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Comparison of adsorption and post-adsorption behavior of oxyanions between ferrihydrite and schwertmannite

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of the requirements for the degree of
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By

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Abstract

Water contamination is a serious problem around the world. Many toxic elements such as arsenic, chromium and selenium are seriously problem in the surface and ground water because most of them are oxyanions in the the natural water and tend to be less adsorbed as the pH increases to alkaline condition. Removing oxyanions is a problematic task, because in the natural water there are coexisting oxyanions which have similar properties with toxic anions, which exist in high concentrations in the natural environment. Therefore, it is important to consider a technology and find out the best material to apply for water contamination treatment.

Chapter 1 refers to the background and research objectives of this study. This chapter describes iron oxides and hydroxides minerals, which are excellent scavengers both for hazardous cations and oxyanions. In iron oxides and hydroxide minerals, there are several mineral species such as goethite, hematite, and ferrihydrite etc. There also exists a mineral; schwertmannite which is a meta-stable iron oxy- and hydroxy-sulfate found in acidic iron and sulfate rich environments such as sulfide metal mines. Schwertmannite and ferrihydrite are both well known to play an important role in the removal of toxic elements from acid mine drainage and in natural attenuation processes of hazardous elements in acid mine water.

Chapter 2 shows the adsorption properties of some/other oxyanions. Schwertmannite and ferrihydrite are meta-stable iron oxide minerals, which are well known as excellent adsorbents for oxyanions such as arsenate, but the comparison behavior of schwertmannite and ferrihydrite with other kinds of oxyanions has not been fully or systematically investigated. With this background, the adsorption properties of oxyanions including arsenate, phosphate, chromate and selenate of schwertmannite and ferrihydrite were investigated. The result of adsorption capacities between schwertmannite and ferrihydrite, under these conditions showed that the schwertmannite's adsorption capacity is higher than the ferrihydrite's adsorption capacity. However, the adsorption selectivity of oxyanion adsorption on both schwertmannite and ferrihydrite decreases in the following order: $\text{arsenate} \geq \text{phosphate} > \text{chromate} \gg \text{selenate}$.

In chapter 3: schwertmannite and ferrihydrite are metastable minerals and both transform to a stable phase as goethite. It was therefore necessary to consider the transformation process of the disposed waste from adsorption process by dissolution and precipitation; after schwertmannite and ferrihydrite adsorbed the oxyanions, as the toxic elements may be released to the environment. The post-adsorption behavior of oxyanion onto schwertmannite and ferrihydrite was investigated. To better understand the stabilization of mineral, the solubility of schwertmannite with different oxyanions was calculated by the solid solution theory. A comparison of

the results of the post-adsorption behavior between schwertmannite and ferrihydrite showed that solubility of ferrihydrite is lower than schwertmannite's solubility. In case of comparison of other oxyanions adsorption on schwertmannite showed that the degree of retardation in transformation to goethite decreased as arsenate=phosphate>chromate>selenate>sulfate. The solubility increases in the following order: arsenate>phosphate<chromate<selenate≡sulfate. Therefore, oxyanions with a high selectivity can stabilize schwertmannite by lowering the solubility of schwertmannite after adsorption of the oxyanions.

Chapter 4 shows that the natural of adsorption for oxyanion species for a wide range of minerals and environmental conditions is fundamental to the prediction of migration and long-term fate of oxyanions in the natural environments. The surface complexation modeling which is known as a theoretical method and a tool for prediction of adsorption in the natural system was applied. However, ferric oxide has already been established in many of the adsorption conditions, such as ferrihydrite adsorbing arsenate and phosphate as inner-sphere complexes, was modeled by extended triple layer modeling (ETLM). Meanwhile, information is lacking about schwertmannite surface complexation modeling. This study characterized schwertmannite by comparison with ferrihydrite because, as explained in chapter 2, schwertmannite and ferrihydrite have similar adsorption tendencies. Thus, the main propose is to apply surface complexation modeling to schwertmannite by using similar input parameters of ferrihydrite. In this present study, oxyanion speciation reaction equations with surface of schwertmannite was predicted theoretically following previous work of ferrihydrite. The ETLM result for some oxyanions were shown as a trial to explain the difference in adsorption behavior of oxyanion on schwertmannite from the oxyanions adsorption on the pure ferrihydrite.

Chapter 5 presents the summary and general conclusion of this study. Following from chapter 2 to 4, it was concluded that the adsorption behavior between schwertmannite and ferrihydrite have similar anions selectivity. Arsenate and phosphate were inner-sphere complexes with both schwertmannite and ferrihydrite. Selenate and sulfate were outer-sphere complexes with both schwertmannite and ferrihydrite. Selenate and sulfate were outer-sphere complexes. Chromate is an intermediate with inner-and outer-sphere with schwertmannite and ferrihydrite. The stabilization of ferrihydrite is higher than schwertmannite due to ferrihydrite's lower stability compared to schwertmannite. Some of oxyanions which made inner sphere complexes with the minerals can change the stabilization of mineral by lowering solubility

Chapter 1

General introduction

1.1. Statement of the problems and objective of this study

Water resources are sources of water that are potentially useful. Uses of water include agricultural, industrial, household, recreational and environmental activities. All the activities above need fresh water. Fresh water is naturally occurring water on earth's surface such as river, lakes, ponds and streams and underground as groundwater in aquifers and underground streams (Figure 1). As shown in Figure 1a, the water contamination by acid mine drainage, Figure 1b, leads to water contamination by arsenate in groundwater. Freshwater is generally characterized by having low concentration of dissolved salts and other total dissolved solids. Much of the surface fresh water and ground water is unsuitable for drinking without some form of purification because of the presence of chemical or biological contamination

Water contamination is the contamination of water bodies including lakes, rivers, oceans, aquifers and groundwater. Water contamination is a major global problem which requires ongoing evaluation and revision of water resource policies at all levels. It has been suggested that water contamination is the leading worldwide cause of deaths and diseases. There are anions that can remain in solution in relatively high contents. Therefore, oxyanions such as chromate, arsenate and selenate are the most common trace contaminants in surface and ground water. Arsenic is the most problematic element in the natural conditions, because it is highly mobile over a wide range of redox conditions as shown in Figure 2 (Smedley & Kinniburgh 2002; David & Kosmus 2002; Mohan & Pittman 2007). Selenium is usually mobile as the selenate oxyanion (SeO_4^{2-}) under highly oxidizing conditions but is immobilized under reducing conditions due to adsorption of selenite (SeO_3^{2-}) on mineral surfaces (Dzombak & Morel 1990; Drever 1997) or due to reduction to metal. On other hand chromium, can also be mobilized as chromate oxyanion species (CrO_4^{2-}) under oxidizing conditions. However, chromium forms cationic Cr(III) species in reducing environments and performs like other trace cations. Other oxyanions also appear to be less mobility under reducing conditions.

The migrations of dissolved trace species in the surface condition are initially retarded by the adsorption process at mineral water interface. Especially, low crystalline ferric oxides are known to be the most effective scavengers for these species. The interactions of low crystalline ferric oxide with cationic metal species have been widely investigated by laboratory experi-

ments and field observations. However, these with anionic species have been lacking information investigated due to their complex behavior in the natural systems. Ferrihydrite and schwertmannite are iron oxide minerals and low crystalline minerals had high specific surface area (Bigham et al. 1990; Cornell & Schwertmann 1979). Ferrihydrite and schwertmannite occur in nature with different pH conditions (Figure 3), ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) precipitated in soil and sediment with pH in neutral conditions (Jambor & Dutrizac 1998), schwertmannite occurrence in pH acidic condition in mining tailing (Bigham, Udo Schwertmann, et al. 1996; Fukushima, Sasaki, et al. 2003), there are different surface properties, ferrihydrite surface has hydroxyl group which had ligands exchange with oxyanions as shown in Figure 4a,b. Meanwhile, schwertmannite has hydroxyl group and SO_4 (Figure 4c) some of which adsorption information by arsenate is shown in Figure 4b (Fukushi, Sasaki, et al. 2003; Fukushima, Sato, et al. 2003). Moreover, although the retardation has been thought to be initially attained by adsorption process, the long-term stability of adsorbed species had some information which were already understood especially for the anionic species (Fukushi et al. 2003a; Fukushima et al. 2003a). The low crystalline Fe(III) oxide are metastable phase and eventually transform to more a stable phase with time. Therefore, it is important to understand the stability of the host mineral and sorbed species for the prediction and assessments of long term behavior of anionic species. Ferrihydrite and schwertmannite are both metastable and transform to stable phase as goethite by dissolution and reprecipitation (Figure 5). Ferrihydrite is known as a ferric iron oxide mineral, which is highly effective for waste water treatment and has application to predict the adsorption capacity such as surface complexation modeling, meanwhile, information is lacking in which surface complexation modeling of schwertmannite is applied to predict the adsorption properties. The comparison of both ferrihydrite and schwertmannite is important to better understand the adsorption and post-adsorption properties.

Particularly, this study aims to

- (1) To understand the differences and similarities in adsorption behavior of oxyanions by ferrihydrite and schwertmannite.
- (2) To understand differences and similarities in post-adsorption behaviors of oxyanions between ferrihydrite and schwertmannite
- (3) To apply surface complexation modeling for different kinds of oxyanions on ferrihydrite and schwertmannite to check applicability of existing double layer model.

1.2. Oxyanions in natural water

Aqueous anions, from elements such as arsenate, chromate, selenite and sulfate to anionic functional groups on biomolecules, adsorb on the electrically charged surfaces of oxides, influencing the motilities of toxic species in the environment (Dixit & Hering 2003). Arsenic, chromium and selenium, when they are form the aqueous solution in the natural water, they are types of toxicity oxyanions which occurrence in both by anthropogenic and natural dissolution from the weathering soil and bedrock itself.

Arsenic is a metalloid that can form inorganic and organic compounds (Choi et al. 2009). Arsenic can occur in inorganic form as oxyanions of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)) in natural water. Organic arsenic forms may be produced by biological activity, mostly in surface water, but are rarely important (Smedley & Kinniburgh 2002). Redox potential and pH are the most important factors controlling arsenic speciation (David & Kosmus 2002; Mohan & Pittman 2007; Terlecka 2005). The toxicity and the mobility of arsenic is highly dependent on the speciation; it is important to understand what form of arsenic take in the specific condition. The distributions of the species as a function of pH and Eh are shown in Figure 2a, Under oxidizing conditions, H_2AsO_4^- is dominant at low pH (less than about pH 6.9), while HAsO_4^{2-} is dominant at higher pH. Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite speciation H_3AsO_3^0 is predominate. In the condition of resultant acid mine drainage, arsenic is usually existing as mainly H_2AsO_4^- due to the low pH and high redox potential. Oxyanions which coexist with the water such as sulfate, nitrate and phosphate have important effects to the water treatment system. Phosphate is an oxyanion, whose factor to control phosphate is pH (Figure 2,b), phosphate is competition adsorption with the arsenate oxyanions, so the phosphate is become one important oxyanions need to study (Violante & Pigna 2002; Manning & Goldberg 1996)

For other oxyanions, such as chromate and selenate redox potential and pH conditions are also controlling factors (Figure 2, c and d). They are common trace contaminants in surface and groundwater.

1.3. Poorly crystalline iron (hydr) oxide mineral

Iron (Fe) is a ubiquitous element in the earth surface and often occurs as Fe(III)oxides under the surface conditions. The iron oxide under the surface conditions are goethite, hematite, lepidocrocite, maghemite, ferrihydrite and schwertmannite (Schwertmann & Cornell 2008; Cornell et al. 1996) Among them, ferrihydrite and schwertmannite are generally categorized as poorly crystalline Fe (III) oxides. Ferrihydrite is a hydrous ferric oxide found in soils and rocks,

lakes and rivers, in air and in organisms (Cornell et al. 1996). Schwertmannite is a ferric oxy-hydroxysulfate and frequently found in acid mine drainage which are characterized by acidic and high sulfate condition (Bigham et al. 1990; Regenspurg et al. 2004; Bigham, U. Schwertmann, et al. 1996; Schwertmann & Cornell 2008; Bigham et al. 1994). These minerals play an important role as a regulator of dissolved trace element concentrations in the surface conditions due to their ubiquitous distribution in the surface, large specific surface area, unique surface characteristics and participating redox reaction.

The above two poorly crystalline Fe(III) oxides are directly produced from natural water. The products are recognized reddish brown to yellow precipitates in nature and also easily form in laboratory conditions (Schwertmann & Cornell 2008). The well-known method for synthesis of ferrihydrite is titration of alkaline solution to ferric nitrate or chloride solution. Alternatively, addition of ferric nitrate or chloride to preheated water (80°C), hydrolysis and dialysis of the resultant suspension also yield ferrihydrite. Schwertmannite is formed by titration of the sodium sulfate solution to preheated ferric nitrate or chloride solution. Alternatively, schwertmannite is formed by incubating the iron oxidized bacterium in ferrous sulfate solution (Bigham, Udo Schwertmann, et al. 1996; Fukushi et al. 2004; Fukushi, et al. 2003)

For the formula and structure of ferrihydrite have not been understood completely (Cornell et al. 1989; Cornell & Schwertmann 1979; Waychunas et al. 1993). The main reasons for the uncertainties are due to the fact that the formula and crystallinity are frequently changed according to the synthesis methods and aging periods (Cornell et al. 1989). On the other hand, the structure of schwertmannite was thought to be similar to akageneite which was composed of double chains of $\text{FeO}_3(\text{OH})_3$ octahedra sharing corners to produce square tunnel extending parallel to the c axis (Bigham et al. 1990). In akageneite, structure is stabilized by Cl^- or F^- or OH^- occupations in every second cavity. Therefore, it has been suggested that SO_4^{2-} may play a similar role in schwertmannite (Figure 4c-d). However, because of size restrictions, the structural cavities cannot be occupied by SO_4^{2-} without sharing the O atoms with surrounding Fe atoms and without severe distortion of the structure. The distortion undoubtedly leads to the poor crystallinity. Therefore, a significant amount of excess SO_4 adsorbs to the surface sites of schwertmannite as well as the tunnel sites (Bigham et al. 1990). The formula of schwertmannite has been proposed as $\text{Fe}_8\text{O}_8(\text{OH})_{8-2x}(\text{SO}_4)_x$ ($1 < x < 1.75$) (Bigham et al. 1990). The variation of SO_4 contents in the formula has been thought to be dependent on the extent of adsorbed SO_4 . Moreover, due to the poorly crystallinity, these minerals possess large specific surface area. The specific surface areas of ferrihydrite and schwertmannite are 200 to 600 m^2/g , and about 250 m^2/g , respectively (Bigham & Nordstrom 2000).

Poorly crystalline oxides are commonly produced at the surface environment during rock weathering (Appelo & Postma 2004; Schwertmann & Cornell 2008). The important hosts for Fe (II) are magnetite (Fe_3O_4), illumenite (FeTiO_3), pyrite (FeS_2), siderite (FeCO_3) and Fe (II) silicate such as pyroxenes, amphiboles, biotite and olivine. These minerals dissolve during weathering processes and release Fe(II) to the solution. When the groundwater containing much amount of Fe(II) reacts with surface oxidized water, Fe(II) oxidizes to Fe(III). Because of the low solubility of Fe (III) at neutral pH condition, the dissolved Fe (III) rapidly is hydrolyzed and precipitates as a ferrihydrite or schwertmannite. The resultant mineral speciation is determined by the solution chemistry (Bigham, Udo Schwertmann, et al. 1996; Yu et al. 1999). As shown in the Eh-pH diagram of Fe-S-O₂-H₂O system (Figure 4) with relevant minerals, ferrihydrite forms under oxidative and weak acidic to alkaline condition (Bigham & Nordstrom 2000; Yu et al. 1999), while schwertmannite forms under oxidative, acidic and high sulfate concentration (Bigham, Udo Schwertmann, et al. 1996; Carlson et al. 2002; Yu et al. 1999). In acidic conditions, oxidation rate of Fe (II) is very slow (Singer & Stumm 1970; Bigham & Nordstrom 2000). Therefore, the formation of schwertmannite is thought to be usually mediate by biotic oxidation (Clarke et al. 1997; Bigham, Udo Schwertmann, et al. 1996; Bigham et al. 1990). Because the formation rates of these minerals are so rapid, Fe concentration in the surface water should be limited by the formations (Appelo & Postma 2004).

The concentration of dissolved trace elements in natural water are usually much lower than those expected from solubility of minerals containing these elements. The limited concentration of these species is probably due to sorption processes on the surfaces of solid phases (Stumm 1992; Drever 1997). The solid phases participating in sorption processes are typically composite materials, i.e., they consist of mixtures of various minerals and organic debris with a wide range of intrinsic chemical properties (Davis & Kent 1990; Sposito 1984). In many cases, the surface chemical properties of natural materials are dominated by secondary minerals (Davis & Kent 1990). Specifically, ferrihydrite and schwertmannite are some of the most important adsorbent for dissolved trace elements because these minerals occur ubiquitously in nature and possess large specific surface area.

The adsorption mechanisms by ferrihydrite are known to be the surface complexes formations between surface hydroxyl groups and dissolved trace elements (Dzombak & Morel 1990). In general, mineral edge exposures surface hydroxyl groups ($>\text{FeOH}$). The surface hydroxyl groups adsorb protons and positively charge under acidic conditions:



On the other hand, these desorb protons and negatively charge under alkaline condition:



The pH, where the amount of protonated surface hydroxyl group is equal to that of deprotonated surface hydroxyl group, refers to point of zero charge (PZC), (Sposito 1984; Davis et al. 1987; Dzombak & Morel 1990; Stumm 1992; Stumm & Morgan 1996). Ferrihydrite has relatively higher pzc and higher increment of surface charge with relation to pzc than those of normal silicate minerals. It indicates that ferrihydrite has high positive charge under the natural water condition (pH5-8) while the surface charge of silicate mineral is negative under the condition. Therefore, anionic species in natural water electrostatically adsorb to the surface (Figure3a) and/or exchange with protonated surface hydroxyl. As a result of the process, the concentrations of these species in solution would be kept low. Oxyanions such as arsenate and phosphate are known to form a strong inner-sphere complexes with the surface of ferrihydrite via ligand exchange (Drever 1997). However little is known about the surface characteristics and the change in the surface reactivity of schwertmannite as function of the environmental parameters such as pH, temperature and so on (Bigham & Nordstrom 2000).

1.4. Stabilization of the poorly crystalline iron (hydr) oxide mineral

Ferrihydrite and schwertmannite are metastable and transform to goethite or hematite with time and pH condition (Bigham, Udo Schwertmann, et al. 1996; Cornell et al. 1989). Kinetics of the transformation and factors influencing the transformation of ferrihydrite have been extensively investigated (Clarke et al. 1997; Cornell et al. 1987; Cornell et al. 1989; Carlson et al. 2002). The most important factor that affects the kinetics and formed mineral speciation is solution pH (Cornell & Schwertmann 1979). However, the temperature and the additives in solution also effect on kinetics and formed mineral speciation (Cornell et al. 1989).

The transformation from ferrihydrite to hematite is attained by aggregation of ferrihydrite particle and dehydration, while the transformation to goethite is attained by dissolution of ferrihydrite and subsequent crystallization (Fischer & Schwertmann 1975; Cornell et al. 1989). Therefore, the formation of hematite is favored at low solubility condition of ferrihydrite under neutral pH whilst that of goethite is favored at high solubility condition under high pH and low pH (Fischer & Schwertmann 1975). In the case of schwertmannite, transformation to goethite has been reported (Bigham, Udo Schwertmann, et al. 1996; Yu et al. 1999). The pure ferrihydrite synthesized in laboratory has transformed to crystalline mineral during a few days by suspending solution. Schwertmannite also has transformed to goethite during several months

(Bigam, Udo Schwertmann, et al. 1996). These minerals, as mentioned above, play an important role as a sink for dissolved trace metal despite the labile properties, because the transformation is significantly retarded by several factors. The transformation rate of ferrihydrite to crystalline minerals is retarded by adsorbing or incorporating silica (Cornell et al. 1987), organic anions (Cornell & Schwertmann 1979), other anions and several cations (Cornell et al. 1992) as impurities. On the other hand, the factors influencing the transformation of schwertmannite have been investigated that arsenic was formed with oxyanion and can stabilize schwertmannite (Fukushi, Sato, et al. 2003; Fukushi, Sasaki, et al. 2003), there is lacking information with other anions adsorption onto schwertmannite.

1.5. Surface complexation modeling

Surface complexation models (SCMs) which are based on thermodynamics and which are analogous to aqueous speciation models, are a powerful approach to surface reaction modeling (Dzombak & Morel 1990; Davis & Kent 1990). Surface complexation models represent an improvement over empirical models of adsorption because the intrinsic equilibrium constants (K^{int}) derived from SCMs are much less system-dependent than those derived from empirical models. Values of K^{int} depend on the identity of the solid and the adsorbing solute (and for some models, on ionic strength), but do not depend on the pH, concentration of adsorbate or the solution composition.

First, it is assumed that mineral surface can be described as flat planes of surface hydroxyl sites and that equations can be written to describe reactions at these specific sites. So, for example, a surface protonation was written as follow:



The second assumption common to all SCMs is that reactions at mineral surface may be described using mass law equations; in other words, these reactions are assumed to be in a state of local equilibrium. For reaction above, the associated mass law equation is

$$K^{\text{int}} = \frac{\{> \text{SOH}_2^+\}}{\{> \text{SOH}\} \{\text{H}^+_{\text{aq}}\}} \quad (4)$$

Where $\{\}$ shown activity of the species in the brackets

The third assumption adopted in all SCMs is that variable charge at the mineral surface is the direct result of chemical reactions at the surface. It has been observed that the mineral has zero surface charge at a particular pH, termed the pH_{pzc} , or pH of the pristine point of zero, which is a predictable function of mineral structure (Sverjensky 1994).

1.6. Outline of the dissertation

This dissertation is composed of five chapters. The key contents of each chapter are outlined as following here:

Chapter1: Introduction of the background, statement of the problem and objective of the study. Some explanations about oxyanions in the natural water, poorly crystalline iron mineral and the stability of the iron oxide minerals.

Chapter2: Adsorption behavior of oxyanions onto ferrihydrite and schwertmannite with difference kind of oxyanions. The chapter describes the adsorption capacities, the selectivity of oxyanions on iron oxide (ferrihydrite and schwertmannite), mechanism of the oxyanions adsorption onto schwertmannite and ferrihydrite, which were described by changing of zeta potential before and after adsorption.

Chapter3: Post-adsorption behavior of oxyanions onto ferrihydrite and schwertmannite was conducted to better understand the stabilization of the minerals before and after adsorption process. The solubility is an important factor to understand the stability of the mineral, applied solid-solution theory to calculate solubility of schwertmannite and schwertmannite after adsorbed oxyanions was necessary.

Chapter4: Surface complexation modeling for many kinds of oxyanions onto ferrihydrite and schwertmannite. In this study, we specifically use extended triple layer modeling (ETLM), which explains the mechanism of oxyanions adsorption on the mineral surfaces. For ferric oxide or ferrihydrite there is some parameter data that are used to apply in this ETLM. Information for schwertmannite is lacking. In this chapter, a better understanding of the adsorption behavior of schwertmannite which assumed to be similar to the behavior of ferrihydrite sorbing SO_4 , for input data for ETLM of schwertmannite, we predicted by using previously work of ferrihydrite equilibrium constants.

Chapter 5: the summary and conclusion of the dissertation



Figure 1. (a) acid mine water pollution, McCarthy (2012), (b) arsenic safe deep tubewell in Satkhira, Bangladesh, Mazurul Hassan (2010)

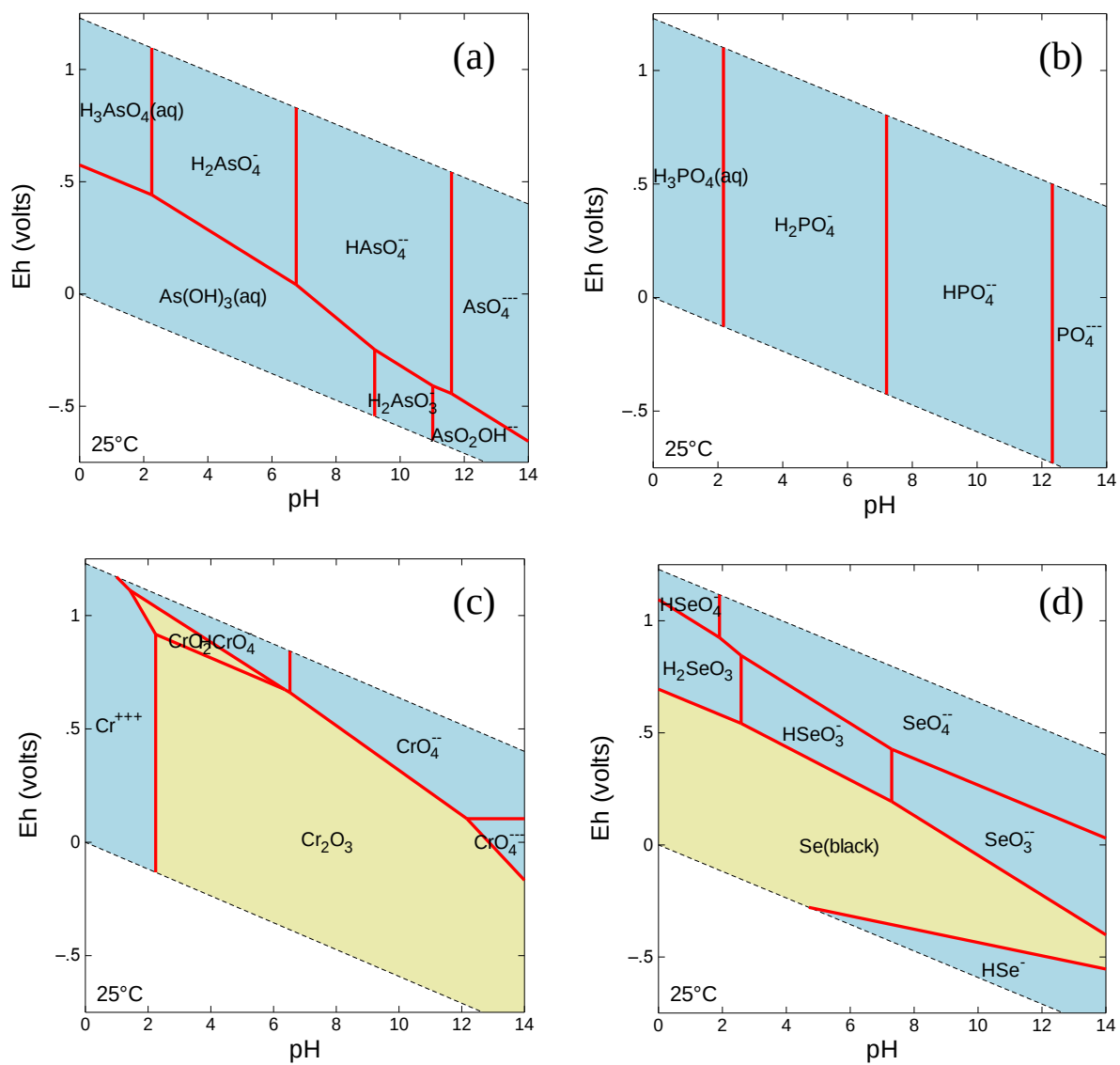


Figure 2. pH and Eh diagrams of the focused oxyanions

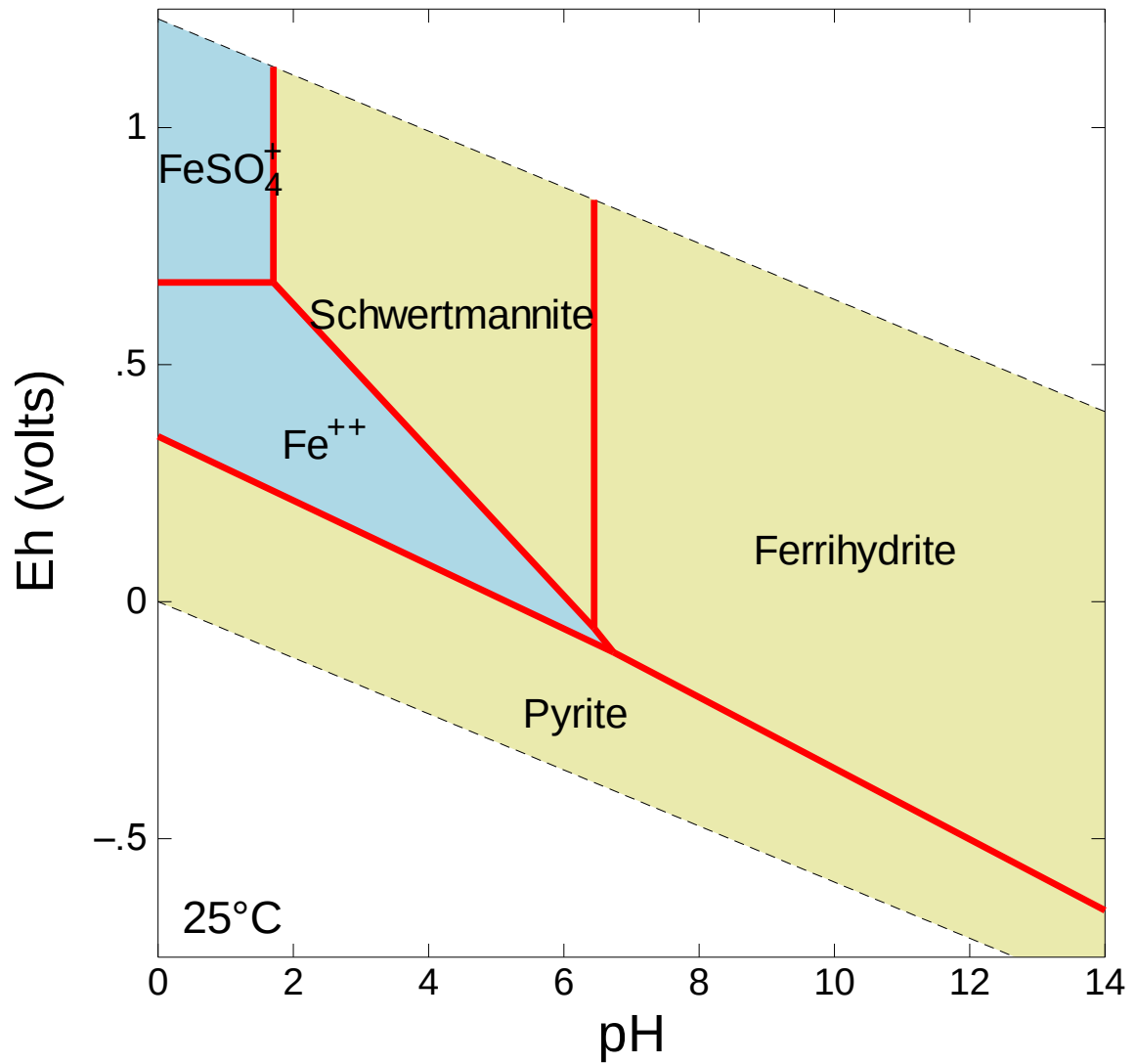


Figure 3. Eh-pH diagram for Fe-S-H₂O system with relevant minerals at 25°C, where log activities of Fe= -5 and S=-3. The thermodynamic data of schwertmannite and ferrihydrite were used from Yu et al., (1999). Other aqueous solutions use database incorporated in the Geochemist's workbench (GWB) using the latest thermodynamic database released from Lawrence Livermore National Laboratory in USA.

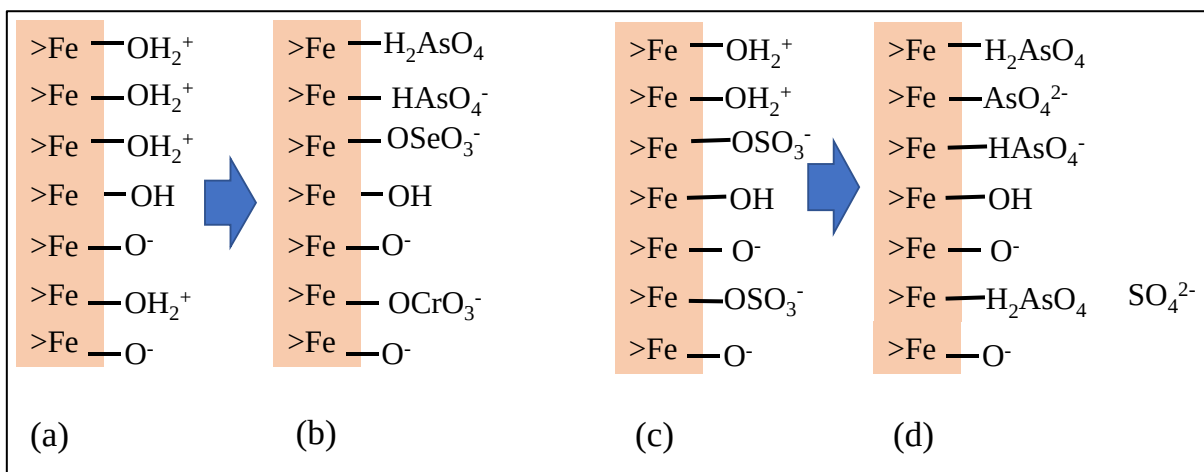


Figure 4. (a) Surface hydroxyl group of ferrihydrite, (b) ferrihydrite's surface after adsorbed oxyanions, (c) schwertmannite's surface group included hydroxyl group and SO_4 , (d) schwertmannite's surface after adsorbed oxyanions.

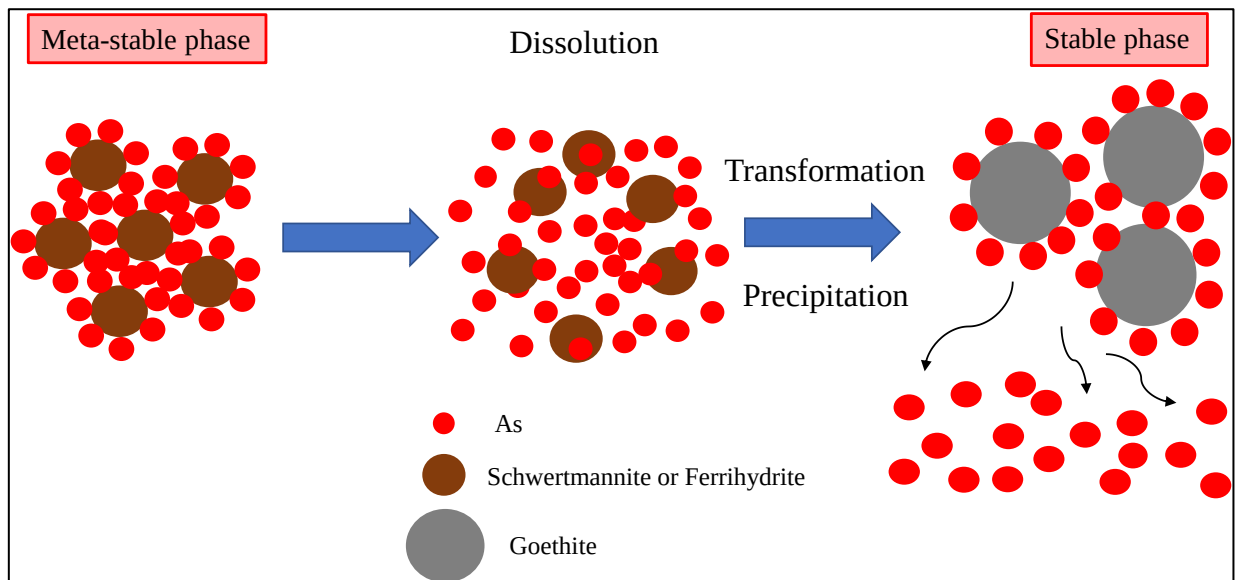


Figure 5. Schwertmannite and ferrihydrite transformation process to goethite

Chapter 2

Adsorption behavior of oxyanions onto ferrihydrite and schwertmannite

2.1. Introduction

Toxic element dissolved in the aqueous solutions, dominated form ions in the solutions there are cations and anions. For cations was effected by pH, when pH increased the toxic element was precipitate with the mineral (Stumm 1992; Drever 1997) and these cations more likely adsorb to the clay mineral and organic matter (Sposito 1984; Davis et al. 1987; Dzombak & Morel 1990). Anion can remain in solution with relatively high contents. Consequently, the oxyanions such as arsenate, chromate and selenate are most common trace contamination in the natural water in both surface water and groundwater (Smedley & Kinniburgh 2002; David & Kosmus 2002). To treat of oxyanions toxicity was established processes such as coagulation/co-precipitation, adsorption, and ion-exchange etc. (Saxena et al. 2004; Rubio et al. 2002; Gonzalez et al. 2010). Adsorption is an example of simply easily application techniques. Adsorption has been reported in removal of hazardous cations using activated carbon, zeolites and clays (Sawhney 1972; Erdem et al. 2004). Iron oxides and hydroxides are known well as an excellent material both for hazardous cations and hazardous oxyanions. In iron oxides and hydroxide, there are several mineral species such goethite, hematite, ferrihydrite and schwertmannite etc.

Ferrihydrite and schwertmannite a nanocrystal-line Fe (hydr)oxide commonly found in soils, sediments, and mine-drainage channels. Ferrihydrite is a mineral name for poorly crystalline hydrous ferric oxide that is widely occurring in low-temperature geochemical and hydrometallurgical processes (Jambor & Dutrizac 1998; Cornell et al. 1996). There is new mineral such schwertmannite is a meta-stable iron oxy-and hydroxy-sulfate found in acidic iron- and sulfate rich environments such as sulfide metal mines (Bigham et al. 1990; Bigham et al. 1994; Bigham, Udo Schwertmann, et al. 1996; Waychunas et al. 2001). Schwertmannite well known to play an important role in the removal toxic elements from the acid mine drainage (Webster et al. 1998; Liao et al. 2011; Paikaray & Peiffer 2012) and in natural attenuation processes of hazardous elements in acid mine water (Fukushi, Sasaki, et al. 2003).

Because of its high surfacearea and density of reactive surface-sites, both schwertmannite and ferrihydrite are the most important mineral sorbents affecting the mobility of nutrients trace elements and contaminants in aquatic environments, ferrihydrite is also used commercially for

removing heavy-metal contaminants from industrial wastewater (Richmond et al. 2004; Arai & Sparks 2001; Wang et al. 2013; Zachara et al. 1987; Johnston & Chrysochoou 2016). Therefore, the lacking information of comparison the mechanism of oxyanions adsorption onto ferrihydrite and schwertmannite.

This background, the adsorption properties of oxyanions including arsenate, phosphate, chromate and selenate of schwertmannite and ferrihydrite were investigated. The waste water treatment such as precipitation method and column method which common use in groundwater treatment (Figure 6), which material is the appropriate materials use for both method need to be investigate. The comparison of adsorption behavior between schwertmannite and ferrihydrite is important to better understand what is different and similarity of many kinds of oxyanions adsorption onto ferrihydrite and schwertmannite

2.2. Method and material

2.2.1. Prepare adsorbents

Ferrihydrite was prepare as adsorbent by using digital titration machine TOADKK-AUT-701, 0.1M of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 500 ml was prepared and set on the stirrer, 0.1 of KOH solution was also prepared about 500 ml set into the machine, Auto titration was added 0.04ml/min (KOH) to the solution, until reach to pH7 (Schwertmann & Cornell 2008), sample was centrifuge 3000rpm, 40 minutes' wash in 6 times, then filtered through 0.2 μm cellulose membrane. The resulting of solids was freeze dried and identify the synthesized phases solids was examined by Rigaku X-Ray diffractometer with $\text{CuK}\alpha$ radiation (40kV and 40 mA), the result of XRD pattern (Figure 7a) was identical to that of the previously reported of ferrihydrite (Cornell et al. 1987; Drits 1993).

Schwertmannite was prepared by the method previously reported by Bigham et al (1996). Mixing solution prepared by 0.04 M Na_2SO_4 solution and 0.04 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution was held at 60°C for 12 minutes, then cooled and dialyzed for 30 days, deionized water used for the dialyzing was changed every day. To remove the salt in the surface of mineral the product was clean by using deionized water and was filtered through a 0.2 μm cellulose membrane then immediately freeze-dried to prevent transformation to another phase. Further, X-ray diffraction (XRD) analyses were conducted to identify the synthesized phases by Rigaku X-Ray diffractometer with $\text{CuK}\alpha$ radiation (40kV and 40mA). From the XRD analyses (Figure 7b), the synthesized products were identified as a schwertmannite because the XRD pattern was identical to that of the previously reported schwertmannite by Bigham et al (1990).

2.2.2. Adsorption experiment

All adsorption experiments were conducted at a constant ionic strength ($I=0.01$ M, NaNO_3) by using a 50 ml centrifuge tube adding 40 ml solution of Na_2HPO_4 , Na_2HAsO_4 , Na_2CrO_4 , and Na_2SeO_4 with concentrations from 0 to 2 mM and 40 mg of the synthetic schwertmannite and ferrihydrite. The pH of the adsorption media was adjusted to 7.00 ± 0.15 by 0.1M NaOH solution. The samples were placed in a reciprocal shaker at 25°C , 100 rpm for 24 hours. The filtered solids were freeze-dried for measurements of Zeta potential (Malvern Zetasizer Nano series Nano-ZS90 instrument) and liquid samples were used for the inductively coupled plasma atomic emission spectroscopy, (ICPE-9000, ICP-AES) and ion-chromatography (Metrohm 861 Advanced Compact IC instrument) to determine the concentration of elements after the adsorption. The released SO_4^{2-} in the equilibrium solutions were also determined for schwertmannite

The amount of anions adsorbed were calculated by the difference between the initial concentration and concentration in the solution after adsorption as shown in the equation reported previously (Vanderborght & Van Grieken 1977).

2.3. Results

2.3.1. Oxyanions adsorption on ferrihydrite

As shown in Figure 8 a, from the result of adsorption without pH adjustment (pH 7.5 to 8.5) the amounts of adsorbed oxyanions increased with increasing initial concentration of anions. Arsenic ion adsorbed on ferrihydrite with the highest adsorption capacities, while only small amount of selenate adsorbed on mineral. From both without pH adjustment and pH adjustment (Figure 8a) by the observation for oxyanions adsorption on ferrihydrite, the selectivity was shown in following order: arsenate $\geq$ phosphate > chromate >> selenate.

Ferrihydrite before adsorption has a point of zero charge (PZC) at round 7.9. The ferrihydrite had positive and negative potentials at pH less and more than 7.9, respectively. Ferrihydrite with selenate changes shift to negative charge but less than other oxyanions. PZC of selenate-ferrihydrite is at around 5.8. ferrihydrite with arsenate, phosphate and chromate shown different change from that of schwertmannite with sulfate with PZC at about 4.5. Among arsenate, phosphate and chromate, schwertmannite with chromate change is slightly different curve at pH range between 6 and 10 with less negative potentials (Figure 10a).

2.3.2. Oxyanions adsorption on schwertmannite

As shown in Figure 8b and Figure 9b, the amounts of adsorbed oxyanions increased with increasing initial concentration of anions. The maximum adsorbed anion contents on schwertmannite were 1.023, 0.934, 0.723 and 0.313 mmol/g for arsenate, phosphate, chromate, and selenate, respectively. From the different in capacity, if determine the selectivity adsorption on schwertmannite in the following order: arsenate $\geq$ phosphate> chromate>> selenate.

This decrease would be due to release of protons from schwertmannite during the adsorption. Further, the SO_4^{2-} concentration in the reaction solutions was determined after the adsorption because SO_4^{2-} originally adsorbed on schwertmannite. The SO_4^{2-} concentration in the reaction solution initially 0.123 ± 0.002 mmol/g without adsorption of any other oxyanions, which is a value similar to that in previously work (Fukushi et al. 2004).

Schwertmannite before adsorption, sulfate-schwertmannite, has a point of zero charge (PZC) at round 7. The schwertmannite had positive and negative potentials at pH less and more than 7, respectively. Schwertmannite with selenate changes like that of schwertmannite with sulfate. PZC of selenate-schwertmannite is at around 6.2. Schwertmannite with arsenate, phosphate and chromate shown different change from that of schwertmannite with sulfate with PZC at about 5. Among arsenate, phosphate and chromate, schwertmannite with chromate change is slightly different curve at pH range between 6 and 10 with less negative potentials (Figure 10b).

2.4. Discussion

2.4.1. Mechanism of oxyanions onto ferrihydrite

The change in the Zeta potential after adsorption by arsenate, phosphate and chromate were very different from the adsorption by selenate and that of original ferrihydrite. As shown in Figure 10a, the zeta potential curve of original ferrihydrite shown high positive charge in pH acidic condition and negative charge in pH alkaline condition. Anion had negative charge, when adsorbed on mineral surface, can change the potential of mineral surface from positive charge shift to negative charge as shown in Figure 10b. In this different implies that the adsorption mechanism on ferrihydrite as inner- or outer sphere complexes. The inner-sphere complexes can change the potential charge because anions close to mineral surface and can made ligand exchange with mineral surface (Figure 11b), meanwhile outer-sphere complexes is the electrostatic with mineral surface (Figure 11c), the zeta potential was not change when compare with original zeta potential of mineral surface (Morimoto et al. 2012). For arsenate and phosphate and chromate is different from selenate and sulfate. The curves of the zeta potential after adsorption for oxyanions shifted to negative. The degree of the

shift increased in the following order: selenate << chromate < phosphate < arsenate. This shift may be attributed to interaction between oxyanions and the iron oxide mineral surface. An inner sphere complexation induced the modification of surface charge of the minerals. The inner-sphere complexation with anions make the surface charge negative. Therefore, in this study may assume that arsenate, phosphate and chromate form inner-sphere complexes with the surface of the ferrihydrite and this result correspond to the previous work which described by using surface complexation modeling (Fukushi & Sverjensky 2007a). The curves of selenate and sulfate was between chromate and original ferrihydrite, then already establish by previously work by surface complexation modeling (Fukushi & Sverjensky 2007b) from the result we can assume that the mechanism of oxyanions adsorption onto ferrihydrite was included both inner and outer-sphere complexes (Figure 10,a).

2.4.2. Mechanism of oxyanions onto schwertmannite.

In case of schwertmannite, shown in Figure 10b arsenate and phosphate is similar with adsorbed on ferrihydrite, it implied that arsenate and phosphate made inner-sphere complexes with schwertmannite, then selenate and sulfate was not shift in different with the original schwertmannite, indicate that anions was not effected to surface charge of schwertmannite, it could assume that selenate and sulfate made an outer-sphere complexes with surface of schwertmannite. For chromate was in between phosphate and selenate. Chromate ions might be intermediate reaction with the schwertmannite.

2.5. Conclusion

In this study, the adsorption behavior of ferrihydrite and schwertmannite with various kinds of oxyanions were investigated and compared, from the result of comparison adsorption the capacities of difference kinds oxyanions between schwertmannite and ferrihydrite, in this condition of adsorption experiments, schwertmannite had more high capacity to adsorbs oxyanions much more than ferrihydrite. The result of the adsorption experiments shows that the selectivity of oxyanion adsorption on schwertmannite decreases as the following order: arsenate $\geq$ phosphate > chromate >> selenate. The adsorption mechanism on ferrihydrite with arsenate, phosphate and chromate is different from that with selenate and sulfate. Arsenate, phosphate and chromate ions form inner-sphere complexes with the surface of schwertmannite. The selenate and sulfate ions form outer-sphere complexes with the surface of schwertmannite. Strong base anions such as arsenate and phosphate can form inner-sphere complexes, which induces a strong adsorption with schwertmannite as well as provides a high adsorption capacity.

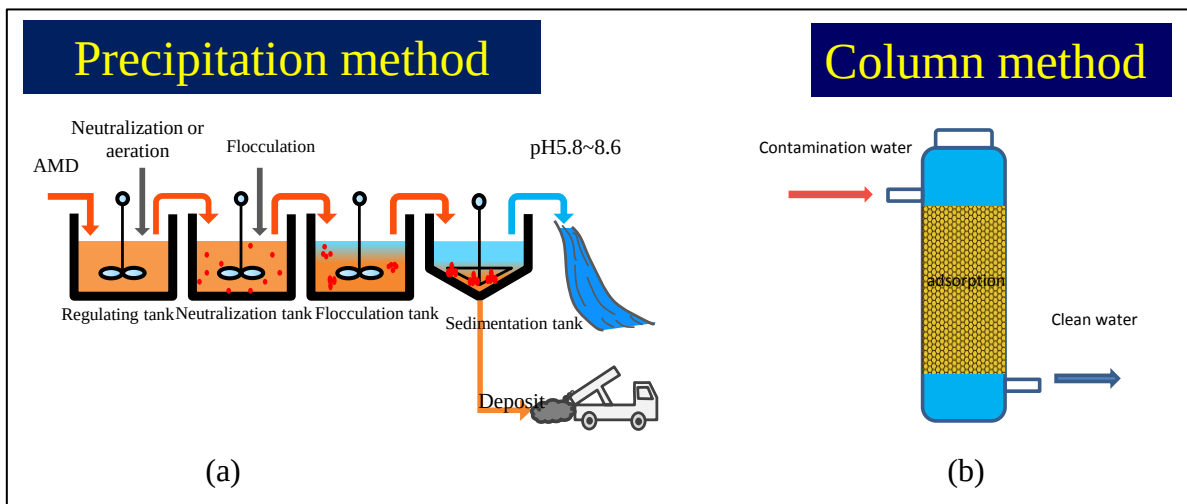


Figure 6. Waste water treatment concept, (a) precipitation method and (b) column method

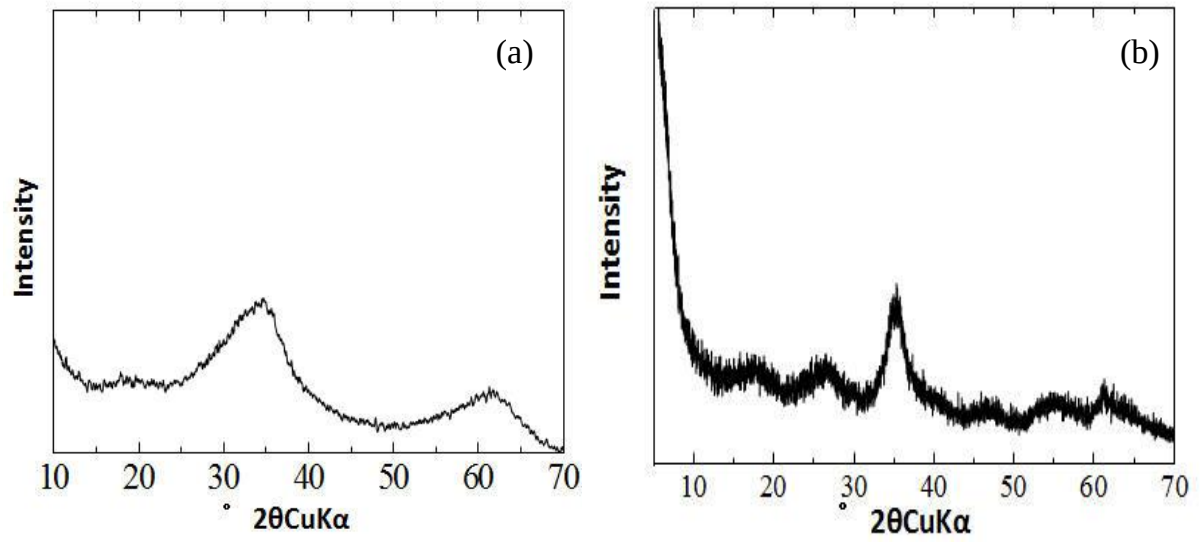


Figure 7. (a) XRD pattern for ferrihydrite and (b) XRD pattern for schwertmannite

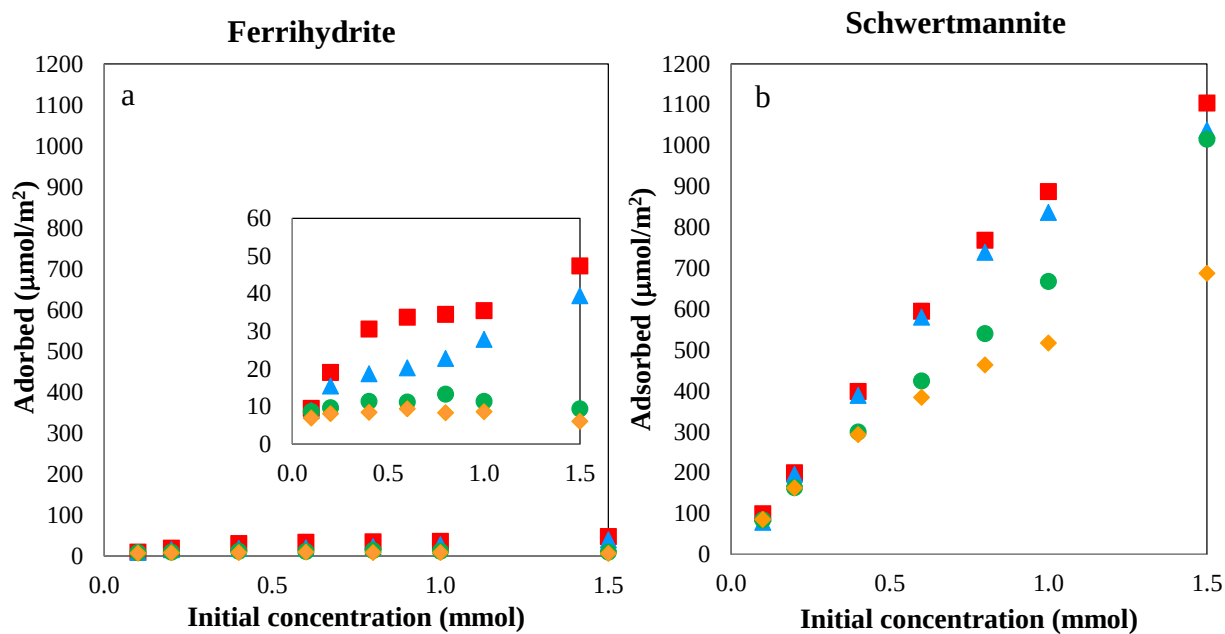


Figure 8. Oxyanions adsorption on ferrihydrite and schwertmannite as function of the initial concentration of oxyanion in solution, without pH adjustment (■: Arsenate, ▲: Phosphate, ●: Chromate and ◆: Selenate).

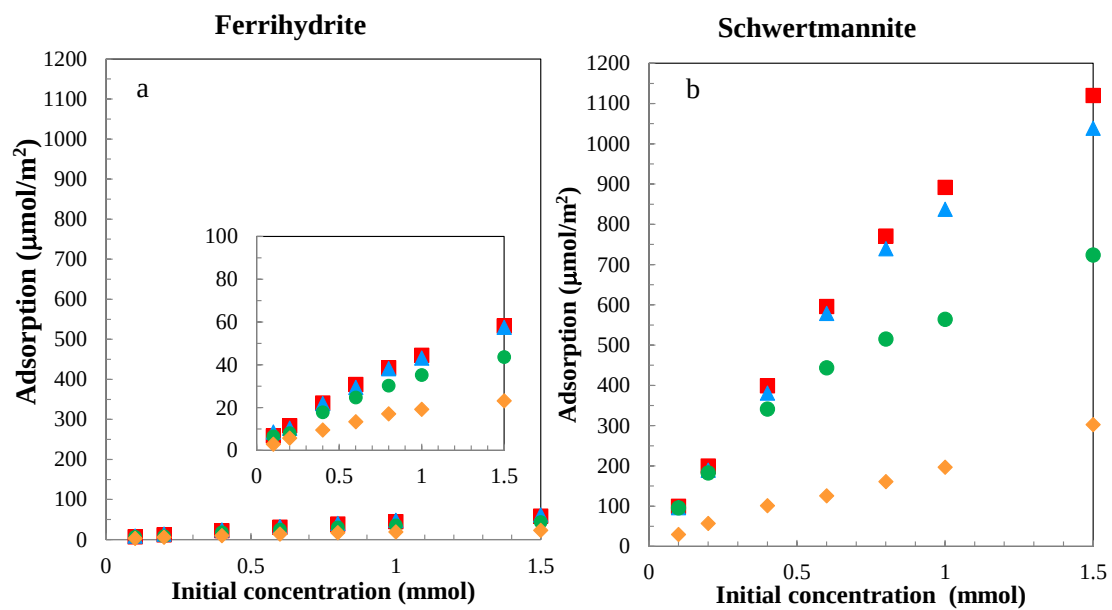


Figure 9. Oxyanions adsorption on ferrihydrite and schwertmannite as function of the initial concentration of oxyanion in solution, with pH adjustment ($\blacksquare$: Arsenate, $\blacktriangle$: Phosphate, $\bullet$: Chromate and $\blacklozenge$: Selenate).

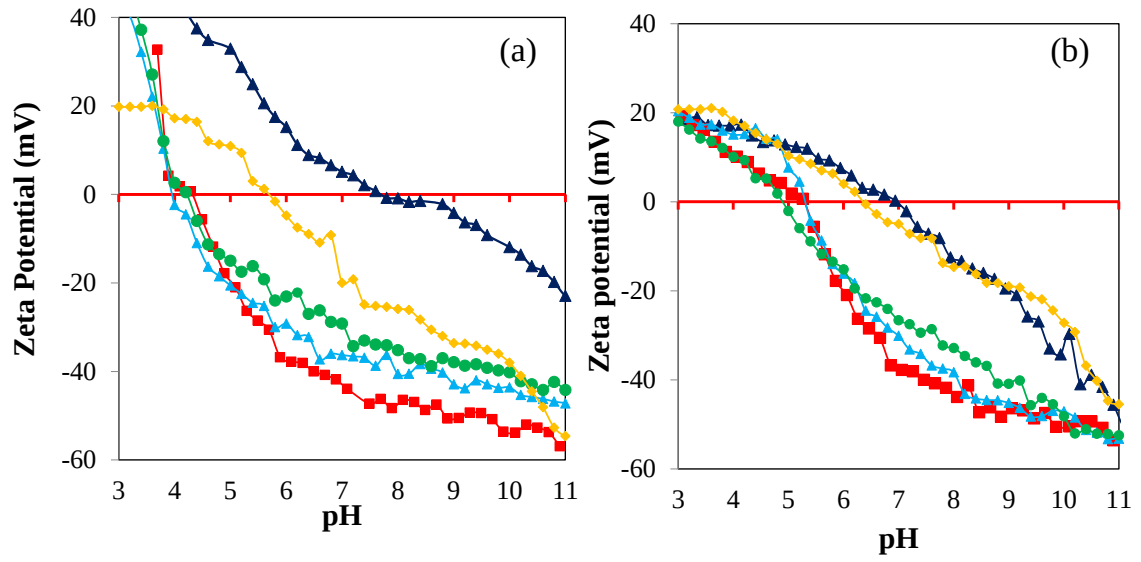


Figure 10. The zeta potential with function of pH, (a) display Zeta potential for ferrihydrite, (b) display zeta potential for schwertmannite (▲: Original, ■: Arsenate, ▲: Phosphate, ●: Chromate and ◆: Selenate)

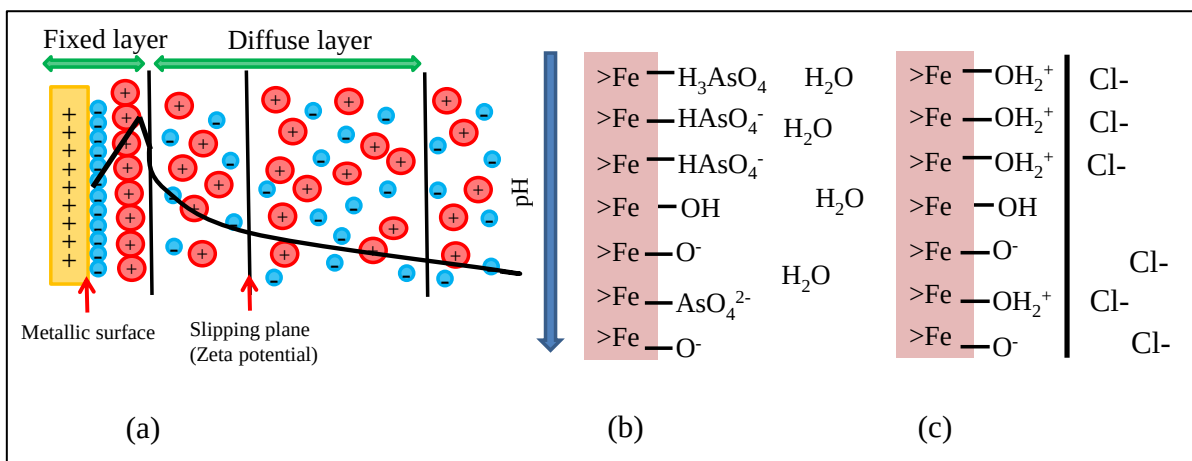


Figure 11. Adsorption mechanism, (a) zeta potential concept, (b) inner-sphere complexes and (c) outer-sphere complexes (Morimoto et al. 2012)

Chapter 3

Post-adsorption behavior of oxyanions onto ferrihydrite and schwertmannite

3.1. Introduction

Poorly crystalline iron oxide mineral is widely distributed in surface environments, is well known as a scavenger for dissolved species because of its high specific surface area. The mobility of almost all trace elements in surface water is affected considerably by adsorption process on ferrihydrite (Dzombak & Morel 1990). Other new mineral as schwertmannite is also poorly crystalline iron oxide mineral, it is a meta-stable iron oxy- and hydroxy-sulfate found in acidic iron- and sulfate rich environments such as sulfide metal mines (Bigham et al. 1990; Bigham et al. 1994; Bigham, Udo Schwertmann, et al. 1996; Waychunas et al. 2001). Schwertmannite well known to play an important role in the removal toxic elements from the acid mine drainage (Webster et al. 1998; Liao et al. 2011; Paikaray & Peiffer 2012) and in natural attenuation processes of hazardous elements in acid mine water (Fukushi, Sasaki, et al. 2003).

Schwertmannite and ferrihydrite are metastable and tend to be stable phase as goethite by dissolution and precipitation, the disposal waste from adsorption process was necessary to consider when schwertmannite and ferrihydrite adsorption oxyanion, the transformation process, the toxic element may be released to the environment (Figure 12). The alteration adsorption was necessary to consider. Schwertmannite is also well known well known that the stability of schwertmannite is changed and stabilized after arsenate adsorption (Fukushi, Sato, et al. 2003).

The stability of schwertmannite and ferrihydrite need to pay attention safety at the sites where schwertmannite is deposited. The stability of schwertmannite with other kinds of oxyanions have not been fully or systematically investigated. With this background, the adsorption properties of oxyanions including arsenate, phosphate, chromate and selenate of schwertmannite were investigated to conducted post-adsorption to understand the transformation rate and stabilization of mineral before and after adsorption. To better understand the solubility of schwertmannite after adsorbs oxyanions was studied to better understand the stability of schwertmannite with many kinds of oxyanions.

3.2. Material and method

3.2.1. Preparation

Schwertmannite was prepared by the method previously reported by Bigham et al (1996). Mixing solution prepared by 0.04 M Na_2SO_4 solution and 0.04 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution was held at 60°C for 12 minutes, then cooled and dialyzed for 30 days, deionized water used for the dialyzing was changed every day. To remove the salt in the surface of mineral the product was clean by using deionized water and was filtered through a $0.2\ \mu\text{m}$ cellulose membrane then immediately freeze-dried to prevent transformation to another phase. Further, X-ray diffraction (XRD) analyses were conducted to identify the synthesized phases by Rigaku X-Ray diffractometer with $\text{CuK}\alpha$ radiation (40kV and 40mA). From the XRD analyses, the synthesized products were identified as a schwertmannite because the XRD pattern was identical to that of the previously reported schwertmannite by Bigham et al (1990).

Ferrihydrite was prepared as adsorbent by using digital titration machine TOADKK-AUT-701, 0.1M of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 500 ml was prepared and set on the stirrer, 0.1 of KOH solution was also prepared about 500 ml set into the machine, Auto titration was added 0.04ml/min (KOH) to the solution, until reach to pH7 (Schwertmann & Cornell 2008), sample was centrifuge 3000rpm, 40 minutes' wash in 6 times, then filtered through $0.2\ \mu\text{m}$ cellulose membrane. The resulting of solids was freeze dried and identify the synthesized phases solids was examined by Rigaku X-Ray diffractometer with $\text{CuK}\alpha$ radiation (40kV and 40 mA), the result of XRD pattern was identical to that of the previously reported of ferrihydrite (Cornell et al. 1987; Drits 1993).

After adsorbent was prepared, the adsorption process was performed, a constant ionic strength ($I=0.01\ \text{M}$, NaNO_3) by using a 50 ml centrifuge tube adding 40 ml solution of Na_2HPO_4 , Na_2HAsO_4 , Na_2CrO_4 , and Na_2SeO_4 with concentrations from 0 to 2 mM and 40 mg of the synthetic schwertmannite and ferrihydrite. The pH of the adsorption media was adjusted to 7.00 ± 0.15 by 0.1M NaOH solution. The adsorption batch were controlling the concentration of oxy-anion onto the mineral. After adsorption experiment, all of samples were conducted ICP-AES to determine the concentration of solution and Fe dissolve from the schwertmannite and ferrihydrite also examined.

3.2.2. Alteration experiment

The dried powders of schwertmannite and ferrihydrite were added to the solutions of the anions, for the adsorption process, the pH was adjusted by 0.1 M NaOH and 0.1 HNO_3 to

7.00±0.12 and 30-35 mg/g of the solid phase of anions of arsenate, phosphate, chromate or selenite were adsorbed on the schwertmannite, separately. The solids after the adsorption were mounted and dried on silica glass. The glasses with the mounted solid samples were kept in boxes with wet cotton at 60°C to accelerate alterations in a moisture condition (Figure 13). At the different aging times, the samples were analyzed by XRD to determine the extent of the phase transformation.

3.3. Result

3.3.1. *Dissolution of ions from the adsorbent*

From the Figure 16a, explain the Fe dissolve from the ferrihydrite structure, as increasing of the initial concentration, the Fe will have decreased to release from ferrihydrite, as compare with different kinds of oxyanions, arsenate adsorbed with the high concentration can stabilized the ferrihydrite. Figure 16b Fe dissolve from schwertmannite was decreased with increased of initial concentration the tendency comparison with high concentration with lowering dissolve Fe by following order: arsenate<phosphate<chromate<selenate

3.3.2. *Aging experiment result.*

From the results of the aging experiments, the XRD patterns of samples clearly indicate the difference in the stability of schwertmannite and ferrihydrite with different oxyanions and aging times as shown in Figure 19 and Figure 20. From this result ferrihydrite's XRD pattern was not change, ferrihydrite more stable schwertmannite (Figure 14). In case of many kinds oxyanions on schwertmannite, the schwertmannite with sulfate ions (pure schwertmannite), the peaks from goethite appeared after 7 days, while the peaks from goethite appeared after 14 days in schwertmannite with selenate. In schwertmannite with chromate, the XRD pattern showed peaks form goethite after 30 days. There are no differences in the XRD pattern for schwertmannite with arsenate and phosphate even after 30 days. In comparison with pure schwertmannite, transformation to goethite was retarded for schwertmannite after adsorption with selenate, chromate, phosphate and arsenate. The degree of retardation in transformation to goethite decreased as arsenate= phosphate>chromate>selenate>sulfate.

3.4. Discussion

3.4.1. *Difference of adsorption with different anions*

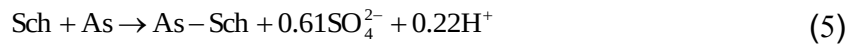
Among the oxyanions, there are differences in the adsorption capacity. As mentioned

above the selectivity of oxyanion adsorption on schwertmannite decreases in the following order: arsenate $\geq$ phosphate > chromate > selenate. At the pH after reaction, the dominant species of oxyanions were H_2AsO_4^- , H_2PO_4^- , HCrO_4^- and SeO_4^{2-} from the thermodynamic calculation by Geochemist's workbench (GWB) using the latest thermodynamic database released from Lawrence Livermore National Laboratory in USA. From the comparison of anion adsorptions, strong base anions can achieve a strong adsorption with schwertmannite surface, and with high adsorption capacity. In case of ferrihydrite adsorption by many kind of oxyanions was reported by previously study (Figure 15), oxyanions were effected to the mineral stabilization (Fukushi & Sato 2005).

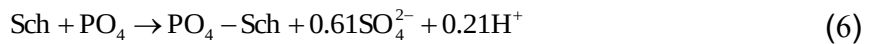
3.4.2. Anion-exchange with different anions

As the result of the adsorption of oxyanions with schwertmannite such as with arsenate, phosphate and chromate is represented by the release of SO_4^{2-} and proton in the adsorption process (Figure 17 and Figure 18), These stoichiometric ion-exchange are confirmed by a plot in Figure 21, which is from the previous study for the case of sorption of As (III) and As(V) onto schwertmannite (Burton et al. 2009).

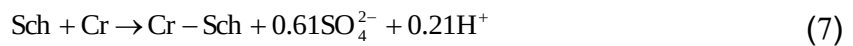
The quantity of released protons was estimated from the differences in proton concentration which were calculated from the speciation analytical by REACT in GWB package (Bethke 2007). From the slope of the regression line in Figure 21, schwertmannite released 0.61 mmol of SO_4^{2-} after 1 mmol of As(V) adsorption. This value is corresponding the value previously reported by Fukushi, et al (2003). Overall, the anion-exchange reaction can be expressed as below:



Where sch indicates schwertmannite with sulfate and As-Sch is the schwertmannite with arsenate. Similarly, the anion-exchange reaction of phosphate with sulfate and chromate with sulfate become express as follows, respectively.

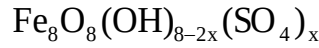


And



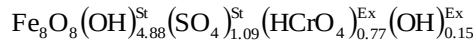
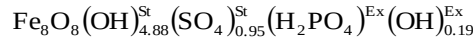
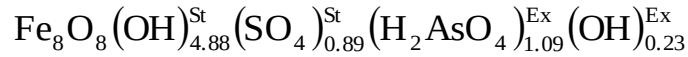
In this study, selenate adsorption on schwertmannite was not considered to be an ion-exchange

with sulfate because the capacity of selenate adsorption is limited. Bigham, et al (1996)

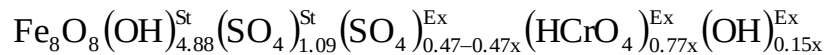
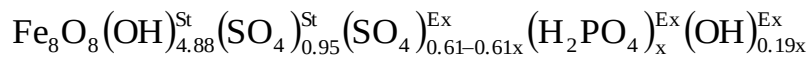
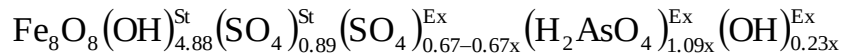


Where x is $1 < x < 1.75$. The mole numbers of SO_4 and mole number of each oxyanion in chemical formula were calculated by setting the mole number of Fe equal to 8 in Table 1, Table 2 and Table 3 for As-Sch, PO_4 -Sch and Cr-Sch, respectively. As shown in the composition of schwertmannite and schwertmannite adsorbed oxyanions; the maximum adsorbed oxyanions are about half of SO_4 which remains in schwertmannite. In the natural states based on field observations it was established that As/(As+S) ratio was 0.7, by using synthetic co-precipitation prepared with different amounts of As(V), the result showed that half of SO_4 is basically need to stabilize the structure of schwertmannite whereas the other half functions as exchangeable anions during As(V) adsorption (Carlson et al. 2002)

From the chemical composition of schwertmannite and schwertmannite adsorbed by oxyanions, the mole number of SO_4 which could be exchanged are 0.67, 0.61 and 0.47 which correspond to arsenate, phosphate and chromate adsorption, respectively. Therefore, schwertmannite with the maximum number of oxyanions was follows:



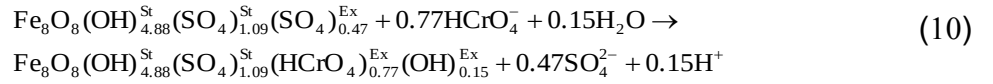
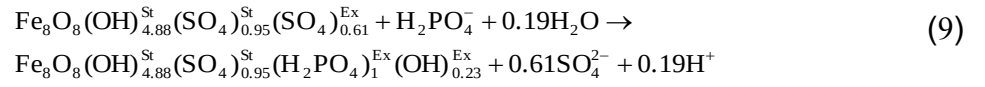
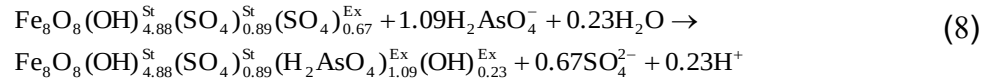
Where St is the principal structural component and Ex is the exchangeable component. This shows that schwertmannite sorbing arsenate (Sch-As), phosphate (Sch- PO_4) and chromate (Sch-Cr), which all behave as a solid-solution, are represented by the following chemical formulas, respectively



In the formula above, x is the mole fraction of Sch-As, Sch- PO_4 and Sch-Cr, respectively.

3.4.3. Estimate the equilibrium constant for anion-exchange reaction

The exchange reaction is described by an equilibrium constant and distribution coefficient ordinarily expressed separately for solid and aqueous solutions (Sverjensky 1984; Tesoriero & Pankow 1996; Rimstidt et al. 1998). The equilibrium constant can be used to predict the amount of an element in the solid phase when the solution chemistry is known. The anion-exchange reaction from Equation (5) to Equation (7) can then be formulated with end-number composition, similar to the previous work by Fukushi et al (2003).



The equilibrium constant for Equation (8) to Equation (10) are represented below:

$$K_{ex} = \frac{a_{\text{SO}_4^{2-}}^{0.67} a_{\text{H}^+}^{0.23} X_{\text{sch-As}} \gamma_{\text{sch-As}}}{a_{\text{H}_2\text{AsO}_4^-}^{1.09} X_{\text{sch}} \gamma_{\text{sch}}} \quad (11)$$

$$K_{ex} = \frac{a_{\text{SO}_4^{2-}}^{0.61} a_{\text{H}^+}^{0.19} X_{\text{sch-PO}_4} \gamma_{\text{sch-PO}_4}}{a_{\text{H}_2\text{PO}_4^-}^1 X_{\text{sch}} \gamma_{\text{sch}}} \quad (12)$$

$$K_{ex} = \frac{a_{\text{SO}_4^{2-}}^{0.47} a_{\text{H}^+}^{0.15} X_{\text{sch-Cr}} \gamma_{\text{sch-Cr}}}{a_{\text{HCrO}_4^-}^{0.77} X_{\text{sch}} \gamma_{\text{sch}}} \quad (13)$$

where X_{sch} , $X_{\text{sch-As}}$, $X_{\text{sch-PO}_4}$ and $X_{\text{sch-Cr}}$ shows the mole fraction of schwertmannite, Sch-As, Sch-PO₄, Sch-Cr, respectively in the solid solution, whereas γ_{sch} , $\gamma_{\text{sch-As}}$, $\gamma_{\text{sch-PO}_4}$ and $\gamma_{\text{sch-Cr}}$ symbolized

the activity coefficient of components of schwertmannite and schwertmannite adsorbed oxyanions. Equation (11) to Equation (13) could be converted to:

$$K_{ex} \frac{\gamma_{sch}}{\gamma_{sch-As}} = \frac{a_{SO_4^{2-}}^{0.67} a_{H^+}^{0.23} X_{sch-As}}{a_{H_2AsO_4^-}^{1.09} X_{sch}} = K_d \quad (14)$$

$$K_{ex} \frac{\gamma_{sch}}{\gamma_{sch-PO_4}} = \frac{a_{SO_4^{2-}}^{0.61} a_{H^+}^{0.19} X_{sch-PO_4}}{a_{H_2PO_4^-}^1 X_{sch}} = K_d \quad (15)$$

$$K_{ex} \frac{\gamma_{sch}}{\gamma_{sch-Cr}} = \frac{a_{SO_4^{2-}}^{0.47} a_{H^+}^{0.15} X_{sch-Cr}}{a_{HCrO_4^-}^{0.77} X_{sch}} = K_d \quad (16)$$

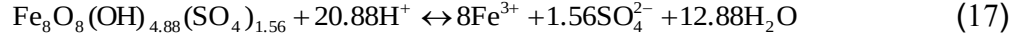
where K_d is the distribution coefficient. The distribution coefficients were calculated by replacing the solution activities of each dissolved species and mole fraction of schwertmannite. That adsorbed by oxyanions as shown in Equation (14) to Equation (16) were used input data, from Table 4 to Table 6. The average distribution coefficient, $\log K_d$ is 2.82 ± 0.45 , 2.23 ± 0.57 and 1.38 ± 0.14 for Sch-As, Sch- PO_4 , Sch-Cr, respectively.

According to the previous study Fukushima, et al (2003), the K_d value was very similar to K_{ex} because in an ideal solid solution model it is assumed that the activity coefficient of this system is unity. Hence, the high value of the equilibrium constant for the anion-exchange reaction corresponds to the ratio of dissolution reaction of the mineral and mineral adsorbed by trace element. At high equilibrium constants, the adsorption capacity was highly adsorbed onto schwertmannite.

3.4.4. Stability of schwertmannite with different oxyanions

The transformation process of schwertmannite to goethite involves dissolution and re-precipitation processes. The results from the calculation of solubility shows that a low solubility suggests a high stability of the mineral (Knorr & Blodau 2007). In the previous studies, the stability of the mineral was described from consideration of the activity of dissolved species in aqueous solution; this was used to estimate the solubility products to calculate the stability mineral (Dove & Rimstidt 1985; Yu et al. 1999). This corresponds to the experimental results where the association of the solubility between schwertmannite and schwertmannite adsorbed

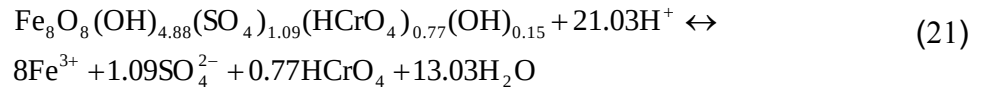
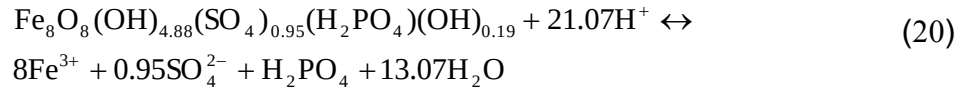
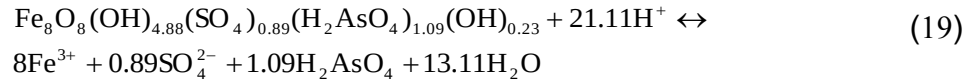
by oxyanions could be a result of the equilibrium constant of the exchange reaction from Equation (11) to Equation (13) (Busenberg & Niel Plummer 1989; Glynn 1990; Plummer et al. 1992; Barham 1997). The dissolution reaction equation of the synthesized schwertmannite can be expressed as:



From Equation (17), the equilibrium constant of schwertmannite could be expressed by:

$$K_{sch} = \frac{a_{\text{Fe}^{3+}}^8 a_{\text{SO}_4^{2-}}^{1.56}}{a_{\text{H}^+}^{20.88}} \quad (18)$$

Where, the activity of H_2O and the mineral is unity. The dissolution reaction equation for schwertmannite which has adsorbed different kinds of oxyanions could be written by:



From Equation (19) to Equation (21), the equilibrium constants could be represented by:

$$K_{sch-As} = \frac{a_{\text{Fe}^{3+}}^8 a_{\text{SO}_4^{2-}}^{0.89} a_{\text{H}_2\text{AsO}_4}^{1.09}}{a_{\text{H}^+}^{21.11}} \quad (22)$$

$$K_{sch-PO_4} = \frac{a_{\text{Fe}^{3+}}^8 a_{\text{SO}_4^{2-}}^{0.95} a_{\text{H}_2\text{PO}_4}^1}{a_{\text{H}^+}^{21.07}} \quad (23)$$

$$K_{sch-Cr} = \frac{a_{Fe^{3+}}^8 a_{SO_4^{2-}}^{1.09} a_{HCrO_4^-}^{0.77}}{a_{H^+}^{21.03}} \quad (24)$$

As explained previously, K_d corresponds to K_{ex} which is the equilibrium constant for anions-exchange reaction. Further, K_{ex} could be expressed as the ratio between the dissolution reaction of schwertmannite and schwertmannite adsorbed by different kinds of oxyanions as:

$$K_{ex-As} = \frac{K_{sch}}{K_{sch-As}} \quad (25)$$

$$K_{ex-PO_4} = \frac{K_{sch}}{K_{sch-PO_4}} \quad (26)$$

$$K_{ex-Cr} = \frac{K_{sch}}{K_{sch-Cr}} \quad (27)$$

The K_{ex} for the oxyanions indicate the relative solubility of each of the schwertmannite with oxyanions, which are compared with schwertmannite with sulfate (Table 7). The schwertmannite with arsenate has the lowest solubility and is the most stable among the oxyanions. From Table 7, could be shown as solubility diagram (Figure 22) which were calculated from the solubility analytical by REACT and ACT2 in GWB package (Bethke 2007), the relative solubility of schwertmannite with chromate is smaller than that of schwertmannite with arsenate and phosphate. This implies that schwertmannite with chromate would be less stable than with arsenate and phosphate. This is consistent with the results of the aging experiments as shown in Figure 20. This is also consistent with the finding of the released Fe concentrations after the oxyanion adsorption as shown in Figure 16 b. Consequently, adsorption by oxyanions with the higher selectivity may be expected to result in meta-stable schwertmannite becoming stable.

3.5. Conclusion

In this study, the post adsorption behavior of oxyanions onto ferrihydrite and schwertmannite was investigated. From the result of the XRD pattern Figure 19 and Figure 20 shown ferrihydrite more stable than schwertmannite. The solubility was used to determine the stability of mineral, as low solubility the mineral is more stable. As shown in Figure 22 the solubility of

ferrihydrite is lower than schwertmannite's solubility. Within one month, ferrihydrite and ferrihydrite after adsorbed oxyanions was not shown peak change in XRD pattern, in Figure 22 oxyanions adsorption on ferrihydrite led to change of Fe(III) solubility to more lower than the anion-free system or ferrihydrite without adsorbed oxyanions (Fukushi & Sato 2005). The stability of schwertmannite and schwertmannite after the adsorption increased in the following order: sulfate $\cong$ selenate $\ll$ chromate $<$ phosphate $\cong$ arsenate. The solubility of schwertmannite with different oxyanions was calculated with solid solution theory. The solubility of ferrihydrite and schwertmannite decreased after adsorption by oxyanions with high selectivity. The magnitude of the decrease in Fe(III) solubility for arsenate and phosphate coordinated with both mineral is greater than that for chromate and selenate. Therefore, oxyanions with high selectivity can stabilize ferrihydrite and schwertmannite by decreasing the solubility of them after adsorption of the oxyanions.

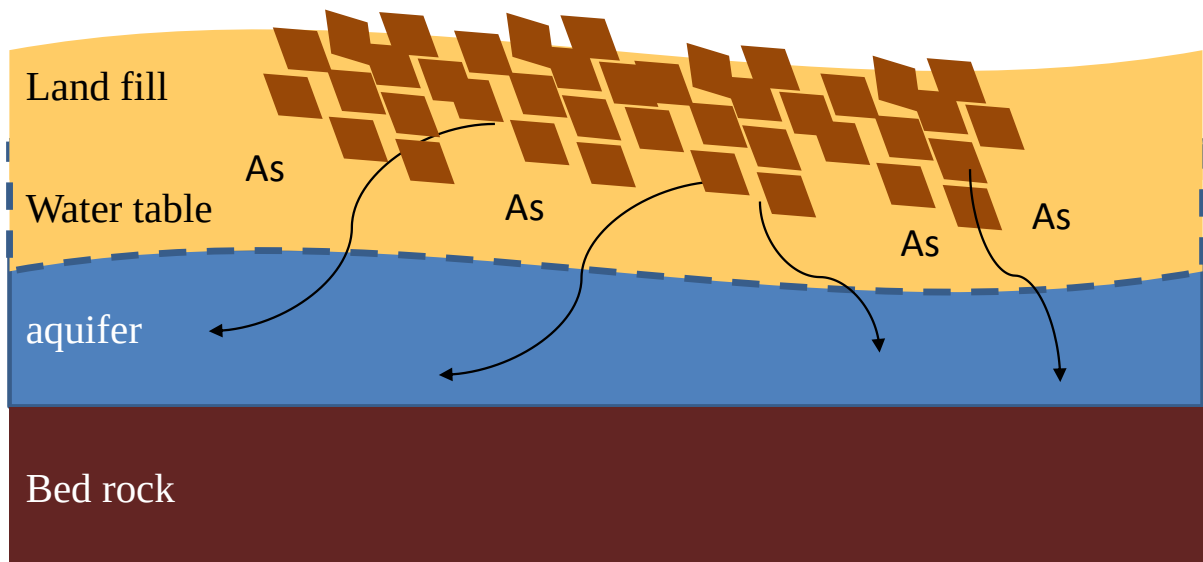


Figure 12. Disposal site concept for adsorbent after adsorption

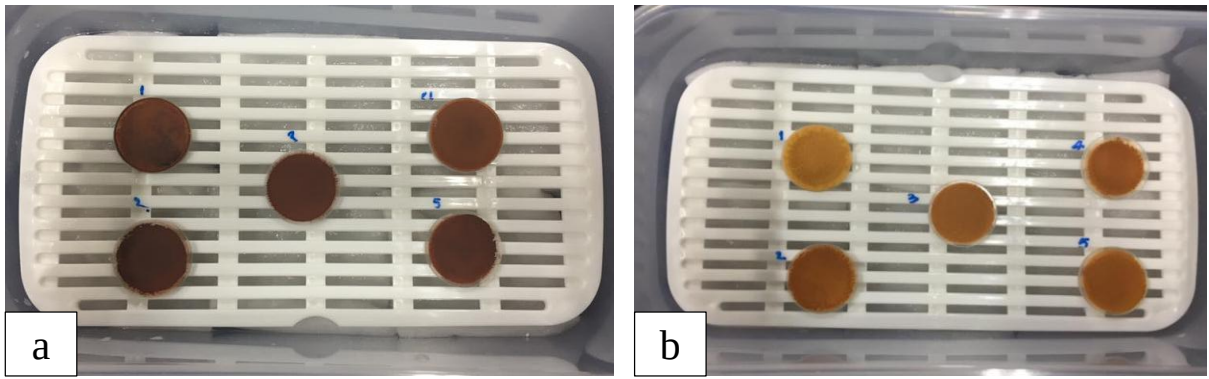


Figure 13. Alteration experiment, (a) ferrihydrite and ferrihydrite after adsorbed oxyanions and (b) schwertmannite and schwertmannite after adsorbed oxyanions

Solubility diagram of Fe-SO_4^{2-}

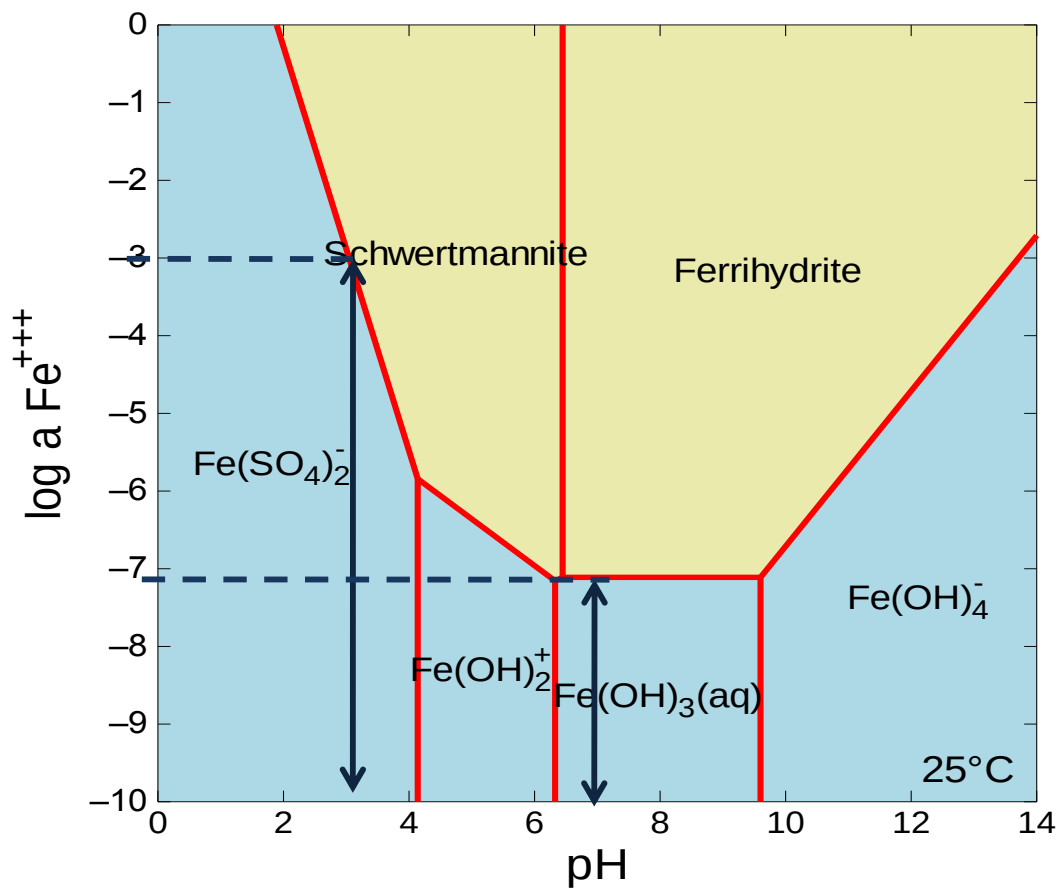


Figure 14. Solubility of ferrihydrite and schwertmannite

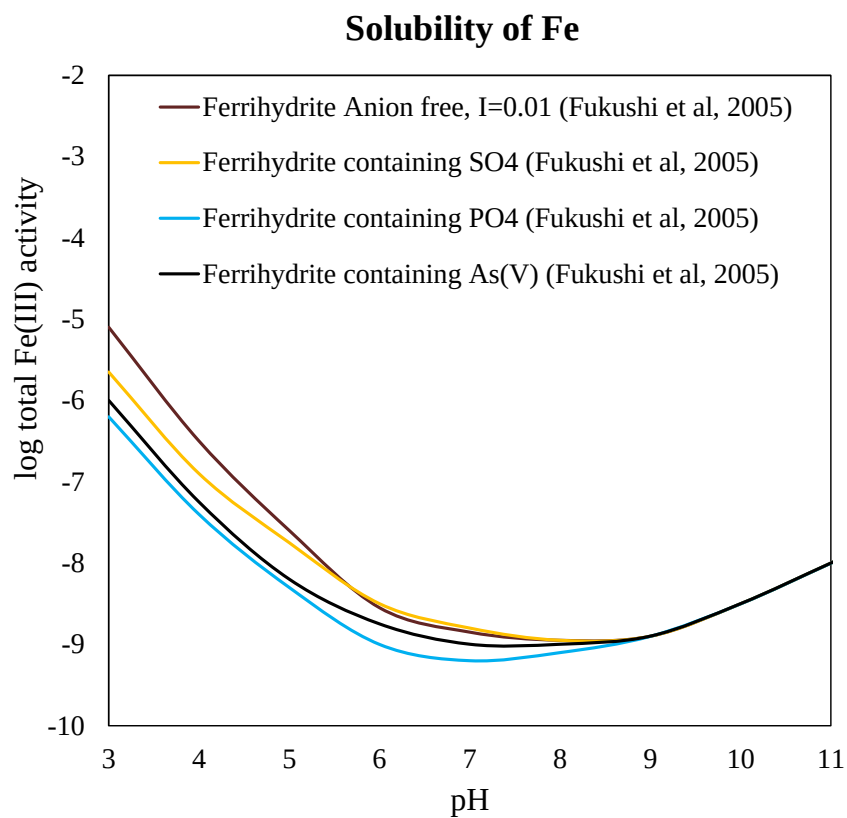


Figure 15. Solubility of ferrihydrite and ferrihydrite after adsorbed oxyanions (Fukushi et al 2005)

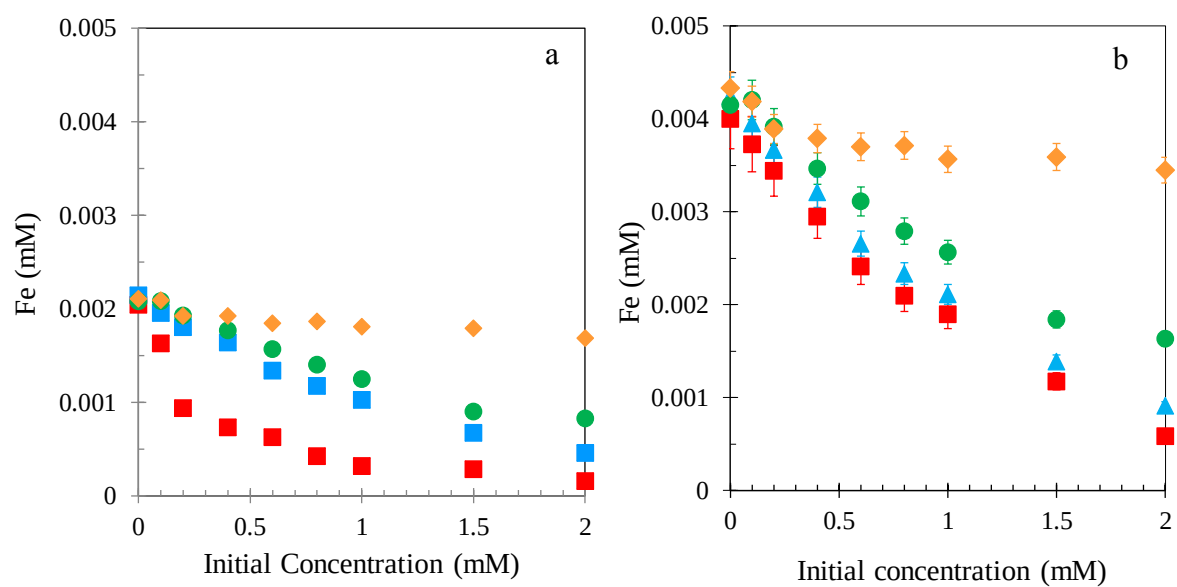


Figure 16: Fe dissolved from ferrihydrite (a) and schwertmannite (b) (■: Arsenate, ▲: Phosphate, ●: Chromate and ♦: Selenate).

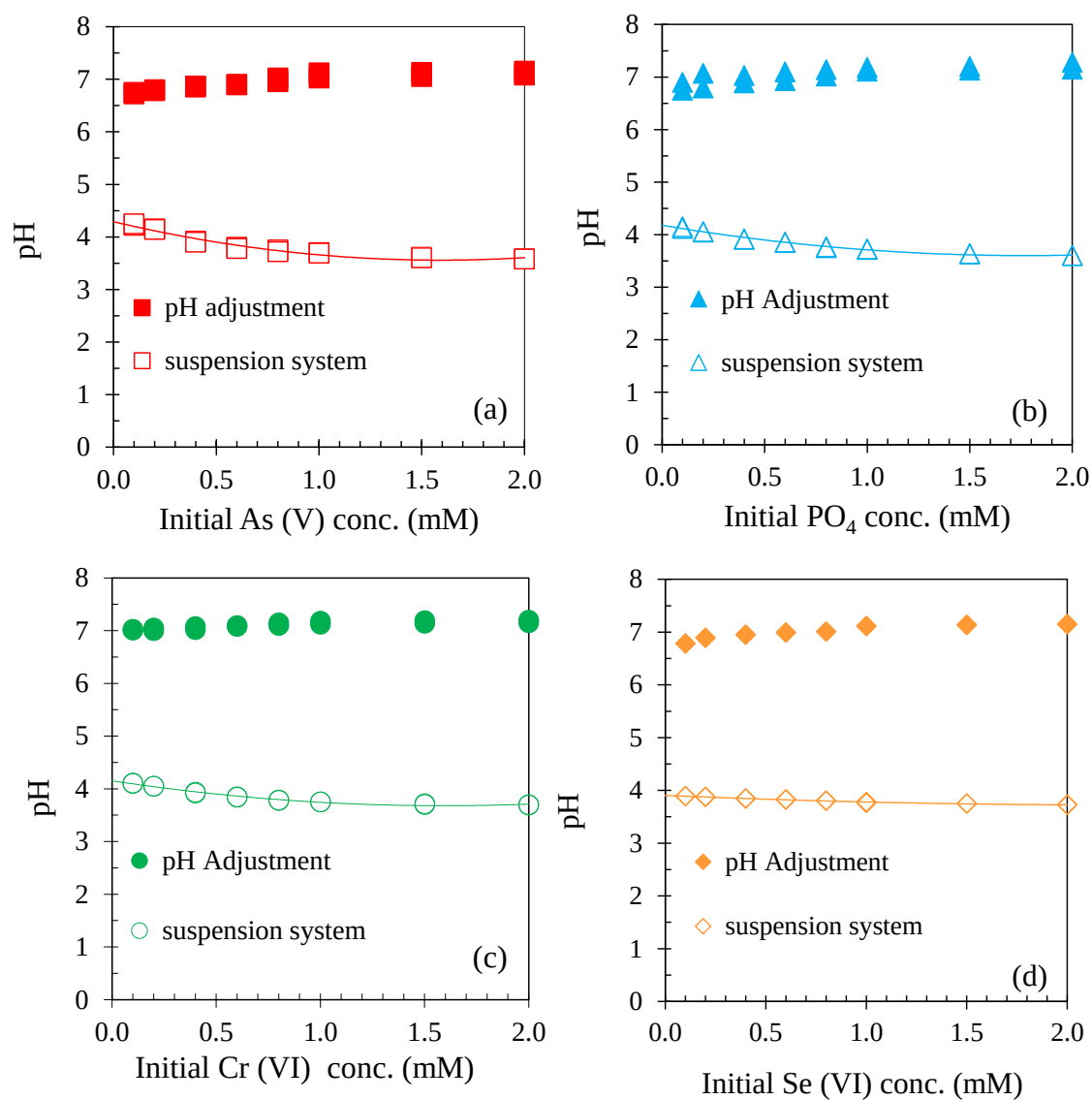


Figure 17: Changes in pH of the solution at the different initial concentration of anions during adsorption processes; (a) Arsenate, (b) Phosphate, (c) Chromate and (d) Selenate.

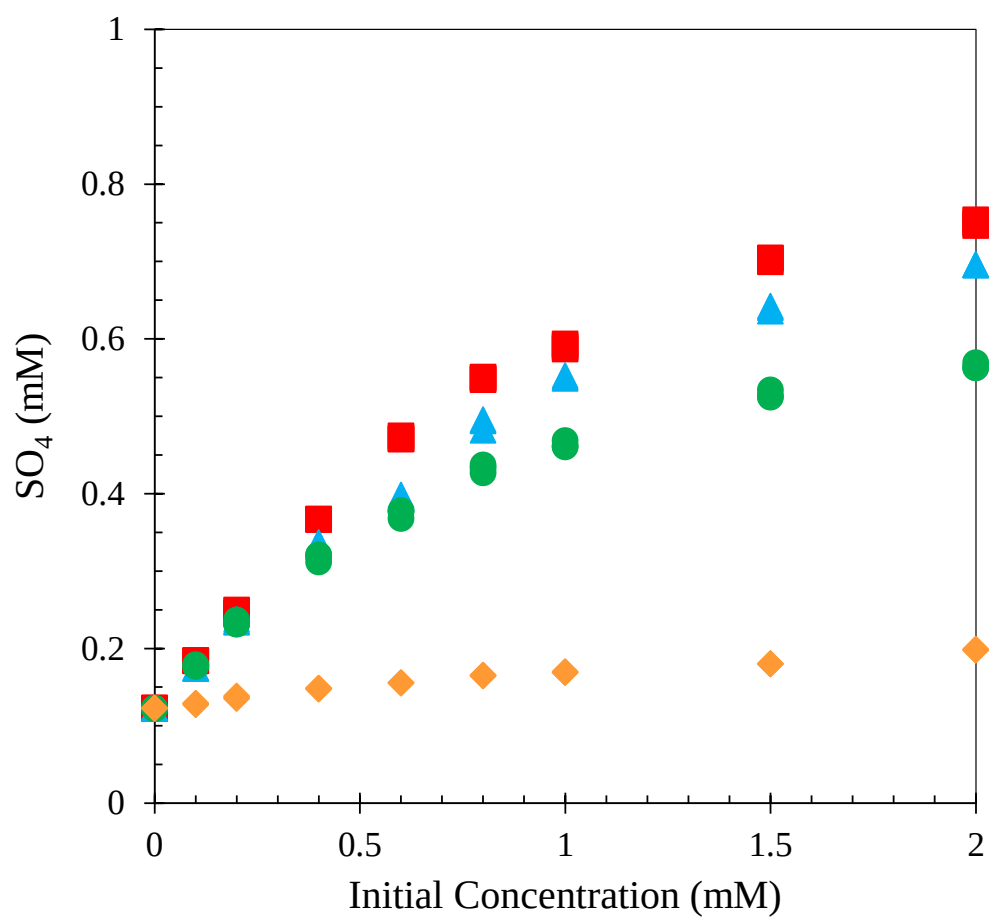


Figure 18: Released SO_4 concentrations from schwertmannite as function of the initial concentration of anions during adsorption process (■: Arsenate, ▲: Phosphate, ●: Chromate and ◆: Selenate)

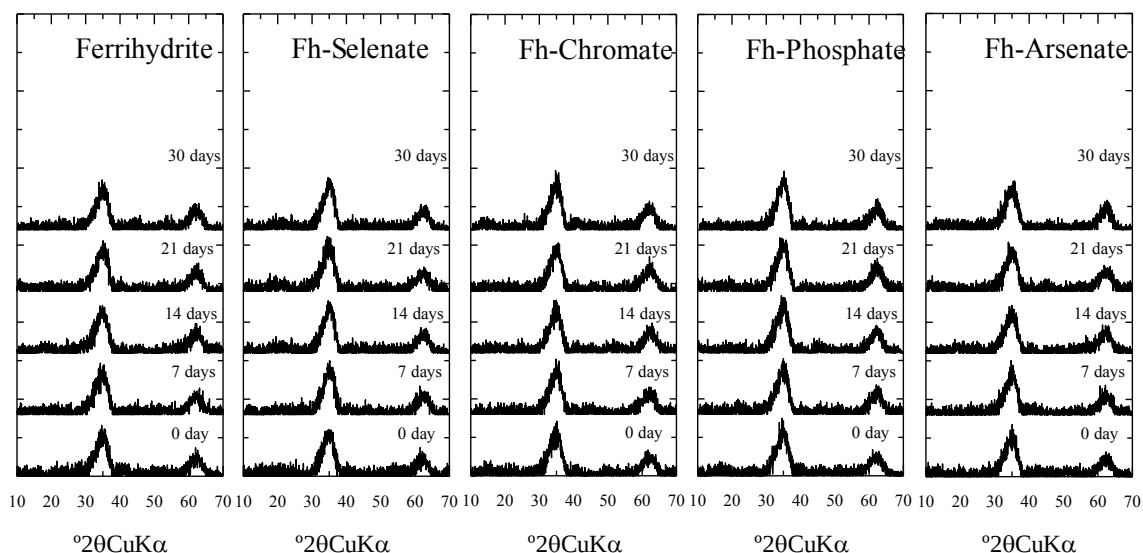


Figure 19. X-ray diffractogram of the synthetic ferrihydrite and ferrihydrite after adsorption of each oxyanion with different aging times.

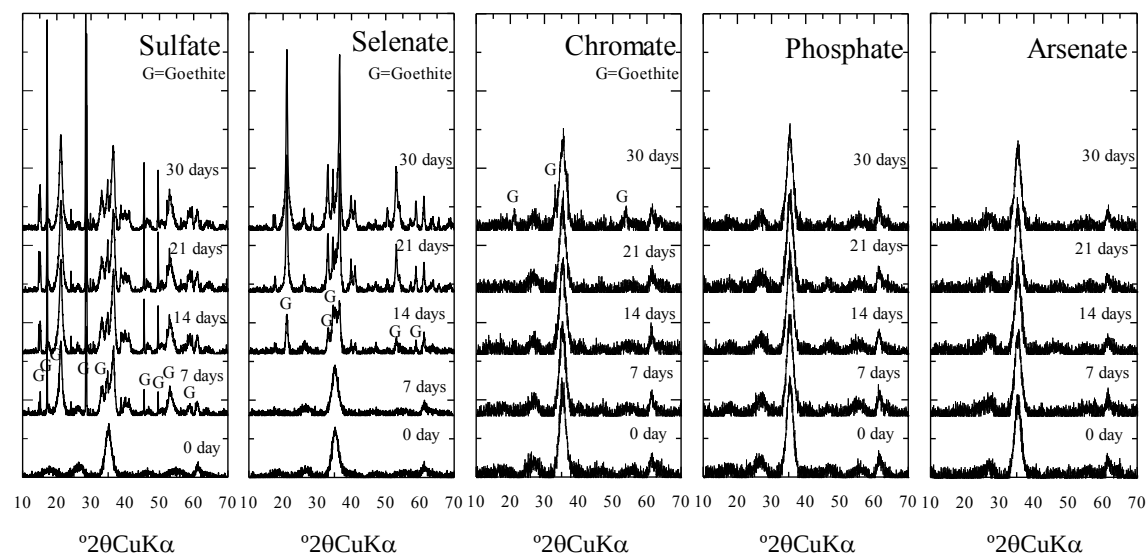


Figure 20: X-ray diffractogram of the synthetic schwertmannite and schwertmannite after adsorption of each oxyanion with different aging times.

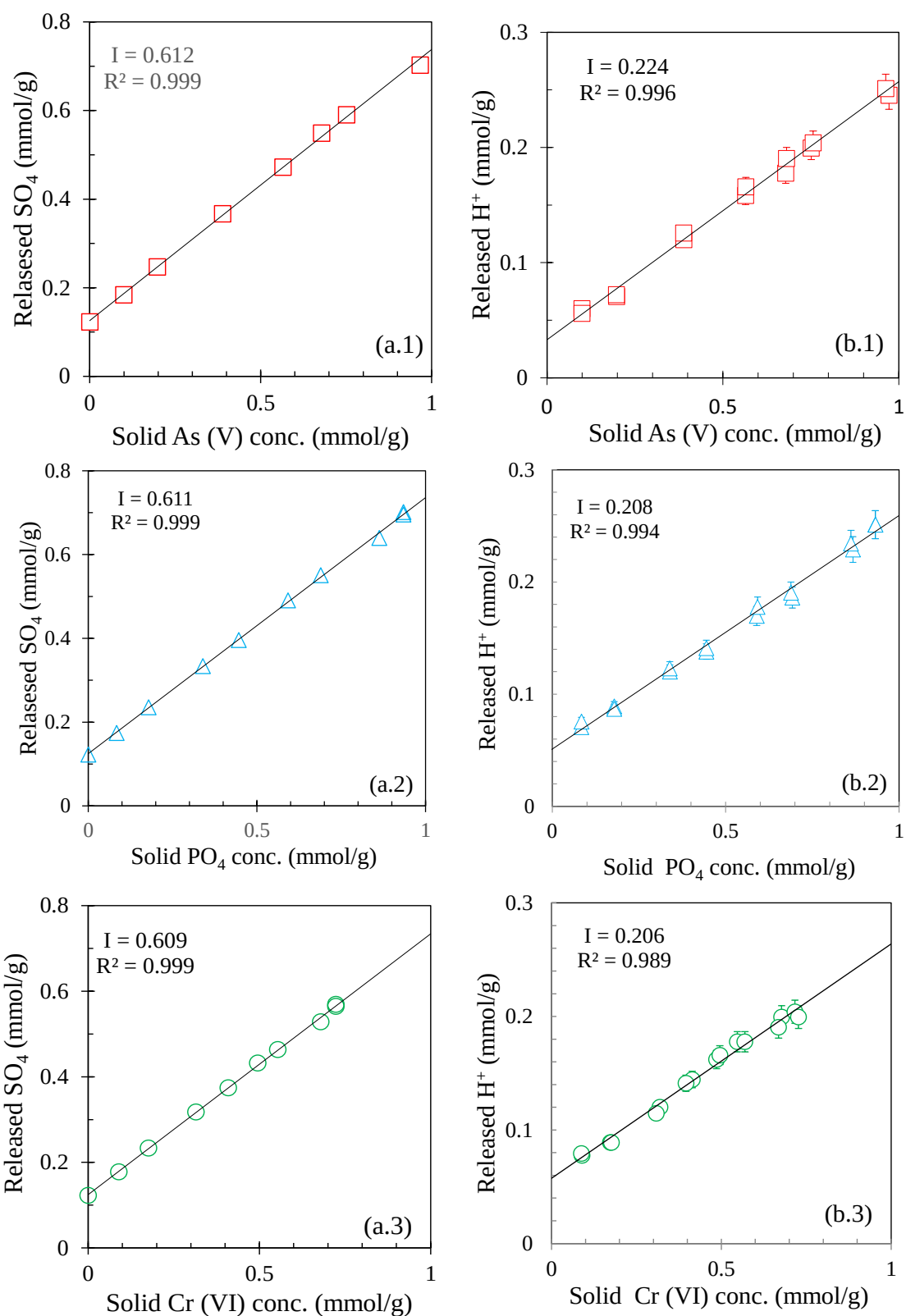


Figure 21: Relationship between the amount solid-phase (oxyanions) concentration with (a) released SO_4 and (b) released of H^+

Solubility of Fe

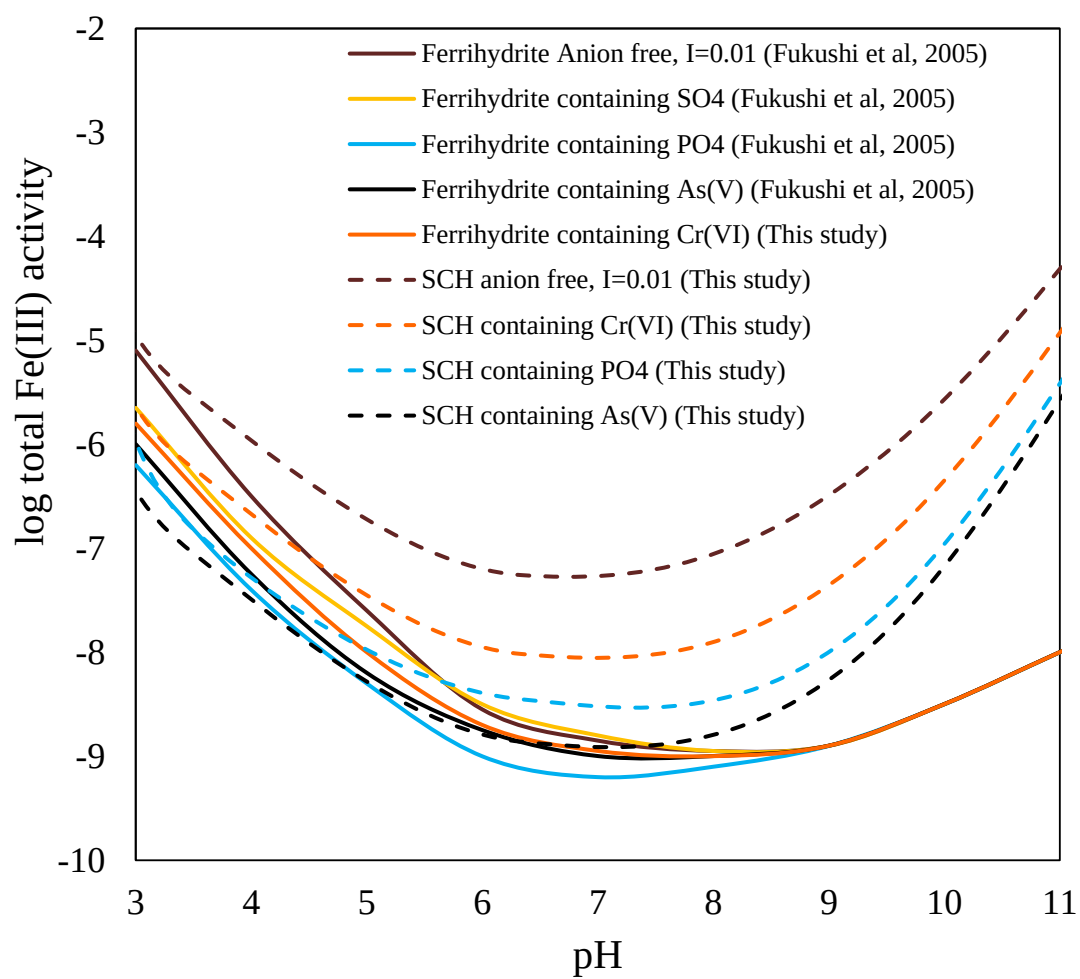


Figure 22. Solubility of diagram of Fe (III) for ferrihydrite and schwertmannite

Table 1: Chemical composition of schwertmannite adsorbed by arsenate

x	As/ (As+S)	Fe mmol/g	SO ₄ mmol/g	As mmol/g	Fe no./unit cell	H ₂ AsO ₄ no./unit cell	SO ₄ no./unit cell	Cal SO ₄ no./unit cell	Cal OH no./unit cell
0.00	0.00	7.49	1.46	0.00	8	0.00	1.56	1.56	0.00
0.01	0.01	7.49	1.46	0.01	8	0.01	1.55	1.55	0.00
0.05	0.03	7.49	1.43	0.05	8	0.05	1.53	1.52	0.01
0.10	0.07	7.49	1.40	0.10	8	0.11	1.49	1.49	0.02
0.25	0.16	7.49	1.31	0.26	8	0.27	1.39	1.39	0.06
0.50	0.31	7.49	1.15	0.51	8	0.55	1.23	1.22	0.11
0.75	0.44	7.49	0.99	0.77	8	0.82	1.06	1.06	0.17
0.90	0.51	7.49	0.90	0.92	8	0.98	0.96	0.96	0.21
0.95	0.53	7.49	0.87	0.97	8	1.04	0.92	0.92	0.22
0.99	0.55	7.49	0.84	1.01	8	1.08	0.90	0.90	0.23
1.00	0.55	7.49	0.83	1.02	8	1.09	0.89	0.89	0.23

Table 2: Chemical composition of schwertmannite adsorbed by phosphate

x	PO ₄ / (PO ₄ +S)	Fe mmol/g	SO ₄ mmol/g	PO ₄ mmol/g	Fe no./unit cell	H ₂ PO ₄ no./unit cell	SO ₄ no./unit cell	Cal SO ₄ no./unit cell	Cal OH no./unit cell
0.00	0.00	7.49	1.46	0.00	8	0.00	1.56	1.56	0.00
0.01	0.06	7.49	1.41	0.08	8	0.09	1.50	1.55	0.00
0.05	0.12	7.49	1.35	0.18	8	0.19	1.44	1.52	0.01
0.10	0.21	7.49	1.23	0.34	8	0.36	1.33	1.49	0.02
0.25	0.27	7.49	1.19	0.45	8	0.48	1.27	1.39	0.06
0.50	0.30	7.49	1.09	0.47	8	0.50	1.17	1.22	0.11
0.75	0.40	7.49	1.03	0.70	8	0.75	1.10	1.06	0.17
0.90	0.46	7.49	0.99	0.84	8	0.90	1.06	0.96	0.21
0.95	0.46	7.49	0.94	0.88	8	0.94	1.01	0.92	0.22
0.99	0.46	7.49	0.90	0.92	8	0.98	0.96	0.90	0.23
1.00	0.49	7.49	0.89	0.93	8	1.00	0.95	0.89	0.23
	0.51								

Table 3: Chemical composition of schwertmannite adsorbed by chromate

x	Cr/ (Cr+S)	Fe mmol/g	SO ₄ mmol/g	Cr mmol/g	Fe no./unit cell	HCrO ₄ no./unit cell	SO ₄ no./unit cell	Cal SO ₄ no./unit cell	Cal OH no./unit cell
0.00	0.00	7.49	1.46	0.00	8	0.00	1.56	1.56	0.00
0.01	0.06	7.49	1.40	0.09	8	0.10	1.50	1.55	0.00
0.05	0.12	7.49	1.35	0.18	8	0.19	1.44	1.53	0.01
0.10	0.20	7.49	1.26	0.31	8	0.34	1.35	1.51	0.01
0.25	0.25	7.49	1.21	0.41	8	0.44	1.29	1.44	0.04
0.50	0.30	7.49	1.15	0.49	8	0.53	1.23	1.32	0.07
0.75	0.33	7.49	1.12	0.55	8	0.59	1.19	1.21	0.11
0.90	0.37	7.49	1.09	0.65	8	0.69	1.16	1.14	0.13
0.95	0.39	7.49	1.08	0.68	8	0.73	1.15	1.11	0.14
0.99	0.40	7.49	1.05	0.69	8	0.74	1.13	1.09	0.15
1.00	0.42	7.49	1.02	0.72	8	0.77	1.09	1.09	0.15

Table 4. Activities of dissolved solution speciation and mole fraction of schwertmannite adsorbed by arsenate

x	log(As)	log(SO ₄ ²⁻)	log(Fe ³⁺)	log(H ⁺)
0.00		-4.10	-8.31	-4.25
0.01	-7.75	-4.11	-8.20	-4.14
0.05	-7.66	-4.03	-7.83	-3.90
0.10	-6.28	-3.95	-7.70	-3.78
0.25	-5.76	-3.77	-7.67	-3.72
0.50	-5.36	-3.58	-7.68	-3.70
0.75	-4.89	-3.45	-7.62	-3.63
0.90	-4.42	-3.39	-7.80	-3.60
0.95	-4.10	-3.37	-7.97	-3.58
0.99	-3.59	-3.35	-7.97	-3.55
1.00	-3.50	-3.33	-7.97	-3.50

Table 5: Activities of dissolved solution speciation and mole fraction of schwertmannite adsorbed by phosphate

x	$\log(\text{PO}_4)$	$\log(\text{SO}_4^{2-})$	$\log(\text{Fe}^{3+})$	$\log(\text{H}^+)$
0.00		-4.12	-8.53	-4.35
0.01	-7.65	-4.10	-8.13	-4.12
0.05	-7.57	-4.03	-8.04	-4.06
0.10	-5.30	-3.96	-7.80	-3.91
0.25	-4.71	-3.80	-7.74	-3.85
0.50	-4.35	-3.61	-7.65	-3.75
0.75	-4.17	-3.48	-7.70	-3.72
0.90	-4.09	-3.42	-7.62	-3.63
0.95	-4.06	-3.39	-7.60	-3.60
0.99	-3.50	-3.39	-7.82	-3.58
1.00	-3.45	-3.39	-7.88	-3.55

Table 6: Activities of dissolved solution speciation and mole fraction of schwertmannite adsorbed by chromate.

x	$\log(\text{Cr})$	$\log(\text{SO}_4^{2-})$	$\log(\text{Fe}^{3+})$	$\log(\text{H}^+)$
0.00		-4.10	-8.29	-4.25
0.01	-7.14	-4.11	-8.13	-4.10
0.05	-5.84	-4.05	-7.98	-4.05
0.10	-5.30	-3.99	-7.98	-3.92
0.25	-4.57	-3.85	-7.77	-3.84
0.50	-4.02	-3.68	-7.67	-3.80
0.75	-3.69	-3.56	-7.65	-3.77
0.90	-3.54	-3.50	-7.70	-3.75
0.95	-3.47	-3.48	-7.76	-3.72
0.99	-3.39	-3.47	-7.75	-3.70
1.00	-3.31	-3.47	-7.73	-3.69

Table 7. Comparison of the solubility of schwertmannite adsorbed different kinds of oxyanions

	Solubility of schwertmannite after adsorbed oxyanions		
	Arsenate	Phosphate	Chromate
K_{ex}	$10^{2.82}$	$10^{2.23}$	$10^{1.38}$

Chapter 4

Surface complexation modeling for many kinds of oxyanions onto ferrihydrite and schwertmannite

4.1. Introduction

Many inorganic compounds are necessary in plant and animal nutrition while others may be toxic to living matter. Inorganic environmental contaminants are particularly problematic because unlike most organic contaminants they do not undergo degradation. Redox reactive metals, however, often do have different degrees of toxicity depending on the specific metal oxidation state. Arsenic, chromium and selenate are metal ion that persists in the environment which are toxic to both plants and animals, being a strong oxidizing agent, corrosive, and a potential carcinogen (Smedley & Kinniburgh 2002; Gonzalez et al. 2010; Richard & Bourg 1991; Kotaś & Stasicka 2000)

To predict the migration and long-term fate of many kinds of oxyanions in natural environment, the behavior and the natural of adsorbed oxyanions species must be known for a wide variety of mineral and over the full range of environmental conditions. In natural system, the changing of pH and concentration depending on changing of time as shown in Figure 23. The surface speciation of different kinds of oxyanions as specially arsenate and phosphate on oxide powders and on single crystal surface has been studied through X-ray spectroscopic and infrared investigation as well as theoretical molecular calculations. On powders, a variety of surface species have been inferred from extended X-ray adsorption fine structure (EXAFS) studies (Waychunas et al. 1993). Therefore, iron oxide mineral such as ferrihydrite and schwertmannite are excellent adsorbents used to adsorb oxyanions such as arsenate and phosphate. In case of ferrihydrite adsorption arsenate and phosphate the mechanism was described as inner-sphere complex (Dzombak & Morel 1990; Davis & Kent 1990; Boukema & Boukhalfa 2012; Butkus et al. 1998; Jiang et al. 2015) and adsorbs selenate and sulfate as outer sphere complex as shown in Figure 24 (Fukushi et al. 2013; Fukushi & Sverjensky 2007b). There is the theoretical tool, used to predict adsorption properties for oxyanions onto iron oxide. It is surface complexation modeling. This model is powerful use for wastewater and groundwater treatment, which implies to predict the adsorption properties and mechanism of toxic element in the aqueous solutions. Surface complexation modeling was established with ferric oxide or ferrihydrite, but there is lacking information for schwertmannite surface complexation modeling.

Schwertmannite and ferrihydrite are both is a nanocrystalline iron (hydro) oxide mineral and will transform to be crystalline mineral as goethite by similar process, by dissolution and precipitation. In this study, would like to describe the chromate adsorption behavior onto schwertmannite and apply surface complexation modeling for chromate adsorption onto iron oxide by comparison with previous work for ferrihydrite and apply the surface complexation of ferrihydrite to schwertmannite.

4.2. Method and material

4.2.1. Preparation for adsorbent (*schwertmannite and ferrihydrite*)

Ferrihydrite was prepare as adsorbent by using digital titration machine TOADKK-AUT-701, 0.1M of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 500 ml was prepared and set on the stirrer, 0.1 of KOH solution was also prepared about 500 ml set into the machine, Auto titration was added 0.04ml/min (KOH) to the solution, until reach to pH7, sample was centrifuge 3000rpm, 40 minutes' wash in 6 times, then filtered through 0.2 μm cellulose membrane. The resulting of solids was freeze dried and identify the synthesized phases solids was examined by Rigaku X-Ray diffractometer with $\text{CuK}\alpha$ radiation (40kV and 40 mA), the result of XRD pattern was identical to that of the previously reported of ferrihydrite (Drits 1993; Cornell et al. 1989).

Schwertmannite was prepared by the method previously reported by Bigham et al (1996). Mixing solution prepared by 0.04 M Na_2SO_4 solution and 0.04 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution was held at 60°C for 12 minutes, then cooled and dialyzed for 30 days, deionized water used for the dialyzing was changed every day. To remove the salt in the surface of mineral the product was clean by using deionized water and was filtered through a 0.2 μm cellulose membrane then immediately freeze-dried to prevent transformation to another phase. Further, X-ray diffraction (XRD) analyses were conducted to identify the synthesized phases by Rigaku X-Ray diffractometer with $\text{CuK}\alpha$ radiation (40kV and 40mA). From the XRD analyses, the synthesized products were identified as a schwertmannite because the XRD pattern was identical to that of the previously reported schwertmannite by Bigham et al (1990).

4.2.2. Adsorption experiment

After prepare both schwertmannite and ferrihydrite as adsorbents, the adsorption experiments were performed as function of pH from pH 3 to pH 12. The oxyanions solutions (Na_2HPO_4 , Na_2HAsO_4 , Na_2CrO_4 , and Na_2SeO_4) were prepared in 50ml centrifuge tube about 40 ml, the concentration was set in variety value 0.2mM, 0.6 mM, and 1 mM for each sample,

and sets ionic strength (0.01-0.1 M, NaNO₃). The adsorbents (40mg) were added to each solution by ratio 1g/liter, then all sample were adjusted pH by using 1M, NaOH and 1M, HNO₃. The adsorption samples were place on shaker 100rpm, 25°C in the equilibrium times (24 hours). After adsorption process the solid and solution were separate by using membrane 0.2µm. then the solids were freeze and dried for measurement zeta potential (Mavern Zetasizer Nano series Nano-ZS90 instrument) for the solutions were measurement by using the inductively coupled plasma atomic emission spectroscopy, (ICPE-9000, ICP-AES) and ion-chromatography (Metrohm 861 Advanced Compact IC instrument) to determine concentration of oxyanions.

4.2.3. *Estimation of Extend triple layer modeling (ETLM) basic parameter*

- **Aqueous speciation, surface protonation and electrolyte adsorption**

Aqueous speciation calculations were carried out taking into account aqueous ionic activity coefficients appropriate to single electrolytes up to high ionic strengths calculated with the extended Debye-Huckel equation (Helgeson et al. 1981; Criscenti & Sverjensky 1999). Electrolyte ion pairs used were consistent with previous studies (Criscenti & Sverjensky 1999; Criscenti & Sverjensky 2002). Aqueous arsenate, phosphate, chromate, selenate and sulfate protonation and aqueous complex equilibria are summarized in Table 8

The sample characteristics and surface protonation and electrolyte adsorption equilibrium constants used in the present study are summarized in Table 9. Surface protonation constants referring to site-occupancy standard states (indicated by the superscript “θ”), i.e. $\log K_1^0$ and $\log K_2^0$, were calculated from values of pH_{ZPC} and $\Delta \text{p}K_n^0$ (Sverjensky 2005)

$$\log K_1^0 = \text{pH}_{\text{ZPC}} - \frac{\Delta \text{p}K_n^0}{2} \quad (28)$$

and

$$\log K_2^0 = \text{pH}_{\text{ZPC}} - \frac{\Delta \text{p}K_n^0}{2} \quad (29)$$

Value of pH_{ZPC} were taken from measured low ionic strength isoelectric points or point of zero salt effects corrected for electrolyte adsorption (Sverjensky 2005). For HFO or ferrihydrite examined in previous study (Dixit & Hering 2003), neither isoelectric points nor surface titration data were reported. The value of $\Delta \text{p}K_n^0$ were predicted theoretically (Sverjensky 2005).

For convenience, protonation constants referring to the hypothetical 1.0 molar standard state (denoted by the superscript “0”) are also given (Table 9). The relationship between the

two standard states is given by (Sverjensky 2003).

$$\log K_1^0 = \log K_1^0 - \log \left(\frac{N_s A_s}{N^+ A^+} \right) \quad (30)$$

$$\log K_2^0 = \log K_2^0 - \log \left(\frac{N_s A_s}{N^+ A^+} \right) \quad (31)$$

Where,

N_s represents the surface site density on the s th solid sorbent (site m^{-2})

N^+ represents the standard state sorbate species site density (site m^{-2})

A_s represents the BET surface area of the s th solid sorbent (m^2g^{-1})

A^+ represents standard state BET surface area (m^2g^{-1})

In the present study, values of $N^+ = 10 \times 10^{18}$ sites m^{-2} and $A^+ = 10 \text{ m}^2\text{g}^{-1}$ are selected for all solids.

Electrolyte adsorption equilibrium constants referring to site-occupancy standard states, $\log K_{M^+}^0$ and $\log K_{L^-}^0$, and capacitances, C_1 , were obtained from regression of proton surface charge data when such data were available. In other instances, these parameters were obtained by the theoretical prediction (Sverjensky 2005) or from similar samples as noted in Table 9. For convenience, value for the hypothetical 1.0 molar standard state relative to $>\text{SOH}$ species, $\log^* K_{M^+}^0$ and $\log^* K_{L^-}^0$ (where the superscript “*” represents a reaction relative to the species $>\text{SOH}$), are also shown in Table 9. The relationships between $\log^* K_{M^+}^0$ and $\log^* K_{L^-}^0$, and $\log K_{M^+}^0$ and $\log K_{L^-}^0$ are given by (Sverjensky 2003; Sverjensky 2005)

$$\log^* K_{M^+}^0 = \log K_{M^+}^0 - \text{pH}_{\text{ZPC}} - \frac{\Delta \text{p}K_n^0}{2} - \log \left(\frac{N_s A_s}{N^+ A^+} \right) \quad (32)$$

$$\log^* K_{L^-}^0 = \log K_{L^-}^0 - \text{pH}_{\text{ZPC}} - \frac{\Delta \text{p}K_n^0}{2} - \log \left(\frac{N_s A_s}{N^+ A^+} \right) \quad (33)$$

Surface area (A_s) and (N_s) in this study was assumed from the previous study (Davis & Kent 1990; Dzombak & Morel 1990; Fukushima & Sverjensky 2007a; Fukushima & Sverjensky

2007b). Theoretical estimation of these site densities is impossible for powdered samples when proportions of the crystal faces are unknown, as is the case for all the experimental studies analyzed below. In this present study was used a single site density for each sample applied to all the surface equilibria as described previously (Sverjensky 2005; Fukushi et al. 2013; Fukushi & Sverjensky 2007a; Fukushi & Sverjensky 2007b). All the calculations were carried out with the aid of the computer code GEOSURF (Sahai & Sverjensky 1998).

4.3. Result and discussion

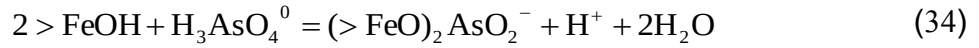
4.3.1. Arsenate adsorption

Figure 25 and Figure 26 shown, adsorption of arsenate onto ferrihydrite and schwertmannite in different pH and different ionic strength, base on the result the tendency of adsorption fraction between ferrihydrite and schwertmannite was similar in the pH range from neutral to alkaline conditions. For ionic strength as increasing of the concentration of arsenate the adsorption fraction was increase in th alkaline condition for both minerals.

Double layer modeling (DLM) following from (Dzombak & Morel 1990), by using RE-ACT in the Geochemist's workbench (GWB) (Bethke 2007), the result of arsenate adsorption onto ferrihydrite with DLM shown in Figure 27a, the experimental data was fitting well with the model. To better understand and comparison with other model, extend triple layer modeling (ETLM) was also apply for arsenate adsorption onto ferrihydrite with different concentration and diferent ionic strength. The difference of DLM and TLM as shown in Figure 28, the DLM was had to layer which devide fixed layer and diffuse layer Figure 28a, the TLM had fixed layer and difuse layer divide one more plan, may adsorbed the intermediate complexes (Figure 28b).

ETLM for arsenate adsorption on oxide by choosing surface species based on the *in situ* X-ray and infrared spectroscopic studies of phosphate and arsenate and the molecular calculations for arsenate and phosphate interaction with metal oxide clusters. There are three reaction stoichiometry expressed as the formation of inner-sphere surface species as illustrated in Figure 31 . Additional species could be incorporated into the model, but even the data analyzed in the present study, which refers to a wide range of experimental conditions, did not permit retrieval of equilibrium constants for more than three surface species. In previous study Fukushi et al (2007a) was confirmed three reaction stoichiometry involved surface species identical to the ones proposed in the *in situ* ATR-FTIR study of phosphate adsorption on goethite (Tejedor-Tejedor & Anderson 1990) discussed above. For the most part, these species are also consistent with the X-ray studies cited above. The three reactions produced:

1st a deprotonated bidentate-binuclear species according to:



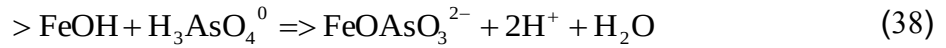
$$^* K_{(>\text{FeO})_2 \text{AsO}_2^-}^\theta = \frac{a_{(>\text{FeO})_2 \text{AsO}_2^-} a_{\text{H}^+} a_{\text{H}_2\text{O}}^2}{a_{>\text{FeOH}}^2 a_{\text{H}_3\text{AsO}_4^0}} 10^{\frac{F(\Delta\Psi_{r,10})}{2.303RT}} \quad (35)$$

2nd a protonated bidentate-binuclear species according to



$$^* K_{(>\text{FeO})_2 \text{AsOOH}}^\theta = \frac{a_{(>\text{FeO})_2 \text{AsOOH}} a_{\text{H}_2\text{O}}^2}{a_{>\text{FeOH}}^2 a_{\text{H}_3\text{AsO}_4^0}} 10^{\frac{F(\Delta\Psi_{r,12})}{2.303RT}} \quad (37)$$

3rd a deprotonated mono-dentate species according to



$$^* K_{(>\text{FeO})_2 \text{AsO}_2^-}^\theta = \frac{a_{>\text{FeOAsO}_3^{2-}} a_{\text{H}^+}^2 a_{\text{H}_2\text{O}}}{a_{>\text{FeOH}} a_{\text{H}_3\text{AsO}_4^0}} 10^{\frac{F(\Delta\Psi_{r,14})}{2.303RT}} \quad (39)$$

Here, the superscript “ θ ” again represents site-occupancy standard states (Sverjensky 2003; 2005). The exponential terms contain the electrostatic factor, $\Delta\Psi_r$, which is a reaction property arising from the work done in an electric field when species in the reaction move on or off the charged surface. It is evaluated taking into account the adsorbing ions and the water dipoles released in Equation (34), (36) and (38). Electrostatic work is done in both instances and is reflected in the formulation of $\Delta\Psi_r$ (Sverjensky & Fukushima 2006a;b).

In the ETL model was place the charge of the adsorbing protons on the 0-plane and the charge of the oxyanion on the β -plane. This is a departure from the practice of placing the oxyanion charge on the 0-plane for inner-sphere complexes in the TLM (Hayes et al. 1988). In this present’s calculations, with the dipole modification and the arsenate or protonated arsenate

charge on the β -plane, the ETLM can describe a wide variety of arsenate adsorption data.

In the ETLM, the water dipole (s) leaving the charged surface experience a change in potential equal to $-n(\Psi_0 - \Psi_\beta)$ where n is the number of desorbed waters per reaction. For the reaction in Equation (35), (37) and (39), this result in

$$\Delta\Psi_{r,10} = 2\Psi_0 - 3\Psi_\beta - 2(\Psi_0 - \Psi_\beta) = -\Psi_\beta \quad (40)$$

$$\Delta\Psi_{r,12} = 2\Psi_0 - 2\Psi_\beta - 2(\Psi_0 - \Psi_\beta) = 0 \quad (41)$$

$$\Delta\Psi_{r,14} = \Psi_0 - 3\Psi_\beta - (\Psi_0 - \Psi_\beta) = -2\Psi_\beta \quad (42)$$

As shown in Figure 29, the percent arsenate adsorption with function of changing pH, at low pH condition adsorption fraction was shown in high adsorption indicated that surface speciation of mineral is positive charge which inclined to react with the anion. The solid curves in Figure 29, a represent regression calculations gain using the three reactions as mentioned above the equilibrium constant for the arsenate speciation as shown in Table 10 and site density used previously for arsenate calculations for this sample (Table 9). The solid point symbol was represented the experimental data. It is predicted that deprotonated bidentate-binuclear species is dominant for most pH conditions. However, the importance of the mononuclear species is again predicted to increase with pH similar to HFO, consistent with EXAFS and IR spectroscopic results (Waychunas et al. 2001; Arai & Sparks 2001)

The relationships of the site-occupancy standard states to the hypothetical 1.0 M standard state for the arsenate surface are following (Fukushi & Sverjensky 2007a)

$$\log^* K_{(>\text{FeO})_2 \text{AsO}_2^-}^\theta = \log^* K_{(>\text{FeO})_2 \text{AsO}_2^-}^0 + \log\left(\frac{(N_s A_s)^2}{N^+ A^+} C_s\right) \quad (43)$$

$$\log^* K_{(>\text{FeO})_2 \text{AsOOH}}^\theta = \log^* K_{(>\text{FeO})_2 \text{AsOOH}}^0 + \log\left(\frac{(N_s A_s)^2}{N^+ A^+} C_s\right) \quad (44)$$

$$\log^* K_{>\text{FeOAsO}_3^{2-}}^\theta = \log^* K_{>\text{FeOAsO}_3^{2-}}^0 + \log\left(\frac{N_s A_s}{N^+ A^+}\right) \quad (45)$$

Where C_s represented solid concentration (g L^{-1}). The equilibrium constants represented relative to the species $>\text{FeOH}$, expressed by the superscript “*” in Equation (35), (37) and (39) depend on the pH_{ZPC} and ΔpK_n^θ of solid samples. It is convenient to correct for differences in the pH_{ZPC}

and ΔpK_n^θ with following equations (Sverjensky 2005)

$$\log K_{(>\text{FeO})_2 \text{AsO}_2^-}^\theta = \log {}^*K_{(>\text{FeO})_2 \text{AsO}_2^-}^\theta - 2\text{pH}_{\text{ZPC}} + \Delta pK_n^\theta \quad (46)$$

$$\log K_{(>\text{FeO})_2 \text{AsOOH}}^\theta = \log {}^*K_{(>\text{FeO})_2 \text{AsOOH}}^\theta - 2\text{pH}_{\text{ZPC}} + \Delta pK_n^\theta \quad (47)$$

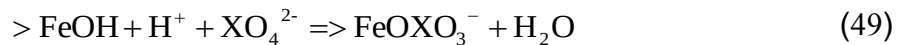
$$\log K_{>\text{FeOAsO}_3^{2-}}^\theta = \log {}^*K_{>\text{FeOAsO}_3^{2-}}^\theta - \text{pH}_{\text{ZPC}} + \frac{\Delta pK_n^\theta}{2} \quad (48)$$

The resultant values of three equilibriums above are independent of the site density, surface area or solid concentration of the specific samples, as well as the pH_{ZPC} and ΔpK_n^θ used in the experiments. Values of the logarithms of the above equilibrium constants are summarized in Table 10.

4.3.2. Selenate and sulfate adsorption

DLM can apply and fitted well with arsenate adsorption onto ferrihydrite base on previously study, the mechanism of arsenate is inner-sphere complexes and base on the previously study for *in situ* X-ray and infrared spectroscopic studies of selenate, the DLM was apply for selenate base on the data base of previously study (Dzombak & Morel 1990) by using REACT in GWB program. As shown in the Figure 27b, the experiment data was not fitted well with this model which just fit some of the data base, because selenate was involved both surface species equation inner-sphere and outer-sphere complexes. To better fitted model, in this present study, surface complexation modeling ETLM was applied for selenate adsorption onto ferrihydrite.

In the ETLM treatment of sulfate and selenate adsorption on ferrihydrite, was investigated the applicability of the inner-sphere and outer-sphere (or H-bonded) complexes, in this presents study was input some parameter similar with the previously work (Fukushi & Sverjensky 2007b; Fukushi et al. 2013). The inner-sphere species is a mono-dentate-mononuclear species represented by



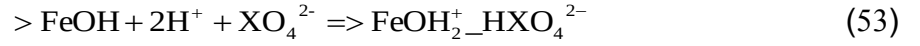
$${}^*K_{>\text{FeOXO}_3^-}^\theta = \frac{a_{>\text{FeOXO}_3^-} a_{\text{H}_2\text{O}}}{a_{>\text{FeOH}} a_{\text{H}^+} a_{\text{XO}_4^{2-}}} 10^{\frac{F(\Delta\Psi_r)}{2.303RT}} \quad (50)$$

The outer-sphere species is represented by



$${}^*K_{(>\text{FeOH}_2^+)_2\text{XO}_4^{2-}}^\theta = \frac{a_{(>\text{FeOH}_2^+)_2\text{XO}_4^{2-}}}{a_{>\text{FeOH}}^2 a_{\text{H}^+}^2 a_{\text{XO}_4^{2-}}} 10^{\frac{F(\Delta\Psi_r)}{2.303RT}} \quad (52)$$

And



$${}^*K_{>\text{FeOH}_2^+ \text{HXO}_4^{2-}}^\theta = \frac{a_{>\text{FeOH}_2^+ \text{HXO}_4^{2-}}}{a_{>\text{FeOH}} a_{\text{H}^+}^2 a_{\text{XO}_4^{2-}}} 10^{\frac{F(\Delta\Psi_r)}{2.303RT}} \quad (54)$$

Where is X represented S or Se. In this case, placed the charge of the proton in Equation (49) on the 0-plane and the charge of the anions on the β -plane. Almost of the explanation was like arsenate adsorption, the different is there is equation of outer-sphere complex.

The relationships of the site-occupancy standard states to the hypothetical 1.0 M standard state for the selenate surface are following (Fukushi & Sverjensky 2007a)

$$\log {}^*K_{>\text{FeOXO}_2^-}^\theta = \log {}^*K_{>\text{FeOXO}_2^-}^0 + \log \left(\frac{N_s A_s}{N^+ A^+} \right) \quad (55)$$

$$\log {}^*K_{(>\text{FeOH})_2^+/\text{XO}_4^{2-}}^\theta = \log K_{(>\text{FeOH})_2^+ \text{XO}_4^{2-}}^0 + \log \left(\frac{(N_s A_s)^2}{N^+ A^+} C_s \right) \quad (56)$$

$$\log {}^*K_{>\text{FeOH}_2^+ \text{HXO}_4^-}^\theta = \log K_{>\text{FeOH}_2^+ \text{HXO}_4^-}^0 + \log \left(\frac{N_s A_s}{N^+ A^+} \right) \quad (57)$$

Where C_s represented solid concentration (g L^{-1}). The equilibrium constants represented relative

to the species $>\text{FeOH}$ (using superscript “*”) in Equation (50), (52) and (54) depend on the pH_{ZPC} and $\Delta\text{p}K_n^\theta$ of solid samples. It is convenient to correct for differences in the pH_{ZPC} and $\Delta\text{p}K_n^\theta$ by eliminating contributions of surface protonation from equilibrium constants. These conversions can be made with following equations (Sverjensky 2005)

$$\log K_{>\text{FeOXO}_3^-}^\theta = \log {}^*K_{>\text{FeOXO}_3^-}^\theta - \text{pH}_{\text{ZPC}} + \frac{\Delta\text{p}K_n^\theta}{2} \quad (58)$$

$$\log K_{(>\text{FeOH}_2^+)_2-\text{XO}_4^{2-}}^\theta = \log {}^*K_{(>\text{FeOH}_2^+)_2-\text{XO}_4^{2-}}^\theta - 2\text{pH}_{\text{ZPC}} + \Delta\text{p}K_n^\theta \quad (59)$$

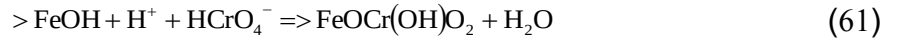
$$\log K_{>\text{FeOH}_2^+-\text{HXO}_4^-}^\theta = \log {}^*K_{>\text{FeOH}_2^+-\text{HXO}_4^-}^\theta - \text{pH}_{\text{ZPC}} + \frac{\Delta\text{p}K_n^\theta}{2} \quad (60)$$

The resultant values of three equilibriums above are independent of the site density, surface area or solid concentration of the specific samples, as well as the pH_{ZPC} and $\Delta\text{p}K_n^\theta$ used in the experiments. Values of the logarithms of the above equilibrium constants are summarized in Table 11

For the outer-sphere complex in Equation (52), it was continue to express the electrostatic factor in the traditional way for β -plane complexes in the triple-layer model (Davis & Leckie 1980). It can be seen in Figure 30 that the combination of reactions (49) and (51) results in a close description of the experimental adsorption data over wide range of pH values. Ionic strengths and surface coverages. The data shown in Figure 30 cover such a wide range of conditions, including surface coverage, that they were used to regress for the two equilibrium constants and the site density. In Figure 30 d, the speciation of selenate had shown the proportion of the outer-sphere complex is predicted to increase as function of pH.

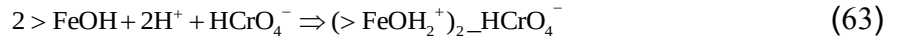
4.3.3. Predicted adsorption reaction for chromate

For chromate adsorption on iron oxide, there is unknown of the ETLM applications, in this study was predicted and used some parameter of the electrolytes equilibrium constants and capacitances from the previously work as shown in Table 8 and Table 9, from the adsorption experimental data, it was be seen the adsorption capacities of chromate on ferrihydrite compare with arsenate and selenate it shown in between and accordingly from the zeta potential data, the curves was shift in between arsenate, phosphate which known as inner-sphere complexes and selenate which known as outer sphere complexes. In this present study of ferrihydrite chromate reaction can be represented by formation of inner-sphere according to:



$$^* K^\theta_{>\text{FeOCr}(\text{OH})\text{O}_2} = \frac{a_{>\text{FeOCr}(\text{OH})\text{O}_2}}{a_{>\text{FeOH}} a_{\text{H}^+} a_{\text{HCrO}_4^-}} 10^{\frac{F(\Delta\Psi_r)}{2.303RT}} \quad (62)$$

In addition, for reaction equation represented in outer-sphere (H-bonded) species according to



$$^* K^\theta_{(>\text{FeOH}_2^+)_2 \text{HCrO}_4^-} = \frac{a_{(>\text{FeOH}_2^+)_2 \text{HCrO}_4^-}}{a_{>\text{FeOH}}^2 a_{\text{H}^+}^2 a_{\text{HCrO}_4^-}} 10^{\frac{F(\Delta\Psi_r)}{2.303RT}} \quad (64)$$



$$^* K^\theta_{>\text{FeOH}_2^+ \text{HCrO}_4^-} = \frac{a_{>\text{FeOH}_2^+ \text{HCrO}_4^-}}{a_{>\text{FeOH}} a_{\text{H}^+} a_{\text{HCrO}_4^-}} 10^{\frac{F(\Delta\Psi_r)}{2.303RT}} \quad (66)$$

The relationships of the site-occupancy standard states to the hypothetical 1.0 M standard state for the chromate surface are following (Fukushi & Sverjensky 2007a)

$$\log ^* K^\theta_{>\text{FeOCr}(\text{OH})\text{O}_2} = \log ^* K^0_{>\text{FeOCr}(\text{OH})\text{O}_2} + \log \left(\frac{N_s A_s}{N^+ A^+} \right) \quad (67)$$

$$\log ^* K^\theta_{(>\text{FeOH}_2^+)_2 \text{HCrO}_4^-} = \log K^0_{(>\text{FeOH}_2^+)_2 \text{HCrO}_4^-} + \log \left(\frac{(N_s A_s)^2}{N^+ A^+} C_s \right) \quad (68)$$

$$\log ^* K^\theta_{>\text{FeOH}_2^+ \text{HCrO}_4^-} = \log K^0_{>\text{FeOH}_2^+ \text{HCrO}_4^-} + \log \left(\frac{N_s A_s}{N^+ A^+} \right) \quad (69)$$

Where C_s represented solid concentration (g L^{-1}). The equilibrium constants represented relative to the species $>\text{FeOH}$ (using superscript “*”) in Equation (62), (64) and (66) depend on the

pH_{ZPC} and $\Delta\text{p}K_n^\theta$ of solid samples. It is convenient to correct for differences in the pH_{ZPC} and $\Delta\text{p}K_n^\theta$ by eliminating contributions of surface protonation from equilibrium constants. These conversions can be made with following equations (Sverjensky 2005)

$$\log K_{>\text{FeOCr}(\text{OH})\text{O}_2}^\theta = \log {}^*K_{>\text{FeOCr}(\text{OH})\text{O}_2}^\theta - \text{pH}_{\text{ZPC}} + \frac{\Delta\text{p}K_n^\theta}{2} \quad (70)$$

$$\log K_{(>\text{FeOH}_2^+)_2\text{-HCrO}_4^-}^\theta = \log {}^*K_{(>\text{FeOH}_2^+)_2\text{-HCrO}_4^-}^\theta - 2\text{pH}_{\text{ZPC}} + \Delta\text{p}K_n^\theta \quad (71)$$

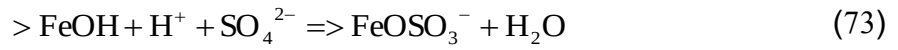
$$\log K_{>\text{FeOH}_2^+\text{-HCrO}_4^-}^\theta = \log {}^*K_{>\text{FeOH}_2^+\text{-HCrO}_4^-}^\theta - \text{pH}_{\text{ZPC}} + \frac{\Delta\text{p}K_n^\theta}{2} \quad (72)$$

The resultant values of three equilibriums above are independent of the site density, surface area or solid concentration of the specific samples, as well as the pH_{ZPC} and $\Delta\text{p}K_n^\theta$ used in the experiments. Values of the logarithms of the above equilibrium constants are summarized in Table 12

From equations above, the calculation surface reaction and chromate species, the adsorption fraction was change depend on pH conditions. As chromate is oxyanions which as negative charge and need to attract with the positive with the mineral surface, as shown in the result, chromate was adsorbing well in the low pH condition and effected by different surface coverages. The chromate surface species as inner-sphere complex was decreasing with the increase of pH (Figure 31)

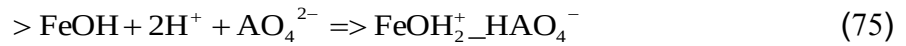
4.3.4. *Applied ETLM on schwertmannite*

In case of applied ETLM onto schwertmannite for oxyanions, in this present study surface protonation and electrolytes adsorption equilibrium constants and capacitances was calculated following previous study of ferrihydrite (Fukushi & Sverjensky 2007a) as shown in Table 9 and Table 10. Because from the comparison adsorption capacities, oxyanions selectivity and surface speciation of ferrihydrite and schwertmannite (Figure 32). As known that schwertmannite and ferrihydrite are precipitate in mining site whereas rich iron; therefore, the different is schwertmannite had SO_4 sorbs in the tunnel structure (Figure 32c-d). Although, the between schwertmannite and ferrihydrite had similar, but additional to apply schwertmannite ETLM, one reaction should be included:



$$^* K_{>\text{FeOSO}_3^-}^\theta = \frac{a_{>\text{FeOSO}_3^-} a_{\text{H}_2\text{O}}}{a_{>\text{FeOH}} a_{\text{H}^+} a_{\text{SO}_4^{2-}}} 10^{\frac{F(\Delta\Psi_{r_s})}{2.303RT}} \quad (74)$$

The experiment data and ETLM was fitting well in the pH between neutral to alkaline condition. In case schwertmannite adsorbe arsenate was shown in Figure 33 display schwertmannite adsorbed arsenate in different concentration and different ionic strength, all most range of pH there is experiment data fitted well to the ETLM, indicate that the oxyanion which made inner-sphere complexes with schwertmannite can apply ETLM to predicted adsorption fraction by following data base of ferrihydrite which reported by previously work (Fukushi & Sverjensky 2007b) in case of schwertmannite adsorption selenate and sulfate was consider into only outer-sphere complexes and according to the zeta potential curves after schwertmannite adsorbs selenate and sulfate was not different with the original schwertmannite (mentioned in chapter 2). In additional outer-sphere speciation was shown here:



$$^* K_{>\text{FeOH}_2^+ \text{--} \text{HAO}_4^-}^\theta = \frac{a_{>\text{FeOH}_2^+ \text{--} \text{HAO}_4^-}}{a_{>\text{FeOH}} a_{\text{H}^+}^2 a_{\text{AO}_4^{2-}}} 10^{\frac{F(\Psi_0 - \Psi_\beta)}{2.303RT}} \quad (76)$$

As shown in Figure 34, schwertmannite had SO_4 in surface group and also surface hydroxyl group, when chromate adsorption on schwertmannite may had competition between chromate and sulfate on surface of schwertmannite. According from the chromate, selenate and sulfate adsorption on ferrihydrite made inner- and outer-sphere complexes and had similar properties.

Figure 35 represented schwertmannite adsorption chromate, the result shown that chromate and sulfate which sorbing on tunnel structure of schwertmannite had competition with chromate according from previously work sulfate made intermediate with surface (HFO) and from the presente study the equation which use to apply the ETLM modeling for chromate was predicted following previous work(Xie et al. 2015), in the model shown as high adsorption fraction, meanwhile the experiment data in acidic condition to neutral condition (about 6.9, pH_{ZPC}), when

decreasing of pH adsorption fraction was also decreased. In Figure 35 a-c, dashed line is the estimating modeling, in this model involve only two species surface reaction of chromate monodentate inner-sphere complexes and bidentate outer-sphere complexes (Table 12). From the result of estimated modeling was fitted to the experiment data, indicated that in the solution experiment might included in high HCrO_4^- which is stronger basis compare to SO_4^{2-} speciation.

4.3.5. Prediction of equilibrium constants for oxyanions

The ETLM calculations summarized above for arsenate had three reactions producing the species $(>\text{FeO})_2\text{AsO}_2^-$, $(>\text{FeO})_2\text{AsOOH}$ and $>\text{FeOAsO}_3^{2-}$ can describe a variety of arsenate adsorption data for this study with wide range of pH, ionic strength and two oxide minerals as ferrihydrite and schwertmannite. The equilibrium constants for adsorption on different solids, it is essential to use site-occupancy standard states ($\log K_j^0$). On this basis, it had established by previously work Fukushima et al (2007a).

This present study for arsenate, we assume the equilibrium constant for adsorption by following the equation bellow (Fukushi & Sverjensky 2007a):

$$K_{>\text{FeOAsO}_3^{2-}}^\theta = -80.0 \left(\frac{1}{\varepsilon} \right) + 1.02 \quad (77)$$

$$K_{(>\text{FeO})_2\text{AsO}_2^-}^\theta = -68.5 \left(\frac{1}{\varepsilon} \right) + 5.40 \quad (78)$$

$$K_{(>\text{FeO})_2\text{AsOOH}}^\theta = -51.4 \left(\frac{1}{\varepsilon} \right) + 6.78 \quad (79)$$

Where ε represented the dielectric constant of the solid, the equation above was used to predict the equilibrium constants for arsenate adsorption on ferrihydrite and schwertmannite, the predictive equations indicate that the Born solvation effect for mononuclear species is much stronger than for binuclear species (Table 10)

In case of chromate and selenate adsorption onto ferrihydrite and schwertmannite, the equilibrium constants were theoretically predictive following from previous work (Fukushi & Sverjensky 2007a; Fukushima & Sverjensky 2007b; Fukushima et al. 2013) and consistent with previous work of EXAF data, the equilibrium constants were compare with previous works as

shown in Table 11 and Table 12

4.4. Conclusion

The extended triple layer model (ETLM), which takes into account the electrostatics of water dipole desorption caused by inner-sphere surface complexation, was developed to help from the published experimental spectroscopic and theoretical molecular evidence of the identity of oxyanions surface species with a surface complexation model of adsorption (Sverjensky & Fukushima 2006a; b). Accordingly, to the previous work, the model can predict change in the proportions of inner- and outer-sphere surface species with changes in environmental variables, such as pH, ionic strength and surface coverages, consistent with independent spectroscopic evidence.

From the previous work (Fukushi & Sverjensky 2007a), the other was compare with variety published experimental data, in wide range of pH, surface coverage and was used evidence from X-ray and infrared spectroscopic and theoretical molecular, then the authors can found the reaction stoichiometry forming inner-sphere complexes for arsenate adsorptions. By following three reactions for arsenate with present experiment data was fitting well to the model, indicate that the applicable of the model can also predicted by using previously parameters for ferric iron oxide. In case of schwertmannite, the ETLM was applied by using the parameters from ferrihydrite. From the result in case of adsorption oxyanion which inner-sphere complexes, the model was fitting well with the experiment data, implied that, for more understand, the EXAFS data and experimental spectroscopic need to include.

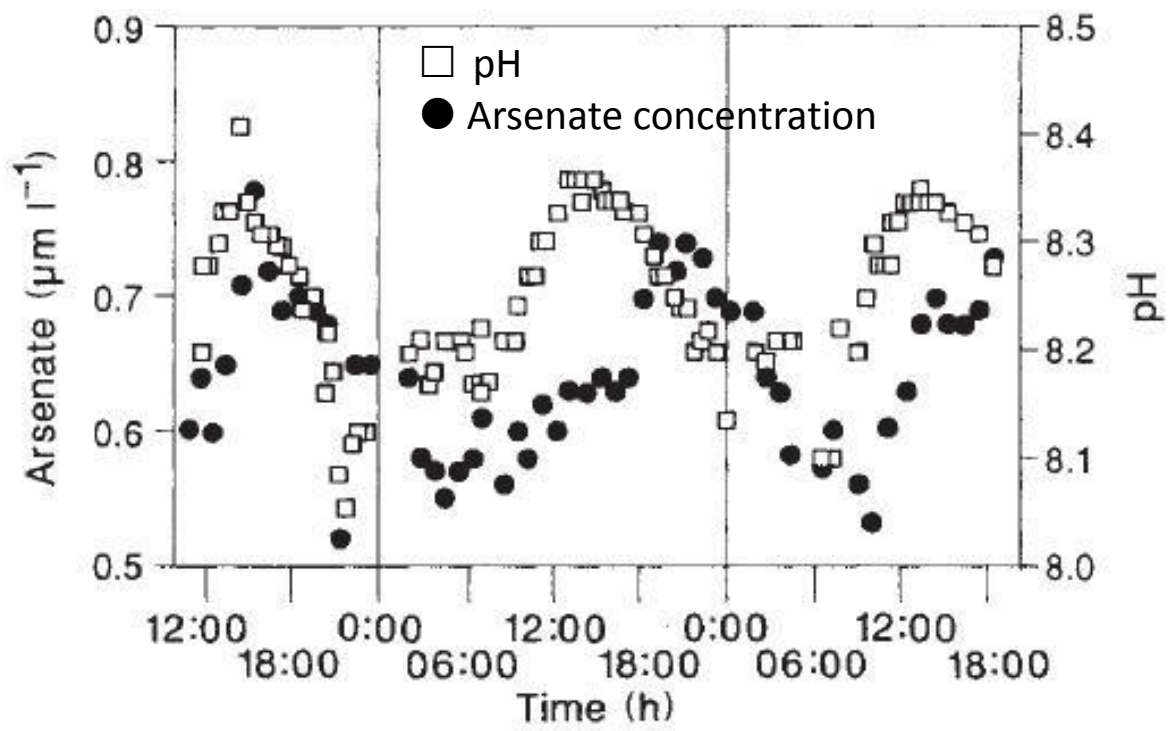


Figure 23. Diagram representation of arsenate and pH changing with changing of time (Fuller & Davis 1989)

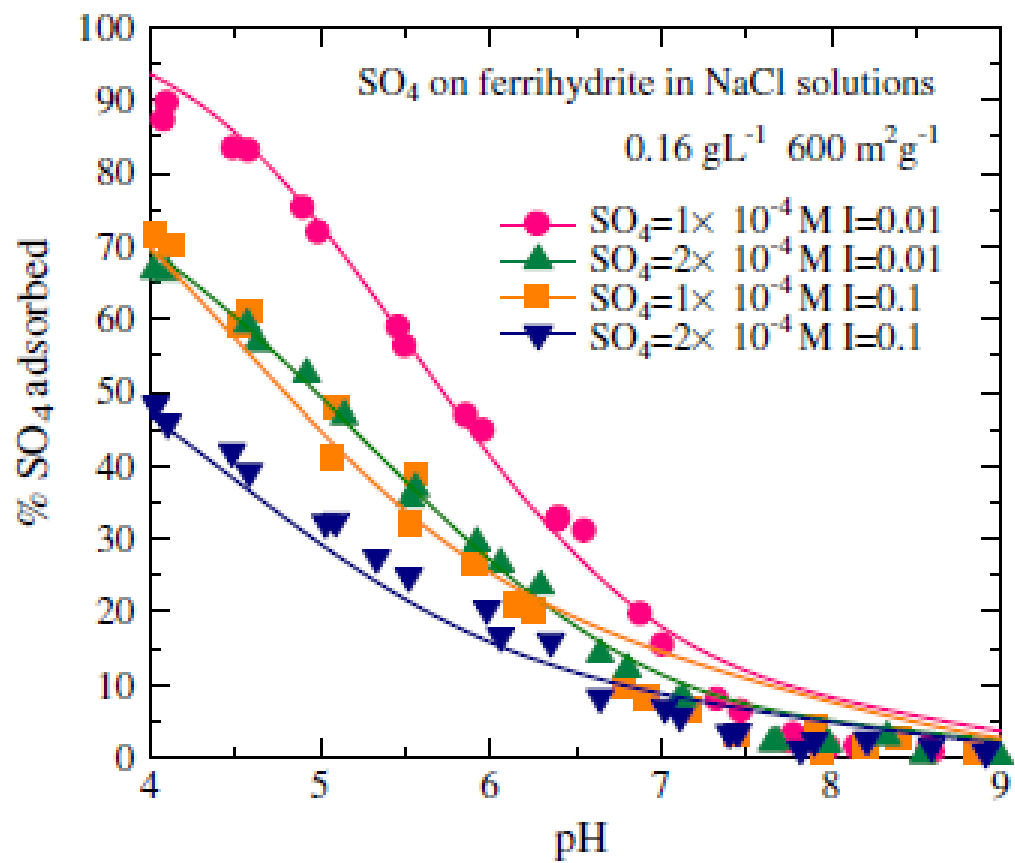


Figure 24. SO₄ adsorption onto ferrihydrite and apply ETLM (Fukushi et al. 2013)

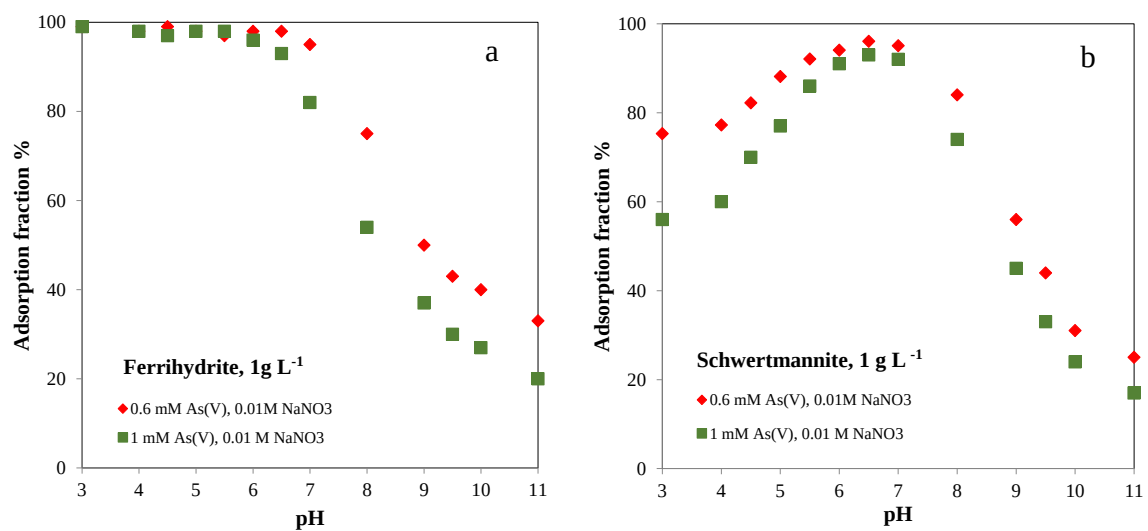


Figure 25. (a) ferrihydrite adsorbed As(V) in functional of pH, (b) schwertmannite adsorbed As(V) in function of pH

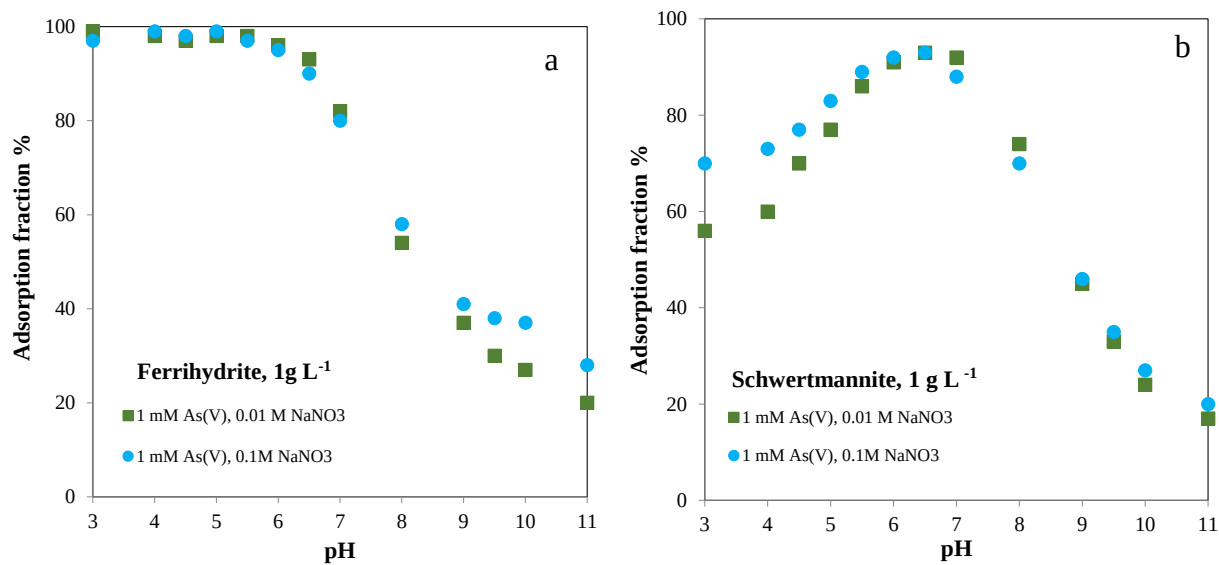


Figure 26. (a) ferrihydrite adsorbed As(V) in functional of pH with different ionic strenght, (b) schwertmannite adsorbed As(V) in function of pH with different ionic strength

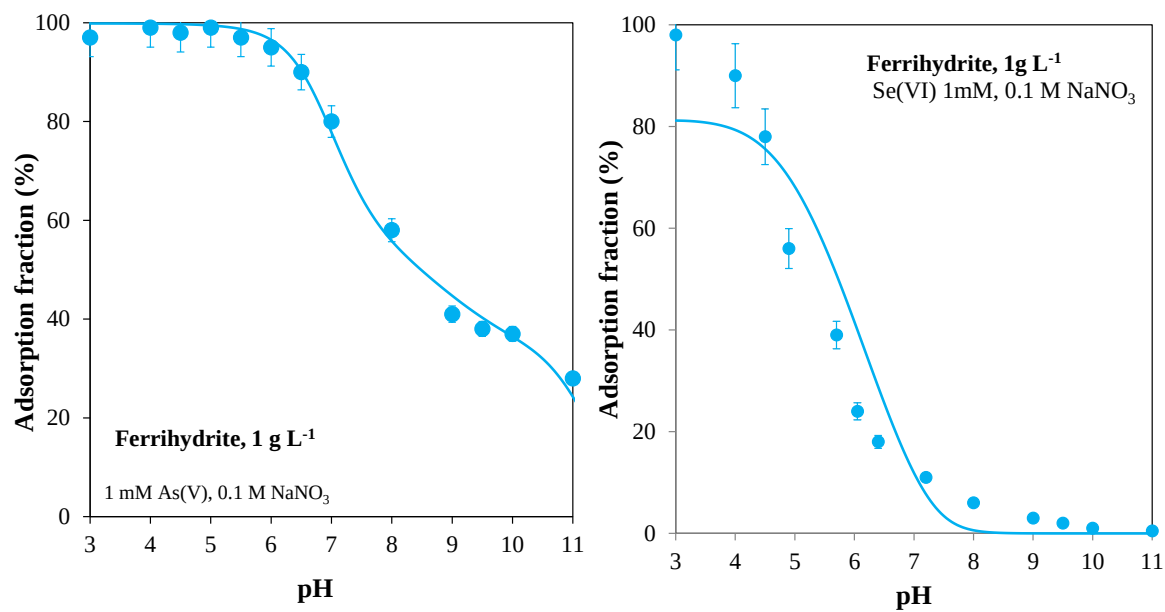


Figure 27. Surface complexation double layer modeling for As(V) and Se(VI) onto ferrihydrite

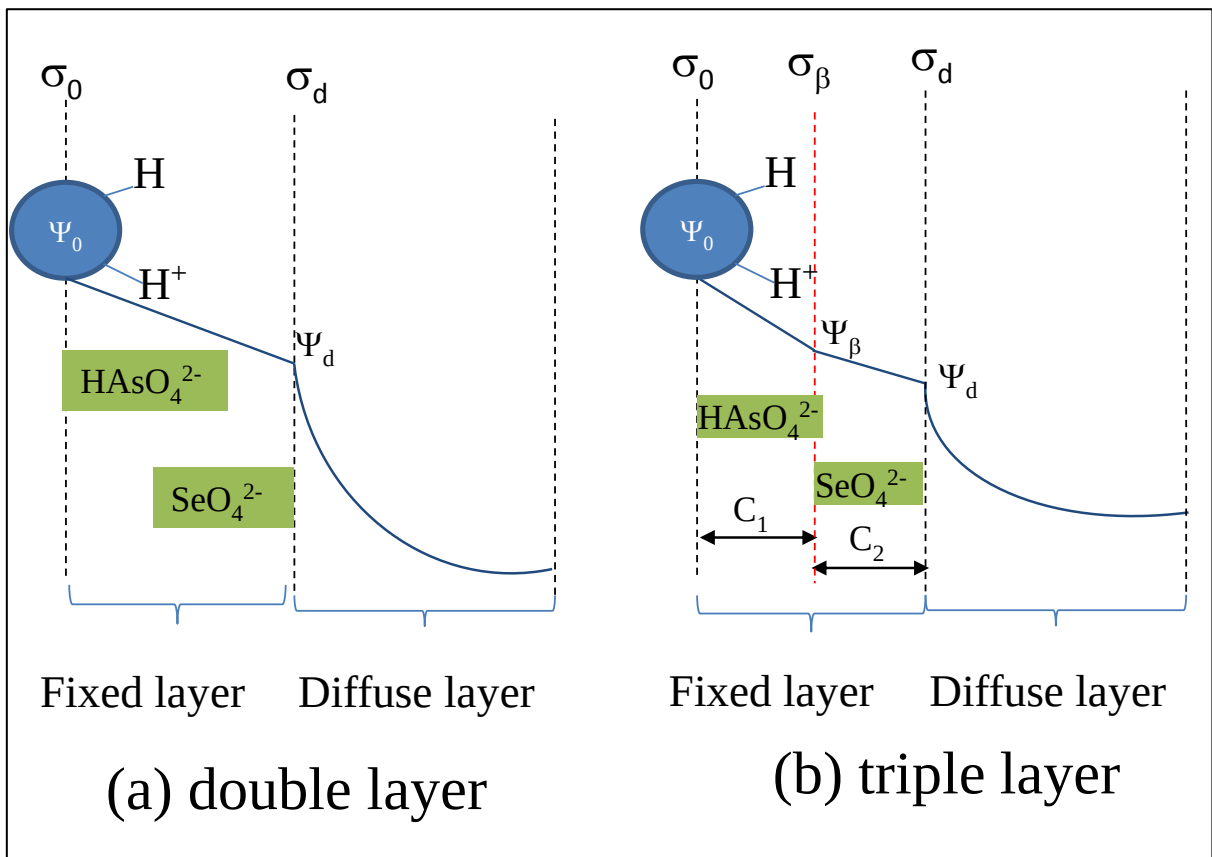


Figure 28. Diagrammatic representation of oxyanions adsorption. (a) double layer modeling (Koretsky 2000) and (b) triple layer modeling (Hayes et al. 1988; Sverjensky & Fukushima 2006b)

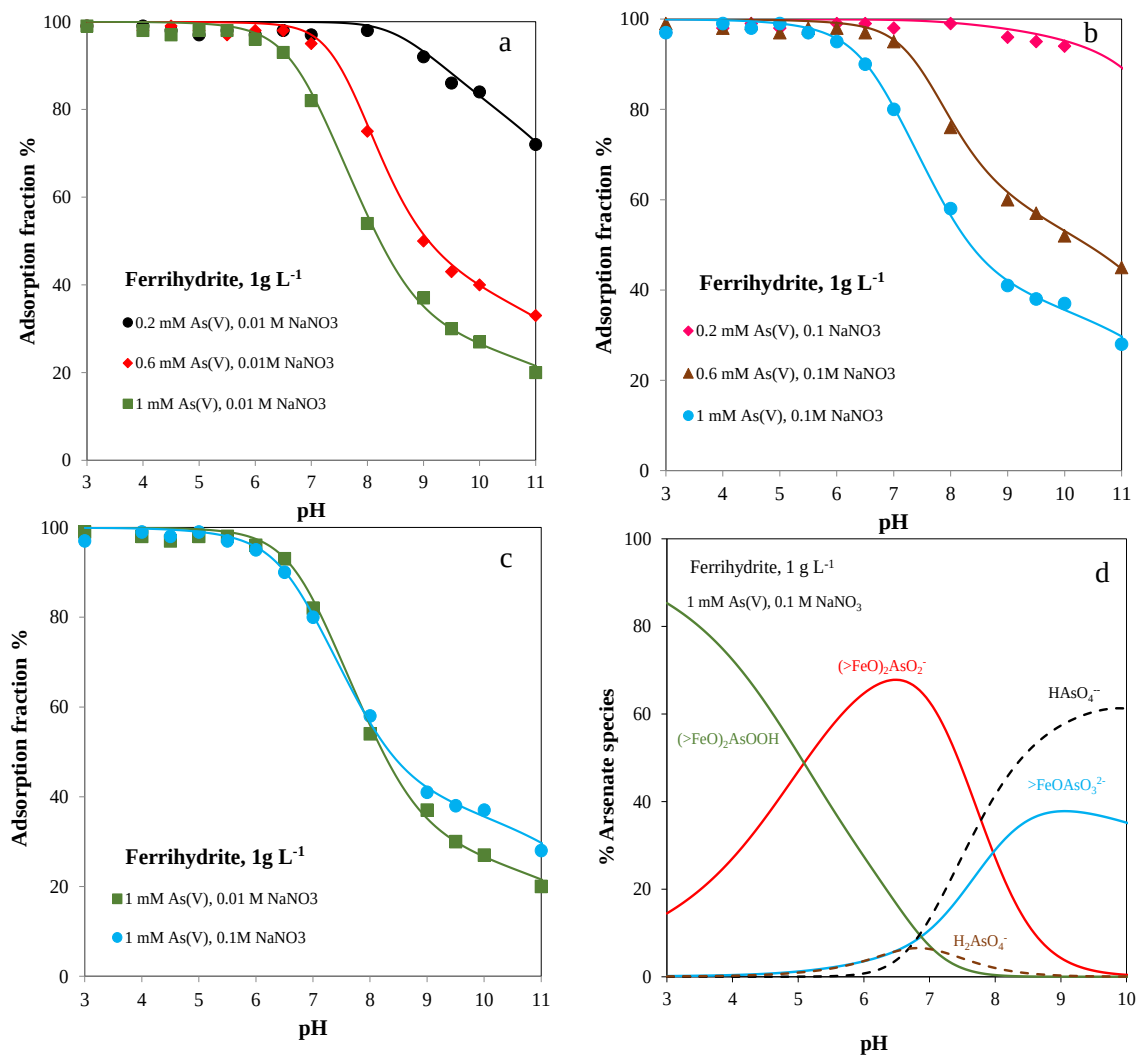


Figure 29. ETLM for ferrihydrite adsorption arsenate

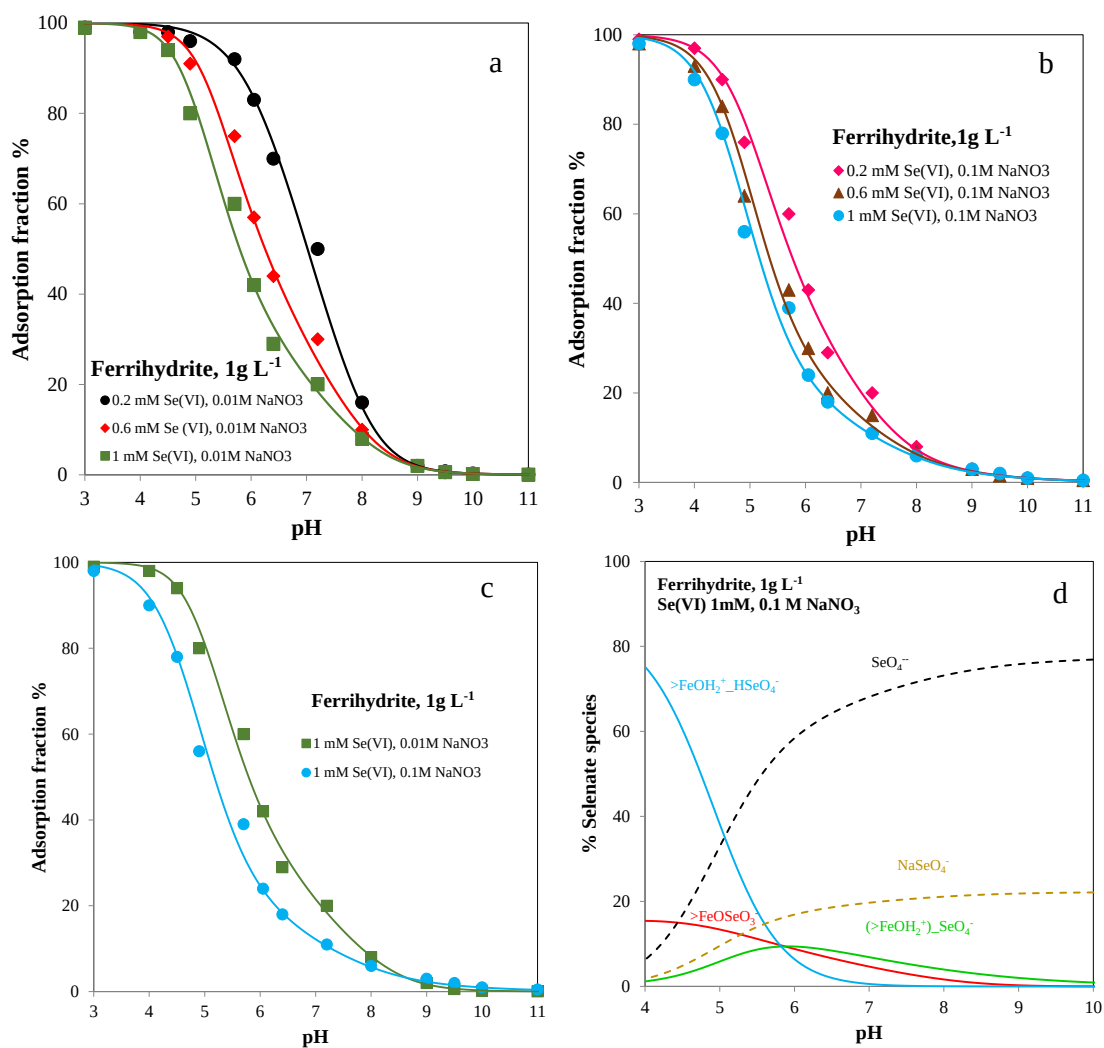


Figure 30. ETLM for ferrihydrite Selenate

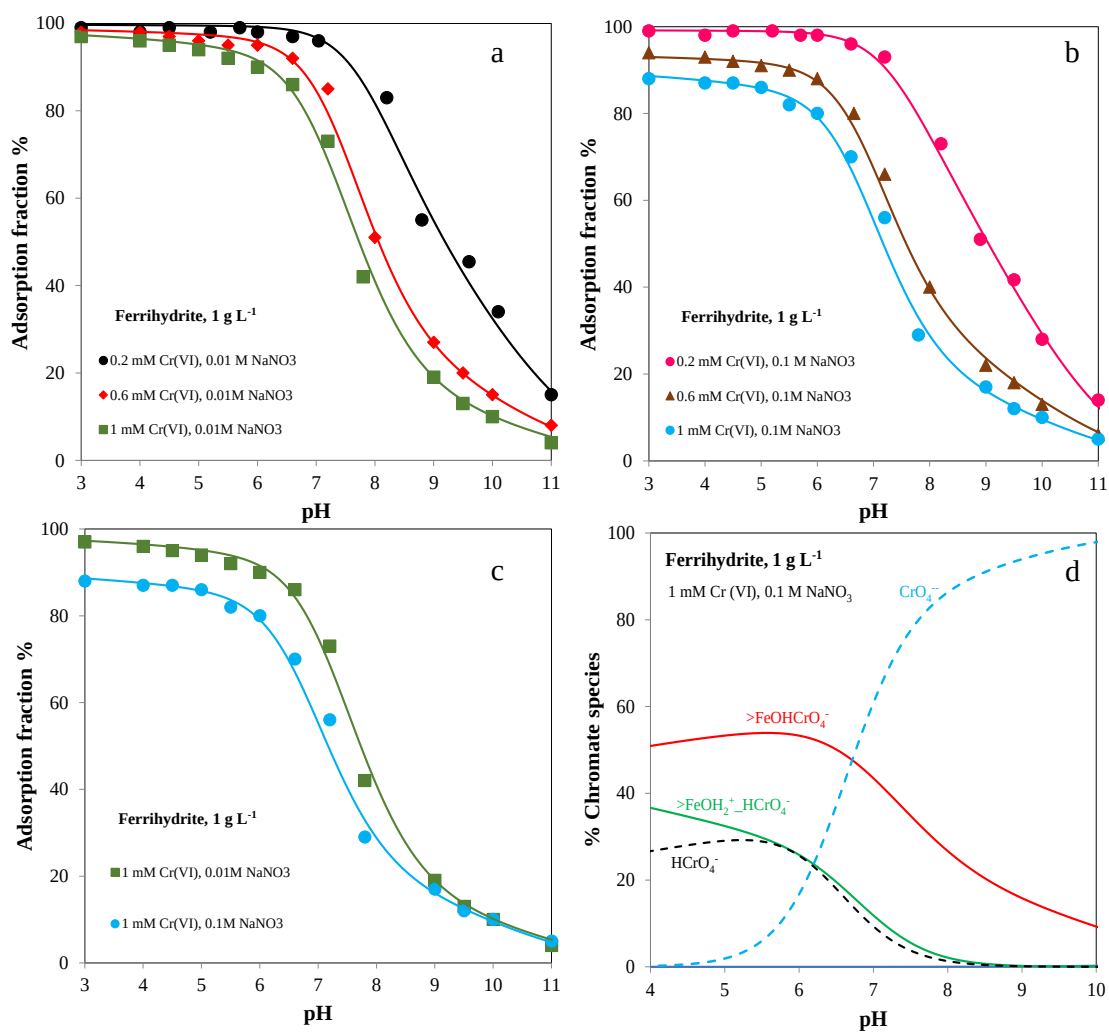


Figure 31. ETLM for ferrihydrite adsorption chromate

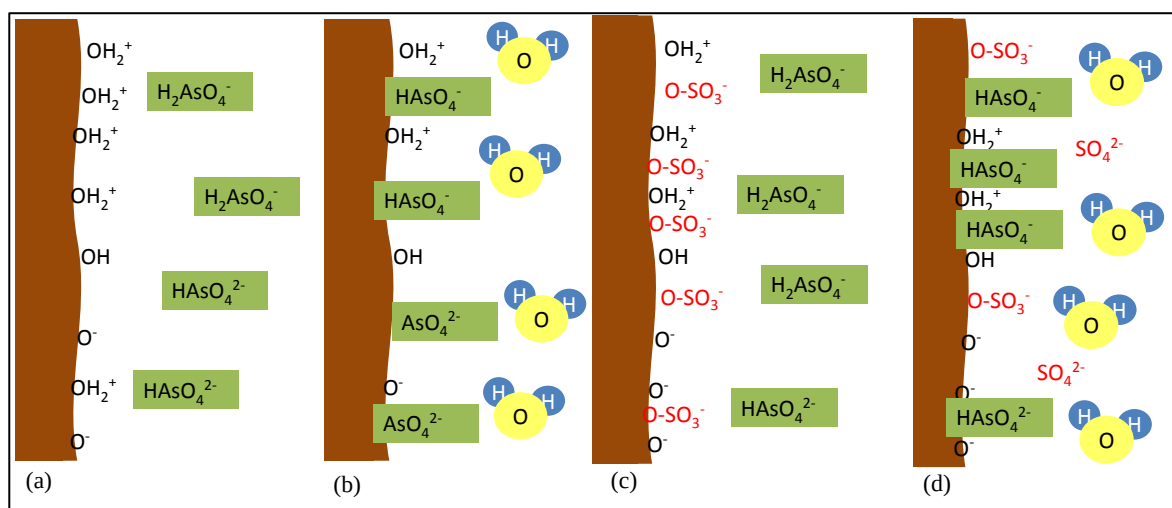


Figure 32. Comparison of ferrihydrite and schwertmannite surface. (a) ferrihydrite's surface, (b) ferrihydrite adsorbed oxyanions, (c) schwertmannite's surface and (d) schwertmannite adsorbed oxyanions.

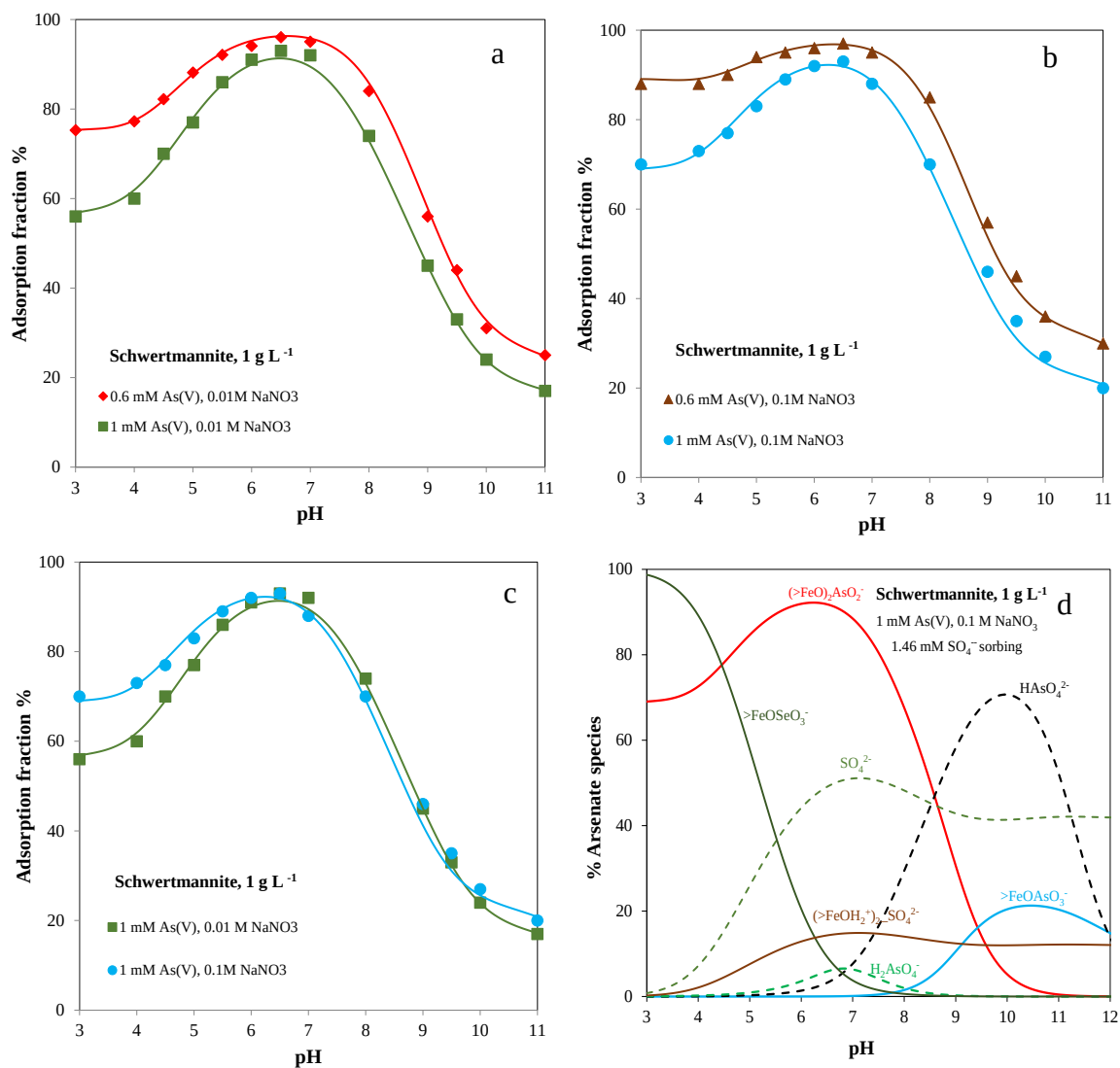


Figure 33. ETLM for schwertmannite adsorption arsenate

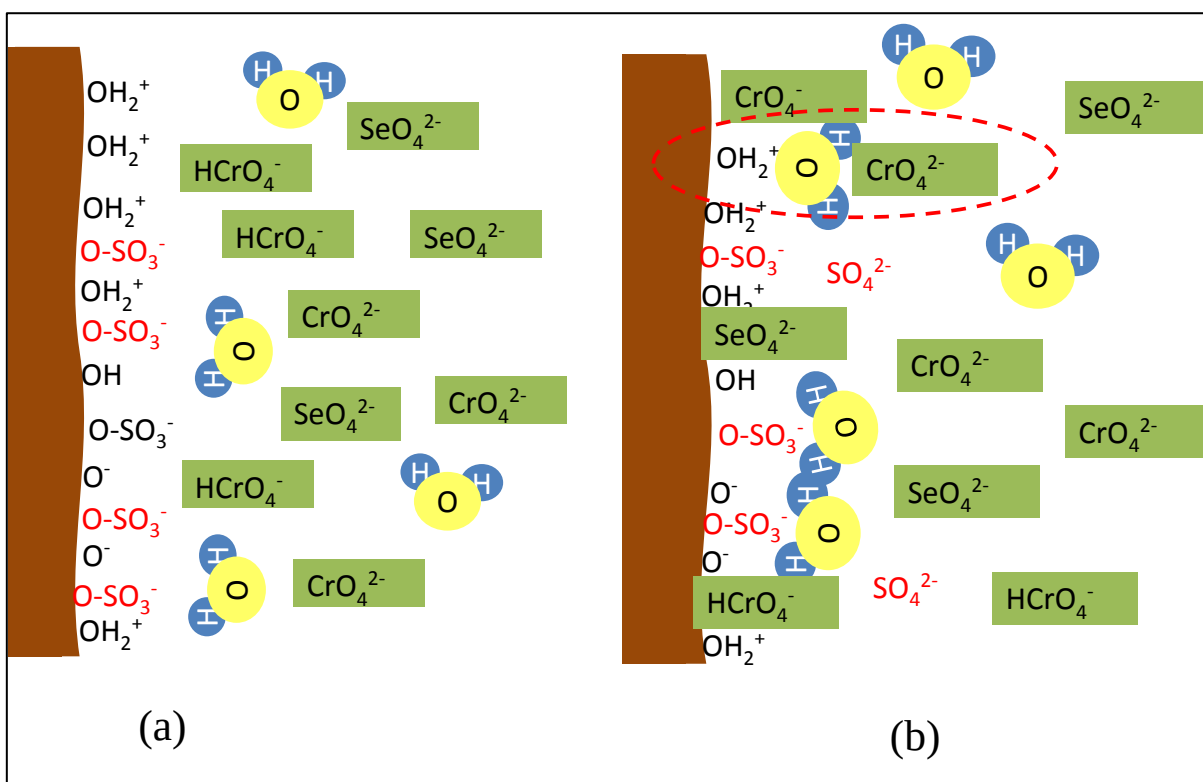


Figure 34. Oxyanions made competition adsorption on schwertmannite's surface. (a) schwertmannite's surface and (b) schwertmannite adsorption and competition of oxyanions with SO_4

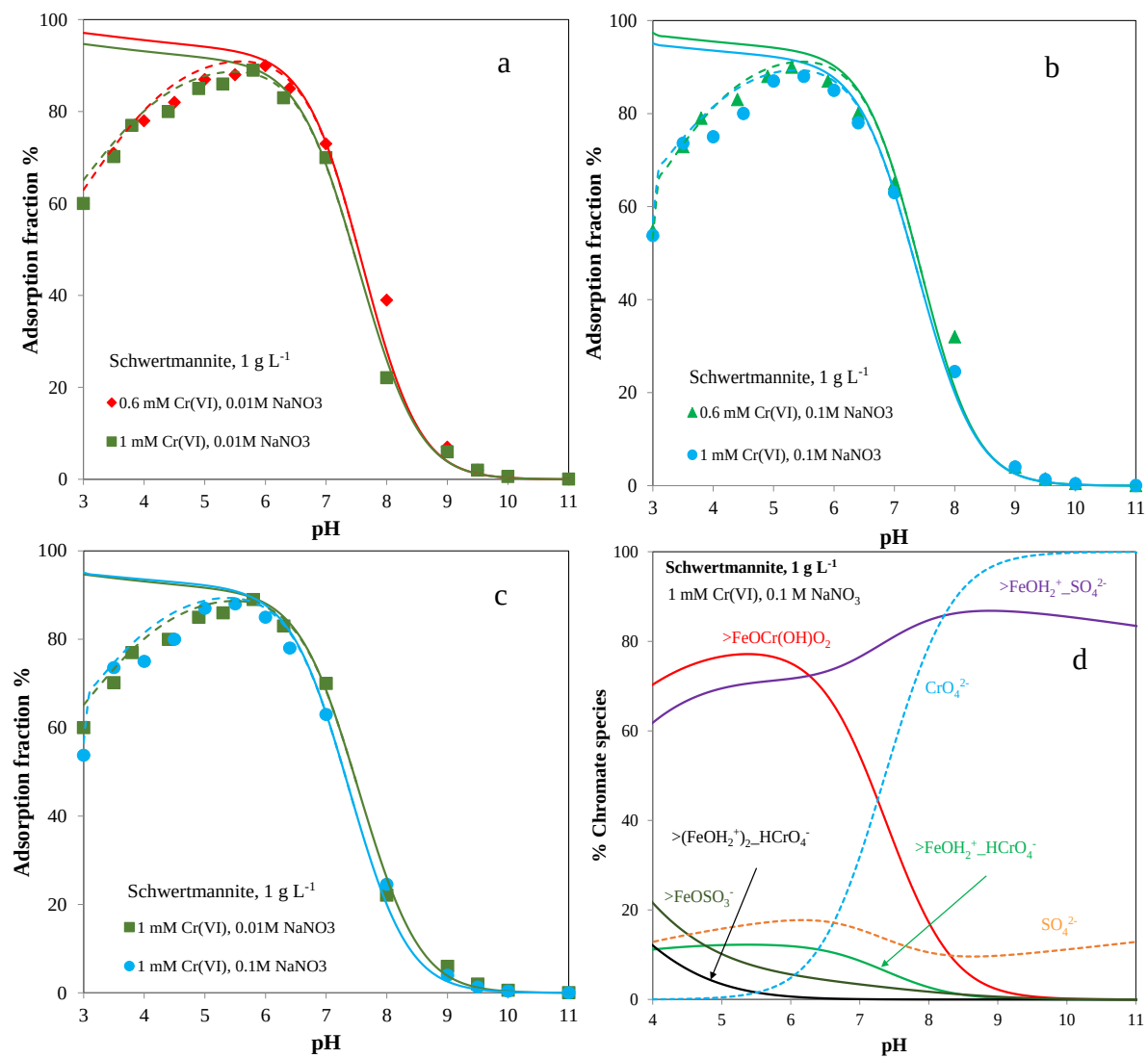


Figure 35. ETLM for schwertmannite adsorption chromate

Table 8. Aqueous protonation and aqueous complex formation constants for oxyanions at 25°C used in present study

Reactions	log K	Reference:
$\text{HSO}_4^- = \text{SO}_4^{2-} + \text{H}^+$	-1.98	(Shock et al. 1997)
$\text{HSeO}_4^- = \text{SeO}_4^{2-} + \text{H}^+$	-1.80	(Shock et al. 1997)
$\text{NaSO}_4^- = \text{SO}_4^{2-} + \text{Na}^+$	-0.88	(Fukushi & Sverjensky 2007b)
$\text{NaSeO}_4^- = \text{SeO}_4^{2-} + \text{Na}^+$	-0.88	(Fukushi & Sverjensky 2007b)
$\text{H}^+ + \text{CrO}_4^{2-} = \text{HCrO}_4^-$	6.53	(Dzombak & Morel 1990)
$2\text{H}^+ + \text{CrO}_4^{2-} = \text{H}_2\text{CrO}_4^0$	6.31	(Dzombak & Morel 1990)
$\text{H}^+ + \text{H}_2\text{AsO}_4^- = \text{H}_3\text{AsO}_4^0$	2.30	(Nordstrom & Archer 2003)
$\text{H}^+ + \text{HAsO}_4^{2-} = \text{H}_2\text{AsO}_4^-$	6.99	(Nordstrom & Archer 2003)
$\text{H}^+ + \text{AsO}_4^{3-} = \text{HAsO}_4^{2-}$	11.8	(Nordstrom & Archer 2003)
$\text{H}^+ + \text{H}_2\text{PO}_4^- = \text{H}_3\text{PO}_4^0$	21.7	(Dzombak & Morel 1990)
$\text{H}^+ + \text{HPO}_4^{2-} = \text{H}_2\text{PO}_4^-$	19.55	(Dzombak & Morel 1990)
$\text{H}^+ + \text{PO}_4^{3-} = \text{HPO}_4^{2-}$	12.35	(Dzombak & Morel 1990)

Table 9. Sample characteristics, surface protonation and electrolyte adsorption equilibrium constants, and capacitances used in present study

Solid	Salt (ml)	N_s^c (site nm ⁻²)	A_s^d (m ² g ⁻¹)	pH _{ZCP} ^e	ΔpK_n^{of}	$\log K_1^\theta$	$\log K_2^\theta$	$\log^* K_1^\theta$	$\log^* K_2^\theta$	$\log K_M^\theta$	$\log K_L^\theta$	$\log^* K_M^\theta$	$\log^* K_L^\theta$	C_l ($\mu\text{F cm}^{-2}$)	Reference
HFO	NaClO ₄	3.8	600	7.9	5.6	5.1	10.7	3.7	-12.1	4.3	4.5	-7.8	8.2	100	(Davis et al. 1978)
FH	NaCl	3.8	600	8.5	5.6	5.7	11.3	4.3	-12.7	4.0 ^f	4.0 ^f	-8.7	8.3	110	(Jain & Loeppert 2000)
FeOOH	NaNO ₃	2.3	27.7	8.5	5.6	6.5	12.1	6.2	-12.4	3.5	3.2	-8.9	9.4	120	(Dixit & Hering 2003)
FH ^g	NaNO ₃	3.8	600	7.9	5.6	5.1	10.7	3.7	-12.7	4.3	4.5	-7.8	8.2	100	(Davis et al. 1978a,b)
SCH ^g	NaNO ₃	15	300	6.9	5.6	4.1	9.7	2.4	-11.7	4.3	4.5	-7.1	6.9	100	(Sverjensky 2005)
Value of $\log K_1^\theta$, $\log K_2^\theta$, $\log K_{M+}^\theta$ and $\log K_{L-}^\theta$ refer to site-occupancy standard state for the reactions listed below. Value of $\log K_1^\theta$ and $\log K_2^\theta$, were predicted using the given values of pH_{ZCP} and ΔpK_n^θ. Values of $\log K_{M+}^\theta$, $\log K_{L-}^\theta$ and C_l were estimated from regression of proton surface charge data unless otherwise noted. Values for $\log^* K_{M+}^\theta$ and $\log^* K_{L-}^\theta$ refer to the hypothetical 1.0 M standard state and the reactions listed below. They were calculated from the values of $\log K_1^\theta$, $\log K_2^\theta$, $\log K_{M+}^\theta$ and $\log K_{L-}^\theta$ with the aid of Equation (30) to Equation (33) using the tabulated values of N_s, A_s, pH_{ZPC} and ΔpK_n^θ. ^a $\log K_1^\theta: >\text{SOH}+\text{H}^+=>\text{SOH}_2^+$; $\log K_2^\theta: >\text{SO}^-+\text{H}^+=>\text{SOH}$; $\log K_{M+}^\theta: >\text{SO}^-+\text{M}^+=>\text{SO}^-_M^+$; $\log K_{L-}^\theta: >\text{SOH}_2^++\text{L}^-=>\text{SOH}_2^+_L^-$ ^b $\log K_1^\theta: >\text{SOH}+\text{H}^+=>\text{SOH}_2^+$; $\log K_2^\theta: >\text{SO}^-+\text{H}^+=>\text{SOH}$; $\log^* K_{M+}^\theta: >\text{SOH}+\text{M}^+=>\text{SO}^-_M^++\text{H}^+$; $\log^* K_{L-}^\theta: >\text{SOH}+\text{H}^++\text{L}^-=>\text{SOH}_2^+_L^-$ ^c Values generated by regression of oxyanions adsorption data as a function of surface coverage. ^d Surface area from BET measurement ^e Zero point of charge taken from point of zero salt effect or reported point of zero charge (Sverjensky 2005) ^f Predicted theoretically (Sverjensky 2005) FH=Ferrihydrite, SCH=Schwertmannite															

Table 10. Equilibrium constants for As(V) adsorption, predictive by following previous work (Fukushi & Sverjensky 2007a)

Solid	ϵ_s	N_s	$\log^* K^0_{>FeOAsO_3^{2-}}$	$\log K^\theta_{>FeOAsO_3^{2-}}$	C_s	$\log^* K^0_{(>FeO)_2AsO_2^-}$	$\log K^\theta_{(>FeO)_2AsO_2^-}$	$\log^* K^0_{(>FeO)_2AsOOH}$	$\log K^\theta_{(>FeO)_2AsOOH}$	Adsorption data
HFO	1000	3.8	3.9	0.2	0.03	12.0	5.0	13.5	6.5	(Dixit & Hering 2003)
Ferrihydrite ^a	32	3.8	3.5	-0.8	2	10.4	4.0	12.0	5.6	(Jain & Loeppert 2000)
Ferrihydrite ^b	31.7	3.8	2.2	-1.5	1	8.7	3.2	10.6	5.1	This present study
Goethite	15	4.5	2.5	-3.6	0.234	12.6	2.8	13.9	4.1	(Dixit & Hering 2003)
SCH	50	15	1.8	-0.6	1	9.5	4.0	-	-	This present study
a The equilibrium constant from the previous work (Fukushi & Sverjensky 2007a)										
b The ferrihydrite in this present study, the dielectric constants was calculate theoretically (Sverjensky 2003; Sverjensky 2005)										
SCH= Schwertmannite										

Table 11. Equilibrium constants for Se(VI) and SO₄ adsorption, predictive by following previous work (Fukushi & Sverjensky 2007b)

Solid	ϵ_s	N_s	$\log^* K^0_{(>\text{FeOH}_2^+)_2\text{--SeO}_4^{2-}}$	$\log K^\theta_{(>\text{FeOH}_2^+)_2\text{--SeO}_4^{2-}}$	C_s	$\log^* K^0_{>\text{FeOSeO}_3^-}$	$\log K^\theta_{(>\text{FeOSeO}_3^-)}$	$\log^* K^0_{>\text{FeOH}_2^+\text{--HSeO}_4^-}$	$\log K^\theta_{>\text{FeOH}_2^+\text{--HSeO}_4^-}$	Adsorption data
HFO	1000	3.8	22.4	15.9	0.088	9.3	5.6	16.9	13.5	(Davis & Leckie 1978)
HFO	1000	3.8	21.5	14.8	0.0264	9.6	6.1	16.8	13.3	(Balistrieri & Chao 1990)
HFO	1000	3.8	20.4	13.9	0.088	10.5	6.8	15.8	12.1	(Hayes et al. 1988)
Ferrihydrite	31.7	3.8	20.3	14.8	1	9.6	6.1	15.8	12.1	Present study
	ϵ_s	N_s	$\log^* K^0_{(>\text{FeOH}_2^+)_2\text{--SO}_4^{2-}}$	$\log K^\theta_{(>\text{FeOH}_2^+)_2\text{--SO}_4^{2-}}$	C_s	$\log^* K^0_{(>\text{FeOSO}_3^-)}$	$\log K^\theta_{(>\text{FeOSO}_3^-)}$			
SCH	50	15	24.1	15.9	1	14	11.1	Present study		
a The equilibrium constant from the previous work (Fukushi & Sverjensky 2007a)										
b The ferrihydrite in this present study, the dielectric constants was calculate theoretically (Sverjensky 2003; Sverjensky 2005)										
SCH=Schwertmannite										

Table 12. Equilibrium constants for Cr(VI) adsorption, predictive by following previous (Xie et al. 2015)

Solid	ϵ_s	N_s	$\log^* K^0_{(>FeOH_2^+)_2-HCrO_4^-}$	$\log K^\theta_{(>FeOH_2^+)_2-HCrO_4^-}$	C_s	$\log^* K^0_{>FeOCr(OH)O_2}$	$\log K^\theta_{(>FeOCr(OH)O_2)}$	$\log^* K^0_{>FeOH_2^+-HCrO_4^-}$	$\log K^\theta_{>FeOH_2^+-HCrO_4^-}$	Adsorption data
HFO	1000	3.8	-	-	-	-	-	-	12.8	Zachara et al (1987)
Gothite	15	2.3	-	-	-	-	8.96	-	14.49	Grossl et al (1997)
A waste	-	2.31	-	-	-	-	13.39	-	-	Smith et al (2006)
Ferrihydrite	31.7	3.8	25.5	16.7	1	15.0	11.3	10.7	7.0	Present study
SCH (a)	50	15	17.0	10.5	1	11.3	8.9	10.5	8.1	Present study
SCH (b)	50	15	-	-	1	11.3	8.9	10.5	8.1	Present study
a The equilibrium constant from the previous work (Fukushi & Sverjensky 2007a)										
b The ferrihydrite in this present study, the dielectric constants was calculate theoretically (Sverjensky 2003; Sverjensky 2005)										
SCH (a) =Schwertmannite use 3 equations (model solid line), SCH (b)= Schwertmannite use 2 equations (model dush line)										

Chapter 5

General conclusion

The mineralogical and chemical characterization of schwertmannite and ferrihydrite are studied and better understand the adsorptions and post-adsorption behavior of both mineral by comparison in similar experiment conditions. As known well schwertmannite and ferrihydrite are iron (hydr) oxide mineral, which had ability to be as adsorbent for acid mine drainage and water treatment system. Both mineral is metal stable and will transform to stable phase as goethite. The stabilization is also important to more understand for both mineral. In this study was explain the detail in each chapter and for more conclusion in each chapter, as following here:

Chapter 2 described about many of oxyanions adsorption on schwertmannite and ferrihydrite. The result of the adsorption experiments shows the different and similarity of adsorption behavior such as selectivity of oxyanion adsorption was similar on ferrihydrite and schwertmannite decrease as the following order: arsenate $\geq$ phosphate $>$ chromate $\gg$ selenate. The adsorption mechanism on ferrihydrite and schwertmannite with arsenate, phosphate and chromate is different from that with selenate and sulfate. The change of zeta potential for ferrihydrite and schwertmannite before and after adsorption shown the changing of zeta potential, when decreasing of zeta potential consistant with previous work which explain the mechanism of oxyanion adsorption. Arsenate, phosphate might form inner-sphere complexes with the surface of ferrihydrite and schwertmannite. The different behavior is the selenate and sulfate ions form outer-sphere complexes with the surface of schwertmannite. Chromate in between arsenate and selenate with surface of schwertmannite assumed that chromate might make intermediate complexes. For ferrihydrite chromate and selenate might be made similar behavior as intermediate on ferrihydrite. Strong base anions such as arsenate and phosphate can form inner-sphere complexes, which induces a strong adsorption with ferrihydrite and schwertmannite as well as provides a high adsorption capacity

Chapter 3 the stability of ferrihydrite and schwertmannite was investigated by observation of XRD pattern before and after the adsorption. By following the result of XRD pattern, solubility curves were explained as lower solubility made the more stability of mineral surface. The result of XRD pattern of ferrihydrite before and after adsorption during our experiment there was not change peak to goethite. Even as explain in background, that ferrihydrite will change to stable phase as goethite and hematite. However, solubility of ferrihydrite is very lows

which already reported previously (Fukushi & Sato 2005). The authors were introduced modeling for stability of nanoparticle, from this theory could be useful for next future work for explain the stability of the mineral by using the solubility. The schwertmannite and schwertmannite after adsorbed many kinds of oxyanions with were investigated to determine the stability of the schwertmannite. The solubility of schwertmannite after the adsorption decreased in the following order: sulfate $\cong$ selenate $\gg$ chromate $>$ phosphate $>$ arsenate. The solubility of schwertmannite with different oxyanions was calculated with solid solution theory. The solubility of schwertmannite decreased after adsorption by oxyanions with high selectivity. The solubility of schwertmannite with arsenate and phosphate is lower by two orders of magnitude than that with sulfate. Therefore, oxyanions with high selectivity can stabilize schwertmannite by decreasing the solubility of schwertmannite after adsorption of the oxyanions. The similar characteristic of post adsorption is the oxyanions effected to the stabilization of both minerals. The different shown solubility of ferrihydrite is lower than schwertmannite's solubility. But in acidic condition to neutral condition schwertmannite's solubility decreased to similar with ferrihydrite's solubility.

Chapter 4 presented the theoretical method to explain the adsorption mechanism of oxyanions adsorption on the mineral surface of schwertmannite and ferrihydrite. But in this study, there is no information about evidence which conducted experiment by EXAFS and infrared microscopic experiment data for schwertmannite, the data was used from previous study which conducted for arsenate, phosphate and chromate on ferrihydrite. The input parameters for the model was theoretically predicted referring with the previous study. However, for this chapter, we more better understand the behavior of oxyanions adsorption on ferric oxide mineral such ferrihydrite and schwertmannite. When ferrihydrite containing SO_4 , it might be had surface potential in similar with synthetic schwertmannite, but the concentration of SO_4 containing is also important and might affected to adsorption capacities, in this study we could apply ETLM of ferrihydrite to that of schwertmannite for arsenate, phosphate and chromate. The information of this chapter could be a guideline for apply surface complexation for other kinds of ions onto schwertmannite

Base on this present study, schwertmannite's adsorption capacities is higher than ferrihydrite's adsorption capacities. For oxyanions, classified arsenate and phosphate are inner-sphere complexes, chromate, selenate and sulfate are intermediat complexes. From the solubility curves in Chapter 3, Ferrihydrite's solubility lower than schwertmannite's solubility indicate that ferrihydrite more stable than schwertmannite. Oxyanions were effected to stabilization of both minerals, which oxynions made inner-sphere comlexs in high adsorption capacities can change

the stabilization of mineral more stable when compare with the original minerals (Figure 36). In the natural is complex system, surface complexation model as ETLM is useful to predicted the adsorption capacities for oxyanions adsorption on ferrihydrite and schwertmannite. In the natural water treatment systems for both acid mine drainage and groud water system, schwertmannite is the appropriate material to use for water treatment system, because schwertmannite had high adsorption capacities and in the acid water the pH is low and schwertmannite can precipitate in low pH conditions. But to choose the materials are depending on excisting of the materials in the water treatment system site and the concentration of the toxic elements. In case of disposal site for materials, if used schwertmannite adsorption arsenate and phosphate, the disposal of adsorbent is safe. Base on the elementary graph of cation (Figure 37) and base on this studies result, other oxyanions which had similar properities such as arsenate and vanadate may have made inner-sphere complexes; selenate, manganate and chromate may have made intermediate complexes, but to better understand we need experiments to support this prediction. For oxyanions which made intermediate and outer-sphere complex we can consider to choose ferrihydrite and use surface complexation modeling to predict the concentration of adsorbents.

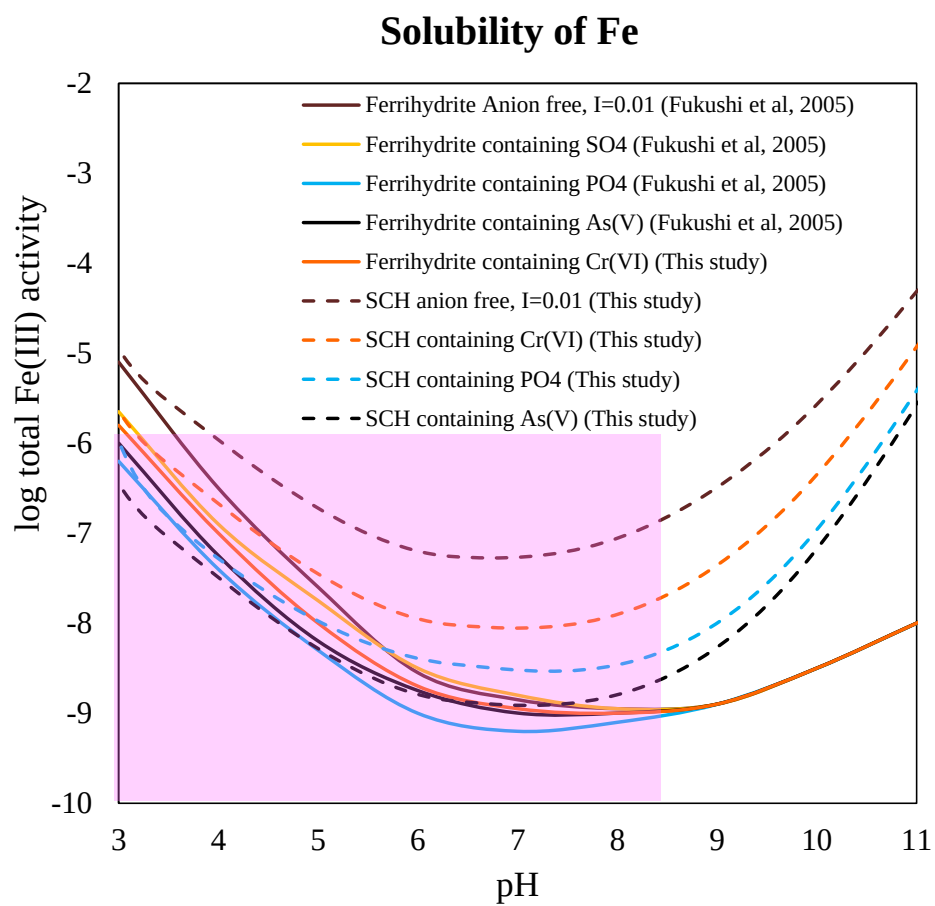


Figure 36. Oxyanions change stabilization of schwertmannite



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