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## Mineral Processing and Extractive Metallurgy Review: An International Journal

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gmpr20

# Arsenic Removal from Water by Adsorption Using Iron Oxide Minerals as Adsorbents: A Review

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Available online: 04 Jul 2011

To cite this article: Marisol Gallegos-Garcia, Kardia Ramírez-Muñiz & Shaoxian Song (2012): Arsenic Removal from Water by Adsorption Using Iron Oxide Minerals as Adsorbents: A Review, Mineral Processing and Extractive Metallurgy Review: An International Journal, 33:5, 301-315

To link to this article: http://dx.doi.org/10.1080/08827508.2011.584219

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### ARSENIC REMOVAL FROM WATER BY ADSORPTION USING IRON OXIDE MINERALS AS ADSORBENTS: A REVIEW

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This review highlights the adsorption process by using iron oxide minerals as the adsorbent for arsenic removal from water. It includes the characteristics of arsenic in water and its toxicities, the adsorption process for arsenic removal from contaminated water, iron oxide minerals as the adsorbent, arsenic adsorption capacity on iron oxide minerals, main factors of the adsorption, and arsenic removal from water by the adsorption process, as well as the mechanisms by which arsenic species adsorb on iron oxide minerals.

Keywords: adsorption, arsenic removal, iron oxide minerals

#### ARSENIC IN WATER AND ITS TOXICITY

#### Arsenic in Water

Arsenic occurs naturally in water in many parts of the world. Natural processes, including soil erosion, mineral leaching, and weathering, are responsible for introducing arsenic into surface water (Welch et al. 1988). Arsenic-enriched geothermal water can also significantly contribute to arsenic contamination in surface waters (Seong, Ujan, and Le Clech 2004). Drinking water is derived from a variety of sources depending on local availability: surface water (rivers, lakes, reservoirs, and ponds), groundwater (aquifers), and rainwater. These sources are very variable in terms of arsenic risk, among which groundwater has high concentration of arsenic (Smedley and Kinniburgh 2002).

Thermodynamic predictions provide a useful understanding of the equilibrium chemistry of inorganic arsenic species in water; see Figure 1. Arsenic is perhaps unique among the heavy metalloids and oxyanion-forming elements (e.g., As, Se, Sb, Mo, V, Cr, U, Re) in its sensitivity to mobilization at the pH values typically found in ground waters (pH 6.5-8.5) and under both oxidizing and reducing conditions. Arsenic can occur in the environment in several oxidation states (at the valences of -3, 0, +3, and +5), but in natural waters, it is mostly found in inorganic

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Figure 1 Equilibrium chemistry of inorganic arsenic aqueous species in the system As– $O_2$ – $H_2O$  at 25°C and 1 bar total pressure.

form as oxyanions of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)) (Ioannis and Zouboulis 2004). The mobility of As(III) was commonly considered to be greater than that of As(V), which has recently been successfully challenged. It remains true that iron oxyhydroxide phases probably play a key and complex role in controlling the mobility and fate of arsenic in groundwater. Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Under oxidizing conditions,  $H_2AsO_4^{1-}$  is dominant at low pHs (between pH 2.2 and 6.9), while at higher pHs,  $HAsO_4^{2-}$  becomes dominant. At extremely acidic and alkaline conditions, arsenic may be present as  $H_3AsO_4^{0}$  and  $AsO_4^{3-}$ , respectively. Under reducing conditions at pH less than 9.2, the uncharged arsenite species  $H_3AsO_3^{0}$  will predominate (Smedley and Kinniburgh 2002).

Several forms of arsenic undergo acid-base equilibrium; thus, different major and minor species are present depending on the pH. As(V) dissociates sequentially in water as follows:

$$H_3AsO_4 \leftrightarrow H^+ + H_2AsO_4^- \qquad pK_{a1} = 2.1 \tag{1}$$

$$H_2AsO_4^- \leftrightarrow H^+ + HAsO_4^{2-} \qquad pK_{a2} = 6.7 \tag{2}$$

$$HAsO_4^{2-} \leftrightarrow H^+ + AsO_4^{3-} \qquad pK_{a3} = 11.2$$
 (3)

#### Arsenic-Contaminated Water and Its Toxicity

Arsenic contamination of drinking water has been an increasing concern worldwide because of toxicity (Viet et al. 2003). This contamination is from mineral dissolution in mining sites, arsenical pesticides, disposal of fly ash, geothermal discharge, agricultural drainage waters from some soils in arid regions, and pyritic sedimentary rocks (mine drainage) in contact with the aquifer (Goldberg and Johnston 2001). It has been reported that many countries, including Bangladesh (Meng et al. 2001), New Zealand (Roddick-Lanzilotta, McQuillan, and Craw 2002), United States (Tempel et al. 2000), Italy (Frau and Ardau 2003), and Malaysia (Morgensen et al. 2001), are facing the problem of high-arsenic concentration in drinking water. Arsenic concentration in contaminated water was observed to range between 0.01 and 0.55 mg/l, while maximum arsenic levels reached 0.125 mg/l in sediment and 0.003 and 0.08 mg/l in fish and plant, respectively.

High concentration of arsenic in drinking water has resulted in signs and symptoms of arsenic poisoning, especially in developing countries, where millions of people are at acute risk. Inorganic arsenic species (As(III) and As(V)) have long been known for their toxic properties (Lafferty and Loeppert 2005). Long-term exposure to arsenic in drinking water can lead to cancer of the bladder, lungs, skin, kidney, nasal passages, liver, and prostate. Noncancer effects of ingesting arsenic include cardiovascular, pulmonary, immunological, neurological, and endocrine (e.g., diabetes) disorders. Besides its tumorigenic potential, arsenic has been shown to be genotoxic (Guo and Chen 2005). Primary route of exposure to arsenic in humans is ingestion. Exposure via inhalation is considered minimal, though there are regions where elevated levels of airborne arsenic occur periodically (Hering and Chiu 1998).

In 1958, an international guideline established an allowable level of 0.20 mg/l for arsenic in drinking water. However, the recognition of the harmful health risk of arsenic exposure has resulted in the standard being reduced to 0.05 mg/l and more recently to 0.01 mg/l.

#### **Processes for Arsenic Removal from Water**

Arsenic removal technologies that are commercially available, such as aeration, prechlorination, and sedimentation, do not comply with the proposed maximum contaminant level for arsenic (Kim et al. 2004). Therefore, many enhanced treatment processes have been developed to deeply eliminate arsenic from water. Precipitation/coprecipitaion process causes dissolved arsenic to form low-solubility solid minerals. Adsorption process for arsenic removal is realized through arsenic species on special solid adsorbents, such as activated carbon (Dambies et al. 2002). Ion exchange process uses synthetic resins to remove dissolved ions from water. Membrane separation process, including microfiltration, reverse osmosis, electrodialysis, ultrafiltration, and nanofiltration, has also proved to be effective for arsenic removal from water (Feenstra, van Erkel, and Vasak 2007). Biological process has attracted attention recently in this area (Johnston and Heijnen 2001). Among the possible treatment processes, adsorption is considered to be less expensive than membrane separation, easier and safer to handle as compared with the contaminated sludge produced by precipitation, and more versatile than ion exchange.

This review highlights arsenic removal from water by adsorption using iron oxide minerals as adsorbents, including the adsorption mechanism of arsenic on iron oxide minerals as well as techniques for studying the mechanisms.

#### ADSORPTION PROCESS FOR ARSENIC REMOVAL

Adsorption is a traditional process to separate solutes from solvent or gases, where the solute increases on the adsorbent surfaces and decreases in the solvent.

It can be classified into two categories: coagulation adsorption and ion exchange adsorption.

#### **Coagulation Adsorption**

In this process, colloidal solid particles in arsenic-contaminated water first aggregate through the addition of coagulants ( $Al^{3+}$  or  $Fe^{3+}$  ions) because the ions appear in the Stern layers of the colloidal particles in the form of hydrolyzed species. It is the same as the conventional electrolytic coagulation. Then, arsenate ions (As(V)) in water form ferric arsenate (FeAsO<sub>4</sub>) or aluminum arsenate (AlAsO<sub>4</sub>) with the hydrolyzed species in the Stern layers and thus adsorb on the coagulates. This step is also termed as precipitation or co-precipitation.

#### Ion Exchange Adsorption

Various solid materials, such as iron and aluminum hydroxide flocs, have a strong affinity for dissolved arsenic. Arsenic is strongly attracted to adsorption sites on solid surfaces and is effectively removed from solution. Ion exchange can be considered as a special adsorption, though it is often considered separately. Ion exchange involves the reversible displacement of an ion adsorbed onto a solid surface by a dissolved ion. Other forms of adsorption involve stronger bonds and are less easily reversed (Johnston and Heijnen 2001).

Adsorption process depends primarily on adsorbent. Effective adsorbents have a highly porous structure so that their surface area-to-volume ratio is very large (Jiang 2001). Various adsorbents (natural and synthetic origin) have been developed for arsenic removal from water, including polymer resins, activated carbon (Mohan and Pittman 2007), ion exchange resins (DeMarco, Gupta, and Greenleaf 2002), hydrous metal oxides such as activated alumina (Kartinen and Martin 1995), metal-loaded coral limestone (Ohki et al. 1996), hematite (Singh, Prasad, and Rupainwar 1996), sandy soils (Khulmeier 1997), lanthanum-loaded silica gel (Kumar, Pal, and Pal 2008), hydrous zirconium oxide (Suzuki et al. 1997), ferric hydroxides (Sperlich et al. 2005), etc. New adsorbents such as kaolinite acid complexes, activated red mud (Saada et al. 2003), ferruginous manganese ore (Chakravarty et al. 2002), and porous resin loaded with crystalline hydrous zirconium oxide (Suzuki et al. 2000) are currently being developed and evaluated (Seong, Ujan, and Le Clech 2004). Iron oxides have higher capacity for the adsorption of arsenic from water than activated alumina in fixed-bed systems (Leeuw and Cooper 2007).

Adsorption is generally considered as a promising method for arsenic removal. It is mainly affected by pH, adsorbent pretreatment, and the presence of others ions (sulfate, chloride etc). Organic components in aqueous solutions can decrease sharply the arsenic removal efficiency (Seong, Ujan, and Le Clech 2004; Carabante et al. 2009). This could be explained by the competitive effects of co-occurring solutes on the adsorption, such as surface complexation reaction. Phosphate ion is a typical competitor during arsenic adsorption because of its similar chemistry as As(V) (Hiemstra and Van Riemsdijk 1999). The parameters that affect arsenic removal by adsorption will be described in details later.

#### ADSORPTION OF ARSENIC ON IRON OXIDE MINERALS

#### Iron Oxide Minerals as Arsenic Adsorbents

The iron oxide minerals used as adsorbents of arsenic in water are goethite, hematite, siderite, limonite, ferrihydrite, and magnetite.

Goethite ( $\alpha$ -FeOOH) is an iron oxide mineral containing 62.9% Fe, 27% O, and 10.1% H<sub>2</sub>O. It consists of double bands of FeO(OH) octahedral, which share edges and corners to form a 2 × 1 octahedral tunnel partially bonded by H-bonds. It exhibits needle-shaped crystals with grooves and edges.

Hematite ( $Fe_2O_3$ ) consists of 70% Fe and 30% O. The structure is based on hexagonal closet packing of oxygen atoms with the cations in octahedral coordination (Klein and Hurbut 1993). Hematite is widely distributed in rocks of all ages and forms the most abundant and important iron ore.

Siderite (FeCO<sub>3</sub>) is frequently found as clay ironstone, impure by admixture with clay materials, in concretions with concentric layers (Klein and Hurbut 1993). Limonite (FeOOH  $\cdot n$ H<sub>2</sub>O) is a natural hydrous iron oxide mineral of uncertain identity.

The exact composition of ferrihydrite is uncertain, being variously given as FeO(OH),  $Fe_5O_6(OH)_3 \cdot 3H_2O$ ,  $5Fe_2O_3 \cdot 9H_2O$ , or  $Fe_2O_3 \cdot 2FeO(OH) \cdot 6H_2O$ . Ferrihydrite, a primary precipitate of iron-fixing bacteria or of the natural hydrolysis of iron salts in solution, is probably a precursor of goethite (limonite), feroxhyte, and many other iron minerals (Gaines et al. 1997).

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) is one of the most abundant and widespread of iron oxide minerals. It is often pseudomorphously altered to hematite or goethite (Gaines et al. 1997). Magnetite frequently occurs as octahedral crystals, with 22.4% Fe and 27.6% O (Klein and Hurbut 1993).

#### Adsorption Capacity of Iron Oxide Minerals

There are numerous reports on the adsorption capacity of iron oxide minerals in adsorbing arsenic. It has been found that goethite is the best iron oxide mineral for arsenic adsorption in water. Mamindy-Pajany et al. (2009) studied the adsorption of As(V) on commercial goethite in water as a function of pH and ionic strength. A strong As(V) retention on goethite appeared in acidic pH. There is no effect of the ionic strength on the adsorption of As(V) on goethite surfaces. Similar results were also obtained by Gimenez et al. (2007) for the adsorption of As(III) and As(V) on goethite in water. On a synthesized goethite, arsenic adsorption capacity of 5 mg/g was achieved at pH 5.0 (Mohan and Pittman 2007).

Asta et al. (2009) carried out batch tests to examine arsenic adsorption capacity on synthetic goethite at pH 1.5–2.5 with varying ionic strengths (0.02–0.15 mol/l NaCl). The arsenic adsorption on goethite fitted to a noncompetitive Langmuir isotherm. Ionic strength and pH had little effect on the adsorption capacity in lower pHs. Sulfate ion negatively affected arsenic removal from water since it competed with arsenate for the adsorption sites on goethite surfaces.

Hematite was also studied for As(V) removal from aqueous systems. The adsorption of As(V) on hematite fitted to the Langmuir isotherm (Singh, Prasad, and Rupainwar 1996). As(V) adsorption was favored electrostatically up to the

PZC (point of zero charge) of hematite (pH 7.1). At this point, specific adsorption predominated. The decrease in the extent of adsorption below pH 4.2 attributed to the dissolution of hematite and a consequent decrease in the number of adsorption sites.

Lafferty and Loeppert (2005) compared the adsorption and desorption behavior of As(V) and As(III) on a two-line ferrihydrite within the pH range from 3 to 11. It has been found that As(V) and As(III) strongly adsorbed on the iron oxide mineral. Generally, it is accepted that As(V) has a stronger affinity than As(III) for iron oxide surfaces. However, recent studies (Thirunavukkarasu, Viraraghavan, and Subramanian 2003) showed that at high initial arsenic concentration, As(III) more strongly adsorbed on ferrihydrite than As(V) throughout the pH range of 3–11. It has also been found that at relatively high arsenic concentration, arsenic adsorption on ferrihydrite was almost complete in a few hours (Raven, Jain, and Loeppert 1998). As(V) adsorption was faster than As(III) adsorption at low initial arsenic concentrations and low pH, while As(III) retained in much larger amounts than As(V) at higher pH (approximately > 7.5) or at high arsenic initial concentrations. The high As(III) retention was due to the fact that ferrihydrite was transformed to a ferric As(III) phase and not simply adsorbed at the surface.

Few researches have been carried out to use magnetite, siderite, and limonite as the adsorbent for removing arsenic from water. Viet et al. (2003) reported that the adsorption capacity of limonite for As(V) was about 900 mg/kg in adsorption column tests.

Figure 2 illustrates the adsorption capacity of As(V) and As(III) on goethite, hematite, and magnetite in aqueous solutions as a function of solution pH. The data in the graphs come from the reports made by Gimenez et al. (2007), Mamindy-Pajany et al. (2009), and Matis et al. (1997). It shows that the adsorption capacity decreased with increasing pH. Arsenic adsorption on goethite reached  $2 \times 10^{-6} \text{ mol/m}^2$ .

The adsorption kinetics of As(V) on goethite showed two regimes (Carabante et al. 2009). The first high adsorption rate might correspond to the adsorption of As(V) on more accessible sites of goethite external surfaces, whereas the low second adsorption rate might be related to the slow diffusion of As(V) into the pores of goethite particles. The adsorption of As(V) on hematite has been found to follow first-order kinetics (Singh, Prasad, and Rupainwar 1996).

#### Main Factors of Arsenic Adsorption on Iron Oxide Minerals

Solution pH affects significantly the speciation of arsenic in solution. The distribution of As(V) and its hydrolyzed species as a function of pH is shown in Figure 3. As(V) species are only stable in the corresponding pH ranges, for instance, pH < 2 for H<sub>3</sub>AsO<sub>4</sub>, pH 2–7 for H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>, pH 7–11 for HAsO<sub>4</sub><sup>2-</sup>, and pH > 12 for AsO<sub>4</sub><sup>3-</sup>. As(III) is stable at pH < 9 in the form of neutral H<sub>3</sub>AsO<sub>3</sub>, pH 9–12 in H<sub>2</sub>AsO<sub>3</sub><sup>-</sup>, pH 12–13 in HAsO<sub>3</sub><sup>2-</sup>, and pH > 13 in AsO<sub>3</sub><sup>3-</sup>, respectively (Liu and Zhang 2008). As it is known, the affinity of each arsenic species to iron oxide mineral surfaces is different in strength. Therefore, the capacity of chemical adsorption of arsenic on iron oxide mineral surfaces varies with the arsenic species and thus with solution pH. It has been found that As(V) adsorption on iron oxide minerals



Figure 2 Adsorption of As(V) and As(III) on various iron oxide minerals in aqueous solutions.

decreased with increasing solution pH and reached the maximum value at a very low pH (Gimenez et al. 2007), while As(III) adsorption on these materials had a maximum value around pH 8.5 (Goldberg 2002).

Surface charges on iron oxide mineral particles are also influenced by solution pH. The surfaces are negatively charged in the pH range above PZC. Accordingly, in the pH range above PZC, the adsorbent and the adsorbate are charged in the same sign, so there is electrostatic repulsion between arsenic species and iron oxide mineral surfaces, leading to the adsorption being weakened (Kosmulski et al. 2003).

The presence of competing anions would reduce the amount of arsenic adsorption on iron oxide minerals. For example, As(V) and As(III) adsorption on goethite was significantly reduced in the presence of phosphate ions, although some sites exhibited considerably higher selectivity for As(III) than for phosphate (Goldberg 2002).



Figure 3 Distribution of As(V) and the hydroxide species as a function of pH at 25°C.

The presence of other anionic components such as sulfate, chloride, or natural organic matters can also decrease sharply the arsenic removal efficiency by adsorption using iron oxide minerals as the adsorbent (Wilson et al. 2009). This could be explained by the competitive effects of co-occurring solutes on the arsenic adsorption, such as surface complexation reaction. Because of its similar chemistry with As(V) and its common presence in natural waters, phosphate is a typical competitor during arsenic adsorption (Kuan, Ujang, and Le-Clech 2004). In addition, the effects of oxyanions (such as phosphate, sulfate, carbonate, and silicate) on arsenic adsorption is complicated by not only competition for active sites but also by redox process and coprecipitation (Sharma and Sohn 2009).

#### Arsenic Removal from Water by Adsorption on Iron Oxide Minerals

Several kinds of iron oxide minerals have been studied for arsenic removal from contaminated water through adsorption. High arsenic removal has been achieved. Figure 4 illustrates arsenic (As(III) and As(V)) removal from water as a function of pH by using iron oxide minerals as adsorbents. The data in the graphs come from the reports made by Gimenez et al. (2007), Raven, Jain, and Loeppert (1998), Singh, Prasad, and Rupainwar (1996), and Mamindy-Pajany et al. (2009). Arsenic removal is maximum at acidic pH values and negligible at basic pH values. With hematite as the adsorbent, the maximum As(V) removal was close to 100% at pH 3–6 and 13.35-µmol/l arsenic concentration (Singh, Prasad, and Rupainwar 1996).

Guo, Stuben, and Berner (2007) performed batch and column tests to examine the capability of natural hematite to remove arsenic from drinking water. It was reported that the arsenic removal efficiency increased parallel to the decrease in grain size of hematite. Nitrate ion had no significant effect on the uptake of As(V), while phosphate greatly impeded the adsorption.



Figure 4 Arsenic removal as a function of pH by adsorption on various iron oxide minerals.

Natural siderite had similar characteristics as hematite as an adsorbent for arsenic removal from water but was more effective than hematite (Guo, Stuben, and Berner 2007).

Iron oxide minerals as adsorbents for arsenic adsorption in water are summarized in Table 1. As it is known, arsenic adsorption on iron oxide minerals correlates with the physical and chemical properties of the mineral powder, such as grain size, specific surface area, surface active sites, and surface micro-morphology. Therefore, the arsenic adsorption capacities presented in the table are different from each other.

#### MECHANISMS OF ARSENIC ADSORPTION ON IRON OXIDE MINERALS

As(V) adsorption on iron oxide minerals have been studied using the extended X-ray absorption fine-structure (EXAFS) technique (Sherman and Randall 2003). It is concluded that As(V) complexes in the form of bidentate binuclear inner spheres

				Table 1. Arsenic adsor	rption c	apacity	on iron e	oxide mineral	S		
			Solid	Initial arsenic			Surface		Adsor capacity	ption (mg/g)	
Adsorbent	Ηd	Size (mm)	(g/L)	(mol/L)	T (°C)	$\mathrm{pH}_\mathrm{pzc}$	$(m^2/g)$	Isotherm	As(III)	$A_{S}(V)$	Reference
Siderite	I	0.25, 0.50	2-40	$1.3  imes 10^{-5}$	20	I	I	Langmuir Freundlich	I	0.098	Guo, Stuben, and Berner (2007)
Hematite	I	0.25, 0.50	2-40	$1.3  imes 10^{-5}$	20	I	I	Temkin Langmuir Freundlich	I	0.204	
Hematite	4.2	I	I	$1.335  imes 10^{-5}$	30	7.1	14.40	Temkin Langmuir	Ι	0.20	Singh et al. (1996)
Synthetic	4.6, 9.2	I	I	$2 imes 10^{-4}  ext{-} 0.028$	I	8.5	202	Langmuir	266.5	111.02	Raven, Jain, and Loeppert
ferrihydrite								Freundlich Temkin			(1998)
Ferrihydrite	7	Ι	0.44	$0-2 imes 10^{-3}$	Ι	8	Ι	Langmuir	Ι	87.6	Lafferty and Loeppert (2005)
Goethite	7	I	0.44	$0{-5} imes 10^{-4}$	I	8.3	I	Langmuir	I	442.8	
Goethite	$2^{-10}$	0.01	4	$6.6 imes 10^{-6}$	I	6.9	11.61	I	I	0.500	Mamindy-Pajany et al. (2009)
Hematite	$2^{-10}$	0.053	4	$6.6 imes 10^{-6}$	I	8.1	1.66	I	I	0.500	
Synthetic	1.5 - 2.5	I	2.5	$3 \times 10^{-5}$ a $1 \times 10^{-2}$	22	Ι	29	Langmuir	Ι	15	Asta et al. (2009)
goethite											
Goethite	7.5	I	5	$10^{-6}, 10^{-3}$	I	6.8	7	Langmuir	0.374	0.449	Giménez et al. (2007)
Magnetite	6.5	0.1	5	$10^{-6}, 10^{-3}$	Ι	6.5	0.89	Langmuir	0.206	0.253	
Hematite	7.3	0.25	5	$10^{-6}, 10^{-3}$	Ι	6.7	0.38	Langmuir	0.265	0.827	



Figure 5 Schematic representation of arsenic complexes formed on iron oxide mineral surfaces.

(Figure 5) are the most thermodynamically favored and thus are the most abundant species on iron oxide surfaces. However, there are some contradictions regarding the formation of bidentate mononuclear and monodentate complexes, leading to As(V) adsorption on iron oxides not being fully understood. The formation of the bidentate binuclear complex has also been studied by FTIR (fourier transform infrared) spectroscopy on dry samples (Sun and Doner 1996). It showed that arsenic complexes were formed via hydroxyl groups at iron oxide surfaces. The proposed mechanism consists of two steps: formation of an inner-sphere monodentate surface complexes are defined as covalent linkages between the adsorbed ion and the reactive surface functional group (Manning, Fendorf, and Goldberg 1998). Inner-sphere surface complexes (such as  $\equiv$ Fe–OAsO<sub>3</sub>H<sup>-</sup>), or with 1:2 stoichiometry, forming bidentate complex (Hubbard 2002).

$$\equiv Fe - OH + HAsO_4^{2^-} \leftrightarrow \equiv Fe - OAsO_3H^- + OH^-$$
(4)

Most As(V) and As(III) oxyanions replaced two singly coordinated OH groups on iron oxide mineral surfaces to form binuclear bridging complexes Fe–O– AsO(OH)–O–Fe and Fe–O–As(OH)–O–Fe (Sun and Doner 1996). As(III) mainly reacted with doubly coordinated surface OH groups, whereas As(V) reacted with triply coordinated surface OH groups.  $HAsO_2^{2-}$  ion participates in ligand exchange reactions, displacing singly coordinated surface hydroxyl groups to adsorb on iron oxide minerals as a binuclear species (Lumsdon et al. 1984). Bidentate binuclear complexation remains the major bonding mechanism for As(V) adsorption on goethite. The three types of arsenate–goethite surface complexes also depend on the surface-covering oxides' age. At extremely low surface coverage, a ligand exchange reaction of  $H_2AsO_4^{2-}$  with surface OH groups formed the monodentate complex (Gao et al. 2006). At high surface loadings, the adsorption of As(V) was dominated by the formation of bidentate surface complexes after a second ligand exchange reaction occurred. As(V) forms inner-sphere bidentate complexes on both goethite and ferrihydrite. But, at very low surface coverage, monodentate complexes may form on crystalline goethite under the conditions. It has been found that the fraction of monodentate bonds decreased as the As(V) coverage for amorphous iron oxide minerals was increased and that the primary adsorptive complex was a bidentate binuclear bridging complex (Gao et al. 2006). The interaction between arsenic and iron oxide surface is highly dependent on pH and the arsenic species. Maximum As(V) adsorption occurred on ferrihydrite within the pH range of 3.5–5.5, while maximum As(III) adsorption was between pH 8 and 10. These trends have been attributed to the variable charge characteristics of both the iron oxide mineral surfaces and the arsenic species (Lafferty and Loeppert 2005).

It has also reported that the mechanism involves electrostatic attraction and surface complexation between the arsenic species in solution and Fe(II) and/or Fe(III) hydroxides on the minerals, which leads to the adsorption of arsenic on iron oxide above the PZC (Guo, Stuben, and Berner 2007).

Various techniques such as FTIR spectroscopy, ATR-FTIR (attenuated total reflection—Fourier transform infrared), XAS (X-ray adsorption spectroscopy), and SEM-EDAX (scanning electronic microscopy-energy dispersive spectroscopy) have been utilized for the studies of arsenic adsorption on iron oxide minerals. FTIR spectroscopy has been considered as a kind of direct means for investigating mechanisms of arsenic adsorption on iron oxide minerals. The specific adsorption of arsenic on the mineral surfaces involves ligand exchange reactions where the anions displace  $OH^-$  and/or  $H_2O$  from the surface and therefore changes in intensity of bands after and before the adsorption, which could be determined through FTIR spectroscopy (Zhang et al. 2003).

#### SUMMARY

It is an acceptable fact that iron oxide minerals are good adsorbents for arsenic adsorption in water in order to eliminate arsenic from contaminated water. They feature low costs and high efficiency of arsenic removal. The mechanism by which arsenic species adsorb on iron oxide minerals in water is mainly attributed to chemical adsorption through forming binuclear bridging complexes Fe–O–AsO(OH)–O–Fe on the minerals, as well as electrostatic attraction and surface complexation between the species and iron hydroxides on the minerals.

Of the iron oxide minerals, synthesized goethite showed the largest arsenic adsorption capacity, which might be attributed to the larger specific surface area. However, the operation cost is much higher for synthesized goethite than natural iron oxide minerals.

#### ACKNOWLEDGMENTS

The financial supports for this work from the Consejo Nacional de Ciencia y Tecnología (CONACyT) of Mexico under the grants 48436-Y and 92506 are gratefully acknowledged. Also, K. Ramirez-Muñiz would like to thank the CONACyT for the scholarship 225618 during her PhD studies.

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