; Leuz and Johnson, 2005; Quental et al., 2004). A recent study suggested that oxidation of Sb(III) occurred after Sb(III) was adsorbed on goethite and thus any Sb(V) in the aqueous phase was a result of desorption from the surface (Xi et al., 2013). Belzile et al. (2001) reported the complete oxidation of Sb(III) by synthetic iron oxyhydroxides within six days. Another study indicated that Sb(III) adsorbed on goethite was partly oxidized at pH 3, 5, 9 and 9.7 within seven days (Leuz et al., 2006b). Xi et al. (2014) also reported significant oxidation of Sb(III) to Sb(V) under certain experimental conditions during the adsorption of Sb(III) on kaolinite.

Hydrous ferric oxides (HFO), such as ferrihydrite are recognized as effective solid phases for the adsorption and attenuation of Sb in anthropogenic and geogenic systems (Ahmed et al., 2006; Craw et al., 2004; Xi et al., 2013). However, the assessment of Sb(III) adsorption by HFO is complicated because adsorption and oxidation of Sb(III) occur more or less simultaneously. The newly formed Sb(V) could behave differently than the original Sb(III) in solution. Currently next to nothing is known about the mobility of this Sb(V) and its interaction with the remaining Sb(III). Thus Sb(III) adsorption remains somewhat ambiguous and particularly the competition between the two Sb species need further investigation.

Here we present new data for Sb(III) adsorption experiments focusing on Sb speciation analyses in the supernatant following adsorption. The key objective was to examine the kinetics of Sb speciation at varying Fe/Sb molar ratios and pH. In addition, the competition between the two Sb species for adsorption sites as a function of pH in binary systems was evaluated.

## **5.2 Experimental section**

### **5.2.1 Reagents and materials**

All chemicals were of analytical grade. Two types of Sb(III) stock solutions were prepared by dissolving potassium antimonyl tartrate ( $C_8H_4K_2O_{12}Sb_2 \cdot 3H_2O$ , Sigma-Aldrich) in de-ionized distilled (DDI) water or by dissolving antimony trioxide ( $Sb_2O_3$ , Aldrich) in 2 M HCl. Unfortunately the solubility of the latter is low and thus the dissolution of  $Sb_2O_3$  had to be performed in highly concentrated acid solutions. Despite the difference in aqueous complexing, antimony tartrate anions and  $Sb(OH)_3$  behave similar (Thanabalasingam and Pickering, 1990) and both form inner-sphere complexes during adsorption (Verbinnen et al., 2013; Vithanage et al., 2013; Watkins et al., 2006; Xi et al., 2011). This was once more confirmed prior to conducting the experiments and their adsorption onto ferrihydrite was found to be similar (Figure S1). Thus the more soluble potassium antimonyl tartrate was used in the adsorption experiments since it was necessary to evaluate the removal efficiency of Sb at high concentrations commonly found in water samples influenced by mining activities (Hiller et al., 2012). Sb(V) stock solutions were prepared by dissolving potassium hexahydroxoantimonate ( $H_6KO_6Sb$ , Fluka) in DDI water.

Ferrihydrite was synthesized following an established method (Qi and Pichler, 2014), by adding dropwise and under constant stirring a one molar solution of KOH (Sigma-Aldrich, Germany) to 500 mL of 0.2 molar  $Fe(NO_3)_3 \cdot 9H_2O$  (Alfa Aesar, Germany), until the pH increased to  $7.4 \pm 0.1$ . The precipitated material was then 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. The surface area of freeze-dried ferrihydrite was analyzed by the BET (Brunauer-Emmett-Teller) method and found to be 120 m<sup>2</sup>/g.

### 5.2.2 Experimental procedure

All experiments were carried out at room temperature, with a background electrolyte of 0.01 M NaCl. In the individual adsorption experiments of Sb(III), the Sb(III) working solutions were mixed with ferrihydrite in 100 mL conical flasks with plugs, and the pH of the suspensions was adjusted to 7.0 ± 0.2 with HCl or NaOH. The molar ratios of Fe to Sb were 8, 100 and 500. Suspensions were capped and maintained under constant stirring. Aliquots of suspensions were collected after 1, 5, 24, 48, 96 and 120 h and filtered immediately through syringe filters with a pore size of 0.25 µm. The samples were preserved using a combination of 0.2 M EDTA and HCl and stored at 4°C in the dark (Wu and Pichler, 2015). To test for the possibility of oxidation by atmospheric oxygen during the experiment a blank Sb(III) solution was prepared and analyzed at the same time intervals. To study the influence of pH the same experimental setup was used at pH 3.8 ± 0.2 and pH 9.0 ± 0.2 at a Fe to Sb ratio of 100. The samples were collected and analyzed for Sb speciation at the same time intervals of 1, 5, 24, 48, 96 and 120 h. The percentage of Sb(III) adsorbed onto ferrihydrite was calculated according to the following equation:

$$\% \text{ Sb(III)adsorbed} = \frac{[\text{Sb(III)}]_{\text{tot}} - [\text{Sb(III)}]_{\text{aq}} - [\text{Sb(V)}]_{\text{aq}}}{[\text{Sb(III)}]_{\text{tot}}} \times 100\% \quad (1)$$

To assess if Sb(III) converted to Sb(V) after adsorption, three replicates of 5 mL ferrihydrite suspensions were collected at the end of the experiments (pH 3.8 and 9) and dissolved in 2 M EDTA and 6 M HCl. After complete dissolution of ferrihydrite the samples were diluted to 20 mL with DDI water and filtered for Sb speciation analyses. A combination of EDTA and HCl was chosen, because HCl can dissolve ferrihydrite without a change in redox conditions and EDTA is known to complex Sb(III) in a way that prevents oxidation (Daus and Wennrich, 2014).

Individual and co-adsorption experiments as a function of pH were performed in 50 mL tubes, by adding either Sb(III) or Sb(V) or a combination of both to a ferrihydrite suspension. The concentrations of each Sb species at each pH in the single and binary systems were identical with a concentration of 50 mg/L, and the adsorbent dosage was 0.5 g/L. The pH was adjusted from 4 to 10, and the suspensions were continuously shaken for 24 h in case of long time contact promoting oxidation interference. At the end of the experiment the suspensions were filtered and the supernatant was analyzed for total Sb concentration and Sb speciation. These experiments were performed in triplicates and one blank was prepared for each pH studied.

### **5.2.3 Analytical methods**

The Sb speciation was determined by hydride generation-atomic fluorescence spectroscopy (HG-AFS) on a PSA 10.055 Millennium Excalibur system. Prior to analysis the two Sb species were separated chromatographically in an anion exchange column (Hamilton PRP-X100) using 20 mM EDTA at pH 4.7 as the mobile phase. The detection limits for Sb(III) and Sb(V) were 0.02 and 0.2 µg/L, respectively.

The total Sb concentration was measured using inductively coupled plasma-optical emission spectrometry (ICP-OES), and the detection limit was 0.02 mg/L. If Sb concentration were below the detection limit of ICP-OES, total Sb was determined by HG-AFS by reducing Sb(V) to Sb(III) with potassium iodide (KI) and ascorbic acid. The limit of detection of that method was 0.01 µg/L.

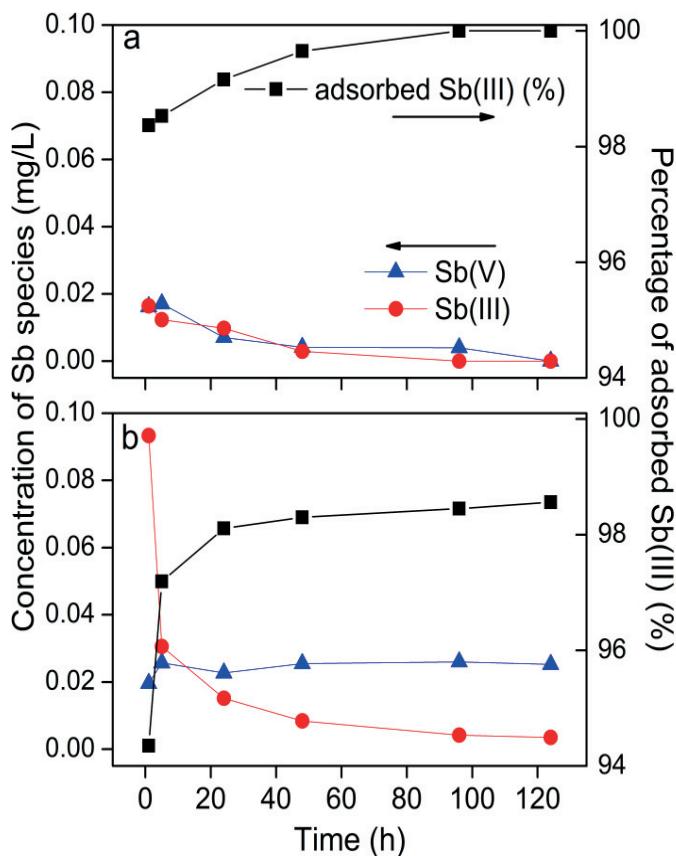
## **5.3 Results**

### **5.3.1 Effect of Fe/Sb ratios**

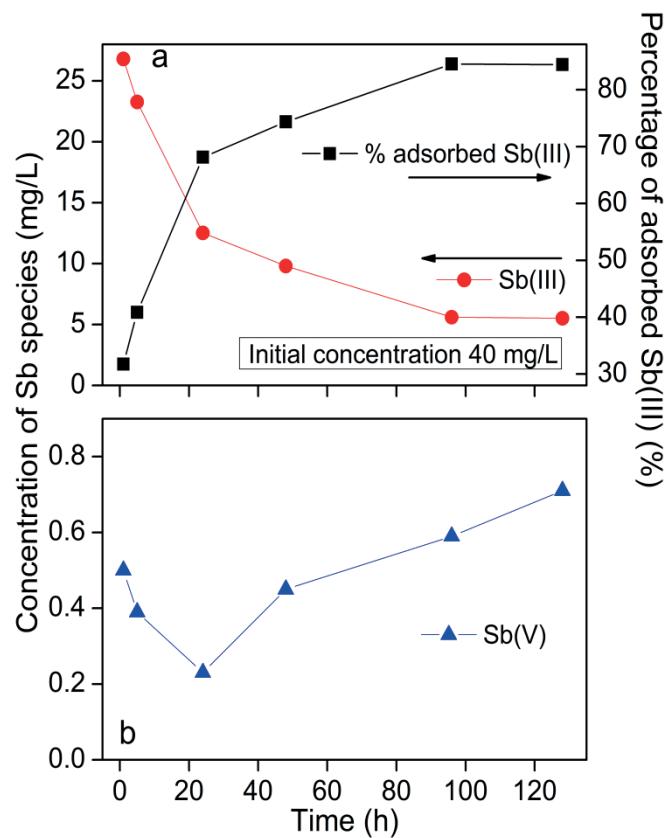
The data for Sb speciation in the supernatant of the Sb(III) adsorption experiments are shown in Figures 1 and 2 as well as the adsorption percentage of Sb(III) as a function of time. At a Fe/Sb ratio of 500, the concentration of Sb(III) in the aqueous phase decreased from 2 mg/L to less than 0.02 mg/L (Figure 1a), indicating almost complete removal of Sb(III) within the 58

first hour of the experiment. However, a small amount of Sb(V) was detected in solution likely due to the oxidation of Sb(III). Previous studies also reported the rapid uptake of Sb(III) and rapid formation of Sb(V) in solution due to the oxidation of Sb(III) for example by manganite (Wang et al., 2012). The newly formed Sb(V) can then be subsequently removed from solution and thus Sb(V) was only detectable for a short period during the experiment. After 96 h, neither Sb(III) nor Sb(V) were detected in the solution and adsorption of Sb(III) was close to 100 %. This indicated that the oxidation of Sb(III) to Sb(V) did not affect the overall adsorption behavior of Sb(III) at a high adsorbent to adsorbate ratio, since there were sufficient adsorption sites to adsorb the initial Sb(III) and the newly formed Sb(V).

At the lower Fe/Sb ratio of 100, the adsorption of Sb(III) was found to be less effective than that at the Fe/Sb ratio of 500 (Figure 1b). After 1 hour Sb(V) was observed in the aqueous phase and remained in solution until the end of the experiment. This observation was in contrast to the result of the experiment at a Fe/Sb ratio of 500 where Sb(V) was completely removed by the end of the experiment (Figure 1a). At the Fe/Sb ratio of 100 only 1.97 mg/L (98.5 %) of Sb(III) were removed from the aqueous phase after 120 h. Of the remaining of 0.03 mg/L (1.5 %) Sb, approximately 0.025 mg/L (1.25 %) were Sb(V) and 0.005 mg/L (0.25 %) were Sb(III). That indicated that Sb(III) was preferentially adsorbed onto ferrihydrite at the lower Fe/Sb ratio (i.e., less adsorption sites per adsorbate) at neutral pH, leaving some Sb(V) which formed due to the oxidation of Sb(III) in the aqueous phase after all possible adsorption sites were occupied. At the even lower Fe/Sb ratio of 8 and at a high initial concentration of 40 mg/L, this effect was magnified, generating substantially more Sb(V) in solution. The concentration of Sb(V) decreased with time having a low peak at 24 h but then increased to a final value of more than 0.6 mg/L (1.5 %) at 120 h (Figure 2b). That indicated that the oxidation of Sb(III) and the fate of generated Sb(V) was dependent on Fe/Sb molar ratios.



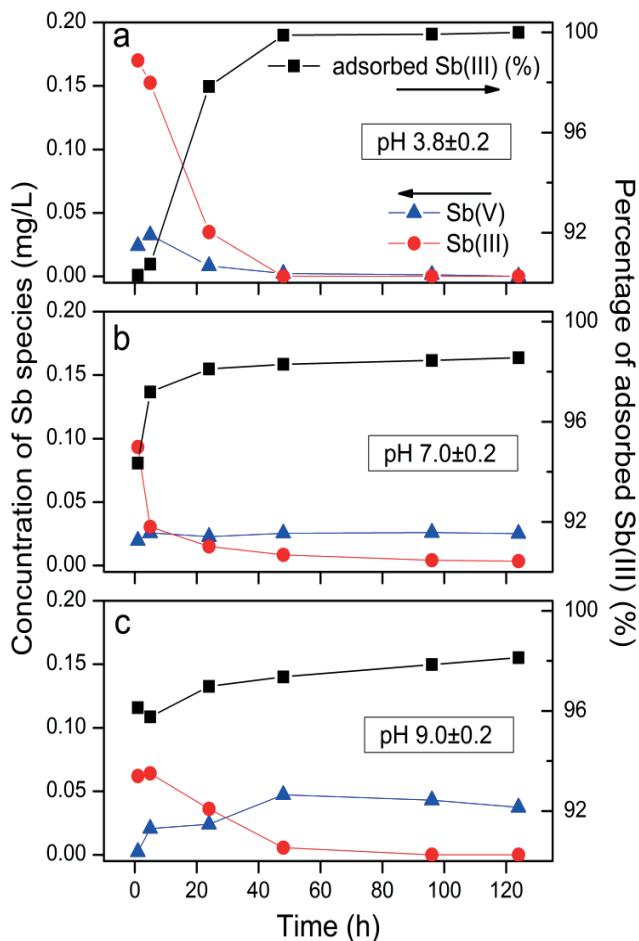
**Figure 1.** Sb speciation in the supernatant during Sb(III) adsorption experiments and the adsorption percentage of Sb(III) as a function of time at a Fe/Sb molar ratio of 500 (a) and at a ratio of 100 (b) (volume of suspensions: 100 mL, initial concentration of Sb(III): 2 mg/L, pH:  $7.0 \pm 0.2$ ).



**Figure 2.** Sb speciation in the supernatant during Sb(III) adsorption experiments and the adsorption percentage of Sb(III) as a function of time. (a): Concentration of Sb(III) in solution and Sb(III) adsorption percentage as time; (b) Concentration of Sb(V) in solution (volume of suspensions: 100 mL, Fe/Sb molar ratio: 8, pH:  $7.0 \pm 0.2$ ).

### **5.3.2 Effect of pH**

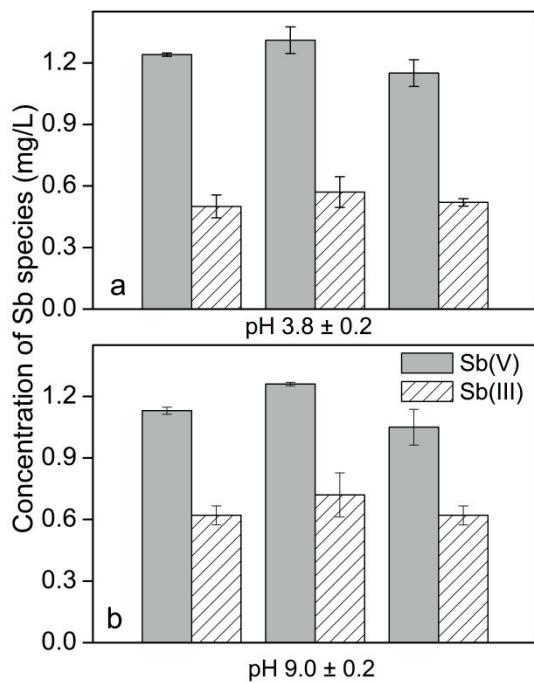
The effect of pH on Sb speciation in the supernatant during the Sb(III) adsorption experiments and the adsorption behavior of Sb(III) are shown in Figure 3. The molar ratio of Fe/Sb was 100 and the initial concentration of Sb(III) was 2 mg/L. At pH 3.8 Sb(V) was initially detected in the aqueous phase, but immediately decreased to below detection after 48 hours (Figure 3a). At pH 7 approximately 0.025 mg/L (1.25%) of Sb(V) were detected, which remained constant throughout the experiment (Figure 3b). At pH 9 the initial concentration of Sb(V) was lower than the other two experiments (Figure 3c), but continuously increased until reaching a maximum of 0.047 mg/L (2.35 %) after 48 h, and followed by a slight decrease to just below 0.04 mg/L (2%) at the end of the experiment (Figure 3c). The percentages of Sb(III) adsorbed were approximately 100 % at pH 3.8, 98.5 % at pH 7 and 98 % at 9. Thus under acidic conditions the Sb(V), which was formed by Sb(III) oxidation was subsequently removed from solution. However, the newly formed Sb(V) was still present in solutions at neutral and alkaline pH. Meanwhile, the Sb(III) concentration declined constantly until it was below or near detection after 96 h at each of the 3 pH settings (Figure 3). The Sb(III) oxidation was stronger under alkaline conditions and the mobility of formed Sb(V) in solutions was affected by the pH. Buschmann et al. (2005) found a similar degree of pH dependence for photo-induced oxidation of Sb(III) on humic acid.



**Figure 3.** Sb speciation in the supernatant during Sb(III) adsorption experiments and the adsorption percentage of Sb(III) as a function of time at different pH values (volume of suspensions: 100 mL, Fe/Sb molar ratio: 100, initial concentration of Sb(III): 2 mg/L).

### 5.3.3 Dissolution of ferrihydrite suspensions after adsorption

The ferrihydrite suspensions of the adsorption experiments at pH 3.8 and 9 were dissolved after completion and the results of Sb speciation analyses are presented in Figure 4. The recovery efficiency was calculated according to the ratio between the total concentration of dissolved Sb species and the initial Sb(III) concentration, which was approximately 88 % at a pH of 3.8 and 90 % at a pH of 9. The results clearly show that a large amount of the adsorbed Sb(III) was converted to Sb(V) on the surface sites.

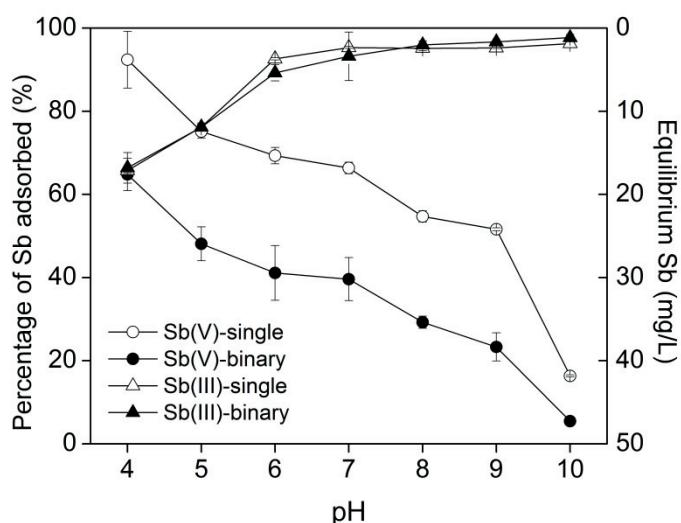


**Figure 4.** Speciation analysis for Sb, which was removed from ferrihydrite suspensions at the end of the adsorption experiments at (a) pH  $3.8 \pm 0.2$  and (b)  $9.0 \pm 0.2$  (same experimental conditions as in Figure 3). Three replicates from each experiment were analyzed. Error bars are the standard deviation of triplicates.

### 5.3.4 Sb(III) and Sb(V) adsorption under competitive conditions

Figure 5 presents the adsorption behavior of Sb(III) and Sb(V) as a function of pH under individual (single) and competitive (binary) conditions. In the single system, the adsorption of Sb(V) decreased significantly with increasing pH. The strong pH dependence of Sb(V) adsorption and the fact that adsorption was favored at acidic pH were reported for kaolinite and goethite (Guo et al., 2014; Leuz et al., 2006b; Xi et al., 2010). The adsorption behavior of Sb(V) in terms of pH is attributed to the electrostatic attraction between  $\text{Sb}(\text{OH})_6^-$  and the surface of ferrihydrite (Zhao et al., 2014). The pH dependence of Sb(III) adsorption was less pronounced than that of Sb(V), showing an increase in adsorption to the pH at which adsorption was almost complete (Figure 5). This was in good agreement with the earlier studies, which showed that Sb(III) adsorption by iron oxides can be optimized over a broad pH range (Guo et al., 2014; Leuz et al., 2006b; Shan et al., 2014).

As seen in the time series experiments (Figure 2), the amount of Sb(V) formed by Sb(III) oxidation at a high initial Sb(III) concentration seemed to be negligible compared to the initial concentration used during competitive adsorption experiments. The adsorption of Sb(III) in single systems was more or less identical as that observed in binary systems (Figure 5). On the other hand, the percentage of Sb(V) adsorbed in binary systems decreased by approximately 25% compared to those adsorbed in single systems between pH 4 to 9. Sb(III) adsorption was not affected by the presence of Sb(V), while Sb(III) had an inhibitory effect on the adsorption of Sb(V). Competition took place between Sb(III) and Sb(V), and Sb(III) outcompeted Sb(V). Thus the adsorption of Sb(V) was diminished by the presence of Sb(III) in binary systems.



**Figure 5.** Sb(III) and Sb(V) adsorption envelopes as a function of pH in single and binary systems respectively (pH from 4 to 10; initial concentration of each Sb species: 50 mg/L; adsorbent dosage: 0.5 mg/L). Error bars are the standard deviation of triplicates.

## 5.4 Discussion

### 5.4.1 Implications of oxidation accompanying Sb(III) adsorption

The Sb(V), which was detected in the supernatant of Sb(III) adsorption experiments showed a different behavior for each of the Fe/Sb ratios and pH values studied. Independent of

experimental conditions Sb(V) appeared immediately at the start of each experiment, but subsequently disappeared from solution at a high Fe/Sb ratio (500) or a low pH (Figure 1a and 3a). While at a lower Fe/Sb ratio of 100 or under non-acidic conditions, the concentration of Sb(V) remained more or less constant with time (Figure 1b and 3b-c). There are several possible explanations, (1) due to insufficient adsorption sites the newly formed Sb(V) was in competition and Sb(III) showed a stronger affinity, (2) the removal of Sb(V) was significantly affected by an increasing pH or (3) oxidation of Sb(III) on the surface of ferrihydrite. It was reported that Sb(III) adsorbed on goethite was oxidized to Sb(V) and then its release resulted in the observed Sb(V) in the solution (Leuz et al., 2006b). However, it cannot be simply inferred that the release of Sb(V) caused the detected Sb(V) in aqueous solution, since both Sb(III) and Sb(V) can be bound strongly to the surface sites by the formation of inner-sphere surface complexes (Guo et al., 2014; McComb et al., 2007). Thus the release of Sb(V) into solution does not occur rapidly and easily in the presence of sufficient adsorption sites or at an acidic pH or in the absence of interferences. According to our observations, the appearance of Sb(V) during Sb(III) adsorption experiments show that Sb(V) is outcompeted by Sb(III) in the case of insufficient adsorption sites or at a basic pH.

#### **5.4.2 Sb(III) oxidation mechanism**

The initial appearance and subsequent disappearance of Sb(V) from the aqueous phase during Sb(III) adsorption indicated a two-step process for the occurrence of Sb(V): (1) oxidation of Sb(III) and (2) removal of formed Sb(V) by ferrihydrite. The speciation analyses of the blank solution of Sb(III) (in the absence of ferrihydrite) did not detect any Sb(V) (Figure S2), which indicated that dissolved oxygen alone is unlikely to be an oxidant for Sb(III) in our experiments. However, Sb(V) was detected in the supernatant in the presence of ferrihydrite. This suggests that the ferrihydrite surface acts as a catalyst for the oxidation of Sb(III) by dissolved oxygen (Guo et al., 2014) or via an abiotic electron transfer from Sb(III) to Fe(III) (Belzile et al., 2001) to promote oxidation during the adsorption of Sb(III). Moreover, the assumption that adsorbed Sb(III) converted to Sb(V) on the ferrihydrite surfaces was

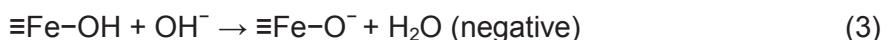
corroborated by the results from the dissolution experiments (Figure 4). Similar observations were made using XANES, XAFS and XPS to determine the Sb species adsorbed on ferrihydrite, manganite and goethite (Fan et al., 2014; Guo et al., 2014; Wang et al., 2012). These results are similar to those reported for As where the adsorbed As(III) was partially converted to As(V) on the surface of ferrihydrite (Zhao et al., 2011). However, the oxidation of Sb(III) was detected at a lower Fe/Sb molar ratio than the oxidation of As(III). Oxidation of As(III) on ferrihydrite did not occur at low Fe/As ratios or at short contact times (Oscarson et al., 1981; Zhao et al., 2011). This is also supported by the observation that Sb(III) was oxidized more easily at a lower Eh than As(III) and that Sb(V) was a stable oxidation state found over a wide range of Eh in the environment (Mitsunobu et al., 2006). It was reported that the Fe mediated oxidation of Sb(III) proceeded 10 times faster than that of As(III), which was only partly oxidized under the same experimental conditions (Leuz et al., 2006a). The oxidation of Sb(III) by Fe(III) in acid aerated solutions was also found to be faster than that of As(III), and the oxidation rate was highly dependent on the ratio of Fe(III)/Sb(III) or Fe(III)/As(III) (Asta et al., 2012).

#### **5.4.3 Competition between Sb(III) and Sb(V)**

The detection of Sb(V) in the aqueous phase during the Sb(III) adsorption experiments indicated that some Sb(III) was oxidized and that Sb(III) and Sb(V) competed for adsorption sites on ferrihydrite. Particularly since there is evidence that both Sb(III) and Sb(V) can be adsorbed on iron hydroxides via inner-sphere complexes (Guo et al., 2014; He et al., 2015). However, to the best of our knowledge there was no study about the simultaneous removal of Sb(III) and Sb(V) from an aqueous phase via adsorption by ferrihydrite. This could be attributed to the observed oxidation of Sb(III) during adsorption. Another reason could be that Sb-speciation is a rather complex analytical procedure, which is not routinely applied. Nevertheless, a close look at the competitive interaction during simultaneous adsorption of Sb(III) and Sb(V) should further elucidate Sb adsorption in the presence of both Sb species.

Our findings indicated that Sb(III) impeded Sb(V) adsorption, while the presence of Sb(V) had no influence on the adsorption of Sb(III) (Figure 5).

The protonation and deprotonation reactions for the hydroxyl functional group can be written as:



and thus depending on the pH of the aqueous phase, the surface of ferrihydrite has either a neutral, positive or negative charge. The surface of ferrihydrite has a neutral charge at a pH of approximately 7 to 8. This pH is called the point of zero charge (PZC) and above this pH the surface has a negative and below this pH a positive charge. In the pH range of 2 to 11,  $\text{Sb}(\text{OH})_6^-$  is the dominant Sb(V) species existing in the solution and thus should be adsorbed preferentially at low pH when the ferrihydrite surface is positively charged. This was observed in the single adsorption experiments, while in the presence of Sb(III) the adsorption of Sb(V) was impeded significantly (Figure 5). This would indicate that Sb(V) is not attached strongly to the ferrihydrite surface, potentially due to a combination of both outer- and inner-sphere complexes (Wang et al., 2015) instead of inner-sphere complexes only. Sb(III) adsorption, on the other hand was not affected by the presence of Sb(V) nor significantly affected by pH indicating that the uncharged Sb(III) is bound strongly on ferrihydrite by specific inner-sphere binding.

Due to their similar chemical properties, As and Sb should share a similar adsorption behavior. For example, it was reported that As(III) outcompeted As(V) for adsorption sites on ferrihydrite (Qi and Pichler, 2014), similar to what was observed for Sb (Figure 5). In natural systems, such as hot springs (Pichler et al., 1999a), both As and Sb can be present leading to competition during adsorption of different redox states of the same element and between different redox states of two elements. However, no study thus far focused on the simultaneous removal and competitive interactions of As(III,V) and Sb(III,V) in the presence of ferrihydrite. Since As and Sb are recognized pollutants and can occur together in the

environment, understanding the simultaneous adsorption of As(III,V) and Sb(III,V) should be the next step.

## 5.5 Conclusions

Our study demonstrated that ferrihydrite is an effective adsorbent for Sb(III) and Sb(V) in single and binary systems, with a higher efficiency for Sb(III) than Sb(V). Under competitive conditions, the adsorption of Sb(III) was not affected by the presence of Sb(V) over a wide of pH range. On the other hand Sb(III) had an inhibitory effect on the adsorption of Sb(V). The presence of ferrihydrite not only removed Sb(III) via adsorption, it also catalyzed the oxidation of Sb(III) to Sb(V), while at the same time leading to competition between the newly formed Sb(V) and the original Sb(III) for adsorption sites on ferrihydrite.

These results can also be used to understand the mobility and transport of Sb. In the presence of ferrihydrite and under redox conditions, which would allow the presence of both Sb species, Sb(V) should be the dominant species in aquatic environments, since Sb(III) is adsorbed preferentially.

## Acknowledgements

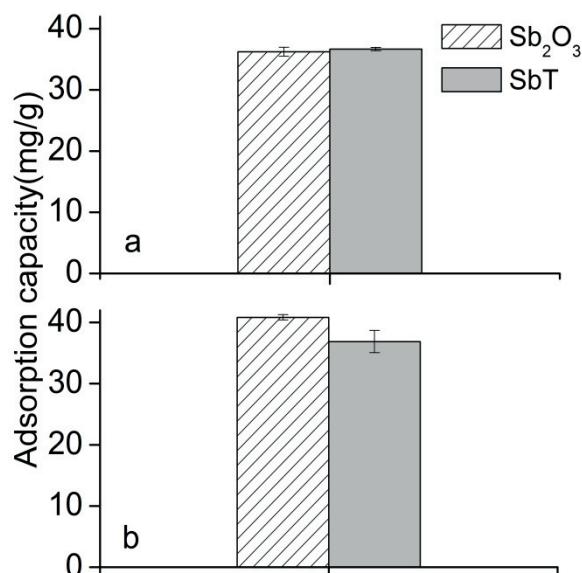
The authors thank Laura Knigge for the ICP-OES analysis and PQ thanks the China Scholarship Council (CSC) for funding support. TP acknowledges support by the German Research Foundation (DFG).

## Appendix A. Supplementary data

Comparison of two Sb(III) chemical forms on adsorption capacity (Figure S1) and antimony speciation analysis of Sb(III) blank solution (Figure S2) are provided.

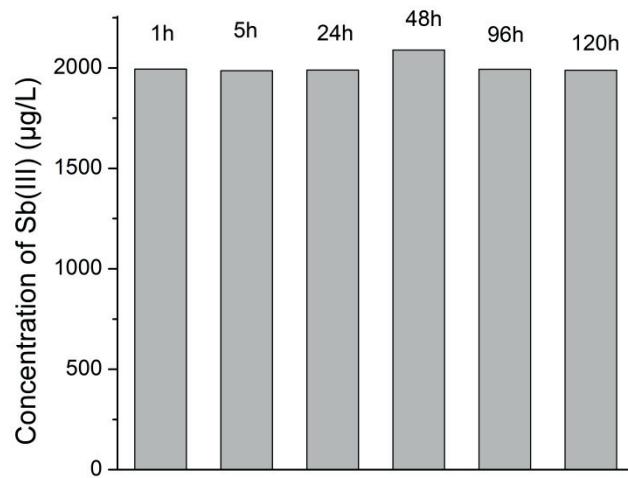
## 5.6 Supplementary Information

The comparison of adsorption capacity of Sb(III) onto ferrihydrite was tested using two chemicals, (1) potassium antimonyl tartrate ( $C_8H_4K_2O_{12}Sb_2 \cdot 3H_2O$ ) dissolved in distilled de-ionized water and (2) antimony trioxide ( $Sb_2O_3$ ) dissolved in 2 M HCl followed by dilution to the required concentrations. In the pH range of the adsorption experiments, the dissolution of reagent 1 results in the formation of a Sb-tartrate complex (SbT), while dissolution of reagent 2 results in the formation of the  $Sb(OH)_3$  oxyanion. Regardless, both reagents yielded similar results during the comparison of adsorption experiments of Sb(III) (Figure S1).



**Figure S1.** Comparison of the adsorption capacity of Sb onto ferrihydrite depending on two Sb(III) chemical reagents at neutral pH and room temperature. Experimental conditions: (a): Initial Sb(III) concentration: 2 mg/L; adsorbent dosage: 40 mg/L; Time: 24 h; (b): Initial Sb(III) concentration: 0.8 mg/L; adsorbent dosage: 12.5 mg/L; Time: 24h. Error bars are the standard deviation of triplicates.

The stability of Sb(III) in the experimental blank, i.e., in the absence of ferrihydrite, is shown in Figure S2. During the experimental period of 120 h only Sb(III) was detected in the blank, which indicates that the Sb(V) observed during the adsorption experiments was not directly oxidized by dissolved oxygen, but rather through surface oxidation on ferrihydrite.



**Figure S2.** The variation of Sb(III) in the experimental blank solution with time (pH value: 7.0 ± 0.2; initial Sb(III) concentration: 2000 µg/L)

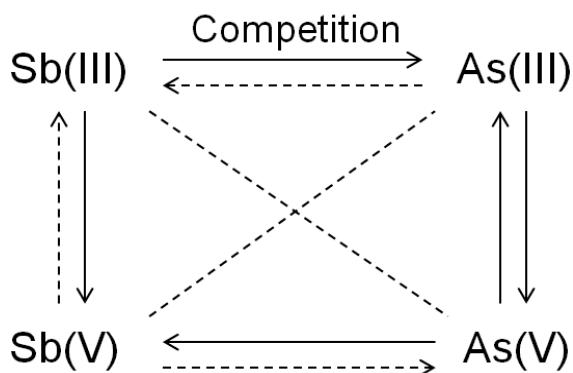
**6. Simultaneous adsorption of As(III), As(V), Sb(III) and Sb(V) in  
aqueous media by ferrihydrite**

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## Graphical abstract



## Abstract

The simultaneous adsorption behavior and competitive interaction between As(III), As(V), Sb(III) and Sb(V) during adsorption by ferrihydrite were evaluated in multi-component (binary, ternary, quaternary) systems. The presence of Sb(III) had a stronger inhibitory effect on As(III) adsorption than Sb(V), and the presence of As(V) had a stronger inhibitory effect on Sb(V) adsorption than As(III). The adsorption behavior of the four redox species under quaternary conditions, i.e., all four species are present at the same time, was pH dependent. Sb(III) always showed the strongest affinity on ferrihydrite. At low pH As(III) showed the lowest affinity could be due to the presence of Sb(III) and As(V), which both have a negative influence on the adsorption of As(III). Also, both the presence of Sb(III) and As(V) had a greater inhibitory impact on the adsorption of Sb(V). The Freundlich model provided a good fit for the simultaneous adsorption data under quaternary conditions. The major anions of  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  did not compete for the adsorption of As(III) and Sb(III) in ternary systems. The presence of  $\text{PO}_4^{3-}$  had a negative influence on the adsorption of As(V) and Sb(V) in ternary systems, while both  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  had no distinct effect on the adsorption of As(V) and Sb(V). This study indicates that Sb(III) and As(V) are adsorbed on ferrihydrite by inner-sphere complexes, while a combination of outer- and inner-sphere complexes is involved for the adsorption of Sb(V) and As(III).

**Keywords:** Simultaneous adsorption; Competition; As(III, V); Sb(III, V); Ferrihydrite

## 6.1 Introduction

Environmental contamination by coexisting toxic elements, such as arsenic (As) occurring together with antimony (Sb), is difficult to assess and remediate (He et al., 2012; Hiller et al., 2012; Wu et al., 2011). A mechanism that may immobilize one element could at the same time immobilize the other. Arsenic and Sb are metalloids of the fifth main group of the periodic table and both occur in the same range of oxidation states (-3 to +5). They are mostly found in inorganic forms as trivalent (As(III) and Sb(III)) and pentavalent (As(V) and Sb(V)) species in aquatic systems. Thus they are expected to share numerous similarities in chemical properties and toxicity. Both As and Sb are strongly adsorbed onto hydrous ferric oxide (HFO) and exhibit a similar adsorption behavior (Ilgen and Trainor, 2011; Masue et al., 2007; Pierce and Moore, 1982; Wu et al., 2010). For example, the adsorption of As(V) and Sb(V) was found to be dependent on pH with increased adsorption under acidic pH conditions (McComb et al., 2007; Xi et al., 2010), while the adsorption of As(III) and Sb(III) was reported as being less pH dependent (Guo et al., 2014; Qi and Pichler, 2014). The presence of other potential adsorbates has similar effects on adsorption behavior of As and Sb. For example, sulfate ( $\text{SO}_4^{2-}$ ), carbonate ( $\text{HCO}_3^-$ ) and nitrate ( $\text{NO}_3^-$ ) have minor influence on the individual adsorption of As and Sb, while phosphate ( $\text{PO}_4^{3-}$ ) is a well-known competitor for both the adsorption of As(V) and Sb(V) (Biswas et al., 2009; He et al., 2015; Luther et al., 2012; Zhang et al., 2009). Moreover, the formation of inner sphere complexes is part of the adsorption of As(III,V) and Sb(III, V) (Mittal et al., 2013; Sun and Doner, 1996; Vithanage et al., 2013). Considering that As and Sb share similar adsorption properties, it is crucial to evaluate the adsorption behavior of As and Sb when both compete for the same adsorption sites. So far, only a few studies were conducted concerning the simultaneous removal of As and Sb. Sb(V) adsorption was observed to be disturbed by As(V) onto akaganeite, while conversely, the addition of Sb(V) did not have any influence on the adsorption of As(V) (Kolbe et al., 2011). Xu et al. (2001) 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. However, there has been no study focusing on simultaneous adsorption of As(III,V) and

Sb(III,V) in quaternary aqueous solutions, i.e., all four possible species are present at the same time.

The main objectives of this study were to compare the competitive interaction and 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 with addition of  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  at constant pH and (3) in quaternary systems varying pH.

## 6.2 Experimental section

### 6.2.1 Materials

All reagents used were of analytical grade. Stock Sb(III, V) and As(V) solutions were prepared by dissolving potassium antimonyl tartrate trihydrate ( $\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2 \cdot 3\text{H}_2\text{O}$ , Sigma-Aldrich), potassium hexahydroxoantimonate ( $\text{H}_6\text{KO}_6\text{Sb}$ , Fluka), sodium arsenate  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (Sigma-Aldrich) in deionized distilled (DDI) water, respectively. Another stock solution of As(III) was prepared by dissolving  $\text{As}_2\text{O}_3$  (Sigma-Aldrich) in a 4% NaOH solution. Ferrihydrite was prepared following an established method (Qi and Pichler, 2014) by drop wise adding a 1 molar solution of KOH (Sigma-Aldrich, Germany) to 500 mL of a 0.2 molar  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Alfa Aesar, Germany). The suspension was kept under constant stirring until the pH increased to  $7.4 \pm 0.1$ . 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 (Qi and Pichler, 2014).

### 6.2.2 Adsorption experiments

All experiments were conducted in batch mode, with a background electrolyte of 0.01 M NaCl in 50 mL polyethylene tubes. In order to study the competition between As and Sb, experiments were carried out in various binary systems as a function 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 identical and the solution pH was adjusted to 3.5, 4.5, 5.5, 6.5, 7.5 and 8.5 by HCl or NaOH. The tubes were capped tightly

and shaken for 24 hours and allowed to settle. Then the solution was filtered through a 0.45 µm membrane filter, and the total concentration of each species in the binary system was determined.

To study the adsorption behavior of As(III, V) and Sb(III, V) onto ferrihydrite in the presence of all four species as a function of pH, 12.5 mg of ferrihydrite were suspended in a solution containing the four species at equal concentrations of 20 mg/L. The pH of all suspensions was adjusted to the same range as in the binary systems. Adsorption equilibrium isotherms studies were carried out at a pH of 5 at room temperature under quaternary conditions with identical concentrations for all four species at 4 mg/L, 10 mg/L, 15 mg/L, 20 mg/L and 25 mg/L. The suspensions were filtered after 24 hours of shaking using syringe filters and the speciation analysis of the supernatant was determined.

To study the effect of interfering ions, such as, phosphate ( $\text{PO}_4^{3-}$ ), sulfate ( $\text{SO}_4^{2-}$ ) and nitrate ( $\text{NO}_3^-$ ) on the simultaneous adsorption of As(III) and Sb(III), or As(V) and Sb(V), batch experiments were performed under ternary conditions in 40 mL suspensions containing 25 mg ferrihydrite. The concentration of the interfering ions varied, while the concentrations of As and Sb species were kept constant throughout the experiments. The ratios of the interfering ions to the As and Sb species were 0, 0.5, 1, 2 and 2.5. The pH of the suspensions was adjusted to 6 and then shaken for 24 hours. The total concentrations of As and Sb in the supernatant were measured after filtration.

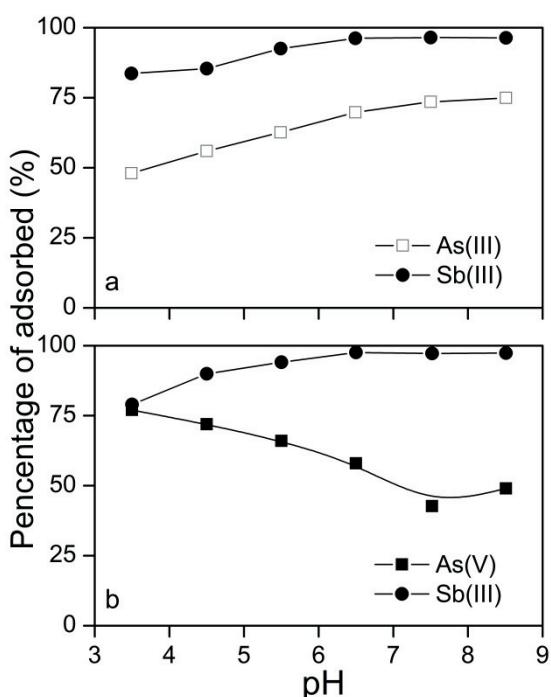
### **6.2.3 Analytical methods**

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 Scientific Accela 1250 Pump and an Hamilton PRP-X100).

A thorough description of this method can be found in the published literature (Wu and Pichler, 2014). 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 %.

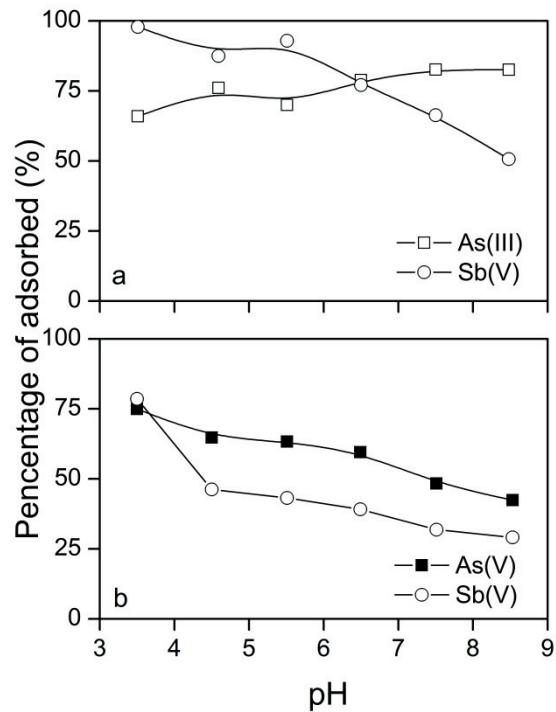
### **6.3 Results**

In Figure 1 the simultaneous adsorption behavior of As and Sb as a function of pH is shown for 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 (Table 1). The adsorption percentage of As(III) increased with increasing pH from approximately 50 % to 75 % (Figure 1a), while at the same time the adsorption percentage of As(V) decreased from 75 % to less than 50 % (Figure 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.



**Figure 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)

Figure 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 (Figure 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) (Figure 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) (Figure 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 (Figure 1b and 2b), indicating that the effect of the two Sb species on the adsorption of As(V) was almost similar.

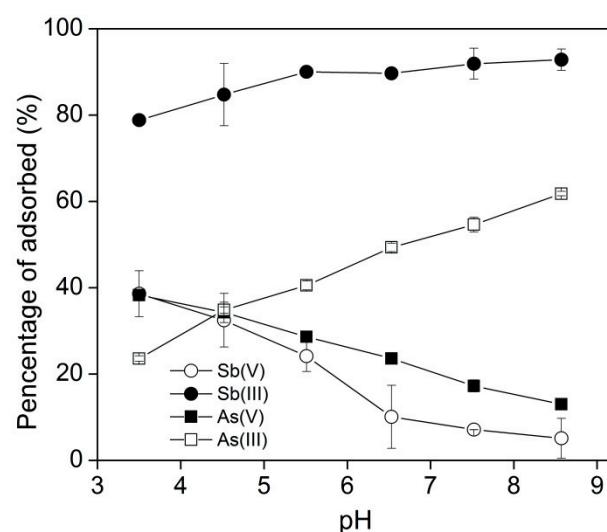


**Figure 2.** Adsorption envelopes of As and Sb as a function of pH in the binary systems of As(III)/Sb(V) and As(V)/Sb(V) (Initial concentration: 40 mg/L; pH: 3.5 – 8.5; adsorbent dosage: 0.625 g/L)

**Table 1.** The effect of pH on simultaneous adsorption of As and Sb in binary and quaternary systems onto ferrihydrite

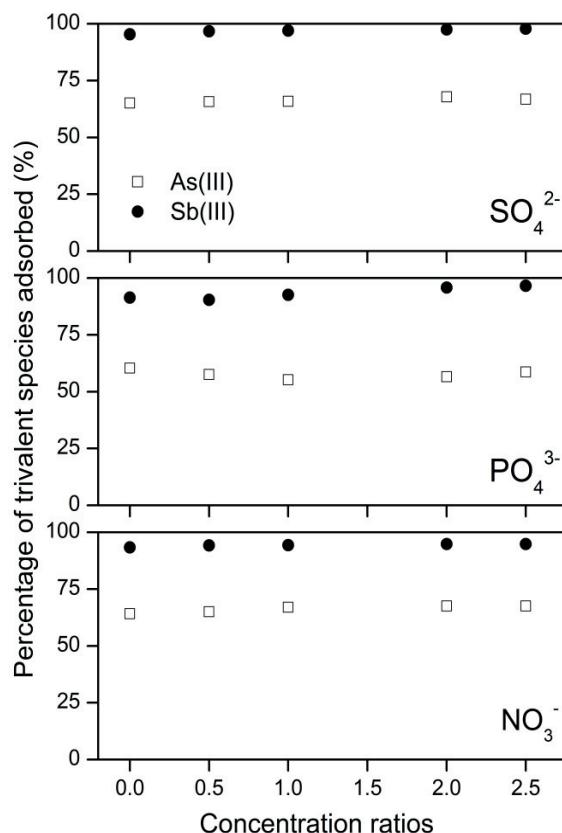
pH	binary systems (adsorption percentage)								quaternary system (adsorption percentage)			
	As(III)/Sb(III)		As(V)/Sb(III)		As(III)/Sb(V)		As(V)/Sb(V)					
	As(III)	Sb(III)	As(V)	Sb(III)	As(III)	Sb(V)	As(V)	Sb(V)	As(III)	Sb(III)	As(V)	Sb(V)
3.5	48.0	83.6	77.0	79.0	65.9	97.8	74.9	78.5	23.6	78.8	38.3	38.6
4.5	56.0	85.4	71.9	90.0	76.1	87.5	64.7	46.2	34.9	84.8	34.3	32.5
5.5	62.7	92.5	66.0	94.1	70.0	92.9	63.3	43.2	40.5	90.0	28.6	24.2
6.5	69.8	96.2	58.0	97.6	78.9	77.1	59.5	39.1	49.4	89.7	23.6	10.1
7.5	73.5	96.5	42.7	97.3	82.6	66.3	48.3	31.9	54.6	91.9	17.3	7.1
8.5	75.0	96.4	49.0	97.4	82.5	50.7	42.3	29.1	61.8	92.9	13.0	5.1

The effect of pH on the adsorption of As(III), As(V), Sb(III) and Sb(V) by ferrihydrite under competitive quaternary conditions (i.e., all four species were present at the same time) is shown in Figure 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 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. Compared to the adsorption under binary conditions adsorption efficiency in the quaternary systems was less for all species (Figure 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).

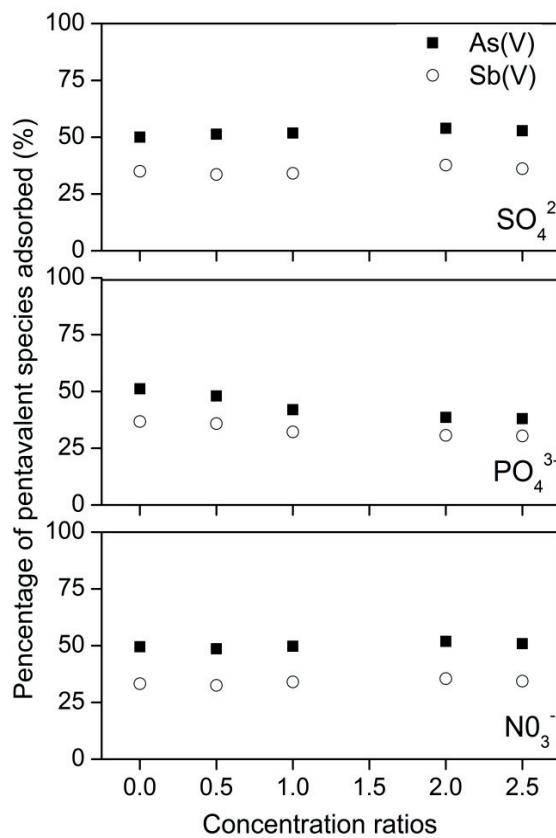


**Figure 3.** Simultaneous adsorption envelopes of As(III), As(V), Sb(III) and Sb(V) as a function of pH in the quaternary systems (Initial concentration: 20 mg/L; pH: 3.5 – 8.5; adsorbent dosage: 0.3125 g/L)

The influences of the oxyanions  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  on the adsorption of As(III) and Sb(III) are presented in Figure 4. None of the three oxyanions had a distinct influence on the simultaneous adsorption behavior of As(III) and Sb(III). At pH 6 both As(III) and Sb(III) were adsorbed in the same proportions as in the experiment without competing oxyanions (Figure 1). Adsorption envelopes remained more or less constant across the range of  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  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 adsorption of As(III) and Sb(III) under the ternary conditions nor do they affect the order of adsorption affinity. The influence of the presence of  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  on the adsorption of As(V) and Sb(V) are presented in Figure 5. The adsorption envelopes of As(V) and Sb(V) in the presence of  $\text{NO}_3^-$  were similar to that in the presence of  $\text{SO}_4^{2-}$ , but a difference was discovered in the presence of  $\text{PO}_4^{3-}$ . The adsorption of As(V) decreased noticeably with increasing of  $\text{PO}_4^{3-}$  concentration, while the adsorption of Sb(V) also decreased, but to a lesser extent (Figure 5).



**Figure 4.** The simultaneous adsorption behavior of As(III) and Sb(III) under the presence of increasing amounts of oxyanions ( $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ ) in the ternary systems. (Initial concentration: 40 mg/L; pH: 6; concentration ratios of competing ions with objective ions R: 0 – 2.5)



**Figure 5.** The simultaneous adsorption behavior of As(V) and Sb(V) under the presence of increasing amounts of oxyanions ( $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ ) in the ternary systems. (Initial concentration: 40 mg/L; pH: 6; concentration ratios of competing ions with objective ions R: 0 – 2.5)

## 6.4 Discussion

In the binary and ternary systems Sb(III) was stronger adsorbed by ferrihydrite than As(III) (Figure 1a and Figure 4), as well as in the quaternary systems (Figure 3). The removal of Sb(III) being preferred to As(III) was reported previously (Guo et al., 2009; Shan et al., 2014). The relatively stronger adsorption of Sb(III) compared to As(III) could be attributed to on the one hand that Sb(III) is a stronger Lewis base than As(III) (Leuz et al., 2006b), having a higher  $pK_a$  value ( $pK_{a1}(\text{H}_3\text{AsO}_3) = 9.22$ ;  $pK_a(\text{Sb(OH)}_3) = 11.9$ ). 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,

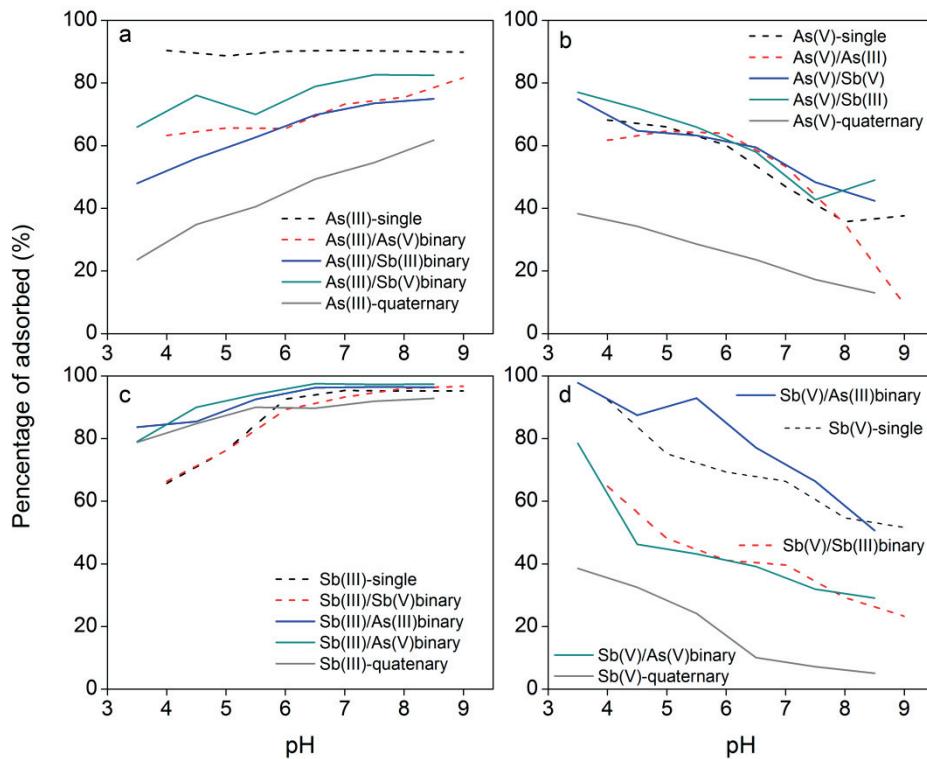
the adsorption of As(III) was weaker in the presence of Sb(III) compared to its adsorption in the presence of Sb(V) (Figure 1a and 2a), suggesting that Sb(III) is a stronger competitor for As(III) adsorption by ferrihydrite than Sb(V). It is ascribed that As(III) and Sb(III) have similar atomic structures and species distribution.

As(V) was adsorbed more effectively than Sb(V) onto ferrihydrite in the binary systems except at the low pH of 3.5 (Figure 2b). This was also confirmed under ternary conditions in the presence of interfering oxyanions (Figure 5). Under quaternary conditions, also showing slightly higher adhesion ability than Sb(V) from pH more than 5 (Figure 3). Firstly, as reviewed by Wilson et al. (2010), the observed successive deprotonation of arsenic acid ( $\text{H}_3\text{AsO}_4$ ) ( $\text{pK}_1=2.2$ ;  $\text{pK}_2=6.97$ ) caused the As(V) complex to reach a higher negative charge, in contrast to the single deprotonation of antimonic acid ( $\text{H}_3\text{SbO}_4$ ) ( $\text{pK}_a = 2.72$ ), i.e.,  $\text{HAsO}_4^{2-}$  vs.  $\text{H}_2\text{SbO}_4^-$ . A more positive charge could be required from the surface adsorption sites to offset and balance the more negatively charged As(V). Secondly, Sb(V) has a larger spatial structure 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 in the presence of As(III) (Figure 2).

Apparently  $\text{PO}_4^-$  had no effect on the adsorption of Sb(III) and As(III), while the adsorption of As(V) and Sb(V) was impeded. Although arsenic and antimony have similar chemical properties and share the same electronic configuration in their outer shell ( $s^2p^3$ ), the presence of  $\text{PO}_4^-$  had a stronger negative influence on As(V) adsorption than on Sb(V) adsorption under ternary conditions (Figure 5). A previous study reported that the adsorption of Sb(V) was disturbed to a higher extent by As(V) than by  $\text{PO}_4^-$  onto akaganeite, and As(V) adsorption was only disturbed by  $\text{PO}_4^-$  (Kolbe et al., 2011). The stronger competition between As(V) and  $\text{PO}_4^-$  could be ascribed to the fact that the structures of As(V) and  $\text{PO}_4^-$  are analogous with tetrahedral linkages and similar  $\text{pK}_a$  values, while Sb(V) is octahedral coordinated to 6 oxygen atoms (Kolbe et al., 2011; Scheinost et al., 2006).

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, a previous study reported that As(III) adsorption on activated alumina decreased with increasing Sb(III) at both low and high initial concentrations (Bullough et al., 2010). Another study also concluded that the coexisting As(V) substantially suppressed Sb(V) adsorption on activated alumina (Xu et al., 2001). But taken together our previous and current results, as shown in Figure 6, not merely Sb(III) but also As(V) had a significant negative influence on As(III) adsorption especially at low pH. Which could cause the lowest adsorption efficiency for As(III) at a pH of 3.5 in the quaternary system. Also, both the presence of Sb(III) and As(V) significantly reduced the adsorption efficiency of Sb(V) under binary conditions (Figure 6). Under quaternary conditions Sb(III) showed a distinctly strongest affinity onto ferrihydrite than that of any of the other three species (Figure 3). However, only Sb(III) envelopes under quaternary conditions (less adsorption sites available) was more or less identical to those in the binary systems (Figure 6), 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 (Wang et al., 2015) and for As(III) adsorption on iron oxides

(Goldberg and Johnston, 2001). 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) (Guo et al., 2014).



**Figure 6.** Comparisons 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. (The data for the dashed lines were obtained from our previous study (Qi and Pichler, 2014; Qi and Pichler, 2016).

#### 6.4.1 Adsorption isotherms

To evaluate contaminant transport and plume movement in groundwater the one-dimensional advection-dispersion equation must include a term, which addresses retardation (Miller and Weber, 1984). This term is

$$-\frac{B_d}{\theta} \frac{\partial C^*}{\partial t} \quad (1)$$

where  $B_d$  is the bulk density of the aquifer,  $\theta$  is the volumetric moisture content and  $C^*$  is the amount of solute adsorbed per unit weight solid. To solve this term,  $C^*$  can be calculated with 84

the help of equilibrium adsorption isotherms, which describe the relationship between adsorption capacity and concentration. Two widely used isotherms are the Langmuir and Freundlich isotherms (Travis and Etnier, 1981). The Langmuir isotherm theory assumes that the adsorption takes place on the specific homogeneous sites of the adsorbent (Kundu and Gupta, 2006b):

$$C^* = \frac{\alpha\beta C}{1 + \alpha C} \quad (2)$$

where  $\alpha$  is an adsorption constant related to binding energy (L/mg) and  $\beta$  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 (Sarı et al., 2011). The equation is:

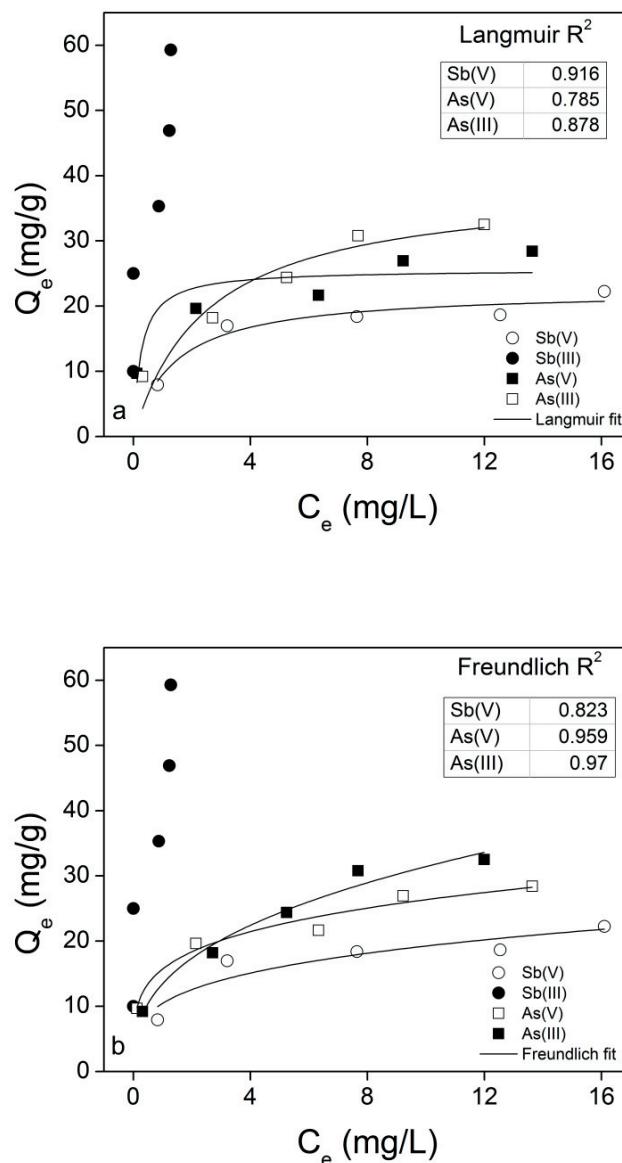
$$C^* = KC^N \quad (3)$$

where  $K$  and  $n$  are constants.

Figure 7 shows the experimental results under quaternary conditions and non-linear adsorption isotherm fittings for the data. Although Sb(III) showed the strongest adsorption ability and 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 Langmuir and Freundlich adsorption isotherm models. As(III) displayed a slightly stronger adsorption affinity than As(V) and Sb(V) with increasing initial concentrations. More effective As(III) than As(V) adsorption by ferrihydrite was previously observed at high initial As concentrations (Raven et al., 1998).

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 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.



**Figure 7.** Adsorption isotherms for simultaneous adsorption of As(III), As(V), Sb(III) and Sb(V) on ferrihydrite in the quaternary systems 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

#### 6.4.2 Implications of competition

Knowledge about the competition and simultaneous removal of individual adsorbates in a multi-component system where several adsorbates compete for the same adsorption sites is crucial to understand their fate, mobility and transport in the environment. Although As and Sb have similar chemical properties, discrepancies in their geochemical behavior were evident. For example, a recent study reported that As and Sb exhibited some differences in geochemical behavior in mine waters, and that competition for adsorption sites was the most likely explanation for the observed distribution of concentrations (Fawcett et al., 2015). The much stronger adsorption of As(III) than As(V) may also explain the unusual species distribution in natural aqueous systems (Price et al., 2007).

The four possible redox species As(V), As(III), Sb(V) and Sb(III) were in competition and their affinity order on ferrihydrite was dependent on pH and initial concentrations. The presence or absence of Sb(III) would have a tremendous impact on the mobility of As(III), As(V) and Sb(V). The mobility of As(III) is particularly enhanced at low pH and in the presence of multiple species (Figure 3). With increasing pH however, As(III) is adsorbed stronger than either As(V) and Sb(V). Thus increasing the pH in an environmental system, such as mine water, has the advantage that the trivalent species are preferentially removed from an aqueous phase. Since As(III) adsorption was affected strongest at low pH and As(V) and Sb(V) adsorption diminished at higher pH, ferrihydrite has the highest efficiency for the simultaneous removal of As and Sb at around neutral pH. 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).

#### 6.5 Conclusions

The simultaneous adsorption behavior of As(III), As(V), Sb(III) and Sb(V) onto ferrihydrite was evaluated in multi-component systems under competitive conditions for available surface

sites on ferrihydrite. 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 isotherm adsorption data 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 mechanisms of the four possible redox species should contribute to a better dispose of As and Sb contaminated water and soil and a better understanding of their mobility and transport in the environment.

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## 7. Conclusions and outlook

### 7.1 Conclusions

Numerous studies have been carried out concerning the adsorption behavior of either As species and either Sb species individually. However, different redox species of As and Sb coexist in natural environment (e.g. Fawcett et al., 2015; Okkenhaug et al., 2012). As and Sb are often considered to behave similarly and they could compete for the surface sites. Only a few studies were involved about the competition between different redox species of the same element, i.e., As(III) and As(V) (Goldberg, 2002; Kanematsu et al., 2013). However, the competition between As and Sb and their four redox species has never been studied. Therefore in this project, the simultaneous/competitive adsorption between different redox species of As and Sb on ferrihydrite was individually studied. More importantly, the simultaneous adsorption of As(III), As(V), Sb(III) and Sb(V) was studied in multi-component systems. As far as I know, this is the first time it has been considered applying the four redox species of the two elements into the same system. This project presented that the synthetic ferrihydrite was suitable as an adsorbent for the simultaneous adsorption of As(III), As(V), Sb(III) and Sb(V) from aqueous media. It also showed that the four redox species could compete for the available surface sites. The main results and general conclusions are summarized in the following paragraphs:

- 1) A competition between As(III) and As(V) was confirmed to occur on the surface sites of ferrihydrite. Contrary to the theoretical prediction that As(V) should adsorb stronger than As(III) at pH values below the point of zero charge (pzc) of ferrihydrite of about 7 to 8, As(III) more or less outcompeted As(V) across the pH scale from 4 to 10. The adsorption of As(III) was impeded largely by the presence of As(V) especially at low pH, corresponding to the range from  $pK_1$  to  $pK_2$  of arsenate acid. The effect of the presence of As(V) on As(III) adsorption was lower with increasing pH. In the binary systems, the percentage of As(III) adsorbed also depended on the concentrations of As(V) coexisting. On the contrary, the presence of As(III) has an insignificant effect on the adsorption of

## CONCLUSIONS AND OUTLOOKS

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As(V). The order of species addition had a significant effect on their competitive adsorption, since each As species could occupy the adsorption sites successfully when in contact with ferrihydrite first.

- 2) Both adsorption isotherm and kinetic studies showed that As(III) adsorption onto ferrihydrite was largely impeded by the presence of As(V) at pH 5 whereas the presence of As(III) had an insignificant influence on As(V) adsorption. The adsorption isotherms of As(III) and As(V) onto ferrihydrite in single and binary systems were good fit with 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 As(III) and As(V) was adsorbed by a rate-determining mechanism. The FTIR spectral analysis offered a direct evidence that both of the two As redox species could be adsorbed by inner-sphere complexes. It implied that As(III) and As(V) could share similar adsorption mechanism, and thus they could compete for the surface sites on ferrihydrite in the binary systems.
- 3) The presence of ferrihydrite not only removed Sb(III) via adsorption, it also catalyzed the oxidation of Sb(III) to Sb(V). The competitive adsorption could take place between the newly formed Sb(V) and the original Sb(III). The formed Sb(V) is outcompeted by Sb(III) in the case of insufficient adsorption sites or at a basic pH. The mobility of the formed Sb(V) was related to Fe/Sb ratios and pH. Specifically, at a high Fe/Sb ratio (500) or a low pH, the Sb(V) was initially detected but subsequently removed from the solution. While at a lower Fe/Sb ratio of 100 or under non-acidic conditions, the formed Sb(V) was still remained in the solution.
- 4) The pH of the solution significantly influenced the adsorption of Sb(V), while the adsorption of Sb(III) was less dependent on pH. Under competitive conditions, i.e., the two Sb species present together, Sb(III) was bound strongly on the surface sites and not affected by the presence of Sb(V) over a wide pH range. On the other hand Sb(III) had an inhibitory effect on the adsorption of Sb(V).
- 5) The competition mainly occurred between Sb(III) and As(III) or between Sb(V) and As(V)

under binary conditions. Both the adsorption of As(III) and Sb(V) onto ferrihydrite were 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).

- 6) Under ternary conditions, the presence of  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  did not compete for the simultaneous adsorption of As(III) and Sb(III).  $\text{PO}_4^{3-}$  was a stronger competitor for As(V) than for Sb(V) in ternary systems, while both  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  had no distinct effect on the adsorption of As(V) and Sb(V).
- 7) The simultaneous adsorption isotherm data in quaternary systems was well described by the Freundlich model, suggesting the heterogeneous nature of the surface sites for the adsorption of As and Sb onto ferrihydrite.
- 8) The adsorption affinities between As and Sb and their four redox species in the quaternary system were related to pH. Sb(III) was the strongest adsorbed species on ferrihydrite independent on pH. As(III) adsorption was the most affected at low pH and both As(V) and Sb(V) adsorption diminished with increasing of pH. It seems that ferrihydrite has the highest efficiency for the simultaneous removal of As and Sb at around neutral pH values.

This study indicated that ferrihydrite was a promising adsorbent to dispose the contaminated As and Sb water. In addition, the study of simultaneous/competitive adsorption of the four possible redox species on ferrihydrite also contributed to better understanding their distribution, mobility and transport in the environment. For example, in the presence of iron hydrous oxides and under redox conditions, which would allow the presence of the four redox species, Sb(V) should be the most dominant species in the aquatic environment, since Sb(V) was significantly affected and had the lowest adsorption capacity in the presence of the four redox species.

### 7.2 Outlook

The contamination of coexisting of As and Sb in aqueous environment is a big challenge for

## CONCLUSIONS AND OUTLOOKS

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scientists. More efforts are required to well understand the simultaneous adsorption of As and Sb, and it would be of interest to study it according to the following aspects:

- 1) Spectral evidences are required to further identify the nature of the simultaneous oxidation and adsorption of Sb(III) on the surfaces of ferrihydrite. For example, it was reported that the adsorbed Sb(III) was slowly oxidized to Sb(V) on iron oxyhydroxides by X-ray photon spectroscopy (XPS) and Extend X-ray absorption fine structure spectroscopy (EXAFS) (Guo et al., 2014). In addition, the effect of other parameters on the simultaneous adsorption of Sb(III) and Sb(V) by ferrihydrite also needs more studies.
- 2) The simultaneous/competitive adsorption behavior between different redox species of As and Sb on HFO could be affected by other factors, such as the sequence of addition of species, adsorbate/adsorbent ratios, ionic strength and the presence of natural organic matters. For example, our previous study reported that the order of addition of the two As redox species had an significant influence on their competitive adsorption behavior (Qi and Pichler, 2014). The competitive adsorption mechanism of As and Sb need more explanations by using spectroscopy methods, moreover, a quantitative model such as a surface complexation model would be expected to explain and compare with the experimental results.
- 3) There are several limitations in the laboratory experiments compared to the natural aquatic environment, i.e., the utilization of elevated As and Sb concentrations and their adsorption behavior in deionized water. The efficiency of ferrihydrite to remove As and Sb should be studied in different water matrices such as in groundwater systems. It also would be interesting to apply ferrihydrite into the real contaminated waters.

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## **Appendix**

This Appendix (CD) contains three files: a Microsoft word file involving the detailed experimental results corresponding to each figure presented in Chapter 3 to 6, and two Excel files including some replicated experimental data.