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The adsorption of arsenic (V) by iron (Fe_2O_3) and aluminum (Al_2O_3) oxides

by

Youngran Jeong

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Civil Engineering (Environmental Engineering)

Program of Study Committee:
J. (Hans) van Leeuwen, Major Professor
Robert C. Brown
Timothy Ellis
Shihwu Sung
Roy R. Gu

Iowa State University

Ames, Iowa

2005

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Committee Member

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Major ~~Professor~~

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For the Major Program

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ABSTRACT

Arsenic (As), one of most toxic contaminants found in water, is well known to have adverse effects, such as skin cancer, on human health. The consumption of arsenic-contaminated water has led to human health crises in many countries such as Bangladesh, China, and even the western United States. The new Environmental Protection Agency (EPA) standard for arsenic in drinking water is 10 μg/L, and many smaller drinking water treatment plants are in need of additional treatment to achieve this standard. Recently, many researchers have been trying to find cost-effective and disposable adsorbents for the many small-scale water systems or individual ground wells that are used in most arsenic endemic areas. The adsorption of As(V) using iron- and aluminum-based adsorbents has been considered one of the most effective small-scale techniques for arsenic removal.

Two types of nonporous iron- and aluminum-based adsorbents were used in this dissertation: iron oxide (Fe_2O_3) from a byproduct of the steel industry, and aluminum oxide (Al_2O_3) as a chemical powder. Due to their fast adsorption of As(V) anions and low cost, Fe_2O_3 and Al_2O_3 were found to be good and cost-effective adsorbents in lowering As(V) initial concentrations in drinking water at a lower pH (< 7). In the presence of competing ions, the adsorption of As(V) on Fe_2O_3 was decreased by selenium (IV), vanadium (V), phosphate, and silica while that on Al_2O_3 was reduced by these same ions, and also by sulfate. The phosphate anion is the most competitive ion in As(V) adsorption with either Fe_2O_3 or Al_2O_3 as the adsorbent. When the cost and As(V) adsorption capacity of Fe_2O_3 and Al_2O_3 in the presence and absence of competing solutes are compared, Fe_2O_3 is the more cost-effective adsorbent for As(V) removal from drinking water.

CHAPTER 1. INTRODUCTION

Adsorption of arsenic (As) using metal oxides is considered effective removal technology in drinking water treatment because of its relatively low cost, reliable removal efficiency, and simplicity of installation and maintenance. It has been reported that many small-scale water systems or individual groundwater wells, which are spread out over most arsenic endemic areas such as China, Bangladesh, the eastern India, and the western United States, are facing difficulties in removing arsenic from drinking water efficiently and economically. Therefore, many researchers have focused on the development of effective adsorbents of As(V) for Point of Entry (POE) and Point of Use (POU) water treatment systems, such as small-scale commercial or individual home water treatment systems. Recently, the use of iron- or aluminum-based adsorbents as disposable adsorbent media is being considered as a good alternative for arsenic removal from drinking water. This study focuses on two concerns: (1) evaluation of the possibility of Fe_2O_3 and Al_2O_3 as effective adsorbents of As(V) for POE and POU water treatment systems, and (2) quantifying the effects of variables such as initial concentration of arsenic, dosage of adsorbents, pH, and competing solutes.

This dissertation comprises five chapters.

Chapter 2 presents a literature review on arsenic species, describing their characteristics, sources, and occurrences; their effects on human health; analytical methods used for identification and measurement of arsenic species; the available removal techniques for As(V) recommended by the US Environmental Protection Agency (US EPA); and adsorption of arsenic using various iron- and aluminum-based adsorbents—a necessity in developing new adsorbents. Additionally, the basic theories of adsorption, such as adsorption isotherm models and kinetic mechanisms, are discussed. The objectives of this chapter are based on two premises: (1) the necessity for removing arsenic from drinking water and (2) the availability of iron- and aluminum-based adsorbents as effective adsorbents for the removal of As(V).

Chapter 3 describes the evaluation of Fe_2O_3 and Al_2O_3 as potential arsenic (V) adsorbents in water. Fe_2O_3 is introduced as a new and cost-effective adsorbent of arsenic (V) compared with Al_2O_3, which has characteristics similar to those of Fe_2O_3. The properties of Fe_2O_3 and Al_2O_3 are described and the experimental apparatus and procedures used in this study are explained. Chapter 3 also summarizes the results obtained under various conditions for the best operational protocols, the As(V) adsorption capacities of Fe_2O_3 and Al_2O_3, and the kinetic mechanism of these adsorbents.

Chapter 4 presents an investigation into the effect of competing solutes such as chloride, nitrate, sulfate, selenium(IV), vanadium(V), phosphate and silica on As(V) adsorption using Fe_2O_3 and Al_2O_3. The chapter includes a discussion of the various chemicals used for competing solutes and of the instruments for identifying and measuring the components of solutes. It also describes the comparison of the As(V) the removal efficiency and adsorption capacity of Fe_2O_3 and Al_2O_3 with and without competing solutes, and suggests mechanisms of solute competition with Fe_2O_3 and Al_2O_3 in As(V)-contaminated water.

Finally, Chapter 5 presents a general conclusion, including the results from Chapters 3 and 4. It also provides few recommendations for future research and for the application of Fe_2O_3 in practical water treatment systems.

CHAPTER 2. LITERATURE REVIEW:

OCCURRENCE OF ARSENIC AND ADSORPTION OF As(V) USING IRON- AND ALUMINUM- BASED OXIDES

2.1 PROPERTIES OF ARSENIC

Elemental arsenic is yellow or metallic gray in color, very brittle, and not soluble in water, and it has a semi-metallic crystalline structure. Arsenic smells of garlic in air and oxidizes to arsenous oxide on heating. Arsenic and its compounds are poisonous (Buchanan, 1962; Ferguson and Gavis, 1972). Table 2.1 summarizes the physical properties of arsenic. Arsenic has various industrial applications. It is used in bronzing and making agricultural pesticides and insecticides. It is used as a doping agent in solid-state devices such as transistors. It is also used as a laser material to transform electricity directly into coherent light (LANL, 2004).

Table 2.1. Physical properties of arsenic

Atomic symbol	As
Classification	Metalloid
Color	Gray
Crystal structure	Rhombohedral
Density @ 293 K	5.72 g/cm^3
Atomic mass	74.9216
Atomic number	33
Electronic configuration	[As]$4s^2 3d^{10} 4p^3$
Oxidation states	5, 3, 0, -3
Atomic radius	125 pm
Melting point	~817°C
Boiling point	603°C (sublimation)

Arsenic exists in both organic and inorganic forms. Arsenic combined with carbon and hydrogen is referred to as organic arsenic. In general, organic arsenic is found in marine animals and plants such as seaweed. Monomethyl arsenic acid (MMAA), dimethyl arsenic acid (DMAA), and arseno-sugars are some examples of organic arsenic compounds (NAS, 2001). Arsenic combined with at least one other element like oxygen, chlorine, or sulfur, but no carbon is referred to as inorganic arsenic (US NLM, 2003).

Inorganic arsenic exists in four main oxidation states, of which +3 [As(III)] and +5 [As(V)] are the most common. The existence of arsenic in a specific oxidation state in the hydrosphere depends on various environmental factors such as reduction-oxidation reactions, pH conditions, general hydrochemistry, microbial activity, and other ionic distribution states, but the concentration of arsenic species mainly depends on redox potential and pH (Masscheleyn et al., 1991; Dzombak and Morrel, 1990; Hering et al., 1996). Figures 2.1 and 2.2 show the distribution of the arsenic species as functions of redox potential (Eh) and pH, respectively (Ghimire et al., 2003; Brookins, 1988; Yan et al., 2000). As shown in the figures, under reducing conditions arsenite [As(III)] is the dominant form; however, arsenate [As(V)] is generally the thermodynamically more stable form in well-oxygenated environments. The major As(V) species is $H_2AsO_4^-$ at a pKa of 6.9 and $HAsO_4^{2-}$ at higher pH; however, both species of As(V) exist at the intermediate region (between pH 6 and 8). The dominant As(III) species is arsenious acid (H_3AsO_3) at a pKa of pH 9.3. Based on the typical pH of 6 to 8.5 in groundwater (CEES, 2005), the main arsenic species should be changed from arsenite to arsenate anions, specifically $HAsO_4^{2-}$, depending on oxidation conditions.

2.2 SOURCES AND OCCURRENCE OF ARSENIC

Arsenic combined with other metals such as arsenical irons ($FeAs_2$ and Fe_4As_3) or

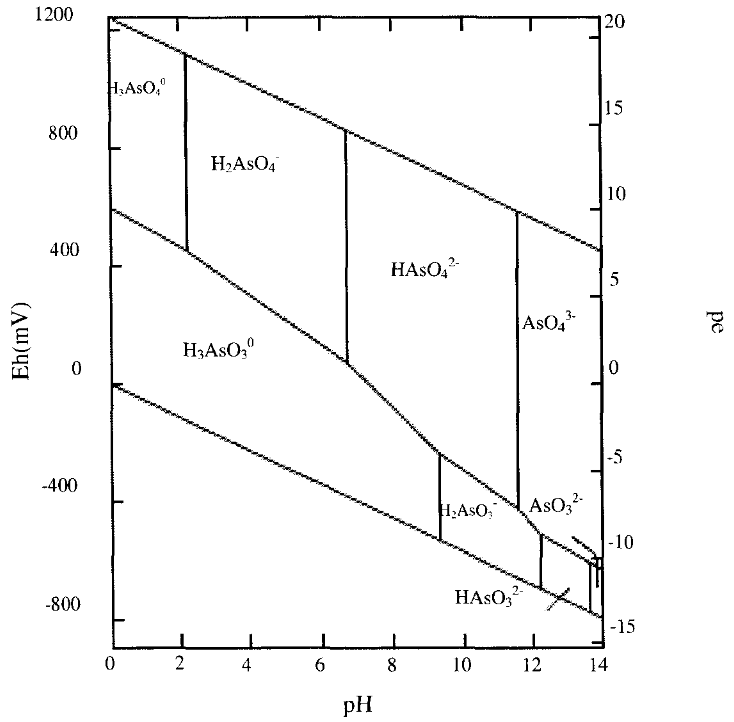

Figure 2.1. Eh-pH diagram for aqueous As species in the system As–O_2–H_2O at 25°C and 1bar total pressure (Brookins, 1988; Smedly and Kinniburgh, 2002)

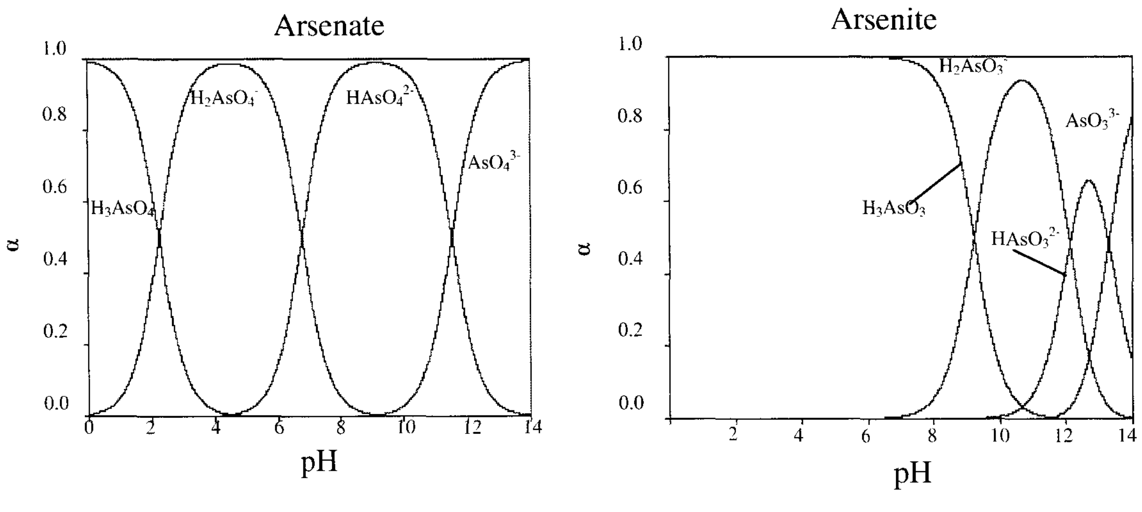

Figure 2.2. Distribution of arsenate and arsenite as a function of pH (Ghimire et al., 2003)

arsenical pyrites (FeSAs) exists in small quantities in crystalline rocks (Buchanan, 1962; Smedley and Kinniburgh, 2002). Volcanic eruptions and forest fires are other natural sources of arsenic.

Arsenic is also a by-product of some anthropogenic activities including mining; smelting; petroleum refining; manufacturing of pharmaceuticals, glass, and cement; combustion of fuels and wastes; pulp and paper production; insecticides; pesticides; landfill leaching; and wood preservation (Nordstrom and Alpers, 1999; US EPA, 1999; Murphy and Guo, 2003). The US Environmental Protection Agency (US EPA) reported that approximately 8 million pounds of arsenic and arsenic containing compounds such as mine tailings, herbicides, and wood preservatives were distributed into the environment in 1997. In addition, 90% of all arsenic consumed in the United States came from one chemical wood preservative, chromated copper arsenate (CCA). This preservative was used to protect wood from decaying due to insects and microbial agents (US EPA, 2005).

Arsenic is released into groundwater or surface water through erosion, dissolution, and weathering (Ferguson and Gavis, 1972; Reynolds et al., 1999). For example, ferric arsenate ($FeAsO_4$) is distributed into the hydrosphere in less than a week under a reduction and dissolution environment (Deuel and Swoboda, 1972).

Arsenic concentrations in ground or surface water vary from 0.01 to more than 500,000 μg/L depending on the physical and hydrogeological environment, based on the data of some researchers (Smedley and Kinniburgh, 2002). Large aquifers with higher concentrations of arsenic (over 50 μg/L) are found in some parts of the world such as Bangladesh, India, China, Chile, Taiwan, and the western United States. Arsenic concentrations in groundwater in the alluvial and delta aquifers of Bangladesh and West Bengal vary from less than 0.5 to 3200 μg/L (BGS, 2001). Wickramasinghe et al. (2004) reported that the average arsenic concentration of well water at Sonargaon in Bangladesh was 138 μg/L. According to Wang and Huang (1994), deep groundwater of the Tianshan plains in China contains arsenic at a maximum concentration of 2400 μg/L. Some researchers found that arsenic concentrations in groundwater in Taiwan vary from 10 to 1820 μg/L (Tseng et al., 1968; Kuo, 1968). Although arsenic concentrations in US source waters are generally low, some investigators have reported that the arsenic concentration is high in the water of some special environments such as mining tails, lake sediments, volcanic deposits, hydrothermal inputs, and underground aquifers (Welch et al., 1998; Welch and Lico, 1988; Mok and Wai, 1990; Judy et al., 2004).

Figure 2.3 shows areas in the United States where at least 25% of the ground samples were found to have arsenic concentrations above a specified level. Orange and red colors on the map indicate the areas where more than 25% of the groundwater samples exceeded the revised arsenic maximum contamination level (MCL) of 10 ppb (USGS, 2000). In addition, the US EPA reported that over 6% of the community water systems (CWS) in many western states, Michigan, and some New England states have mean arsenic concentrations above the revised MCL (US EPA, 2000).

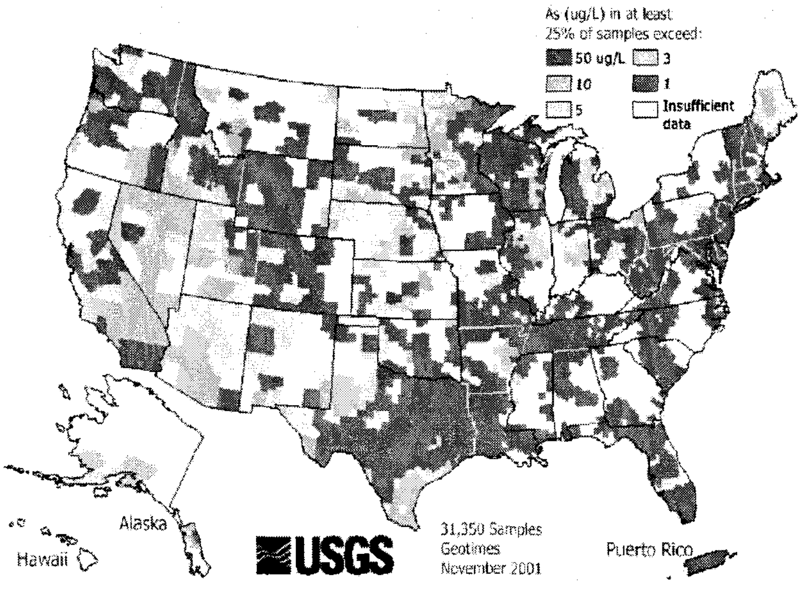

Figure 2.3. The areas in the United States where at least 25% of the ground samples will have arsenic concentrations above a specified level (USGS, 2000).

2.3 ENVIRONMENTAL TRANSPORT AND DISTRIBUTION

Arsenic is released into the atmosphere from fossil-fuel combustion power plants, smelter operations, burning vegetation, volcanism, and other high-temperature processes (LANL, 2004). The above mentioned operations emit arsenic primarily in the form of As_2O_3 adsorbed on particulate matter (Cullen and Reimer, 1989). These particles are dispersed by the wind and are returned to the earth by wet or dry deposition. According to Nriagu and Pacyna (1988), about 70% of the global atmospheric As flux comprises approximately 18,800 tons/acre of atmospheric arsenic from anthropogenic sources. Although not enough is known about the effects of airborne As compounds on the overall As cycle, these anthropogenic sources are still regarded as important contributors to airborne As compositions.

In addition, arsines are known to release as biomethylate arsenics, from many activities of microorganisms (bacteria, molds, and yeasts) and animals present in soils or sediments, which on oxidation in the air reconvert to both volatile (e.g., methylarsines) and nonvolatile (e.g., methylarsonic acid and dimethylarsinic acid) arsenic compounds and settle back to the ground (Bentley and Chasteen, 2002). Furthermore, wind and water erosion weathers away rocks and soils, resulting in the transportation of these arsenic compounds. Many arsenic compounds tend to adsorb to soils, which on leaching usually results in transportation over short distances within soils. Figure 2.4 depicts the arsenic cycle in a mining environment (Bowell and Parshely, 2002). Mining does not produce arsenic directly; however, the primary host mineral containing arsenic is sometimes unstable. The unstable host mineral emits arsenic on oxidation or weathering in certain condition such as dumping or heaping of waste rock associated with arsenic. Also, when As-hosting ore is chemically treated (for example, smelting) prior to the extraction of the ore element, the arsenic composition may be released from its matrix, and in this form it becomes mobile.

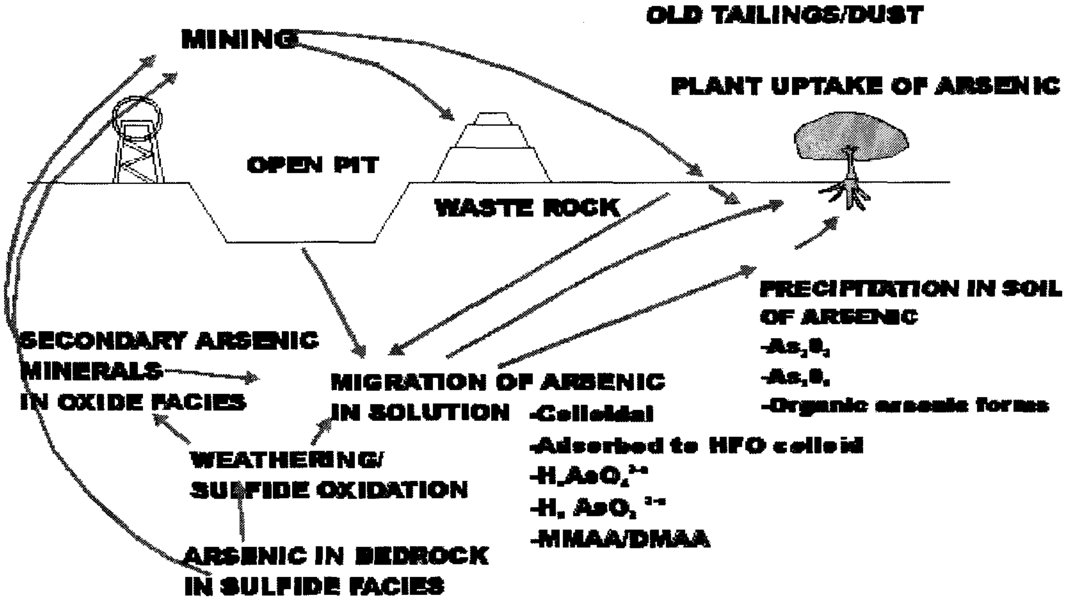

Figure 2.4 Arsenic cycling in mining environment (Bowell and Parshely, 2002).

2.4 PREOXIDATION OF As(III) TO As(V)

As(V), bearing a negative charge, is more efficiently removed by metal oxidation than As(III), which exists in neutral form in groundwater. As(V) can be removed easier and faster than As(III) in water treatment systems. In addition, As(III) is gradually changed to As(V) in the presence of O_2 from air.

Based on the above, a preoxidation step is required to convert As(III) to As(V) to remove arsenic from drinking waters with higher concentrations of As(III). Many different oxidizing agents such as oxygen, ozone, free chlorine, hypochlorite, permanganate, and hydrogen peroxide can be used for the oxidation of As (III) to As (V) (Oscarson et al., 1983; Frank and Clifford, 1986; Lauf and Waer, 1993). Recently, the US EPA has reported that chlorine, potassium permanganate, and ozone are useful oxidants for oxidizing As(III) to As(V); however, use of chlorine as a disinfectant should be restricted as it results in the production of unwanted by-products and membrane fouling in some water treatment facilities using various processes such as reverse osmosis (Clifford, 2003; US EPA, 2001b). Equations (1), (2), and (3) describe the oxidation reactions for some of the most commonly used oxidizing agents for the oxidation of As(III) to As(V).

$$2H_3AsO_3 + O_2 \Leftrightarrow 2H_2AsO_4^- + 2H^+ \tag{1}$$

$$H_3AsO_3 + HClO \Leftrightarrow HAsO_4^{-2} + Cl^- + 3H^+ \tag{2}$$

$$3H_3AsO_3 + 2KMnO_4 \Leftrightarrow 3HAsO_4^{-3} + 2MnO_2^- + 2K^+ + 4H^+ + H_2O \tag{3}$$

Pierce and Moore (1982) stated that oxidation of arsenite to arsenate takes weeks in basic solution before considerable air oxidation occurs.

2.5 HEALTH EFFECTS

In general, organic metal compounds such as tin, mercury, and lead (simple methylated species) tend to be more harmful than the respective inorganic species. However, inorganic arsenic compounds are known to be 100 times more toxic than organic arsenic compounds (Ferguson and Gavis, 1972; Prange and Jantzen, 1995). It is said that the toxic level of variable arsenic species is in the following order: arsenite > arsenate > monomethylarsenate (MMA) > dimethylarsenate (DMA) (Penrose, 1974; Stugeron et al., 1989).

Arsenic toxicity is of two types, acute and subacute. The main sources of acute arsenic poisoning are contaminated food or drink. The symptoms of acute arsenic poisoning include burning sensation and dryness of mouth and throat, muscular cramps, projectile vomiting, and diarrhea (Done and Peart, 1971). The symptoms of subacute arsenic poisoning mainly link to cardiovascular, pulmonary, immunological, and neurological effects. Long-term exposure causes loss of hair, brittle nails, and darkened skin exfoliation (Holmquist, 1951; Pinto and McGill, 1953). Specifically, long-term exposure to arsenic-contaminated water causes various diseases such as cardiovascular diseases and conjunctivitis. In addition, many researchers revealed the relationship of arsenic to cancers of the bladder, lungs, kidney, nasal passages, liver, and prostate, as well as to skin cancer and Blackfoot disease according to several researchers' reports (Tseng et al., 1968; Wu et al., 1989; Chen et al., 1992; Smith et al., 1992). In addition, Csanady and Straub (1995) reported that high concentrations of arsenic in drinking water lead to an increase in stillbirths and spontaneous abortions.

Figures 2.5 and 2.6 show symptoms of gangrene and actinic keratosis. In gangrene, tissues in a specific part of the body die due to infection. The infection can be due to injury and subsequent contamination with bacteria, or lack of blood flow. An actinic keratosis (AK), also known as a solar keratosis, is a scaly or crusty bump that arises on the skin surface. AK can eventually grow into skin cancer (Willson and DCH, 2004).

Figure 2.5. Gangrene (Worldbank, 2005)

Figure 2.6. Keratosis sole (Willson and DCH, 2004)

2.6 ARSENIC STANDARDS

Since 1958, the World Health Organization (WHO) has been the primary authority in settling the international standards (allowable concentrations) for arsenic in drinking water. According to the last edition (1993) of the WHO guidelines for Drinking Water Quality, the guideline value for arsenic in drinking water is less than 10 μg/L (WHO, 2001). The new suggested guideline value was based on expanding awareness of the toxicity of arsenic, mainly its carcinogenicity; developing technology; and the use of advanced instruments that can measure the amount arsenic more accurately. In the United States, the current standard for arsenic in drinking water is 50 ppb (ppb = μg/L). To protect consumers against the effects of long-term, chronic exposure to arsenic in drinking water, the US EPA announced a new arsenic standard for drinking water of 10 μg/L that will be effective from January 23, 2006 (US EPA, 2001a).

2.7 ANALYTICAL METHODS FOR ARSENIC

In the past few decades, developing the technology for detecting arsenic in drinking water has become increasingly important due to the toxicity of arsenic. A variety of instrumental techniques including atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and inductively coupled plasma-mass spectrometry (ICP-MS) are currently being used for the determination of arsenic in drinking water (Jain and Ali, 2000). The US EPA currently accepts six methods for the analysis of arsenic in drinking water, which including ICP-MS; graphite furnace atomic absorption (GFAA); stabilized temperature platform graphite furnace atomic absorption (STPGFAA); electrothermal atomic absorption spectrometry (EAAS); manual hydride generation atomic absorption spectrometry; and hydride generation atomic absorption (GHAA) (US EPA, 2003).

Inductively coupled plasma-mass spectrometry (ICP-MS) is a very powerful tool for tracing extremely small amounts of elements. Nowadays, this technique is in high demand for analysis of toxic elements owing to its precision and accuracy in measurement. In ICP-MS, argon gas produces a plasma or gas consisting of ions, electrons, and neutral particles. The elements in a sample are atomized and ionized by the plasma, and then these ionized elements are passed through a series of apertures (cones) into the high vacuum mass analyzer. The isotopes of the elements are acknowledged by their mass-to-charge ratio (*m/e*), and the intensity of a specific peak in the mass spectrum is comparable to the amount of that isotope (element) in the original sample (Houk, 1986; APHA, 1999). ICP-MS can achieve the arsenic detection limit of less than 0.1 μg/L recommended by the US EPA. ICP-MS has many other advantages, which include a short analysis time, lower detection limits, and multianalyte capabilities. However, instrumentation is expensive and the analysis for arsenic is subject to interference from the formation of an argon chloride in high chloride water samples (US EPA, 1994).

Graphite furnace atomic absorption (GFAA) is another of the most broadly used methods for measuring arsenic as it has high sensitivity and low detection limits. In GFAA, in order to detect the concentrations of a specific metal in a sample, the sample is heated very rapidly through the coated graphite tube up to 3000°C and atomized. The atomic adsorption lamp for the metal emits its characteristic atomic line spectra, and the instrument's monochromator selects one of those wavelengths. The amount of light absorbed by the atomized sample is proportional to its concentration in solution. GFAA needs very small amounts of sample, approximately 20 μL, but it takes a long time for multianalyte detection (Aggett and Boyes, 1989; Howard and Comber, 1992; Beaty and Kerber, 1993).

Stabilized temperature platform graphite furnace atomic absorption (STPGFAA) is GFAA with an attached stabilized temperature platform to delay atomization until stable temperature conditions are achieved. STPGFAA, which was approved by the US EPA in 1994, is used in depositing multiplication and can measure down to 0.1 μg/L of arsenic (Beaty and Kerber, 1993; US EPA, 2003).

Electrical atomic absorption spectrometric method (EAAS) is based on the same theory as direct flame atomization except that an electrically heated atomizer or graphite furnace replaces the standard burner head. EAAS has better sensitivity and detection limits (20 to 1000 times) than those of conventional flame techniques without extraction or sample concentration. EAAS requires only very small volumes of sample (APHA, 1999).

The manual hydride generation atomic absorption spectrometry (manual GHAA) has a principle similar to that of atomic absorption spectrometry; however, manual GHAA is a better method than AAS for analyzing arsenic with interferences that cannot be overcome by standard electrothermal techniques. In manual GHAA, the interferences are minimized because the arsenic hydrides are removed from the solution by sodium borohydride reagent and transported to an atomic absorption atomizer. This method has a lower detection limit of 0.5 μg/L, but, the analysis time is longer due to multiple injections (APHA, 1999).

The continuous-flow automated hydride generation atomic absorption (automated GHAA) is preferable to manual hydride generators because the effect of sudden hydrogen generation on light-path transparency is removed. Also, any blank response from contamination of the HCl reagent by the elements of concern is incorporated into the background base line (APHA, 1999).

2.8 THE METHODS OF ARSENIC REMOVAL

Various common treatment technologies have been used for removal of inorganic arsenic from drinking water. Large-scale treatment facilities often use conventional coagulation and precipitation with alum or iron salts and filtration to remove arsenic (Hering et al., 1996; Edwards, 1994; Chen et al., 2002). Lime softening is another conventional treatment process that potentially removes arsenic from source waters. Smaller scale systems and point of entry systems often use anion exchange resins, reverse osmosis, or activated alumina (Clifford, 1990; Lee et al., 2003). The new MCL of 10 ppb for arsenic publicized by the US EPA has led researchers to improve newer treatment techniques for more effective arsenic removal from drinking water. The US EPA suggested the criteria for the best available technology (BAT) are as follows: (1) the capability of achieving a high removal efficiency, (2) a history of full-scale operation, (3) general geographic applicability, (4) reasonable cost based on large and metropolitan water systems, (5) reasonable service life, (6) compatibility with other water treatment processes, and (7) the ability to bring all of the water in a system into compliance (US EPA, 2001b).

After evaluating previous As removal techniques from drinking water with BAT criteria, the US EPA recommended ion exchange, activated alumina, reverse osmosis, modified coagulation/filtration, modified lime softening, electrodialysis reversal, and oxidation/filtration as best available technologies to achieve 80–95 % arsenate [As(V)] removal efficiency after oxidation of As(III) to As(V) prior to removal (US EPA, 2000). The

US EPA is also evaluating other technologies such as coagulation-assisted microfiltration and granular ferric hydroxide, not yet designated as BAT, as adsorption absorbents.

Table 2.2. Best available technologies (BAT) and removal rates (US EPA, 2000)

Treatment technology	Max. As(V) removal (%)	Limitation
Ion Exchange	95	Sulfate $\leq$ 50 mg/L
Adsorption (Activated Alumina)	95	pH sensitive, low regeneration rate
Reverse Osmosis	> 95	Low water recovery rate, high cost
Modified Coagulation/Filtration	95	pH < 7, high dosage required
Modified Lime Softening	90	pH > 10.5
Electrodialysis Reversal	85	Low water recovery rate, high cost
Oxidation/Filtration	80	20:1= iron:arsenic

Ion exchange, especially using anion exchange resins, is suggested at lower sulfate concentrations for removing arsenate (US EPA, 2000). Anion exchange resins must be regenerated frequently due to shorter run lengths caused by sulfate. Frequent column bed regeneration leads to increasing costs and volumes of waste produced by the process. Although Clifford and Zhang (1994) noted that anion exchange may be operated for as high as 120 mg/L of sulfate, the US EPA suggested 50 mg/L as an appropriate upper limit for sulfate concentration in anion exchange for removing arsenic.

Reverse osmosis (RO) is a well-known process for small water treatment systems to remove arsenic from water and to achieve the new arsenic standard. RO membranes have extremely small pores (< 0.001 μm). The solvent is passed through these pores and the free volume between the segments of the polymer of which the membrane consists. In the RO system, osmotic pressure across the membrane is higher than in other membrane processes (Shih, 2005). Reverse osmosis was reported to provide greater than 95% removal efficiency in ideal operation conditions, but it may not be suitable in water-scarce regions because of low water recovery rates (75–85%) and high cost (Chen et al., 1999).

McNeill and Edwards (1995) reported that modified coagulation/filtration is a cost-effective arsenic treatment process. In general, the system needs to be at a pH lower than 7 or requires larger amount of coagulant to achieve higher removals. For example, modified lime softening, which is regarded as one of the better processes for As removal, needs to be operated at a pH of greater than 10.5 to achieve a high percentage of As removal (Chen et al., 2002).

Electrodialysis is another type of membrane process. The membranes separating the electrodialysis unit consist of cation and anion ion exchange resins. In electrodialysis, an electric current attracts the ions (dissolved solids) through the membranes, leaving the "fresh" water behind. The concentration of dissolved solids on the other side of the membrane (not the "fresh" water side) increases. The cations (e.g., calcium and magnesium) are drawn to a negatively charged electrode, and the anions (e.g., sulfate and arsenic) are attracted to a positively charged electrode (Kartinen and Martin, 1995).

Electrodialysis reversal (EDR), generally a fully automated system, has many advantages; for example, no addition of chemicals and little operator attention are required. However, it is typically expensive and has a lower water recovery of 70–80%. Additionally, oxidation/filtration is particularly effective for waters containing lower concentrations of arsenic and higher concentrations of iron (Subramanian et al., 1997).

Adsorption is a separation or purification process in which organic or inorganic compounds are adsorbed onto porous solid media with large surface areas for removal from the solution (Do, 1998). Adsorption easily separates a small amount of toxic elements from large volumes of solutions. For the removal of arsenic, the US EPA recently approved adsorption using activated alumina (AA) as one of the best available technologies (BAT). AA used for removal of contaminants by adsorption is nonhazardous and could safely be disposed of in landfills. However, AA is very pH sensitive and needs regeneration. In addition, it has a low regeneration rate of 50–70% (US EPA, 2001a). It is therefore necessary to develop new adsorbents that are more effective in removing arsenate in drinking water.

2.9 ADSORPTION THEORY

Before studying the adsorption of arsenic using iron- and aluminum-based adsorbents from drinking water, it is necessary to review the adsorption theory briefly.

Adsorption phenomena have been known for a very long time. Adsorption can be utilized as a treatment process to remove highly undesirable compounds from feedwater. It involves the separation of undesirable compounds from the liquid phase, the binding of components to a surface, and their accumulation at the surface of the adsorptive media. The binding to the surface is usually weak and reversible. Adsorption is distinguished from absorption, which is the filling of pores in a solid. Chemical adsorption (chemisorption) and physical adsorption (physisorption) are the two broad classifications of adsorption. In chemisorption, formation of strong bonds between adsorbate molecules and specific surface locations, also known as active sites, take place. Thus, chemisorption is primarily used to evaluate quantitatively the number of surface active sites, which participate in promoting (catalyze) chemical reactions. Van der Waals forces and electrostatic forces between adsorbate molecules and the atoms that compose the adsorbent surface result in physical adsorption. Thus, surface properties such as surface area and polarity play a significant role in adsorbent characterization. The problem of distinguishing between chemisorption and physisorption is basically the same as that of distinguishing between chemical and physical interactions in general. An absolutely sharp distinction is rare, and intermediate cases (e.g., adsorption involving strong hydrogen bonds or weak charge transfer) exist.

The major factors affecting adsorption are the nature and concentration of the adsorbate, the temperature and pH of the solution, the presence of competing solutes, and properties of the adsorbents such as surface area and pore size. A porous solid adsorbent is very significant in the adsorption process. Adsorbents can be classified, based on their porosity, as nonporous or porous adsorbents. Nonporous adsorbents have relatively small external adsorptive surface areas; such adsorbents include glass, steel beads, and clay. Porous adsorbents have relatively large internal adsorptive surface areas. Particularly, some of the important adsorbent characteristics affecting isotherms are surface area, pore size distribution, and surface chemistry. For nonporous adsorbents, the maximum amount of adsorption is proportional to the amount of surface area that is accessible to the adsorbate. However, the surface area of porous adsorbents is not the chief influence on adsorption capacity (Lin and Wu, 2001; APHA, 1999).

Adsorption separation is based on three distinct mechanisms: steric, equilibrium, and kinetic mechanisms (Do, 1998; Lee et al., 2004).

Thermodynamic adsorption is associated with the steric mechanism, specifically isosteric heat emitted during adsorption of a specific quantity of adsorbate. In liquid-phase adsorption systems, adsorption of solute molecules is generally accompanied by the desorption of water molecules, and therefore relatively low amounts of steric heat are evolved in such cases. For adsorption equilibria that follow a Langmuirian pattern, the isosteric heat of adsorption is constant because of the implied energetic homogeneity of the adsorbing surface. Therefore, the equilibria isotherm and the kinetic mechanism are more important for liquid-phase adsorption systems.

The two main characterizations of any adsorption process are adsorption equilibria (i.e. adsorption isotherms) and the rate of adsorption (i.e. adsorption kinetics). These two aspects will be discussed further below.

2.9.1 Adsorption Isotherms (Adsorption Equilibria)

The adsorption equilibrium for any particular adsorbent-adsorbate system can be called an adsorption isotherm because an isotherm is the distribution of solute between the liquid phase and the adsorbed phase at a specified temperature.

The adsorption phenomena can be described based on any one of the several adsorption isotherms, including Freundlich, Langmuir, Brunauer, Emmet and Teller (BET), Dubinin and Raduskevich (D-R), and Polanyi. The appropriate model for a particular component depends on the characteristics of the system. The energetic heterogeneity or uniformity of the adsorptive surfaces is an important factor in finding a suitable model for a particular adsorbate.

For single-solute adsorption, the Freundlich and the Langmuir are the more common isotherm models (LeVan, 1996; Snoeyink and Summers, 1999). The following well-known empirical and practical Freundlich equation explains adsorption data reasonably well:

$$q_e = KC_e^{1/n} \tag{4}$$

The linear form is as follows:

$$\log q_e = \log K + \frac{1}{n}\log C_e \tag{5}$$

where q_e (units mass of adsorbate/mass of adsorbent) and C_e (units of mass/volume) are equilibrium surface and solution concentrations, respectively. K and $1/n$ are constants for a given system; $1/n$ is unitless, and the units of K are determined by the units of q_e and C_e. K states the capacity of the adsorbent for the adsorbate and $1/n$ is a function of the strength of adsorption. For fixed values of C_e and $1/n$, the larger the value of K, the larger the capacity q_e. For fixed values of K and C_e, the smaller the value of $1/n$, the stronger the adsorption bond. As *1/n* becomes very small, the capacity tends to be independent of C_e, and the isotherm plot approaches the horizontal level; the value of q_e is then basically constant, and the isotherm is termed irreversible. If the value of *1/n* is large, the adsorption bond is weak, and the value of the q_e changes obviously with small changes in C_e.

The Freundlich isotherm is based on the assumption that the adsorbent has a heterogeneous surface composed of different classes of adsorption sites. The Langmuir equation can be linearized as shown below.

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad \text{or} \quad \frac{1}{q_e} = \frac{1}{q_{\max} b C_e} + \frac{1}{q_{\max}} \tag{6}$$

where b and q_{max} are constants. q_{max} represents the maximum value of q_e that can be achieved as C_e is increased. The constant q_{max} corresponds to the surface concentration at monolayer coverage. The constant b is related to the energy of adsorption and increases with the increase in adsorption bond strength. The basic assumption of the Langmuir isotherm is that adsorption of solutes occurs at specific homogeneous sites and forms a monolayer.

2.9.2 Kinetic Mechanisms

The rate of sorption is one of the most important factors in evaluating the efficiency of sorption and in determining the size of water treatment unit processes. In order to estimate the rates of adsorption and to identify the behavior of the adsorptive, the pseudo first-order Lagergren equation and the pseudo-second order equation are widely used (Ho and McKay, 1998a; b). A simple kinetic analysis of adsorption is the pseudo first-order equation in the form.

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{7}$$

where k_1 (1/min) is the rate constant of pseudo first-order adsorption, q_c (mg/g of dry weight) is the amount of metal ion sorbed at equilibrium, and q_t (mg/g of dry weight) is the amount of metal ion on the surface of the sorbent at any time t (min). By applying the boundary condition $q_t = 0$ at $t= 0$, equation (4) becomes

$$\log(q_e - q_t) = \log q_e - k_1 t \tag{8}$$

Instead of the pseudo first-order Lagergren equation, a pseudo second-order equation was recently described to explain the adsorption kinetics. The pseudo second-order equation is as follows.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{9}$$

where k_2 is the rate constant of adsorption (g/mg min) and h is the initial sorption rate (mg/g min). As time approaches zero (t → o), h can be defined as

$$h = k_2 q_e^2 \tag{10}$$

The initial sorption rate (h), the equilibrium sorption capacity (q_e), and the pseudo second-order rate constant (k_2) can be determined experimentally from the slope and intercept of the plot of t/q versus t.

To explain the diffusion state of adsorbate on adsorbent, the rate constant for intraparticle diffusion (k_{id}) is given by Weber and Morris (Kim et al., 2004; Namasivayam and Ranganathan, 1995; Peak and Sparks, 2002; Sun and Yang, 2003). The equation is as follows:

$$q = k_{id} t^{1/2} \tag{11}$$

The steep linear portions generally represent intraparticle diffusion within pores of adsorbent, while the plateaus are attributed to the equilibrium.

2.10 ADSORPTION OF ARSENIC USING VARIOUS IRON- AND ALUMINUM-BASED ADSORBENTS

Adsorption of arsenic(As) using metal oxides has been reported as an effective arsenic removal technology in drinking water because of its advantages: comparatively low cost, reliable arsenic removal efficiency, and simplicity of installation and maintenance. The metal oxides generally described as absorbents are manganese green sand (Subramanian et al., 1997), activated alumina (Singh et al., 2001; Rosenblum and Clifford, 1983), granular ferric hydroxide (Thirunavukkarasu et al., 2003a;b), lanthanum oxide (Davis and Misra, 1997), soil and clay minerals (Livesey and Huang, 1981; Altundogan et al., 2002; Goldberg, 2002), titanium oxide (Abe et al., 1992), and zirconium hydroxide (Lee et al., 2004). However, iron- or aluminum-based adsorbents have been reported by several investigators to be especially effective for removing arsenic from drinking water.

2.10.1 Iron (Fe) Based Adsorbents

Several researchers have found that iron-based oxides adsorb arsenic compounds in drinking water to a significant extent. Pierce and Moore (1982) described the adsorption of arsenic by amorphous iron (Fe) hydroxide as varying as a function of pH and concentration, and obeyed a Langmuir isotherm at low concentrations of arsenic. Hsia et al. (1992) reported that the adsorption of As(V) by amorphous ferric oxide was observed to vary as functions of pH (4–10) and initial As(V) and Fe(III) concentrations. They used the triple-layer model to simulate As(V) adsorption on the Fe oxide surface and showed that the surface complexes of $Fe(H_2AsO_4)^0$, $Fe(HAsO_4)^-$, and $Fe(AsO_4)^{2-}$ with an inner sphere of amorphous ferric oxide are more consistent with experimental adsorption data.

Dzombak and Morrel (1990) invoked the surface complexation modeling to explain the adsorption of cations on hydrous ferric oxide (HFO). Several researchers have presented this concept as a theory for adsorption of arsenic in water. To explain the factors affecting arsenic adsorption, Wilkie and Hering (1996) compared the extent of arsenic adsorption on HFO in the range of pH 4 to 9 with the result calculated by the generalized two-layer model, a surface complexation model in which the columbic term is fixed by double-layer theory. To explain the effect of adsorbate/adsorbent ratios on arsenic adsorption using HFO, they introduced the concept of surface heterogeneity, which is common in modeling transition metal cation adsorption. They also showed that high concentrations of sulfate decreased the removal of As(V) and that the effect of sulfate was greatest at lower pH. They further reported that calcium ions had a cooperative effects on adsorption of As(V) at high pH due to its favorable electrostatic behavior.

Safiullah et al. (2004) tested hydrated ferric oxide (HFO), activated Al_2O_3 (AA), and acidified or HFO-coated activated Al_2O_3 for the removal of arsenic, and concluded that HFO-based materials were better adsorbents than activated Al_2O_3 for the removal of arsenic from water and were environmentally more acceptable in terms of desorption behavior. Meng et al. (2002) discovered that the combined effects of phosphate and silicate can significantly affect the removal of arsenic by iron hydroxides. Meng et al. (2000) showed that using the triple-layer model (TLM), the removal of As(V) by coprecipitation and adsorption with ferric chloride was moderately affected in the presence of silicate, and that up to 300 g/L of sulfate concentration had no apparent effect on the removal of As(V) with ferric chloride at a pH 6.8 because sulfate binding affinity for ferric hydroxide maybe much weaker than that of As(V).

Manning and Goldberg (1996a; b) reported that the adsorption of arsenate on goethite [α-FeOOH] was affected by pH and competing anions such as phosphate and molybdenum, and that the competitive adsorption of these solutes with arsenic was observed in binary adsorption envelopes, which is embodies the concept of the one-site (monodentate) and two-site (monodentate + bidentate) oxide surface. Waltham and Eick (2002) reported that in the presence of silicic acid (H_2SiO_3), the adsorption of arsenate on goethite decreased as compared with that of arsenite. They explained this as possibly due to a decrease in the goethite's surface potential upon specific adsorption of silicic acid and deprotonation of the arsenate, creating an unfavorable electrostatic field.

Ferrihydrite, a kind of iron oxide with poorly crystallized oxides, plays a significant role in controlling arsenic concentrations and in the mobility of arsenic. Jain et al. (1999) indicated the bonding mechanism of arsenic on the surface of ferrihydrite to explain arsenic adsorption on ferrihydrite: during arsenite adsorption at lower pH, the oxygen of the Fe-O-As bond remains partially protonated as Fe-O(H)-As, while during arsenate adsorption at a pH of more than 8, monodentate bonds play a significant role. Jain and Loeppert (2000) found that the presence of phosphate resulted in a severe reduction in arsenate adsorption by ferrihydrite. Chaudhury et al. (2003) tried to incorporate manganese oxide into the ferrihydrite structure to improve adsorption capacity and increase the rate of adsorption.

Granular ferric hydroxide, which has a large specific surface area (approximately 150 m^2/g), has been described by some investigators as a good adsorbent for removing arsenic in drinking water. Recently, the US EPA is testing granular ferric hydroxide as an appropriate arsenic absorbent of BAT. Driehaus et al. (1998; 2002) described the adsorption using GFH for the removal of arsenic as simple and effective, particularly for small water facilities, due to its high adsorption capacity and short contact time in model systems and natural waters. Thirunavukkarasu et al. (2003a) tested GFH as an arsenic adsorbent in drinking water with an arsenic concentration of 100 μg/L of at a pH of 7.6, a typical pH value in drinking water supplies. They found that the observed data of arsenic adsorption fitted well in the Freundlich and Langmuir models, and they suggested that GFH could be effectively applied to small water utilities because it can achieve As(V) levels of less than 5 μg/L of in drinking water. Chang et al. (2003) reported that of three adsorbents (iron-modified activated alumina, high porosity activated alumina, and GFH) used to remove arsenic from Southern California Water Company (SCWC) wells, GFH was the better adsorbent. Lee et al. (2004) discovered that 35.5 mg/L of silica and 13 μg/L of vanadium (V) in groundwater had an unfavorable impact on As(V) adsorption using GFH because competing solutes reduced media surface sites available for arsenic.

Yuan et al. (2002) evaluated several iron-treated natural materials, such as Fe-treated activated carbon (FeAC), Fe-treated gel beads (FeGB), and iron oxide-coated sand (IOCS), for removing arsenic in drinking water for household use (cooking and drinking) and showed that IOCS had a good performance in terms of As(III) and As(V) removal in batch tests, column tests, and field experiments. They also reported that As(V) adsorption decreased slightly with increasing pH and that the observed adsorption data followed the Langmuir isotherm model quite well. To regenerate the columns of IOCS, 0.2 N NaOH was used. For application to simple and affordable household type of arsenic removal instruments, iron-coated sand (ICS) and iron-impregnated granular activated carbon (IGAC) were tested, and similar results were obtained. The results showed that the arsenic adsorption capacities decreased at high pH values (Petrusevski et al., 2002). Thirunavukkarasu et al. (2003b) developed iron oxide-coated sand (IOCS) through a high temperature coating process to increase its effectiveness and suitability for batch and column tests. Also, they reported that the fixed bed column of IOCS showed good performance for the removal of arsenic from tap water at pH 7.6, that the observed data fitted the Langmuir isotherm, and that the As(V) adsorption capacity of IOCS was 42.6 mg As/g IOCS.

Yean et al. (2005) evaluated the sorption and desorption behaviors of arsenic to magnetite (Fe_3O_4) nanoparticles, and they found that the sorption capacity is dependent on the pH value and surface area of the adsorbent. They also reported that the observed adsorption data followed the Langmuir isotherm and that nanoparticle-sized magnetite had a stronger desorption hysteresis for arsenic sorption than did larger particles. The presence of natural organic matter (NOM) decreased arsenic sorption to magnetite nanoparticles. Zeng (2004) also found that sulfate concentration of less than 460 mg/L produced little interference with As(V) adsorption when using an iron (III) oxide-silica binary oxide adsorbent.

2.10.2 Aluminum (Al) Based Adsorbents

Aluminum-based adsorbents are also well known to significantly adsorb arsenic species in drinking water. Anderson et al. (1976) studied arsenate absorption on amorphous

Al hydroxide and measured the adsorption and electrophoretic mobility of adsorbent particles as a function of equilibrium pH.

Adsorption on activated alumina (AA) has been one of the most commonly used methods for As(V) removal from drinking water. Activated alumina, with a high surface area of approximately 370 m^2/g, is recognized as an appropriate adsorbent for the removal of arsenate by the US EPA. Gupta and Chen (1978) studied the adsorption of As(V) and As(III) using activated alumina at various pH values and salinities, and they found that arsenic removal can be best accomplished in the As(V) state. Rosenblum and Clifford (1983) also found that arsenic (V) was effectively removed from water onto activated Al_2O_3. Singh et al. (2001) reported that activated Al_2O_3 can remove more than 90% of As(V), depending on pH, initial arsenic concentration, and dose of adsorbent, and it can be an effective adsorbent for the removal of As(V) from water at pH 5–7. Shugi et al. (2003) tried to coat activated alumina with iron oxide to increase the adsorption of As(III). They found that the adsorption process followed the first-order kinetics, and the adsorption isotherms fitted both Langmuir and Freundlich equations well. They also observed that the equilibrium time of arsenic adsorption was independent of initial arsenic concentration, but percentage removal decreased with increasing initial concentration. Lin and Wu (2001) studied the equilibrium and kinetic adsorption of arsenic onto activated alumina using a pore diffusion model, coupled with the observed Freundlich or Langmuir isotherm equations, and they found that the model fitted the experimental data well. They calculated pore diffusion coefficients. To find an ideal adsorbent having uniformly accessible pores, an interlinked pore system, a high surface area, and physical and/or chemical stability, Kim et al. (2004) developed mesoporous alumina by a templating method. This method produces a spongelike interlinked pore system through a posthydrolysis method, using stearic acid as an anionic surfactant and aluminum sec-butoxide (Fluka) as the aluminum precursor. They reported that the mesoporous alumina was insoluble and stable within the range of pH 3 to 7, had seven times higher maximum uptake of As(V) than that of conventional AA, and had rapid adsorption kinetics (5 hours) compared with the conventional AA (2 days). To desorb the adsorbate from the mesoporous alumina, a sodium hydroxide solution was used. They also found that the most significant key factor affecting adsorption capacity wase not the surface area of the adsorbents: the key factors were a uniform pore size and an interlinked pore system. Goldberg (2002) stated that the adsorption of As(V) on alumina decreased with high concentrations of sulfate.

David and Misra (1997) developed and tested several mixtures of lanthanum oxide and activated alumina for adsorbing selenium (IV) and arsenic (V) as a function of time and pH, and they showed that selenium (IV) was a competing solute in the adsorption of Se(IV) and As(V) onto aluminum-based adsorbents.

Manning and Goldberg (1996b) studied the effects of pH and competing anions on the adsorption of arsenate [As(V)] on gibbsite [γ-Al(OH)$_3$]. They found that the presence of phosphate resulted in a severe reduction in arsenate adsorption on gibbsite; they also described the binary adsorption envelopes for competitive adsorption of these solutes with arsenic. In addition, Manning and Goldberg (1996a) tested the arsenic adsorption using kaolinite, montmorillonite, and illite at varying pH and competing anion concentrations. To explain As(V) adsorption on these three clay minerals at varying pH and in the presence of competing oxyanions, specifically, phosphate anions, the surface complexation model was indicated.

Xu et al. (1998) developed the aluminum-loaded Shirasu-zeolite (Al-SZP1) by treating a P1 type Shirasu-zeolite (SZP1) with an aluminum surface solution. Xu et al. (2002) found that this adsorbent was better than activated alumina and other aluminum-loaded zeolites in terms of adsorption ability for As(V), and they demonstrated that the As(V) adsorption process using aluminum-loaded zeolites followed the first-order kinetic equation and the Freundlich isotherm. Phosphate anions significantly affected the arsenate adsorption on this adsorbent. The suggested adsorption mechanism was a ligand-exchange process between As(V) and the hydroxide groups present on the surface of Al-SZP1. In addition, NaOH solutions were used to desorb As(V) that had been adsorbed on Al-SZP1.

It can generally be concluded that the adsorption of As(V) using iron- and aluminum-based adsorbents is dependent on the pH value, adsorbate concentration, and amount of adsorbent. Specifically, the arsenate adsorption on these adsorbents increases at a pH value of less than 7 due to a decrease in the formation of complexes of arsenate with the surface of these adsorbents. The formation of complexes can be illustrated at lower pH by the following reactions:

$$\equiv \mathbf{Fe-OH+H_2AsO_4^- + H^+ \rightarrow Fe-H_2AsO_4 + H_2O} \ : \mathrm{pH}\ 2\text{–}7$$

$$\equiv \mathbf{Fe-OH+H_3AsO_3 \rightarrow Fe-H_2AsO_3 + H_2O} \ : \mathrm{pH} \leq 2$$

where $\equiv \mathbf{Fe-OH}$ is a hydroxide surface site. The observed adsorption data followed Langmuir or Freundlich isotherms and obeyed first-order kinetic equation. Phosphate anions are the most important solute competing with arsenate adsorption on iron- and aluminum-based adsorbents in water. Other competing solutes are sulfate, nitrate, and silicate. Additionally, the adsorption of As(V) onto iron-based adsorbents was found to be more efficient than that on aluminum based adsorbents.

2.10.3 Needs of New Fe- or Al-Based Adsorbents

The literature, as consulted, showed that iron- or aluminum-based adsorbents are good adsorbents for removing arsenic from water. However, previous studies of Fe- and Al-based adsorbents have focused on adding chemicals to enhance adsorption capacity, (e.g., coatings and heat or acid treatment) and on reusing adsorbents to reduce cost after regeneration—usually with sodium hydroxide. The sodium hydroxide solution is frequently used as a desorption agent to recover expensive adsorbent media. However, pretreatment of adsorbents or use of a desorption agent increases operating cost. The reality of the present situation is that the demand for effective and inexpensive adsorbents is constantly increasing. The use of pretreatment or desorption chemicals also results in pollution. Researchers are gradually realizing the importance of as nonregenerative adsorbent media in terms of economics and environmental impact.

In addition, it was reported that the arsenic contamination of many small-scale water systems and individual ground wells is widespread in most endemic areas such as China, Bangladesh, and the western United States. In these areas, centralized water treatment and distribution facilities are unavailable for the removal of arsenic due to the difficulty and expense of installing and operating regeneration processes. Besides, these small water systems need different approaches to removing arsenic from water. Simple and affordable arsenic treatment systems at the household level should be suggested, and the development of new, cheap, and easy-to-manage adsorbents would be quite worthwhile. Therefore, iron and aluminum oxides can be effective adsorbents of As(V) for Point of Entry (POE) and Point of Use (POU) water treatment systems, such as small-scale commercial or individual home water treatment systems.

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CHAPTER 3. EVALUATION OF IRON OXIDE AND ALUMINUM OXIDE AS POTENTIAL ARSENIC (V) ADSORBENTS

A paper to be submitted to The Journal of WATER RESEARCH

Youngran Jeong, Maohong Fan, Na Li, Shilpi Singh[1], *Chia-Line Chuang*[2], *Basudeb Saha*[3] *and J. (Hans) van Leeuwen*[4*]

Center for Sustainable Environmental Technologies, Iowa State University, Ames, IA, 50011, U.S.A.

[1] Sanborn, Head & Associates, Inc., Concord, NH, 03301, U.S.A
[2] Department of Research and Development, Allied Biotech Corp., Tao-Yuan, Taiwan
[3] Department of Chemistry, Iowa State University
[4] Department of Civil, Construction and Environmental Engineering, Iowa State University Ames, IA, 50011, U.S.A. (leeuwen@iastate.edu)

1. Abstract

Iron (Fe_2O_3) and nonactivated aluminum oxide (Al_2O_3) were found to be good and inexpensive adsorbents for As(V) removal in drinking water despite their relatively small surface area. The experimental results for this study suggest that by careful selection of the relative concentration of arsenic, pH, and dosages of Fe_2O_3 and Al_2O_3, As(V) removal efficiency as high as 99% can be achieved. At lower pH (< 7), and also depending on the dosages of Fe_2O_3 and Al_2O_3 and the initial concentration of As(V), over 95% of As(V) adsorption was observed within a contact time of 20 to 60 minutes. The adsorption of As(V) on Fe_2O_3 and Al_2O_3, like that on other nonporous adsorbents, is mainly controlled by the surface area. The adsorption of As(V) on Fe_2O_3 and Al_2O_3 was found to follow the Langmuir isotherm between the pH values of 5 and 9. The maximum As(V) uptake values at pH 6 – the optimal pH value for adsorption – using Fe_2O_3 and Al_2O_3, were calculated as 0.66 mg/g and 0.17 mg/g, respectively. No significant variation in the uptake of As(V) on Fe_2O_3 as compared with Al_2O_3 was observed at different pH values. The initial sorption rate of Fe_2O_3 is higher than that of Al_2O_3. All these factors make Fe_2O_3 a better adsorbent than Al_2O_3. Fe_2O_3 is a useful and effective adsorbent for POE (pint of entry) and POU (point of use) water treatment systems, such as small-scale commercial or individual home water treatment systems. Even though the adsorption capacities of Fe_2O_3 and Al_2O_3 for As(V) are quite low compared with those of other absorbents, their low cost makes them useful adsorbents. They may be very useful in arsenic removal from water in endemic areas such as China, India, and Bangladesh.

Keywords: Adsorption; Arsenic; As(V); Iron oxide; Aluminum oxide

2. Introduction

Arsenic is one of the most common natural contaminants found in water that has adverse effects on human health. Arsenic mainly originates from arsenic-containing rocks and soil and from some anthropogenic sources including mining, glass processing, insecticides, pesticides, and landfill leaching (Nordstrom and Alpers, 1999; US EPA, 1999). It is transported into natural waters through erosion and dissolution. It occurs in natural waters in both inorganic and organic forms, such as monomethyl arsenic acid (MMAA), dimethyl arsenic acid (DMAA), and arseno-sugars (NAS, 2001). The inorganic form of arsenic is most toxic to humans. Inorganic arsenic usually occurs in two valence states, arsenite [As(III)] and arsenate [As(V)]. In natural waters, As(III) species primarily consist of arsenious acid (H_3AsO_3), while As(V) species consists of $H_2AsO_3^-$ and $HAsO_3^{2-}$ (Ferguson and Gavis, 1972). The previous research has shown that As(V) in aerobic surface water has better removal efficiency than As(III) in anaerobic groundwater (Penrose, 1974). Besides, As(III) is easily converted to As(V) by oxidizing agents such as oxygen, ozone, free chlorine, hypochlorite, permanganate, and hydrogen peroxide (Frank and Clifford, 1986; Oscarson et al., 1983; Lauf and Waer, 1993). Thus, it is convenient to consider only As(V) compounds to be removed in drinking water treatment.

Long-term exposure to inorganic arsenic such as arsenite [As(III)] and arsenate [As(V)] in drinking water leads to adverse health effects such as cancer of the bladder, lungs, skin, kidney, nasal passages, liver, and prostate (Chen et al., 1992; Wu et al., 1989; Smith, et al., 1992). These adverse health effects of arsenic have mainly been reported in third world countries such as Bangladesh, India, Chile, and China, but a few incidences have been found even in affluent nations like the United States (Murphy and Guo, 2003; US EPA, 2000; Mazumder et al., 2000; Smith et al., 2000).

Based on the above-discussed adverse health effects of arsenic, changes in WHO's arsenic standard for drinking water (WHO, 2001), and the need to protect citizens against the effects of long-term, chronic exposure to arsenic in drinking water, the US Environmental Protection Agency (US EPA) has revised the current maximum contaminants level (MCL) of 0.05 mg/L (50 ppb) for arsenic in drinking water to 0.01 mg/L (10 ppb), which will be effective from January 23, 2006 (US EPA, 2003). In addition, the USEPA suggests the criteria of the best available technology (BAT) for arsenic removal, that is, technology that provides high removal efficiency, has a history of full-scale operation and a reasonable service life, and is cost effective. The new MCL standard and BAT for arsenic have led researchers to find new and improved treatment techniques for more effective removal of arsenic from drinking water (US EPA, 2001).

Adsorption is a separation or purification process in which organic or inorganic compounds are adsorbed, for removal from the solution, onto porous solid media with a large surface area (Do, 1998). Adsorption has a comparatively low cost and easily separates a small amount of toxic elements from large volumes of solutions. These benefits of adsorption have motivated several researchers to use adsorption for arsenic removal from drinking water. Some of the common adsorbents used for the process include activated alumina, manganese green sand, granular ferric hydroxide, soil, and mud (Rosenblum and Clifford, 1983; Subramanian et al., 1997; Thirunavukkarasu et al., 2003; Livesey and Huang, 1981; Altundogan et al., 2002). Adsorption by activated alumina (AA) was approved recently as one of the best available technologies (BAT) for arsenic removal. It has an advantage over other adsorbents in that AA used during the removal process is nonhazardous and could be safely disposed of in landfills. However, AA is very pH sensitive and has a low regeneration rate of 50–70% (US EPA, 2001). It is necessary to consider development of new adsorbent, one that is more effective in removing arsenate in drinking water.

Several researchers have found that Fe- and Al-based adsorbents adsorb arsenic compounds in drinking water to a significant extent. Of these, amorphous ferric hydroxide (Pierce and Moore, 1982), ferric oxide (Dzombak and Morrel, 1990), hydrous ferric oxide (Wilkie and Hering, 1996), ferrihydrite (Jain et al., 1999), granular ferric hydroxide (Thirunavukkarasu et al., 2003), goethite and gibbsite (Manning and Goldberg, 1996), amorphous aluminum oxide (Anderson et al., 1976), activated alumina (Gupta and Chen, 1978; Singh et al., 2001) are most frequently described. However, previous studies of Fe-and Al-based adsorbents have focused on adding chemicals for augmenting adsorption capacity (e.g., coating, heat, or acid treatment) and on reusing adsorbents to reduce cost after regeneration (usually with sodium hydroxide). Maeda et al. (1992) and Vaughan and Reed (2005) used Fe-impregnated coral and Fe-impregnated activated carbon to enhance arsenic removal. Altundogan et al. (2002) demonstrated that the acid treatment with 1 M HCl solution to red mud, which removes sodalite ($Na_2O{\cdot}Al_2O_3{\cdot}1.68SiO_2{\cdot}1.73H_2O$), increases the adsorption ability of red mud in industrial wastes treatment. A desorption agent (e.g., sodium hydroxide solution) is commonly used to recover expensive adsorbent media such as mesoporous alumina prepared by the templating method (Kim et al., 2004). However, pretreatment of the adsorbent or use of a desorption agent increases the operating cost. In addition, waste solution containing HCl and NaOH discarded from pretreatment for boosting adsorption capacity also result in pollution. The development of new, inexpensive, and easy-to-manage adsorbents would be quite worthwhile.

Arsenate adsorption using Fe and Al oxides without pretreatment or regeneration processes may offer a useful new technology, particularly in Point of Use (POU) or Point of Entry (POE) treatment units (such as household drinking water faucets). It would require no hazardous desorption agents, and offers easy maintenance of the adsorption system (MDE, 2004). Additionally, iron and alum oxides are inexpensive chemicals and are readily available at water treatment plants, where they are sometimes used in other unit processes (Scott et al., 1995; McNeill and Edwards, 1997).

In this research, we studied the adsorption of arsenate [As(V)] onto Fe_2O_3 and Al_2O_3. The objectives of this study were to evaluate the use of Fe_2O_3 and Al_2O_3 as possible adsorbents for the removal of arsenate from drinking water through a series of experiments conducted by changing various parameters such initial concentration, dosage of adsorbents, and pH that are known as critical parameters in other researches.

3. Theoretical study

3.1. Adsorption kinetic equation

The pseudo second-order rate equation was developed by Ho (1995) to describe the adsorption systems of divalent metal ions using sphagnum moss peat. This equation derives the adsorption capacity of solid from the solution concentration. The pseudo second-order rate equation has recently been applied to discussions of various reactions such as the adsorption of metal ions or organic substances from liquid solutions and the design of multistage or batch adsorption facilities. The pseudo second-order equation was used to explain the arsenic adsorption kinetics. The pseudo second-order equation is as follows;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (1)$$

where k_2 is the rate constant of adsorption (g/mg min) and h is the initial sorption rate (mg/g min). As time approaches zero (t → o), h can be defined as

$$h = k_2 q_e^2 \qquad (2)$$

The initial sorption rate (h), the equilibrium sorption capacity (q_e), and the pseudo second-order rate constant (k_2) can be determined experimentally from the slope and intercept of the plot of t/q versus t.

3.2 Adsorption isotherm

Several adsorption isotherms including Brunauer, Emmet, and Teller (BET), Dubinin and

Raduskevich (D-R), and Polanyi are available to describe adsorption phenomena, but none of them are based on or derived from the Freundlich and the Langmuir (LeVan, 1996), which are more common isotherm models for single-solute adsorption.

The Langmuir equation can be linearized as below:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad \text{or} \quad \frac{1}{q_e} = \frac{1}{q_{\max} b C_e} + \frac{1}{q_{\max}} \qquad (3)$$

where b and q_{max} are constants. q_{max} represents the maximum value of q_e that can be achieved. b is related to the energy of adsorption and increases with the increase in adsorption bond strength. The basic assumption of the Langmuir isotherm is that adsorption of solutes happens at specific homogeneous sites and forms a monolayer.

Some important adsorbent characteristics affecting isotherms are surface area, pore size distribution, and surface chemistry. For nonporous adsorbents, like ferrihydrite, the maximum amount of adsorption is proportional to the amount of surface area within pores that is accessible to the adsorbate. However, the surface area of porous adsorbents is not the chief influence on adsorption capacity (AWWA, 1999; Lin and Wu, 2001).

4. Experimental sections

4.1. Adsorbents

Ferric oxide (Fe_2O_3-PVS; Physical Vapor Synthesis) by Bailey-PVS and aluminum oxide (Al_2O_3-ALO101) by Praxair are the two metal oxides used in our experiments as adsorbents. Iron oxide is produced from the decomposition of iron chloride solution within the spray roasting reactor. This reaction requires the presence of water vapor and oxygen at a temperature between approximately 600 and 1600°F (589 and 1144°K). The basic reactions are as follows:

$$2FeCl_2 + 2H_2O + 1/2\ O_2 \rightarrow Fe_2O_3 + 4HCl$$

$$2FeCl_3 + 2H_2O \rightarrow Fe_2O_3 + 6HCl$$

This also makes the recovery of hydrochloric acid possible. In order to elucidate the possibility of using of iron oxide as an appropriate adsorbent for removal of As(V), aluminum oxide, having characteristics similar to those of iron oxide was chosen as a comparable adsorbent. Aluminum oxide (Al_2O_3) comes from Praxair (Wisconsin, USA), a manufacturing company that produces thermal spray powders. This Al_2O_3 is coated at high temperature to resist to abrasion, erosion, alkali, and acids.

The colors of iron and aluminum oxide are reddish brown and grayish white, respectively. As shown in Figure 3.1, the SEM (Scanning Electron Microscope) images obtained with a Philips XL-30 (25kV LaB_6 filament) show that Fe_2O_3 particles exist as clustered and aggregated shapes while Al_2O_3 particles occurs as acicular forms with a smooth surface. The actual particle sizes of Fe_2O_3 can not be determined, but those of Al_2O_3 are much larger. The length and width of the Al_2O_3 particle in the SEM figure seem to be 10–50 μm and 5–20 μm, respectively. This matches 5–45 μm of average particle size of Al_2O_3 provided by the manufacture. The average particle size of Fe_2O_3 was 0.7 μm according to the company and was 7 to 70 times smaller than that of Al_2O_3. As provided by manufacturers, the iron oxide consists of 99.1% Fe_2O_3 and a small portion of other metals such as Cu and Zn, while aluminum oxide contains 99.5% Al_2O_3 and a small portion of other elements such as Ca and Si. The effective pore size, total pore volume, and specific surface area of the two adsorbents were measured using BET gas adsorption methods (ASAP2010, Micromeritics, USA) and are provided in Table 3.1. The effective pore size of Fe_2O_3 and Al_2O_3 was found to be 80.49 Å and 75.69 Å, respectively, which means that these Fe_2O_3 and Al_2O_3 particles generally have mesopores (20–500 Å) and not micropores (< 20 Å). Total pore volume was 1.02×10^{-2}cm^3/g for Fe_2O_3 and 1.02×10^{-3}cm^3/g for Al_2O_3. Finally, the specific surface area of Fe_2O_3 was found to be ca. 5.05m^2/g, and that of Al_2O_3 was ca. 0.55 m^2/g.

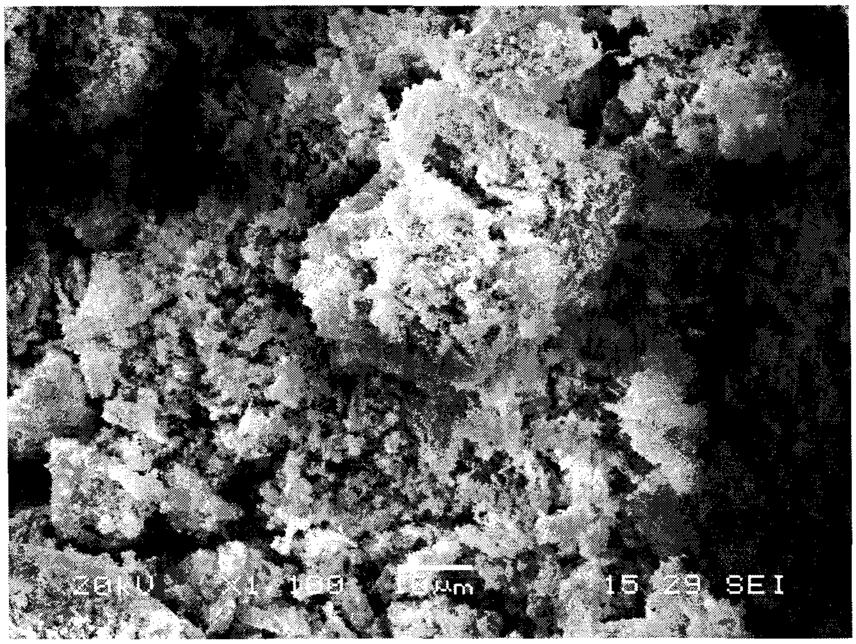
Table 3.1. Absorbents Properties

	Fe_2O_3	**Al_2O_3**
Manufacturer	Bailey-PVS Oxides (USA)	Praxair (USA)
Purity	Fe_2O_3 (99.1%)	Al_2O_3 (99.5%)
Particle size (μm)	0.7	5–45
Average pore size (Å)	80.49	75.69
Pore volume (cm^3/g)	1.02×10^{-2}	1.02×10^{-3}
Specific surface area (m^2/g)	5.05	0.55

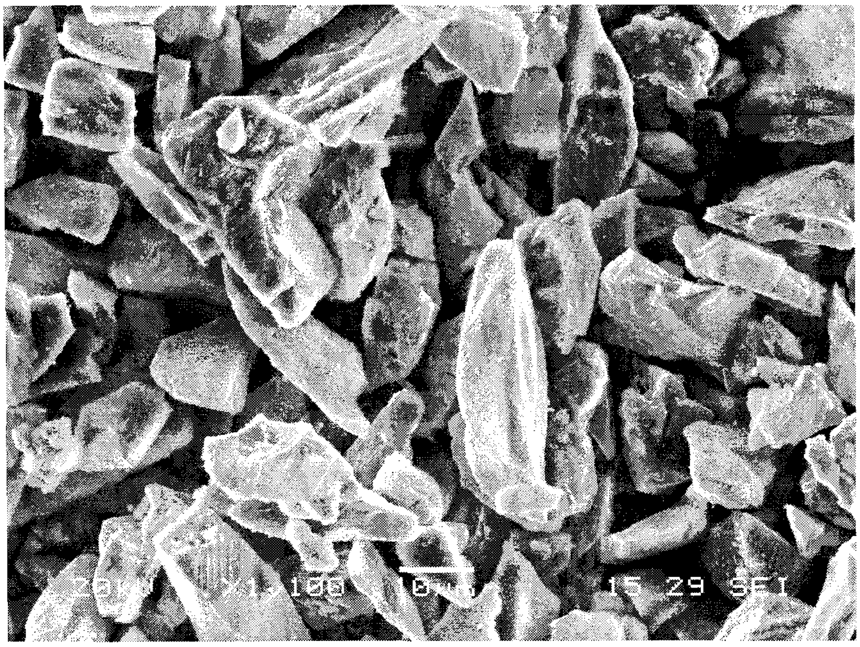
The specific surface areas of some of the adsorbents have been reported by several investigators; for example, 200 m^2/g for ferrihydrite (Raven et al., 1998), 290 m^2/g for amorphorous ferric oxide (Goldberg and Johnston, 2001), 840 m^2/g for iron oxide impregnated activated carbon (FeAC) (Vaughan and Reed, 2005), and from 15 m^2/g for aluminum-loaded Shirasu-zeolite to 300 m^2/g for highly porous activated alumina (Xu et al., 2002; Kim et al., 2004). Fe_2O_3 and Al_2O_3 have very small surface areas compared with the surface areas of the above absorbents. However, Fe_2O_3 has a much larger surface area than Al_2O_3. In general, metal oxides or metal hydroxides do not dissolve in neutral solutions but are easily soluble in acidic and strongly basic solutions because of their amphoteric characteristics. Mesoporous alumina was reported to dissolve in both acids (pH < 3) and bases (pH > 8) (Kim et al., 2004). However, Fe_2O_3 and Al_2O_3 are almost insoluble in acid and alkaline solutions, and once filtered, they do not have significant adverse effects on water quality, such as imparting color. Because of these properties, Fe_2O_3 and Al_2O_3 were found to be stable and reliable adsorbents for drinking water treatment, and they have been used in our As(V) adsorption experiments without further purification.

4.2. Batch experiment

Batch experiments were conducted in a jar tester (PB-700TM, Phipps & Bird, USA) to study the removal of As(V) with Fe_2O_3 and Al_2O_3 in drinking water. All chemicals were reagent grade from Fisher Chemicals, while sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) was from Matheson Coleman and Bell (Norwood, Ohio, USA). Arsenate solutions were freshly prepared by dissolving sodium arsenate in deionized water. The pH values were measured using a Corning model 320 pH meter, calibrated using commercial pH 4.01 and 7.0 buffers. The pH values of the test solutions were adjusted to 5 to 9 (± 0.1 pH unit) using either diluted 0.1 M hydrochloric acid (HCl) or 0.1 M sodium hydroxide (NaOH) solutions before adsorption. As(V) concentrations were controlled at 200, 400, and 600 μg/L ($2.67–8 \times 10^{-6}$M) considered reasonable concentrations encountered in the United States and Bangladesh (Wickramasinghe et al., 2004). Approximately 0.05–1 g/L of Fe_2O_3 or 0.5–6 g/L of Al_2O_3 was added to a solution prepared at a predetermined arsenate concentration using deionized water, followed by stirring at 23 ± 0.5°C for 1 hour and 2 hours, respectively. The pH was measured, and for analysis, supernatant was collected directly from the jar after reaction



(a) Fe_2O_3



(b) Al_2O_3

Figure 3.1. (a) SEM figure of Fe_2O_3 at 1100 × magnification, clustered and aggregated shapes; (b) SEM figure of Al_2O_3 at 1100 × magnification, acicular forms with a smooth surface

using a 10 ml disposable syringe. The samples were filtered through 0.45 μm syringe filters (Millipore Millex) and analyzed for arsenic. The adsorption capacities were calculated from the difference between the initial and the equilibrium concentrations.

4.3. Kinetics

Kinetic studies were also conducted at different intervals of time and concentrations in a 500 mL jacketed reactor vessel (Chemglass, New Jersey, USA) equipped with a constant-temperature circulating bath (Cole-Parmer, USA) to determine the rate of arsenate removal by Fe_2O_3 and Al_2O_3. Kinetic studies were done at the three different temperatures of 5, 25, and 45 ± 0.5°C. The same procedure was used for analysis as in adsorption experiments.

4.4. Arsenate Analysis

Arsenate concentrations in all the samples were analyzed using Inductively Coupled Plasma–Mass Spectrometry (ICP-MS, 4500 Series, HP) following Standard Methods (APHA, 1999). The detection limit of ICP-MS was 0.1 μg/L for arsenic. The measurements were accepted as reasonable data in cases of less than 5 or 10% relative standard deviation (RSD) when the arsenic concentration in the samples was greater than or less than 50 μg/L, respectively. In order to amplify the consistency of results, the experiments were performed in triplicate and the mean values considered. No detectable As(V) adsorbed on the walls of the jar was ascertained through the blank experiments.

5. Results and discussion

5.1. The Effects of contact time with adsorbent dosages or initial As(V) concentrations

The adsorption rate is influenced by many factors, including solubility and molecular size of the adsorbate, characteristics of the adsorbent, and agitation. In addition, temperature commonly affects the adsorption rate, solute hydrolysis status, and ionization constant concurrently (Do, 1998). The rates of As(V) adsorption on Fe_2O_3 were not dependent on temperature, while those on Al_2O_3 were slightly dependent on temperature (figure not shown). The effect of temperature may not have a significant impact on As(V) adsorption using Al_2O_3 because of the relatively stable variation of water temperature in water treatment systems.

Figures 3.2 and 3.3 show the rates of As(V) adsorption on Fe_2O_3 and Al_2O_3 at different dosages of adsorbents and different As(V) initial concentrations. The rates of As(V) adsorption on Fe_2O_3 and Al_2O_3 were found to be significantly time dependent. The rate of As(V) adsorption was found to be higher with high dosages of Fe_2O_3 and Al_2O_3 to As(V) and to be higher with lower initial As(V) concentrations to the same dosages of Fe_2O_3 and Al_2O_3. To achieve the less than 10 μg/L of the new arsenic standard from 200 μg/L of initial As(V) concentration at pH 6, the dosages are 0.5 g/L of Fe_2O_3 or 3 g/L of Al_2O_3. That means that to achieve the same equilibrium As(V) concentration for both the adsorbents, Al_2O_3 was required at a dosage of more than six times the dosage of Fe_2O_3. Additionally, the As(V) adsorption onto Fe_2O_3 was rapid in the first 20 minutes and then slowed down considerably as the reaction approached equilibrium. However, the majority of adsorption onto Al_2O_3 was achieved in the first 60 minutes. Pierce and Moore found that the 99% of As(V) adsorption onto amorphous Fe hydroxide was achieved after 4 hours of stirring at each of three final pH values (4.0, 8.0, and 9.9). They also observed that the removal rate was somewhat faster for higher As(V) concentrations (1 mg/L) than for lower As(V) concentrations (50 μg/L). They suggested that an adequate time for As(V) equilibrium on amorphous Fe hydroxide was 24 hours (Pierce and Moore, 1982). Iron oxide-coated sand was observed to adsorb As(V) completely in 50 minutes (Yuan et al., 2002). Activated alumina grains (100 mesh, Macherey-Nagel, Germany) have been reported to typically have low adsorption rates, and up to 2 days are required to reach half of the equilibrium value (Lin and Wu, 2001). Mesoporous alumina prepared by a templating method as an adsorbent may take approximately 5 hours to meet the equilibrium As(V) concentration (Kim et al., 2004). Compared with those of amorphous Fe hydroxide, activated alumina, and mesoporous alumina, the adsorption rates of Al_2O_3 and Fe_2O_3 were found to be higher. Furthermore, the adsorption rates of Fe_2O_3 were faster than those of Al_2O_3.

5.2. Adsorption kinetics

The rate of sorption is one of the most important factors in evaluating the efficiency of sorption and in determining the size of water treatment unit processes. In order to estimate the rates of adsorption and to identify the behavior of the adsorptive, we conducted experiments related to the kinetics of As(V) removal on Fe_2O_3 and Al_2O_3.

The adsorption rates of As(V) using Fe_2O_3 and Al_2O_3 are found to fit this pseudo second-order kinetics equation well. The pseudo second-order rate constant (k_2) and the initial sorption rate (h) are estimated in Figure 3.4 and are listed in Table 3.2. It is shown that the h value for Fe_2O_3 (0.26 mg/g min) is higher than that for Al_2O_3 (0.04 mg/g min), which means Fe_2O_3, having small particles (0.7 μm), needs a shorter adsorption time than Al_2O_3, with its larger particles (5–45 μm). This result is supported by Fick's second law of diffusion.

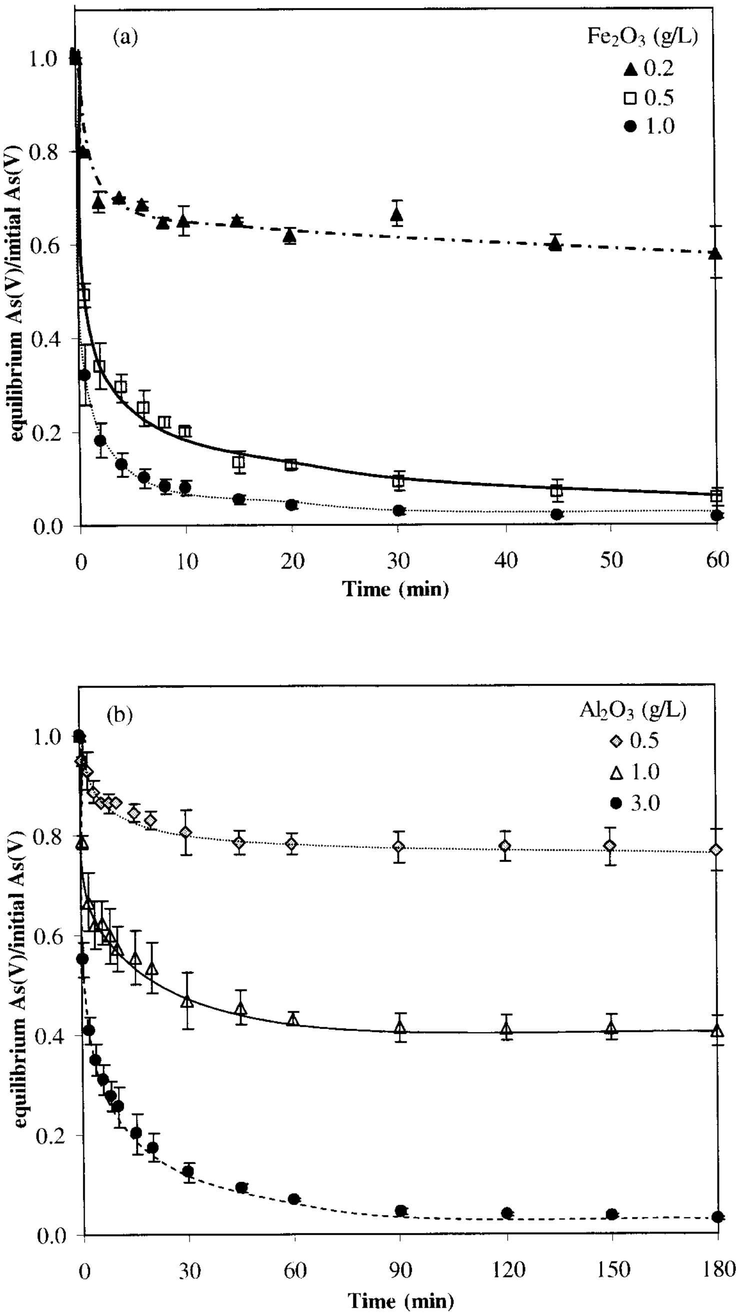
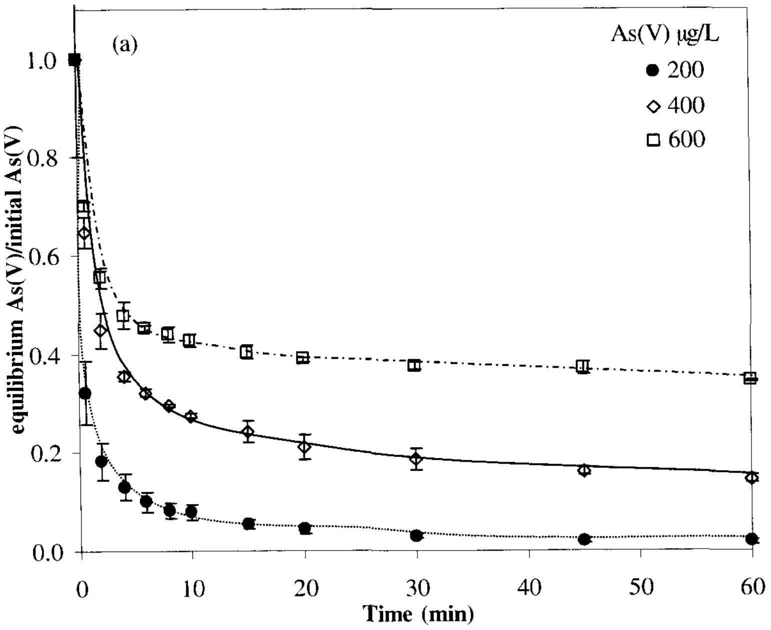


Figure 3.2. Time courses of As(V) adsorption for different dosage of (a) Fe_2O_3 and (b) Al_2O_3. Initial As(V) concentration, 200 µg/L; Sample volume, 0.5 L; Stirring speed, 83 ± 5 rpm; pH 5 ± 0.1; 25°C; error bars = standard error



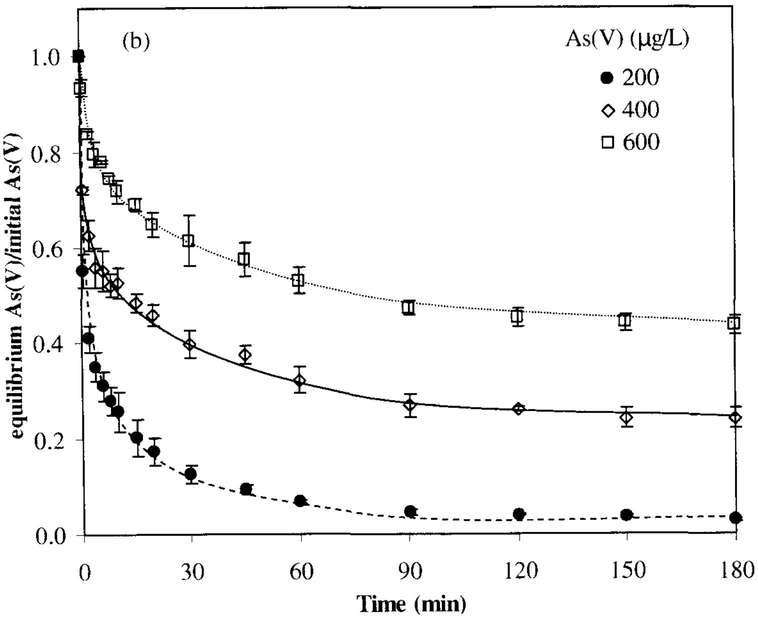


Figure 3.3. Time courses of As(V) adsorption onto (a) Fe_2O_3 and (b) Al_2O_3 for different As(V) initial concentrations. Sample volume, 0.5 L; Stirring speed, 83 ± 5 rpm; pH 6 ± 0.1; 25°C (a) Dosage, 0.8 g/L, (b) Dosage, 3.0 g/L.

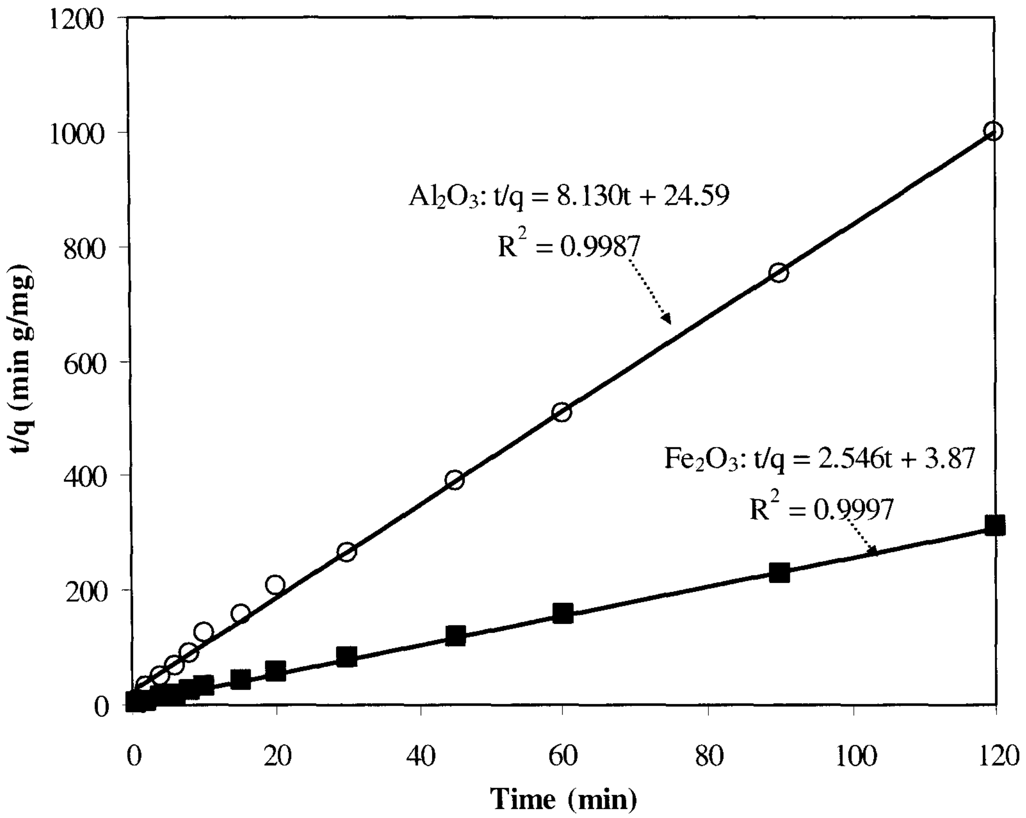


Figure 3.4. Pseudo second-order sorption kinetics of As(V) onto Fe_2O_3 and Al_2O_3. Initial As(V) concentration, 200 μg/L; pH 5 ± 0.1; 25°C; dosage of Fe_2O_3 and Al_2O_3, 0.5 g/L respectively.

Table 3.2. Pseudo second-order rate constants

	Pseudo second-order rate constants	
	***h* (mg/g min)**	**k_2 (g/mg min)**
Fe_2O_3	0.26	1.68
Al_2O_3	0.04	2.64

5.3. The Effect of pH

The uptake of As(V) per mass unit of adsorbent as a function of pH was studied to find the optimum pH value for adsorption of As(V) using iron or aluminum oxides. The stirring time for arsenate adsorption was kept at 1 hour for iron oxide and 2 hours for aluminum oxide. Fe_2O_3 and Al_2O_3 were able to remove more than 95% of As(V) from 200 μg/L of arsenate contaminated water and met the new 10 μg/L drinking water standard.

Figures 3.5 and 3.6 show the arsenic (V) uptakes of Fe_2O_3 and Al_2O_3 as a function of pH for different dosages of adsorbents and different initial As(V) concentrations. The maximum As(V) uptakes of both Fe_2O_3 and Al_2O_3 were achieved at a pH 6. At pH less than 8, increasing As(V) uptake rates were observed with decreasing dosages of Fe_2O_3 and Al_2O_3, and increasing As(V) initial concentrations; however, for pH greater than 8, As(V) uptakes were little affected by adsorbent dosages or As(V) initial concentrations. Besides, regardless of varying pH values, equal As(V) uptake rates for Fe_2O_3 and Al_2O_3 were observed for 1 g/L of Fe_2O_3 and 4 g/L of Al_2O_3. Thus, it can be concluded that the As(V) uptake rates of Fe_2O_3 and Al_2O_3 are significantly affected by pH in conditions of comparatively lower dosages of adsorbent and higher As(V) initial concentrations, which further means comparatively lower As(V) concentrations or higher adsorbent dosages are better for As(V) adsorption on Fe_2O_3 and Al_2O_3 at varying pH conditions. The uptake of As(V) on Fe_2O_3 does not change significantly from pH 5 to pH 7 but decreases rapidly at pH 8, while that of Al_2O_3 decreases rapidly at pH 6. This result with Fe_2O_3 is comparable to that with amorphous $Fe(OH)_3$, where As(V) adsorption was not affected significantly at lower pH (< 7) but decreased rapidly at $pH > 7$ (Pierce and Moore, 1982; Singh et al., 2005). Similar observations were made in another study in which FeAC (iron oxide impregnated activated carbon) was used.

The adsorption uptake rate of Fe oxides on the surface of FeAC decreases significantly at high pH values (Vaughan and Reed, 2005). According to some reports, the decrease in adsorption rate occurs because the surface of the adsorbent becomes negatively charged and columbic repulsion is enhanced (Hsia et al., 1992; Xu et al., 2002; Yuan et al., 2002). According to Stumm and Sulzberger (1992), the decrease is because of ligand exchange, where anions react with surface hydroxides on the adsorbents. Others have described these observation as the formation of an inner-sphere surface complex on adsorbents such as goethite (α-FeOOH) or iron oxide-coated sand (IOCS) (Benjamin et al., 1996; Grossl et al., 1997). Thus, it can be concluded that the form of $H_2AsO_4^-$ may be primarily adsorbed on Fe_2O_3 at a lower pH. However, with increasing pH, the monovalent arsenate anion does not get adsorbed on Fe_2O_3 due to a negative surface charge and coulombic repulsion (Brookins, 1988; Zouboulis et al., 1993). Finally, the arsenate anions interact with the surface sites of Fe_2O_3 that are occupied by hydrogen ions and transform to $Fe(H_2AsO_4)^0$, $Fe(HAsO_4)^-$, and $Fe(AsO_4)^{2-}$.

The As(V) uptake of Al_2O_3 decreases sharply at pH values differing from 6 when compared with the Fe_2O_3 as shown in Figure 3.6. Thus, it is concluded that Al_2O_3 is more likely than Fe_2O_3 to absorb $H_2AsO_4^-$ at lower pH but may prefer OH^- to $H_2AsO_4^-$ at higher pH (> 6). According to some researchers, Fe is superior to Al in ligand exchange with arsenate anions on the surface of Fe and Al oxide, that is, arsenic removal efficiencies with different electrode materials in an electrocoagulation process follow the sequence: iron > aluminum (Ratna Kumar et al., 2004) and therefore supports the above-noted observations. This result is also supported by several studies where activated alumina used in the pH range of 5.5 to 8.5 preferred OH- to $H_2AsO_4^-$ (Trussell et al., 1980; Rosenblum and Clifford, 1983;

AWWA, 1999). Based on studies of activated alumina and aluminum-loaded Shirasu-zeolite (Xu et al., 2002; AWWA, 1999), the As(V) adsorption mechanism of Al_2O_3 can also be considered a ligand exchange process between As(V) and the hydroxide groups. According to these results for Fe_2O_3 and Al_2O_3, we can conclude that the favorable arsenate adsorption of both adsorbents takes place at pH 6. This experimental result, where As(V) removal uptake on Fe_2O_3 and Al_2O_3 increased at low pH and decreased at high pH, was the same as that observed with other absorbents of Fe and Al oxides such as ferric chloride (Hering et al., 1996), ferrihydrite (Raven et al., 1998), ferric oxide (Dzombak and Morrel, 1990), hydrous ferric oxide (Wilkie and Hering, 1996), goethite and gibbsite (Manning and Goldberg, 1996), amorphous aluminum oxide (Anderson et al., 1976), and activated alumina (Singh et al., 2001) as well as amorphous ferric hydroxide and ferric-impregnated activated carbon. It was revealed that surface or groundwater should be controlled in the pH range of less than 7 to achieve better arsenate removal efficiency when Fe_2O_3 or Al_2O_3 is used as an absorbent, and that Fe_2O_3 is less sensitive to pH than Al_2O_3. The pH values of the solution were not changed significantly on using Fe_2O_3 and Al_2O_3 and were almost between 4 and 7 for Fe_2O_3 and 5.3 and 7.4 for Al_2O_3 (note that pH values were adjusted from 5 to 9 ± 0.1 before adsorption with Fe_2O_3 and Al_2O_3).

Surface area, pore size distribution, and surface chemistry are the main characteristics of an adsorbent that can affect its organic or inorganic compound removal efficiency (AWWA, 1999). For nonporous adsorbents, the surface area is reported as the most important factor in removal efficiency and uptake capacity by several investigators (Lin and Wu, 2001; Xu et al., 2002). Both Fe_2O_3 and Al_2O_3 belong to the group of nonporous adsorbents, although the total pore volume and total specific surface area of Fe_2O_3 are 10 times greater than those of

Al_2O_3, as stated previously. Therefore, it can be inferred that the surface area is the most important factor influencing As(V) adsorption on Fe_2O_3 and Al_2O_3. Our experimental results support the observation that Fe_2O_3, with a higher surface area, has a higher As(V) uptake rate than Al_2O_3.

5.4. Adsorption isotherm

To design an appropriate sorption system for removing As(V) in drinking water, it is important to find the well-fitted isotherm curves of Fe_2O_3 and Al_2O_3.

Figure 3.7 shows the relationship between As(V) equilibrium concentration and the adsorption capacity of Fe_2O_3 and Al_2O_3 at the range of pH 5 to 9. With increasing pH, a decreasing trend in the amount of arsenate taken up by Al_2O_3 was observed. In the isotherm studies, it was found that the experimental data for adsorption on Fe_2O_3 and Al_2O_3 fitted well with the Langmuir adsorption isotherm in the range of pH 5 to 9. Plots of adsorption capacity (mg/g) vs. equilibrium As(V) concentration in Figure 3.7 yielded straight lines for each of five different pH values. The Langmuir curves and parameters for As(V) removal using Fe_2O_3 and Al_2O_3 as shown in Figure 3.8 and in Table 3.3. The calculated parameters of the Langmuir isotherm model for Fe_2O_3 and Al_2O_3, as well as the correlation coefficients (R^2) are listed in Table 3.3. It is found that, at pH 6, the correlation coefficient (R^2) values for the Langmuir isotherm for As(V) on Fe_2O_3 and Al_2O_3 are 0.92 and 0.90, respectively. Therefore, the maximum adsorption capacities of Fe_2O_3 and Al_2O_3 at pH 6 were estimated from the Langmuir isotherm, and found to be 0.66 mg/g and 0.17 mg/g, respectively. These results show that Fe_2O_3 is a better absorbent than Al_2O_3. As noted above, the parameter *b* is a function of the strength of adsorption. The larger *b* means that the adsorption bond is stronger. With a larger *b* value, Langmuir isotherm curves approach a saturation plateau. The isotherm shows that no more adsorbate can be removed even at low loading ratios of adsorbate to adsorbent. In turn, the adsorption capacity is independent of the equilibrium As(V) concentration. As shown in Table 3.3, the value of *b* for Fe_2O_3 and Al_2O_3 increases with decreasing pH. Thus, we can conclude that at lower pH, the As(V) adsorption bond with Fe_2O_3 and Al_2O_3 is stronger and more irreversible, and that the As(V) adsorption bond with Fe_2O_3 is stronger than with Al_2O_3. However, at pH 9, As(V) adsorption bonds with Fe_2O_3 and Al_2O_3 are very weak, and the q_e values change remarkably with even small changes in the equilibrium As(V) concentration, C_e. Based on the assumptions of the Langmuir isotherm, it can be estimated that both Fe_2O_3 and Al_2O_3 should have mainly homogenous sites.

Compared with some adsorbents that having high As(V) adsorption capacity such as ferrihydrite, amorphous aluminum hydroxide, and mesoporous alumina, (Thirunavukkarasu et al., 2001; Anderson et al., 1976; Kim et al., 2004), the adsorption capacities of Fe_2O_3 and Al_2O_3 are quite low. However, compared with other adsorbents that have lower As(V) adsorption capacities such as IOCS, activated alumina, and activated red mud (Thirunavukkarasu et al., 2001; Lin and Wu, 2001; Altundogan et al., 2002), Fe_2O_3 can specifically be considered as a very useful adsorbent for As(V) removal in drinking water due to its very low cost.

6. Conclusions

Iron oxide (Fe_2O_3) and aluminum oxide (Al_2O_3) were found to be good and inexpensive adsorbents for lowering As(V) initial concentration in drinking water due to the fast

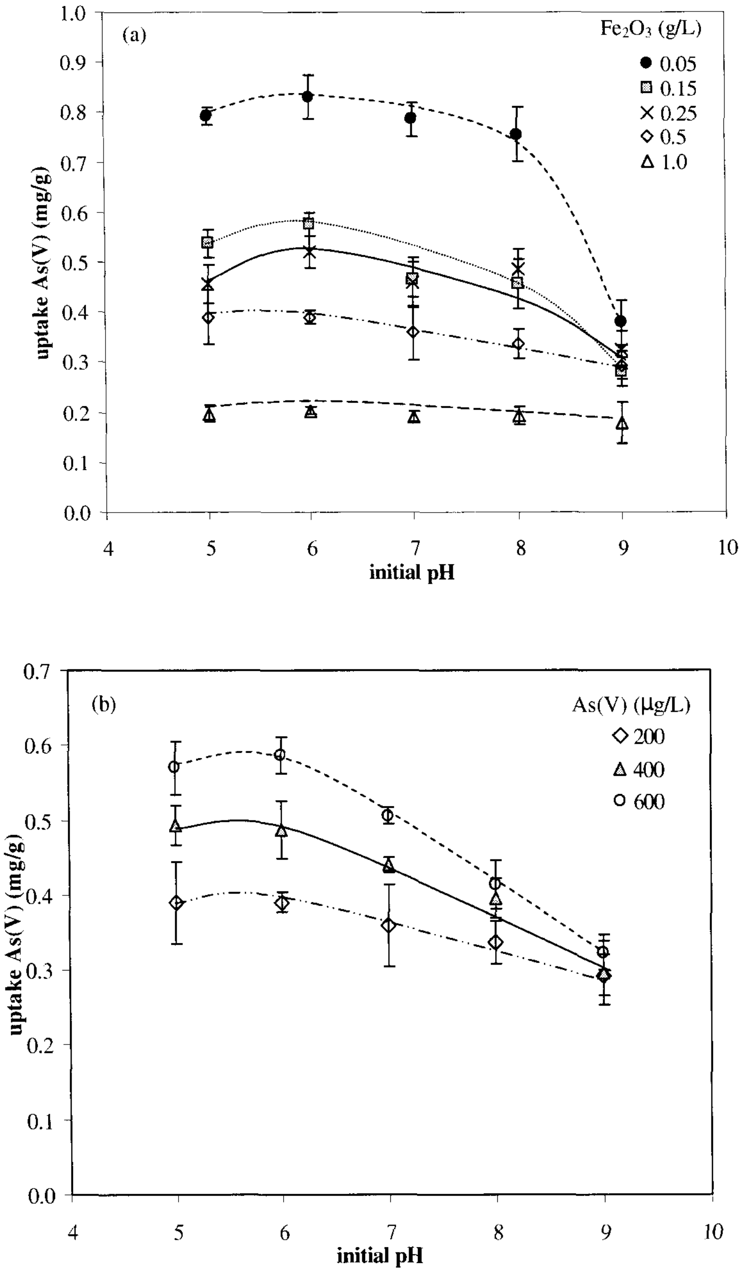


Figure 3.5. Arsenate adsorption onto Fe_2O_3 as a function of pH at (a) different dosages and (b) As(V) initial concentrations. Sample volume, 1 L; Stirring speed, 130 ± 5 rpm; 25°C; Stirring time, 1 hour (a) Dosage of Fe_2O_3, 0.05–1.0 g/L; As(V) initial concentration, 200 μg/L; (b) Initial As(V) concentration, 200–600 μg/L; dosage of Fe_2O_3, 0.5 g/L

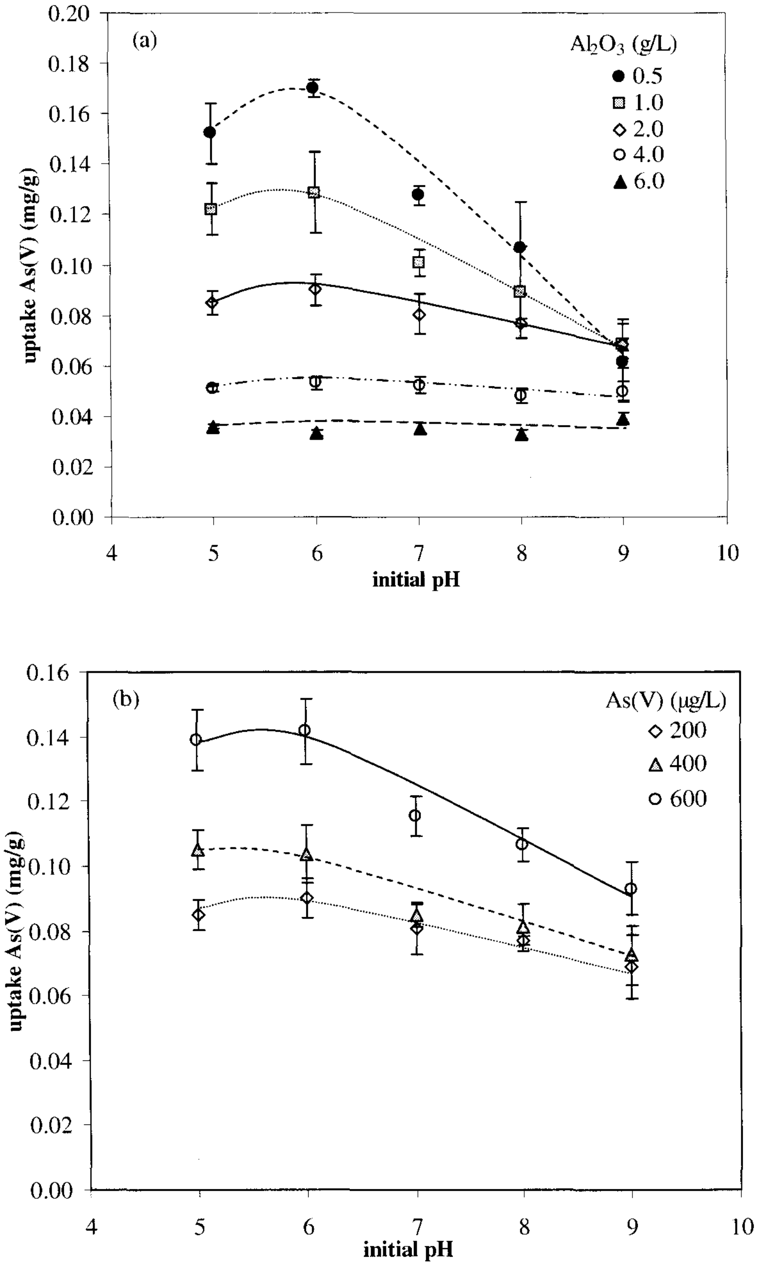


Figure 3.6. Arsenate adsorption onto Al_2O_3 as a function of pH at (a) different dosage and (b) As(V) initial concentrations. Sample volume, 1 L; Stirring speed, 130 ± 5 rpm; 25°C; Stirring time, 2 hours (a) Dosage of Al_2O_3, 0.5–6.0 g/L; As(V) initial concentration, 200 μg/L (b) Initial As(V) concentration, 200–600 μg/L; dosage of Al_2O_3, 2.0 g/L

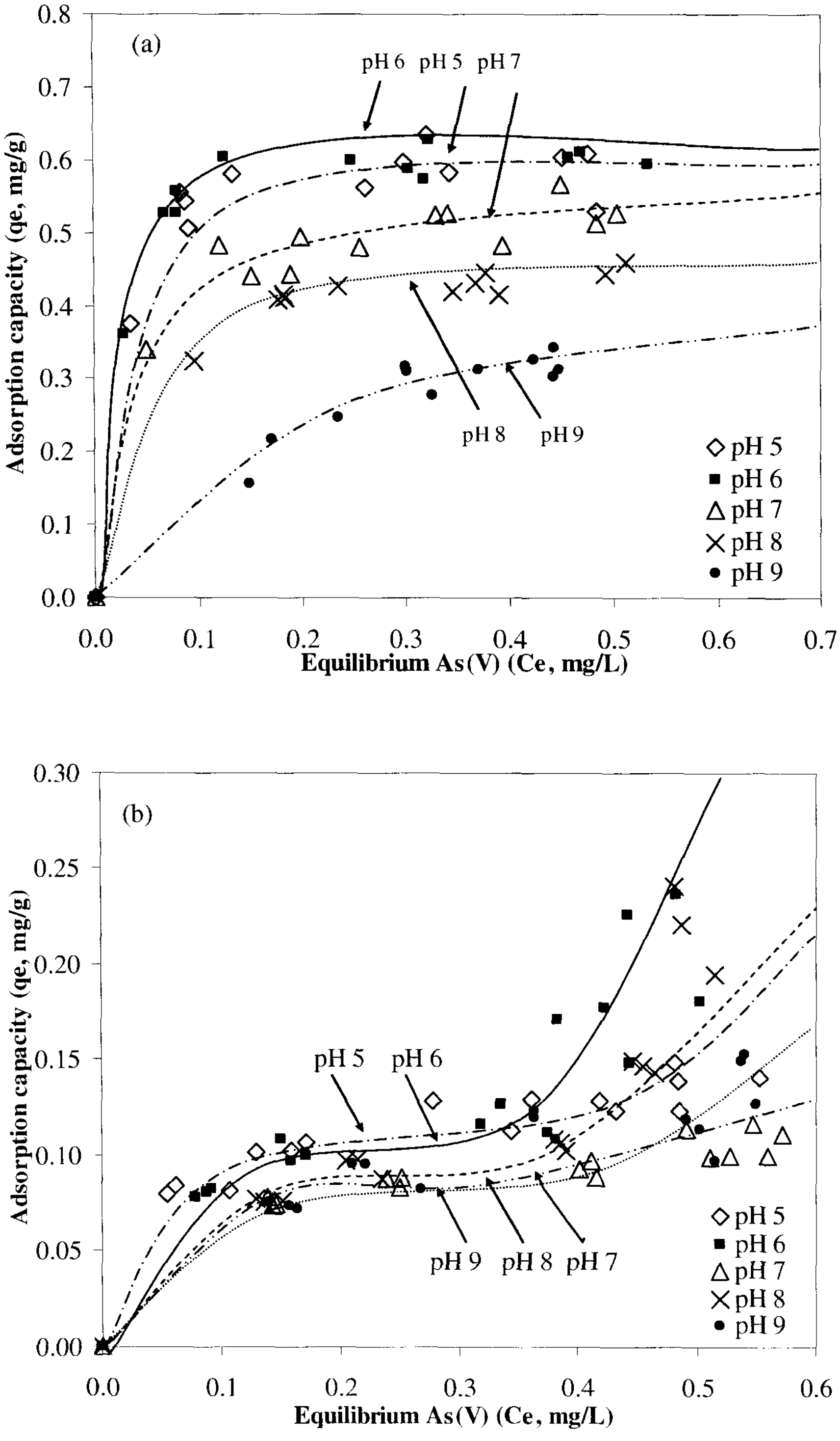


Figure 3.7. Adsorption isotherm plots for As(V) onto (a) Fe_2O_3 and (b) Al_2O_3. As(V) initial concentration, 600 μg/L; pH 5–9 ± 0.1 (a) Dosage, 0.05–1 g/L, (b) Dosage, 0.5–6 g/L

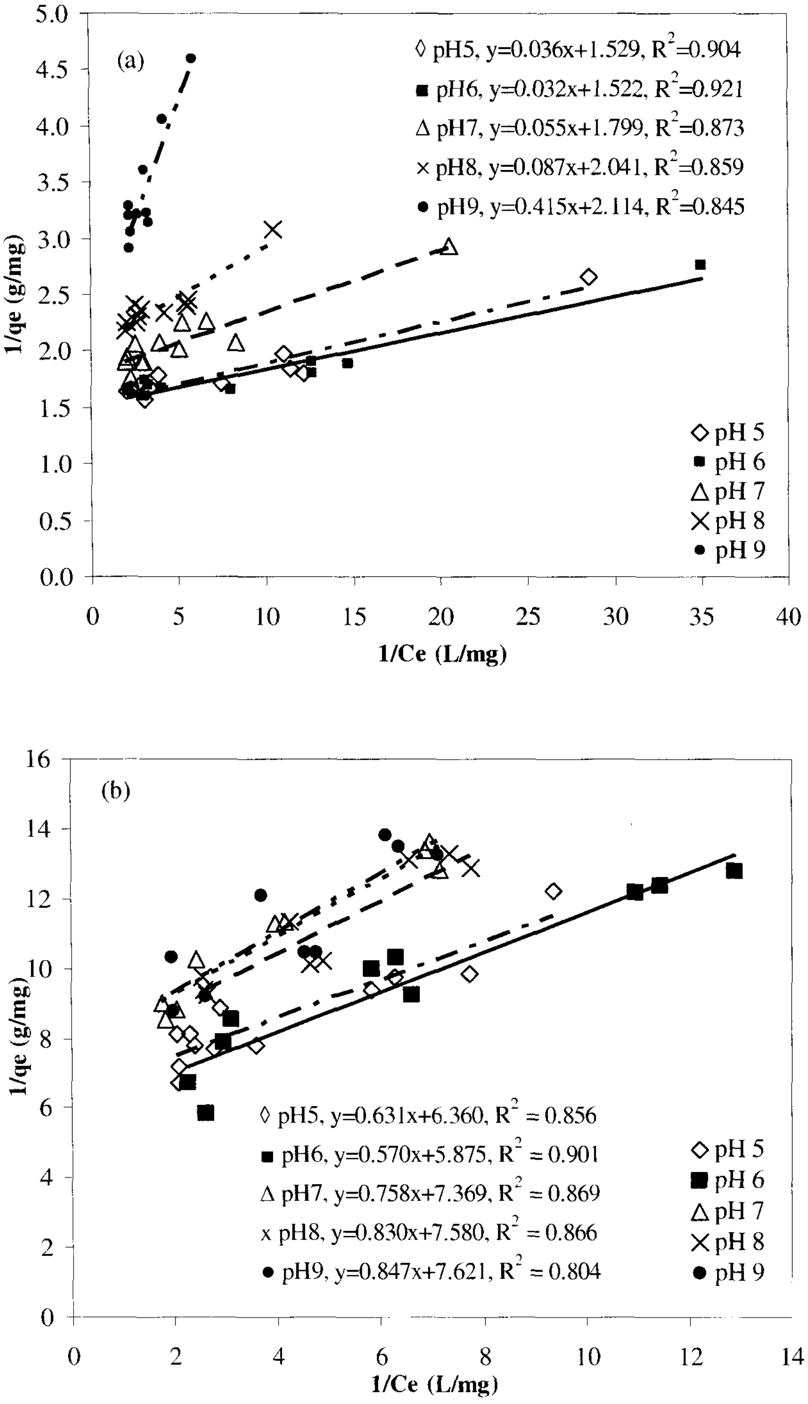


Figure 3.8 Linearized Langmuir isotherm plots for As(V) onto (a) Fe_2O_3 and (b) Al_2O_3. As(V) initial concentration, 600 μg/L; pH 5–9 ± 0.1 (a) Dosage, 0.05–1 g/L, (b) Dosage, 0.5–6 g/L

Table 3.3. Arsenate adsorption isotherm parameters of Fe_2O_3 and Al_2O_3

adsorbents	adsorption isotherms	parameters	pH 5	6	7	8	9
Fe_2O_3	*Langmuir*	b (L/mg)	42.01	47.12	32.83	23.36	5.09
		q_{max} (mg/g)	0.65	0.66	0.56	0.49	0.47
		R^2	0.90	0.92	0.87	0.86	0.85
Al_2O_3	*Langmuir*	b (L/mg)	10.08	10.31	9.76	9.13	8.99
		q_{max} (mg/g)	0.16	0.17	0.14	0.13	0.13
		R^2	0.86	0.90	0.87	0.87	0.80

7. Recommendations

Fe_2O_3 seems to be good for POE and POU water treatment systems because of the advantages outlined above. POE and POU arsenate removal systems utilizing iron oxide or aluminum oxide can be considered for either small-scale commercial water treatment systems for community water supplies or individual home treatment systems. These absorbents (Fe_2O_3 and Al_2O_3) for removing arsenate should be very useful in most endemic areas where arsenate-contaminated wells are used as water resources (e.g., China, India, and Bangladesh) as simplicity in application and low cost are often the essential factors for successful performance of adsorbents.

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CHAPTER 4. EFFECT OF COMPETING SOLUTES ON ARSENIC (V) ADSORPTION USING IRON AND ALUMINUM OXIDES

A paper to be submitted to The Journal of WATER RESEARCH

Youngran Jeong, Maohong Fan, Shilpi Singh[1]*, Chia-Line Chuang*[2]*, Basudeb Saha*[3]*, and J. (Hans) van Leeuwen*[4*]

Center for Sustainable Environmental Technologies, Iowa State University, Ames, IA, 50011, U.S.A.

[1] Sanborn, Head & Associates, Inc., Concord, NH, 03301, U.S.A
[2] Department of Research and Development, Allied Biotech Corp., Tao-Yuan, Taiwan
[3] Department of Chemistry, Iowa State University
[4] Department of Civil, Construction and Environmental Engineering, Iowa State University, Ames, IA, 50011, U.S.A. (leeuwen@iastate.edu)

1. Abstract

Iron oxide (Fe_2O_3) and nonactivated aluminum oxide (Al_2O_3) were found to be good and cost-effective adsorbents for removal of As(V) in drinking water in the presence of competing solutes including chloride, nitrate, sulfate, vanadium (V), selenium (IV), phosphate, and silica. It was observed that in a solution with an As(V) concentration of 200 μg/L and a pH 6, As(V) adsorption on Fe_2O_3 was not affected by 500 mg/L of chloride, nitrate, or sulfate, respectively, but it was slightly affected by 100 μg/L of selenium (IV) and vanadium (V). This behavior of these competing solutes can be explained by the fact that the complexes of As(V) with Fe_2O_3 are stronger than those formed by competing solutes; however, binding of Se(IV) and V(V) with Fe_2O_3 can occur even though the binding affinities of Se(IV) and V(V) are weaker than that of As(V) with Fe_2O_3. The adsorption of As(V) on Al_2O_3 was not affected by 500 mg/L concentration levels of chloride and nitrate anions, and very little by 100 μg/L concentration levels of Se(IV) and V(V) ions, respectively. However, despite the nonvariant concentration levels of sulfate after adsorption, the adsorption of As(V) on Al_2O_3 was moderately affected by more than 250 mg/L concentration levels of sulfate. Such an effect of sulfate on adsorption of As(V) may be due to surface heterogeneity. Both phosphate and silica had significant adverse effects on As(V) adsorption onto Fe_2O_3 and Al_2O_3 because the structure of phosphate is very close to that of arsenic and because silica ions form negatively charged surface sites and thus increase electrostatic repulsion. The As(V) adsorption capacities of Fe_2O_3 and Al_2O_3 were observed to be 0.616 mg/g and 0.098 mg/g, respectively, at a concentration of 200 μg/L of As(V) in the absence of competing solutes in a previous work (Jeong et al., 2005). Phosphate anion is found to be the most prominent solute competing against As(V) for adsorption on Fe_2O_3 and Al_2O_3, at even at concentration levels that are low in comparison with those of other competing solutes. Therefore, Fe_2O_3 was found to be a better adsorbent than Al_2O_3 for removing As(V) in the presence of competing solutes in water in the range of concentrations tested.

Keywords: Adsorption; Arsenic; As(V); Iron oxide; Aluminum oxide; Sulfate; Selenium(IV); Vanadium(V); Phosphate; Silica

2. Introduction

Arsenic(As) is well known as a useful compound in industrial applications such as smelting, agricultural pesticides and insecticides (LANL, 2004). However, arsenic (As) has also been considered as a strong poisonous chemical due to its odorless and nearly tasteless nature (Buchanan, 1962; Ferguson and Gavis, 1972). Even small amounts of arsenic in drinking water can have adverse effects on human health. Known consequences include cardiovascular diseases, conjunctivitis, and skin cancer (Tseng et al., 1968; Klaassen et al., 1996; Zhang et al., 2004; Safiullah et al., 2004; Yean et al., 2005; Zhang and Stanforth, 2005). Of organic and inorganic arsenic, inorganic arsenic commonly exists in two valence states, arsenite [As(III)] and arsenate [As(V)], in groundwater or surface water (Ferguson and Gavis, 1972; Reynolds et al., 1999). Erosion, dissolution, and weathering are some of the sources of inorganic arsenic in groundwater. Inorganic arsenic also has adverse effects on human health. As(III) effects on human health are more adverse than those of As(V); however, it is known to transform easily to As(V) in oxygenated environments (Brookins, 1988). In addition, arsenate removal efficiency using mineral oxides is found to be greater than that of arsenite. Therefore, the preoxidation of As(III) to As(V) using oxidizing agents including oxygen and ozone, prior to adsorption is recommended (Oscarson et al., 1983; Frank and Clifford, 1986).

Since the WHO (World Health Organization) has recommended 10 μg/L as the guideline value for arsenic in drinking water (WHO, 2001), the US Environmental Protection Agency (USEPA) has also promulgated 10 μg/L as their new arsenic standard for drinking water (US EPA, 2001a). Adsorption on metal oxides such as iron (Fe) and aluminum (Al) oxide is recommended by several researchers as one of most promising arsenic removal technologies. Other effective adsorbents for arsenic are amorphous ferric hydroxide (Pierce and Moore, 1982), granular ferric hydroxide (GFH) (Thirunavukkarasu et al., 2003), amorphous aluminum oxide (Anderson et al., 1976), and activated alumina (Rosenblum and Clifford, 1983).

We elucidated the possibility of Fe_2O_3 and Al_2O_3 being considered as nonregenerative adsorbent medias in a previous work (Jeong et al., 2005). It was observed that arsenate adsorption capacity varied between pH 5 and 9, and the highest adsorption of As(V) on both Fe_2O_3 and Al_2O_3 was observed at pH 6. Specifically, based on the simplicity in application and economics, Fe_2O_3 was proposed as a better adsorbent of As(V) for small point of use (POU) systems such as a single water tap delivering arsenic-contaminated ground or surface water. However, some soluble solutes in water were reported to reduce the adsorption of arsenic on metal oxides. Specifically silicate, phosphate, and sulfate were notorious as competing solutes when metal oxides were used for arsenic removal, and these competing solutes are commonly found in the groundwater and surface water in Bangladesh or in New Hampshire in the United States (Meng et al., 2002; Roberts et al., 2004; Hug et al., 2005). Welch et al. (1998) reported that more than 4 mg/L of phosphate (as P) occurs in the shallow groundwater from the southern Carson Desert in the United States.

Several researchers have reported that the presence of competing solutes results in a reduction of the amount of As(V) adsorbed on Fe and Al oxides. In one study, the presence of phosphate resulted in a severe reduction in arsenate adsorption by ferrihydrite (Jain and Loeppert, 2000), goethite [α-FeOOH] and gibbsite [γ-$Al(OH)_3$] (Manning and Goldberg, 1996b), kaolinite [$Al_2Si_2O_5(OH)_4$], montmorillonite [$(Na, Ca)(Al, Mg)_6(Si_4O_{10})_3(OH)_6$–$nH_2O$], and illite [$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}\{OH)_2,(H_2O)\}$] (Manning and Goldberg, 1996a). In another study, the high concentration of sulfate slightly reduced the removal of arsenate on alumina and hydrous ferric oxide, although the competing effect of sulfate anions was of a lesser degree than that of phosphate anions (Wilkie and Hering, 1996; Xu et al., 1988). Meng et al. (2000) showed that when using the triple-layer model (TLM), the removal of As(V) by coprecipitation and adsorption with ferric chloride was moderately affected in the presence of silicate, but not in the presence of sulfate. Lee et al. (2004) discovered that 35.5 mg/L of silica and 13 μg/L of vanadium (V) in groundwater had an unfavorable impact on As(V) adsorption using GFH. Davis and Misra (1997) showed that selenium (IV) could be a competing solute in the adsorption of Se(IV) and As(V) onto aluminum-based oxides. Thus, it is necessary to analyze the competitive effect of co-occurring solutes on As(V) adsorption onto Fe_2O_3 and Al_2O_3, and to evaluate the possibility of these oxides as appropriate adsorbents for removing As(V) in drinking water.

The competing effect of solutes on As(V) removal with Fe_2O_3 and Al_2O_3 was quantified by comparing As(V) removal efficiencies or adsorption capacities with and without the presence of solutes. Our experiments were conducted with the most common solutes in ground or surface water, such as chloride, nitrate, and sulfate, as well as phosphate and silicate. Vanadium (V) and selenium (IV) were also tested as competing solutes in As(V) adsorption onto Fe_2O_3 and Al_2O_3 because vanadium (V) is known as one of the phosphate-like mononuclear anions (Wehrli and Stumm, 1989; Wanty and Goldhaber, 1992); and because selenium (IV) plays an important role in soil and environmental chemistry due to its toxicity at high concentrations (Balistrieri and Chao, 1987; Tokunaga et al., 1996). A study of solutes competing with As(V) adsorption onto Fe_2O_3 and Al_2O_3, as in this paper, will be very helpful for developing more effective water treatment processes for removal of As(V) in drinking water.

3. Materials and Methods

3.1. Preparation of adsorbents and solutions

Iron oxide (Fe_2O_3-PVS; Physical Vapor Synthesis, Bailey-PVS, USA) and aluminum oxide (Al_2O_3-ALO101, Praxair, USA), as mentioned in a previous paper (Jeong et al., 2005), were used in our experiments for studying the competing effect of solutes on As(V) adsorption. These oxides, Fe_2O_3 and Al_2O_3, are nonporous adsorbents with small specific surface areas (5.05 and 0.55 m^2/g) and have been used in our experiments without further purification.

Chemicals including NaCl, $NaNO_3$, Na_2SO_4, Na_2HPO_4, $Na_2SiO_3 \cdot 9H_2O$, and V_2O_5 were reagent grade materials from Fisher Chemicals (USA). Sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) and sodium selenite (Na_2SeO_3) were from Matheson Coleman and Bell (Norwood, Ohio, USA) and from Sigma-Aldrich (USA), respectively. Stock solutions of arsenate ($HAsO_4^{2-}$, 10 mg/L), chloride (Cl^-, 1 g/L), sulfate (SO_4^{2-}, 1 g/L), nitrate as nitrogen (NO_3-N, 1 g/L), phosphate (HPO_4^{2-}, 1 g/L), silica (SiO_3^{2-}, 1 g/L), vanadium as vanadate (V^{5+}, 5 mg/L), and selenium as selenite ion (SeO_3^{2-}, 5 mg/L) were prepared by dissolving the respective chemicals in deionized water. All of these solutions, with the exception of the silica solution, were further diluted to suitable concentrations on the day of use. Silica stock solution was prepared every week and rapidly mixed with arsenate-contaminated water to maintain the main silicate species found in natural aquatic systems (monomeric H_4SiO_4); the quick dilution was proposed to avoid the formation of silicate polymers (Stumm and Morgan, 1996; Roberts et al., 2004).

3.2. Batch Experiment

Batch experiments were performed in a jar tester (PB-700TM, Phipps & Bird, USA) having six jars each of 2 L volume and six two-paddle stirrers to study the effect of competing ions on As(V) adsorption using Fe_2O_3 and Al_2O_3 in drinking water. The As(V) concentration was 200 μg/L (2.67×10^{-6}M), and the dosages of Fe_2O_3 and Al_2O_3 were 0.05–1 g/L and 0.5–6 g/L, respectively. Each of the competing solutes was added into separate water samples. Amounts of solutes added in the samples were based on the concentration of solutes in the natural water and drinking water quality standard of the US EPA (Meng et al., 2002; US EPA, 2001b; APHA, 1999; Heinz Center, 2000). Generally, the concentrations of sulfate and chloride were much higher than those of nitrate and silica in the water. The concentrations of phosphate, vanadium (V) and selenium (IV) were usually less than 1 mg/L in ground or surface water. The pH values of the test solutions were adjusted to 6 ± 0.1 using either diluted 0.1 M hydrochloric acid (HCl) or 0.1 M sodium hydroxide (NaOH) solutions before adsorption. To avoid the interference of other ions, all glassware was cleaned by soaking in 0.1 M HNO_3 and 0.5 M HCl and rinsed four times with deionized water. In order to avoid silica leaching from the glass beaker, polyethylene beakers were used in the experiments with silica and As(V) following Standard Methods (APHA, 1999). No detectable solutes adsorbed on the walls of the jar were ascertained through the blank experiments. At room temperature (25 ± 0.5°C), As(V) adsorption onto Fe_2O_3 and Al_2O_3 with competing solutes was conducted by stirring (130 ± 5 RPM) for 1 hour and 2 hours, respectively. For analysis after adsorption, supernatant of samples was collected from the jar using a 10 mL disposable syringe. The samples were filtered through 0.45 μm syringe filters (Millipore Millex) and analyzed for arsenic and competing anions. The As(V) adsorption uptakes were estimated from the difference between the initial and the equilibrium As(V) concentrations. The experiments were performed in triplicate and the mean values were accepted.

3.3. Methods of Analysis; arsenate and solutes

Arsenate [As(V)], vanadium [V(V)], and selenium [Se(IV)] concentrations in all the samples were measured by Inductively Coupled Plasma-Mass Spectrometry [ICP-MS, 4500 Series, Hewlett Packard (HP)] following Standard Methods (APHA, 1999). Because high concentrations of chloride interfere in measuring As(V), the interference correction equation provided by HP was applied to identify and measure arsenic concentrations. The analysis of phosphate (HPO_4^{2-} as total P) was also performed using ICP-MS (Dixit and Hering, 2003). The detection limits of ICP-MS were 0.1 μg/L for arsenic, and 1 μg/L for phosphate, vanadium (V), and selenium (IV), respectively. The measurements were considered as reasonable data in cases of less than 10% relative standard deviation (RSD) for lower concentrations and the RSD was ± 5% in the range of 50 to 600 μg/L solute concentration.

According to Standard Methods (APHA, 1999), the analysis of anions, such as nitrate (NO_3-N), sulfate (SO_4^{2-}), and chloride (Cl^-), was conducted in our laboratory using an ion chromatograph (IC-DX-120, Dionex) equipped with a Dionex Ion Pac As14 (4mm × 250mm) column and conductivity detection. The eluent solution used for ion chromatography (IC) was 3.5 mM Na_2CO_3/1 mM $NaHCO_3$. The molybdosilicate method was used for detecting silica concentrations (APHA, 1999). The concentration of silica was analyzed using a UV visible spectrophotometer (DMS 100, Varian) with a 1 cm light path at a 410nm wavelength. The detection limit for silica was 1 mg/L. The digestion with

$NaHCO_3$ was not used for checking the existence of molybdate-unreactive silica. Prior to each analysis, standard solutions of each solute were prepared by diluting stock solutions of each solute with deionized water.

4. Results and discussion

Adsorption of As(V) onto Fe_2O_3 and Al_2O_3 in the presence of some ions including sulfate (SO_4^{2-}), chloride (Cl^-), nitrate (NO_3-N), vanadium (V), selenium (IV), silica (SiO_3^{2-}), and phosphate (HPO_4^{2-}) was observed respectively for 200 μg/L As(V) concentrations at pH 6 ± 0.1, which was shown to be the best pH for removal of As(V) in a previous study (Jeong et al., 2005). Figure 4.1 shows the As(V) removal efficiencies of 0.5 g/L of Fe_2O_3 and 4 g/L of Al_2O_3 in the presence of high concentrations of competing solutes. Figure 4.1(a) shows that at the 0.5 g/L dosage of Fe_2O_3, chloride, nitrate, and sulfate solutes hardly affected the As(V) removal efficiencies, while vanadium (V) and selenium (IV) slightly affected the As(V) adsorption and silica and phosphate ions significantly decreased As(V) removal efficiencies. Figure 4.1(b) shows that at the 4 g/L dosage of Al_2O_3, chloride, nitrate, vanadium (V), and selenium (IV) solutes have little effect on the As(V) removal efficiencies; sulfate ions moderately reduced As(V) removal efficiencies; silica and phosphate ions significantly decreased As(V) removal efficiencies.

4.1. Chloride and Nitrate

The adsorption of As(V) on Fe_2O_3 and Al_2O_3 was found to be independent of the concentration of chloride and nitrate at pH 6 (figure not shown). Also, it was observed that the concentrations of these ions remained the same before and after adsorption (figure not shown). Xu et al. (2002) reported that the chloride and nitrate anions did not affect the adsorption of As(V) on aluminum-loaded shirasu-zeolite, which was similar to what we observed for Al_2O_3 in our study. This observation can be attributed to the fact that complexes of chloride and nitrate with Fe_2O_3 and Al_2O_3 are much weaker than those of arsenate.

4.2 Sulfate

The As(V) adsorption isotherm curves for Fe_2O_3 and Al_2O_3 are shown on Figure 4.2. The As(V) adsorption isotherm curves were hardly affected by lower concentrations of sulfate; however, the isotherms showed a moderately decreasing trend at higher sulfate concentrations, specifically at concentrations greater than 250 mg/L. This result is supported by several studies. Meng et al. (2000) reported that up to 300 mg/L of sulfate concentration had no apparent effect on the removal of As(V) with ferric chloride at a pH value of 6.8. This behavior was attributed to the fact that the binding affinity of sulfate for ferric hydroxide was much weaker than that of As(V). Zeng (2004) revealed that the interference of 460 mg/L of sulfate ions on arsenate adsorption onto an iron (III) oxide-silica binary oxide adsorbent (with an iron/silicate molar ratio of 3) was insignificant. Xu et al. (1988) stated that a high concentration of sulfate slightly reduced the removal of arsenate on alumina, although the competing effect of sulfate anions is smaller than that of phosphate anions. The heterogeneous surface of an adsorbent is known to affect adsorption more in muti-adsorbate than in single-adsorbate solutions (Balistrieri and Chao, 1990). The adsorption of As(V) on the heterogeneous surface of Al_2O_3, which was shown in the SEM picture of Al_2O_3 in a

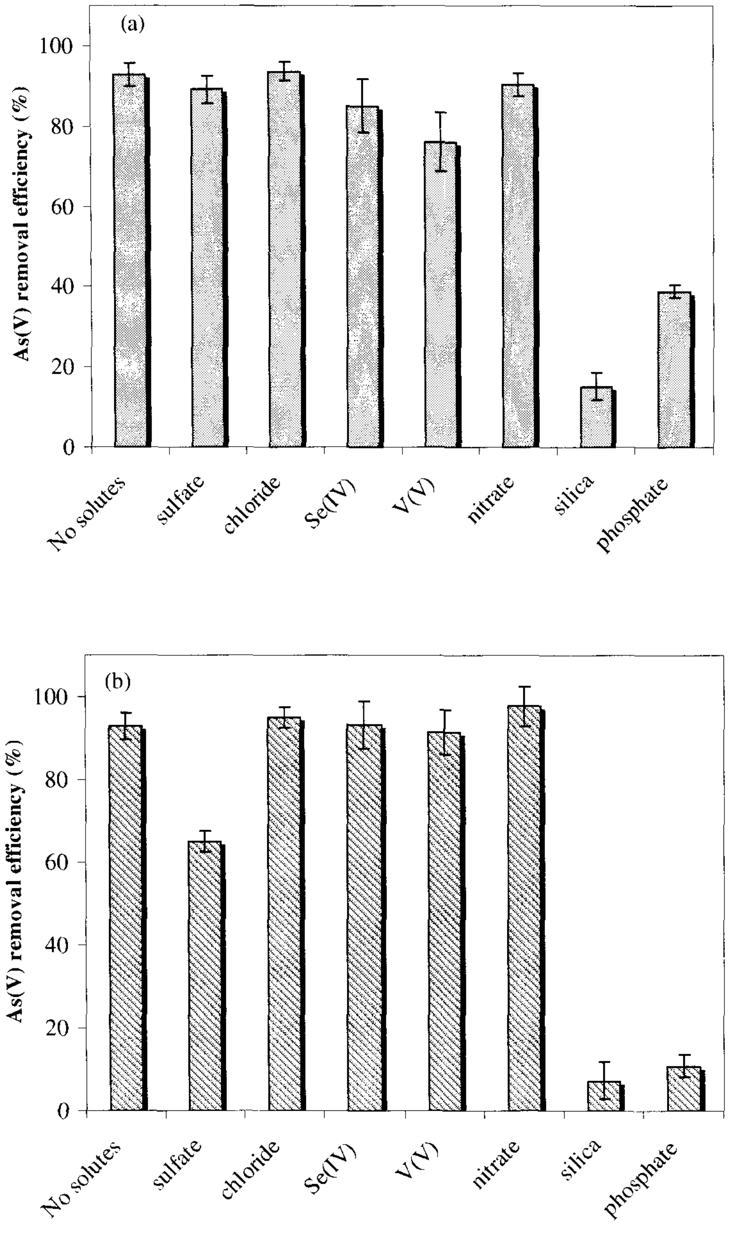


Figure 4.1. Effects of various competing solutes on As(V) removal efficiency using (a) Fe_2O_3 and (b) Al_2O_3. Initial As(V) concentration, 200 μg/L; sulfate and chloride, 500 mg/L for each; Se(IV) and V(V), 100 μg/L for each; nitrate, 20 mg/L; silica, 10 mg/L; phosphate, 1000 μg/L; pH 6 ± 0.1 (a) Dosage, 0.5 g/L, (b) Dosage, 4.0 g/L

previous work (Jeong et al., 2005), is affected by sulfate concentrations that are relatively high in comparison with the initial As(V) concentration.

As shown in Figure 4.3, the concentration of sulfate after As(V) adsorption on Al_2O_3 remained unchanged from its initial concentration, although Wijnja and Schulthess (2000) observed through Raman and attenuated total reflectance-Fourier transformed infrared (ATR-FTIR) that both inner- and outer-sphere surface complexes of sulfate ions occur on goethite and aluminum hydroxide surfaces without arsenate anions. By comparing the spectral intensities of sulfate anions on goethite and Al oxide, they further revealed that complexation of sulfate anions with aluminum oxide is weaker than that with Fe oxide. Thus, we conclude that the interaction of sulfate ions with surfaces of Fe_2O_3 and Al_2O_3 is weaker than that of As(V).

4.3 Selenium

The selenium (Se) ion, one of the essential micronutrients, is known to play an important role in soil and environmental chemistry due to its toxicity at high concentrations (Balistrieri and Chao, 1987; Tokunaga et al., 1996). High concentrations of selenium in soil often accumulate in plants and can then have toxic effects on herbivores (Peak and Sparks, 2002). The primary drinking water standard for selenium is 50 μg/L in the United States (US EPA, 1999b). The selenate anion (SeO_4^{2-}) (oxidation state VI) is the stable species under oxidizing conditions and adsorbs relatively weakly onto metal oxide surfaces. However, the selenite anion (SeO_3^{2-}) (oxidation state IV) is the stable species under slightly suboxic conditions and binds strongly to metal oxide surfaces (Balistrieri and Chao, 1987; Elrashidi et al., 1987).

As shown on Figure 4.4, the As(V) adsorption capacity of Fe_2O_3 slightly decreases while that on Al_2O_3 was little affected. In addition, as shown on Figure 4.5, the concentration of selenium (IV) after adsorption reduces rapidly with increasing of Fe_2O_3 dosage, while it reduces moderately with increasing Al_2O_3 dosage. At 50 μg/L initial Se(V) concentration, 95% of Se(IV) was adsorbed on 0.5 g/L Fe_2O_3, while only 10% of Se(IV) was removed by 0.5 g/L of Al_2O_3.

Our result with Se(IV) is supported by the study of Peak and Sparks through experiments of Extended X-ray adsorption fine structure and ATR-FTIR. According to Peak and Sparks (2002), selenate ions form inner-sphere and/or outer-sphere surface complexes and are adsorbed on iron oxides and hydroxides such as hematite, goethite and hydrous ferric oxide (HFO) by pH and ionic strength. Wijnja and Schulthess (2000), using ATR-FTIR spectroscopy, reported that selenate (SeO_4^{2-}) ions are adsorbed on goethite and Al oxide and that complexation of selenate with Fe oxide is stronger than that with Al oxide. These results indicate that the binding affinity of As(V) with Fe_2O_3 and Al_2O_3 is stronger than that of selenite, and the complexation of selenite with Fe_2O_3 is stronger than that with Al_2O_3.

4.4 Vanadium

Vanadium exposure is known to cause lung irritation, chest pain, cough, and sore throat, but no significant health effect on human has yet been found (US EPA, 1999b). The maximum level of vanadium recommended for irrigation by the United Nations Food and Agriculture Organization is 0.1 mg/L (APHA, 1999). Vanadium occurs in the +3, +4, and +5 oxidation states under aqueous conditions and exists in the +5 oxidation state in oxic seawater.

As shown on Figure 4.6, vanadium (V) slightly affects the As(V) adsorption capacity of

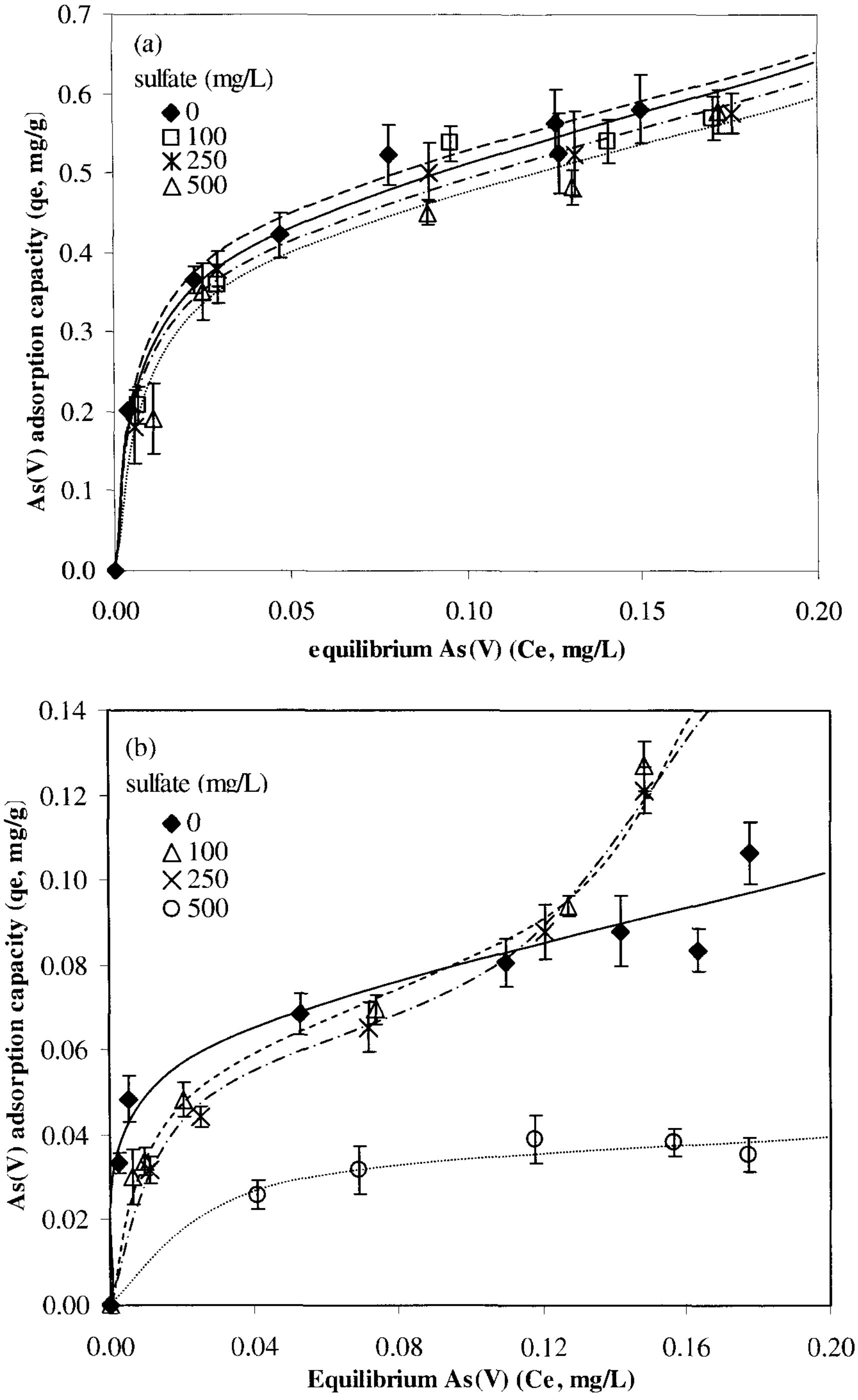


Figure 4.2. Adsorption isotherm of As(V) onto (a) Fe_2O_3 and (b) Al_2O_3 as a function of sulfate concentration. Initial As(V) concentration, 200 μg/L; pH 6 ± 0.1

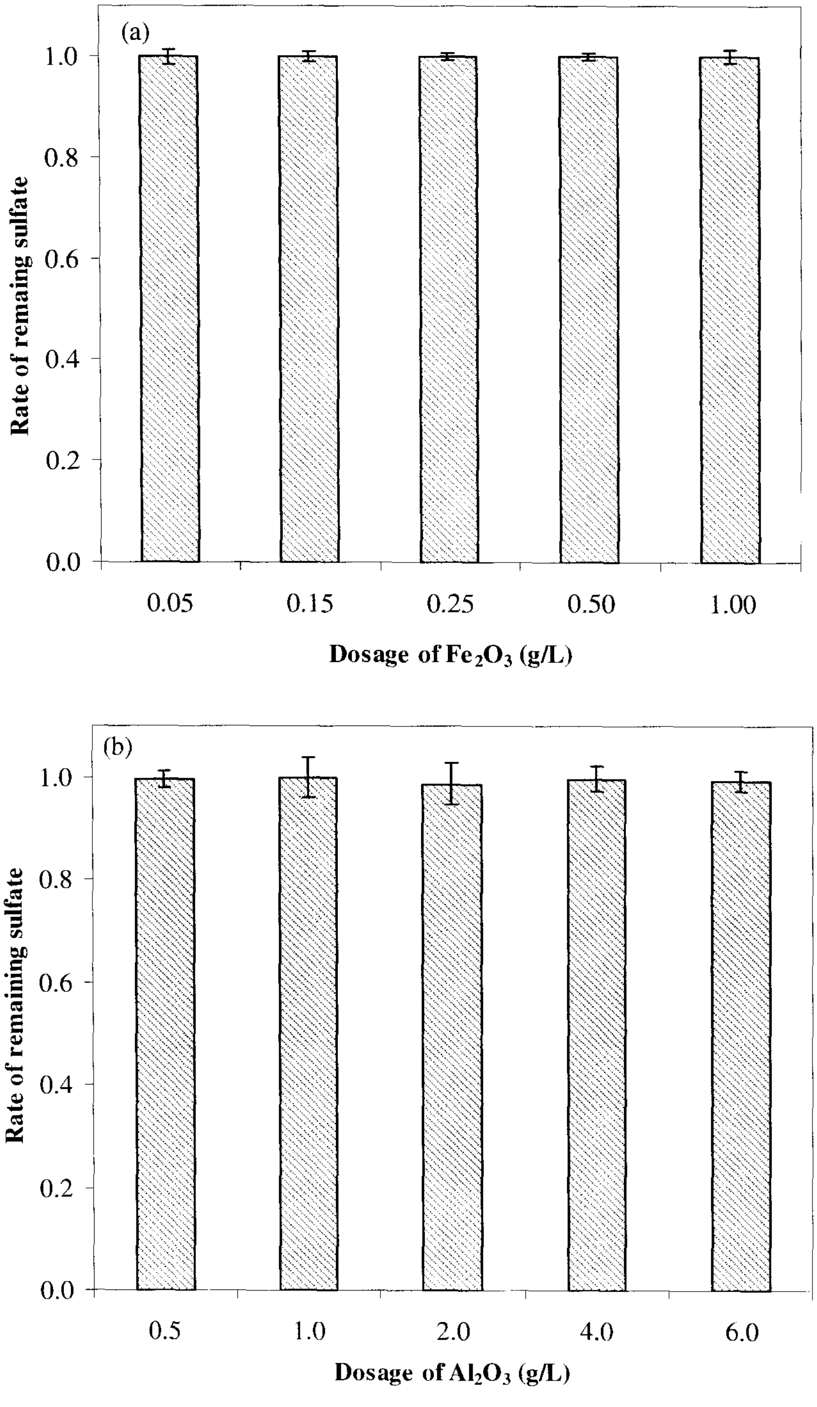


Figure 4.3. Comparison of remaining sulfate concentrations after As(V) adsorption on various dosages of (a) Fe_2O_3 and (b) Al_2O_3. Initial sulfate concentration, 250 mg/L; pH 6 ± 0.1

Fe_2O_3 but has little effect on that of Al_2O_3. The As(V) adsorption capacity of Fe_2O_3 was not changed in the presence of V(V) at 10 μg/L concentration. Similar results were observed with Al_2O_3 in the presence of V(V) at 50 μg/L concentration. In high V(V) concentrations (>50 μg/L), however, the adsorption isotherm curve of As(V) on Fe_2O_3 showed a gradual decrease. It was found that the isotherm curves reach a saturation plateau with increasing vanadium (V) concentrations. This result matches with the report by Lee et al. (2004) that 13 μg/L of vanadium (V) in groundwater had an unfavorable impact on As(V) adsorption using granular ferric hydroxides.

As shown in Figure 4.7, the remaining V(V) concentration after adsorption decreased significantly with an increasing dosage of Fe_2O_3. From a 50 μg/L initial V(V) concentration, 0.5 g/L of both adsorbents adsorb 90% or 10% of the V(V), respectively. Vanadium (V) can be more easily adsorbed on Fe_2O_3 than on Al_2O_3. This result matches the findings of Shieh and Duedall (1988) that suggest that the removal of V(V) on amorphous ferric oxyhydroxide can be reached in quasi-equilibrium condition within 1 hour. Golob et al. (1971) reported that vanadium (V) is absorbed poorly on activated aluminum oxide. Several investigators discovered that in dilute solutions the principal species of V(V) are mononuclear vanadate oxyanions [$VO_2(OH)_2^-$ and $VO_3(OH)^{2-}$], which are similar to phosphate anions (Wanty and Goldhaber, 1992; Wehrli and Stumm, 1989), and that vanadate oxyanions can particularly adsorb through ligand exchange onto the negatively charged iron oxide or clay mineral surfaces such as goethite (α-FeOOH) (Cruywagen and Heyns, 1991; Sigg and Stumm, 1980; Peacock and Sherman, 2004). Because of these characteristic of vanadium (V), we can assume that V(V) competes with As(V) for adsorption on surface sites on Fe_2O_3 but the interaction of As(V) with the surface of Fe_2O_3 is still stronger than that of V(V).

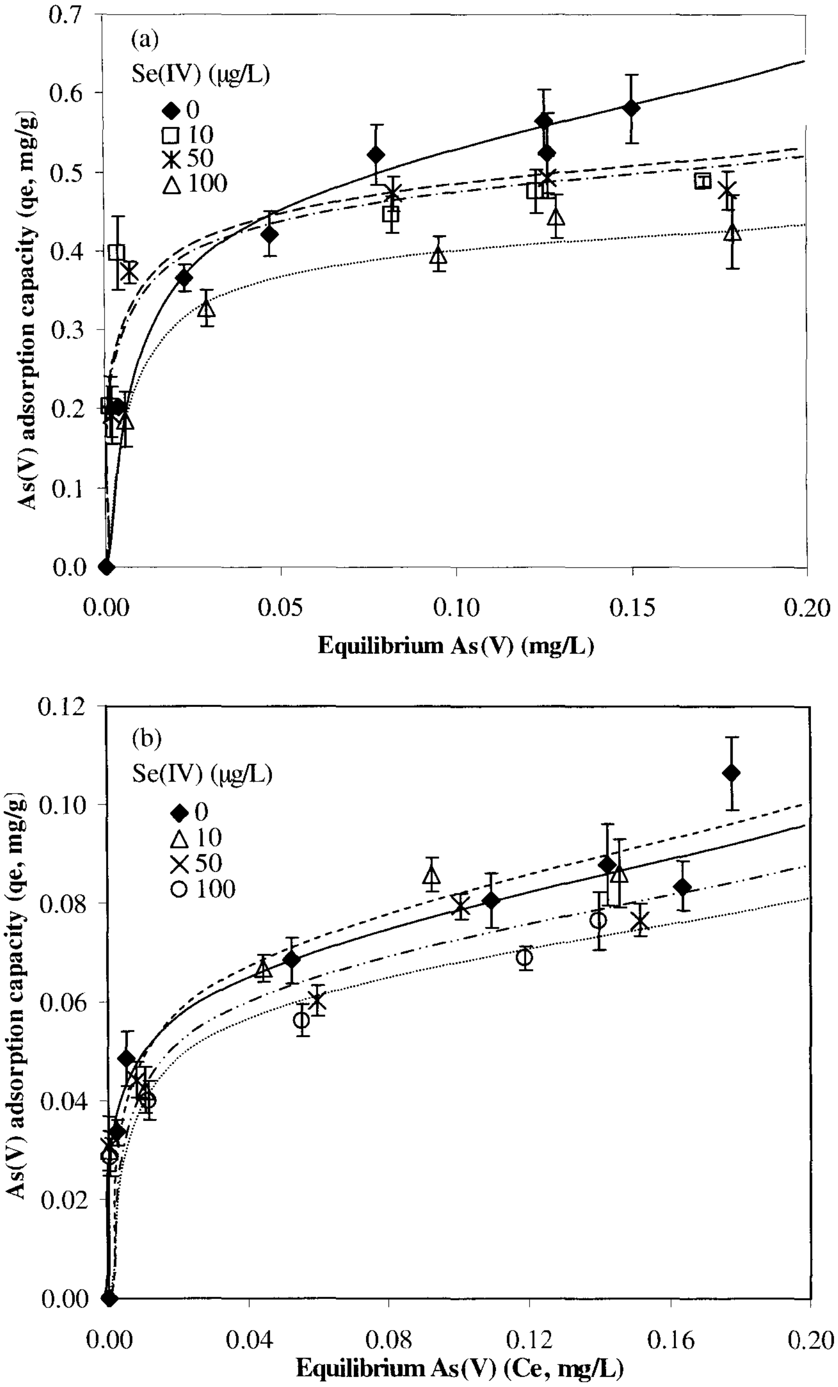


Figure 4.4. Adsorption isotherm of As(V) onto (a) Fe_2O_3 and (b) Al_2O_3 as a function of Se(IV) concentration. Initial As(V) concentration, 200 μg/L; pH 6 ± 0.1

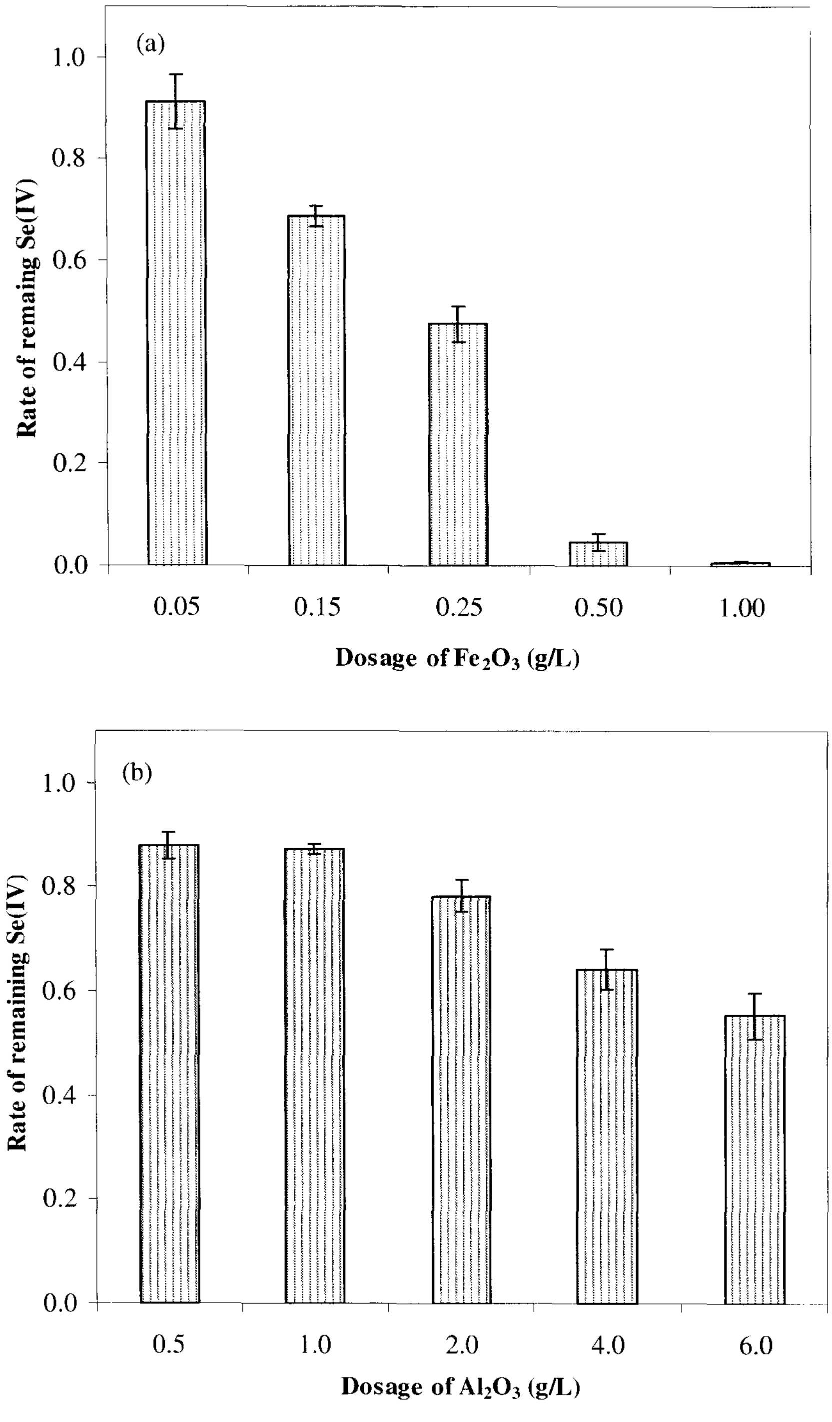


Figure 4.5. Comparison of remaining Se(IV) concentrations after As(V) adsorption on various dosages of (a) Fe_2O_3 and (b) Al_2O_3. Initial Se(IV) concentration, 50 μg/L; pH 6 ± 0.1

4.5 Phosphate

Phosphate is known as a growth-limiting nutrient, which plays an important role in the growth of organisms. Phosphates, classified as orthophosphates, condensed phosphate, and organically bound phosphate, occur in natural water and wastewater through laundering, fertilizing, and weathering (US EPA, 1999b). Depending on the pH value, phosphates can have any of the following four forms in dilute aqueous solution: phosphate ion (PO_4^{3-}), hydrogen phosphate ion (HPO_4^{2-}), dihydrogen phosphate ion ($H_2PO_4^-$), or aqueous phosphoric acid [H_3PO_4(aq)]. PO_4^{3-} ions are more prevalent in strongly basic conditions, and HPO_4^{2-} ions are more common in weakly basic conditions. $H_2PO_4^-$ ions and aqueous H_3PO_4 predominate in weakly acid conditions and strongly acid conditions, respectively (Wikipedia, 2005).

Figure 4.8 shows that phosphate (HPO_4^{2-}) can sharply decrease the As(V) adsorption capacity of Fe_2O_3 and Al_2O_3 as a function of phosphate concentration. Less than 50 μg/L phosphate concentration does not affect the adsorption of As(V) using either of the two adsorbents (Fe_2O_3 and Al_2O_3). However, As(V) adsorption on Al_2O_3 is influenced more than that on Fe_2O_3 by phosphate concentrations over 50 μg/L. In fact, to achieve the same results for As(V) adsorption with Al_2O_3 as with Fe_2O_3, higher dosages of Al_2O_3 are required. As shown in Figure 4.8, the As(V) adsorption isotherm data for Fe_2O_3 and Al_2O_3 satisfactorily fit the lower concentration of phosphate, but the isotherm curves for Al_2O_3 show a significantly decreasing trend in the presence of more than 50 μg/L of phosphate. This result matches several researchers' findings. Meng et al. (2002) reported that phosphate (HPO_4^{2-}) in concentrations over 0.25 mg/L was an important factor affecting the removal of As(V) on iron hydroxides. Manning and Goldberg (1996b) also studied the decreased As(V)

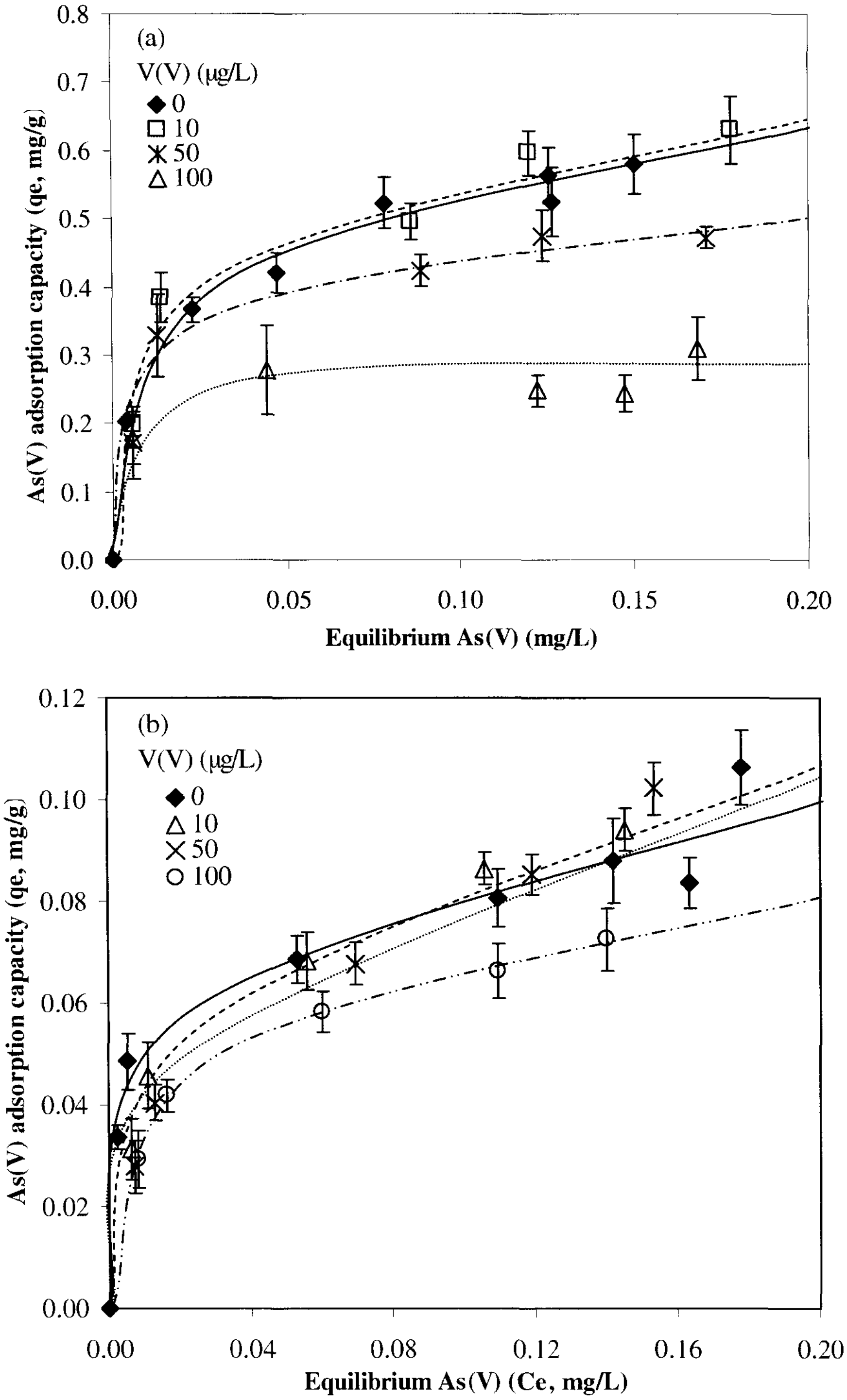


Figure 4.6. Adsorption isotherm of As(V) onto (a) Fe_2O_3 and (b) Al_2O_3 as a function of V(V) concentration. Initial As(V) concentration, 200 μg/L; pH 6 ± 0.1

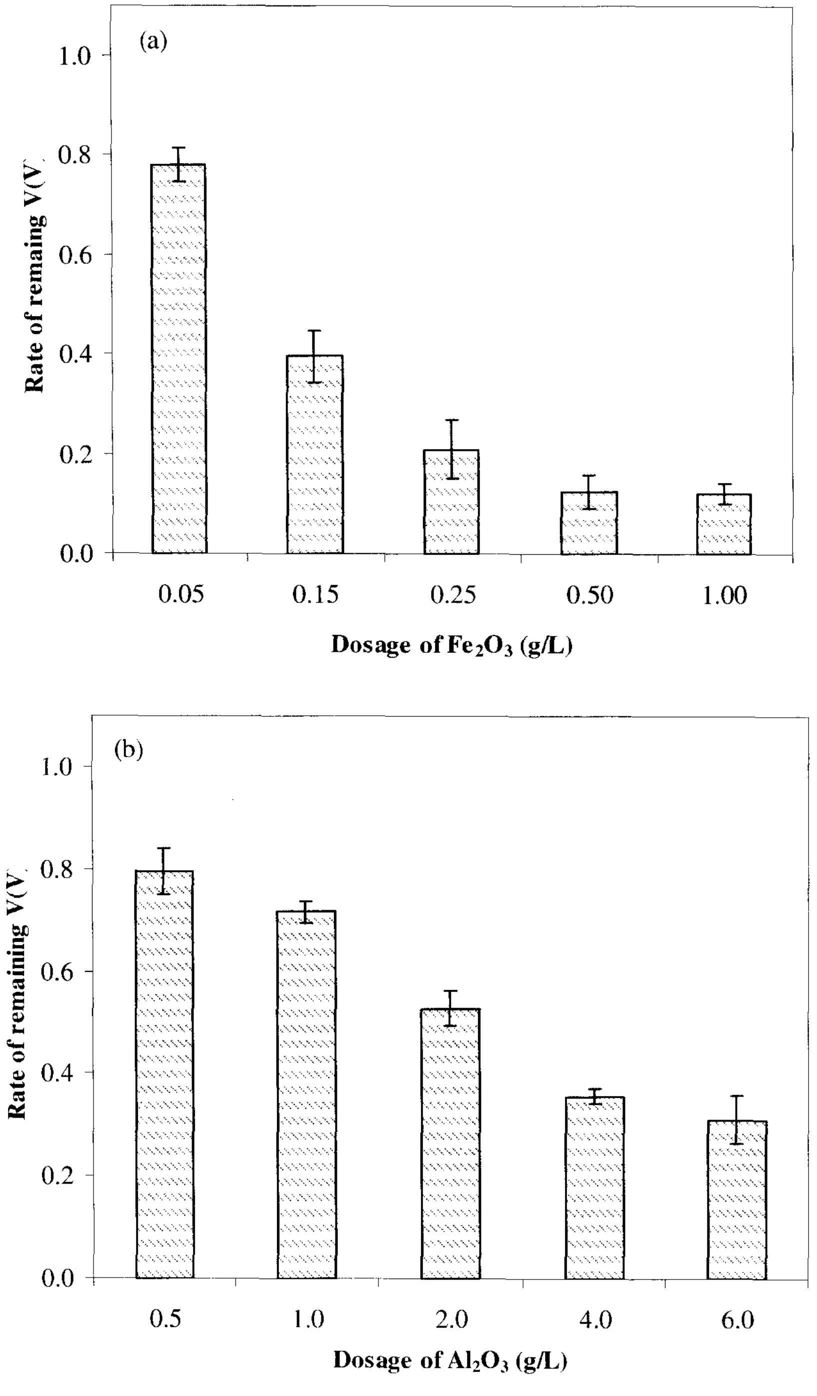


Figure 4.7. Comparison of remaining V(V) concentrations after As(V) adsorption on various dosages of (a) Fe_2O_3 and (b) Al_2O_3. Initial V(V) concentration, 50 μg/L; pH 6 ± 0.1

adsorption in the presence of phosphate within the pH range of 2 to 11 on goethite (α-FeOOH) and gibbsite (γ-Al(OH)$_3$). Xu et al. (2002) observed that the adsorption of As(V) on aluminum-loaded Shirasu-zeolite was significantly reduced by the addition of phosphate ions. Figure 4.9 shows that phosphate anions compete with arsenate ions and adsorb onto Fe_2O_3 and Al_2O_3 in the water. The remaining phosphate concentration following adsorption decreased significantly with increasing dosages of Fe_2O_3 and moderately with increasing dosages of Al_2O_3. At 500 μg/L initial phosphate concentration, 1 g/L of Fe_2O_3 can remove 78% of phosphate, while same dosage of Al_2O_3 adsorbs only 25% of the phosphate anion. This result seems reasonable considering the fact that it is consistent with the results of several reports regarding phosphate adsorption. Madrid et al. (1974) indicated that phosphate ions can easily adsorb onto three kinds of Fe oxides (goethite, lipidocrocite, and hematite) at pH 3.2 to 9.6 and they found that the reactions fit well to both Langmuir and Freundlich isotherms. Nooney et al. (1996) also found that phosphate uptake was rapid on a thin Fe_2O_3 film of adsorbent in 10 minutes of exposure time. Javid et al. (2004) reported that gibbsite (γ- Al_2O_3) was an effective anion exchange material for phosphate anions at a low pH and that phosphate uptake on γ- Al_2O_3 results from electrostatic interactions (ion exchange) rather than nonelectrostatic adsorption.

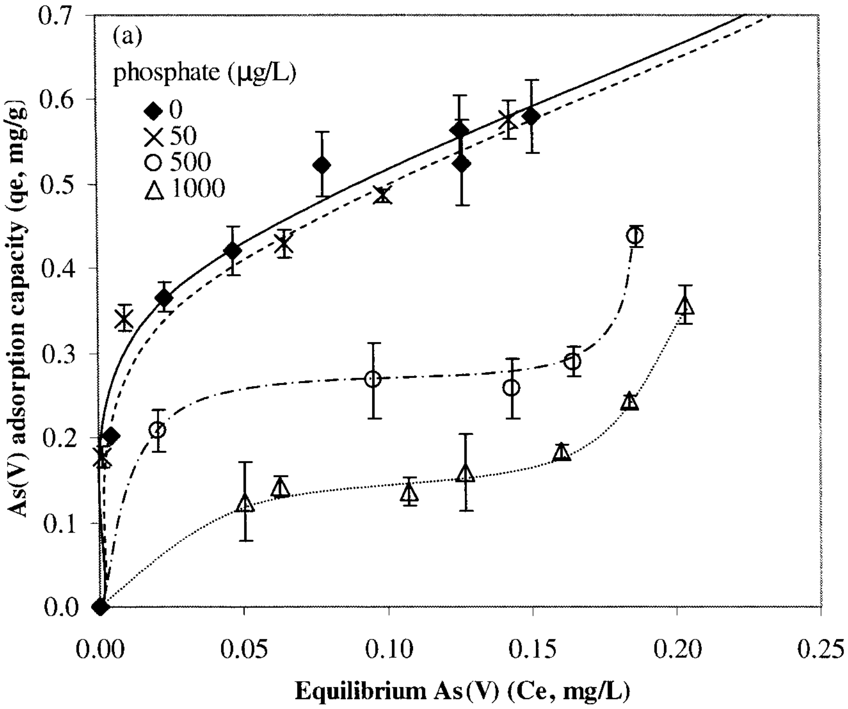
The competing effect of phosphate anions on Fe_2O_3 and Al_2O_3 can be explained using several investigators' statements. Phosphate is very adsorptive on the surfaces of iron and aluminum oxides and has significant effects on the adsorption of arsenic at low concentration because of the structural resemblances between arsenic and phosphate ions (Pierce, 1981; Wasay et al., 1996; El Khatib and Balba, 2004). Therefore, we have conclusions similar to those discussed above. Phosphate competes with arsenate for binding sites on Fe_2O_3 and

Al_2O_3 due to the similarity of their structure. But the complexes of As(V) with Fe_2O_3 and Al_2O_3 should be stronger than those of phosphate according to the findings of Meng et al. (2002), which suggest that the constant of binding affinity (Kapp) value of As(V) is seven times greater than that of phosphate on iron hydroxides.

4.6 Silica

Commonly found soluble forms of silica in natural water are H_2SiO_4 and $H_2SiO_4^-$, and the average concentration of silica is 14 mg/L as Si in surface and groundwater (APHA, 1999). There is no maximum contaminant level (MCL) for silica in drinking water, but high levels of silica can form precipitates, increasing turbidity (US EPA, 1999b).

The results in Figure 4.10 show the As(V) adsorption capacity of Fe_2O_3 and Al_2O_3 as a function of silica concentration. The As(V) adsorption isotherms of Fe_2O_3 and Al_2O_3 are found to show significant decreasing trends in relation to silica concentrations. The adsorption of As(V) on Fe_2O_3 at 1 mg/L silica concentration increases slightly while that on Al_2O_3 increases moderately. We assume that very low concentrations of silica have an enhancing effect on the adsorption of As(V) because of favorable electrostatic effects at the surface of $Fe_2O_3$and Al_2O_3 (Wilkie and Hering, 1996). The adsorption of As(V) decreased significantly with the increasing silica concentrations from 5 to 10 mg/L and decreasing dosages of Fe_2O_3 and Al_2O_3. The silica solute has more adverse effects on Al_2O_3 than on Fe_2O_3. Considering the average silica concentration of 14 mg/L in surface and groundwater (APHA, 1999), the effect of silica is very important on As(V) adsorption using Fe_2O_3 and Al_2O_3. This result matches the results of several reports regarding the effect of silica or silicate on arsenic removal. Meng et al. (2000) reported that with 10 mg/L of silicate



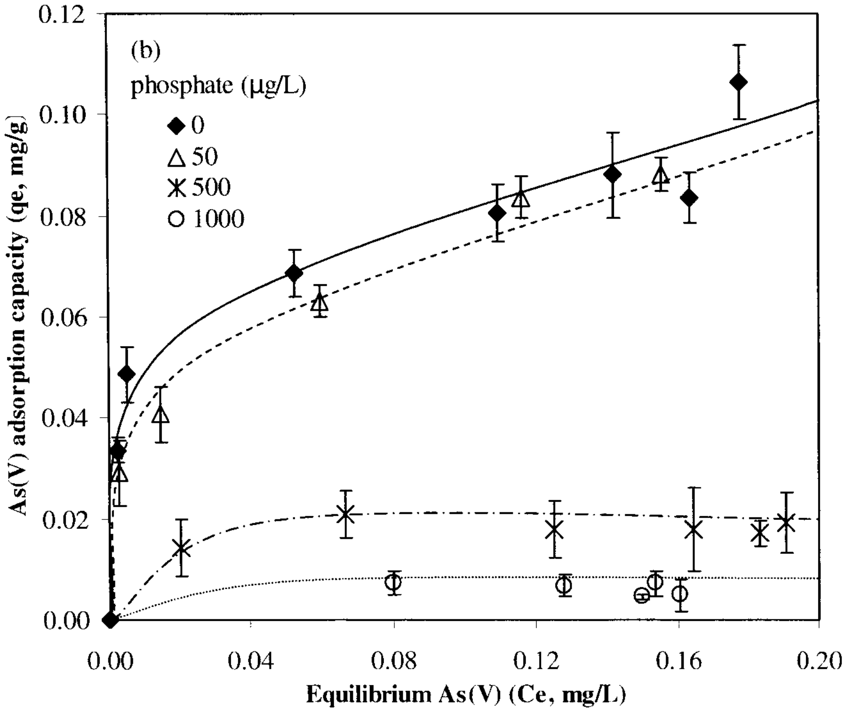


Figure 4.8. Adsorption isotherm of As(V) onto (a) Fe_2O_3 and (b) Al_2O_3 as a function of phosphate concentration. Initial As(V) concentration, 200 μg/L; pH 6 ± 0.1

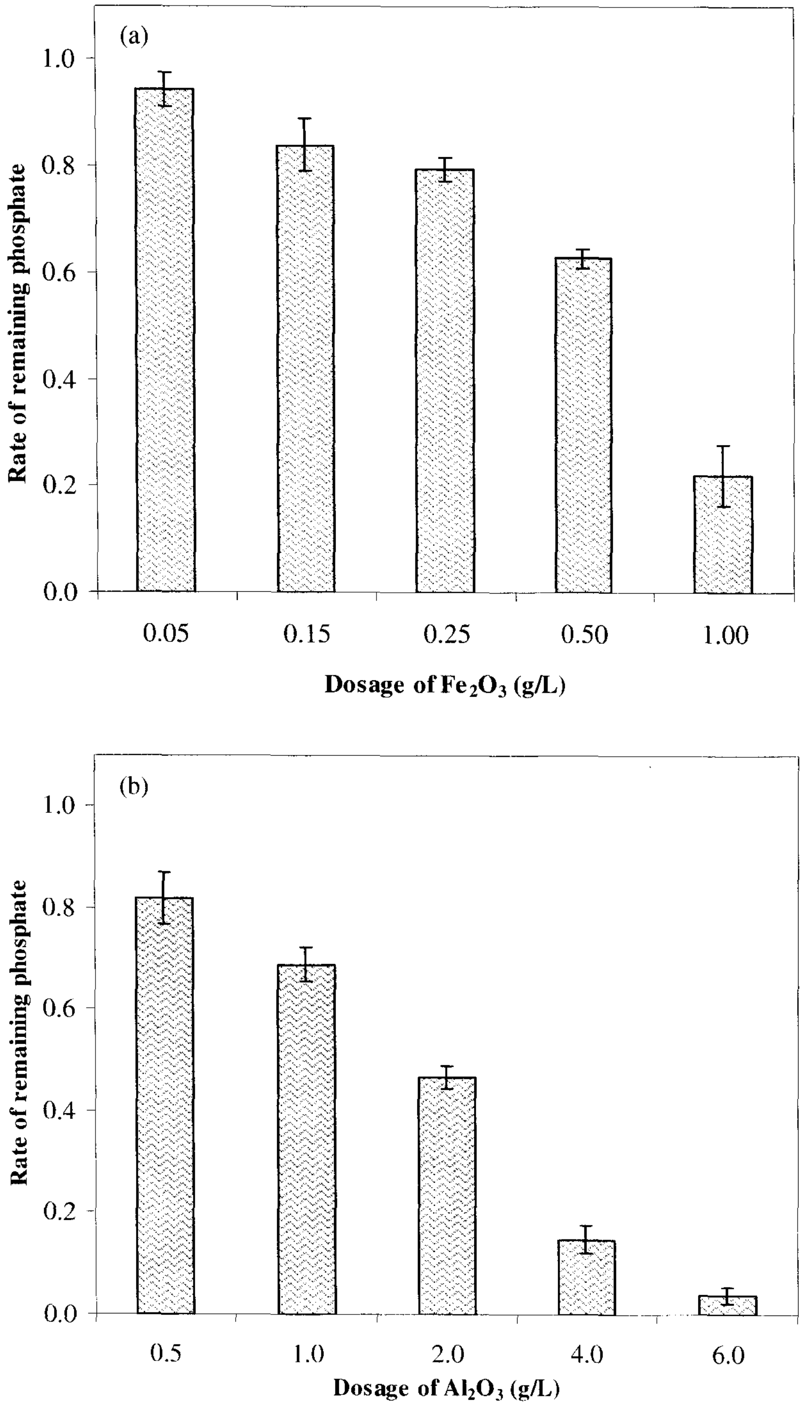


Figure 4.9. Comparison of remaining phosphate concentrations after As(V) adsorption on various dosages of (a) Fe_2O_3 and (b) Al_2O_3. Initial phosphate concentration, 500μg/L; pH 6±0.1

concentration, the removal of As(V) on ferric chloride decreased from approximately 90 to 45%, and the As(V) adsorption capacity was also reduced from 0.96 to 0.27 mg/g Fe. In addition, they suggested that the As(V) adsorption reduction resulted from the strong association of silicate with ferric hydroxide, which reduced the surface sites available for As(V) and increased electrostatic repulsion between As(V) and the negatively charged surface sites. Meng et al. (2002) also showed that the adsorption of As(V) on iron hydroxides was not changed at SiO_2 concentrations of less than 1.4mg/L because the binding constant of silicate was 800 times inferior to that of As(V), but it was reduced from 99% to 85% at silica concentrations higher than 1.5 mg/L. Singh et al. (2005) found that the dissolved silicate competes with As(V) in the coprecipitation and adsorption removal processes using ferrihydrite, and they proposed that the effect of silicate is to cause a combination of complexation reactions between Fe(III), Si(IV), and As(V) species, and competition between As(V) and Si(IV) for adsorption sites on ferrihydrite. Our finding is also supported by the fact that 35.5 mg/L of silica and 13 μg/L of vanadium (V) in groundwater had an unfavorable impact on As(V) adsorption using granular ferric hydroxides (Lee et al., 2004). Therefore, we infer that comparatively high concentrations of silica affect the adsorption of As(V) on Fe_2O_3 and Al_2O_3 due to a reduction in available surface sites and increasing electrostatic repulsion.

As shown in Figure 4.11, the concentration of silica after As(V) adsorption on Fe_2O_3 did not change, compared with its initial concentration, and changed very little after As(V) adsorption on Al_2O_3. Some researchers have shown by estimating the apparent adsorption constants that the binding affinity of the anions for iron hydroxide sites decreased in the following order: OH- >arsenate > phosphate > silicate > sulfate (Madrid et al., 1974; Meng et al., 2002). Based on the low binding affinity of silica, we can infer that silica can hardly be adsorbed on Fe_2O_3 and Al_2O_3.

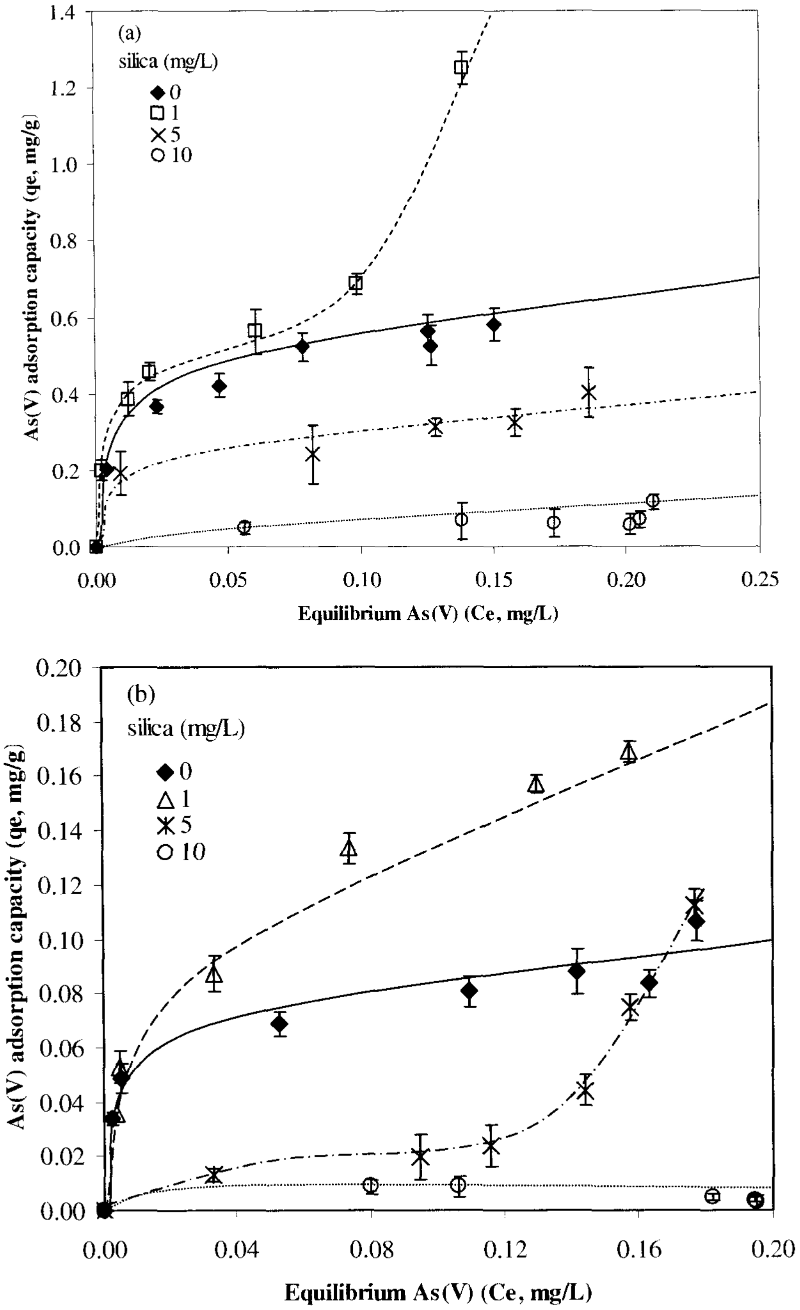


Figure 4.10. Adsorption isotherm of As(V) on (a) Fe_2O_3 and (b) Al_2O_3 as a function of silica concentration. Initial As(V) concentration, 200 μg/L; pH 6 ± 0.1

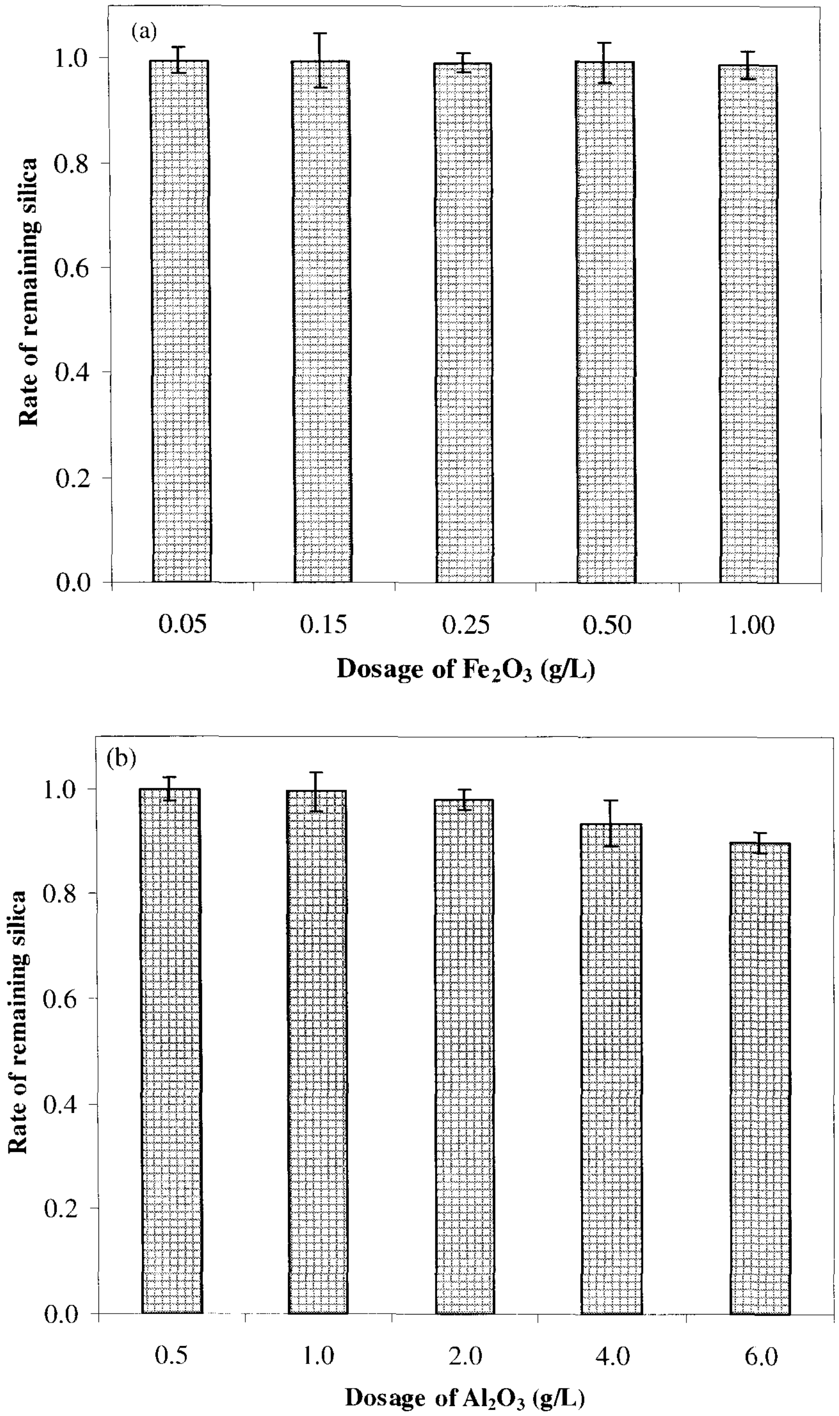


Figure 4.11. Comparison of remaining silica concentrations after As(V) adsorption on various dosages of (a) Fe_2O_3 and (b) Al_2O_3. Initial silica concentration, 10 mg/L; pH 6 ± 0.1

4.7. Comparison of As(V) adsorption parameters of Fe_2O_3 and Al_2O_3 with competing solutes

In the previous study (Jeong et al., 2005), the adsorption of As(V) on both Fe_2O_3 and Al_2O_3 fitted the Langmuir isotherm well. To compare the adsorption capacity of As(V) on Fe_2O_3 and Al_2O_3 in typical concentrations of competing solutes such as phosphate and silica, plots of adsorption capacity (mg/g) vs. equilibrium As(V) concentration were linearized using mean values of experimental data (figure not shown). Table 4.1 shows the As(V) adsorption parameters of the Langmuir isotherm on Fe_2O_3 and Al_2O_3 in the presence of competing solutes such as sulfate, Se(IV), V(V), phosphate, and silica. For 200 μg/L of initial As(V) concentration at pH 6, the maximum As(V) adsorption capacity (q_{max}) and correlation coefficient (R^2) in the absence of competing solutes were observed to be 0.616 mg/g and 0.93 using Fe_2O_3, and 0.098 mg/g and 0.94 using Al_2O_3, as estimated from the Langmuir isotherm in a previous study (Jeong et al., 2005). In the presence of phosphate at 500 μg/L concentration, the adsorption capacity (q_{max}) and the correlation coefficient (R^2) were reduced to 0.327 mg/g and 0.59, respectively, using Fe_2O_3; and 0.019 mg/g and 0.61, respectively, using Al_2O_3. Silica at 5 mg/L concentration also reduced q_{max} and R^2 to 0.327 mg/g and 0.74, respectively, using Fe_2O_3; and 0.045 mg/g and 0.82, respectively, using Al_2O_3. Considering the adsorption bond strength, b, selenite ion bonds on Fe_2O_3 and Al_2O_3 were much weaker than those of the other competing solutes. Silica ion bonds are stronger than the others on Fe_2O_3, while phosphate ion bonds are much stronger than the others on Al_2O_3. These results show that Fe_2O_3 is a better absorbent than Al_2O_3 in the presence of competing solutes, specifically, phosphate and silica.

Therefore, based on the lower concentration level of phosphate compared with other competing solutes, and the values of the adsorption capacity and correlation coefficient (R^2)

discussed above, phosphate anions are found to be the most prominent solute competing against As(V) for adsorption on Fe_2O_3 and Al_2O_3. Considering the values of adsorption capacity and dosages, Fe_2O_3 is found to be a better adsorbent than Al_2O_3 for removing As(V) in the presence of competing solutes in water.

Table 4.1. Langmuir adsorption isotherm parameters of As(V) on Fe_2O_3 and Al_2O_3 in the presence of competing solutes

Adsorbents	**200 µg/L of As(V), pH 6 + competing solutes**	**As(V) adsorption parameters**		
		***b* (L/mg)**	**q_{max} (mg/g)**	**R^2**
Fe_2O_3	No solutes	60.53	0.616	0.93
	Sulfate, 250 mg/L	81.33	0.572	0.96
	Selenium(IV), 50 µg/L	32.84	0.503	0.95
	Vanadium(V), 50 µg/L	91.49	0.521	0.96
	Phosphate, 500 µg/L	82.56	0.327	0.59
	Silica, 5 mg/L	145.58	0.327	0.74
Al_2O_3	No solutes	44.56	0.098	0.94
	Sulfate, 250 mg/L	50.31	0.087	0.96
	Selenium(IV), 50 µg/L	7.06	0.076	0.87
	Vanadium(V), 50 µg/L	55.19	0.098	0.89
	Phosphate, 500 µg/L	154.98	0.019	0.61
	Silica, 5 mg/L	11.86	0.045	0.82

Conditions: initial As(V) concentration 200 µg/L, pH 6 ± 0.1

5. Conclusions

This study, describing the effect of competing solutes on adsorption of As(V) on Fe_2O_3 and Al_2O_3 was performed as an extension to our previous work. The subject solutes of our study include sulfate, chloride, nitrate, Se(IV), V(V), phosphate, and silica. In the presence of these competing solutes, the adsorption of As(V) onto Fe_2O_3 and Al_2O_3 was conducted to estimate the possibility of these oxides as appropriate adsorbents for removing As(V) from drinking water. High concentrations of chloride and nitrate did not affect the adsorption of As(V) on Fe_2O_3 and Al_2O_3. This observation was ascertained by the fact that the concentrations of these anions did not change before and after adsorption, and was attributed to the possibility of the formation of weak complexes of these solutes with Fe_2O_3 and Al_2O_3. Due to surface heterogeneity, high concentration of sulfate has a moderate adverse effect on the adsorption of As(V) on Al_2O_3. However, high concentration levels of sulfate did not seem to affect the adsorption of As(V) on Fe_2O_3 because sulfate binding affinity for Fe oxide may be much weaker than that of As(V). Besides, the concentration of sulfate anions did not change before and after adsorption on either adsorbent. Because the complexes of Se(IV) and V(V) with Fe_2O_3 are stronger than those with Al_2O_3, these Se(IV) and V(V) ions may compete with As(V) ions on the surface of Fe_2O_3. Therefore, the relatively higher concentration (100 μg/L) of Se(IV) and V(V) had a slightly unfavorable impact on the As(V) removal efficiency and adsorption isotherm for Fe_2O_3 but not those for Al_2O_3. However, the most significant interference with the removal of As(V) on Fe_2O_3 and Al_2O_3 occurs in the presence of phosphate and silica solutes. The phosphate anion is found to be the most competitive solute on Fe_2O_3 and Al_2O_3, considering its lower concentration and the value of adsorption capacity and the correlation coefficient (R^2). Besides, a strong bond with Fe_2O_3 and Al_2O_3 occurs in the presence of silica and phosphate solutes, respectively. Considering the value of adsorption capacity and dosage, Fe_2O_3 is found to be a better adsorbent than Al_2O_3 to remove As(V) in the presence of competing solutes in water. In addition, Fe_2O_3 may be used as a preliminary adsorbent to minimize the competing effect for some solutes prior to As(V) adsorption, considering that Fe_2O_3 can easily adsorb phosphate, Se(IV), and V(V) in water.

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CHAPTER 5. CONCLUSIONS

GENERAL DISCUSSION

Iron oxide (Fe_2O_3) and aluminum oxide (Al_2O_3) have been studied as prospective adsorbents for removing arsenic (V) from drinking water under various conditions of temperature, concentration, time, and competing solutes. Fe_2O_3 and Al_2O_3, both of which are nonporous adsorbents, were found to be good and inexpensive adsorbents for As(V) removal from drinking water at lower pH (< 7), specifically pH 6, due to their fast adsorption of arsenate anions and high As(V) removal efficiencies. The adsorption of As(V) onto Fe_2O_3 was affected by the same solutes, such as phosphate, silica, Se(IV), and V(V), while that onto Al_2O_3 was affected by sulfate as well as by phosphate and silica. Both phosphate and silica had significant adverse effects on adsorption of As(V) with Fe_2O_3 and Al_2O_3; however, the phosphate anion was found to be the most prominent solute competing against As(V). Considering the cost and the adsorption capacity of As(V) with and without competing solutes, Fe_2O_3 is a more suitable adsorbent than Al_2O_3 to remove As(V) from drinking water.

RECOMMENDATIONS FOR APPLICATION

Fe_2O_3 and Al_2O_3 have many advantages including possibly low cost, easy maintenance, fast adsorption rate, and no need for regeneration, and they have no adverse effects on water quality after adsorption. Specifically, Fe_2O_3 is more economical than Al_2O_3 because it is generated from the ferrous metals industry as a by-product. Due to its low cost and simplicity in application, Fe_2O_3 should be useful to apply to small-scale commercial water treatment systems or individual home treatment systems as POE or POU unit processes in most endemic areas where arsenate-contaminated wells are used as water resources, such as China, Chile, Taiwan, Bangladesh, and the western United States. Pilot-scale studies are recommended for developing appropriate types of adsorption process units using these adsorbents (e.g., columns, filters, or dosing in powdered form). In addition, it is suggested that Fe_2O_3 can be used as a preliminary adsorbent to minimize the competing effect of other solutes prior to As(V) adsorption because Fe_2O_3 has a better ability than Al_2O_3 to remove competing solutes, specifically, phosphate, selenium (IV) and vanadium (V).

APPENDIX A. ADDITIONAL FIGURES

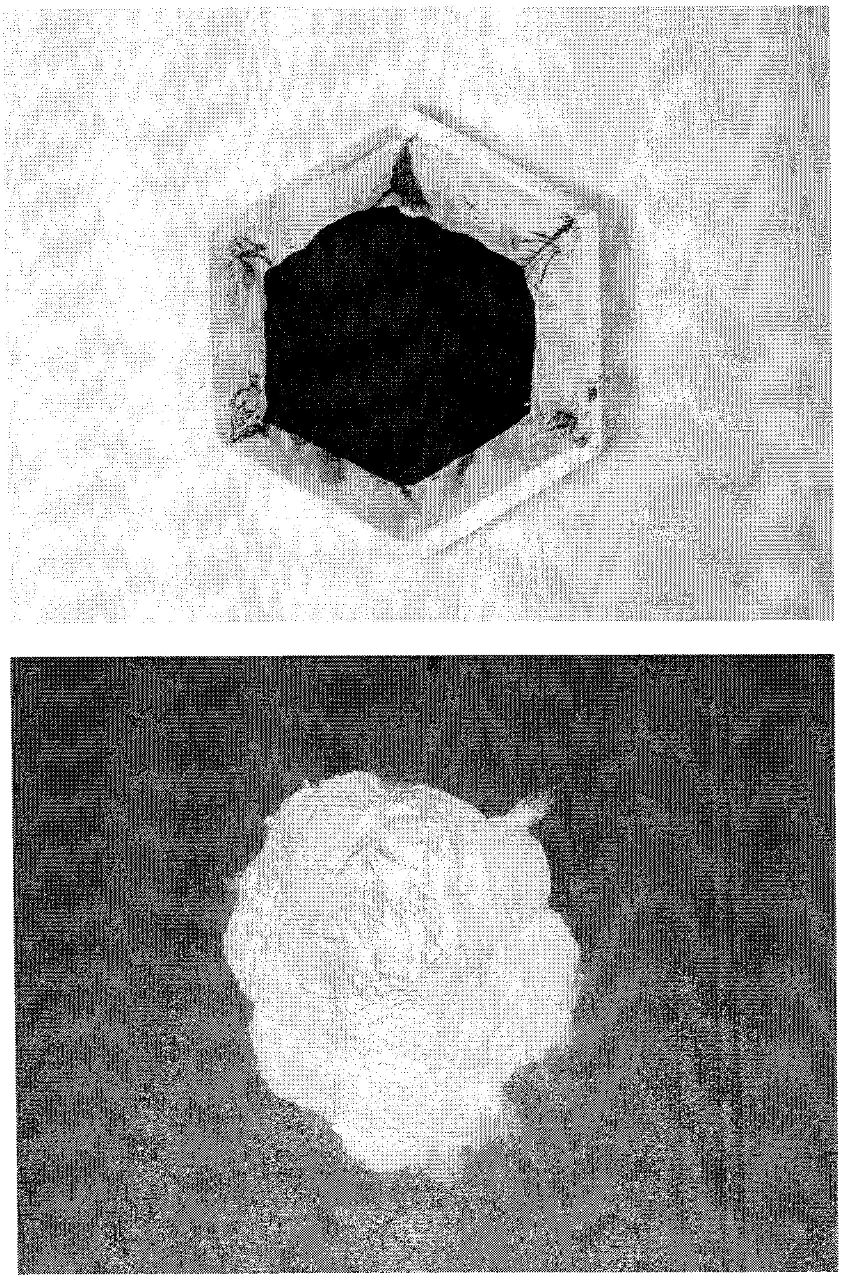

Figure A1. The colors of Fe_2O_3 (top) and Al_2O_3 (bottom)

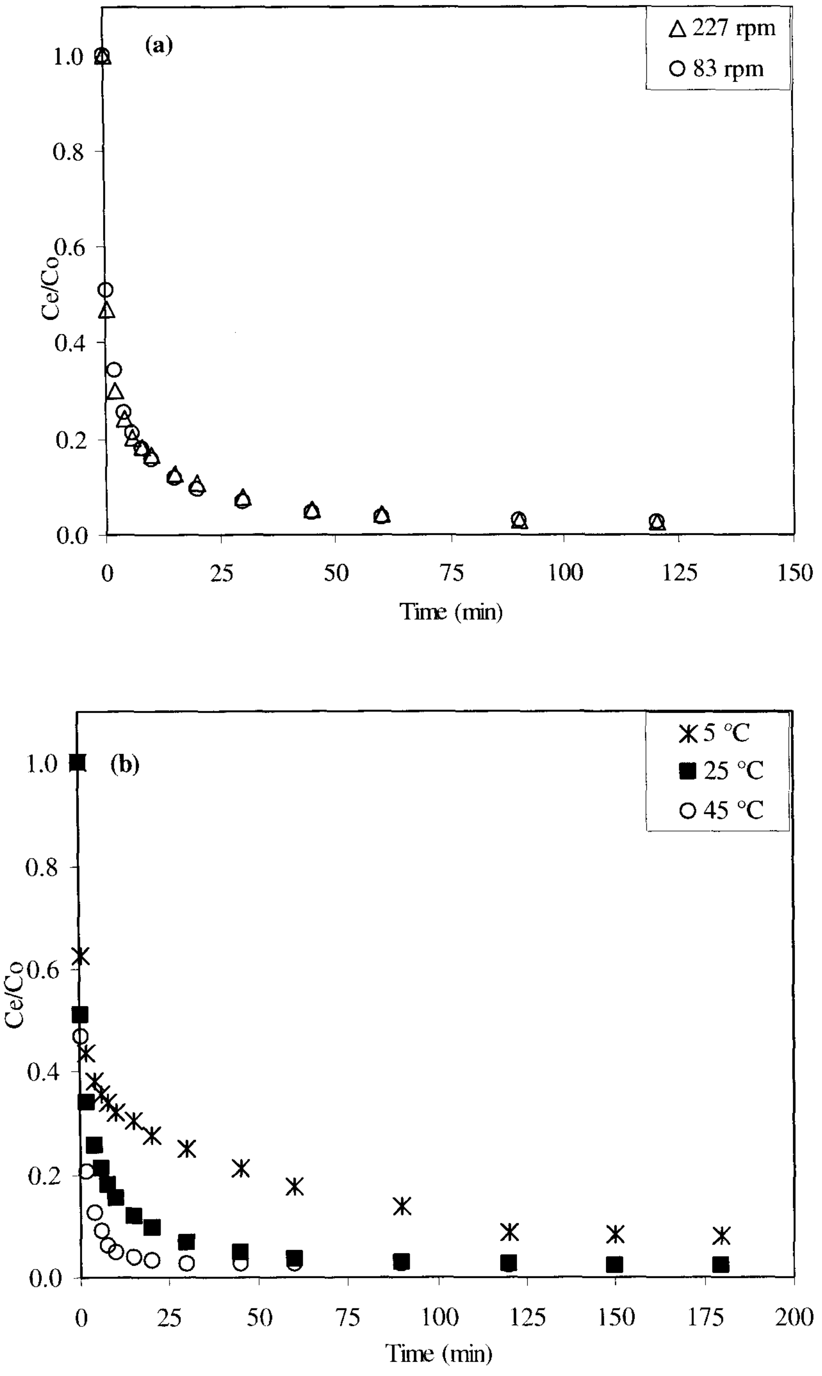

Figure A2. As(V) adsorption onto Al_2O_3 as functions of (a) stirring speed and (b) temperature. Initial As(V) concentration (Co), 200 μg/L; Dosage of Al_2O_3, 3 g/L; Sample volume, 0.5 L; pH 6 ± 0.1; (a) Temperature, 25 ± 0.5°C; (b) Stirring speed, 83 ± 5 rpm