

# Removal of Selenium from Aqueous Solutions Using Magnetite Nanoparticles as Adsorbent

Xinchao Wei<sup>\*</sup>, Shilpa Bhojappa<sup>\*\*</sup>, Lian-Shin Lin<sup>\*\*</sup>, Roger C. Viadero, Jr.<sup>\*</sup>

<sup>\*</sup>State University of New York Institute of Technology, Utica, NY, USA, weix@sunyit.edu

<sup>\*\*</sup>West Virginia University, Morgantown, WV, USA, lian-shin.lin@mail.wvu.edu

<sup>\*\*\*</sup>Western Illinois University, Macomb, IL, USA, rc-viadero@wiu.edu

## ABSTRACT

Selenium (Se) is a problematic contaminant for many regions worldwide. Adsorption is by far the most researched and most promising method in treating Se laden waters. The major limitations in using those adsorbents are the preferential adsorption for either selenite ( $\text{SeO}_3^{2-}$ ) or selenate ( $\text{SeO}_4^{2-}$ ) and interferences by anions such as phosphates. The objective of this study was to remove Se from aqueous solutions using the synthesized magnetite nanoparticles as an adsorbent. In this study, a series of batch adsorption experiments were performed to study the effects of pH, temperature, concentration, contact time, and presence of competing anions on Se removal efficiency. Compared with either natural magnetite ( $<5\mu\text{m}$ ) or nano-iron ( $\sim 10\text{ nm}$ ), magnetite nanoparticles ( $10\text{-}20\text{ nm}$ ) were more effective as an adsorbent for selenite, while nano-iron was found to perform better to remove selenate.

## 1 INTRODUCTION

Selenium (Se), is a problematic contaminant for many regions globally. Although Se can be released to the environment naturally due to its natural occurrence in the soil, rocks, coal and minerals, Se pollution is often caused by anthropogenic processes such as mining of coal and minerals and utilization of these resources (Lemly, 2004; Adams and Pennington, 2005; Renner, 2005). At low concentrations, Se is an essential micronutrient for humans and animals, but considered toxic when ingested in amounts higher than those needed for optimum nutrition. Drinking water regulations on Se vary from country to country and most countries adopt the  $10\text{ }\mu\text{g-Se/L}$  limit of World Health Organization (WHO) guideline (WHO, 2003). In the U.S., the current limit for both the maximum contaminant level (MCL) and the MCL goal (MCLG) for Se is still  $50\text{ }\mu\text{g-Se/L}$  set by Environmental Protection Agency (EPA), although a new limit of  $5\text{ }\mu\text{g-Se/L}$  is being proposed. In the U.S. Clean Water Act (CWA), Se is listed as a priority toxic pollutant. The freshwater acute and chronic criteria are  $20\text{ }\mu\text{g-Se/L}$  and  $5\text{ }\mu\text{g-Se/L}$ , respectively, and Se concentrations above these levels can pose a serious risk

to aquatic life and humans due to the possibility of Se bioaccumulation through the food chain.

Different processes have been developed to remove Se from water and wastewater. The conventional water treatment practices such as lime neutralization, softening and ferric coagulation can remove Se to certain levels. The shortcomings of these processes are the high residual Se concentrations in the treated water and Se-containing sludges. Ion exchange and membrane processes such as reverse osmosis, nanofiltration, and emulsion liquid membranes can effectively remove Se species. However, they are complicated processes and very expensive in treating large amount of Se containing wastewater. (Twidwell, 2005; Mavrov et al., 2006; Gleason et al., 1996). Reduction of Se to other species can facilitate its removal. However, generation of large volumes of sludge, high cost of reagents and interferences by dissolved oxygen and other anions are factors that affect the wide application of this technique (Mavrov et al., 2006). Se can also be removed biologically (Hunter and Manter, 2009; Takada et al., 2008). However, the operating time and size of bioreactors are the obvious challenges. Various adsorbents have been tested for Se removal, such as alumina, activated carbon, manganese nodule leached residues sulphuric acid-treated peanut shell and various iron oxides/hydroxides (El-Shafey, 2007; Dash and Parida, 2007). The iron-based adsorbents include amorphous iron oxyhydroxide (Parida et al., 1997; Balistrieri and Chao, 1990; Benjamin, 1983), goethite (Zhang and Sparks, 1990), ferrihydrite (Parida et al., 1997), 'waste' iron (III) hydroxide (Namasivayam and Prathap, 2006), hematite and magnetite (Martinez et al., 2006), goethite and hematite (Rovira et al., 2008), and iron-coated granular activated carbon (Zhang et al., 2008). The drawback of those adsorbents is their preferential adsorption for either selenite ( $\text{SeO}_3^{2-}$ ) or selenate ( $\text{SeO}_4^{2-}$ ) and their performance can be hindered by anions such as phosphates.

Magnetite nanoparticles, as a nano-sorbent, have received significant attention because they are relatively inexpensive to make, safe to handle, and friendly to the environment. Magnetite particles have been studied as an adsorbent to remove such contaminants as  $\text{Cr}^{6+}$  (Hu et al., 2004), methylene blue (Mak and Chen, 2004), and Cu,

Zn, As and dichlorophenol (Cumbal and SenGupta, 2005) from aqueous solutions. This work was to develop an adsorption process to remove selenite and selenate from water and wastewater using magnetite nanoparticles. In order to compare the effectiveness of magnetite nanoparticles, tests were also performed using natural magnetite (< 5 µm) and zero-valent nano-iron (~10 nm).

## 2 MATERIALS AND METHODS

Analytical grade chemicals were used for this study. All chemical solutions were prepared using Millipore de-ionized water. A stock solution of 100 mg-Se/L (either selenite or selenate) was prepared with de-ionized water and working solutions (50, 100, 250, 500 and 1000 µg-Se/L) for the adsorption experiments were prepared from the stock solution. Synthesis of magnetite nanoparticles was performed under room temperature using a coprecipitation method developed by Wei and Viadero (2007). Particle sizes were analyzed by a transmission electron microscope (TEM) and estimated to range from 10 to 20 nm. The amounts of adsorbents applied in the experiments were reported in grams of dry weight. Natural magnetite (<5 microns, Fe<sub>3</sub>O<sub>4</sub>) was acquired from Cerac Inc. (Milwaukee, WI) and zero-valent nano-iron (~10 nm, element Fe) was obtained from Quantum Sphere (Santa Ana, CA).

Batch adsorption experiments were conducted by agitating 100 ml of Se (selenite or selenate) solutions of varying concentrations with predetermined amounts of the three adsorbents (0.1, 0.5, 1.0, 2.0 and 5.0 g/L) in a temperature-controlled shaker (200 rpm) at 25°C for 24 h. After adsorption, each mixture was then subject to a magnet to separate magnetite nanoparticles from the solution and the supernatant was subsequently filtered through a 0.45 µm membrane filter. Se concentration was measured using a graphite furnace atomic absorption spectrometer (GFAAS, Varian SpectrAA 210 Zeeman). To study the effect of contact time, adsorption tests were allowed to take place for different periods of time ranging from 5 to 1440 min with two initial Se concentrations (100 or 250 µg-Se/L) at pH 4 and at 25°C. The effect of pH was studied for the range of 2 – 9. Temperature effects were evaluated for the range of 25 – 45°C for three initial Se concentrations (100, 250 and 500 µg-Se /L).

Three competing anions (chloride, sulfate and nitrate) were studied for their effect on Se adsorption. The experiments were conducted at 25°C, pH 4.0 ± 0.1 and adsorbent dose of 0.1 g/L for a contact time of 24 h. The concentrations of the various anionic species were controlled at 0.05 M. The effect of sulfate anions was further investigated by varying its concentrations (0.01, 0.03, 0.05 and 0.1 M). All adsorption tests were carried out in triplicates and the mean values were reported.

## 3 RESULTS AND DISCUSSION

From the contact time tests for two initial Se concentrations of 100 µg-Se/L and 200 µg-Se/L, rapid adsorption was observed in the first 30 min (with almost 50% removal of selenite), thereafter the adsorption slowed down and gradually reached equilibrium after 24 h. A similar behavior was reported by Goh and Lim (2004) and the Se adsorption on a tropical soil was rapid in the first hour, plateaued after 8 h and approached equilibrium at about 24 h. Other studies in the literature using iron oxide as adsorbents reported comparatively shorter time required to reach adsorption equilibrium, such as 2 h for adsorption of selenite on different forms of iron oxyhydroxides and ferrihydrite (Parida et al., 1997).

From the tests using different doses of three types of adsorbents, it was found the Se concentration decreased with increasing doses for all adsorbents. The magnetite nanoparticles synthesized for this study demonstrated a superior adsorption capacity in removing selenite compared to the nano-iron and natural magnetite. A final concentration of < 5 µg-Se/L was achieved at a dose of 0.1 g/L and the adsorption capacity is about 1 mg-Se per gram of adsorbent. The greater surface area of the magnetite nanoparticles in comparison to the natural magnetite (<5 µm) might be responsible for better selenite adsorption. The poor performance of nano-iron could be due to the severe agglomeration and/or surface oxidation during storage.

In the case of selenate adsorption, natural magnetite was clearly ineffective in removing selenate from aqueous solutions. Nano-iron was found to have best adsorption for selenate among the three adsorbents, which might be contributed to its reducing power which can convert selenate to selenite (Mavrov et al., 2006). From the results of both Se species, nano-iron demonstrated similar adsorption performance for both selenite and selenate, while magnetite nanoparticles showed lower adsorption for selenate than for selenite. The lower adsorption of magnetite for selenate is not in agreement with a previous study by Martinez et al. (2006), who found that magnetite had similar or greater adsorption for selenate as compared to selenite.

The pH had significant effect on selenite adsorption by magnetite nanoparticles. The final Se concentration increased as pH increased from 4.0 to 9.0, indicating that lower pH favored Se adsorption. This behavior could be attributed to two theories, namely surface charge and speciation of Se in aqueous solution. From the results of temperature tests, it was observed that the final selenite concentration decreased as temperature increased from 25°C to 45°C, indicating high temperatures favored selenite adsorption. This finding was in an agreement

with previous studies, in which selenite removal was achieved using iron-coated granular activated carbon (GAC) (Zhang et al., 2008).

The thermodynamic parameters of adsorption, such as free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ_{ads}$ ), and entropy ( $\Delta S^\circ$ ), were calculated using the test data. The value of  $\Delta G^\circ$  was negative indicating the spontaneity of the adsorption process. The value of  $\Delta H^\circ_{ads}$  was positive, which explains why the elevated temperature led to enhanced selenite adsorption. The positive value of entropy change ( $\Delta S^\circ$ ) revealed an increase in randomness at the solid/liquid interface due to the adsorption of selenite onto magnetite nanoparticles. Adsorption isotherm study indicated adsorption of selenite onto the surface of nano-magnetite followed the Freundlich isotherm, and Se adsorption took place heterogeneously. Kinetic study revealed the pseudo-second-order kinetic was suitable to model the adsorption process.

The presence of chloride and nitrate caused a slight decrease in selenite adsorption, while sulfate at 0.05 M did not significantly affect the adsorption capacity of magnetite nanoparticles. Because sulfate is commonly presented in mining impacted waters, further investigation with different ionic strength of 0.01, 0.03, 0.05 and 0.1 M of sulfate was carried out and proved the presence of sulfate did not interfere Se adsorption by magnetite nanoparticles.

## 4 CONCLUSIONS

Synthesized magnetite nanoparticles were used as an adsorbent in this study to remove Se from aqueous solutions. Compared with either natural magnetite ( $<5\mu\text{m}$ ) or nano-iron ( $\sim 10\text{ nm}$ ), magnetite nanoparticles (10-20 nm) were a better adsorbent for selenite, while nano-iron showed better adsorption for selenate. The results indicated that magnetite nanoparticles can remove Se to a level of  $< 5\ \mu\text{g-Se/L}$ . The high selenite removal efficiency in low pH range ( $<4$ ) was an advantage for magnetite nanoparticles to be used in treating low pH waters. Adsorption of selenite onto magnetite nanoparticles was found to be a spontaneous, endothermic process. The selenite adsorption followed the Freundlich isotherm model and presence of common anions did not significantly affect the adsorption capacity of magnetite nanoparticles for selenite. The Se adsorption demonstrated magnetite nanoparticles could be a very effective nano-sorbent for Se species.

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