SELENITE SORPTION BY CARBONATE SUBSTITUTED APATITE

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Abstract

The sorption of selenite, SeO_3^{2-} , by carbonate substituted hydroxylapatite was investigated using batch kinetic and equilibrium experiments. The carbonate substituted hydroxylapatite was prepared by a precipitation method and characterized by SEM, XRD, FT-IR, TGA, BET and solubility measurements. The material is poorly crystalline, contains approximately 9.4% carbonate by weight and has a surface area of $210.2 \text{ m}^2/\text{g}$. Uptake of selenite by the carbonated hydroxylapatite was approximately an order of magnitude higher than the uptake by uncarbonated hydroxylapatite reported in the literature. Distribution coefficients, K_d , determined for the carbonated apatite in this work ranged from approximately 4,200 to over 14,000 L/kg. A comparison of the results from kinetic experiments performed in this work and literature kinetic data indicates the carbonated apatite synthesized in this study sorbed selenite 23 times faster than uncarbonated hydroxylapatite based on values normalized to the surface area of each material. The results indicate carbonated apatite is a potential candidate for use as a sorbent for pump-and-treat technologies, soil amendments or for use in permeable reactive barriers for the remediation of selenium contaminated sediments and groundwaters.

Capsule

The sorption of selenite by carbonated apatite including distribution coefficients and kinetic data are reported.

Keywords selenium, selenite, carbonated apatite, apatite, sorption, kinetics

Introduction

Selenium occurs naturally in very low amounts, 50 – 1700 µg/kg sediment, and is ubiquitous in the environment (Parkman and Hultberg, 2002; Preedy and Watson, 2005). Higher concentrations of selenium are from man-made sources including agriculture, mining, and coal ash. Selenium is a nutrient required in small quantities for animals, however, in higher concentration it is highly toxic resulting in selenosis or death (Bond, 2000; U.S. G.A.O., 2012). Selenium is easily taken up by plants that are consumed by animals and as a result selenium poisoning has resulted in significant livestock, elk, deer and fish kills (U.S. G.A.O., 2012). Furthermore, Selenium contamination of groundwater is a worldwide problem.

In the environment, selenium can be found in four oxidation states depending on the local redox conditions. Under strong to moderate oxidizing conditions, selenate (SeO_4^{2-}) is predominant. In mildly reducing conditions, selenite (SeO_3^{2-}) is the predominant species. Under strongly reducing conditions, the HSe^- is the predominant species (Elrashidi et al., 1987; Séby et al., 2001). Selenate and selenite are the most significant species under typical groundwater and surface water conditions and are both very water soluble. However, they are distinctive in that selenate does not absorb extensively to natural materials whereas selenite will sorb weakly to clays and more strongly to Fe and Ca based minerals (Shrimpton et al., 2015). Furthermore, selenites are stable in alkaline to mildly acidic conditions (Shamberger, 1981).

Currently, there are no inexpensive and easily implemented technologies for remediation of selenium contaminated groundwater. Methods to remove selenium from water and groundwater include phytoremediation (Esringü and Turan, 2012), biological

treatment (Hageman et al., 2013), ion exchange, evaporation, chemical treatment and filtration (Bond, 2000) and permeable reactive barriers (PRB) (Zhang et al., 2008). All of these methods with the exception of using PRB are active treatment technologies that have significant capital costs, create waste streams, can expose workers to the contaminant and have significant long-term operational costs (Moore, 2003; Moore et al., 2004; Naftz et al., 2002). Typically, the reactive media used in PRBs are ion exchange media including activated carbon and natural minerals.

The sorption of selenium is reported for several minerals including calcite (Aurelio et al., 2010; Fujikawa and Fukui, 1997; Heberling et al., 2014), magnesium bearing minerals (Opiso et al., 2016), maghemite (Jordan et al., 2013), hematite and magnetite (Fujikawa and Fukui, 1997), iron oxides (Duc et al., 2003) and apatites (Duc et al., 2003; Monteil-Rivera et al., 1999, 2000). The latter and its ability to sorb selenite is the focus of the current study.

The apatite mineral group consists of calcium phosphate compounds with a hexagonal dipyramidal crystal structure and includes hydroxylapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. It has long been recognized that the apatite group has strong sorptive properties for many radionuclides, heavy metals and other compounds, and many different substitutions can be made into the apatite structure (Ewing and Wang, 2002; Rakovan and Pasteris, 2015; White et al., 2005).

Monteil-Rivera et al. (1999, 2000) studied the sorption of selenite by hydroxylapatite in batch sorption experiments. The authors report that selenite substitutes into the apatite structure for orthophosphate and that selenium is not exclusively located at the surface of the hydroxylapatite, but also diffused slightly into the structure. The sorption of selenium as selenite by hydroxylapatite, fluorapatite and iron oxides is reported by Duc et al. (2003). In this study, the sorption of selenite by hydroxylapatite is

shown to be pH dependent with the highest uptake occurring at a pH of approximately 8. Sorption by fluorapatite was not significantly affected by pH but the total uptake of selenite was 2 to 3 orders of magnitude less than that measured for hydroxylapatite. Furthermore, the authors indicate the mechanism for selenite uptake by sorption to the hydroxylapatite surface followed by substitution for orthophosphate in the crystal structure. They conclude that hydroxylapatite can be used as an additive in engineered permeable reactive barriers for sorption of selenium.

In the studies of Monteil-Rivera et al. (1999) and Duc et al. (2003) the kinetics of selenite uptake by hydroxylapatite is reported to be very slow requiring more than 100 hours to reach equilibrium. This suggests that for areas with rapid groundwater flow, the residence time for selenium contaminated groundwater in a PRB may not be sufficient for complete uptake of selenium. Additionally, pump and treat methods would have to be excessively large.

The present study focuses on the use of carbonated apatite as a sorbent for selenite in batch equilibrium and kinetic experiments. The structure and properties of carbonated apatites differ significantly from hydroxylapatite and these differences may affect selenite uptake. Uptake of selenite by apatite through substitution for orthophosphate can be affected by two factors; dissolution rate of the apatite and rate of substitution of selenite for orthophosphate. Carbonated apatites are reported to have faster dissolution rates and higher solubility than hydroxylapatite (Pan and Darvell, 2010). The mechanism of selenite uptake by carbonated apatite may also be different than for hydroxylapatite. Kolmas et al. (2014) report that the substitution of selenite for orthophosphate occurs with simultaneous decalcification and dehydroxylation in order to maintain a charge

balance in the hydroxylapatite structure. Alternatively, the substitution of selenite for orthophosphate could also occur with the simultaneous substitution of a monovalent cation such as sodium for calcium into the apatite to maintain a charge balance in the apatite structure. For carbonated apatites, the substitution mechanism could be through the substitution of selenite for carbonate and/or phosphate. However, it is beyond the scope of this paper to determine the mechanism of selenite uptake by carbonated apatite. In this initial study, we examine selenite uptake rates and distribution coefficients and compare the data to literature data for selenite substitution into hydroxylapatite.

Materials and methods

Carbonate substituted spatite

All chemicals used were reagent grade. Deionized water used in the work was purified by reverse osmosis followed by filtration through activated carbon. Carbonated apatite was prepared using a modification of the precipitation method described by Frank-Kamenetskaya et al. (2011). A 0.35 L solution containing 0.053 M CaNO_3 was slowly mixed with 0.35 L of a solution containing 0.0107 M NaHPO_4 and 0.021M NaHCO_3 over a 4 hr. period in a 1 L flask thermostated at 32°C. In this synthesis method the concentration of NaHPO_4 is low relative to NaHCO_3 to encourage the formation of carbonated apatite. The low temperature precipitation method has been shown produce a poorly crystalline apatite with a high sorption capacity relative to highly crystalline apatites produced by hydrothermal methods (Frank-Kamenetskaya et al., 2011). All solutions were degassed before mixing by sparging with ultrapure argon and the initial pH of each solution was adjusted to 7.4 using 0.01M HCl and/or 0.01M NaOH solutions. After the solutions were mixed the resulting slurry was stirred and maintained at 32°C for

an additional 24 hours. The precipitate was removed by vacuum filtration, rinsed with distilled water and dried under vacuum at ambient temperature for 24 hours. The dried precipitate was then ground into a fine powder.

The precipitate was examined using a Bruker D8 Advanced X-Ray Diffractometer (XRD) (scanning at 2 sec. per data point with a 0.02 degree step size), a Thermo-electron Corporation Nicolet FT-IR 380 Fourier Transform-Infrared Spectrometer (FT-IR) and a JEOL Scanning Electron Microscope (SEM). The surface area of the precipitate was determined by Brunauer, Emmett and Teller (BET) analysis using a Micromeritics Instrument Corp. Tristar 3000.

The amount of carbonate in the apatite was determined by thermogravimetric analysis (Venkatesan et al., 2015) using a SDT Q600 thermogravimetric analyzer. The carbonated apatite sample was heated to different temperatures and held at each temperature for 30 min. The ramping temperature was 10°C per min. Samples were heated to 160°C to remove water adsorbed to the carbonated apatite surface, to 400°C to remove additional water inside the carbonated apatite structure and finally to 950°C to assure that all carbonate in the structure was converted to carbon dioxide. The amount of water and carbonate loss was determined gravimetrically.

Carbonated apatite solubility

The solubility of the carbonated apatite was determined at pH values of 5, 6, 9, and 11. Experiments were performed by placing 40 mg of carbonated apatite in 20 mL of deionized water and gently agitating the mixtures for 7 days. The pH of the solutions was measured and, if necessary, adjusted each day with 0.01M HCl and/or 0.01M NaOH. After 5 days no further change in pH was observed in the mixtures. Samples were

withdrawn using a syringe, filtered through a 0.40 μm syringe filter and acidified with 0.1 M HNO_3 . Calcium and phosphate concentrations were then determined by ion chromatography.

Kinetic experiments

Kinetic experiments were performed by using a batch method. Eighty milligrams of carbonated apatite were added to 40 mL of solution. The background electrolyte was 0.1M KNO_3 (Duc et al., 2003; Monteil-Rivera et al., 2000). It is known that potassium and nitrate do not strongly interact with apatite, carbonated apatite or selenium. The system was gently agitated on a shaker table and allowed to equilibrate for 7 days prior to initiation of kinetic experiments. This step ensures dissolution is not the limiting process in reaching equilibrium (Monteil-Rivera et al., 2000). The pH of the mixture was maintained 8.0 by addition of 0.01M HCl and/or 0.01M KOH , if necessary. After 5 days, the pH of the mixture remained constant. Na_2SeO_3 was added to give an initial selenium concentration of 68 mg/L and the pH was adjusted daily if necessary. Aliquots of the liquid phase, 0.2 mL, were withdrawn periodically using a syringe, filtered through a 40 μm syringe filter and acidified with 0.01M HNO_3 . The amount of selenium in the samples was determined by ICP-MS. Blanks containing only selenite with no carbonated apatite for the kinetic and equilibrium experiments indicated selenium was not sorbing to the containers, syringes or filters.

Equilibrium experiments

Equilibrium experiments were performed by adding 40 mg of carbonated apatite to 20 mL solutions of 0.1M KNO_3 in polycarbonate vials. Experiments were performed over a range of pH from 6 to 12 and at two different initial selenite ion concentrations of

6.33×10^{-3} moles/L and 2.42×10^{-2} moles/L. The carbonated apatite containing solutions were allowed to equilibrate for 7 days prior to adding the selenite and the pH was adjusted each day if necessary with 0.01M NaOH and/or 0.01M HCl. Na_2SeO_3 was added to each mixture and gently agitated on a shaker table for 5 days. The pH of each vessel was monitored and adjusted if necessary with HCL or NaOH. At the end of 5 days, samples of the liquid phase were withdrawn and analyzed.

A single reversibility experiment was performed by combining 80 mg of carbonated apatite with 1.72 mg sorbed selenium in 40 ml of 0.1M KNO_3 solution. The mixture was gently agitated on a shaker table and after 48, 96 and 200 hours the solution phase was analyzed as previously described.

Results and discussion

Analysis of carbonated apatite

Figure 1 is an XRD pattern of 2θ vs. intensity for the carbonated apatite that was scanned from 2θ of 5° to 60° . The pattern clearly indicates the poor crystallinity of the material. Poor crystallinity is typical for apatites prepared at low temperature and for highly-substituted material. The peak at $2\theta = 26.8^\circ$ corresponds to the (002) plane and the peak between $2\theta = 31^\circ$ to 34° corresponds to the (211, 112 and 300) planes in the apatite structure. The FT-IR pattern for the carbonated apatite was determined from 500 to 4000 cm^{-1} and is given in Figure 2. The pattern shown is typical for carbonated apatite with IR vibrational bands for carbonate substituted into the apatite shown at 873 and 1400-1550 cm^{-1} (LeGeros, 1991). Figure 3 is an SEM image of the carbonated apatite. The material is composed of small irregular shaped sub-micron sized agglomerated particles that are

typical for carbonated and poorly crystalline hydroxylapatite (LeGeros, 1991). Analysis of the carbonated apatite by the thermogravimetric method indicates the material contains

Figure 1. XRD pattern for carbonated apatite prepared in this work.

Figure 2. FT-IR pattern of the carbonated apatite.

Figure 3. SEM image of the carbonated apatite.

6% water sorbed onto the surface, 3.5% water in the structure of the material and 9.4% carbonate that has been substituted for phosphate. BET analysis indicated the material has a surface area of 210.2m²/g.

Carbonated apatite solubility

The solubility of the carbonated apatite is shown in Figure 4 as a plot of calcium and phosphate concentration in solution as a function of pH. The propagated error in each measurement, represented in the figure as error bars, was calculated based on the error in the analytical procedures used, the residual standard deviation reported for the ICP-MS, round off error in calculations. The solubility of the carbonated apatite is relatively high

Figure 4. Concentrations of Ca and PO₄ in solution as a function of pH for carbonated hydroxylapatite in 0.1M KNO₃

in acidic solution but rapidly drops off in basic solutions. This is typical for apatites in general (LeGeros, 1991).

For pure hydroxylapatite, solubility values reported in the literature vary widely with significantly higher solubility of apatites in the acidic region. Solubility measurements for hydroxylapatite by Liu et al. (2015) report a Ca^{2+} concentration of approximately 10 mg/L at a pH of 5. This value is significantly lower than the value reported for carbonated apatite used in our study. The difference can be attributed to several factors. The hydroxylapatite used in the Liu et al. (2015) study was heat treated at 150°C for 8 hr. prior to use. The carbonated apatite synthesized in this work was heated only to 32°C. Additionally, the XRD pattern for the Liu et al. (2015) carbonated apatite indicates it is significantly more crystalline than the carbonated apatite used in our study. A comparison of the FT-IR patterns of both materials indicate the carbonated apatite used in our work contains significantly more carbonate than the material used by Liu et al. (2015). All of these factors can significantly affect solubility as discussed by LeGeros (1991) and Pan and Darvell (2010).

Selenium sorption experiments

Kinetic experiments

A kinetic experiment was performed to determine the time required to reach equilibrium between selenite taken up by carbonated apatite and that remaining in solution. This information is required to determine the correct parameters for performing equilibrium experiments. The results from the kinetic experiment are given graphically in Figure 5 as a plot of selenium in solution vs. time. The propagated error in each

measurement is represented by the error bars. Uptake of selenium was complete in approximately 300 min. with 1.72 mg selenium sorbed by 80 mg carbonated apatite.

No other data for selenium uptake by highly carbonated apatite could be located in the literature. However, the data can be compared to data by Monteil-Rivera et al. (1999) for the uptake of selenite by hydroxylapatite. In their study, the researchers used a commercially available hydroxylapatite from Bio-Rad Laboratories. The authors provide two limiting formulae for their hydroxylapatite:

Their kinetic experiments were performed with a solution to solid ratio of 250 mL/g with initial selenium concentrations of 1×10^{-3} and 1×10^{-5} molar.

Figure 5. Sorption of selenium (IV) as a function of time in minutes (min.). 80 mg of carbonated apatite was placed in 40 mL of 0.1M NaNO_3 solution. Initial selenium concentration was 67 mg/L. Selenium in the solution phase was determined by ICP-MS.

With an initial selenite concentration of 1×10^{-3} mol/L, the authors report approximately 1.27 mg of selenium was sorbed by 100 mg hydroxylapatite in 100 hours. In this work, 1.72 mg of selenium was sorbed by 80 mg carbonated apatite in approximately 300 min. A direct comparison between the two studies is complicated because factors other than carbonate substitution must be considered. These include apatite solubility, the presence of other ions in the apatite structure, surface area and experimental conditions. The data are best compared by normalization to the mass of sorbent. In the Monteil-Rivera et al. (1999) study the total mass uptake of selenium is reported to be 12.7 mg/g with an uptake rate of 0.127 mg/g hr. In the present work, the carbonated apatite had a total uptake of 21.5 mg/g at a rate of 4.3 mg/g hr. The total amount of Se sorbed is approximately two times more for the carbonated apatite than for the hydroxylapatite used by Monteil-Rivera et al. (1999). Additionally, the kinetics are significantly faster with the carbonated apatite being twenty times faster than what is reported for the hydroxylapatite. These large differences may be attributed not only to differences in experimental conditions and physical and chemical properties of the sorbents but also to different mechanisms of selenite uptake.

Equilibrium experiments

The equilibrium data was used to calculate distribution coefficients, K_d , values, defined as:

$$K_d = [\text{Se}]_{\text{sorbed}} / [\text{Se}]_{\text{liquid phase}}$$

Where $[\text{Se}]_{\text{sorbed}}$ and $[\text{Se}]_{\text{liquid phase}}$ are the amount of selenium sorbed (mg Se sorbed/kg carbonated apatite) and the amount of selenium in the liquid phase (mg Se in the liquid phase/L of solution), respectively.

Figure 6 gives the K_d values plotted as a function of pH for two different initial selenium concentrations of $6.33 \times 10^{-3} \text{ M}$ and $2.42 \times 10^{-2} \text{ M}$. The error bars represent the propagated error in each measurement. Maximum selenium sorption occurs between pH 8.5 and 9 and drops off as the solution is more acidic and basic regions.

Sorption of selenium in the Monteil-Rivera et al. (2000) study occurs with a maximum at pH 7.8 to 8.0 with K_d values of 200 L/mol (182 L/kg) and 800 L/mol (729 L/kg) for initial selenium concentrations of $1 \times 10^{-3} \text{ moles/L}$ and $1 \times 10^{-6} \text{ moles/L}$, respectively. In the present study, the maximum selenite sorption is observed between pH

Figure 6. Distribution coefficient, K_d , as a function of pH for selenite uptake by carbonated apatite.

8.5 and 9.0 with K_d values of 4,200 L/kg and 14,000 L/kg for initial selenium concentrations of 2.42×10^{-2} moles/L and 6.33×10^{-3} moles/L, respectively. If the K_d values in this work and the work the Monteil-Rivera et al. (2000) for hydroxylapatite are normalized to the mass of sorbent or surface area of sorbent, the K_d values measured in this work for carbonated apatite are still an order of magnitude larger.

A single reversibility experiment was performed by placing 80 mg of carbonated apatite with 1.72 mg sorbed selenium in 40 ml of 0.1M KNO_3 solution. After 48 and 96 hours 0.0652 mg and 0.0812 mg of selenium was released into solution. These values correspond to 3.7 % and 4.7%, respectively. After 96 hours and at 200 hrs. no additional release of selenium was detected.

The kinetic and equilibrium data for carbonated apatite indicate it outperforms hydroxylapatite for selenite uptake in experiments performed under similar conditions reported in the literature. However, to identify the mechanism resulting in faster kinetics and increased uptake of selenite by the carbonated apatite will require additional experiments. Unfortunately, the concentration of selenium sorbed by the carbonated apatite is too low for accurate analysis using the analytical instruments and techniques available to us at the time of this work. Future experiments will be performed with more sensitive analytical methods.

Conclusions

In this work, a poorly crystalline carbonated apatite containing approximately 9.4% carbonate was synthesized by a precipitation method and characterized by multiple analytical methods. Batch kinetic and equilibrium experiments indicate carbonated apatite uptakes selenite more effectively and significantly faster than that reported for

hydroxylapatite in the literature. The results indicate carbonated apatite may be a better candidate than hydroxylapatite for remediation of selenium contaminated sites in pump and treat operations, permeably reactive barriers and as a soil amendment. The next phase of this work will be to investigate selenium uptake and desorption from carbonated apatite under varying chemical conditions as well as to determine the mechanism of selenite uptake by carbonated apatite.

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Declaration of interest

The authors have no conflict of interest to declare.

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