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Study of Chemical States, Composition and Adsorption Behavior of Iron Coated Granular Activated Carbon (Fe-GAC) for Selenate Removal and Feasible Adsorbent Modifications

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**Study of Chemical States, Composition and Adsorption Behavior of
Iron Coated Granular Activated Carbon (Fe-GAC) for Selenate
Removal and Feasible Adsorbent Modifications**

Ning Zhang

**Dissertation submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Doctor of Philosophy
In
Civil and Environmental Engineering**

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**Morgantown, West Virginia
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**Keywords: selenate removal, iron-coated GAC, adsorption isotherm, adsorption
kinetics**

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ABSTRACT

Study of Chemical States, Composition and Adsorption Behavior of Iron Coated Granular Activated Carbon (Fe-GAC) for Selenate Removal and Feasible Adsorbent Modifications

Ning Zhang

This study examined the adsorptive removal of selenate using iron coated granular activated carbon (Fe-GAC) and further investigated its complexation mechanisms and coordination structures using spectroscopic techniques. Adsorption kinetics and equilibrium experiments with initial selenium concentration of 1 mg/L were conducted under three different ionic strengths to study selenate adsorption behavior. Selenate adsorption reached equilibrium within 48 hours with more than 85% of the equilibrium capacities being obtained within the first 6 hours. High removal efficiency (i.e., > 75%) was achieved for pH range 2 - 5. Pseudo-second-order kinetic model characterized selenate adsorption kinetics well ($R^2 = 0.999$) and the rate constant decreased with ionic strength. Adsorption capacity decreased significantly with increasing ionic strength, which was not observed in selenite adsorption with the same adsorbent. Competitive adsorption with other four oxy-anions (SiO_3^{2-} , SO_4^{2-} , PO_4^{3-} and CO_3^{2-}) showed that selenate removal efficiency was reduced to various degrees in the presence of each individual anion. Competitive adsorption of binary adsorbates (selenite and selenate) showed that the Fe-GAC had higher adsorption affinity for selenite over selenate and the adsorption preference increased with ionic strength. Sheindorf-Rebuhn-Sheintuch (SRS) multi-adsorbate competitive adsorption model was applied to quantify the binary competitive adsorption between selenate and selenite.

Acid-base titration experiments were carried out under three ionic strengths (i.e., 0.001, 0.01 and 0.1M) and showed point of zero charge (pH_{pzc}) at pH 7.8 for the tested Fe-GAC. It indicates a preferred positively charged surface for anions under acidic conditions. Raman spectroscopy was used to determine the type of surface complex and the coordination state of adsorbed selenate at different pH with 0.1 M ionic strength. The results showed that inner-sphere and outer-sphere complexes were formed at pH 5 and 8, respectively. Additionally, mixture of mono-dentate and bi-dentate binding was observed at pH 5 with selenate. In comparison, selenite was only observed to form bi-dentate inner sphere bindings with surface sites.

Three electrolytes (LiCl, NaCl and KCl) were used as background electrolytes in this study to investigate their effects on selenate adsorption. Adsorption isotherms carried out under three ionic strengths (0.01, 0.05 and 0.1 M) were all well fitted with the Freundlich isotherm ($R^2 > 0.97$). The results suggested that as ionic strength increased, selenate adsorption decreased to various degrees in the presence of all three electrolytes, which followed the order: $KCl < NaCl < LiCl$. Additionally, under the same ionic strength controlled by three background electrolytes, Kruskal - Wallis Statistical Test showed increasing difference among selenate adsorption as ionic strengths increased from 0.01 to 0.1 M. This result can be attributed to the variations of cation radius.

X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical state and composition of coated iron on GAC surface. The multiplet peak fitting results for high resolution XPS spectra for O1s and Fe2p_{3/2} indicated that Fe(III) was formed after coated with 0.1 M ferrous chloride, and α -FeOOH was the possible chemical composition. Furthermore, the suspension of Fe-GAC in NaCl electrolytes at studied pH range (3 - 8) did not cause appreciable changes of iron chemical states and composition. Raman spectra for selenate loaded Fe-GAC indicated the formation of bidentate inner sphere complex at pH lower than 7 and a mixture of outer sphere and monodentate inner sphere complex at pH 8. These results explained the low selenate adsorption under alkaline conditions. Two modification methods of Fe-GAC preparation were proposed based on the XPS and Raman results: (1) binary coating with other metal oxides in order to increase the point of zero charge (pH_{zpc}); and (2) ferrous iron coating to reduce selenate first followed by high adsorption removal of selenite.

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LIST OF ABBREVIATIONS

1. **GAC** - Granular activated carbon
2. **SEM** - Scanning electron microscopy
3. **EDS** - Energy dispersion spectrometer
4. **BET** - Brunauer-Emmett-Teller
5. **DAN** - 2, 3-diaminonaphthalene
6. **MCL** - Maximum contaminant level
7. **MCLG** - Maximum Contaminant Level Goals
8. **EPA** - Environmental Protection Agency
9. **ZVI** - Zero Valent Iron
10. **BDAT** - Best demonstrated available technology
11. **BASBR** - Baffled anaerobic solids bed reactors
12. **BSeR** - Biological selenium reduction
13. **HFO** – Hydrous ferric oxide

CHAPTER 1: INTRODUCTION

1.1 Background

Selenium (Se) is both beneficial and toxic to animals, plants, and humans. However, it was not until the 1930s that selenium widely drew attention as a result of health and reproduction problems in livestock and poultry caused by seleniferous areas in South Dakota (Moxon and Rhian, 1943). The narrow gap between necessary (i.e., 0.04 to 0.1 mg/L in normal dietary) and toxic (i.e., 4 mg/L in food) concentrations of Se makes it imperative to understand the processes controlling the distribution of this element in the environment (Eisler, 1985).

Selenium can accumulate in some selenium tolerant plants (e.g., *Astragalus*, *Stanleya*, and etc.) to a level as high as thousands mg-Se/kg-dry weight (Terry et al., 2000). In humans, selenium is a trace element which functions as a cofactor for reduction of antioxidant enzymes such as glutathione peroxidases and thioredoxin reductase (Venardos et. al., 2004). Accumulation of selenium in soils, aquifer sediments and drinking water through various pathways has threatened the health of wildlife and humans (Lakin, 1973). It degrades water quality and may accumulate in fishes and birds. Even though selenium contamination does not result in sudden fish kills, it causes deterioration and deformity in fish and wildlife over time. In some contaminated areas, high levels of selenium accumulation in plants, high rates of mortality and deformity in birds have been observed (Bowen, 1966; Ohlendorf, 1989).

Selenium is widely used in industrial processes including the photovoltaic cells, glass and ceramic manufacture. It is also one of the strongly enriched elements in coal, being present as an organoselenium compound, a chelated species, or as an adsorbed element (USEPA, 2006). Coleman et al. (1993) reviewed the selenium data from 9,000 coal samples throughout the U.S. and found the highest concentrations of selenium in coal were in Texas and Mississippi. Neuzil et al. (2007) reported a wide content range of selenium in coal bearing strata in West Virginia (i.e., 0 - 6800 µg/kg). Mountaintop removal and excess spoil valley fills were found to have impacts on the nearby

waterways (WVGES, 2006). In 2002, USEPA conducted a study of the stream chemistry associated with sites classified as mined, unmined, filled, and filled/residence. Of the streams samples, selenium concentrations were found to exceed EPA's water quality criterion (5 µg/L) at most (13 out of 15) sites in the filled category (USEPA, 2003). Other main contamination sources of selenium are listed below (USDA, 2002):

- Coal, gold, silver, nickel, and phosphate mining
- Metal smelting
- Municipal landfills
- Oil transport, refining, and utilization
- Agricultural irrigation

Selenium is chemically and structurally similar to sulfur, a group VI non-metal, which forms oxyacids of strengths similar to those of sulfur (Ghosh *et al.*, 1994). In the environment, selenium exists in different oxidation states, selenide (Se^{2-}), elemental selenium (Se^0), selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) (Tamari, 1998). It can also be present as various organically bound Se^{2-} ; these compounds are analogous to those of sulfur and include seleno-amino acids (i.e. selenocysteine and selenomethionine) and methyl selenides (i.e., dimethylselenide and dimethyldiselenide) (Séby *et al.*, 1998). Selenite and selenate are thermodynamically stable under the neutral pH (e.g., 4 - 8) and mildly redox conditions. They are the predominant chemical forms in aqueous media (Jacobs, 1989). Selenite is present in mildly oxidizing, neutral pH environments and typical humid regions, while selenate is the predominant form under ordinary alkaline and oxidized conditions (Goh and Lim, 2004).

Most of the selenium research conducted currently has focused on either agricultural drainage water or western U.S. coal mines wastewaters (Vesper *et al.*, 2004). A variety of treatment technologies have been reported in the literature for selenium removal (Mari as and Selleck, 1992; Gallup, 1996; Frankenberger Jr. *et al.*, 2004; Mavrov *et al.*, 2006). Examples include ion-exchange, reverse osmosis, nanofiltration, solar ponds, chemical reduction with iron, microalgal-bacterial treatment and biological treatment. While these approaches can remove selenium to a level below 5 µg/L under optimal conditions, most of these systems are expensive and are not suitable for mining

wastewater with high sulfate concentrations. Therefore, there is a need to develop a treatment method suitable for removing selenium originating from mining activities. Adsorption of Se by metal oxides such as iron oxides and aluminum oxide has been demonstrated by several researchers (Ghosh *et al.*, 1994; Parida *et al.*, 1997; Su and Suarez, 2000; Monteil-Rivera *et al.*, 2000), but these adsorbents can be difficult to use in continuous flow systems due to their small particle size. To overcome this difficulty several researchers have combined iron oxides with more traditional adsorbents (e.g., sand and granular activated carbon) (Lo and Chen, 1997; Kuan *et al.*, 1998; Namasivayam and Prathap, 2006; Zhang, *et al.*, 2008). Granular activated carbon (GAC) is one of the most promising adsorbents.

It is well understood that there are several functional groups distributed on the surface of GAC, such as carboxyl, hydroxyl, phenol, and quinone. The structure of GAC can be described as a combination of carbon particles connected with a random distribution of these surface functional groups (Pakula *et al.*, 1998). Fe (III) was reported to form stronger complexes with carboxyl and phenol ligands than Fe (II), therefore, ferric iron were more effective than ferrous iron in the formation of complexes (Gu *et al.*, 2005). Iron coated GAC compared to other adsorbents is expected to achieve higher metal removal and as well as removal of organics simultaneously. It is also easy to be compacted into column and applied to continuous heavy metals treatment (Vaughan Jr. and Reed, 2005). Gu *et al.* (2005) has successfully used Fe-GAC to remove arsenate from drinking water.

Iron coated granular activated carbon (Fe-GAC) was developed by the oxidation of ferrous iron to form ferric iron followed by its precipitation onto GAC porous surface (Gu *et al.*, 2005). Fe-GAC successfully removed arsenic and various other oxyanions from aqueous solutions through adsorption process. As a result of the chemical similarity between selenium and arsenic, Fe-GAC was applied to remove selenite from aqueous solution (Zhang *et al.*, 2008). Slightly lower adsorption was often reported for selenate than that for selenite with different adsorbents used (e.g., goethite, hematite). Therefore, there is a need for the detailed investigation of the physical and chemical properties of synthesized adsorbents in terms of its chemical composition and stabilities at different

pHs, so that some modifications can be proposed in order to obtain an improvement of selenate adsorption.

1.2 Objectives

This study aimed to develop effective adsorbents to remove selenate from aqueous solutions and further examined its complexation mechanisms and coordination structures by using spectroscopic techniques. The major goals were to:

- Study the chemical states and chemical compositions of coated iron on GAC surfaces using X-Ray photoelectron spectroscopy (XPS)
- Evaluate the adsorptive removal of selenate using Fe-GAC through bench-scale experiments
- Investigate the effects of relevant factors (e.g., pH, ionic strength and presence of other oxy-anions) on selenate adsorption
- Determine the type of surface complex and the coordination state of adsorbed selenate under different conditions using Raman spectroscopy.
- Propose feasible methods for adsorbent modification in order to improve the selenate adsorption

CHAPTER 2: LITERATURE REVIEW

2.1 Occurrence of Selenium

Selenium was discovered by Jon Jakob Berzelius in 1817. It has an atomic number of 34 and an electronic configuration of $[\text{Ar}]3d^{10} 4s^2 4p^4$. It is located in the oxygen group of the periodic table between nonmetallic sulfur (S) and metallic tellurium (Te). It was found that there are several naturally occurring isotopes for Se [^{74}Se (0.87%), ^{76}Se (9.02%), ^{77}Se (7.58%), ^{78}Se (23.52%), ^{80}Se (49.82%) and ^{82}Se (9.19%)] (McNeal and Balistrieri, 1989).

Selenium occurs naturally in the environment. Though it is among the rare elements on the surface of the earth, selenium is widely dispersed in nature with a $1.3 \times 10^{-5}\%$ concentration in the earth's crust (Todini and Co s.p.a., 2006). The primary sources of selenium are volcanic emanations and metallic sulfides associated with igneous activity. Biological sinks were reported as the secondary sources of selenium (Lakin, 1973). Black shales, coal and petroleum were found to have 10 - 20 times more abundant in selenium than the earth's crust.

2.1.1 Primary Sources

Wells (1967) reported high selenium content in volcanic ash flows. Selenium is dispersed with the gases emitted from volcanoes and has been deposited on the earth for ages. Rankama and Sahama (1950) estimated that selenium produced by volcanic emissions amounted to 0.1 g-Se/cm^2 -earth surface. Reuter (1975) also revealed that selenium is released as high temperature volatile gases during volcanic eruption. Reuter (1975) further concluded that igneous rocks generally have low selenium concentration due to their ignition. Selenium in volcanic sulfur was found as high as 5.18% (Palache *et al.*, 1944).

Additionally, it was found that selenium was present in coals up to 300 times as much as in other geologic materials (Coleman *et al.*, 1993). Vesper *et al.* (2008) concluded that sulfur and total organic carbon (TOC) have been used as predictors of selenium concentration in coals. Coleman *et al.* (1993) reported a significant relationship existing between total sulfur and selenium concentrations in Powder River Basin coals.

2.1.2 Secondary Sources

Organic selenium substitutes for sulfur in simple amino acids. Selenium distributed by erosion of igneous rocks or by volcanic emanations is locally concentrated in carbonaceous deposits, which are generally present in black shales. Additionally, black shales were reported containing higher selenium than limestones or sandstone as selenium is often present as organo-selenium and iron adsorbed species. Concentrations ranging from 1 to 300 mg-Se/kg were reported in the Cretaceous black shales in Wyoming (NAS-NRC, 1983).

2.1.3 Selenium Production

Production of selenium in 1985 was reported to be 429,515 pounds (USEPA, 2006). Selenium is most commonly produced from selenide in many sulfide ores, such as those of copper, silver, or lead. It is obtained as a byproduct of the processing of these ores, from the anode mud of copper refineries and the mud from the lead chambers of sulfuric acid plants. These muds can be processed by a number of means to obtain free selenium. There are around 40 known selenium-containing minerals, some of which can have as much as 30% selenium - but all are rare. The main selenium producing countries are Canada, USA, Bolivia and Russia. Global industrial production of selenium is around 1.5 million kg a year and about 0.15 million kg of selenium are recycled from industrial waste and reclaimed from old photocopiers (Lenntech, 2007). Selenium main application in industry includes electronic and photocopier components, gas manufacturing, chemicals and pigments. [Figure 1](#) illustrates the percentage of each industrial usage.

2.2 Chemical Species and Transformation of Selenium

Several factors can affect the selenium speciation, including pH, redox conditions, solubilities of its salts and availability of complexation ligands. The sections below discuss the predominant species of selenium under various environmental conditions.

2.2.1 Elemental Selenium (Se^0)

Generally, elemental selenium is stable in reducing environments. The crystalline forms of elemental selenium are alpha-monoclinic and beta-monoclinic Se, which are

commonly known as red crystalline selenium. The amorphous forms of selenium are red amorphous and glassy or black varieties (Vokal-Borek, 1979). Elemental selenium is very insoluble in water, although, certain microorganisms can oxidize elemental selenium to selenite and small amounts of selenate (Sarathchandra and Watkinson, 1981).

2.2.2 Selenide (Se^{2-})

Selenide is chemically similar to sulfide. It usually exists in reducing conditions as hydrogen selenide (H_2Se) and metal selenides. Hydrogen selenide gas has a strong odor and is extremely toxic to animals. Excess exposure to hydrogen selenide may result in hepatotoxicity (Spallholz and Hoffman, 2002). When dissolved in water, hydrogen selenide is a weak acid with pK_{a1} less than 4. Aqueous H_2Se also shows high toxicity and can be easily oxidized to form elemental Se. Metal selenides are usually formed by replacing sulfur in metal sulfide ores (e.g., Fe, Cu, and Pb). Most metal selenides have very low solubilities (Elrashidi *et al.*, 1987). It has also been reported that volatile methylated derivatives of selenium and dissolved organic selenide compounds can be produced by microbial activity (Chau *et al.*, 1976 and Cutter and Bruland, 1984).

2.2.3 Selenite (SeO_3^{2-})

Selenite is usually present in mildly oxidizing environments. Selenous acid (H_2SeO_3) is a weak acid. [Figure 2](#) illustrates the species fraction of Se (IV) at different pH. The fully deprotonated form (SeO_3^{2-}) exists under alkaline conditions, while singly protonated form (HSeO_3^-) predominates under acidic conditions. When pH is lower than 3, selenous acid is dominant. Generally, selenite salts show low solubility (e.g., Ag_2SeO_3).

Selenite can be reduced to elemental selenium via chemical reduction under acidic conditions (e.g., elemental iron reduction). Also, several microbial genera (e.g., *Acinetobacter*, *Aeromonas*, *Bacillus*, *Candida* and etc.) were reported to reduce selenite into insoluble elemental selenium and selenide (Maiers *et al.*, 1988). Scott and Morgan (1996) reported the oxidation of Se (IV) to Se (VI) at pH 4 using synthetic birnessite ($\delta\text{-MnO}_2$).

2.2.4 Selenate (SeO_4^{2-})

Selenate is the fully oxidation form of selenium. It is fairly stable in well oxidized environments. Unlike selenous acid, selenic acid (H_2SeO_4) is a strong acid with a negative pK_{a1} value. Therefore, the fully protonated form is barely present and singly protonated form exists only at low pH. The deprotonated forms predominate over the entire pH range ([Figure 3](#)). Selenate salts are generally more soluble than corresponding selenite salts (McNeal and Balistrieri, 1989), and thus less likely to be adsorbed by minerals oxides (e.g., iron oxides and aluminum oxides). Therefore, selenate readily migrates with natural water in environment. Additionally, selenate is the most plant available species among all selenium forms (Sors et al., 2005), and therefore selenate is more likely to accumulate in plants.

Zero valent iron (ZVI) is widely applied in selenate reduction. Both elemental selenium and selenide was reported to be produced under different reaction conditions. Microbial activities can also result in the reduction of selenate under both aerobic and anaerobic conditions (Oremland *et al.*, 1989).

2.3 Selenium in Environment

Selenium typically can be found in almost all the materials on earth (McNeal and Balistrieri, 1989). Moreover, human activities such as fossil fuel combustion, agricultural irrigations, and mining, increasingly released selenium to environment (Nriagu and Pacyna, 1988). Engberg and Sylvester (1990) reported the detectable amounts of selenium existing in the samples of water, bottom sediment, and biota in the 20 investigated areas in western US. Maximum selenium concentration was reported in seleniferous soils, with the concentrations commonly found within 1 - 1200 mg-Se/kg soils (Trelease, 1945; Fleming, 1962). From 1987 to 1993, according to the Toxics Release Inventory published by USEPA (2006), total selenium released to land and water had exceeded over a half million kilograms. These releases were primarily from copper smelting industries. It was also reported that two of largest selenium releasing states were Utah and Indiana (USEPA, 2006).

2.3.1 Selenium in Waters

Selenite and selenate are the two predominant chemical forms of selenium in aqueous systems due to their relatively high solubility and may readily transport with surface and ground water. Additionally, selenium content in surface water is greatly influenced by pH, presenting high in both acidic ($\text{pH} < 3.0$) and alkaline waters ($\text{pH} > 7.5$). Selenite in surface water can precipitate in the presence of ferric at pH range 6.3 - 6.7 (Lakin, 1973). When pH greater than 8, selenite salts may be oxidized to form selenate which shows relatively high solubility, therefore result in an increase of Se concentrations. It was found that average selenium concentrations in Colorado River and its major tributaries were in the range 1 - 4 $\mu\text{g/L}$ (Engberg, 1999), however, a maximum of higher than 400 $\mu\text{g/L}$ was found in this area also (NAS, 1976). In the Lake Michigan, selenium concentrations were reported in the range of 0.8 - 10 $\mu\text{g/L}$ (Jacobs, 1989). Dissolved concentrations of selenium in San Francisco Bay was found to be 0.1 - 0.2 $\mu\text{g/L}$ (Cutter, 1989).

Lindberg (1968) reported the selenium concentration ranging from 0.06 to 0.15 $\mu\text{g/L}$ in eight ground and surface waters in Sweden. Selenium contents in 43 samples from surface water in Colorado were found from 1 - 400 $\mu\text{g/L}$ (Scott and Vodgeli, 1961). Among these 43 samples, 11 were reported to exceed the drinking water criteria (i.e., 10 $\mu\text{g/L}$).

Trace levels of selenium ranging from 0 - 10 $\mu\text{g/L}$ are commonly found in community drinking water in USA and 10 $\mu\text{g/L}$ is suggested as the upper limit concentration of Se for safety concern (Lakin, 1973). The USEPA regulated selenium concentration in drinking water at 50 $\mu\text{g/L}$ for both MCLG and MCL (US EPA, 2006). The USEPA set the national water quality chronic criterion for selenium at 5 $\mu\text{g/L}$ (USEPA, 1987). However, a controversy has risen, as more adverse effects were found for unaffected areas, regarding to set lower selenium environmental standards (e.g., < 2 $\mu\text{g/L}$) for the protection of aquatic birds and mammals (Hamilton and Lemly, 1999).

2.3.2 Selenium in Soils

Selenium concentrations in soils are generally between 0.01 to 2 $\mu\text{g-Se/g}$, though it can be as high as 1200 $\mu\text{g-Se/g}$ in seleniferous areas (Mayland *et al.*, 1989). A concentration of 38 mg-Se/kg as water soluble selenate has been reported in seleniferous areas (Lakin, 1948; Swaine, 1955). It was reported soils developed from the Cretaceous shales in some middle US states (e.g., South Dakota, Montana, Wyoming, Nebraska and etc.) presented high selenium concentrations (i.e., $>10 \mu\text{g-Se/g}$) (Reeves, 2006). Concentration of selenium in some Hawaiian surface soils was also found at high level (i.e., 1-20 $\mu\text{g-Se/g}$), but they are not readily available for vegetation due to the formation of complexation with Fe and Al minerals (Anderson *et al.*, 1961; Rosenfeld and Beath, 1964).

It was found that selenium in soils is present in several chemical forms which differ widely in their solubility and availability to plants (Anderson and Scarf, 1983). Redox potential and pH play an important role in the chemical forms of Se existing in soils and sediments (van Dorst and Peterson, 1984). Inorganic selenium exists predominately as the oxyanions (i.e., selenite and selenate) in the aqueous solutions of well aerated alkaline soils. In poorly aerated acid soils, inorganic selenium occurs as the relatively insoluble selenide and elemental forms.

Moreover, soils derived from parent materials containing high selenium content under alkaline conditions also present high biologically available selenium. Plants growing on these soils will have sufficient selenium (0.1 $\mu\text{g-Se/g}$ forage) for animal benefits (Kubota *et al.*, 1967). However, natural selenium toxicosis was reported when selenium level was higher than 10 $\mu\text{g-Se/g}$ in soils (Mayland *et al.*, 1989).

2.3.3 Selenium in Atmosphere

Selenium compounds are commonly released to the air during the combustion of coal and petroleum fuels, and also from the smelting and refining of other metals. Therefore, selenium concentrations in air are tremendously influenced by industrial activities. Volatile selenium can also be released via non-accumulative plants (e.g., dimethyl diselenide volatilized from *Astragalus racemosus*). Shrift (1961) revealed that

dimethyl selenide can be given off by certain microorganisms and is exhaled by animals fed on seleniferous diets.

Lakin and Byers (1941) found selenium concentrations in atmospheric dust of 0.05 - 10 mg/L in 10 US cities. Hashimoto and Winchester (1967) reported an average of 0.09 $\mu\text{g-Se}/100\text{-m}^3$ air during the summer of 1965 in Cambridge, MA. Lakin (1973) suggested that selenium is commonly present in air in industrial areas.

2.3.4 Selenium in Biota

Selenium is found widely exist in plants, waterfowls, fishes and mammals. Biomagnify of selenium concentrations was observed by Holland (1979): 2 $\mu\text{g/L}$ in water, 23 - 25 $\mu\text{g/g}$ in plankton, 26 - 31 $\mu\text{g/g}$ in benthic invertebrates, and 18 - 47 $\mu\text{g/g}$ in three fish species. Eisler (1985) suggested that selenium concentrations tended to be higher when collected from locales showing the following characteristics, including highly seleniferous soils or sediments, high human population densities, heavy accumulations of selenium laden wastes and selenium contaminated subsurface irrigation drain water.

Selenium in terrestrial plants was found to tend to accumulate in *Aster*, *Astragalus*, *Oenopsis* and several other genera (Eisler, 1985). These plants are classified as selenium accumulator and typically require 1 to 50 $\mu\text{g/g}$ selenium in either soil or water for growth (Eisler, 1985). Primary selenium accumulator plants (e.g., *Astragalus*, *Oenopsis*, *Stanelya*, and etc.) and secondary selenium accumulator plants (e.g., *Aster*, *Gutierrezia* and etc.) may contain selenium in the range of 100 - 10,000 and 25 - 100 $\mu\text{g/g}$, respectively. Selenium nonaccumulator plants generally contain 1 - 25 $\mu\text{g/g}$ -fresh-weight when growing on seleniferous soil. Chau and Riley (1970) and Lunde (1970) reported the selenium concentrations in marine algae and macro-phytes ranged from 0.04 to 0.24 $\mu\text{g/g-dry-weight}$, selenium in edible seaweeds was found at the level of 0.14 to 0.39 $\mu\text{g/g-dry-weight}$.

High selenium level (e.g., > 12 $\mu\text{g/g-wet-weight}$) was found in liver and kidney tissues of marine and coastal vertebrates (e.g., fishes, birds, and mammals). May and McKinney (1981) reported selenium concentrations in freshwater fishes in US ranging from 0.05 to 2.9 $\mu\text{g/g-fresh-weight}$ (whole fish) and averaged about 0.6 $\mu\text{g/g}$. Harr (1978) reported that selenium concentrations in tissues from animals maintained on high

selenium feeds generally contain 3 - 5 µg-Se/g-fresh-weight, comparing with the concentration of 20 µg-Se/g that resulted animal death from selenium poisoning.

2.4 Toxicity of Selenium

The recommended daily intake of selenium for the reference adult North American male and female are 70 and 55 µg/day, respectively (NAS, 1989). It may increase to 65 and 75 µg/day for female during pregnancy and lactation period, respectively. The Food and Nutrition Board-Institute of Medicine (2000) recommended upper selenium intake level as 400 µg/day. Excess selenium can cause selenosis with clinical signs, such as growth retardation, decreased fertility, embryo toxicity, fetotoxicity and teratogenic effects in animals (IRIS, 1991). It has been observed that concentrations of selenate (SeO_4^{2-} , Se(VI)) as low as 10 µg/L in water can cause death and birth deformities in waterfowl (Letey *et al.*, 1986). The U.S. EPA defined selenium intake level of 1262 µg/day for human as the element intake at which clinical selenosis appeared, which was related to a whole blood selenium level of 1350 µg/L (Navarro-Alarcon and Cabrera-Vique, 2008). Also, a dietary of 2 mg-Se/kg on a continuous basis has been suggested as a maximum tolerable level for all species (NAS-NRC, 1980). However, carcinogenic effects were not found for diets containing up to 8 mg-Se/kg (Tinsley *et al.*, 1967; Harr *et al.*, 1967).

2.4.1 Toxicity of Different Chemical Forms

Combs and Combs (1986) suggested that sodium selenite, sodium selenate, selenomethionine and selenogluthathione are among the more toxic species. In alkaline soils and oxidizing conditions, selenium may be oxidized sufficiently to maintain the availability of its biologically active form, and cause plant uptake of the metal to be increased. In acidic or neutral soils, it tends to remain relatively insoluble and the amount of biologically available selenium should steadily decrease. Selenium volatilizes from soils when converted to volatile selenium compounds (e.g., dimethyl selenide) by microorganisms (FRTR, 2002). Elemental selenium and most metallic selenides have relatively low toxicities because of their low bioavailability. By contrast, selenate and

selenite are very toxic, and have modes of action similar to that of arsenic (Swinden, 2007). Hydrogen selenide is an extremely toxic and corrosive gas. Selenium also occurs in organic compounds such as dimethyl selenide, selenomethionine and selenocysteine, all of which have high bioavailability and are toxic in large doses. Selenium dioxide is the primary source of problems from industrial exposures since the dioxide forms selenious acid with water or sweat, and the acid is an irritant.

2.4.2 Selenosis Symptoms

Selenium toxicity is classified into three types: acute selenosis, subacute selenosis and chronic selenosis (IRIS, 1991). Consuming relatively high amounts of selenium within a short time can cause acute selenosis (IRIS, 1991). Some noticeable symptoms are unsteady walking, labored breathing and finally may result in death. Pathological findings of acute selenosis are inclusive of liver congestion, endocarditis and myocarditis, degeneration of gastrointestinal tract and long bones erosion (Francke and Moxon, 1936). Subacute selenosis is caused by exposure to a large dose of selenium over a longer time. It may result in neurological dysfunction and respiratory distress. It commonly occurred among grazing livestock continuous fed by selenium accumulating plants (Rosenfeld and Beath, 1964). Chronic selenium toxicity to humans is selenosis (Goldhaber, 2003). Some major symptoms of selenosis include hair and fingernail loss, skin rash (e.g., alopecia), hoof necrosis and loss, garlic breath and abnormal functioning of the nervous system (Navarro-Alarcon and Cabrera-Vique, 2008).

2.5 Selenium Reactions

Selenium reactions are complex to understand its general behavior. Several parameters (i.e. pH, redox potential, microbial activity and presence of complexing and precipitation agents) affect its predominant species, motility and toxicity (Séby, et al., 1998). To identify the presence and reactivity for each species, a brief review of their reactions under different conditions is necessary.

2.5.1 Oxidation-Reduction Reactions

Selenium exists on the earth in several valences status, oxidation - reduction reactions are important processes that can affect both the chemical speciation and the stability of selenium in natural environment; these reactions are strongly influenced by the potential and pH (Séby, et al., 1998). In aqueous medium, a potential-pH diagram as [Figure 4](#) for a selenium activity of 10^{-7} mol/L can provide information on the chemical stability and the redox chemistry of this element as a function of these parameters.

At high redox potential values, Se (VI) is predominant in a wide pH range under the SeO_4^{2-} form. In the moderate potential values, Se (IV) is stable and according to the pH, can be present as H_2SeO_3 , HSeO_3^- or SeO_3^{2-} . In reducing environment, elemental selenium can exist in a wide pH range. Under more reducing conditions, Se (-II) is predominant with HSe^- as major Se species in solution. However, these observations based on thermodynamic considerations are often misleading when applied to natural waters particularly at trace levels (Abdullab, 1995). An accurate interpretation of the selenium behavior requires *in situ* speciation determinations (Devereln et al., 1994; Séby et al. 1997; Fio and Fujii, 1990).

2.5.2 Sorption/Desorption Reactions

In oxidized to moderately reduced environment, the selenium distribution between solid and aqueous phases depends mainly on sorption/desorption reactions, particularly at trace levels (Neal et al., 1987a). These reactions can occur on different solid surfaces such as inorganic solids and organic matter (Öhman, 1988), as described below.

2.5.2.1 Sorption Reactions on Inorganic Materials

On the surfaces of inorganic materials (i.e. minerals, soils, iron oxides, alumina, etc.), selenium adsorption behavior depends on its oxidation state: selenate sorption is generally much lower than selenite sorption (Ahlrichs and Hossner, 1987; Balistrieri and Chao, 1987; Saeki et al., 1995). For Se (IV), different studies have shown a strong affinity to materials rich in metallic oxides or/and hydroxides (iron, manganese, aluminium, etc). The sorption mechanism of Se (IV) was broadly studied and involved very often a ligand exchange reaction with formation of an inner-sphere surface complex

(Monteil-Rivera *et al.*, 2000; Namasivayam and Prathap, 2006). Previous studies also indicated that the selenite adsorption was significantly pH dependent. It showed a lower affinity when it was sorbed by Al and Fe oxides or clays (Parida *et al.*, 1997). The mechanism for the sorption was commonly accepted as surface complexation involving the SeO_3^{2-} and HSeO_3^- sorbed onto the surface sites by ligand exchange (Monteil-Rivera *et al.*, 2000).

The adsorbed Se (IV) amounts as a function of time show a two steps behavior: the first part of the curve indicate a fast and linear retention which becomes slower with time (Balistrieri and Chao, 1987; Papelis *et al.*, 1995; Papelis *et al.*, 1995; Del Debbio, 1997). Two general kinetic models had been applied to the selenite adsorption: (1) pseudo-first-order kinetic model and (2) pseudo-second-order kinetic model. The equations are listed below (Azizian, 2004):

$$\frac{dq}{dt} = k_1(q_e - q)$$

$$\frac{dq}{dt} = k_2(q_e - q)^2$$

Where q_e and q are solute sorbed per gram of sorbent at equilibrium and time t ; k_1 and k_2 are pseudo first order and pseudo second order rate constants. Integrate the equations above, gives the following linear forms

$$\log(q_e - q) = \log q_e - \frac{k_1 t}{2.303}$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Previous studies indicated that selenite adsorption kinetics could be characterized better by the pseudo-second-order kinetic model (Kuan *et al.*, 1998; Namasivayam and Prathap, 2006). Goh and Lim (2004) reported that selenite adsorption can be described by Elovich rate law, the rate of selenite adsorption decreased exponentially with the increasing selenium coverage on the surface of adsorbents when tropical soils were utilized to remove selenium. The linear form of the Elovich equation can be expressed as:

$$q = \frac{1}{\alpha} \ln(a\alpha) + \frac{1}{\alpha} \ln\left(t + \frac{1}{a\alpha}\right)$$

where, a and α are Elovich kinetic constants. In other works, it was assumed that adsorption rate is controlled by an intraparticulate mass transfer in the solid (Papelis *et al.*, 1995; Papelis *et al.*, 1995).

For adsorption equilibrium, the Langmuir model and the Freundlich model were widely used. The Langmuir model is used to reveal the equilibrium between surface and solution as a reversible chemical equilibrium between species. It suggests a monolayer sorption, with no lateral interaction between the adsorbed molecules. Equation for Langmuir model can be expressed as follow (Crittenden *et al.*, 2005):

$$q_e = \frac{q_{\max} C_e}{b + C_e}$$

where C_e (mg/L), the equilibrium concentration in the solution; $q_{\max}$ (mg-Se/g-adsorbent), represents the maximum adsorption capacity; adsorption constant b (L/mg), is related to the energy of adsorption, it is both temperature-dependent and related to the Gibbs free energy and hence to the enthalpy change for the adsorption process.

The Freundlich model, originally proposed as an empirical equation, is used to describe the data for heterogeneous adsorbents such as activated carbon. The model can be expressed as follows (Crittenden *et al.*, 2005):

$$q_e = K_f C_e^{1/n}$$

Where K_f and $1/n$ are parameters of the Freundlich isotherm. K_f (mg/g)(L/mg)^{1/n}, reveals the adsorption capacity and $1/n$ unitless, the intensity of adsorption.

Kuan *et al.* (1998) reported that when applied the aluminum-oxide coated sand to the selenite adsorption, the adsorption capacity could reach 1.08 mg-Se (IV)/g-adsorbent with the coefficient of linear regression (R^2) for Langmuir model calculated to be 0.98 at pH 4.6. Lo and Chen (1997) obtained the adsorption capacity value of 0.017 mmol-Se (IV)/g-adsorbent at pH 4.0, as iron-coated sand was used.

The weaker sorption of selenate compared to selenite was observed on different solid surfaces (Masscheleyn and Patrick, 1993; White and Dubrovsky, 1994; Balishtrieri, 1987) and could be explain by the formation of an outersphere complex at the solid surface (Saeki *et al.*, 1995; Davis and Leckie, 1980). Adsorption of Se (VI) is also

strongly affected by the pH with a similar behavior to Se (IV) (Ahlrichs and Hossner, 1987; Saeki *et al.*, 1995; Vuori *et al.*, 1994).

2.5.2.2 Sorption Reactions on Organic Matter

Interactions between selenium and organic matter such as humic substances were reported for Se (IV) (Gustafsson and Johnsson, 1994). From iron oxyhydroxide coated with sodium humate, it was observed a more important immobilization of Se (IV) compared to the mineral alone. In order to clarify the association between selenite and humic substances, some authors have assigned the retention of Se(IV) to a microbial reductive incorporation on soils and aquatic systems and this reaction would occur mainly in the low molecular-weight-fraction of the humic substances (fulvic acids) (Gustafsson and Johnsson, 1994). The mechanism of selenite sorption on organic matter is not yet well understood and incorporation or adsorption reactions could occur alone or in a simultaneous way.

2.5.3 Complexation Reactions

In aqueous phase, selenium can exist in the form of complexes mainly as ion pairs that are in association with inorganic cations (White and Dubrovsky, 1994; Elrashidi *et al.*, 1987; Reddy *et al.*, 1995). A number of works has experimentally shown the presence of these Se compounds. Only a study on Se speciation in groundwater samples has shown the occurrence of $\text{MgSeO}_{4(\text{aq})}$ by using the specific adsorption properties of the divalent Se(IV) and Se(VI) species on CuO solid particles (Reddy *et al.*, 1995).

Equilibrium thermodynamic calculations for a groundwater at pH = 7 containing a total selenium concentration of 300 mg/L have shown that under oxidizing conditions ($E > 400$ mV), SeO_4^{2-} and $\text{CaSeO}_{4(\text{aq})}$ are the predominant species in aqueous solution. For potentials ranging from 0 to 400 mV, the most stable species are $\text{CaSeO}_{3(\text{aq})}$ and SeO_3^{2-} and, under more reducing conditions ($E < 0$ mV), only HSe^- is present in solution (White and Dubrovsky, 1994). A similar study was carried out in soil solutions and none of the 27 complexes studied were found to contribute significantly to the total soluble selenium concentration. Only the SeO_4^{2-} , HSeO_3^- , SeO_3^{2-} , H_2Se and HSe^- dissolved forms predominate according to the pH and potential conditions (Elrashidi *et al.*, 1987).

2.5.4 Precipitation Reaction

Inorganic Se with the oxidation states of -2, +4 and +6 can react with metal cations (e.g, Ag^+ , Fe^{3+} , Al^{3+}) and be immobilized via precipitation. Generally, selenide has very low solubility with most of the metal cations. Selenate salts show higher solubility than corresponding selenite salts.

2.5.4.1 Selenite Precipitation

Selenite anions can only exist at trace level with most of the cations (e.g., Fe^{3+} , Al^{3+}) due to the formation of precipitates. Fairly low solubility product (K_{sp}) (i.e., $10^{-30\sim-33}$) for ferric selenite ($\text{Fe}_2(\text{SeO}_3)_3$) was reported by several researchers (Chukhlantsev and Tomashevsky, 1957; Geering *et al.*, 1968). Al^{3+} was also found to have similar magnitude solubility product with ferric (Essington, 1988). Essington (1988) reported higher solubility for ferrous selenite ($K_{sp} = 10^{-9.99}$) than that for ferric selenite. Comparing with that, selenite can dissolve more when it combines with sodium ($K_{sp} = 10^{-3.51}$), potassium ($K_{sp} = 10^{-1.48}$) and calcium ($K_{sp} = 10^{-5.6}$).

2.5.4.2 Selenate Precipitation

Solubilities of metal selenate salts were less studied than that of metal selenite salts. Similar with selenite, ferric ($K_{sp} = 10^{-23.19}$) and aluminum ($K_{sp} = 10^{-21.46}$) selenate were found to dissolve at trace level. And potassium selenate ($K_{sp} = 10^{0.6}$) and sodium selenate ($K_{sp} = 10^{-0.89}$) were found easier to dissolve in water.

2.6 Selenium Treatment Technologies

A variety of treatment technologies have been reported to remove selenium from contaminated waters (Marinas and Selleck, 1992; Gallup, 1996; Frankenberger *et al.*, 2004; Mavrov *et al.*, 2006). Traditional treatment methods (e.g., coagulation, lime softening and sand filtration) are not effective (Kapoor *et al.*, 1995). Some advanced techniques (e.g., ion-exchange, reverse osmosis, nanofiltration) are not economically feasible in treating large volume of selenium containing water and meeting EPA's high criteria (i.e., 5 $\mu\text{g/L}$) (Zhang *et al.*, 2005). Zerovalent iron reduction and adsorption onto

iron oxide/hydroxides are two major widely used and promising options in removing selenium.

2.6.1 Traditional Treatment Technologies

Since selenium first drove significant public concern in early 80s because of its bioaccumulation in birds at California's Kesterson Reservoir in the San Joaquin Valley (SJV), several treatment technologies were developed for selenium removal from agricultural drainage and industrial wastewater. These conventional treatment technologies include physical, chemical and biological methods. Although much has been learned, the goal of finding practical, cost-effective technology for treating selenium contaminated water has not yet been accomplished (Losi and Frankenberger Jr., 1997). An integrated, multiphased approach to the problem will most likely prove necessary and feasible.

2.6.1.1 Coagulation

Coagulation involves the agglomeration of colloidal particles to form larger particles which can be easily separated from solution by sedimentation and /or filtration (Kapoor *et al.*, 1995). Cherkinski *et al.* (1970) reported removal efficiency of 50-70% for initial selenium concentration of 2 - 10 mg/L using alum coagulation, sedimentation and filtration in the pilot scale studies. However, the effluent still can not meet the EPA criteria. A laboratory jar test study on the spiked water samples collected from the Ohio River with selenium concentration of 0.1 mg/L was conducted (Logsdon *et al.*, 1974). The results indicated that coagulation using alum and ferric sulfate was ineffective for selenate removal. The removal was found to be less than 10% at any pH and high coagulant dosages. The results also showed that removal of selenite in well water collected from Glendale, Ohio reached 80% at pH 6 but dropped dramatically to 20% at pH 8. It was also found that selenite removal was not significantly increased as the coagulant dose increased.

Logsdon *et al.* (1974) also conducted the pilot scale studies to remove selenium from the same water sources. The pilot plant treatment consisted of rapid mix flocculation, settling and filtration. The detention times used in the pilot study for rapid mixing, flocculation and settling were 2 minutes, 1 hour and 6.5 hours, respectively. The

results of pilot plant showed similar removal efficiency of with jar tests, which was 60% for selenite at pH 6.5 and 10% for selenate at pH 8.5 (Sorg and Logsdon, 1976).

2.6.1.2 Precipitation

Selenite was reported to be significantly removed by precipitation with iron hydroxide (80-95%). Comparing with this, removal of selenate via precipitation was reported to be less than 15% (Yodnane *et al.*, 1992). To reduce the concentration of selenium from fly ash leachate from 0.1 to 0.01 mg/L required an iron dosage of 28 mg/L. The continuous iron coprecipitation process consisted of a rapid mix tank for chemical feed, a flocculation tank and a sedimentation tank.

Merrill *et al.* (1986) evaluated the technical and economic feasibility of precipitation with iron oxyhydroxide in removing selenium from ash pond effluent containing 40-60 µg/L selenium. A pilot scale study was conducted consisting of rapid mix, flocculation and sedimentation. The results indicated that high removal efficiency (e.g., 56 -80%) was achieved at pH 6.2 and below. However, precipitation processes were found to be feasible only if the selenite form was the predominant species.

2.6.1.3 Lime Softening

Lime softening was also investigated by researchers to remove selenium from wastewater. A removal efficiency of 40 - 50% at pH 9.0 - 11.5 was reported (Logsdon *et al.*, 1974). Percentage removals did not vary with the change in the initial concentration of selenium from 0.05 to 10 mg/L at pH 11.3. It was also found that lime precipitation did not remove selenate effectively (e.g., <10%) (Kapoor *et al.*, 1995), it is due to relatively high solubility of calcium selenate ($K_{sp} = 10^{-3.09 \sim -4.77}$ for CaSeO_4).

2.6.2 Biological Treatment

Biological treatment for selenium removal is a viable alternative to the physico-chemical treatment (Kapoor *et al.*, 1995). Selenate and selenite can be reduced readily in most systems through interactions with organic matter or via microbiological processes. Activities of microorganisms drive the formation of elemental selenium in order to immobilize and remove aqueous predominant species (i.e., selenite and selenate) by providing reducing conditions and overcoming kinetic barriers to selenium reduction

(Kenward *et al.*, 2006). Many studies have shown that Se-reducing bacteria can effectively catalyze the reduction of selenate into elemental selenium. Other strains of bacteria may further reduce elemental selenium to selenide or oxidize selenide to form elemental selenium (Doran *et al.*, 1977). Most of these microbe-mediated processes actively reduce selenate to elemental selenium by utilizing selenate as a terminal electron acceptor during the respiration of organic carbon. For example, in agricultural drainage water of the San Joaquin Valley, CA, selenate was effectively reduced to elemental selenium by *Enterobacter taylorae* (Zhang and Frankenberger, 2003) using this pathway.

Biological treatment technology has been applied in industry (MSE Technology Applications, Inc., 2001). Applied Biosciences Corporation developed the BSeR™ process using BASBR. Selenium (selenate and selenite) was reduced to elemental selenium by specially developed biofilms containing specific proprietary microorganisms. This process produces a precipitate of elemental selenium. As the elemental selenium formed in biological treatment, it may precipitate and block the microbes carrying media (e.g., biofilms and biosolids). Therefore, biological processes need to be coupled with back flushing procedure and increase the capital costs (Golder Associates Inc., 2009).

Gerhardt *et al.* (1991) studied a biological treatment process using algal-bacteria system (ABSRS) to remove selenium and nitrate from agricultural drainage water. The system was comprised of algal growth ponds, anoxic reduction unit and solid-liquid separation tank. The average alga concentration used in this system was 178 ± 99 mg/L. The results showed a marginal removal in soluble selenium species for initial selenium concentration of 200 - 400 µg/L. It was found that selenate was completely reduced to selenite by selenium reducing bacteria in the anoxic units. However, it was reported that a sufficient growth of algal was difficult to achieve and the reduction was highly temperature dependent (Golder Associates Inc., 2009).

2.6.3. Advanced Treatment Technologies

As discussed above, most of the conventional treatment options were reported ineffective in removing selenium from wastewater, especially with for existence of selenate as predominant form. Therefore, development of feasible and cost-effective techniques is in need for large scale industrial applications.

2.6.3.1 Ion Exchange

Ion exchange involves the exchange of an undesirable dissolved constituent for a more desirable solute electrostatically attached to an ion exchange material (Frankenberger Jr. *et al.*, 2004). Ion exchange is a very simple process to operate and is suitable for intermittent flow. Resin for the ion exchange process is often synthetic. Research indicates that resins work effectively for removing arsenic, selenium and other ionic constituents.

It was found that ion exchange is more effective in removing selenite rather than selenate (Mavrov *et al.*, 2006), which is due to the interference from sulfate. When large amount of sulfate present in wastewater (e.g., acid mine drainage) along with selenate, competition from sulfate inhibits the removal of selenate. Nishimura and Hashimoto (2007) studied the selenate removal by an ion exchange process using Polyamine-type weakly basic resin. They reported a strong adsorption of selenate anions (initial Se concentration of 30 -240 mg/L) by the resin over a wide pH range from 3 to 12. However, a tremendous decrease was revealed in the presence of elevated sulfate concentrations. Furthermore, they suggested small amount of HCl (1M) was effective in eluting selenate anions off from resin.

The cost for selective ion exchange is generally less than that for reverse osmosis (Frankenberger *et al.*, 2004). But the high chemical regeneration cost for the resin makes this technology unattractive, particularly for the wastewater with the high total dissolved solids (i.e. a few hundred mg/L) because of the quick saturation rates.

2.6.3.2 Reverse Osmosis

Reverse osmosis (RO) is the process of separating dissolved ions and other species from water by overcoming the osmotic pressure and forcing water through a semipermeable membrane from the stronger solution (Kapoor *et al.*, 1995). Sorg and Logsdon (1976) studied the selenium removal by RO process using cellulose acetate membrane. The investigated water sources were Cincinnati tap water with pH value at 7.13 and spiked by a selenite concentration to 0.1 mg/L. The operation conditions for cellulose acetate membrane were reported at flow rate of 1.3 L/min and operating

pressure of 190 psi. The results showed that selenite removal was greater than 97%. It was also found that selenate could achieve similar removal level.

2.6.3.3 Chemical Reduction with Zero-Valent Iron

Elemental iron is commonly referred to as zerovalent iron (ZVI). As a transition metal, ZVI is used as a catalyst for chemical synthesis in industry. In contaminant remediation, ZVI serves as both a catalyst and an electron donor in which ZVI immobilizes soluble trace element contaminants (e.g., selenium, chromium and uranium) by surface reduction and precipitation (Huang *et al.*, 1998; Farrell *et al.*, 1999; Qiu *et al.*, 2000). Selenium can be reduced to selenite, elemental Se [Se(0)], and selenide depending upon pH and O₂ in water. Low pH and low oxygen favors the more reduced forms of selenium. The corrosion of ZVI is an electrochemical process during which iron is oxidized to soluble ferrous ion (Fe²⁺). Ferrous ion could react with OH⁻ to form Fe(OH)₃ and then further oxidized to form green rust I. The green rust can also serve as a reducing agent to abiotically reduce Se(IV) to Se(IV) and Se(0) (Myneni *et al.*, 1997). The advantage of zerovalent iron is to reduce the concentration of selenium to very low concentrations and might be useful as a polishing step following microbial treatments (Frankenberger *et al.*, 2004). Besides its low cost, the secondary and ternary reaction products, such as Fe(II) and Fe(III) compounds, impose no harm to the environment (Qiu *et al.*, 2000). However, the waste and sludge (e.g., elemental selenium) need to be removed from the treatment systems and further properly handled which may increase the cost of treatment.

Murphy (1988) studied the chemical process when using treatment systems containing finely divided iron to remove selenate. It was revealed that ZVI had to be converted into ferrous first in order to have the selenate reduction occur. The existence of oxygen was necessary for the transformation of ZVI. The reaction is described as:

However, extra oxygen will cause a decrease in selenate removal due to the further oxidation of ferrous hydroxide to ferric precipitates:

Selenate reduction reactions are also proposed as follow:

This suggests that ZVI must be oxidized to ferrous hydroxide first in order to allow the reduction to proceed (Murphy, 1988). It also suggests that a higher ratio of Se (VI) to ferrous result in different formation of iron product. Both reactions (3) and (4) presented above are spontaneous according to free energy calculations (Murphy, 1988). Olegario *et al.* (2009) reported that selenate could be further reduced to selenide when using ZVI nanoparticle suspensions. However, Se(IV) was barely detected during the reduction of selenate (Murphy, 1988; Olegario *et al.*, 2009).

Selenite also could be removed by ZVI reduction to form Se(0) or Se (II-) (Loyo *et al.*, 2008). The standard electrode potentials for $HSeO_3^-/Se(0)$ and $Se(0)/HSe^-$ redox couples are more positive than that for the $Fe(II)/Fe(0)$ couple, indicating that Se(IV) can be reduced to Se(II-) by Fe(0) in a certain pH range.

2.6.3.4 Adsorption by Various Materials

Kapoor *et al.* (1995) defined adsorption as the interphase accumulation or concentration of a substance onto the solids surface. Activated carbon is a widely used adsorbent in water/wastewater treatment. Logsdon *et al.* (1974) investigated the selenium removal efficiency using powdered activated carbon (PAC). The results showed a less than 4% removal under various pH. A relative increase of selenium removal was observed on the pilot scale studies carried out using granular activated carbon (GAC) for sewage effluent (Linstedt *et al.*, 1971). They reported the removal for selenite was 43%. Linstedt *et al.* (1971) attributed the increase of selenium removal to the formation of complexation between selenium species and organic matter originally present in wastewater.

Selenium adsorption using activated alumina or aluminum oxide treated materials was estimated by several researchers (Sorg and Logsdon, 1978; Trussell *et al.*, 1980; Novak *et al.*, 1987; Kuan *et al.*, 1998). Studies under various conditions were carried out to examine the optimum adsorption conditions for different adsorbents. The adsorption capacity of activated alumina for selenite was reported about 3 times higher than that for

selenate (Trussell *et al.*, 1980). Yodnane *et al.* (1992) evaluated the selenium adsorptive removal for fly ash leachate using activated alumina. Kuan *et al.* (1998) tested selenite and selenate removal using aluminum oxide coated sand in the presence of 0.1 M NaCl electrolytes. The results showed 95% and above removal efficiency for both initial selenite and selenate concentration of 0.8 mM at pH lower than 8 and 7, respectively. The results also revealed that both selenite and selenate batch adsorption can reach equilibrium after 100 minutes.

Ferrihydrite precipitation with concurrent adsorption of selenium onto the ferrihydrite surface (ferrihydrite adsorption) is EPA's BDAT for treating selenium-bearing waters (MSE Technology Applications, Inc., 2001). For adsorption of selenium using ferrihydrite to occur, the ferric ion (Fe^{+3}) must be present in the water. Selenate (Se^{+6}) is most effectively removed from the water at pH levels below 4. The chemical reactions for ferrihydrite precipitation of selenium are (MSE Technology Applications, Inc., 2001):

Parida *et al.* (1997) investigated the selenite adsorption onto different polymorphic forms of iron oxyhydroxides and amorphous ferrihydrite. pH, initial selenite concentration, adsorbent loading rate, temperature and reaction time were tested to identify the optimum adsorption conditions for each adsorbents. The results indicated the adsorption capacity of selenite removal followed the order of β -FeOOH < α -FeOOH < γ -FeOOH < δ -FeOOH < amorphous ferrihydrite. An adsorption percentage of 80% was reported using amorphous ferrihydrite (250 mg/L) at pH lower than 4 for initial selenite concentration of 1.26 μ m/L after 2 hours reaction.

2.7 Surface Chemistry of Various Iron Oxides

The Fe-GAC adsorbents are found to behave similarly with iron oxides when adsorption is taking place. To understand and predict the Fe-GAC adsorption behavior

and mechanisms, it is necessary to have a thorough understanding of the surface structure and crystal properties of various iron oxides.

2.7.1 Iron Oxides Types, Characteristics and Transformations

Iron oxides are widely present in nature (e.g., in pedosphere, biosphere, lithosphere). There are more than 10 types of iron oxides, with the existing form including oxides (e.g., hematite and maghemite), hydroxides (e.g., Bernalite) or oxy-hydroxides (e.g., goethite and lepidocrocite). All the iron oxides were revealed to convert into one or more types under appropriate conditions (Cornell and Schwertmann, 2003). Among these, hematite ($\alpha\text{-Fe}_2\text{O}_3$) and goethite ($\alpha\text{-FeOOH}$) are widely studied and employed in multi-disciplines (e.g., mineralogy, geology, soil science and environmental chemistry) as a result of their high stability under broad environmental conditions. However, all the iron oxides show low solubility in water and some of the Fe atoms might be substituted by other cations, such as Al, Si, Mn. Also, as the very high crystallization energy of iron oxides, only small amount of crystals are formed in both natural environments and industrial products. Moreover, large specific surface areas (i.e., $>100\text{ m}^2/\text{g}$) are observed in most iron oxides, therefore, they can be employed as adsorbents to remove dissolved inorganic ions and organic compounds.

Goethite and hematite are found to be the most thermodynamically stable forms under various conditions (Cornell and Schwertmann, 2003). They are often the first oxides to form or the end member of many transformations. The oxy-hydroxides can be dehydroxylated and transformed into their oxide counterparts. This reaction often takes place with the assist of heat or mechanical stress under dry conditions. It was found that hematite is always the end product of dehydroxylation of the pure phase (e.g., goethite, lepidocrocite, akaganeite ($\beta\text{-FeOOH}$), ferrihydrite ($\text{Fe}_5\text{HO}_8\cdot 4\text{H}_2\text{O}$) and etc.) with the formation of other iron oxides as the intermediate forms, such as lepidocrocite ($\gamma\text{-FeOOH}$) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$). Other transformation may occur as the form of dissolution or precipitation under acidic or alkaline conditions, such as lepidocrocite, akaganeite and $\text{Fe}(\text{OH})_2$ can be converted into goethite under alkaline conditions; ferrihydrite may also be transformed into goethite in aqueous solution within a broad pH range (3 - 14); in the presence of Cl, ferrihydrite can be converted into akaganeite at low pH.

2.7.2 Surface Functional Groups

The surface hydroxyl groups, which typically originate either from adsorption of water or from structural OH, are the functional groups of iron oxides. Generally, hydroxyl groups possess a double pair of electrons together with a dissociable hydrogen atom which enables them to react with both acids and bases (Cornell and Schwertmann, 2003). Hence, iron oxides are typically amphoteric. Crystallographic considerations indicate that the surface hydroxyl groups may be coordinated to one, two or three underlying iron atoms. The structures of these singly, doubly and triply coordinated groups are illustrated in [Figure 5](#). Assuming sixfold coordination for each Fe atom, a charge of +1/2 could be assigned to each Fe-O bond. Hence, the three of surface OH groups carry charges of -1/2, 0 and +1/2.

All three hydroxyl groups are found coexisting on (001) plane, whereas no triply groups are observed on (100) plane; and only singly groups are present on (010) plane. The density of each type of functional group is dependent on the crystal structure and the extent of development of the different crystal faces. It can be measured by various methods, such as acid base titration, BET treatment of water vapour isotherms, D₂O or tritium exchange and by reaction with adsorbing species (e.g., fluoride, phosphate and oxalate). Badlani and Wachs (2001) employed methanol adsorption method to determine surface active sites for various oxides including hematite. However, as different methods used, the results often vary with each other. Generally, singly coordinated hydroxyls are reported its density between 3 to 8 OH/nm² for goethite and hematite. Barr n and Torrent (1996) reported the densities for singly, doubly and triply functional groups on 101 face of goethite are 3, 3 and 9.1 OH/nm², respectively.

2.7.3 Reactivity of Surface Functional Groups

As discussed above, hydroxyl functional groups may vary in structure, charge and acidity. Hence, they typically show different reactivities. Several previous studies (Russel *et al.*, 1974; Lewis and Farmer, 1986; Hiemstra and Van Riemsdijk, 1996) indicated that the doubly coordinated surface hydroxyls on goethite, hematite and lepidocrocite are inert for adsorption over a wide pH range. Furthermore, Eggleston and Jordan (1998) and Hiemstra and Van Riemsdijk (1999) employed scanning field

microscopy and acid base titration to investigate the hydroxyl groups on the (001) plane of hematite. They both suggested that doubly coordinated hydroxyl groups are the predominant type on this plane, which make this face unreactive and no charge contribution. Venema *et al.* (1998) revealed that only singly coordinated hydroxyls on goethite are involved in adsorption of ions on Fe oxides.

2.8 Selenate Adsorption Mechanisms

Adsorption of selenate onto iron oxides or hydroxides has been studied for decades. It is generally accepted that selenate anions are adsorbed via ligand exchange process. Surface complexes are formed between selenate anions and surface sites. Surface complexes are defined as a stable molecular entity formed between surface functional groups on the solid surface and the ions or molecules present in the solution (Sparks, 2003).

The surface complexes are classified as inner-sphere complex and outer-sphere complex according to the complexation location. Based on the electric double layer theory, various models were developed to describe the arrangement of adsorbate ions (i.e., triple layer model, stern layer model, generalized two layer model, and etc.). Generally, the surface of the adsorbent is charged and balanced by counterions (i.e., ions of opposite charge to the surface charge) in the adjacent cloud layer, which is known as the diffuse layer with a distance exceeding molecular dimensions. The triple layer model (TLM) developed by Davis and Leckie (1978) suggests the existence of two capacitance layers (i.e., α layer and β layer) between the adsorbent surface and diffuse layer. Only proton and hydroxide can be adsorbed on α layer, while adsorption of other ions (e.g., metal cations and ligands) typically occurs on the outersphere layer (β layer) and forms outer-sphere complexes. Hayes and Leckie (1986) further modified the TLM and suggested that adsorbate ions can enter into inner sphere (α layer) and form chemical bonds with surface sites to form inner-sphere complexes. Eggleston *et al.* (1998) suggested that main difference between inner and outer sphere complexes lies in the number of water of hydration lost in the coordination of adsorbates and surface sites. Adsorbates lose at least one water molecule to form inner-sphere and retain intervening water of hydration to

form outer-sphere complexes. Inner sphere complexes can be mono-dentate or bi-dentate. Adsorbates are bound to one oxygen atom to form mono-dentate binds, and bidentate binding is caused by binding with two oxygen atoms. Environmental factors such as pH, surface loading, ionic strength and adsorbent type all affect the type of sorption complex and binding mechanisms.

Various micro-scale spectroscopies were involved to understand the binding formation between selenate ions and surface sites. Harrison and Berkheiser (1982) observed formation of inner-sphere bidentate binuclear complexes of selenate on iron oxides using ex-situ Fourier transform infrared (FTIR). Later studies revealed that drying and vacuum treatment in sample preparation for FTIR analysis could result in the inner-sphere formation (Johnston and Sposito, 1987). Hays and Leckie (1987) used extended X-ray absorption fine structure (EXAFS) to study selenate adsorption and concluded that selenate was adsorbed via outer-sphere mechanism onto goethite. Zhang and Sparks (1990) applied the triple layer model to selenate adsorption onto goethite and suggested an outer-sphere mechanism for selenate adsorption. Attenuated total reflectance FTIR (ATR-FTIR) and diffuse reflectance (DRIFT) spectroscopy were utilized to study selenate adsorption by Su and Suarez (2000). They found that selenate formed both monodentate and bidentate inner-sphere complexes on the surface of amorphous iron oxides under aqueous conditions but only bidentate inner-sphere complexes existed when samples became dry. Using EXAFS and ATR-FTIR, Peak and Sparks (2002) reported only inner-sphere complexes were formed in selenate adsorption on hematite but both outer- and inner-sphere complexes were formed on goethite and hydrous ferric oxides. Rovira *et al.* (2008) concluded that adsorption of selenate forms outer-sphere complexes at higher pH (alkaline conditions) on goethite and inner-sphere complexes at lower pH (acidic conditions).

Although selenate-iron (hydr)oxide adsorption systems have been studied for decades, controversies about the adsorption mechanisms still exist. In particular, the complexation mechanisms of selenate adsorption under different adsorption conditions (i.e. pH, ionic strength and surface loading) still remain controversial. Exploration of adsorption mechanisms under various conditions is expected to help explain the low adsorption phenomena for selenate. Surface property investigation and molecular

distribution mapping will promote the understanding of surface site affinity to selenate ions and further improve the adsorbent preparation procedure along with the increase of selenate removal efficiency by adsorptive techniques.

2.9 Characterization of Selenate Adsorption Mechanism and Oxidation States

The use of spectroscopic techniques has generated valuable yet controversial information on the structure on adsorbed Se species on iron oxides/hydroxide minerals and synthetic adsorbents. Chemical states of selenium can be determined by spectroscopic analysis and quantitative analytical methods. Various spectroscopes including Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), Raman spectroscopy and Extended X-ray absorption fine structure (EXAFS) were used in previous studies to characterize the binding mechanism of selenate sorption (Manceau and Charlet, 1994; Su and Suarez, 2000; Wijnja and Schulthess, 2000; Peak and Sparks, 2002). Atomic scale surface imaging tools (e.g., scanning tunneling microscopy (STM) and high resolution transmission electron microscopy (HRTEM)) are also found to be helpful to provide comprehensive information to identify the crystal structure.

2.9.1 Chemical States Determination

X-ray absorption near edge structure (XANES) was widely used in determining the chemical oxidation states. The near-edge structure is characteristic of an environment and valence state. Much chemical information can be extracted from the XANES region: formal valence, coordination environment and subtle geometrical distortions. XANES has been utilized to identify the location, oxidation state and spatial distribution of heavy metal elements in soils and plants.

Olegario *et al.* (2009) investigated the reaction of Se (VI) with zero-valent iron nanoparticles using X-ray spectroscopic techniques. Initial Se (VI) concentrations used in this study ranged from 0.13 to 3.00 mM with 0.01 M NaCl in the solution. The reaction time for batch adsorption experiments lasted for 48 hours. The Se *K*-edge absorption spectra were collected from 12,500–13200 eV. Energy step intervals of 0.2

eV from 12,640–12,683 eV (XANES region) were controlled with a Si(111) monochromator. Energy calibration was performed by assigning the *K*-edge energy (E_0) of 11919 eV to a gold foil which resulted in a measured Se *K*-edge of 12657.4 eV for Se(0) standard. Olegario *et al.* (2009) reported values of E_0 for Se(VI), Se(IV) and Se(0) as 12664.49, 12661.42 and 12657.51 eV, respectively. The measured E_0 for Na₂Se was 12656.17 eV, which makes the Se²⁻ distinctly different from Se (VI), Se (IV) and Se(0) and thus are useful as a fingerprint for Se²⁻ the oxidation state.

The results of XANES spectrum analysis of Se (VI)-adsorbed nano Fe⁰ suggested that Se (VI) had been fully reduced and no evidence for the existence of Se (VI) in final product was shown. The results also indicated that the oxidation state of Se was clearly Se²⁻, however, it was also possible that poorly ordered domains of Se (0) could be present as part of the Fe corrosion layer, especially for the more oxidizing environmental conditions or partial reduction of Se (VI) occurred.

X-Ray Photoelectron Spectroscopy (XPS) is another widely used surface technique for surface elemental composition and chemical oxidation state studies. The working principle of XPS is that the core electron of a target atom receives sufficient energy from an incoming X-ray source and escapes from the atom and emits out to the surface. The kinetic energy (E_k) of the emitted electrons is measured by XPS energy analyzer. The binding energy of the core electron is then calculated by the difference between adsorbed energy and kinetic energy. Qiu *et al.* (2000) studied the oxidation state of Se after reduction by ZVI reduction using XPS. A Se (VI) concentration of 10 mM was prepared in 1 mM NaCl solution. pH was controlled at 8 - 8.5 to simulate field conditions. Qiu *et al.* (2000) indicated that for Se (0) deposited on clean iron foil in the absence of oxygen, the 3p_{3/2} binding energy is 161.0 eV. For the standard Se(VI) powder, the 2p_{3/2} binding energy is 169.7 eV. The 3p_{3/2} binding energy is 166.0 eV for Se collected from iron substrate reacted in 0.5 mL of a 10 mM Na₂SO₄ solution without N₂ purging. The results showed that peak collected without N₂ purging lied between elemental Se and Se (VI), which indicated the presence of partially reduced form Se(IV).

2.9.2 Chemical Binding Identification

Harrison and Berkheiser (1982) observed formation of inner-sphere bidentate binuclear complexes of selenate on iron oxides using ex-situ Fourier transform infrared (FTIR). Watanabe *et al.* (1994) suggested that conclusions of several earlier FTIR studies of selenate and sulfate adsorption are often equivocal because samples were dried before spectroscopic study. Later studies revealed that drying and vacuum treatment in sample preparation for FTIR analysis could result in the inner-sphere formation (Johnston and Sposito, 1987). Parfitt and Russell (1977) also suggested a transition from outer-sphere to inner-sphere complex upon air drying for nitrate and chloride ions. Hence, an *in situ* study is more precise to analyze the interfacial structure of selenate.

Attenuated total reflectance FTIR (ATR-FTIR) spectroscopy was utilized to investigate selenate and selenite sorption onto amorphous Fe oxide [am-Fe(OH)₃] by Su and Suarez (2000). They reported the spectra of free selenite, selenate and selenate, selenite sorbent suspensions recorded in the range of 4000-700 cm⁻¹. Bands at 850, 825 and 731 cm⁻¹ were observed for free selenite anions in solution at pH 5, and bands at 872 cm⁻¹, assigned to ν_3 (asymmetric stretching of Se-O bond), was identified for free selenate anions in solution at pH 8. Su and Suarez (2000) suggested that the coordination of selenate with metal cations could cause the decrease of selenate symmetry resulting in a splitting of the ν_3 band. They concluded based on the data provided by Harrison and Berkheiser (1982) that two bands will appear at C_{3v} symmetry if a monodentate complex forms, three bands are present at C_{2v} symmetry if a bidentate complex forms. Su and Suarez (2000) determined the spectra of selenate complexes at the solid-aqueous solution interface by subtracting the bulk solution IR absorption from the spectrum of the corresponding sorbent suspension. The results for am-Fe(OH)₃ reacted with 0.05 and 0.1 M selenate at pH 5.0 showed two bands at 895 and 885 cm⁻¹ indicating a reduction in symmetry.

Wijnja and Schulthess (2000) studied coordination and speciation of selenate on goethite surfaces using Raman spectroscopy. The Raman spectra for 0.1 M selenate solution at pH 0.8 and 7.5 were reported. According to value of pK_{a2} of selenate, HSeO₄⁻ is the predominant species at pH 0.8 and SeO₄²⁻ is the only species in solution at pH 7.5. Four bands were identified for selenate at pH 7.5: 349, 417, 837 and 873 cm⁻¹ assigned to

doubly degenerate ν_2 OSeO bending, triply degenerate ν_4 OSeO bending, nondegenerate ν_1 symmetric SeO stretching and ν_3 asymmetric SeO stretching, respectively. It was suggested that stretching vibrations are much more intense than the bending vibrations (Wijnja and Schulthess, 2000). Spectra for selenate (0.004 M) adsorbed at various pH on goethite ($I = 0.004$ to 0.006 M) and Al oxide ($I = 0.008$ to 0.014 M) were compared with spectra for adsorbents only. Results showed that bands at 875 and 900 cm^{-1} became clear and sharp as the decrease of pH from 7.2 to 4.2 . A shoulder band at 835 cm^{-1} was also observed to disappear as pH decreased. A shift of ν_1 band for adsorbed selenate (848 cm^{-1}) from selenate in solution (837 cm^{-1}) was also observed. The shift of ν_1 and split of ν_3 indicated the direct coordination of SeO_4 to the goethite surface (i.e., monodentate inner-sphere surface complex). The fade of the shoulder band also indicated that a fraction of the adsorbed SeO_4 exists as an outer-sphere complex.

Peak and Sparks (2002) employed extended X-ray absorption fine structure (EXAFS) to determine the selenate bonding mechanism on goethite. It was found that the hydrated radius for SeO_4^{2-} and HSeO_4^- are $\sim 4\text{ \AA}$ (Stumm and Morgan, 1996). The k^3 -weighted χ function spectra and radial structure functions (RSF) spectra were presented for selenate solution and selenate on various iron oxides by Peak and Sparks (2002). They also fit the spectra with theoretical scattering paths using FEFF7 code. The results showed successful fitting of $k^3\chi$ spectra with a single shell fit of 4 oxygens at $1.64\text{ \AA}$ for both aqueous selenate and selenate on goethite at pH 6. $k^3\chi$ spectra for selenate on goethite at pH 3.5 was reported to fit better with a two shell fit of 4 oxygens at $1.64\text{ \AA}$ and 1.5 Fe at $3.31\text{ \AA}$. It indicated that inner-sphere complexation of selenate occurs on the goethite surface at pH 3.5. They concluded that pH plays a significant effect on selenate adsorption on goethite, however, ionic strength and surface loading have a more subtle effect.

2.9.3 Crystal Structure Investigation

Olegario *et al.* (2009) used x-ray diffraction (XRD) to study the crystal structure of selenium on zero-valent iron nanoparticles. The spectra for untreated 100 mesh Fe^0 powder, Fe^0 nanoparticles, selenate with various concentrations deposited on Fe^0 nanoparticles were presented. Peaks at 27.15 , 36.25 and $46.90^\circ\ 2\theta$ were identified

indicating the formation of γ -FeOOH as a result of the oxidation of nano Fe⁰. The results also showed that the increasing concentration of selenate (from 0.5 to 5 mM) caused a conversion of γ -FeOOH to magnetite (Fe₃O₄)

Other instruments have the potential to increase our understanding of selenium adsorption on iron oxides, but have not been used. For example, scanning tunneling microscope (STM) and high resolution transmission electron microscope (HRTEM) were applied to study the sorbed crystal structure for other cations (e.g., Cr(III)) and anions (e.g., sulfate) (Fendorf and Sparks, 1994; Eggleston *et al.*, 1998). These atomic-scale microscopes could be useful methods used to analyze the crystal structure of surface sorbed selenium.

Figure 1. Selenium production usage in each industry.

Figure 2. Species fraction diagram for Se (IV) as a function of pH.

Figure 3. Species fraction diagram for Se (VI) as a function of pH

Figure 4. Selenium potential-pH diagram at 25°C for a dissolved selenium activity of 10^{-7} mol/L (Séby, et al., 1998).

Figure 5. Structures of singly, doubly and triply coordinated surface hydroxyl groups on iron oxides (Cornell, 2003).

Table 1. Standard thermodynamic data used to establish the potential-pH diagram (Séby, et al., 1998).

Redox reactions	Standard potential (V)
Se(0)/Se(-II)	
$Se(s) + 2H^+ + 2e^- \rightleftharpoons H_2Se(aq)$	-0.115
$Se(s) + H^+ + 2e^- \rightleftharpoons HSe^-$	-0.227
$Se(s) + 2e^- \rightleftharpoons Se^-$	-0.641
Se (IV)/Se (0)	
$H_2SeO_3(aq) + 4H^+ + 4e^- \rightleftharpoons Se(s) + 3H_2O$	0.740
$H_2SeO_3 + 5H^+ + 4e^- \rightleftharpoons Se(s) + 3H_2O$	0.780
$SeO_3^{2-} + 6H^+ + 4e^- \rightleftharpoons Se(s) + 3H_2O$	0.903
Se(VI)/Se(IV)	
$HSeO_4^- + 3H^+ + 2e^- \rightleftharpoons H_2SeO_3(aq) + H_2O$	1.090
$HSeO_4^- + 2H^+ + 2e^- \rightleftharpoons HSeO_3^- + H_2O$	1.008
$HSeO_4^- + H^+ + 2e^- \rightleftharpoons SeO_3^{2-} + H_2O$	0.760
$SeO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons H_2SeO_3(aq) + H_2O$	1.139
$SeO_4^{2-} + 3H^+ + 2e^- \rightleftharpoons HSeO_3^- + H_2O$	1.060
$SeO_4^{2-} + 2H^+ + 2e^- \rightleftharpoons SeO_3^{2-} + H_2O$	0.811
Acid-Base reactions	pK_a
Se (-II)	
$H_2Se + H_2O \rightleftharpoons HSe^- + H_3O^+$	3.8
$HSe^- + H_2O \rightleftharpoons Se^{2-} + H_3O^+$	14
Se (IV)	
$H_2SeO_3 + H_2O \rightleftharpoons HSeO_3^- + H_3O^+$	2.68
$HSeO_3^- + H_2O \rightleftharpoons SeO_3^{2-} + H_3O^+$	8.4
Se (VI)	
$H_2SeO_4 + H_2O \rightleftharpoons HSeO_4^- + H_3O^+$	-2.01
$HSeO_4^- + H_2O \rightleftharpoons SeO_4^{2-} + H_3O^+$	1.73

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials

All the chemical solutions used in this study were analytical grade and prepared using de-ionized water. Sodium selenite (Na_2SeO_3) and sodium selenate (Na_2SeO_4) were purchased from MP Biomedicals (Solon, OH).

Sodium bicarbonate (NaHCO_3), sodium carbonate (Na_2CO_3), sodium chloride (NaCl), sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), sodium hydroxide (NaOH), sodium phosphate (Na_3PO_4), sodium silicate (Na_2SiO_4), potassium acetate (KAc), potassium chloride (KCl), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and cyclohexane (spectrophotometric, 99+%) were purchased from Fisher Scientific, Inc. (Rochester, NY).

Sodium hypochlorite (NaClO , 13%), sodium sulfate (Na_2SO_4), 2, 3-Diaminonaphthalene (97%) (DAN) and hydroxylamine hydrochloride reagents were obtained from ACROS Organics (Geel, Belgium).

Iron-coated GAC adsorbent used in this study was prepared using Darco 12×20 GAC provided by Norit Americas Inc. (Marshall, TX).

3.2 Reagent Preparation

3.2.1 Selenium Stock Solutions

A selenate stock solution (1,000 mg-Se/L) was prepared by dissolving Na_2SeO_4 into 50 mL deionized water containing 0.5 mL concentrated HCl. A selenite stock solution was prepared for the same concentration. Separate working solutions (4 mg/L) of selenite and selenate were prepared by further diluting the stock solutions and they were used in all adsorption experiments.

3.2.2 Selenium Analysis Reagents

The DAN solution was prepared by dissolving 200 mg DAN in 200 mL HCl (0.1 N), and then extracted three times using 25 mL cyclohexane, followed by filtration into

an opaque container. It was then stored in cool place for no longer than 8 hours. An HA-EDTA solutions prepared by adding 2.25 g Na₂EDTA and 6.25 g hydroxylamine hydrochloride (NH₂OHHCl) into 250 mL de-ionized water was used to eliminate negative interferences from Fe²⁺.

3.2.3 Iron Extraction Reagents

A sodium citrate solution (0.3 M) was prepared by adding 22.05 g Na₃C₆H₅O₇·2H₂O to approximately 50 mL de-ionized water, completely dissolved and brought the volume to 250 mL.

3.2.4 Electrolytes and Other Salt Solutions

Electrolyte solutions (LiCl, NaCl and KCl, 0.5 M) were prepared by dissolving the solid salts into 100 mL de-ionized water and brought the volume to 250 mL in volumetric flasks. Solutions for competitive anions experiments (Na₂SO₄, Na₂SiO₄, Na₂CO₃ and Na₃PO₄) were also prepared for the anion concentration of 0.5 M by dissolving corresponding salts into de-ionized water..

3.3 Adsorbent Preparation and Characterization

3.3.1 Adsorbent Preparation

The adsorbents were prepared by oxidizing ferrous iron into ferric iron using sodium hypochlorite on the outside surface and inner porous structures of GAC. The detailed synthesis procedure was described elsewhere (Gu *et al.*, 2005; Zhang *et al.*, 2008). [Figure 6](#) illustrates the ferrous mixing process incorporated with NaClO titration.

3.3.2 Iron Percentage Measurement

To investigate the efficiency of the coating procedure, total iron percentage and amorphous iron percentage on virgin GAC and Fe-GAC were determined using iron extraction methods followed by Inductively Coupled Plasma Spectroscopy Optical Emission Spectrometer (Optima 2100 DV, Perkin Elmer, CT) measurements.

3.3.2.1 Total Iron Percentage

Total iron was extracted from GAC surface following an acid digestion procedure (Lu, 1995; Gu *et al.*, 2005). Specifically, each type of adsorbents (0.1 g) was suspended in 30 mL HCl (3:1) and shook for 2 hours. The mixture solution was then heated in a water bath at 90 °C for 20 minutes. The liquid phase was separated by vacuum filtration through a 0.45 µm membrane. Remaining solids were washed with de-ionized water several times and followed by filtration after each washout. All the aqueous filtrates were collected and mixed for iron determination using ICP-OES.

3.3.2.2 Active/Amorphous Iron Oxide Percentage

Amorphous iron on Fe-GAC was determined using a dark acid ammonium oxalate method (Schwertman, 1964; McKeague and Day, 1966; Loeppert and Inskeep, 1996). Fe-GAC adsorbents (approximately 1 g) were ground to pass through a 100 mesh in^{-1} (0.15 mm nominal pore size) sieve and transferred into a 50-mL light-proof tube. Thirty (30) mL of ammonium oxalate solution (pH = 3) was added and the tube was immediately capped. The suspension was agitated and placed on reciprocating shaker for 2 hours. The suspension was filtered through a 0.45 µm membrane and solids were washed several times with de-ionized water following by filtration after each washout. All the aqueous filtrates were collected for iron determination as described above.

3.3.3 Iron Composition Analysis

Iron on Fe-GAC surface was studied to determine its chemical composition at various pH (e.g., 2 - 10) using X-ray Photoelectron Spectroscopy (XPS, PHI 5000 VersaProbe, Physical Electronics, Inc., MN). To obtain a high content of iron on GAC surface, Fe-GACs were prepared with 0.1 M ferrous and at a solid loading rate of 5 g/L. A ratio of 1:20 was used for ferrous iron to hypochlorite. Fe-GAC adsorbents were suspended in electrolyte solutions (NaCl, 0.1 M) for 24 hours. The solution pH was adjusted to values (i.e., 2, 5 and 8) using HCl (0.1 N) or NaOH (0.02 N) and monitored every 6 hours. Then, aqueous and solids phases were separated by vacuum filtration through 45 µm membranes. Solids were dried at room temperature and characterized by XPS along with raw GAC and non-suspended Fe-GAC.

3.3.4 Acid-Base Titration

Point of zero charge (pH_{pzc}) of the Fe-GAC under two ionic strengths (0.01 and 0.1 M NaCl) was determined using an acid-base titration method. For each ionic strength, two suspension samples (50 mL) each containing de-ionized water with a predetermined amount of NaCl, and Fe-GAC (0.1 g to obtain adsorbent loading 2 g/L) were prepared in flasks. The suspension samples were mixed for 12 hours to equilibrate. Thereafter, one of the two suspension samples was filtered through a 0.45 μm membrane by vacuum to remove the solids. The remaining suspension sample and the filtrate were then adjusted to pH 3 with a HCl solution (0.1 N) as the initial titration point. Prior to the titration, nitrogen gas was bubbled into the samples to removal CO_2 . The solutions were then titrated to pH 10 with a NaOH solution (0.02 N). Titration was performed by a 50 mL Digitrate Pro™, digital burette (Jencons, UK), during which pH was monitored by a pH meter (Accumet Basic AB15 Plus, Fisher Scientific, NY). During the titration, the aqueous solution along with burette and pH electrode was sealed with parafilm to prevent CO_2 exchange between the atmosphere and the aqueous solution. Equilibrium for each data point were assumed if there was no change of 0.2 units for pH observed within 30 seconds and it ranged from a few seconds to 10 minutes to reach equilibrium. A net titration curve was obtained by subtracting the total added acid/base concentration for titrating the filtrate to pH 10 from the added acid/base concentration for every titration data point of the suspension sample. The concentration of acid/base on the net titration curve can be calculated using the equation reported by Wen *et al.* (1998). The concentrations of added acid (-) or base (+) were plotted as a function pH, and pH_{pzc} was determined by the intersection of the two net titration curves for two ionic strengths (Huang, 1981; Schulthess and Sparks, 1986; Reed and Matsumoto, 1991).

3.4 Selenium Analysis

3.4.1 Selenite Analysis

A colorimetric method was used to measure selenium concentration (USEPA standard methods 3500C, 1998). The method relied on a reaction of selenite ion with DAN that produced a brightly colored and strongly fluorescent piazselenol compound,

which was extracted in cyclohexane and measured colorimetrically. The DAN solution was prepared by dissolving 200 mg DAN in 200 mL HCl (0.1 N), and then extracted three times using 25 mL cyclohexane, followed by filtration into an opaque container. An HA-EDTA solution prepared by adding 2.25 g Na₂EDTA and 6.25 g hydroxylamine hydrochloride (NH₂OHHCl) into 250 mL de-ionized water was used to eliminate negative interference from Fe²⁺. For the colometric measurements, 2 mL of the HA-EDTA solution was added to a 50 mL test tube containing 10 mL selenium aqueous sample or deionized water (as blank). The mixture solution pH was adjusted to 1.5 ± 0.3 using a 0.1 N HCl solution. All the samples solution along with blank control were then added with 5 mL of the DAN solution and put into a covered water bath at 45 °C for one and half hours to allow color formation. The sample solution was allowed to cool down and followed by the addition of 2 mL cyclohexane. The sample test tube was capped with phenolic screw caps (PTFE rubber lined) securely and shaken vigorously for 5 minutes, followed by 5-minute without mixing to separate the organic layer from the aqueous solution. The aqueous phase was removed using a disposable pipet attached to a vacuum line. Organic layer was transferred into methacrylate disposable cuvettes for UV/Visible spectrophotometer (Cary 50, Varian) analysis at wavelength of 480 nm for selenium concentration.

3.4.2 Selenate Analysis

Selenate in the aqueous samples was first reduced to selenite using an acid digestion method (Blaylock and James, 1993) and the selenite concentration was then quantified using a colorimetric method with a detection limit of approximately 0.01 mg/L (Standard Methods 3500 C, USEPA, 1998). For samples containing both selenite and selenate, total selenium was measured as selenite after the reduction of selenate. It has been shown in previous studies that the recovery of selenate varied under different reaction conditions and several chemical digesters could be used for the selenate reduction (Bye, 1983). Among those, concentrated HCl was reported to be the most effective and reliable reductant. In this study, 8 mL of a concentrated HCl (12.1 N) was added to 10 mL selenate sample in a 50 mL tube. The tube was then loosely capped and put into a 90 °C water bath for an hour, followed by sample cooling to room temperature

with the cap tightly closed. Excess HCl was neutralized by a NaOH solution (5 N) before final adjustment of pH to 1.5 ± 0.1 for selenite measurement.

3.6 Adsorption Kinetics

All the adsorption batch experiments were prepared as follow unless particularly indicated: specifically, 12.5 mL of the selenate working solution (4 mg/L) was mixed with 0.5, 2.5, 5 mL NaCl solution (1 M) in separate flasks and brought to a final volume of 50 mL with de-ionized water. As a result, the solutions contained 1 mg/L of selenium with ionic strengths of 0.01, 0.05 and 0.1 M. An acetate buffer solution (1 mL) was added to each mixture to obtain 0.01 M buffer concentration, and its interference with ionic strength was insignificant. Control experiments without solids for same initial selenium concentration were carried out under each ionic strength in the same type of flask. All the flasks were sealed with caps (phenolic screw caps with PTFE rubber liner) and placed in an incubator shaker for mixing. All the adsorption experiments along with control experiments were conducted at $\text{pH } 5 \pm 0.2$ and 25°C . Figure 6 illustrates the selenate batch adsorption process in continuous shaking incubator. After adsorption experiments, vacuum filtration through $0.45\ \mu\text{m}$ membranes of all the samples was performed to separate solids and other possible precipitates from liquid phase, and a 10 mL filtrate was collected for each batch experiment for selenate reduction and concentration analysis.

Adsorption kinetics was examined for the initial selenium concentration of 1 mg/L under three ionic strengths (i.e., 0.01, 0.05 and 0.1 M) for 48 hours. Adsorbent loading rate of 3.5 g/L was used. The experiments were performed in triplicates for each ionic strength for data validation. A pseudo second-order kinetic model was applied to the kinetic data:

$$\frac{t}{q} = \frac{1}{kq_e^2} + \frac{t}{q_e}$$

where q and q_e (mg-Se/g-adsorbent) are the amount of selenate adsorbed at time t and equilibrium, respectively; t (min) is the adsorption time; k (g/(mg·min)) is the second

order kinetic rate constant. The linear regression for $\frac{t}{q}$ over t was performed, intercept and slope were used to calculate the values of k and q_e .

3.5 Adsorption Isotherm Experiments

Adsorption isotherms of the Fe-GAC for selenate under three ionic strengths (0.01, 0.05 and 0.1 M) were determined. Adsorbent loading rates ranging from 0.5 to 7 g/L with an increment of 0.5 g/L were used. Adsorption was lasted for 48 hours. The adsorption isotherms were characterized by the Langmuir and the Freundlich isotherms. The Langmuir isotherm is given as below:

$$q_e = \frac{q_{\max} C_e}{b + C_e}$$

where b (L/mg) is the Langmuir adsorption constant; $q_{\max}$ (mg-Se/g-adsorbent) is maximum adsorption capacity; C_e (mg/L) is the equilibrium selenium concentration in the aqueous phase; q_e (mg-Se/g-adsorbent) is the solid-phase concentration at equilibrium.

The Freundlich isotherm is described by the following equation:

$$q_e = K_f C_e^{\frac{1}{n}}$$

where K_f (mg/g)(L/mg) ^{n} and n , (unitless) are model parameters related to adsorption capacity and intensity, respectively.

To describe the isotherm and calculate the parameters in each isotherm, nonlinear regression fitting were performed using SigmaPlot 11.0 (Systat Software Inc., IL). To evaluate the relative goodness of fit, Akaike's Information Criteria (AIC) analysis was performed. The AIC value was calculated according to the following equation (Faraway, 2005):

$$AIC = n \times \ln\left(\frac{RSS}{n}\right) + 2k$$

where n is the number of data points; RSS is the residual sums of squares; k is the number of parameters in the model. The Akaike weights (w_i) for each model was also calculated:

$$w_i = \frac{\exp[-0.5 \times (AIC_i - \min AIC)]}{\sum_{r=1}^R \exp[-0.5 \times (AIC_r - \min AIC)]}$$

AIC_i is AIC for model i ; $\min AIC$ is the minimum AIC value of all models; R is the number of models compared.

3.7 Relevant Factors Effect

3.7.1 Effect of pH

A range of pH (2 – 11) was used to evaluate pH effects on selenate adsorption. For each batch experiment, pH was monitored every 6 hours and maintained within ± 0.2 of each pH value by adding 0.1 N HCl or 0.02 N NaOH to the mixture. Control experiments were conducted at each pH without the addition of solids. After 24-hour, a 10 mL liquid sample was collected from each batch experiment following the procedure described in section 3.5 and processed for analysis.

3.7.2 Effect of Background Electrolytes

Three different electrolytes (LiCl, NaCl and KCl) were used to study the effects of electrolytes' hydrated radius on selenate adsorption by Fe-GAC. Selenate adsorption was conducted under a range of ionic strength controlled by three electrolytes (0.01, 0.5 and 0.1 M) with initial selenium concentration of 1 mg/L. An acetate buffer solution (1 mL) was added to each mixture to obtain 0.01 M buffer concentration. Solid loading rates ranging from 0.5 to 6 g/L was employed in the adsorption experiments. Adsorption lasted for 48 hours at room temperature and 10 mL of aqueous sample was collected following the procedure described in section 3.5 from each batch experiment to determine selenate concentration. Kruskal - Wallis Test using Systat 12 (Systat Software Inc., IL) was performed to examine the possibility of graphical overlapping among three isotherms under the same ionic strength.

3.7.3 Effect of Competitive Oxy-anions

Four anions (SiO_3^{2-} , SO_4^{2-} , PO_4^{3-} and CO_3^{2-}) were used to study their effects on selenate adsorption. Tests were conducted for initial selenium concentration of 1 mg/L with different competitive anion concentrations (0, 0.1, 1 and 5 mM). Experiments were carried out at room temperature at pH 5 under ionic strength controlled by 0.05 M NaCl for 24 hours. A 10 mL aqueous sample was collected from each batch experiment following the procedure described in section 3.5.

3.8 Selenite and Selenate Competitive Adsorption

Both selenite and selenate working solutions were added to a series of flasks to obtain initial Se concentration of 1 mg/L for both anions. NaCl (1 M) and acetate (0.01 M) solutions were used to control ionic strength and stabilize pH at 5. Adsorbent loading rate was varied from 0.5 to 3.5 g/L to obtain an isotherm for each chemical form. After 48-hour adsorption, two 10 mL sub-samples were collected from each flask with one sample used for selenite determination and the other for total selenium determination. Selenate concentration was calculated by subtracting the selenite concentration from the total Se concentration.

Freundlich-type multi-adsorbate adsorption isotherm model developed by Sheindorf *et al.* (1981) was used to characterize the competitive adsorption between selenite and selenate. The general Sheindorf-Rebuhn-Sheintuch (SRS) model equation for adsorbate i in an N -component system is given as:

$$q_{e,i} = K_{F,i} c_{e,i} \left(\sum_{j=1}^N a_{ij} c_{e,j} \right)^{\frac{1}{n_i} - 1}$$

where $q_{e,i}$ (mg-Se/g-adsorbent) is the adsorption capacity for adsorbate i ; $c_{e,i}$ and $c_{e,j}$ (mg/L) are equilibrium concentrations in the solution for adsorbate i and j , respectively.

The pre-exponential coefficient $K_{F,i}$ and exponent $\frac{1}{n_i}$ are Freundlich parameters that determined from its single-adsorbate system. The competition coefficient a_{ij} (unitless) describes the inhibition on the adsorption of adsorbate i caused by adsorbate j . The SRS

equation assumes that (i) each adsorbate individually follows the Freundlich isotherm; and (ii) there exists an exponential distribution of site adsorption energies for each component in a multi-component adsorbate adsorption system.

The competition coefficient a_{ij} in the competitive model was estimated using the competitive adsorption data of selenite and selenate by minimizing the Marquardt's percent standard deviation (MPSD), which is described as below:

$$MPSD = 100 \sqrt{\frac{1}{n_m - n_p} \sum_{i=1}^n \sum_{j=1}^N \left(\frac{q_{e,i,exp} - q_{e,i,cal}}{q_{e,i,exp}} \right)^2} \%$$

where n_m is the number of measurements and n_p is the number of parameters in the model. In this study, n_m and n_p equal to 7 and 3, respectively. N is the number of experimental data points and n is the number of adsorbates in the system. The subscripts "exp" and "cal" represent the solid phase concentrations determined from the competitive adsorption experiments and model predictions, respectively. Sheindorf *et al.* (1982) suggested that values for a_{ij} typically are larger than zero and normally smaller than 10. An iterative algorithm was implemented in MS EXCEL to estimate the values of a_{ij} that minimizes the MPSD. In the algorithm, an initial value ranging from 0 to 1000 was assigned to a_{12} (inhibition on selenite adsorption caused by selenate) in order to obtain the global minimum MPSD, and a_{21} which was equal to $1/a_{12}$ (by default for binary systems was calculated). The MPSD value was then calculated. The value of a_{12} was then adjusted iteratively until the minimum MPSD was obtained.

3.10 Raman Spectrum Collection

Raman spectra were collected using an inVia Renishaw Raman imaging microscope (Renishaw Inc., Schaumburg, IL). The instrument is comprised of several components including a laser source with a wavelength of 532 nm, a Leica microscope, a single spectrograph and a Pertier cooled CCD detector. The laser power was 100 mW, and excitation laser power could be adjusted from 0.001% to 100% by passing the laser through different filters. The laser beam was focused on the sample with a $\times 20$ lens to give a spot size of approximately 1 μm . Before the data collection for selenium loaded

Fe-GAC samples, the instrument was calibrated using pure Si at 521.5 cm^{-1} . All the data were collected using effective laser power no higher than 10 mW to avoid sample damage or chemical degradation, unless for assessing the effect of laser power on spectra noise elimination.

Selenium loaded Fe-GAC samples were prepared by suspending small amount of Fe-GAC adsorbents into 10 mL selenate (0.1 M) solutions. pH of each suspension was adjusted from 3 to 8 with increment of 1 to investigate its effect on the bridging structure and coordination mechanism. To perform an *in situ* measurement, all the selenium loaded suspension samples were spread out on a microscope slide and analyzed immediately. The exposure time was 20s/scan and the final spectra were obtained as a result of 10 accumulated scans.

3.11 XPS Spectrum Collection

Core level X-ray photon electron (XPS) spectra were collected using PHI 5000 VersaProbe XPS (Physical Electronics, inc., Chanhassen, MN). Prior to analysis, all the samples were put into vacuum chamber to remove the impurities. Monochromatic Al X-rays (1486.6 eV) were used for both low resolution survey and high resolution scans. The analysis passing energy of 117.4 eV and step size of 0.5 were used for survey scans, passing energy of 23.5 eV and step size of 0.05 eV were used for high resolution scans. All the spectra were charge corrected using C1s line at 284.8 eV . Background of high resolution spectra for Fe and O were deducted by Shirley type background to remove spectra distortion. Gauss-Lorentz Multiplet peak fitting was conducted using PHI Multipak Software (ULVAC-PHI, Inc., MN).

Figure 6. Illustration of FeGAC preparation procedure.

Figure 7. Illustration of batch adsorption experiments incubated in a reciprocating shaker.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Investigation of Iron Chemical States and Composition on Fe-GAC

4.1.1 Iron Coating Percentage

Percentages of coated total iron and amorphous iron in Fe-GAC (Darco 12×20) are listed in [Table 2](#). The data showed that amorphous iron was approximately half of the total iron. Also, the coated iron percentage increases from 0.18% to 2.8% with the increase of ferrous concentration employed in coating process. Gu *et al.* (2005) reported a total amount of 3.32% iron coated onto Darco 12×20 GAC when treated with 0.1 M Fe (II). They also suggested that the Darco GAC produced by steam activation of lignite may result in structures and reactive moieties with high abilities for Fe impregnation.

Table 3 shows the percentage of iron (in total coated iron) dissolved in aqueous solutions after suspended in 0.1 M NaCl solution at different pHs. The values of iron concentration in aqueous phase indicated that when pH was greater than 3, there was no dissolved iron detected; as pH was increased to 2, approximately 12% coated iron was found dissolved in aqueous phase. Therefore, within the mild pH range (e.g., 4 to 8), coated iron was stable on GAC surface.

4.1.2 Chemical States of Oxygen

XPS survey scans for the Virgin GAC (Darco 12X20), 0.1 M iron coated Fe-GAC, and suspended Fe-GAC in 0.1M NaCl solution at pH 5 are shown in [Figures 8](#) and [9](#). Peaks for C and O were readily identified for Virgin GAC. Small amount of Si are also recognized. After GAC was coated with 0.1 M ferrous, strong peaks for Fe and Cl are present in survey scan, indicating that effective iron coating was achieved on the GAC surface.

The high resolution core level XPS spectra for Fe2p, Fe2p_{3/2} and O1s for Virgin GAC, Fe-GAC and Fe-GAC suspended in NaCl solution at pH 5 are shown in [Figure 10 - 15](#). As no iron identified in virgin GAC, high resolution XPS spectrum investigation was not performed. The Gauss-Lorentz multiplet peak fitting was conducted for Fe2p_{3/2} spectra. The summation of the peak fitting is also shown as bold line in order to compare

the peak fitting results with experimental data. The parameter values of peak fitting are listed in Table 4. For O1s on virgin GAC, the multiplets found at 530.8, 532.1 and 533.4 eV can be assigned to metal oxides (Ismail et al., 1996), carbon oxygen double bonds (Hontoria-Lucas et al., 1995), and carbon-oxygen single bonds (e.g, phenols and ethers) (de La Puente et al., 1997). After coated with ferrous chloride, the O1s spectrum of the Fe-GAC was found to fit well with peaks for metal oxides (529.9 eV), hydroxyl (OH) (531.3 eV) (Moulded *et al.*, 1995) and silicon dioxides (532.4 eV). The peak area ratio of hydroxyl to oxides was estimated around 1. The missing peak bonds of carbon-oxygen can be attributed to the shallow detection of laser caused by thin layer coating of ferric on GAC surface. McIntyre and Zetaruk (1977) reported the similar multiplet peak fittings results for α -FeOOH XPS spectra. They found the hydroxyl peak at binding energy of 531.4 ± 0.2 eV and oxides peak at 530.3 ± 0.2 eV. Additionally, they found the peak area ratio to be 0.9 for α -FeOOH. After the Fe-GAC was suspended in 0.1 M NaCl solutions for 24 hours, the spectrum for O1s is found to fit with peaks at similar position with those for non suspended Fe-GAC. It indicates no transformation of chemical composition occurred after Fe-GAC was suspended in electrolytes solution. Moreover, an increasing in peak area for hydroxyl was observed.

4.1.3 Iron Oxide Compositions

[Figure 13](#) shows the XPS Fe2p core level spectrum for Fe-GAC. The center of gravity for Fe2p_{3/2} and Fe2p_{1/2} were estimated at 711.3 eV and 725.0 eV. The binding energy difference between two peaks was approximately 13.7 eV. A shakeup satellite was also observed between Fe_{2p3/2} and Fe_{2p1/2} peaks. According to the literatures, the 2p peaks for Fe element are around 707 and 720 eV for 2p_{3/2} and 2p_{1/2}, respectively ((Moulded et al., 1995); and 2p_{3/2} peak for Fe(II) ferrous oxide (FeO) is reported within binding energy range of 709.1 - 709.6 eV. Comparing the peak positions for different chemical states of iron, peak shifting to higher binding energy region and the relative large binding energy difference between peaks were both observed in this study. These facts indicate that the Fe (III) was successfully precipitated onto the GAC surface.

Fe2p_{3/2} spectra is also widely used to identify iron compounds compositions and structures. Fe2p_{3/2} spectrum for Fe-GAC and suspended Fe-GAC can be fitted well with

four multiplet peaks, ranging from 710.2 eV to 713.4 eV. Based on the peak shapes and peak fitting parameters (Table 3), it can be concluded that there is no difference between Fe2p_{3/2} spectra for suspended and non suspended Fe-GAC. The most intense fitted peaks were both found at low binding energy region (i.e., 710.2 eV) with slightly higher area percentage than those for second intense fitted peaks. The difference in positions among peaks is 1.0 eV except that between peak 3 and peak 4. Grosvenor et al. (2004) reported the similar peak fitting results for α -FeOOH. They found the most intense peak at 710.3 eV with full width at half maximum (FWHM) of 1.4 and area percentage of 31.4%. They also observed the position difference between peak 1 and 2 (711.2 eV) is 1.0 eV. Comparing with their results, it implies a possible chemical composition for iron on Fe-GAC is α -FeOOH and suspension in background electrolytes may not result in any changes for this composition.

4.2 Adsorption Kinetics

Adsorption kinetic experiments were carried out in triplicates to examine the replicability of the experiments. The averages of the adsorption capacities and the removal percentage were plotted over time in Figure 16, 17 and 18. The error of the adsorption capacity for each data is indicated by the upper and lower bar. The errors were generally within 10% indicating the experimental procedures are replicable and reliable. The figures illustrated that selenate adsorption equilibrium was reached within 48 hours for all three ionic strengths (0.01, 0.05 and 0.1 M) with more than 85% of the equilibrium capacities being obtained in 6 hours. Removal efficiency increased from 62% to 78% with the decrease of ionic strength from 0.1 M to 0.01 M. Pseudo second-order kinetic model characterized the selenate adsorption kinetics well ($R^2 > 0.99$). Adsorption rate constants and equilibrium adsorption capacities obtained from the kinetic model are listed in Table 5. The decrease of adsorption capacity and increase of the rate constant were both observed along with the increase of ionic strength. This significant effect of ionic strength was not observed in selenite adsorption. The obtained rate constants under all three ionic strengths were larger than that for selenite adsorption (0.018 g/(mg·min)) under 0.1 M ionic strength using the same adsorbent (1.5 g/L loading rate) obtained in

previous studies (Zhang *et al.*, 2008). Nonetheless, the adsorption capacities were much smaller than that of selenite (i.e., 0.66 mg-Se/g-adsorbent) (Zhang *et al.*, 2008). This could be attributed to the lower adsorption capacities for selenate, which maintained a relatively high concentration gradient for mass transfer across the liquid film around the adsorbent particles. This resulted in rapid removal of the adsorbate due to large mass diffusion flux across the liquid film, thereby exhibiting faster adsorption kinetics. These explain the trend of adsorption capacity and rate constant observed in this study.

4.3 Adsorption Isotherms

Adsorption isotherm data and model fits for the Freundlich model under three ionic strengths are shown in Figure 19. The parameters for the Freundlich model are listed in Table 6. Overall, there were no observed isotherm plateaus, suggesting that the adsorption capacities observed were well below the maximum adsorption capacity of the Fe-GAC for selenate given the initial selenium concentration (i.e., 1 mg/L) and adsorbent loading rates. The Fe-GAC adsorbent exhibited lower adsorption capacities for selenate than those for selenite given the same initial selenium concentration and other conditions (e.g., pH, ionic strength) (Zhang *et al.*, 2008). The difference in the affinity for selenate and selenite is consistent with other studies using different adsorbents (Goh and Lim, 2004; Rovira *et al.*, 2008). In this study, the results show that adsorption capacity increased as ionic strength decreased. This effect of ionic strength was not observed in selenite adsorption (Zhang *et al.*, 2008). Su and Suarez (2000) reported that adsorption capacity of amorphous-Fe(OH)₃ and goethite was 20 and 444 mg-Se/g-adsorbent, respectively with a solid loading rate of 4 g/L under 0.01 M ionic strength. Since substantially higher initial selenium concentrations (79 to 790 mg/L) and different adsorbent sizes were used in their study, the comparison of the values with those reported in this study is not appropriate.

A comparison between the Freundlich model and the Langmuir model fits results (Table 7) was conducted for 0.01 and 0.05 M ionic strength. For higher ionic strength (e.g., 0.1 M), the maximum adsorption capacity (q_{max}) and the Langmuir coefficient (b) obtained from the Langmuir model fit are dramatically large, which are not physically

reasonable, therefore the Langmuir model fit results for 0.1 M ionic strength are not present. Values of the nonlinear regression coefficient (R^2) and AIC weights calculated from the Freundlich model are both slightly larger than the values for the Langmuir model under the studied ionic strengths (0.01 and 0.05M). It indicates that the experimental data are fitted better with the Freundlich model than the Langmuir model. Overall, the results show that selenate adsorption was lowered by 30% as ionic strength increased from 0.01 M to 0.1 M. The value of K_f decreased with the increase of ionic strength, reflecting the fact that selenate adsorption capacity decreased in the presence of higher ionic strength. In contrast to selenate, selenite was not affected by ionic strength and found to follow the Langmuir isotherm better for similar adsorbent loading rates (Zhang *et al.*, 2008). Goh and Lim (2004) used an initial selenium concentration of 15.8 mg/L in adsorption experiments with tropical soil and found that selenate adsorption followed the Freundlich isotherm model ($R^2 = 0.929$) under 0.01 M ionic strength. Rovira *et al.* (2008) applied initial selenium concentrations ranging from 0.2 to 4.0 mg/L to goethite and hematite adsorption and found that selenate adsorption followed the Langmuir model for the two adsorbents ($R^2 = 0.96$ for goethite and $R^2 = 0.91$ for hematite) under ionic strength of 0.1 M.

4.4 Investigation of Relevant Factors Effect on Selenate Adsorption

4.4.1 pH effect

Figure 20 shows that removal efficiency of selenate as a function of pH. Percent selenate removal was above 80% for pHs below 4 and ~75% at pH 5, and showed a decreasing trend for higher pHs. For treatment of acid mine drainage with a typical pH range of 2 - 6 (Gazea *et al.*, 1996), adsorptive removal of selenate could be operated in the optimal pH range of the Fe-GAC. The pH-dependent result exhibited an adsorptive removal pattern similar to that of selenite but to a lower degree under the same adsorption conditions (Zhang *et al.*, 2008). The pH-dependent removal pattern was consistent with other adsorbents reported in the literature. Su and Suarez (2000) reported a dramatic decrease in selenate adsorption onto goethite when pH was raised above 4. Rovira *et al.*

(2008) observed that adsorptive removal of selenate by goethite and hematite decreased at alkaline pHs.

The pH-dependent adsorption of selenate observed in this study can be attributed to electrostatic interactions between the dominant selenate ion (i.e., fully deprotonated SeO_4^{2-} given its pK_{a2} 1.73) and the Fe-GAC surface charges. Figure 21 shows the titration results for determining point of zero charge of the Fe-GAC. The titration curves gave an estimate of the pH_{pzc} at 7.8. The result is consistent with the conclusion drawn by Vaughan and Reed (2005) for iron impregnated GAC (using virgin GAC1240), which was reported to be pH 7.5. This result provides a reasonable explanation for the pH dependent adsorptive removal of selenate. At low pHs (e.g., 2 - 5), adsorbent surface was dominated by positive charge, which was favorable for the electrostatic attraction between positive functional groups and SeO_4^{2-} . The decreasing trend of the selenate removal reflected the change in surface charges of the adsorbent for pHs above 5.

4.4.2 Oxyanions Competitive Effect

Figure 22 shows that all four types of anions (e.g., SiO_3^{2-} , PO_4^{3-} , SO_4^{2-} and CO_3^{2-}) competed individually with selenate adsorption to various degrees depending on types and concentrations of the anions. In general, the oxy-anions had more significant impacts on selenate than selenite for the same adsorbent (Zhang *et al.*, 2008). Among the four anions, PO_4^{3-} was the most competitive anion which reduced selenate remove efficiency from 70% to zero as its concentration increased from 0 to 5 mM. With the same Fe-GAC, a decrease in selenite adsorption in the presence of PO_4^{3-} was also found but to a lesser degree than selenate (Zhang *et al.*, 2008). Goh and Lim (2004) reported a significant impact of PO_4^{3-} in a low concentration range on both selenate and selenite adsorption onto tropical soil. Sulfate ion was also found to compete with selenate significantly. Selenate removal decreased to 11% in the presence of 5 mM SO_4^{2-} , which is believed to be due to the similar anion structure and adsorption behavior between sulfate and selenate. These two anions both tend to form weak bonds with surface sites and be more easily released (Davis and Leckie, 1980; Goh and Lim, 2004). At 5 mM of SiO_3^{2-} and CO_3^{2-} , only 14% and 9% selenate removals were achieved.

4.4.3 Background Electrolyte Effect

It was found that the background electrolyte could affect ion adsorption when anions or cations are adsorbed by iron oxides (Crisenti and Svenjensky, 1999), especially result in the decline of adsorption under high ionic strength (e.g., 0.1 M). As in the same alkaline group, LiCl, NaCl and KCl were selected to control the ionic strength at 0.01, 0.05 and 0.1 M in this study. To investigate the effect of these three electrolytes on selenate adsorption by Fe-GAC, adsorption isotherms were conducted under the same condition except different electrolytes were used. The adsorption isotherms and corresponding Freundlich isotherm modeling are shown in Figure 23, 24 and 25. The calculated parameters for Freundlich fitting and statistical analysis are listed in Table 8. The results of statistical analysis show a much higher p value (i.e., 0.872) calculated for 0.01 M ionic strength than those for 0.05 and 0.1 M. It indicates high possibility of variation among isotherms existing under high ionic strength (i.e., 0.05 and 0.1 M). Additionally, under high ionic strength (Figure 24 and 25), relatively high selenate adsorption is observed along with the increase of molecular weight of electrolyte cations. This result can be attributed to the changes of cation hydrated radii. It is well understood that large ions with small charges tend to bind water less tightly, hence, resulting smaller hydration number as well as hydrated radius. In this study, the hydrated radii for electrolyte cations decline in the order: $\text{Li} > \text{Na} > \text{K}$. As the increase of hydrated radii, it becomes hard for ions to transfer into inner sphere layer and bind with surface sites. Under elevated ionic strength, when KCl is present, a large number of K cation are adsorbed by surface, therefore, the adsorbent surface possesses more positive zeta potential and higher affinity to anions (Ma and Pawlik, 2005). Therefore, anion adsorption is increased. Under low ionic strength (Figure 23), there is no significant difference due to background electrolytes, which is consistent with the finding of statistical analysis (i.e., p value). It can be explained by the lack of sufficient cations in aqueous solution to cause distinguishable difference. The fact that KCl shows the least interference to selenate adsorption also implies an inner sphere complex formation of selenate adsorption.

Furthermore, when same electrolyte is used, the selenate adsorption is found decrease by various percentages as ionic strength increases (i.e., 25% for KCl, 35% for

NaCl and 49% for LiCl). It implicates an improvement of selenate adsorption in the presence of large amount of KCl in the treatment system.

4.5 Competitive Adsorption between Selenite and Selenate

Results of the competitive adsorption of selenate and selenite are shown in Figure 26, 27 and 28. As both selenite and selenate adsorption follow the Freundlich model in single adsorbate system, the SRS competitive model was applied to predict the adsorption behavior of the two adsorbates in the binary system. The model parameter values are listed in Table 9. Overall, selenite showed an adsorption advantage over selenate for the Fe-GAC under all three ionic strengths.

Selenite and selenate adsorption was only lowered slightly compared to its respective single-adsorbate system. Total adsorbed amounts of selenium in the binary system were also slightly lower than the summations of the two single-adsorbate capacities. A comparison of adsorption capacities between the binary (initial Se concentration of 2 mg/L) and single (initial selenium concentration of 1 mg/L) adsorbate systems is presented in Table 3. The results indicate that co-occurrence of selenate and selenite would only slightly decrease the overall removal efficiency. For treatment of mine drainage impacted water, the Fe-GAC can achieve a similar level of removal efficiency of selenium for water containing both selenate and selenite as for water with only one Se form. The competition coefficient of selenite (i.e., a_{21}) increased as ionic strength increased, accompanied with decreased values of the competition coefficient of selenate (i.e., a_{12}) (Table 9). This suggests that selenate competed against selenite more effectively under high ionic strengths. The competitive model can potentially be used as a predicting tool for Se removal from water containing both the chemical forms.

4.6 Selenate Adsorption Mechanism

4.6.1 Selenate Anion Normal Vibration

To make a comparison of adsorbed and free selenate anions, it is necessary to understand the normal vibration of selenate anion first. Selenate structure is tetrahedral

with its molecular symmetry belonging to T_d point group (Nakamoto, 2009). Point group is defined as a possible combination of symmetry operations whose axes intersect at the same point. For T_d point group, there are three mutually perpendicular two-fold (C_2) axes, four three-fold (C_3) axes and a reflection plane (σ_d) through each pair of C_3 axes. All these symmetric axes intersect at the tetrahedral center, which, in this case, is selenium atom.

There are four normal vibration modes for fully de-protonated selenate anions and they are all Raman active as shown in Figure 29 and as reported by Schulze *et al.* (1973). They are nondegenerate symmetric SeO stretching at 836 cm^{-1} , which is denoted as ν_1 ; doubly degenerated OSeO bending at 349 cm^{-1} , ν_2 ; triply degenerated SeO stretching at 873 cm^{-1} , ν_3 ; and triply degenerated OSeO bending at 413 cm^{-1} , ν_4 . It is found that the peak intensity for stretching vibrations are generally stronger than those for bending vibrations (Wijnja and Schulthess, 2000; Nakamoto, 2009). As fully deprotonated selenate is the predominant species at a broad pH range (i.e., $\text{pH} > 2$), therefore, the Raman spectra in Figure 29 conducted at pH 3, 5 and 8 are generally for selenate deprotonated form only. Comparing the three spectra, neither peak shifting nor splitting is observed. It indicates that as pH higher than 2, the spectra for selenate solutions show no variations. The results are consistent with previous finding reported by Wijnja and Schulthess (2000).

4.6.2 Raman Spectra for Adsorbed Selenate

Figure 30, 31 and 32 show the Raman spectra for adsorbed selenate on Fe-GAC at different pH. All spectra were conducted under the same conditions (i.e., 10 mw laser power, 20 s exposure time, $\times 20$ lens and 10 accumulation times) except spectra in Figure 31 (a), which was conducted with a higher laser power (i.e., 50 mw) to minimize noise level. In Figure 31, both spectra were taken for the same spot but with different laser power. Overall, both peak shifting (ν_1) and splitting (ν_3 and ν_4) are clearly observed for selenate adsorption at pH lower than 6. Obscure peak splitting is also shown for ν_2 band. Specially, at pH 6, ν_2 splitting is intense and obvious. At pH 7, peak splitting is not distinguishable for ν_3 under excitation of low laser power. When further increasing pH to 8, only peak shifting is observed.

Theoretically, when molecules coordinate with surface sites, their symmetry will vary from their free status and further lead the change of vibration modes. When one selenate anion with its original symmetry of T_d coordinates with one surface site to form mono-dentate bind, its molecular symmetry is lowered to C_{3v} , which results the ν_1 vibration peak shifting to either higher or lower wave number depending on the type of coordinating ions. Meanwhile, the triply degenerated vibration peaks will split into two bands. When one selenate anion coordinates with two surface sites and form bi-dentate bind, its molecular symmetry is further lowered to C_{2v} . In addition to ν_1 vibration peak shifting, the doubly degenerated and triply degenerated binds are found to split into two and three vibration bands, respectively (1970; Benelli et al., 1977; Wijnja and Schulthess, 2000; Nakamoto, 2009).

In this study, as ν_1 vibration peak shifting is observed for all studied pH, it indicates an inner sphere coordination occurring for adsorbed selenate adsorption on Fe-GAC. The conclusion is consistent with the deduction drawn from electrolytes effect results. The intense double splitting of ν_3 and ν_4 bands at pH lower than 7 reveals the formation of mono-dentate complex for adsorbed selenate. Moreover, the weak splitting of ν_2 doubly degenerate band implies the presence of bi-dentate complex as well. The missing of triple splitting bands may be attributed to low content of bi-dentate complex on adsorbent surface for the instrument to detect. At pH 7 (Figure 32), low bands intensities are observed even with high laser power excitation. It indicates selenate adsorption is decreased dramatically when pH is close or higher than adsorbent pH_{zpc} (i.e., 7.5). At pH 8 (Figure 32.a), a shoulder band at 837 cm^{-1} for ν_1 non-degenerated vibration is identified along with a strong band at 846 cm^{-1} . Also, the splitting of other vibration bands (i.e., ν_2 , ν_3 , and ν_4) are either obscure or absent. Comparing the spectra of adsorbed selenate at pH 8 with that for free selenate solution, similarity in peak positions and peak shapes can be found, which indicates the formation of outer sphere complex. In addition, the variation features (e.g., peak shifting of ν_1 band) between two spectra reveals the presence of inner sphere complex. Therefore, it can be concluded that at pH greater than 7, inner sphere and outer sphere complexes both occur. Wijnja and Schulthess (2000) also reported the formation of outer sphere complex for selenate adsorbed by goethite at pH 7.2 along with inner sphere complex. As partial selenate is

retained as the form of outer sphere complex by the surface, the coordination is easily broken and therefore result in the much lower adsorption comparing with that occurring at acidic condition.

4.7 Proposed Fe-GAC Modifications

The pH_{zpc} for the Fe-GAC was reported to be at pH of 7.5 (Zhang et al., 2010). Our results showed that selenate adsorption mechanism does not vary when pH was lower than pH_{zpc} . As pH was close to pH_{zpc} (e.g. around 7), selenate was adsorbed only via mono-dentate complex. Portion of selenate anions form outer sphere complex with surface sites, which may lead to desorption as pH higher than 8. These results explained the low selenate adsorption under alkaline conditions. As pH_{zpc} plays a key role in selenate adsorption, Fe-GAC can be modified to increase the pH_{zpc} in order to extend the effective selenate adsorption to high pH. To increase the pH_{zpc} , other metal oxides may be coated with iron oxides together, such as aluminum oxides ($pH_{zpc} = 9.1$) and magnesium oxides ($pH_{zpc} = 12.4$) (Stumm and Morgan, 1981; Fierro, 2006). Some of the binary metal oxides adsorbents have been successfully applied to arsenic and other similar oxyanions' removal. Substantial increase of the removal was reported for arsenic. Up to 100% of adsorptive removal of As (III) was reported by Zhang et al. (2007) when they used the Fe-Mn binary oxide adsorbent in As (III) and As (V) adsorption. Ren et al. (2011) reported the similar adsorptive removal (approximately 90%) for As (III) and As (V) using Fe-Zr binary oxide adsorbent. Generally, As (III) was observed to experience noticeable lower adsorption than that for As (V) for most of adsorbents. This phenomenon of lower adsorption was also found in selenate comparing with selenite. Considering the similarity between arsenic and selenium, it is very promising to increase the selenium adsorption by using the binary oxides adsorbents.

Alternatively, as selenite was reported to be easily removed by Fe-GAC adsorption (Zhang et al., 2008), it is possible to first reduce selenate to selenite and then remove it by adsorption. This process involves the coating of reducing agents, such as

Fe(II), along with Fe(III) oxides. The redox potential for selenate reduction and ferrous oxidation half reactions are as follow (Séby, et al., 1998):

According to the values of redox potentials, at acidic condition, selenate reduction by ferrous can occur spontaneously. Green Rust (iron(II)-iron(III) hydroxyl-salts) was synthesized and found effective to remove selenate by combining processes of reduction, precipitation and adsorption (Refait et al., 2000; Hayashi et al., 2009). Therefore, virgin GAC coated with green rust precipitants will create a promising material with large specific surface areas consisting of both reducing agents (Fe(II)) and adsorbing sites (Fe(III)). It can easily be packed into columns and applied in large scale.

Table 2. Total and amorphous iron on GAC surface coated with four initial ferrous iron concentrations.

Iron Percentage (%)	Ferrous Concentration (M)			
	0	0.01	0.05	0.1
Total Iron	0.06	0.18	2.10	2.80
Amorphous Iron	0.00	0.10	1.00	1.20

Table 3. Percentage of iron dissolved in aqueous solutions at different pH.

Iron Percentage (%)	pH			
	2	3	5	10
Dissolved / Total Coated	11.7	0	0	0

Table 4. Parameters values of Gauss - Lorentz multiplet peak fittings for Fe2p_{3/2} and O1s XPS spectra.

Sample	Element	Peak1 (eV)	Area %	Peak2 (eV)	Area %	$\Delta E_{\text{Peak 2 - Peak 1}}$	Peak3 (eV)	Area %	$\Delta E_{\text{Peak 3 - Peak 2}}$	Peak4 (eV)	Area %	$\Delta E_{\text{Peak 4 - Peak 3}}$
		[FWMH]		[FWMH]			[FWMH]			[FWMH]		
Virgina GAC	O1s	530.8 [1.7]	28.80	532.1 [1.7]	46.74	1.3	533.4 [1.7]	24.47	1.3		NA	
Fe-GAC	Fe2p _{3/2}	710.2 [1.4]	34.02	711.2 [1.4]	32.83	1.0	712.2 [1.4]	21.09	1.0	713.3 [1.4]	12.06	1.1
		529.9 [1.4]	41.17	531.3 [1.4]	47.78	1.4	532.4 [1.4]	11.05	1.1		NA	
FeGAC in NaCl at pH 5	Fe2p _{3/2}	710.2 [1.4]	32.45	711.2 [1.4]	31.82	1.0	712.2 [1.4]	23.64	1.0	713.4 [1.4]	12.07	1.2
		529.9 [1.7]	27.16	531.4 [1.7]	56.78	1.5	532.6 [1.7]	16.06	1.2		NA	
FeGAC in NaCl at pH 2	Fe2p _{3/2}	710.1 [1.6]	40.50	711.2 [1.6]	31.55	1.1	712.3 [1.6]	20.01	1.1	713.5 [1.6]	7.92	1.2
		529.6 [1.7]	39.47	531.1 [1.7]	45.67	1.5	532.3 [1.7]	14.85	1.1		NA	
FeGAC in NaCl at pH 10	Fe2p _{3/2}	710.3 [1.7]	25.75	711.2 [1.7]	35.46	0.9	712.3 [1.7]	25.63	1.1	713.5 [1.7]	13.00	1.2
		529.9 [1.7]	25.56	531.2 [1.7]	44.97	1.3	532.4 [1.7]	29.46	1.2		NA	

Table 5. Second-order adsorption rate constants (k) and adsorption capacities (q_e) of Fe-GAC (loading rate = 3.5 g/L) for selenate (initial Se concentration = 1 mg/L) at pH 5 and 25 °C.

Initial Se conc. (mg/L)	Ionic strength (M)	k g/(mg·min)	q_e mg-Se/g-FeGAC	R^2
1.0	0.01	0.13	0.22	0.999
1.0	0.05	0.15	0.21	0.999
1.0	0.1	0.28	0.17	0.998

Table 6. Parameter values of the Freundlich model for selenate and selenite adsorption.

Initial Selenate Conc. (mg-Se/L)	Ionic Strength (M)	Selenate			Selenite		
		K_f (mg / g)(L / mg) ⁿ	$\frac{1}{n}$	R^2	K_f (mg / g)(L / mg) ⁿ	$\frac{1}{n}$	R^2
1.0	0.01	0.55	0.70	0.98	1.70	0.45	0.99
1.0	0.05	0.44	0.82	0.97	1.57	0.53	0.99
1.0	0.1	0.36	1.10	0.98	1.61	0.48	0.99

Table 7. Parameter values of the Freundlich model and the Langmuir model for selenate adsorption under two ionic strengths and AIC comparison results for the two models.

Initial Selenate Conc. (mg-Se/L)	Ionic Strength (M)	The Freundlich Model					The Langmuir Model			
		K_f (mg / g)(L / mg) ⁿ	$\frac{1}{n}$	R^2	AIC	w	q_{max} (mg-Se/g)	b (L/mg)	R^2	AIC
1.0	0.01	0.55	0.70	0.98	-55.1	0.87	0.96	0.88	0.97	-51.4
1.0	0.05	0.44	0.82	0.97	-47.6	0.57	1.42	2.30	0.96	-47.0

Table 8. Parameter values of the Freundlich model for selenate adsorption in presence of different background electrolytes and Kruskal - Wallis testing values (p).

Ionic Strength (M)	Electrolyte	K_f (mg / g)(L / mg) ⁿ	$\frac{1}{n}$	R ²	K-W p
0.01	LiCl	0.55	0.83	0.99	0.872
	NaCl	0.55	0.70	0.98	
	KCl	0.59	0.84	0.99	
0.05	LiCl	0.44	1.12	0.93	0.358
	NaCl	0.44	0.82	0.97	
	KCl	0.53	0.91	0.99	
0.1	LiCl	0.28	1.06	0.97	0.419
	NaCl	0.36	1.10	0.98	
	KCl	0.44	1.11	0.99	

Table 9. Adsorption capacities (mg-Se/g-adsorbent) of the Fe-GAC (loading rate = 1 g/L) for selenite and selenate in a binary adsorbate system (initial Se concentration = 1 mg/L for each) and single-adsorbate system (initial Se concentration = 1 mg/L) at pH 5 and 25 °C. SRS model parameter values: a_{12} - competition coefficient of selenate against selenite, and vice versa for a_{21} .

Ionic Strength (M)	Capacity, Binary (Selenate+Selenite)	a_{12}	a_{21}	MPSD (%)	Capacity Single (Selenite)	Capacity Single (Selenate)
0.01	1.22	0.25	40.0	23.7	0.93	0.39
0.05	1.19	0.37	27.0	21.1	0.90	0.32
0.10	1.12	0.42	23.8	25.6	0.91	0.23

Figure 8. XPS survey scan for Virgin GAC (Darco 12X20).

Figure 9. XPS survey scan for 0.1 M iron coated Fe-GAC (Darco 12X20).

Figure 10. XPS spectrum with multiplet peak fittings (thin solid lines) for O1s on virgin GAC. Summation of the peak fittings is shown as bold solid line. Experimental data are indicated by solid dots.

Figure 11. XPS spectrum with multiplet peak fittings (thin solid lines) for O1s on 0.1 M iron coated Fe-GAC. Summation of the peak fittings is shown as bold solid line. Experimental data are indicated by solid dots.

Figure 12. XPS spectrum with multiplet peak fittings (thin solid lines) for O1s on 0.1 M iron coated Fe-GAC suspended in 0.1 M NaCl. Summation of the peak fittings is shown as bold solid line. Experimental data are indicated by solid dots.

Figure 13. XPS spectrum for Fe2p on 0.1 M iron coated Fe-GAC.

Figure 14. XPS spectrum for Fe $2p_{3/2}$ on 0.1 M iron coated Fe-GAC with multiplet peak fittings (thin solid lines). Summation of the peak fittings is shown as bold solid line. Experimental data is indicated by solid dots. Center of gravity at 711.3 eV for spectrum is indicated by arrow.

Figure 15. XPS spectrum with multiplet peak fittings (thin solid lines) for Fe_{2p_{3/2}} on 0.1 M iron coated Fe-GAC suspended in 0.1 M NaCl. Summation of the peak fittings is shown as bold solid line. Experimental data is indicated by solid dots. Center of gravity at 711.3 eV for spectrum is indicated by arrow.

Figure 16. Selenate adsorption kinetics for initial Se concentration of 1 mg/L at pH 5 and 0.01 M ionic strength in the presence of 3.5 g/L Fe-GAC. The pseudo-second order kinetic model is indicated by the curve.

Figure 17. Selenate adsorption kinetics for initial Se concentration of 1 mg/L at pH 5 and 0.05 M ionic strength in the presence of 3.5 g/L Fe-GAC. The pseudo-second order kinetic model is indicated by the curve.

Figure 18. Selenate adsorption kinetics for initial Se concentration of 1 mg/L at pH 5 and 0.1 M ionic strength in the presence of 3.5 g/L Fe-GAC. The pseudo-second order kinetic model is indicated by the curve.

Figure 19. Adsorption isotherms of the Fe-GAC for selenate (initial Se concentration = 1 mg/L) at pH 5 and 25 °C. The Freundlich models are indicated by the curves.

Figure 20. Adsorptive removal of selenate (initial Se concentration = 1 mg/L) as a function of pH under ionic strength 0.05 M and 25 °C.

Figure 21. Acid base titration curves for the Fe-GAC (loading rate = 2 g/L) under ionic strengths 0.01, 0.05 and 0.1 M.

Figure 22. Oxy-anion competitive adsorption against selenate (initial Se concentration = 1 mg/L) under ionic strengths 0.05 M, pH 5, and 25 °C after 24 hours.

Figure 23. Adsorption isotherms of the Fe-GAC for selenate (initial Se concentration = 1 mg/L) with the presence of different background electrolytes (LiCl, NaCl, and KCl) at pH 5, 0.01 M ionic strength and 25 °C. The Freundlich models are indicated by the curves.

Figure 24. Adsorption isotherms of the Fe-GAC for selenate (initial Se concentration = 1 mg/L) with the presence of different background electrolytes (LiCl, NaCl, and KCl) at pH 5, 0.05 M ionic strength and 25 °C. The Freundlich models are indicated by the curves.

Figure 25. Adsorption isotherms of the Fe-GAC for selenate (initial Se concentration = 1 mg/L) with the presence of different background electrolytes (LiCl, NaCl, and KCl) at pH 5, 0.1 M ionic strength and 25 °C. The Freundlich models are indicated by the curves.

Figure 26. Competitive adsorption isotherms of the Fe-GAC for selenite and selenate (initial Se concentration 1 mg/L for each) under ionic strength of 0.1 M, pH 5 and 25 °C. Pairs of the same symbols represent selenate/selenite concentrations in the same batch reactor. ×: 0.5 g/L; □: 1.0 g/L; +: 1.5 g/L; ○: 2.0 g/L; *: 2.5 g/L; Δ: 3.0 g/L and ◇: 3.5 g/L.

Figure 27. Competitive adsorption isotherms of the Fe-GAC for selenite and selenate (initial Se concentration 1 mg/L for each) under ionic strength of 0.05 M, pH 5 and 25 °C. Pairs of the same symbols represent selenate/selenite concentrations in the same batch reactor. ×: 0.5 g/L; □: 1.0 g/L; +: 1.5 g/L; ○: 2.0 g/L; *: 2.5 g/L; △: 3.0 g/L and ◇: 3.5 g/L.

Figure 28. Competitive adsorption isotherms of the Fe-GAC for selenite and selenate (initial Se concentration 1 mg/L for each) under ionic strength of 0.05 M, pH 5 and 25 °C. Pairs of the same symbols represent selenate/selenite concentrations in the same batch reactor. ×: 0.5 g/L; □: 1.0 g/L; +: 1.5 g/L; ○: 2.0 g/L; *: 2.5 g/L; Δ: 3.0 g/L and ◇: 3.5 g/L.

Figure 29. Raman spectra of Na_2SeO_4 solutions (0.1 M) at pH (a) 3; (b) 5; and (c) 8.

Figure 30. Raman spectra for adsorbed selenate with 0.1 M initial selenate concentration at pH (a) 7; (b) 6; (c) 5; (d) 4; and (e) 3.

Figure 31. Raman spectra for adsorbed selenate with 0.1 M initial selenate concentration at pH = 7 under excitation of laser power (a) 50 mW; and (b) 10 mW.

Figure 32. Raman spectra for adsorbed selenate with 0.1 M initial selenate concentration at pH (a) 8 and (b) 7.

CHAPTER 5: CONCLUSION

The adsorptive removal of ppm-level selenate by Fe-GAC was studied along with detailed investigation for the adsorbed selenate coordination structures in this study. Main conclusions are summarized in the followings:

- Removal efficiency of the Fe-GAC for selenate achieved more than 75% for pH range 2 - 5. It is promising to use the Fe-GAC for selenate removal from acid mine drainages typically found in acidic conditions.
- Selenate adsorption equilibrium was reached within 48 hours with more than 85% of the equilibrium capacity being obtained in 6 hours. Adsorption capacities showed a decreasing trend as ionic strength increased from 0.01 to 0.1 M.
- Adsorption isotherms were characterized by the Freundlich isotherm model. The lack of plateaus in the adsorption isotherms suggested that the maximum adsorption capacity of Fe-GAC was substantially higher than the adsorption capacities observed in the study.
- Effect of background electrolytes was examined on selenate adsorption. The results showed that the increasing of hydrated radius caused variations in selenate adsorption at pH 5, which implied that an inner sphere complexation occurred.
- Four oxy-anions (SiO_3^{2-} , SO_4^{2-} , PO_4^{3-} and CO_3^{2-}) were found to compete with selenate adsorption to various degrees, with phosphate showing the most impact on selenate adsorption.
- Competitive adsorption of binary adsorbates (selenite and selenate) was modeled by SRS multi-adsorbate competitive adsorption isotherms. Selenate was found to compete against selenite more strongly under low

ionic strengths. Only slight decreases in the selenite and selenate adsorption capacities in binary system were observed as they were compared to their respective single-adsorbate systems. This suggests the feasibility of removing selenite and selenate simultaneously.

- Various chemical and physical properties of Fe-GAC were examined in details. The acid base titration results showed that pH_{zpc} for Fe-GAC is 7.5. High resolution XPS spectra conducted for $\text{Fe}2\text{p}_{3/2}$ and $\text{O}1\text{s}$ indicated the ferrous was successfully oxidized to form ferric on GAC surface. The possible chemical composition for the coated iron was α - FeOOH . Additionally, spectra obtained at different pHs suggested that Fe-GAC was stable and no transformation was observed as pH changed.
- Raman spectra showed that selenate was adsorbed via mixing coordination structure of mono-dentate and bi-dentate inner sphere complexation at acidic conditions (i.e., $\text{pH} < 6$). When pH was close to pH_{zpc} , bi-dentate complexation was not clearly observed. When pH was further increased to 8, portion of selenate was adsorbed via outer sphere complexation. These results explained the low selenate adsorption when pH was higher than pH_{zpc} .
- Two feasible modification methods to the adsorbent preparation were proposed in order to improve selenate adsorption. One was to coat other oxides (e.g., magnesium oxides) along with iron oxides to increase pH_{zpc} and broaden effective pH range for selenate adsorption. Alternatively, reduced iron (e.g., ferrous) could be precipitated with ferric oxides in order to reduce selenate to selenite first, followed by high adsorption of selenite.

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