2010

Selenium Removal by Nano-Magnetite Impregnated Diatomaceous Earth

Isabel Cardona
West Virginia University

Follow this and additional works at: <https://researchrepository.wvu.edu/etd>

Recommended Citation

Cardona, Isabel, "Selenium Removal by Nano-Magnetite Impregnated Diatomaceous Earth" (2010).
Graduate Theses, Dissertations, and Problem Reports. 4568.
<https://researchrepository.wvu.edu/etd/4568>

This Thesis is protected by copyright and/or related rights. It has been brought to you by the The Research Repository @ WVU with permission from the rights-holder(s). You are free to use this Thesis in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you must obtain permission from the rights-holder(s) directly, unless additional rights are indicated by a Creative Commons license in the record and/ or on the work itself. This Thesis has been accepted for inclusion in WVU Graduate Theses, Dissertations, and Problem Reports collection by an authorized administrator of The Research Repository @ WVU. For more information, please contact researchrepository@mail.wvu.edu.

Selenium Removal by Nano-Magnetite Impregnated Diatomaceous Earth

Isabel Cardona

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

Master of Science
in
Engineering

Xinchao Wei, Ph.D., Chair
Lian-Shin Lin, Ph.D.
Radhey Sharma, Ph.D.

Department of Civil and Environmental Engineering

Morgantown, West Virginia
2010

Keywords: Adsorption, Selenium Removal, Diatomaceous Earth, Nano-magnetite
Copyright 2010 Isabel Cardona

ABSTRACT

Selenium Removal by Nano-Magnetite Impregnated Diatomaceous Earth

Isabel Cardona

The purpose of this study was to remove selenium from aqueous solution using nano-magnetite impregnated diatomaceous earth (DE) as an adsorbent. The adsorbent was prepared at the laboratory with a ratio of magnetite/DE of 10%. Batch adsorption experiments were conducted to evaluate the effects of pH, temperature, adsorbent concentration, selenium speciation, contact time and presence of competing anions on selenium removal efficiency in conjunction with studies on adsorption kinetics, isotherms, and adsorptive thermodynamics. Rapid adsorption occurred within 30 min and selenium uptake decreased with increase in temperature. Low pH values (i.e. 2 – 4) favored selenium adsorption as expected for anion adsorption but the adsorption of selenate (Se(VI)) was more strongly dependent on pH than that of selenite (Se(IV)). The adsorption isothermal and kinetic data of selenium were well fitted to the *Freundlich* isotherm and pseudo-second-order kinetic models. The nano-magnetite impregnated DE showed an adsorption capacity of 0.5 mg-Se/g for selenite and 0.25 mg-Se/g for selenate at pH 3.0. At an initial selenium concentration of 250 µg-Se/L, more than 96% removal of selenite and 50% removal of selenate were achieved. It was observed that selenate adsorption was significantly affected by the presence of competing anions such as chloride, nitrate and sulfate, whereas selenite removal was mostly affected by the presence of sulfate in solution. Column tests demonstrated that diatomaceous earth by itself was not able to remove selenite or selenate anions from water; therefore all the adsorption capacity could only be attributed to the nano-magnetite coating. Column adsorption tests using nano-magnetite impregnated DE showed higher adsorption efficiency for selenite anions compared to selenate. However, the adsorption capacity decreased when a natural water sample from Monongahela River was used. In conclusion, it was found that nano-magnetite impregnated diatomaceous earth is a promising low-cost adsorbent to treat aqueous solutions containing low levels of selenium. Besides, this new adsorbent is porous and stable, making it suitable for adsorptive filtration in column applications.

ACKNOWLEDGEMENT

As an international student, studying at WVU has been a completely new and wonderful experience. The completion of this journey was possible thanks to the collaboration and support of many people.

First, I would like to express my sincere gratitude to my research advisor, Dr. Wei, for his teaching, patience, and support during this research. His guidance was essential for the completion of my thesis work.

I would also like to thank Dr. Lin and Dr. Sharma for their valuable time to have been part of my committee.

I acknowledge the Center for Advanced Separation Technologies (CAST) for funding this study. I would like to thank Mr. Kenneth Stewart, Analytical Laboratory Director of the National Research Center for Coal and Energy (NRCCE) and his staff for their time, collaboration, and generosity in allowing me to complete some analysis at their laboratory.

My greatest thanks to my lovely boyfriend, Alejandro; my parents, Norman and Rocio; and my sister, Lorena, for their encouragement, understanding and support during all this years.

I really appreciate the help of my friends and fellow students: Jinyan Sun, Khaled Elbriki, Shilpa Bhojappa, and Ning Zhang.

All the advices and collaboration received from Dr. Karen Buzby and Research Assistant Will Ravenscroft are profoundly acknowledged.

TABLE OF CONTENTS

ABSTRACT.....	ii
ACKNOWLEDGEMENT	iii
TABLE OF CONTENTS.....	iv
LIST OF TABLES	vi
LIST OF FIGURES	vii
CHAPTER 1: INTRODUCTION	1
1.1 Environmental Impact and Regulations.....	4
1.2 Selenium Removal Technologies	5
1.2.1 Physical Treatment.....	5
1.2.2 Chemical Treatment.....	6
1.2.3 Biological processes.....	9
1.3 Research objective	9
CHAPTER 2: MATERIALS AND METHODS	11
2.1. Materials	11
2.2. Adsorbent preparation and characterization	11
2.3. Determination of the Point of Zero Charge	13
2.4. Batch adsorption studies	13
2.4.1 Effect of pH.....	14
2.4.2 Effect of contact time.....	14
2.4.3 Effect of temperature	15
2.4.4 Adsorption isotherms	15
2.4.5 Effect of Interfering anions	17
2.5 Desorption Tests	17
2.6 Column adsorption studies.....	18
CHAPTER 3: RESULTS AND DISCUSSION.....	20
3.1 Sample Characterization	20
3.2 Point of Zero Charge (PZC).....	22
3.3 Batch Adsorption Studies	25
3.3.1 Effect of pH.....	25

3.3.2	Effect of contact time.....	28
3.3.3	Effect of Temperature and Adsorption Thermodynamics	30
3.3.4	Adsorption Isotherms.....	35
3.3.5	Adsorption Kinetics	37
3.3.6	Effect of interfering anions	40
3.4	Desorption tests.....	41
3.5	Column adsorption experiments	43
CHAPTER 4: CONCLUSION		46
CHAPTER 5: REFERENCES		48
VITA.....		57

LIST OF TABLES

Table 1. Thermodynamic parameters for the adsorption of selenite and selenate on nano-magnetite impregnated DE at different temperature values.	34
Table 2. Freundlich parameters for the adsorption of selenite and selenate on nano-magnetite impregnated DE	36
Table 3. Pseudo-second-order parameters for the adsorption of selenite and selenate on nano-magnetite impregnated DE	39
Table 4. Water chemistry of the Monongahela River sample used for column adsorption studies	45

LIST OF FIGURES

Figure 1. Potential–pH stability diagram for selenium at 25°C, 1 bar total pressure, and dissolved selenium activity of 10^{-6} M (Séby et al., 2001)	2
Figure 2. Apparatus for chemical precipitation of nano-magnetite particles on the surface of diatomaceous earth	12
Figure 3. Batch experiment apparatus used in selenium adsorption onto nano-magnetite impregnated DE.	14
Figure 4. Scheme of column adsorption experiments for selenite and selenate adsorption onto nano-magnetite impregnated DE.	18
Figure 5. Diatomaceous earth (a) before and (b) after the impregnation process with nano-magnetite.....	20
Figure 6. SEM images of (a) pure diatomaceous earth, (b), (c), and (d) nano-magnetite impregnated DE showing a uniform coating.	21
Figure 7. X-ray diffractograms of nano-magnetite and nano-magnetite impregnated DE particles.	22
Figure 8. Batch titration of raw diatomaceous earth (DE) at various ionic strengths with HCl and NaOH. Adsorbent concentration: 4 g/L, total volume: 50 ml, pH of suspension after equilibrating overnight.....	23
Figure 9. Batch titration of raw nano-magnetite at various ionic strengths with HCl and NaOH. Adsorbent concentration: 4 g/L, total volume: 50 ml, pH of suspension after equilibrating overnight	23
Figure 10. Batch titration of nano-magnetite impregnated DE at various ionic strengths with HCl and NaOH. Adsorbent concentration: 4 g/L, total volume: 50 ml, pH of suspension after equilibrating overnight.....	24
Figure 11. Effect of pH on final selenite concentration (adsorbent dose 0.5g/L; mixing time 24h; 25°C; initial concentrations 250 and 500µg-Se/L).	25
Figure 12. Effect of pH on final selenate concentration (adsorbent dose 0.5g/L; mixing time 24h; 25°C; initial concentration 100 and 250µg-Se/L).....	26

Figure 13. Effect of contact time on final selenite concentration (adsorbent dose 0.5g/ L; pH 3.0 ± 0.1 ; 25°C; 24 h mixing time; initial concentrations 250 and 500 $\mu\text{g-Se/L}$).	29
Figure 14. Effect of contact time on final selenate concentration (adsorbent dose 0.5g/ L; pH 3.0 ± 0.1 ; 25°C; 24 h mixing time; initial concentrations 100 and 250 $\mu\text{g-Se/L}$).	29
Figure 15. Effect of temperature on final selenite concentration (adsorbent dose 0.5g/L; pH 3.0 ± 0.1 ; mixing time 24h; initial concentrations 250 and 500 $\mu\text{g-Se/L}$).	31
Figure 16. Effect of temperature on final selenate concentration (adsorbent dose 0.5g/L; pH 3.0 ± 0.1 ; mixing time 24h; initial concentrations 100 and 250 $\mu\text{g-Se/L}$).	31
Figure 17. Van't Hoff plot for selenite adsorption (adsorbent dose 0.5g/L; pH 3.0 ± 0.1 ; mixing time 24h; initial concentrations 250 and 500 $\mu\text{g-Se/L}$).	33
Figure 18. Van't Hoff plot for selenate adsorption (adsorbent dose 0.5g/L; pH 3.0 ± 0.1 ; mixing time 24h; initial concentrations 100 and 250 $\mu\text{g-Se/L}$).	33
Figure 19. Selenite adsorption isotherms of nano-magnetite impregnated DE (Initial concentration: 250 $\mu\text{g-Se/L}$; mixing time 24h; 25°C).	35
Figure 20. Selenate adsorption isotherms of nano-magnetite impregnated DE (Initial concentration: 250 $\mu\text{g-Se/L}$; mixing time 24h; 25°C).	36
Figure 21. Pseudo-second-order kinetics for sorption of selenite by nano-magnetite impregnated DE (adsorbent dose 0.5g/L; pH 3.0 ± 0.1 ; mixing time 24h; 25°C).	38
Figure 22. Pseudo-second-order kinetics for sorption of selenate by nano-magnetite impregnated DE (adsorbent dose 0.5g/L; pH 3.0 ± 0.1 ; mixing time 24h; 25°C).	39
Figure 23. Effect of anions on selenite removal by nano-magnetite impregnated DE (mixing time 24h; 25°C; pH 3.0 ± 0.1 ; initial concentration 250 $\mu\text{g-Se/L}$; adsorbent dose 0.5g/L).	40
Figure 24. Effect of anions on selenate removal by nano-magnetite impregnated DE (mixing time 24h; 25°C; pH 3.0 ± 0.1 ; initial concentration 250 $\mu\text{g-Se/L}$; adsorbent dose 0.5g/L).	41
Figure 25. Desorption of selenite and selenate from nano-magnetite impregnated DE as a function of pH for an adsorption process at pH = 3.0 ± 0.1 (mixing time 24h; 25°C; initial concentration 250 $\mu\text{g-Se/L}$; adsorbent dose 0.5g/L).	42

Figure 26. Breakthrough curves for selenite and selenate adsorption by nano-magnetite impregnated DE and plain DE (control tests). Initial concentration 500 $\mu\text{g-Se/L}$; pH = 3.0 for selenate adsorption, pH = 4.0 for selenite adsorption; 1BV $\sim 12\text{ cm}^3$.

..... 43

Figure 27. Breakthrough curves for selenite and selenate adsorption when Monongahela River water was used as feeding solution. Initial concentration 500 $\mu\text{g-Se/L}$; pH = 3.0 for selenate adsorption, pH = 4.0 for selenite adsorption; 1BV $\sim 12\text{ cm}^3$ 44

CHAPTER 1: INTRODUCTION

Selenium (Se) is a naturally occurring element that is distributed widely in the environment in most rocks and soils though it is among the rare elements on the surface of the earth. Although it has chemical and physical properties intermediate between metals and nonmetals, it is usually described as a nonmetal (Plant et al., 2007). In its pure form, selenium exists as metallic gray to black hexagonal crystals, but in nature it is usually combined with sulfide or with silver, copper, lead, and nickel minerals.

Due to its photovoltaic and photoconductive properties, most selenium is used in the electronics industry. Its other applications include: 1) as a nutritional supplement; 2) as a minor additive in the glass industry; 3) as a component of pigments in plastics, paints, enamels, inks, and rubber; 4) as a composition in the preparation of pharmaceuticals; 5) as a nutritional feed additive for poultry and livestock; 6) a composition in pesticide formulations; 7) as an ingredient in antidandruff shampoos; and 8) as a constituent of fungicides (MII, 2010).

Selenium is an essential nutrient for humans and animals. However, selenium can be harmful when regularly taken in amounts higher than those needed for optimum nutrition. The range of intake between that leading to selenium deficiency ($<40 \mu\text{g-Se/day}$) and that leading to toxicity (selenosis) ($>400 \mu\text{g-Se/day}$) is very narrow in humans (WHO, 1996). The current DRI (Dietary Reference Intake) for selenium, established by the Institute of Medicine (IOM, 2000), is $55 \mu\text{g-Se/day}$ for male and female adults, and the tolerable upper intake level (UL) for adults is set at $400 \mu\text{g-Se/day}$ based on selenosis as the adverse effect.

Selenium toxicity can lead to hair and nail brittleness and loss, skin rash, garlic breath odor, fatigue, irritability, and disruption of the nervous and digestive systems in humans and to alkali disease in animals (IOM, 2000). Chronic selenosis in animals is not

common but has been reported from parts of Australia, China, Ireland, Israel, Russia, South Africa, USA, and Venezuela (Oldfield, 2002).

Selenium chemistry is quite complicated because its mobility strongly depends on both the redox state of the system and the factors influencing its speciation (pH, presence of organics and kinetics) (Missana et al., 2009). In aqueous medium, the chemical stability and the redox chemistry of this element are represented in potential-pH diagrams as that shown in Fig. 1.

Figure 1. Potential–pH stability diagram for selenium at 25°C, 1 bar total pressure, and dissolved selenium activity of 10^{-6} M (Séby et al., 2001)

Selenium exists in four different oxidation states with very different chemical behaviors: elemental selenium (Se^0), selenide (Se^{2-}), selenite (SeO_3^{2-}), and selenate (SeO_4^{2-}) (Parida et al., 1997). Elemental selenium and metal selenides have a very low

solubility, whereas selenite and selenate are soluble and mobile (Missana et al., 2009). Temperature, moisture, organic matter and microbiological activity usually determine how fast selenium transports through soil and later on into surface waters, resulting in an increased chance of human exposure. According to U.S. EPA report (FRL-5649-7) the acute toxicity of selenite (Se IV) is almost 10 times superior to that of selenate (Se VI) and both species exist simultaneously in surface waters often in comparable concentrations (U.S. EPA, 1996).

The Superfund Amendments and Reauthorization Act (SARA), Section 313, Toxic Release Inventory (TRI99 2001), estimated that a total of 264,267 pounds of elemental selenium was released to air, water, land or injected underground from manufacturing and processing facilities in the United States in 2000 (U.S. Dept of Health and Human Services, 2003).

Selenium is ubiquitous in the environment, being released from both natural and anthropogenic sources. Human activities that have increased the concentration of selenium in the environment include the mining and processing of base-metal, gold, coal, and phosphate deposits, the use of rock phosphate as fertilizer, the manufacture of detergents and shampoo, and the application of sewage sludge to land. The increased use of selenium in the pharmaceutical, glazing, photocopying, ceramic, paint, and electronics industries may also be increasing the amount of selenium entering the environment (Plant et al., 2007). However, the principal releases of selenium into the environment as a consequence of human activities result from combustion of fossil fuels, especially coal (Coleman et al., 1993).

The most dominant forms of selenium in coal are sulfidic and organic although silicate forms could also exist (Yudovich and Ketris, 2006). The predominant selenium species in oxidized and alkaline soils such as surface coal mine soils is selenate, which can be transformed into selenite under reducing conditions, a form that predominates in acidic or neutral soils. Extreme anthropogenic disturbances, as those present in mining

areas, can release toxic levels of selenium into the environment (Sharmasarkar and Vance, 2002). Therefore, the exact characteristics of selenium-containing water depend on the source of selenium, the transport pathways, and the environmental conditions (particularly the redox conditions).

1.1 Environmental Impact and Regulations

The World Health Organization (WHO, 2003) guideline value for selenium in drinking water is currently 10 $\mu\text{g-Se/L}$ and this standard has been adopted by the European Community (EC), Australia, Japan, and Canada. In the US, the Environmental Protection Agency (EPA) set both the maximum contaminant level (MCL) and the maximum contaminant level goal (MCLG) at 50 $\mu\text{g-Se/L}$ in the 1974 Safe Drinking Water Act. According to the EPA, given present technology and resources, this is the lowest level to which water systems can reasonably be required to remove this contaminant should it occur in drinking water (U.S. EPA, 2009). In surface water, selenium is one of the priority toxic pollutants according to the Clean Water Act (CWA). The water quality criteria for acute and chronic aquatic freshwater are 20 $\mu\text{g-Se/L}$ and 5 $\mu\text{g-Se/L}$, respectively. Although most drinking water sources tested in the United States contain very low levels of selenium (around 10 $\mu\text{g-Se/L}$), concentrations exceeding the freshwater criteria pose a serious risk to aquatic life and humans due to the likelihood of bioaccumulation in the food chain (ATSDR, 2003).

Selenium has long been recognized to be enriched in coal beds relative to host strata and relative to the average abundance of selenium in the earth's crust. It is considered that coal contains from 5 to 300 times the amount of selenium as do other rocks (Coleman et al., 1993). In the central Appalachian basin of the eastern US, it has been observed that Se in streams draining areas disturbed by surface mining of coal was higher (median 12 $\mu\text{g-Se/L}$) in comparison to that observed in streams draining undisturbed areas (median 1.5 $\mu\text{g-Se/L}$) (Neuzil et al., 2007).

Selenium is present in West Virginia coals as a trace element (amounts much lower than 1%) together with toxic elements such as arsenic, mercury, lead, antimony, etc. Although they occur in very low concentration, the adverse impacts of these toxic elements can be significant because million of tons of coal are mined and burnt each year (WVGES, 2005).

Since federal studies in 2002 first documented high levels of selenium downstream from some mountaintop removal coal mines in West Virginia, numerous selenium toxic hot spots have been identified in central Appalachia. According to Section 303(d) of the Clean Water Act, a list of waters for which effluent limitations or other controls are not sufficient to meet water quality standards, over 30 streams and reaches in West Virginia are impaired by selenium, affecting a total length of 160 miles (WV DEP, 2008).

1.2 Selenium Removal Technologies

A variety of chemical, physical and biological techniques have been shown to remove selenium from water. Because of the various complexities associated with industry-specific waters, there is no treatment technology that is a “one-size fits all” solution. Selection of the correct technology is highly dependent on the speciation of selenium and the competing and interfering water chemistry of industry-specific waters (NAMC, 2010).

1.2.1 Physical Treatment

Physical treatment technologies include reverse osmosis, nanofiltration, and ion exchange. All of these technologies have been applied to water treatment in other industries; however, with the exception of reverse osmosis, these technologies have only been developed at a laboratory or pilot scale for selenium removal (Golder Associates, 2009).

1.2.1.1 Membrane Filtration

Membrane separations rely on semi-permeable membranes to purify the fluid being treated. During the process, a pressure gradient is applied across the membrane, forcing water through the membrane while retaining the contaminants. Historically, high operating costs have been a drawback to the implementation of membrane filtration processes. Pre-treatment may be required to prevent membrane fouling, particularly if the water contains elevated levels of hardness (Ca, Mg) or total suspended solids (TSS). Other disadvantages of membrane filtration include waste disposal and frequent membrane monitoring and maintenance (NAMC, 2010).

1.2.1.2 Ion Exchange

Ion exchange removes ions from the aqueous phase by the exchange of cations or anions between the contaminants and the exchange medium. Materials employed for this process are either naturally occurring inorganic zeolites or synthetically produced organic resins. Ion exchange is commonly employed to treat industrial wastewater, but until recently, ion exchange has not been successful in removing selenium from mining impaired waters due to the competition between sulfate and selenate (Twidwell, 2000). Pretreatment of the water is generally required. Suspended solids will plug the resin bed and sometimes pH and temperature adjustment is necessary to optimize the performance of the resin (Golder Associates, 2009).

1.2.2 Chemical Treatment

The most common types of chemical treatment involve precipitation, adsorption and oxidation/reduction mechanisms.

1.2.2.1 Precipitation

Because of its high solubility, selenium in the forms of selenite and selenate will not react chemically with a reagent, or soluble chemical added to the water to yield a

precipitate under commonly encountered water temperature, pH and ionic strength (NACM, 2010). Selenocyanate, a soluble form of selenium existing primarily in refining wastewater has been precipitated from aqueous solution upon reaction with gold, silver, cadmium, mercury, thallium, lead, and copper (Manceau and Gallup, 1997). Unfortunately, most of metals that effectively precipitate selenocyanate from aqueous solution are generally regulated in the same way as discharges of selenium.

1.2.2.2 Se reduction

This process involves a chemical method to remove selenium from water by reducing selenate and selenite to an elemental form that settles out of a solution. The reduction takes place when ferrous hydroxide is added to the solution under alkaline conditions (NSMP, 2007). The generation of large volumes of sludge, the high cost of reagents and interferences by dissolved oxygen and other anions are factors that influence the wide application of this technique (Twidwell et al., 2000).

1.2.2.3 Adsorption

Adsorption is defined as process by which atoms, molecules or ions are retained on the surface of a solid by chemical or physical bonding. Ferrihydrite adsorption is a two step chemical treatment process in which selenium is removed by adsorbing to the iron surface and subsequent precipitation of ferrihydrite from solution. According to the U.S. Environmental Protection Agency (EPA), ferrihydrite adsorption is the Best Demonstrated Available Technology (BDAT) for the removal of selenium from wastewater (U.S. EPA, 1990)

Adsorption is by far the most researched method in treating selenium impaired waters and wastewaters. Currently, different adsorbents are being studied for Se removal: alumina, activated carbon, (Twidwell et al., 2000), manganese nodule leached residues (Dash and Parida, 2007), sulphuric acid-treated peanut shell (El-Shafey, 2007a), modified rice husk (El-Shafey, 2007b), Al and Fe-coated sand (Kuan et al., 1998; Chan

et al., 2009), and various iron oxides/hydroxides. The iron-based adsorbents examined in selenium adsorption studies include amorphous iron oxyhydroxide (Parida et al., 1997; Balistrieri and Chao, 1990; Benjamin, 1983), goethite (Balistrieri and Chao, 1987; Zhang and Sparks, 1990), ferrihydrite (Parida et al., 1997), 'waste' Fe(III)/Cr(III) hydroxide (Namasivayam and Prathap, 2006), zerovalent iron (Zhang et al., 2005), magnetite (Jordan et al., 2009; Martinez et al., 2006), crushed granite (Jan et al., 2008), goethite and hematite (Rovira et al., 2008), and iron-coated granular activated carbon (Zhang et al., 2008). The major drawbacks involved in using the above mentioned materials are preferential adsorption of either one selenium species selenite or selenate and interferences by anions such as phosphate, silicate, etc (Twidiwell et al., 2000).

Nano-sized magnetite (Fe_3O_4) with high specific surface area and surface charges has been examined as adsorbent to treat mine water (Navratil and Akin, 2009) and to remove contaminants as Cr^{6+} (Hu et al., 2004), methylene blue (Mak and Chen, 2004), and Cu, Zn, As and dichlorophenol (Cumbal and SenGupta, 2005) from aqueous solution.

Recent studies have also presented nano-magnetite as a potential adsorbent for selenium species (Missana et al., 2009; Bhojappa, 2009; Lopez de Arroyabe et al., 2008). However, a large-scale application of this adsorbent is difficult to achieve since both natural and synthetic nano-magnetite are available only as fine powders, which are not suitable to use in column applications because of their low hydraulic conductivity. Therefore, powdered magnetite must be supported with another material to achieve low backpressure and good water flow through the column (Navratil and Akin, 2009). As a porous supporting material, diatomaceous earth is a lightweight sedimentary rock composed mainly of silica microfossils of aquatic unicellular algae, consisting of various pores with up to 80% - 90% voids. Due to its high permeability, porosity and specific surface area, diatomaceous earth is used as filter media in many industries for the adsorption of chromium, lead and other pollutants (Khraisheh et al., 2004).

The metal sorption capacity of diatomaceous earth can be improved considerably after surface modification. This improvement in diatomaceous earth performance is attributed to an increase in surface area after coating, as well as the resultant surface charge due to the formation of oxide compounds on the surface. The modification of diatomaceous earth using manganese oxide to remove copper and cadmium (Khraisheh et al., 2004) and using ferric oxide to remove arsenic (Jang et al., 2007; Jang et al., 2006; Wu et al., 2005) has been reported as a promising alternative to remove those pollutants. However, surface modification of diatomaceous earth employing magnetite to remove pollutants from water has not been found in the literature.

1.2.3 Biological processes

These technologies include anaerobic bacterial removal, algal-bacterial selenium removal, agroforestry, constructed wetlands, and enzymatic selenium reduction (NSMP, 2007). Bacterial reduction of selenium aqueous species to elemental selenium has been shown to be a potential candidate for treating mine waters (Gusek et al., 2008). However, long operating times and size of bioreactors are challenges to be overcome (Mavrov et al., 2006).

1.3 Research objective

The main objective of this study was to develop an adsorption process using nano-magnetite impregnated diatomaceous earth to remove selenium from water and wastewater. An incipient wetness impregnation method using a vortexing device was developed to disperse and incorporate magnetite nano-particles homogeneously on the pore surfaces of diatomaceous earth (DE).

The removal of selenite (Se(IV)) as well as selenate (Se(VI)) oxyanions by the new material were investigated. A series of batch adsorption experiments were conducted to study adsorption kinetics, isotherms, and adsorptive thermodynamics in

conjunction with studies on the effect of pH, temperature, concentration, contact time, and presence of competing anions on selenium removal efficiency. Finally, column studies were conducted to evaluate the adsorption capacity and the operability of the nano-magnetite impregnated DE.

CHAPTER 2: MATERIALS AND METHODS

2.1. Materials

The analytical grade chemicals used were iron (III) sulfate ($\text{Fe}_2(\text{SO}_4)_3$), ammonium hydroxide (NH_4OH), sodium hydroxide (NaOH), nitric acid (HNO_3), sodium nitrate (NaNO_3), sodium chloride (NaCl), Sodium Sulfate (Na_2SO_4), oleic acid ($\text{C}_{18}\text{H}_{34}\text{O}_2$), and ethanol (anhydrous) purchased from Fisher Scientific, Inc.(Rochester, NY). Iron (II) sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and sodium selenate (Na_2SeO_4) were obtained from ACROS Organics (NJ, USA). Sodium selenite (Na_2SeO_3) was purchased from MP Biomedicals (Solon, OH). Celite 545 (flux calcinated diatomaceous earth) was acquired from World Minerals (CA, USA). All the chemical solutions utilized were prepared using Millipore deionized water.

Taking into account that both selenite and selenate may be present in selenium impaired waters, adsorption of both selenium species onto nano-magnetite impregnated DE was evaluated. A stock solution of 100 mg-Se/L was prepared with de-ionized water using the aforementioned selenium salts, and the working solutions (100, 250, and 500 $\mu\text{g-Se/L}$) for the adsorption experiments were prepared from the stock solution.

2.2. Adsorbent preparation and characterization

In order to obtain a uniform coating, the surface of the diatomaceous earth (DE) was modified using oleic acid. 10 g DE and 50 ml of de-ionized water were mixed in a beaker for 10 min. with a magnetic stirrer, followed by the addition of 1ml of oleic acid and continued stirring for 60 min. Then, 6ml of ammonia solution was added and mixed for a period of 8 hr. The resulting mixture was centrifuged for 5 min at 4,000 rpm, rinsed with 1:1 ethanol/water solution 3-4 times and dried overnight at room temperature.

The synthesis of the nano-magnetite impregnated DE was achieved through coprecipitation at room temperature, in the presence of both ferric and ferrous iron (Fig. 2). In order to avoid the presence of dissolved oxygen in the liquid phase, N₂ bubbling was maintained throughout the process. First, a solution containing 210 ml of de-ionized water and 48 ml of Fe³⁺ solution [10g/L] was stirred for 10 min, followed by the addition of 241 ml of Fe²⁺ solution [1g/L] and 10g of oleic acid-modified DE. After 30 min, 70 ml ammonia was gradually added and a black precipitated was observed. The precipitation process was allowed to occur for additional 30 min with mechanical stirring and continuous N_{2(g)} bubbling. After that, the synthesized particles were separated from the solution by vacuum filtration using 0.45 μm membrane. The dark precipitate was then resuspended and washed 3-4 times by adding de-ionized water followed by filtration. The final sample was dried overnight at room temperature. By this way, a sample of 10% nano-magnetite impregnated diatomaceous earth (w/w) was obtained.

Figure 2. Apparatus for chemical precipitation of nano-magnetite particles on the surface of diatomaceous earth

The morphology of synthesized particles on the DE surface was examined using a Hitachi S-4700 field emission scanning electron microscope (FE-SEM).

The mineralogical composition of the sample was determined by X Ray Diffraction. XRD patterns were recorded at a scanning rate of 4°/min on a X'Pert Pro X-ray diffractometer (XRD) by Panalytical Inc equipped with a Cu K α radiation source under target voltage 40Kv and current 30Ma. For comparison purposes, XRD patterns of raw DE and pure nano-magnetite (prepared following the same procedure previously described but without adding DE particles) were also recorded. Reference data for the different mineral phases were taken from the RRUFF online database.

2.3. Determination of the Point of Zero Charge

Acid/base titrations were performed in order to determine the point of zero charge (PZC) of the new material following the technique described by Schulthess and Sparks (1986). Further, in order to compare the PZC of the nano-magnetite impregnated DE with that of the plain DE and the pure nano-magnetite, acid/base titrations were also carried out for these substrates. The concentration of the acid (HCl) and the base (NaOH) employed for the titrations was 0.02 N. Titration was carried out in three different ionic strength conditions: 0.001 M, 0.01 M and 0.1 M. The point of zero charge (PZC) is indicated by the pH value at which an intersection of three titration curves occurs.

2.4. Batch adsorption studies

Batch adsorption studies were performed to examine adsorption of selenite onto nano-magnetite impregnated DE by agitating 100 ml of solution containing selenium ions of desired concentration with predetermined amounts of adsorbent using a temperature controlled incubator shaker at 25°C for 24 h at 200 rpm (Fig. 3). The resulting mixture was filtered through a 0.45 μ m membrane filter and the selenium

concentration was measured using a Varian SpectrAA 210 Zeeman graphite furnace atomic absorption spectrometer (GFAAS). The amount of adsorbent applied during each test is reported in grams based on its dry weight.

Figure 3. Batch experiment apparatus used in selenium adsorption onto nano-magnetite impregnated DE.

2.4.1 Effect of pH

The effect of pH on selenite removal was studied using a series of 100 ml solutions of selenite (250 and 500 $\mu\text{g-Se/L}$) and selenate (100 and 250 $\mu\text{g-Se/L}$) with 0.5 g/L adsorbent at 25°C. The pH of the solutions was adjusted in the range pH 2-9 by adding dilute solutions of HNO_3 and NaOH and shaken for 24 hrs to ensure the adsorption equilibrium.

2.4.2 Effect of contact time

To test the effect of contact time, a series of conical flasks with 100 ml selenite/selenate solutions (250 $\mu\text{g-Se/L}$) and 0.5 g/L of adsorbent were shaken for

periods of time ranging from 5 min to 24 h at pH 3 and at 25°C. Then, the samples were filtrated for selenium measurement.

2.4.3 Effect of temperature

To examine the effect of temperature on selenium adsorption, a dose of 0.5 g/L nano-magnetite impregnated DE was added to batches of 100 ml solutions of selenite (250 and 500 µg-Se/L) and selenate (100 and 250 µg-Se/L). Then the solutions were shaken for 24 h at five different levels of temperature: 25, 30, 35, 45 and 60°C.

2.4.4 Adsorption isotherms

The affinity of the adsorbate for an adsorbent is quantified using adsorption isotherms, which are used to describe the amount of adsorbate that can be adsorbed onto an adsorbent at equilibrium and at a constant temperature (MWH, 2005). Among the various isotherm models available, two parameter models such as Langmuir and Freundlich models were applied to characterize selenium adsorption capacity.

2.4.4.1 Freundlich model

The Freundlich adsorption isotherm was originally proposed as an empirical equation, used to describe the data for heterogeneous adsorbents such as activated carbon (MWH, 2005). The Freundlich expression is an exponential equation and therefore, assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases (Hamdaoui and Naffrechoux, 2007). This model is consistent with the thermodynamics of heterogeneous adsorption (varying site energies) and it is expressed by the equation given below:

$$q_e = KC_e^{1/n} \quad (1)$$

where: C_e : equilibrium selenium concentration in solution after adsorption (µg/L)

q_e : amount of solute adsorbed per unit weight of adsorbent at equilibrium
($\mu\text{g/g}$)

K : Freundlich adsorption capacity ($\mu\text{g/g})(\text{L}/\mu\text{g})^{1/n}$

n : Constant indicative of the adsorption intensity

A log–log plot of q_e versus C_e using the Eq. 1 will result in a straight line and the parameters K and $1/n$ can be determined.

2.4.4.2 Langmuir model

The Langmuir isotherm is based on the theoretical principle that the energy of adsorption is constant, and the number of binding sites is finite. The adsorbent surface is made up of fixed individual sites where molecules of adsorbate may be chemically bound. Each site is assumed to be capable of binding at most one molecule of adsorbate; that is, the Langmuir model allows accumulation only up to a monolayer (MWH, 2005).

This adsorption model is described by the formula:

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

where: q_m : maximum adsorption capacity on the adsorbent ($\mu\text{g/g}$)
 b : Langmuir adsorption constant related to the free energy of the adsorption ($\text{L}/\mu\text{g}$)

A plot of C_e/q_e versus C_e will result in a straight line with slope of $1/q_m$ and intercept $1/b \cdot q_m$.

For adsorption isotherm study, batch experiments were carried out by mixing 100 ml of selenite or selenate solution (250 $\mu\text{g-Se/L}$) with six different doses of adsorbent:

0.05, 0.1, 0.25, 0.5, 1.0 and 2.0 g/L. The mixtures were shaken for 24 h at 25°C and at different levels of initial pH: 3.0, 4.0 and 5.0 for selenite adsorption, and pH: 2.0 and 3.0 for selenate adsorption.

2.4.5 Effect of Interfering anions

The presence of additional anions that interact with the adsorbent can affect the adsorption behavior of selenium by competing for available binding sites. The effect of competing anions such as chloride, sulfate and nitrate that may coexist with selenium oxyanions in water or wastewater was studied. The experiments were conducted at 25°C, pH 3.0 ± 0.1 and adsorbent dose of 0.5 g/L for a contact time of 24 h with an initial concentration of 250 µg-Se/L. Sodium nitrate (NaNO₃), sodium chloride (NaCl), and sodium sulfate (Na₂SO₄) were used as source for the various anionic species and the ionic strength was controlled at four different levels: 0.1, 1.0, 5.0 and 10 Mm.

2.5 Desorption Tests

The desorption of selenite and selenate was evaluated in order to determine if the adsorbent can be regenerated after Se adsorption for reuse. Initially, a series of conical flasks with 100 ml selenite/selenate solutions (250 µg-Se/L) and 0.5 g/L of adsorbent were shaken for 24 h at pH 3 and at 25°C. Then, samples were taken to measure selenium concentrations in the aqueous phase to determine the amount of selenium adsorption. After that, the pH of the solutions was adjusted in the range pH 4 – 10 using a solution of NaOH and the flasks were shaken for another 24 h. Selenium concentrations in the aqueous phase were measured again to determine the selenium desorption at different pHs.

2.6 Column adsorption studies

Column adsorption tests were carried out by using columns of 1.1 cm diameter and 50 cm length. The columns were packed with ~ 5.5 g (11.4 cm³) of the nano-magnetite impregnated DE and the depth was ~ 12 cm. Thin layers of glass wool (~ 3 cm) and sand (~ 1 cm) were also used at the bottom to provide a base layer of support for the media bed and facilitate the drainage. Figure 4 shows a schematic of the packed column employed.

Figure 4. Scheme of column adsorption experiments for selenite and selenate adsorption onto nano-magnetite impregnated DE.

Columns filled with raw diatomaceous earth (DE) were used as “blank” controls for the experiment.

Feed solutions containing 500 $\mu\text{g-Se/L}$ (selenite or selenate) were continuously supplied to the columns by a squibb pear-shaped funnel. A constant hydraulic head in the column was maintained by making the inflow and outflow rates equal. The pH value of the solutions was fixed at pH 4.0 for selenite adsorption and at pH 3.0 for selenate adsorption. The flow rate was kept at $\sim 0.45\text{ml/min}$, which corresponded to a space velocity of ~ 2.2 bed-volumes/h.

In order to evaluate the applicability of the adsorption process in treating actual selenium-containing waters (such as mining impacted waters), column adsorption tests were also carried out using water from Monongahela River, near Morgantown, WV, which is heavy impacted by mining drainage. The river water sample was spiked with selenite or selenate solutions at 500 $\mu\text{g-Se/L}$ and the pH was adjusted using concentrated nitric acid.

The effluent was collected periodically in 3 ml fractions and subjected to GFAAS analysis in order to determine the concentration of selenium.

CHAPTER 3: RESULTS AND DISCUSSION

3.1 Sample Characterization

The samples of raw DE and nano-magnetite impregnated DE are presented in Fig. 5. The raw DE was a white powder. The color of the dried sample of magnetite-impregnated DE was dark brown (Fig. 5), indicating a possible oxidation of the magnetite since the initial color of the precipitated was black. However, the magnetic response of the material to a magnet was very strong which indicates that if any oxidation took place, it occurred only on the surface of the material.

Figure 5. Diatomaceous earth (a) before and (b) after the impregnation process with nano-magnetite.

SEM images of plain diatomaceous earth and nano-magnetite impregnated DE are presented in Fig. 6. The smooth surfaces of plain DE (Fig. 6(a)) were coated with a layer of magnetite nanoparticles (Fig. 6(b)) and the coverage was relatively uniform (Fig 6 (b, c, d)). It was also found that the porous structure of DE was partially filled by magnetite (Fig. 6(d)).

The X-ray diffraction patterns of nano-magnetite and nano-magnetite impregnated DE particles are showed in Fig. 7.

Figure 6. SEM images of (a) pure diatomaceous earth, (b), (c), and (d) nano-magnetite impregnated DE showing a uniform coating.

The spectra corresponding to raw nano-magnetite sample was in agreement with that of the referenced mineral, and no other mineral phases were detected. For the magnetite-impregnated DE sample, two polymorphs of silica (SiO_2) were clearly identified: cristobalite and quartz. Although diatomaceous earth is mainly composed by amorphous silica compounds, after the calcination process ($>900^\circ\text{C}$) most of the silica is usually transformed to cristobalite (the stable high temperature polymorph). Peaks corresponding to magnetite were also present at very low intensity. The fact that the magnetite fraction in the sample was just 10% (wt%) could be the reason for the low intensity of the peaks associated to these mineral. The detection limit for XRD technique for mixed materials is about 3-5%, which means that a mineral present in concentrations $< 5\%$ can not be easily detected by this method.

Figure 7. X-ray diffractograms of nano-magnetite and nano-magnetite impregnated DE particles.

3.2 Point of Zero Charge (PZC)

The titration curves of raw DE, pure nano-magnetite, and nano-magnetite impregnated DE are presented in Fig. 8, 9, and 10. As shown in Fig. 8, the point of zero charge (PZC) of the raw DE was at pH 2.4, which is in a good agreement with the values reported in the literature for silica (pH $\sim$ 2 – 3) (Persello, 2000) and diatomaceous earth particles (pH 2.0) (Gao et al., 2005).

For magnetite, the PZC is considered to be in the range 6.0 – 7.0 (Cornell and Schwertmann, 2003). According to the titration curves, the PZC obtained for pure nano-magnetite particles was 6.7 (Fig. 9), which coincides with the reported values.

Figure 8. Batch titration of raw diatomaceous earth (DE) at various ionic strengths with HCl and NaOH. Adsorbent concentration: 4 g/L, total volume: 50 ml, pH of suspension after equilibrating overnight

Figure 9. Batch titration of raw nano-magnetite at various ionic strengths with HCl and NaOH. Adsorbent concentration: 4 g/L, total volume: 50 ml, pH of suspension after equilibrating overnight

Figure 10. Batch titration of nano-magnetite impregnated DE at various ionic strengths with HCl and NaOH. Adsorbent concentration: 4 g/L, total volume: 50 ml, pH of suspension after equilibrating overnight

According to the Fig. 10, the PZC of nano-magnetite impregnated DE was at pH 7.2. Therefore, the PZC of DE particles moved from pH 2.4 before modification to pH 7.2 after the impregnation process with nano-magnetite, which was almost the same as the PZC of pure magnetite (6.7) as shown in Fig. 9. The change of DE surface property indicated a good coverage of the magnetite nanoparticles on the surface of DE particles, which is consistent with the results from the SEM images (Fig. 6).

A change in the PZC as a result of modification process has already been reported for other systems of mixed oxides. After the modification of silica particles using aluminum hydroxide ($\text{Al}(\text{OH})_3$), it was observed that the resulting zeta potential of the mixed oxide coincided with the PZC of pure $\text{Al}(\text{OH})_3$ (pH 9.1) (Meng and Letterman, 1993). In contrast to the $\text{Al}(\text{OH})_3/\text{SiO}_2$ system, measurements for the $\text{Fe}(\text{OH})_3/\text{SiO}_2$ system showed that the PZC of the mixed oxide was much lower than that of pure $\text{Fe}(\text{OH})_3$ (Chan et al., 2009). This difference was considered as the overall results contributed by negatively charged silica and positively charged ferric hydroxide.

Furthermore, the $\text{Fe}(\text{OH})_3$ coating on the surface of the silica particles was not as uniform as that observed when $\text{Al}(\text{OH})_3$ was employed.

3.3 Batch Adsorption Studies

3.3.1 Effect of pH

The effect of pH on selenite and selenate adsorption is shown in Figs. 11 and 12, respectively. In general, it was observed that the sorption of both selenite and selenate oxyanions decreased as pH was increased, indicating that lower pH favored selenium adsorption.

Figure 11. Effect of pH on final selenite concentration (adsorbent dose 0.5g/L; mixing time 24h; 25°C; initial concentrations 250 and 500µg-Se/L).

In the case of selenite, it was possible to differentiate three stages or levels of adsorption (Fig. 11), irrespective of the initial concentration (250 and 500 µg-Se/L): (1) First, selenite adsorption was relatively independent of pH at low pH (2.0 – 3.5) with

very high percent adsorption. (2) Then, the adsorption dropped sharply to 47 – 55% in the range of pH 4.0 – 7.0. (3) Finally, very low or no adsorption occurred at pH values > 7.0. In the case of selenate adsorption, maximum removal (80 – 94%) was obtained at pH < 2.5. Thereafter, a significant decrease in selenate adsorption occurred as pH was increased, and no adsorption was observed at pH > 4.0 (Fig. 12).

Figure 12. Effect of pH on final selenate concentration (adsorbent dose 0.5g/L; mixing time 24h; 25°C; initial concentration 100 and 250µg-Se/L).

As a result, the effective pH range for adsorption of both selenium species onto the surfaces of nano-magnetite impregnated DE was pH 2 to 3.5. Considering most mine drainages are acidic and some have very low pH, utilization of nano-magnetite impregnated DE for selenium-impaired mine water can be advantageous. In addition, within pH 2 to 3.5, selenate adsorption was more pH dependent and selenite adsorption was relatively pH independent (Fig. 11 and 12).

The dependence of selenite/selenate adsorption on the pH can be attributed to two theories, namely surface charge and speciation of selenium in aqueous solution. As

shown from Fig. 10, the PZC of nano-magnetite impregnated DE was at pH 7.2, indicating the surfaces of nano-magnetite were negatively charged at pH>7.2. At pH 7.0 or above as illustrated in Fig. 11, there was a sharp decrease in selenite adsorption by nano-magnetite impregnated DE. There were low selenite adsorption for pH>7 (Fig. 12) and negligible selenate adsorption at pH>4. Consequently, the effect of pH on surface charges of nano-magnetite impregnated DE played a significant role in selenium adsorption

On the other hand, the biselenite ion (HSeO_3^-) being the predominant form of selenite in aqueous solution at a pH range 2.6 – 8.5 (Fig. 1) might be responsible for maximum adsorption at low pH, whereas above pH 8.0 selenite (SeO_3^{2-}) species dominates in solution (Plant et al., 2007; Rovira et al., 2008). Similar trends were previously observed in the case of selenite adsorption onto iron oxyhydroxides and ferrihydrite and were attributed to characteristic anionic behavior of selenite species (Parida et al., 1997; Goh and Lim, 2004; Rovira et al., 2008;). Likewise for selenate (Se(VI)), the sorption decreased as pH increased due to a reduced fraction of aqueous species HSeO_4^- in solution (Fig. 1) as well as surface charge variation with pH.

From Figs. 11 and 12 it could be seen that the highest removal efficiency of both selenite and selenate species was achieved at pH 2.5. Besides, the adsorption of selenate was more strongly dependent on pH than that of selenite. At pH > 4.0 the nano-magnetite impregnated DE was not able to adsorb selenate from solution (Fig. 14) but it was still able to adsorb 50% of the selenite oxyanions (Fig. 11). Selenite typically has a significantly greater propensity to adsorb (attach) onto other molecules than selenate due to its level of protonation. Since the $\text{P}k_{\text{a1}}$ for selenate ($\text{P}k_{\text{a1}} = 1.7$) is lower than that of selenite ($\text{P}k_{\text{a1}} = 2.6$), under most naturally occurring conditions the protonation of selenate is diminished which reduces weak bonding with other metal hydroxides. This result is in agreement with previous studies, where it was found that at any given pH value, the binary oxide systems have higher affinities for selenite than selenate, and the

selenium oxyanion removal capacity of the binary oxide systems is strongly influenced by the surface charge and the environmental pH (Chan et al., 2009).

3.3.2 Effect of contact time

The effect of contact time on final selenium concentration for selenite is presented in Fig. 13. Rapid adsorption was observed in the first 30 – 60 min with almost 95% removal of selenite. Thereafter, the adsorption slowed down and quickly reached equilibrium (Fig. 13). A similar behavior was observed for selenium adsorption on binary oxide systems such as $\text{Al}^{3+}/\text{SiO}_2$ and $\text{Fe}^{3+}/\text{SiO}_2$, (Chan et al., 2009) and on different forms of iron oxyhydroxides and ferrihydrite (Parida et al., 1997) where the adsorption rate was rapid in the first minutes and approached equilibrium at about 2 h. In the same way, selenite adsorption on magnetite nanoparticles reached equilibrium in approximately 30 min (Lopez de Arroyabe et al., 2008). Longer times to reach equilibrium have also been reported for selenium adsorption: about 30 h for selenium adsorption onto natural magnetite (Martinez et al., 2006), or 50 h for selenium adsorption onto goethite and hematite (Rovira et al., 2008).

The effect of contact time on final selenium concentration for selenate is presented in Fig. 14. For selenate adsorption, it can be seen that as time increases, part of the selenium already adsorbed by the nano-magnetite impregnated DE was released back to the solution (Fig. 14). This phenomenon occurred independently of the initial concentration of selenium (100 $\mu\text{g-Se/L}$ and 250 $\mu\text{g-Se/L}$) and could be related to the stabilization of the pH in the system during the adsorption test period. Even though an initial pH of 3.0 was set for all the samples tested, after mixing for 24 h the pH values recorded fell in the range 3.2 – 3.5, indicating a consumption of protons from the solution during the sorption process. El-Shafey et al. (2007) reported an increase in the final pH value for a sorption process of selenite using modified rice husk and concluded that the consumption of protons indicated a reduction of selenite.

Figure 13. Effect of contact time on final selenite concentration (adsorbent dose 0.5g/ L; pH 3.0 ± 0.1 ; 25°C; 24 h mixing time; initial concentrations 250 and 500 µg-Se/L).

Figure 14. Effect of contact time on final selenate concentration (adsorbent dose 0.5g/ L; pH 3.0 ± 0.1 ; 25°C; 24 h mixing time; initial concentrations 100 and 250 µg-Se/L).

The fact that this phenomenon was noticeable for selenite adsorption (Fig. 13, especially at the elevated concentration: 500 $\mu\text{g-Se/L}$) and evident for selenate adsorption (Fig. 14) could be attributed to a weaker dependence of selenite adsorption on pH in comparison to selenate (as shown in Section 3.3). Previous studies on selenium adsorption onto activated alumina (Ghosh et al., 1994) and Fe^{3+} -coated silica (Chan et al., 2009) concluded that the adsorption of selenate (Se(VI)) was more strongly dependent on pH than that of selenite (Se(IV)).

The theory of a partial dissolution of the adsorbent was also considered, although the solubility of magnetite at pH 3.0 was very low. It was reported that at pH 2.0 and a concentration of 2g/L, less than 1.2% of the magnetite was dissolved after one month (Missana et al., 2009). The small particle size and large surface area might have facilitated the dissolution of magnetite. Our exploratory tests indicated that the dissolved iron in solution was around 0.06 mg/L after 24 h contact time at pH 3.0, corresponding to 0.17% of the iron contained in the nano-magnetite. Since the dissolution of magnetite was almost negligible, the stabilization of pH over time could be the principal factor affecting selenate adsorption.

In order to adequately ensure adsorption equilibriums were reached, mixing time of 24 h was used in all further adsorption tests since no significant changes in adsorption were observed after that time period.

3.3.3 Effect of Temperature and Adsorption Thermodynamics

The effect of temperature on final selenium concentration is presented in Figs. 15 and 16. It was observed that the final selenite concentration increased as temperature increased from 25°C to 60°C. The removal efficiency was about 60% for selenite ions (Fig. 15) and 10-15% for selenate ions (Fig. 16) at 60 °C. The trend was independent of the initial selenium concentration and the selenium speciation (selenite or selenate),

indicating high temperatures lower selenium adsorption onto the surfaces of nano-magnetite impregnated DE.

Figure 15. Effect of temperature on final selenite concentration (adsorbent dose 0.5g/L; pH 3.0 ± 0.1 ; mixing time 24h; initial concentrations 250 and 500 $\mu\text{g-Se/L}$).

Figure 16. Effect of temperature on final selenate concentration (adsorbent dose 0.5g/L; pH 3.0 ± 0.1 ; mixing time 24h; initial concentrations 100 and 250 $\mu\text{g-Se/L}$).

The results are in agreement with previous studies, where the uptake of selenite decreased with increasing temperature for FeCl₃ coated BFA (Bagasse Fly Ash) (Wasewar et al., 2009) and activated alumina (Jegadeesan et al., 2003).

On the other hand, some studies of selenite adsorption onto different adsorbents such as iron-coated granular activated carbon (Zhang et al., 2008), manganese nodule leached residues (Dash and Parida, 2007), sulphuric acid-treated peanut shell (El-Shafey, 2007a), and nano-magnetite (Bhojappa, 2009) concluded that the selenite uptake increased as temperature increased.

Thermodynamic parameters such as standard free energy (ΔG°), enthalpy (ΔH°_{ads}), and entropy (ΔS°) of adsorption were calculated in order to explain the thermodynamic nature involved in the adsorption process. Free energy change (ΔG°) was calculated from the relation:

$$\Delta G^\circ = -RT \ln K_c$$

where:

R: gas constant (8.314 J/mol·K)

T = absolute temperature in Kelvin

K_c = equilibrium constant (ratio of the concentration of selenite ions adsorbed on the adsorbent to that of selenite ions in the aqueous phase at equilibrium).

Using the Van't Hoff equation given below, the values of enthalpy (ΔH°_{ads}) and entropy (ΔS°) were estimated from the slope and intercept of the linear plots of $\ln (K_c)$ vs. $1/T$ (Figs. 17 and 18).

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ_{ads}}{RT}$$

Figure 17. Van't Hoff plot for selenite adsorption (adsorbent dose 0.5g/L; pH 3.0 ± 0.1 ; mixing time 24h; initial concentrations 250 and 500 $\mu\text{g-Se/L}$).

Figure 18. Van't Hoff plot for selenate adsorption (adsorbent dose 0.5g/L; pH 3.0 ± 0.1 ; mixing time 24h; initial concentrations 100 and 250 $\mu\text{g-Se/L}$).

The thermodynamic parameters obtained from the plots are presented in the Table 1. The spontaneity of the adsorption process was indicated by negative values of ΔG° and the negative values of ΔH°_{ads} indicated exothermic adsorption, which explains why the temperature increase resulted in lower selenite and selenate adsorption onto the surface of nano-magnetite impregnated DE.

Table 1. Thermodynamic parameters for the adsorption of selenite and selenate on nano-magnetite impregnated DE at different temperature values.

<i>Se form</i>	<i>Initial Concentration [$\mu\text{g-Se/L}$]</i>	<i>Temperature [$^\circ\text{C}$]</i>	<i>K_c</i>	<i>ΔG° [Kj/mol]</i>	<i>ΔH°_{ads} [Kj/mol]</i>	<i>ΔS° [Kj/mol*K]</i>
Selenite	250	25	43.17	-9.33	-95.93	-0.29
		30	24.61	-8.07		
		35	10.23	-5.95		
		45	3.97	-3.65		
	500	25	20.85	-7.53	-89.1	-0.27
		30	12.46	-6.35		
		35	5.56	-4.39		
		45	2.27	-2.17		
Selenate	100	25	4.46	-3.70	-101.40	-0.33
		30	1.67	-1.29		
		35	0.80	0.56		
		45	0.32	2.99		
	250	25	1.03	-0.08	-69.52	-0.23
		30	0.70	0.89		
		35	0.39	2.39		
		45	0.18	4.50		

Finally, the negative values of entropy change (ΔS°) reveal a decrease in randomness at the solid/solution interface during the adsorption of selenite onto nano-magnetite impregnated DE.

3.3.4 Adsorption Isotherms

Data obtained from adsorption isotherm study were fitted to two different models of adsorption: Langmuir model and Freundlich model. According to R^2 values from the linear regression, the Freundlich isotherm model (Fig. 19 and 20) presented a better applicability to the adsorption process than the Langmuir model. The parameters of the Freundlich isotherm model are listed in Table 2.

From Fig. 19 it could be seen that the adsorption capacity at pH 3.0 was approximately 125 $\mu\text{g-Se/g-adsorbent}$ with a final selenite concentration of 0.62 $\mu\text{g-Se/L}$ and increased to 1860 $\mu\text{g-Se/g-adsorbent}$ with a final selenite concentration of 157 $\mu\text{g-Se/L}$.

Figure 19. Selenite adsorption isotherms of nano-magnetite impregnated DE (Initial concentration: 250 $\mu\text{g-Se/L}$; mixing time 24h; 25°C).

As depicted in Fig. 20, the adsorption capacity at pH 2.0 was approximately 122 $\mu\text{g-Se/g}$ adsorbent with a final selenate concentration of 5 $\mu\text{g-Se/L}$ and increased to 810 $\mu\text{g-Se/g}$ with a final selenate concentration of 210 $\mu\text{g-Se/L}$.

Figure 20. Selenate adsorption isotherms of nano-magnetite impregnated DE (Initial concentration: 250 $\mu\text{g-Se/L}$; mixing time 24h; 25°C).

Table 2. Freundlich parameters for the adsorption of selenite and selenate on nano-magnetite impregnated DE

<i>Se form</i>	<i>pH</i>	<i>Freundlich Constants</i>		
		K [$\mu\text{g/g})(\text{L}/\mu\text{g})^{1/n}$]	n	r²
Selenite	3.0	282.96	2.60	0.970
	4.0	0.138	0.57	0.995
	5.0	0.017	0.50	0.978
Selenate	2.0	59.95	2.07	0.995
	3.0	15.98	1.80	0.975

Although various studies found in the literature that use iron based adsorbents to remove selenite and selenate could be described by the Langmuir isotherm model (Martinez et al., 2006; Rovira et al., 2007; Zhang et al., 2008; Dash and Parida, 2007; Namasivayam and Prathap, 2006), the Freundlich model resulted in a better fit than the Langmuir isotherm model for adsorption of both selenite and selenate species in surface coal mine environment soils (Sharmasarkar and Vance, 2002) and for adsorption of selenite on nano-magnetite (Bhojappa, 2009).

The applicability of the Freundlich isotherm model indicated that selenite adsorption took place heterogeneously due to the diversity of sorption sites offered by the nano-magnetite impregnated DE. In the Freundlich model, the magnitude of the exponent n gives an indication on the favorability of adsorption. Values of n in the range 2 – 10 represent good, 1 – 2 moderately difficult, and less than 1 poor adsorption characteristics (Treybal, 1981). From Table 2 it is observed that the adsorption of selenite was favorable at pH 3.0 ($n = 2.13$), whereas at pH 4.0 and 5.0 the coefficients indicated poor adsorption ($n < 1$). This finding is consistent with effect of pH on selenite adsorption (Section 3.3). On the other hand, for selenate adsorption the coefficients fell in the range 1.8 – 2.07, indicating moderately difficult to good adsorption at pH 2.0 and 3.0 for selenate, which might explain its poorer adsorption performance by nano-magnetite impregnated DE as opposed to selenite.

3.3.5 Adsorption Kinetics

A pseudo-second-order kinetic model expressed by the equation given below was applied to the kinetic data.

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{t}{q_e}$$

where q_e : sorption capacity at equilibrium [$\mu\text{g-Se/g-adsorbent}$]
 q_t : sorption capacity at time t [$\mu\text{g-Se/g-adsorbent}$]

K: pseudo-second-order equilibrium rate constant [$\text{g}/\mu\text{g}\cdot\text{min}$]

The straight lines obtained by plotting t/q_t vs. t (Figs. 21 and 22) indicated the applicability of the pseudo-second-order rate equation and permitted determining the equilibrium rate constant K (Table 3).

Figure 21. Pseudo-second-order kinetics for sorption of selenite by nano-magnetite impregnated DE (adsorbent dose 0.5g/L; pH 3.0 ± 0.1 ; mixing time 24h; 25°C)

The values of q_e calculated from this model were compared with experimental values of $q_{e(\text{Exp})}$ (Table 3). It was found that they were in excellent agreement exhibiting that the system obeyed the pseudo-second-order kinetic model. Besides, the correlation coefficients were very high, hence affirming the applicability of the aforementioned model.

The calculated pseudo-second order rate constants (Table 3) are higher than the values of $k = 6.1 \times 10^{-8} \text{ g}/\mu\text{g}\cdot\text{min}$ reported for selenite adsorption on modified rice husk (El-Shafey, 2007), $k = 5.07 \times 10^{-7} \text{ g}/\mu\text{g}\cdot\text{min}$ for selenite adsorption on Fe^{3+} coated silica

(Chan et al., 2009), and $k = 1.8 \times 10^{-5}$ for selenite adsorption onto iron-coated granular activated carbon (Zhang et al., 2008).

Figure 22. Pseudo-second-order kinetics for sorption of selenate by nano-magnetite impregnated DE (adsorbent dose 0.5g/L; pH 3.0±0.1; mixing time 24h; 25°C)

Table 3. Pseudo-second-order parameters for the adsorption of selenite and selenate on nano-magnetite impregnated DE

<i>Se form</i>	<i>Concentration</i> [μg-Se/L]	<i>Pseudo-second order kinetic model</i>			
		k [g/μg·min]	q_e [μg-Se/g]	q_{e(Exp)} [μg-Se/g]	R²
Selenite	250	2.98×10^{-3}	488	488.7	1
	500	6.26×10^{-4}	952	951.7	1
Selenate	100	4.06×10^{-4}	132	131.4	0.9985
	250	2.65×10^{-4}	270	271.3	0.9996

3.3.6 Effect of interfering anions

The effect of competing anions as chloride, nitrate and sulfate in the removal of selenite and selenate is shown in Figs. 23 and 24. It was observed that the presence of chloride and nitrate at different concentrations caused a minor decrease in selenite adsorption (from 97% to 93%, Fig. 23) but a significant reduction in selenate adsorption (from 46% to 8-24%, Fig. 24). On the other hand, the presence of sulfate reduced the uptake of both selenite and selenite species significantly (Fig. 23 and 24). At even very small concentration of sulfate (0.1Mm) the removal was reduced in almost 10% for both species and at the highest concentration evaluated (10 Mm), the removal decreased in 15% and 40% for selenite and selenate anions, respectively.

Figure 23. Effect of anions on selenite removal by nano-magnetite impregnated DE (mixing time 24h; 25°C; pH 3.0±0.1; initial concentration 250 µg-Se/L; adsorbent dose 0.5g/L).

These observations suggested that sulfate could compete with selenite and selenate oxyanions for adsorption sites. Nonetheless, the adsorption behavior of selenite was less affected by the changes of SO_4^{2-} ionic strength, which is in agreement with

previous studies for selenite and selenate adsorption using a tropical soil (Goh and Lim, 2004) and goethite (Hayes et al., 1988) as adsorbents. The relative sorption independence of ionic strength in the case of selenite could be macroscopic evidence for strong specific binding mechanism (inner-sphere complex) between selenite and the iron oxide (Hayes et al., 1988; Missana et al., 2009). Conversely, adsorbed selenate anions were more easily displaced by sulfate because both of them might only form weak bonds (outer-sphere complex) with the adsorbent (Goh and Lim, 2004).

Figure 24. Effect of anions on selenate removal by nano-magnetite impregnated DE (mixing time 24h; 25°C; pH 3.0±0.1; initial concentration 250 µg-Se/L; adsorbent dose 0.5g/L).

3.4 Desorption tests

The results for selenite and selenate desorption from the nano-magnetite impregnated DE as a function of pH are shown in Fig. 25. Selenate desorption occurred at lower pH values than selenite desorption. It was observed that a rise in the pH by one unit (pH 3.0 to pH 4.0) produced almost 72% desorption of selenate anions but only 4% of selenite anions. Furthermore, at pH values higher than 5.0 almost all the sorbed

selenate anions were desorbed from the nano-magnetite impregnated DE, indicating that the adsorption process was reversible and the nano-magnetite impregnated DE could be regenerated.

In the case of selenite, as pH was raised from 5.0 to 9.0 the percentage of desorbed anions increased gradually from 10% to 90%, and a further increase in the pH did not produce any additional desorption of selenium. A less exhaustive desorption of selenite anions in comparison to that of selenate indicated that the former was strongly bonded to the adsorbent surface, which is in agreement with previous studies for selenium adsorption/desorption on different oxides as aluminum-oxide-coated sand (Kuan et al., 1998) and goethite (Su et al., 2000). Overall, the desorption results demonstrated nano-magnetite impregnated DE could be easily regenerated and reused after adsorption.

Figure 25. Desorption of selenite and selenate from nano-magnetite impregnated DE as a function of pH for an adsorption process at pH = 3.0 ± 0.1 (mixing time 24h; 25°C; initial concentration 250 $\mu\text{g-Se/L}$; adsorbent dose 0.5g/L).

3.5 Column adsorption experiments

Fig. 26 shows the column breakthrough curves for the adsorption of selenite and selenate onto nano-magnetite impregnated DE and plain diatomaceous earth (DE). The selenium concentrations in the effluents are shown in terms of bed volumes (BV) of selenite/selenate solution. The breakthrough point for the curves was identified at the point where there was a rapid increase of selenium concentration in the effluent.

Figure 26. Breakthrough curves for selenite and selenate adsorption by nano-magnetite impregnated DE and plain DE (control tests). Initial concentration 500 µg-Se/L; pH = 3.0 for selenate adsorption, pH = 4.0 for selenite adsorption; 1BV ~ 12 cm³.

From Fig. 26, it can be concluded that diatomaceous earth itself (control tests) could not remove either selenite or selenate anions from solution, indicating that the selenium adsorption using nano-magnetite impregnated DE can be attributed to nano-magnetite.

When nano-magnetite impregnated DE was used as adsorbent, the column reached saturation earlier for selenate adsorption compared to selenite adsorption, which

is consistent with the batch study results. The effluent concentration at the breakthrough point for selenite was $35\mu\text{g-Se/L}$, corresponding to 773 bed volumes (9.3 L) of solution treated. In the case of selenate, 550 bed volumes (6.6 L) passed through the column to the breakthrough point and the effluent concentration was $12\mu\text{g-Se/L}$. The adsorption capacity of the columns at the breakthrough point was $\sim 845\mu\text{g-Se/g}$ and $\sim 600\mu\text{g-Se/g}$ for selenite and selenate, respectively.

When Monongahela River water was used instead of deionized water as the feeding solution, the breakthrough point was achieved earlier for selenite adsorption (Fig. 27). About 540 BV of selenite solution were treated before breakthrough occurred. However, in the case of selenate the adsorption was almost negligible and no breakthrough point can be identified in the curve. This phenomenon could be attributed to the presence of competing ions such as chloride and sulfate in the natural water sample, as it can be seen from the chemical analyses presented in Table 4.

Figure 27. Breakthrough curves for selenite and selenate adsorption when Monongahela River water was used as feeding solution. Initial concentration $500\mu\text{g-Se/L}$; pH = 3.0 for selenate adsorption, pH = 4.0 for selenite adsorption; $1\text{BV} \sim 12\text{ cm}^3$

Anion competition affected the removal of selenite from Monongahela River water by reducing the volume of water that can be treated in the column to the breakthrough point from 773 to 540 bed volumes (BV). In the case of selenate, the effect produced by the presence of sulfate and chloride in the water was more dramatic since the lowest concentration in the effluent was 377 $\mu\text{g-Se/L}$ and it quickly increased to 500 $\mu\text{g-Se/L}$ after 40 VB passed through the column.

Table 4. Water chemistry of the Monongahela River sample used for column adsorption studies

<i>Parameter</i>	<i>Value</i>
pH	7.9
Total suspended solids (TSS)	1.9 mg/L
Alkalinity	76.1 mg/L as CaCO_3
Acidity	10.6 mg/L as CaCO_3
Chlorides	19.4 mg/L
Sulfates	203 mg/L
Fe	0 mg/L
Ca	51.1 mg/L
Mg	11.2 mg/L
Mn	0 mg/L

These results are in agreement with the anion competition tests (Figs. 23, 24), where it was observed that low concentrations of sulfate, chloride, and nitrate had a greater impact on the adsorption of selenate than selenite.

CHAPTER 4: CONCLUSION

Nano-magnetite was employed to modify the negative surface charge of diatomaceous earth and the former's functionality was combined with the latter's high porous structure, low density, high surface area, chemical and thermo-stability, and low cost. This binary oxide system was successfully applied to remove selenium oxyanions from water.

The new material obtained showed the potential for achieving drinking water maximum contaminant level (MCL) for selenium as required by the EPA. Moreover, the regeneration of this adsorbent could be achieved easily by increasing the pH to a basic range.

The data showed that the maximum removal of selenite and selenate was achieved under acidic conditions (2 – 3.5), indicating the adsorption process was suitable for treating selenium-impaired acid mine drainage. The adsorption of selenate was more strongly dependent on pH than that of selenite.

The adsorption of selenite and selenate onto nano-magnetite impregnated DE fitted well the Freundlich model and the process kinetics could be explained by a pseudo-second-order kinetic model. Thermodynamic data indicated that selenium adsorption is a spontaneous ($\Delta G < 0$) and exothermic ($\Delta H > 0$) process.

The competition adsorption of sulfate with respect to selenite and selenate was more evident than that of nitrate and chloride.

Column studies showed that adsorption columns could be used to remove both selenite and selenate continuously and nano-magnetite impregnated DE can be a practical solution to selenium-impaired waters.

From the column studies it was also observed that competing anions such as sulfate and chloride, commonly present in natural waters, reduce the uptake of selenium by the nano-magnetite impregnated DE.

CHAPTER 5: REFERENCES

- ATSDR (Agency for Toxic Substances and Disease Registry). 2003. Toxicological Profile for Selenium. U.S. Department of Health and Human Services, Public Health Service. Atlanta. Available online at <http://www.atsdr.cdc.gov/toxprofiles/tp92.html>
- Balistreri, S.L., Chao, T.T. 1987. Selenium Adsorption by Goethite. Soil Science Society of America Journal, 51: 1145 – 1151.
- Balistreri, S.L., Chao, T.T. 1990. Adsorption of Selenium by Amorphous Iron Oxyhydroxide and Manganese Dioxide. Geochimica et Cosmochimica Acta, 54(3): 739 – 751.
- Benjamin, M.M. 1983. Adsorption and Surface Precipitation of Metals on Amorphous Iron Oxyhydroxide. Environmental Science and Technology, 17(11): 686 – 692.
- Bhojappa, S. 2009. Removal of Pollutants from Aqueous Solutions by Adsorption Processes. MSc Thesis, West Virginia University.
- Chan, Y.T., Kuan, W.H., Chen, T.Y., Wang, M.K. 2009. Adsorption Mechanism of Selenate and Selenite on the Binary Oxide Systems. Water Research, 43: 4412 – 4420.
- Coleman, L., Bragg, L.J., Finkelman, R.B. 1993. Distribution and Mode of Occurrence of Selenium in US Coals. Environmental Geochemistry and Health, 15(4): 215 – 227.
- Cornell, R.M., and Schwertmann, U. 2003. The Iron Oxides: Structure, Properties, Reactions, Occurrences, and Uses. Wiley-VCH GmbH&Co. KGaA, Weinheim, Germany.

- Cumbal, L.H., Sengupta, A.K. 2005. Preparation and Characterization of Magnetically Active Dual-zone Sorbent. *Industrial & Engineering Chemistry Research*, 44(3): 600 - 605.
- Dash, S.S, Parida, K.M. 2007. Studies on Selenite Adsorption Using Manganese Nodule Leached Residues. *Journal of Colloid and Interface Science*, 307, 333 – 339.
- El-Shafey, E.I. 2007a. Removal of Se(IV) from Aqueous Solution Using Sulphuric Acid Treated Peanut Shell. *Journal of Environmental Management*, 84: 620 – 627.
- El-Shafey, E.I. 2007b. Sorption of Cd(II) and Se(IV) from Aqueous Solution Using Modified Rice Husk. *Journal of Hazardous Materials*, 147(1-2): 546 – 555.
- Gao, B., Jiang, P., An, F., Zhao, S., Ge, Z. 2005. Studies on the surface modification of diatomite with polyethyleneimine and trapping effect of the modified diatomite for phenol. *Applied Surface Science*, 250: 273-279.
- Ghosh, M.M., Cox, C.D., Yuan-Pan, J.R. 1994. Adsorption of Selenium on Hydrous Alumina. *Environmental Progress*, 13: 79 – 88.
- Goh, K. H and Lim, T. T. 2004. Geochemistry of Inorganic Arsenic and Selenium in a Tropical Soil: Effect of Reaction Time, pH, and Competitive Anions on Arsenic and Selenium Adsorption. *Chemosphere*, 55(6): 849 – 859.
- Golder Associates Inc. 2009. Literature Review of Treatment Technologies to Remove Selenium from Mining Influenced Water. Report to Teck Coal Limited, Calgary, AB, 40 p.

- Gusek, J., Conroy, K., Rutkowski, T. 2008. Past, Present and Future for Treating Selenium-Impacted Water. Presentation at the 2008 Annual Meeting of the West Virginia Surface Mine Drainage Task Force, Morgantown, WV.
- Hamdaoui, Q., Naffrechoux, E. 2007. Modeling of Adsorption Isotherms of Phenol and Chlorophenols onto Granular Activated Carbon: Part I. Two-parameter Models and Equations Allowing Determination of Thermodynamic Parameters. *Journal of Hazardous Materials*, 147(1-2): 381 – 394.
- Hayes, K.F., Papelis, L. and Leckie, J.O., 1988. Modeling Ionic Strength Effects on Anion Adsorption at Hydrous Oxide/solution Interfaces. *Journal of Colloid Interface Science*, 125: 717 – 726.
- Hu, J., Lo, I.M., Chen, G. 2004. Removal of Cr(VI) by Magnetite Nanoparticle. *Water Science and Technology*, 50(12) 139 – 146.
- IOM (Institute of Medicine). 2000. Dietary Reference Intakes for Vitamin C, Vitamin E, Selenium and Carotenoids. National Academy Press, Washington DC, 506 p.
- Jan, Y.L., Wang, T.H., Li, M.H., Tsai, S.C., Wei, Y.Y., Teng, S.P. 2008. Adsorption of Se Species on Crushed Granite: A Direct Linkage with its Internal Iron-related Minerals. *Applied Radiation and Isotopes*, 66(1): 14 – 23.
- Jang, M., Min, S.H., Kim, T.H., Park, J.K. 2006. Removal of Arsenite and Arsenate Using Hydrous Ferric Oxide Incorporated into Naturally Occurring Porous Diatomite. *Environmental Science and Technology*, 40: 1636 – 1643.
- Jang, M., Min, S.H., Park, J.K., Tlachac, E.J. 2007. Hydrous Ferric Oxide Incorporated Diatomite for Remediation of Arsenic Contaminated Groundwater. *Environmental Science and Technology*, 41: 3322 – 3328.

- Jegadeesan, G., Mondal, K., Lalvani, S.B. 2003. Comparative Study of Selenite Adsorption on Carbon Based Adsorbents and Activated Alumina. *Environmental Technology*, 24(8): 1049 – 1059.
- Jolivet, J.P., Tronc, E. 1988. Interfacial Electron Transfer in Colloidal Spinel Iron Oxide. Conversion of Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3$ in Aqueous Medium. *Journal of Colloid Interface Science*, 125: 688 – 701.
- Jordan, N., Lomenech, C., Marmier, N., Giffaut, E., Ehrhard, J.J. 2009. Sorption of Selenium (IV) onto Magnetite in the Presence of Silicic Acid. *Journal of Colloid and Interface Science*, 329: 17 – 23.
- Khraisheh, M. A., Al-degs, Y.S., Mcminnb, W. A. 2004. Remediation of Wastewater Containing Heavy Metals Using Raw and Modified Diatomite. *Chemical Engineering Journal*, 99(2): 177 – 184.
- Kuan, W.H., Lo, S.L., Wang, M.K. 1998. Removal of Se(IV) and Se(VI) from Water by Aluminum-oxide-coated Sand. *Water Research*, 32(3): 915 – 923.
- Lopez de Arroyave, R., Nikitenko, S.I., Scheinost, A.C., Simonoff, M. 2008. Immobilization of Selenite on Fe_3O_4 and $\text{Fe/Fe}_3\text{C}$ Ultrasmall Particles. *Environmental Science and Technology*, 42: 2451 – 2456.
- Mak, S.Y., Chen, D.H. 2004. Fast Adsorption of Methylene Blue on Polyacrylic Acid Bound Iron Oxide Magnetite Nanoparticles. *Dyes and Pigments*, 61(1): 93 – 98.
- Manceau, A., Gallup, D.L. 1997. Removal of Selenocyanate in Water by Precipitation: Characterization of Copper-Selenium Precipitate by X-ray Diffraction, Infrared, and X-ray Absorption Spectroscopy. *Environmental Science and Technology*, 31: 968 – 976.

- Martinez, M., Gimenez, J., de Pablo, J., Rovira, M., Duro, L. 2006. Sorption of Selenium(IV) and Selenium(VI) onto Magnetite. *Applied Surface Science*, 252: 3767 – 3773.
- Mavrov, V., Stamenov, S., Todorova, E., Chmiel, H., Erwe, T. 2006. New Hybrid Electrocoagulation Membrane Process for Removing Selenium from Industrial Wastewater. *Desalination*, 201(1-3): 290 – 296.
- Meng, X., Letterman, R. 1993. Effect of Component Oxide Interaction in the Adsorption Properties of Mixed Oxides. *Environmental Science and Technology*, 27: 970 – 975.
- Missana, T., Alonso, U., Scheinost, A.C., Granizo, N., García-Gutiérrez, 2009. Selenite Retention by Nanocrystalline Magnetite: Role of Adsorption, Reduction and Dissolution/co-precipitation Processes. *Geochimica et Cosmochimica Acta*, 73(20): 6205 – 6217.
- MII (Mineral Information Institute). 2010. Selenium. Available online at: <http://www.mii.org/Minerals/photoselenium.html>
- MWH Global, Inc. 2005. *Water Treatment Principles and Design*. 2nd edition, John Wiley & Sons, New York, NY, 1948 p.
- Namasivayam, C., Prathap, K. 2006. Removal of Selenite Using ‘Waste’ Fe(III)/Cr(III) Hydroxide: Adsorption Kinetics and Isotherms. *Toxicological and Environmental Chemistry*, 88(1): 85 – 98.
- NAMC (North American Metals Council). 2010. Review of Available Technologies for the Removal of Selenium from Water, Final Report. CH2M Hill, 233 p.

- Navratil, J. D., Akin, A. C. 2009. Mine Water Treatment Using Magnetite and Iron Ferrites. Abstracts of the International Mine Water Conference, South Africa, 439 – 446.
- Neuzil, S.G., Dulong, F.T., Cecil, C.B., Fedorko, N., Renton, J.J., and Bhumbala, D.K., 2007. Selenium Concentrations in Middle Pennsylvanian Coal-bearing Strata in the Central Appalachian Basin: U.S. Geological Survey Open-File Report 2007-1090.
- Nitrogen and Selenium Management Program (NSMP). Identification and Assessment of Selenium and Nitrogen Treatment Technologies and Best Management Practices. Report, March 2007 available online at <http://ocnsmmp.com/team/NSMP%20Task%202.2%20Update%2030Mar07.pdf>
- Oldfield J. E. 2002 Selenium World Atlas. Selenium-Tellurium Development Association. (STDA).
- Parida, K.M., Gorai, B., Das, N.N and Rao, S.B. 1997. Studies on Ferric Oxide Hydroxides. III. Adsorption of Selenite (SeO_3^{2-}) on Different Forms of Iron Oxyhydroxides. Journal of Colloid Interface Science, 185(2): 355-362.
- Persello, J. 2000. Surface and Interface Structure of Silicas. In Adsorption on Silica Surfaces; Papirer, E., Ed.; Marcel Dekker: New York.
- Plant, J.A., Kinniburgh, D.G., Smedley, P.L., Fordyce, F.M., Klinck, B.A. 2007. Arsenic and Selenium. Treatise on Geochemistry, Chapter 9.02, Pages 17 – 66.
- Rovira, M., Gimenez, J., Martinez, M., Martinez-Llado, X., de Pablo, J., Marti, V., (2) Duro, L. 2008. Sorption of Selenium (IV) and Selenium (VI) onto Natural Iron Oxides: Goethite and Hematite. Journal of Hazardous Materials, 150: 279 – 284.

- Séby, F., Potin-Gautier, M., Giffaut, E., Borge, G., Donard, O.F.X. 2001. A Critical Review of Thermodynamic Data for Selenium Species at 25°C. *Chemical Geology*, 171: 173 – 194.
- Schulthess, C.P., Sparks, D.L. 1986. Backtitration Technique for Proton Isotherm Modeling of Oxide Surfaces. *Soil Science Society of America*, 50: 1406 – 1411.
- Sharmasarkar, S., Vance F.G. 2002. Selenite-Selenate Sorption in Surface Coal Mine Environment. *Advances in Environmental. Research*, 7: 87 – 95.
- Su, T., Guan, X., Gu, G., Wang, J. 2008. Adsorption Characteristics of As(V), Se(IV), and V(V) onto Activated Alumina: Effects of pH, Surface Loading, and Ionic Strength. *Journal of Colloid and Interface Science*, 326: 347 – 353.
- Treybal, R.E. 1981. *Mass-Transfer Operations*, 3rd ed., McGraw-Hill.
- Twidwell, L.G., McCloskey, J., Miranda, P, Gale, M., 2000. Technologies and Potential Technologies for Removing Selenium from Process and Mine Wastewaters. *Proceedings Minor Elements, SME, Salt Lake City, UT.*, pp 53-66.
- U.S. EPA (Environmental Protection Agency). 1990. Final Best Demonstrated Available Technology (BDAT) Background Document for K031, K084, K101, K102, Characteristic Arsenic Wastes (D004), Characteristic Selenium Wastes (D010), and P and U Wastes Containing Arsenic and Selenium Listing Constituents, Treatment Technology Section, 124p. EPA530-SW-90-059A
- U.S. EPA (Environmental Protection Agency), 1996. 40 CFR Part 132: Proposed Selenium Criterion Maximum Concentration for the Water Quality Guidance for the Great Lakes System; Proposed Rule. <http://www.gov/EPA-WATER/1996/November/Day-14/pr-21061DIR/pr-21061.txt.html>

- U.S. EPA (Environmental Protection Agency), 2009. National Primary Drinking Water Regulations. Available online at: <http://www.epa.gov/ogwdw000/consumer/pdf/mcl.pdf>
- Wasewar, K.L., Prasad, B., Gulipalli, S. 2009. Adsorption of Selenium Using Bagasse Fly Ash. *Clean – Soil, Air, Water*, 37(7): 534 – 543.
- WHO. 1996. Trace Elements in Human Nutrition and Health. World Health Organization (Geneva).
- WHO. 2003. Selenium in drinking-water. Background document for preparation of WHO Guidelines for drinking-water quality. Geneva, World Health Organization. (WHO/SDE/WSH/03.04/13).
- Wu, C.C., Wang, Y.C., Lin, T.F., Tsao, H.L., Chen, P.C. 2005. Removal of Arsenic from Waste Water Using Surface Modified Diatomite. *Journal of the Chinese Institute of Environmental Engineering*, 15(4): 255 – 261.
- WV DEP, 2008. West Virginia Integrated Water Quality Monitoring and Assessment Report. West Virginia Department of Environmental Protection, Charleston, WV.
- WV Geological and Economic Survey. 2005. Trace Elements in West Virginia Coals. <http://www.wvgs.wvnet.edu/www/datastat/te/index.htm> (accessed Jan., 2010).
- Yudovich, Ya. E., Ketris, M. P. 2006. Selenium in Coal: A Review. *International Journal of Coal Geology*, 67(1,2): 112 – 126.
- Zhang, N., Lin, L.S. and Gang, D. 2008. Adsorptive Selenite Removal from Water Using Iron-coated GAC Adsorbents. *Water Research*, 42: 3809 – 3816.

Zhang, P., Sparks, D.L. 1990. Kinetics of Selenate and Selenite Adsorption/desorption at the Goethite/water Interface. *Environmental Science & Technology*, 24(12): 1848 – 1856.

Zhang, Y.Q., Wang J., Amrhein, C., Frankenberger W.T. 2005. Removal of Selenate from Water by Zero Valent Iron. *Journal of Environmental Quality*, 34: 487 – 495.

VITA

Isabel Cardona was born in Medellin, Colombia. She enrolled in National University of Colombia at Medellin and received her Bachelor Degree in Geological Engineering in June 2003. Later, she continued her graduate studies at the same University obtaining the M.S. degree in Materials and Process Engineering in Spring 2009. She was admitted into West Virginia University in Fall 2008 and pursued her second Master degree in Engineering. During her studies at WVU she worked under the supervision of Dr. Xinchao Wei and her work focused on removal of selenium from aqueous solutions using nano-magnetite impregnated diatomaceous earth.