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INVESTIGATION OF THE EFFECT OF PHOSPHATE ON IRON(II) SORPTION TO IRON OXIDES

by

Cristina Paola Fernández-Baca

A thesis submitted in partial fulfillment
of the requirements for the Master of
Science degree in Civil and Environmental Engineering
in the Graduate College of
The University of Iowa

May 2010

Thesis Supervisor: Associate Professor Michelle M. Scherer

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Graduate College
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Iowa City, Iowa

CERTIFICATE OF APPROVAL

MASTER'S THESIS

This is to certify that the Master's thesis of

Cristina Paola Fernández-Baca

has been approved by the Examining Committee
for the thesis requirement for the Master of Science degree in Civil and Environmental Engineering at the May 2010 graduation.

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Richard L. Valentine

To my mother.

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I would sincerely like to thank everyone in Scherer lab for showing me the way around a lab, special thanks to Rob Handler, without whom I would not even be able to use a micropipette. Thanks also must be given to all the amazing professors I have had at the University of Iowa, including those on my thesis committee: Michelle Scherer, Gene Parkin, and Richard Valentine. They have all been an essential part of my college career, and have taught me how to be an engineer but also how to live a well-rounded and satisfying life.

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ABSTRACT

Iron is ubiquitous in the environment mostly as stable iron hydr(oxides) such as hematite (α-Fe_2O_3) and goethite (α-FeOOH). The Fe(II)-Fe(III) redox couple plays a vital role in nutrient cycling, bacteria respiration, and contaminant removal. This redox couple, however, can be affected by external influences such as anion adsorption of sulfate, oxalate, and phosphate which can influence various goethite properties including the point of zero charge. This study attempts to determine the effect of phosphate sorption to a goethite surface and its subsequent influence on Fe(II) sorption. The objectives, specifically, were to quantify phosphate sorption on a goethite surface using colorimetric methods and to use Mössbauer spectrometry to determine if electron transfer occurred after a layer of phosphate was adsorbed to the goethite surface. The hypothesis of this study is as follows: an adsorbed layer of phosphate on a goethite surface will inhibit the electron transfer between the Fe(II) and Fe(III) phases at the surface.

The results of the study showed that phosphate follows typical anion sorption as seen in previous works, where more phosphate sorbed at lower pH values. In addition, with increasing aqueous phosphate concentrations there is increasing phosphate adsorption to the goethite surface. However, phosphate sorption was not significantly affected by reaction time after 20 hours or by changes in Fe(II) concentrations. Fe(II) sorption pH edges showed characteristic cation adsorption, where more Fe(II) sorbed at higher pH values. Fe(II) sorption was not affected by the presence or absence of phosphate, but was affected by an increase in the aqueous Fe(II) concentration. With increased Fe(II) there was a pH edge shift to a higher pH, which is consistent with Ca^{2+} sorption results on goethite. An Fe(II) isotherm was also conducted and showed that as Fe(II) concentration increased so did Fe(II) sorption, however the isotherm appeared to be approaching a plateau where the goethite surface sites would be saturated, below this limit the surface sites where not saturated.

Mössbauer analysis was conducted on a sample by Drew Latta, spectra showed that electron transfer was still occurring despite the adsorbed phosphate layer, disproving our initial hypothesis. It is possible that a higher concentration of phosphate could inhibit electron transfer, but at 500 μM PO_4^{3-} and 100 μM Fe(II), electron transfer between the adsorbed Fe(II) and bulk phase Fe(III) still occurred.

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CHAPTER 1: INTRODUCTION

Overview

Iron (Fe) is ubiquitous in the environment as both iron(II) and iron(III), and found most commonly in metal hydr(oxides) such as hematite (α-Fe_2O_3) and goethite (α-FeOOH). It is the fourth most abundant element in the Earth's crust and contributes to metal and nutrient cycling, pollutant removal, and even bacteria respiration [1-3]. Iron has been shown to play a major role in contaminant removal of pollutants such as arsenic [4-5] and chromium [6]. Many important environmental cycles, such as the phosphorous and nitrogen cycles, are also greatly influenced by the Fe(II)-Fe(III) redox couple. This redox couple is prevalent in the environment, and is affected by other ions especially in groundwater systems. Anions such as phosphate have the potential to inhibit the Fe(II)-Fe(III) redox couple's oxidation-reduction potential, subsequently affecting the aforementioned nutrient cycling, pollutant removal, bacteria respiration and more.

Fe(II)-Fe(III) Electron Transfer

Until recently, it was thought that increased reactivity of mineral surfaces was due to an adsorbed layer of an Fe(II) phase which lowered the redox potential of the Fe(II)-Fe(III) couple [7]. Recent studies have proposed that electron transfer may occur between the sorbed Fe(II) phase and the bulk Fe(III) phase [8-9]. Dissolution and recrystallization of the goethite particle through electron transfer depends on the surficial interactions of the dissolved Fe(II) phase with the goethite (α-FeOOH) particles. After sorption of the Fe(II) phase, it appears that electrons are transferred from the adsorbed to the bulk phase, resulting in an oxidized surface layer [9] according to the following reactions (Equations 1 and 2).

$$Fe^{III}OOH + Fe^{II} \rightarrow Fe^{III}OOH - Fe^{II} \qquad \text{(eqn 1)}$$

$$Fe^{III}OOH - Fe^{II} \rightarrow Fe^{II}OOH - Fe^{III} \qquad \text{(eqn 2)}$$

Equation 1 shows the adsorption of Fe(II) to a goethite surface ($Fe^{III}OOH$) and Equation 2 shows the actual electron transfer between the two phases resulting in an adsorbed Fe(III) phase. This electron transfer affects how the iron(III) oxide, goethite, reacts in the environment. Our study attempts to determine whether this electron transfer can be inhibited by the adsorption of phosphate. Goethite was used because it is one of the most common and stable forms of iron (hydr)oxides in the environment.

Phosphate Sorption

Phosphate, like iron, is found everywhere in the environment, and is an essential nutrient for plants. However, excessive runoff of fertilizers containing phosphate can have negative effects on lakes and rivers, causing eutrophication and lowering water quality, even causing anoxic conditions in some cases. Adsorption of phosphate anions to soils is common in water bodies and affects the bioavailability of phosphate in the environment as well as its effectiveness as a fertilizer. Figure 1.1 shows the speciation of phosphate and the strong influence of pH on phosphate sorption. At typical pH values for natural waters (pH 6 to 8) phosphate exists primarily as $H_2PO_4^-$ and HPO_4^{2-}, these species can sorb to metal oxides surfaces such as goethite.

Changes in pH greatly affect the ability of phosphate to sorb to goethite surfaces, as previously shown [11-13]. Typical anion sorption is seen in Figure 1.2 for phosphate adsorption to goethite, where as pH decreases, sorption increases. Sorption also increases with increasing phosphate concentration in solution [13]. Strauss [13] showed that previous studies which found a maximum sorption of 2.51 μmole/m^2 [14], underestimated the value because adsorption measurements were conducted at pH values of 3.5 and 6 where sorption has not yet reached its maximum. At a lower pH of 2, there appears to be higher adsorption and a higher maximum sorption value than was determined in previous works [15-17].

Phosphate Sorption Mechanism

Anions, such as phosphate, are known to affect the surface behavior of cations in environmental systems. Phosphate ions have an affinity for sorption to metal (hydr)oxides and often interact with iron oxides through Fe-O-P bonds [18]. Thus, the effect of phosphate adsorption to the surface of iron oxides on the reactivity of the bulk phase is of interest and has been studied in previous works [13]. Research has shown that phosphate sorbs specifically by an inner sphere sorption mechanism [12, 19]. Several studies confirm that there are three different surface complexes which dominate surface coordination between phosphate and metal oxides [19-21]. These include two bridging bidentate complexes both protonated and nonprotonated and a nonprotonated monodentate complex. The nonprotonated, binuclear bidentate $\equiv Fe_2O_2PO_2$ surface complex is the dominant adsorbed phosphate species at neutral pH values [22]. It may, however, be protonated at low pH values. Metal ions of a solid, bulk phase particle and the central ion of an adsorbed complex can share ligands in an inner sphere complex, which allows the complex to be closer to the surface of the metal hydr(oxide) than is typical for an outersphere complex [22]. Modeling of the phosphate sorption mechanism aids in understanding how and why phosphate sorption occurs on goethite and how it can affect other ions' interactions with the goethite surface.

Anion Sorption in Competition with Phosphate

An adsorbed layer of phosphate may alter how other ions interact and sorb to a metal (hydr)oxide surface. Anions such as carbonate and sulfate have been studied for their effect on phosphate sorption to a goethite surface [11-12, 23]. Phosphate has a higher affinity for goethite than sulfate, demonstrated by the high adsorption rates of phosphate [11]. At lower pH values, however, phosphate sorption decreases in the presence of sulfate, which illustrates the competitive relationship between sulfate and phosphate ions. This competitive sorption may influence phosphate's bioavailability

[11]. There is a similar affect seen between carbonate and phosphate [23] where increasing loading rates of carbonate decrease the adsorption of phosphate; yet phosphate has a higher affinity for goethite. In general, phosphate decreases the ability of other anions to sorb to a goethite surface [11].

Effect of Phosphate on Cation Sorption

Cation sorption can also be influenced by phosphate sorption. Calcium sorption edges shift in the presence of phosphate. As phosphate is added, the calcium sorption edge shifts to a lower pH as can be seen in Figure 1.3 from Rietra and colleagues [24]. Calcium sorbs more at a lower pH when phosphate is present because phosphate alters the surface charge, decreasing the repulsive force, and allowing calcium to sorb to the goethite surface. Thus, adsorption of calcium to a goethite surface in the presence of phosphate is greater when compared to the same system without phosphate [24]. The addition of calcium influences the ability of phosphate to adsorb at high pH values. Aqueous phosphate concentrations at high pH values increase greatly by the addition of only a small concentration of calcium [24] due to the competition between phosphate and calcium at high pH values.

Goethite Properties

Properties of goethite have been extensively studied including many relevant to this study; specifically the point of zero charge (pzc), surface complexation modeling (SCM), and sorption/desorption of phosphate on the goethite surface. The point of zero charge can be defined as the condition at which the net electrical charge density on the surface of a particle is zero. The pzc of goethite under normal conditions is pH 8.1, but it is significantly affected by adsorption of phosphate [16]. The sorption of phosphate onto goethite has been shown to lower the goethite pzc to a pH of 5.1. This shift is due to the addition of phosphate. As previously stated, sorbed phosphate makes the goethite surface

more negative requiring more protons to neutralize the negative charge meaning a lower pH is needed, ultimately resulting in the pzc shift. Figure 1.4, shows this phenomenon.

Similar results were also found for another common iron oxide, hematite. A shift from pH 8.9 for nonphosphated hematite was lowered to pH 5.3 when phosphate was adsorbed [16]. Other anions also appear to have similar effects. This pzc shift to a lower pH could have potential for influencing Fe(II) sorption. It would be expected that more Fe(II) is sorbed at lower pH values as was seen for calcium [24]. I hypothesize that the change in pzc due to phosphate sorption will influence the ability for Fe(II) to sorb to the goethite surface and for electron transfer to occur between Fe(II) and bulk Fe(III).

Objective

The objective of this work is to evaluate the effect of phosphate on Fe(II)-Fe(III) electron transfer at the goethite surface by:

1. Quantifying phosphate sorption on a goethite surface in the presence and absence of Fe(II).
2. Evaluating the effect of phosphate on Fe(II) sorption.
3. Using Mössbauer spectrometry to determine if electron transfer is occurring.

Hypothesis

An adsorbed layer of phosphate on the goethite surface will inhibit the electron transfer between the Fe(II) and Fe(III) phases at the surface.

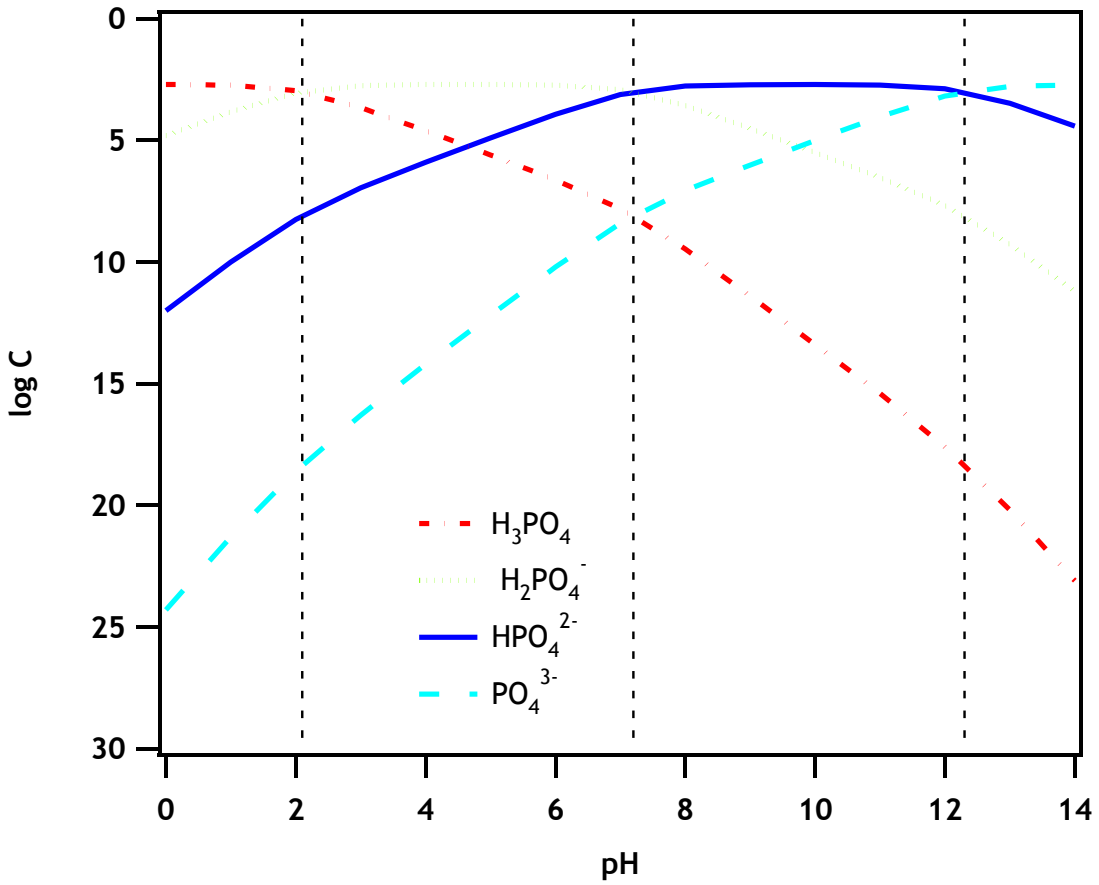

Figure 1.1 Speciation for phosphate in a log C versus pH diagram for an arbitrary concentration of 2 mM total phosphate. In natural waters (pH 6 to 8) $H_2PO_4^-$ and HPO_4^{2-} are the dominant species available for sorption to metal (hydr)oxides. At slightly higher pH there is also the PO_4^{3-} species. The pKa values are represented with dashed lines and are $10^{-2.1}$, $10^{-7.2}$, and $10^{-12.3}$ for H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-}, respectively [10].

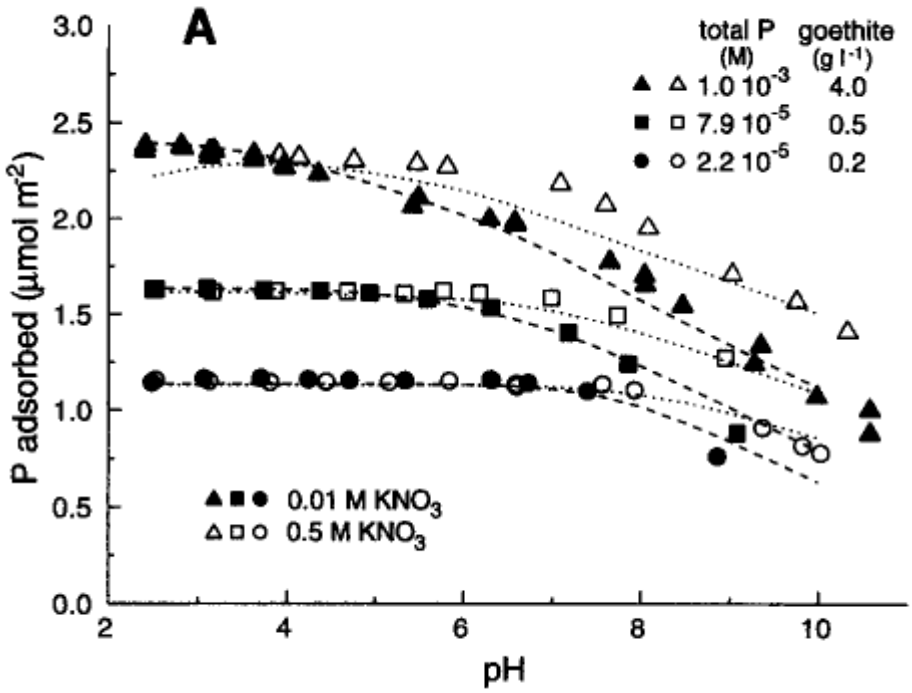

Figure 1.2 The effect of pH on adsorption of phosphate to a goethite surface at two different ionic strengths [11]. Results show typical anion sorption with greater sorption at lower pH values and decreasing sorption as pH increases. Dotted lines represent an ionic strength of 0.1 M KNO_3 while dashed lines represent an ionic strength of 0.5 M KNO_3. Phosphate sorption increases as the phosphate and goethite loadings increase.

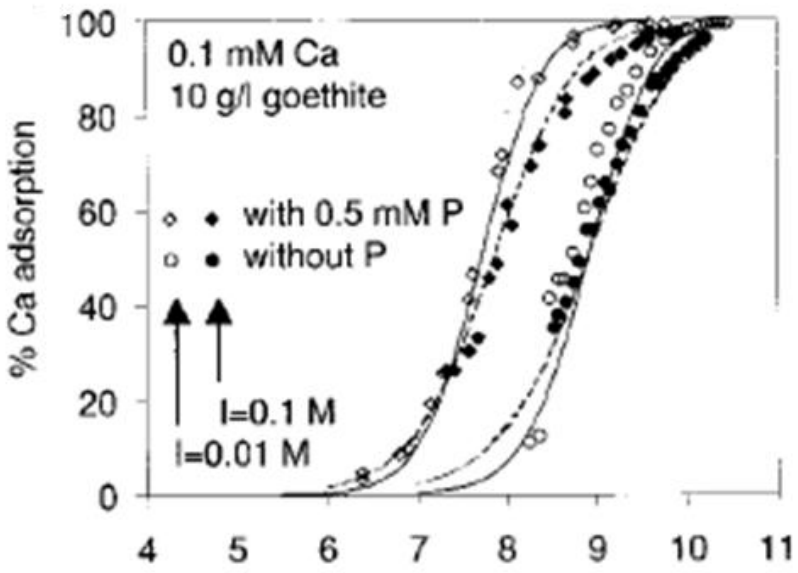

Figure 1.3 Calcium sorption onto goethite in the presence and absence of phosphate at two different ionic strengths. The addition of an adsorbed layer of phosphate shifts the calcium sorption edge to a lower pH due to the decrease in repulsive force allowing calcium to sorb to the negatively charged goethite surface.

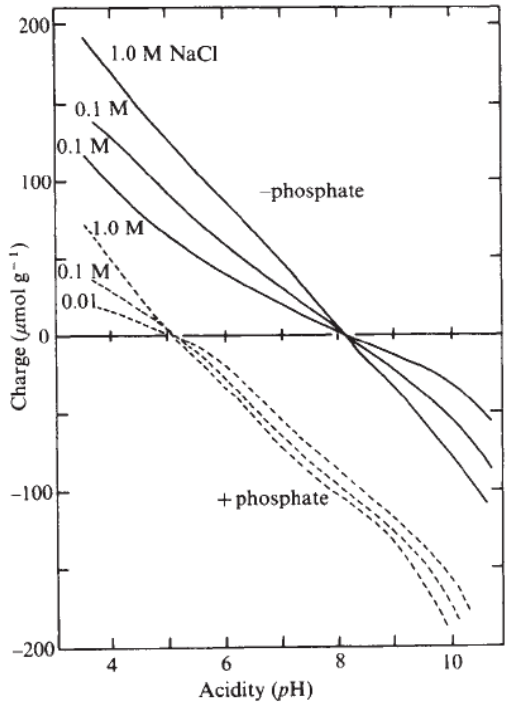

Figure 1.4 Surface charge of goethite (—) and phosphated goethite (- - -), for three different NaCl concentrations to show the effect of ionic strength. The pzc shifts from 8.1 for nonphosphated goethite to 5.1 for phosphated goethite [16].

CHAPTER 2: MATERIALS AND METHODS

Experimental Approach

Isotherms and pH edge experiments were conducted to quantify phosphate adsorption onto goethite. The effect of a phosphate loading rate on Fe(II) sorption to goethite was also studied. Mossbauer analysis was used to determine if electron transfer continued after significant phosphate adsorption to the goethite surface.

Reagents

Reagents were used as received from the manufacturer. Chemicals used for goethite synthesis are as follows: ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$; Sigma Aldrich; ≥98%); sodium bicarbonate (NaOH, Sigma Aldrich, ≥95%), and potassium hydroxide (KOH, Sigma Aldrich). A 100 mM stock solution of KH_2PO_4 was prepared using potassium dihydrogen phosphate (KH_2PO_4). A stock solution of 15 mM Fe(II) was made using anhydrous ferrous chloride beads ($FeCl_2$, Sigma Aldrich, 99.99%) dissolved in 0.1 N HCl. Fe(II) isotherm experiments were conducted in a buffer solution of 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES; Sigma Aldrich, ≥99.5%) with potassium chloride (KCl). Deoxygenated, deionized water was degassed with high purity N_2 gas for 1 hour per liter of water. Reagents used for spectrophotometer analysis of Fe(II) included: 1,10-phenanthroline (Sigma-Aldrich, ≥ 99%), hydroxylamine hydrochloride (Sigma Aldrich, 98%) and ammonium acetate (Fisher, 98.5%). For the colorometric analysis of phosphate the following reagents were used: sulfuric acid (H_2SO_4); potassium antimonyl tartrate ($C_4H_4O_7SbK$); ammonium molybdate; and ascorbic acid ($C_6H_8O_6$).

Synthesis and Characterization of Goethite

The goethite rods used in this study were synthesized in the lab according to the Schwertmann and Cornell recipe [25]. Two solutions were made: A) a 1 M $Fe(NO_3)_3$

solution was prepared by dissolving $Fe(NO_3)_3 \cdot 9H_20$ in distilled water and B) a 5 M KOH solution was also prepared. 180 mL of solution B was added rapidly with stirring to 100 mL of solution A into a polyethylene flask to avoid silicon (Si) dissolution from glass vessels due to the use of a strong base. A red-brown precipitate of ferrihydrite appeared instantly. The solution was immediately diluted to 2 L with deionized water and held in a in an oven for 60 hours at a temperature of 70 °C. A yellow-brown precipitate of goethite formed and once removed from the oven it was cooled to room temperature. The solution was washed to remove OH^- and NO_3^- ions, by pouring the solution into Spectra/Por® dialysis tubes which were placed in a tub of deionized water. The washing water was changed three times daily until its pH was equal to that of deionized water, as measured by pH paper. The solution from the dialysis tubes was then emptied into separate 200 mL bottles and centrifuged three times using an induction drive centrifuge, each time pouring off the supernatant until only the goethite pellets remained. Pellets were freeze-dried and ground to a powder by mortar and pestle. The goethite powder was sieved through a 150 μm sieve to ensure even particle size distribution.

Synthesized goethite rods were characterized by several different methods. X-ray diffraction (XRD) patterns were measured and were consistent with microrod goethite particles. A seven-point N_2 BET adsorption analysis was also conducted on the goethite powder, resulting in a specific surface area of 33.19 m^2/g. Transmission electron microscope (TEM) images were used to determine size and morphology of the goethite microrods. TEM samples were prepared by suspending ~0.2 g/L of the goethite powder into methanol and then sonicating the solution for 2 hours. A drop of the sonicated solution was applied to a holey carbon-coated copper mesh grid. Images were analyzed using the software program ImageJ, which revealed that rods had an average length and width of 1.072 ± 0.59 μm and 0.076 ± 0.038 μm, respectively, resulting in a TEM specific surface area of 28.94 m^2/g. Figure 2.1 shows a TEM image of the synthesized goethite microrods.

Experimental Setup

Adsorption Experiments

All experiments were conducted in an anoxic environment of 95% N_2 to 5% H_2 and all solutions were prepared in deionized (18 MΩ-cm), deoxygenated water. Reactors consisted of 20 mL vials with 15 mL of 10 mM KCl as the electrolytic solution. Nine vials were prepared for pH values ranging from 4 to 10. All reactors were spiked with 100 mM KH_2PO_4 to a concentration of either 500 μM PO_4^{3-} or 100 μM PO_4^{3-} and shaken to ensure proper mixing. Samples were immediately taken after the addition of phosphate to determine the initial phosphate concentration using the spectrophotometer.

Goethite was added to reactors at a loading of 2 g/L and shaken vigorously. The pH was immediately adjusted using either 0.1 M HCl or 0.1 M KOH to the nominal pH; this was done for all pH values. Final pH values after adjustment were recorded and varied ± 0.4 pH units from the nominal pH. All vials were then crimp-sealed and placed on an end-over-end rotator and allowed to mix for 20 hours. After the reaction period, vials were sampled for phosphate determination and pH was again measured and recorded. Reactors were then spiked with 15 mM $FeCl_2$ to a concentration of 0.1 mM or 0.5 mM Fe(II) and shaken. Two controls were made with 15 mL of 10 mM KCl spiked with the corresponding $FeCl_2$ concentration that was being tested. This was done to measure initial Fe(II) spiked concentrations which were later used to determine the percent of iron sorbed to the goethite surface. All vials were then adjusted to their nominal pH ± 0.4 pH units except for controls which were not adjusted. Reactors were again crimp-sealed and placed on a rotator for 20 hours. After the second reaction period, pH was measured and recorded and vials were sampled for both iron(II) and phosphate concentrations. All samples were filtered through a 0.2 μm nylon filter to remove any suspended goethite that might interfere with spectrophotometer

measurements. Each sample taken for phosphate and iron determination was analyzed using the standard method and measured at 880 and 510 nm wavelength, respectively.

Controls were prepared that contained only phosphate and iron to monitor their concentrations in the absence of goethite. Controls were used to determine if phosphate and/or iron was sorbing to the glass surface or precipitating out as $Fe_3(PO_4)_2$ (vivianite), although concentrations used in these experiments were chosen to be below the saturation index for vivianite to avoid precipitation. Initial and final concentrations of iron and phosphate were measured for a 24 hour period, and found to have a less than 10% difference in concentration, a negligible amount; therefore no sorption or precipitation was occurring.

Fe(II) Isotherm

An Fe(II) isotherm was prepared at a high concentration of 500 µM PO_4^{3-} with Fe(II) concentrations varying from 0.1 to 4 mM at a constant pH of 7.5. Triplicates of 20 mL well-mixed batch reactors were filled with 15 mL of a solution containing 25 mM HEPES and 10 mM KCl. Vials were then spiked with 100 mM KH_2PO_4 to the desired concentration and sampled to determine the initial phosphate concentration. Goethite microrods were added to the reactors at a loading of 2 g/L. Vials were adjusted to a pH of 7.5 using 1 M KOH to within ± 0.04 pH units, crimp-sealed and placed on an end-over-end rotator. After 2 hours of equilibration, samples were taken by filtering through a 0.2 µm nylon filter. The pH of the reactors was measured and recorded to ensure they stayed within ± 0.10 pH units; vials were then spiked with $FeCl_2$ at concentrations ranging from 0.1 to 4 mM. The pH of the reactors was again adjusted to within ± 0.06 pH units of the nominal pH. Twenty hours after the initial Fe(II) spike, the vials were again sampled and filtered to measure final concentrations for both iron and phosphate; pH was also measured and recorded. As before, controls were made containing the HEPES buffer and KCl electrolyte solution as well as the spiked Fe(II) to determine

initial Fe(II) concentrations. Controls were crimp-sealed and placed on a rotator, then allowed to equilibrate for 24 hours before measuring the final Fe(II) concentration.

Sample Analysis

Colorimetric Analysis

Analysis of the collected samples was conducted using a colorimetric method for both phosphate and iron(II). Phosphate was measured using the Ascorbic Acid method, from the Standard Methods for the Examination of Water and Wastewater [26]. Briefly, 5 N H_2SO_4, potassium antimonyl tartrate, ammonium molybdate, and ascorbic acid were mixed "fresh" for every sample period. The mixture was added to a sample that was diluted with deionized water to a volume of 1 mL. Phosphate concentrations were measured colorimetrically using a UV/visible spectrophotometer with a wavelength reading of 880 nm. Dissolved iron(II) concentrations were determined using the standard 1,10-phenanthroline method detailed by Komadel [27] at a wavelength of 510 nm. Both of these methods required standard curves to be developed.

Mössbauer Analysis

Electron transfer was determined using isotope specific ^{57}Fe Mössbauer spectroscopy. ^{56}Fe(III) (Mössbauer inactive) and ^{57}Fe(II) (Mössbauer active) were used in the Mössbauer analysis which was conducted as in previous works [8-9]. In brief, the aqueous Fe(II) was prepared using the ^{57}Fe isotope, while the goethite rods were made using the ^{56}Fe isotope, effectively turning off the Mössbauer signal associated with the goethite particles. In this way, any electron exchange occurring between the aqueous and solid phase iron could be measured by the Mössbauer, which only measures the active ^{57}Fe isotope. If electron transfer occurred, the adsorbed ^{57}Fe(II) would be oxidized to ^{57}Fe(III) which would then be seen and measured in the Mössbauer spectra. 13 mm filter discs were used to collect reacted goethite particles which were then analyzed on the

Mössbauer by Drew Latta. Spectra from the analysis were evaluated using the software program Recoil.

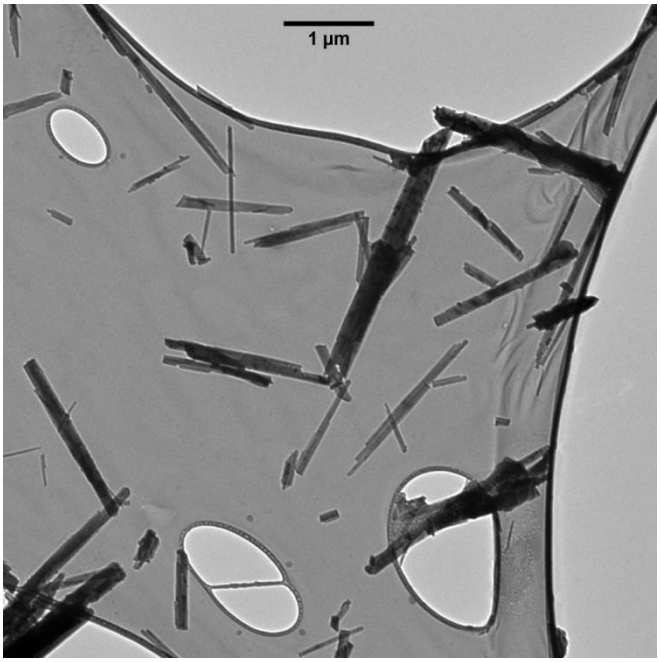

Figure 2.1 A TEM image of goethite rods similar to the particles used in our experiments, made using the same process found in Schwertmann and Cornell [25]. TEM results show that only goethite is present on the holey carbon-coated copper grid and particles appear to have the characteristic rod-shape associated with goethite with no hematite particles present.

CHAPTER 3: RESULTS AND DISCUSSION

Effect of Fe(II) on Phosphate Sorption

Characterization of phosphate sorption onto a goethite surface was accomplished by conducting pH edges for both phosphate and Fe(II) for a pH range of 4 to 10. Figures 3.1 and 3.2 show that phosphate displayed typical anion sorption, where as pH decreased phosphate sorption to the goethite surface increased. This characteristic anion sorption was seen with both low (100 μM) and high (500 μM) concentrations of phosphate, in Figures 3.1 and 3.2, respectively and is consistent with results found by Geelhoed and colleagues [11]. Phosphate adsorption was not greatly affected after a reaction time of 20 hours. Between a 20 and 40 hour reaction time there was no appreciable difference in the adsorbed phosphate even with the addition of 100 μM Fe(II) at the 20 hour time period. Hereafter, 20 hour and 40 hour adsorption data will be presented together, given that no significant changes in phosphate sorption was found between the two time periods.

The site saturation maximum of phosphate onto a goethite surface as determined by Schwertmann [14] is shown on Figures 3.2 through 3.4. Schwertmann calculated a maximum sorption value for phosphate of 2.5 μmole/m^2. However, it can be seen in the following figures that only the lower concentration of phosphate (100 μM) and some of the higher pH measurements at the higher phosphate concentration stayed below this value. Strauss [13] explained this phenomena by suggesting that previous works [15-17] which had found site saturation values close to that of Schwertmann's had underestimated the theoretical value. These previous works had measured maximum sorption at higher pH values, which resulted in lower phosphate sorption. In addition, the crystallinity of the goethite plays a major role in the extent to which sorption can occur. Phosphate sorption was found to be greatest for poorly crystallized goethite, and decreased as goethite samples became more crystalline [13]. Thus, experimental results

which surpass the theoretical site saturation of phosphate on goethite are reasonable, assuming a goethite with poor crystallinity.

Figure 3.3 shows the influence of different aqueous concentrations of phosphate on the amount of phosphate sorbed to the goethite surface. As phosphate concentration increased from 100 μM to 500 μM PO_4^{3-}, adsorption increased as well, these results are consistent with previous works [11, 13] which showed a marked increase in phosphate sorption with an increase in aqueous phosphate concentration. The difference in sorption due to aqueous phosphate concentration increases with decreasing pH. There is significantly more sorption at a pH of 4 in the 500 μM PO_4^{3-} than at 100 μM PO_4^{3-}. At the higher concentration, the sorbed phosphate is almost double the theoretical loading rate of 2.5 μmole/m^2 at pH 4. In fact, the sorbed phosphate is above the theoretical value consistently with the exception of the data point at pH 8. In contrast, the lower phosphate concentrations all result in an adsorbed phosphate value below the site saturation value of 2.5 μmol/m^2.

In Figure 3.4, the results for 500 μM PO_4^{3-} with two different Fe(II) concentrations can be seen. Experimental results show that there is no significant difference in the amount of adsorbed phosphate with increased aqueous concentration of Fe(II) for a reaction period of 40 hours.

Table 1 shows a summary of all the data presented in Figures 3.1 through 3.4 as aqueous concentrations of both phosphate and Fe(II). Phosphate was equilibrated for 20 hours before the spiked addition of Fe(II) which was then allowed to equilibrate an additional 20 hours.

Effect of Phosphate on Fe(II) Sorption

A key step in evaluating the effect of phosphate on Fe(II) sorption onto goethite was the Fe(II) pH edge. Figure 3.5 shows the pH edge ranging from pH 4 to 10 for different phosphate loadings of 100 μM, 500 μM or no phosphate with 100 μM Fe(II).

Results are typical for cation sorption, where greater Fe(II) sorption occurred at higher pH values. Surprisingly, phosphate sorption appeared to have little to no affect on Fe(II) sorption. This was unexpected since phosphate had a significant impact on Ca^{2+} sorption [24]. It was anticipated that with the addition of phosphate, the Fe(II) sorption edge would shift to a lower pH. As phosphate concentration increased, however, Fe(II) sorption stayed relatively stable. This was suspected to occur due to a low Fe(II) concentration, therefore a loading of 500 μM Fe(II) was also tested, with similar results.

Figure 3.6 shows the Fe(II) pH edge for low and high concentrations of Fe(II) of 100 μM and 500 μM, respectively, with 500 μM PO_4^{3-}. Results show only a slight shift in the pH edge with the addition of Fe(II). With the increased sorption of Fe(II), the edge shifted to a higher pH. These results were consistent with a similar system using Ca^{2+} instead of Fe(II). When Ca^{2+} was added, the pH edge of goethite was shifted up, to a higher pH [24] similar to what was seen with the experimental results for Fe(II) sorption to goethite.

Fe(II) Isotherm

The final step towards characterization of Fe(II) sorption to a goethite surface was the Fe(II) isotherm. The isotherm concentrations were chosen based on the previous pH edge experiments, resulting in a constant phosphate loading of 500 μM PO_4^{3-}, with Fe(II) concentrations varying between 0.1 and 4 mM at a constant pH of 7.5. Figure 3.7 shows the experimental results for the Fe(II) isotherm. Sorption of Fe(II) increased with increasing aqueous concentrations of Fe(II), as expected. However, at these concentrations it appears that surface site saturation of the goethite had not yet been achieved, meaning the surface is undersaturated with respect to Fe(II) and surface precipitation has yet to occur. These results are comparable to those for a similar system using calcium instead of Fe(II) [24] when compared to a system without phosphate as seen in a previous study by Cwiertny and colleagues [28]. Cwiertny showed that Fe(II)

sorption increased with increasing aqueous Fe(II) concentrations, but his results show a marked sorption decrease around 300 μmole/g, whereas the results shown here do not appear to be plateau even at 600 μmole/g Fe(II) sorption. This demonstrates that with the addition of phosphate there is an increase in Fe(II) sorption, with increasing aqueous Fe(II). As with the calcium/goethite system [24], the presence of aqueous phosphate allows Fe(II) to sorb by changing the surface charge of the bulk Fe(III) particle in effect reducing the repulsive force, making it easier for Fe(II) as well as other cations to sorb.

Mössbauer Spectra

The objective of this work was to evaluate the effect of an adsorbed phosphate layer on the Fe(II)-Fe(III) electron transfer. To determine if electron transfer still occurs despite the presence of adsorbed phosphate, Mössbauer spectroscopy was used with help from Drew Latta. Concentrations of 500 μM and 100 μM, phosphate and iron(II), respectively, were used. Surprisingly, despite an adsorbed layer of phosphate on the ^{56}Goethite, it appears from the spectra shown in Figure 3.8 that electron transfer is still occurring at a pH of 7.5. By some means, the electron can still be transferred between the aqueous ^{57}Fe(II) phase and the ^{56}Goethite, reducing the structural ^{56}Fe(III) to ^{56}Fe(II). The adsorbed layer is thus oxidized from ^{57}Fe(II) to ^{57}Fe(III) and this change is measured by the Mössbauer, which only “sees” the active ^{57}Fe isotope. Results show a sextet that is ^{57}Fe(III) and is goethite, meaning that electron transfer has taken place which has oxidized the adsorbed ^{57}Fe(II) layer. However, there is also a small doublet that shows that some of the ^{57}Fe(II) remains as Fe(II), and is still measurable by the Mössbauer.

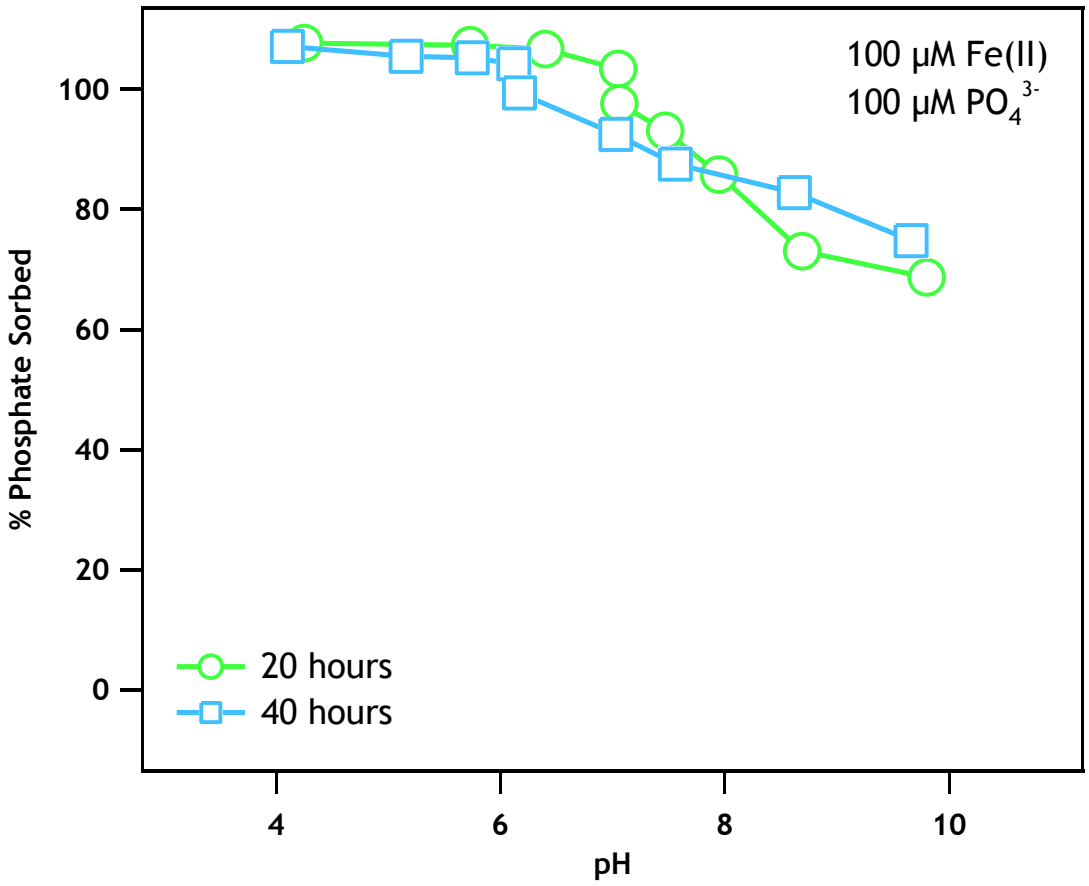

Figure 3.1 Percent of phosphate sorbed to a goethite surface at pH values varying from 4 to 10 showing typical anion sorption. There is no apparent difference in the percent of sorbed phosphate to a goethite surface between a reaction time of 20 hours and 40 hours for a concentration of 100 µM PO_4^{3-} and 100 µM Fe(II) for a goethite loading of 2 g/L. Vials were measured for phosphate concentrations after 20 hours of equilibration, then spiked with Fe(II), and equilibrated another 20 hours before the second sample was taken.

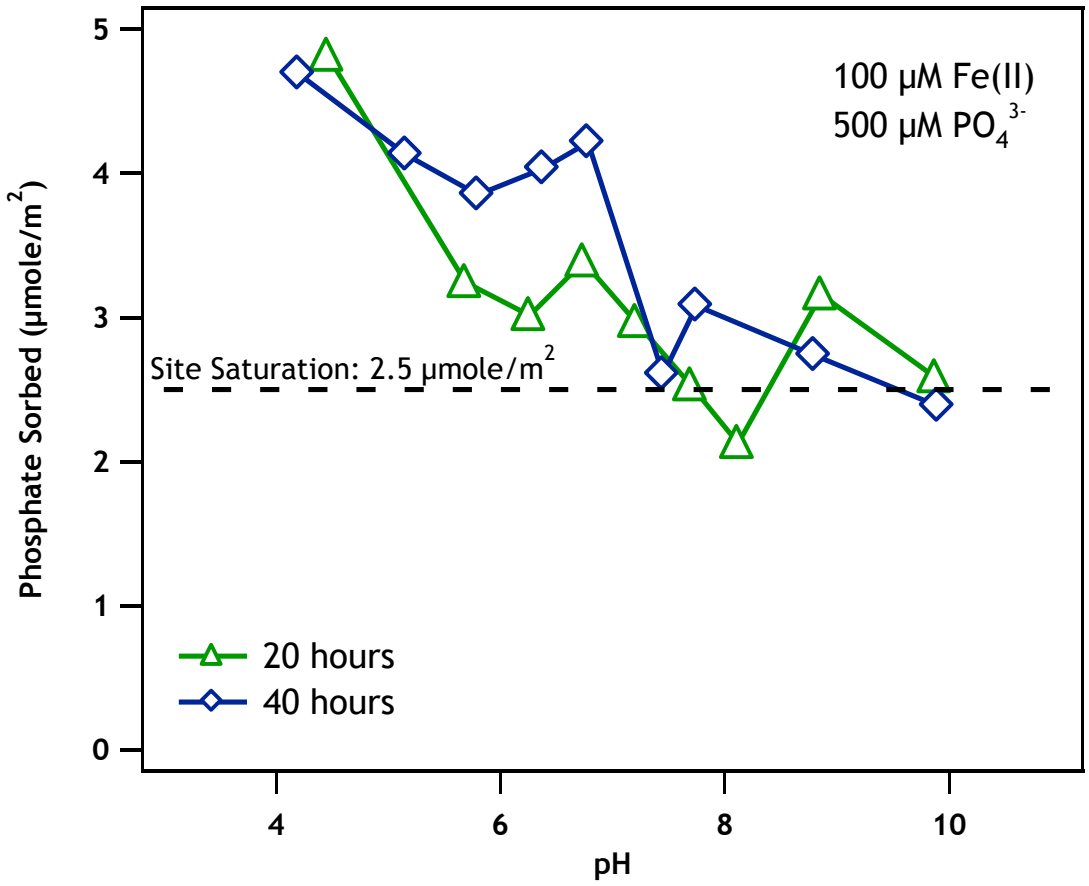

Figure 3.2 Phosphate pH edge results for 500 µM PO_4^{3-} and 100 µM Fe(II) with a goethite loading of 2 g/L. Experimental results show typical anion sorption with more phosphate sorbing at lower pH values. As before, the vials were preequilibrated with phosphate for 20 hours before the spike addition of Fe(II).

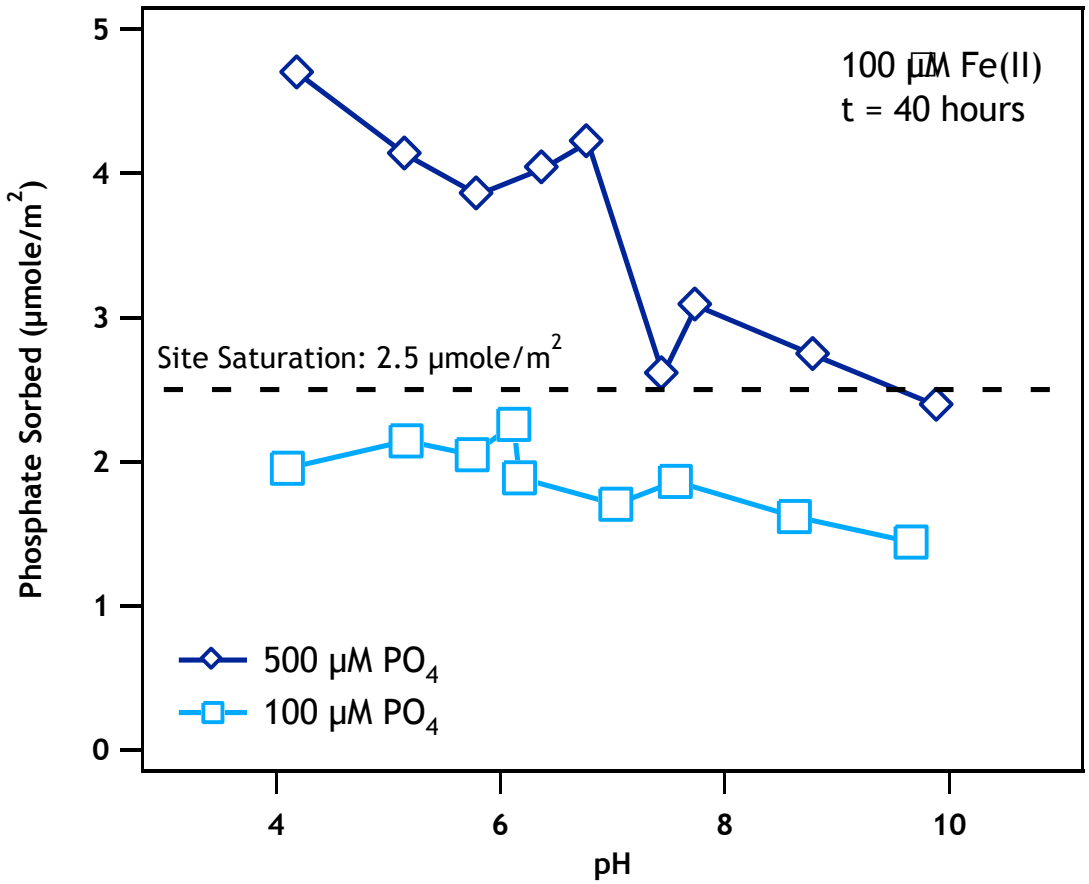

Figure 3.3 Comparison of phosphate sorption on goethite with varying concentrations of phosphate and a constant concentration of 100 µM Fe(II) for a 40 hour reaction period. A significant difference in phosphate sorption between the two concentrations of phosphate especially at lower pH values is seen. Increased sorption with an increased concentration of phosphate is consistent with Strauss [13] and Geelhoed [11].

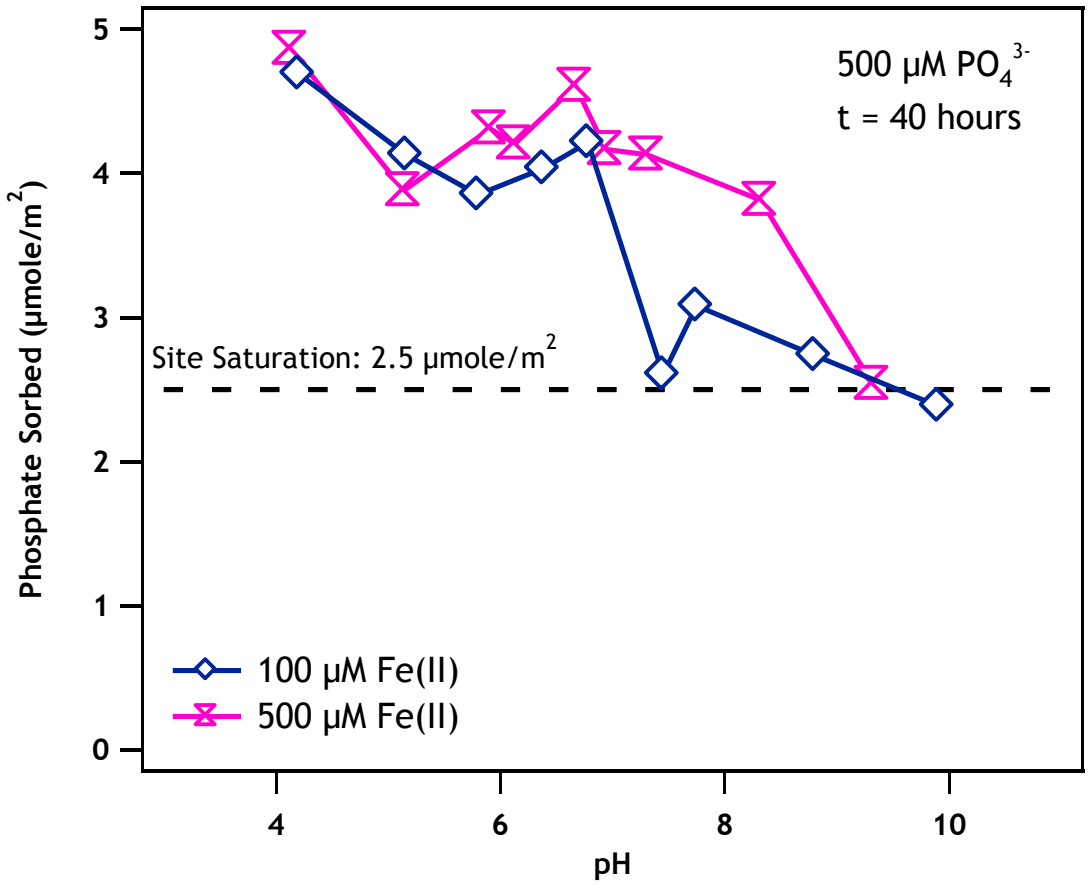

Figure 3.4 Effect of Fe(II) concentration on phosphate sorption on goethite at 500 μM and 100 μM Fe(II) with an aqueous phosphate concentration of 500 μM PO_4^{3-} for a reaction time of 40 hours. There appears to be no significant difference in phosphate sorption with an increase in Fe(II) concentration. Vials were preequilibrated with phosphate for 20 hours then Fe(II) was spiked in and allowed to equilibrate an additional 20 hours.

Table 3.1 Summary of results for Figures 3.1 through 3.4, showing initial, 20 hour, and 40 hour aqueous concentrations of phosphate as well as initial and 20 hour aqueous concentrations for Fe(II). Fe(II) was spiked in after phosphate was equilibrated for 20 hours.

	pH Edge 500 μM PO_4^{3-} and 100 μM Fe(II)					pH Edge 100 μM PO_4^{3-} and 100 μM Fe(II)					pH edge 500 μM PO_4^{3-} and 500 μM Fe(II)				
	Units: μM					Units: μM					Units: μM				
pH	$[PO_4^{3-}]_0$	$[PO_4^{3-}]_{t=20\ hr}$	$[PO_4^{3-}]_{t=40\ hr}$	$[Fe^{II}]_0$	$[Fe^{II}]_{t=20\ hr}$	$[PO_4^{3-}]_0$	$[PO_4^{3-}]_{t=20\ hr}$	$[PO_4^{3-}]_{t=40\ hr}$	$[Fe^{II}]_0$	$[Fe^{II}]_{t=20\ hr}$	$[PO_4^{3-}]_0$	$[PO_4^{3-}]_{t=20\ hr}$	$[PO_4^{3-}]_{t=40\ hr}$	$[Fe^{II}]_0$	$[Fe^{II}]_{t=20\ hr}$
4	588	270	278	105	2	120	0.0	0.0	121	129	590	323	269	509	596
5	593	379	320	114	10	134	0.0	0.0	121	119	554	383	298	509	553
6	587	388	332	114	38	128	0.0	0.0	121	107	588	369	303	509	493
6.5	603	379	337	105	73	143	0.0	0.0	121	80	592	392	314	509	472
7	602	406	323	114	94	125	3.0	0.8	107	47	600	397	296	509	346
7.5	551	385	379	105	102	122	8.4	9.1	107	6	544	369	269	509	199
8	584	444	381	114	115	140	20.0	17.5	107	1	532	393	260	509	116
9	608	400	427	105	105	129	34.8	22.2	107	0	558	424	306	509	20.4
10	597	426	439	105	105	127	39.8	32.0	107	0	535	416	367	509	1.7

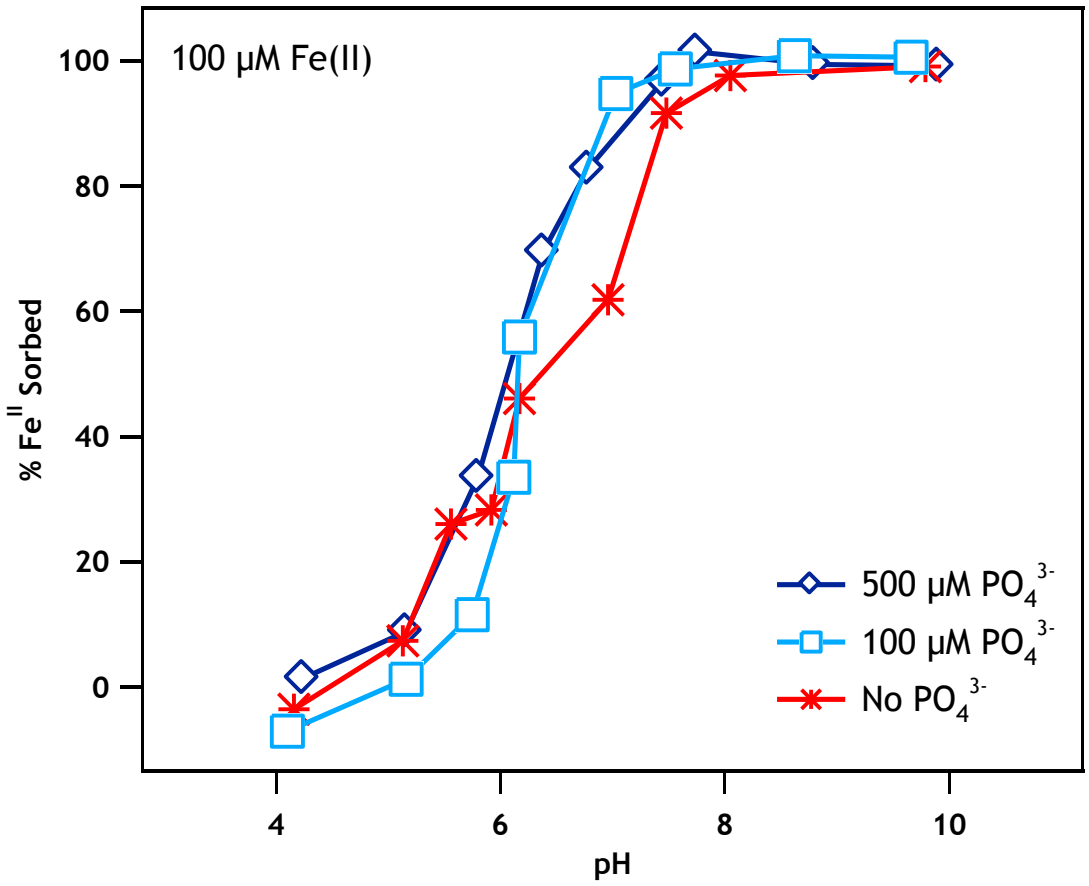

Figure 3.5 Fe(II) adsorption to a goethite surface as function of pH with and without PO_4^{3-}. For reactors with PO_4^{3-}, solutions were preequilibrated with KH_2PO_4 for 20 hours before the addition of Fe(II). Results are typical for cation sorption, with more sorption occurring at higher pH values. Changing the PO_4^{3-} concentration from 500 to 100 µM did not appear to have an effect on the Fe(II) sorbed. Both the 500 µM and 100 µM PO_4^{3-} had similar results, with negligible differences. These results are surprising since the sorption of phosphate dramatically shifted the pzc as show in Figure 1.3, yet there is little to no effect on the Fe(II) sorption. Note that the reactors without phosphate were only equilibrated for 20 hours before sampling, whereas the reactors with phosphate were sampled after 40 hours of equilibration.

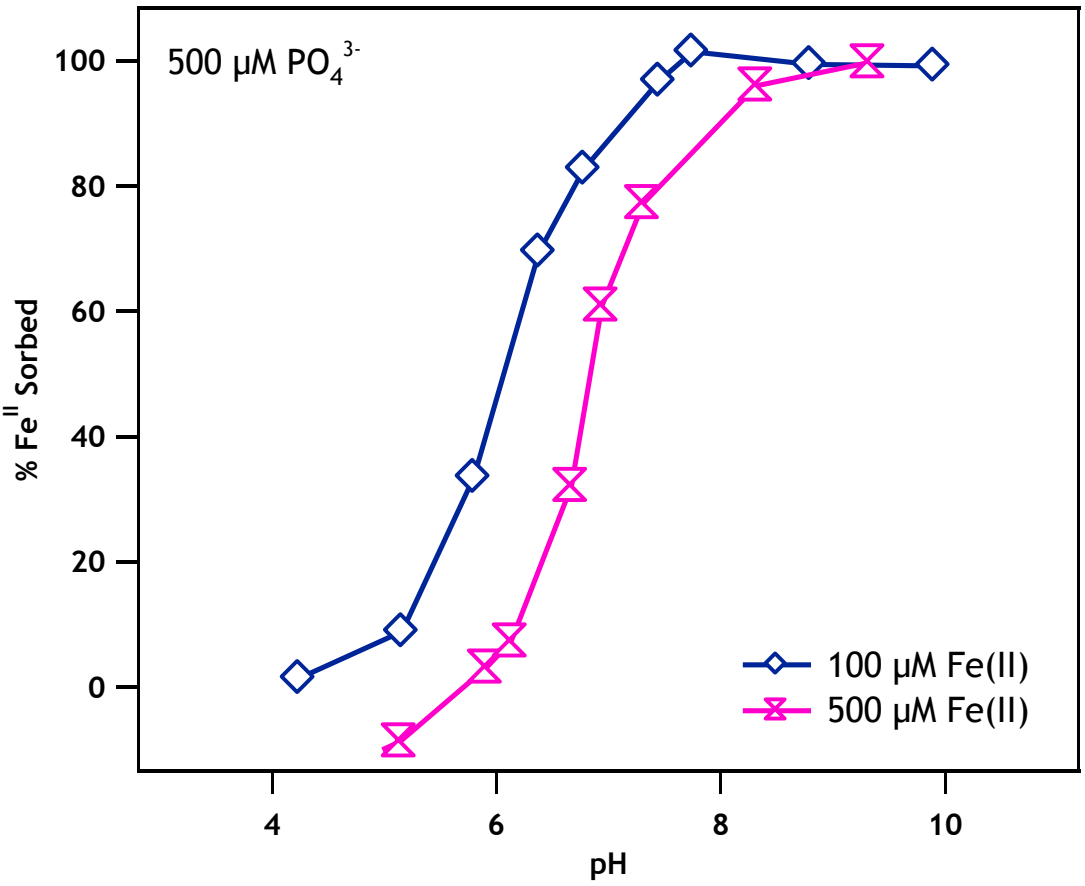

Figure 3.6 Fe(II) sorption to a goethite surface for a low (100 μM) and high (500 μM) concentration of Fe(II), and a high (500 μM) concentration of phosphate. Results show a slight shift to a higher pH with increased Fe(II) concentrations, which is consistent with results seen for Ca^{2+} sorption to goethite [24].

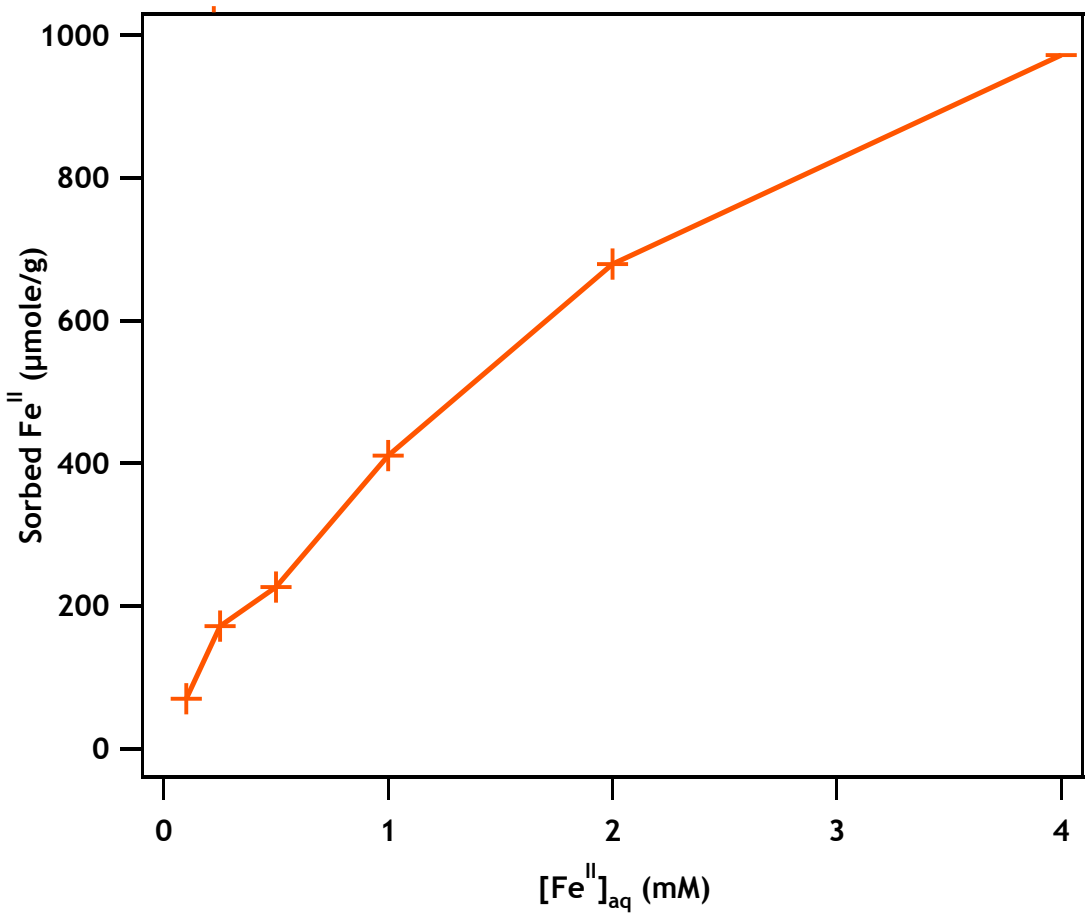

Figure 3.7 Fe(II) isotherm, for 500 µM PO_4^{3-} and Fe(II) concentrations between 0.1 mM and 4 mM Fe(II) at a constant pH of 7.5. As expected, Fe(II) sorption increases with increasing aqueous concentration of Fe(II). The goethite does not appear to have reached surface site saturation with respect to Fe(II), since the isotherm has not reached a plateau. Results are similar to those seen by Rietra [24] for a comparable system using calcium instead of Fe(II).

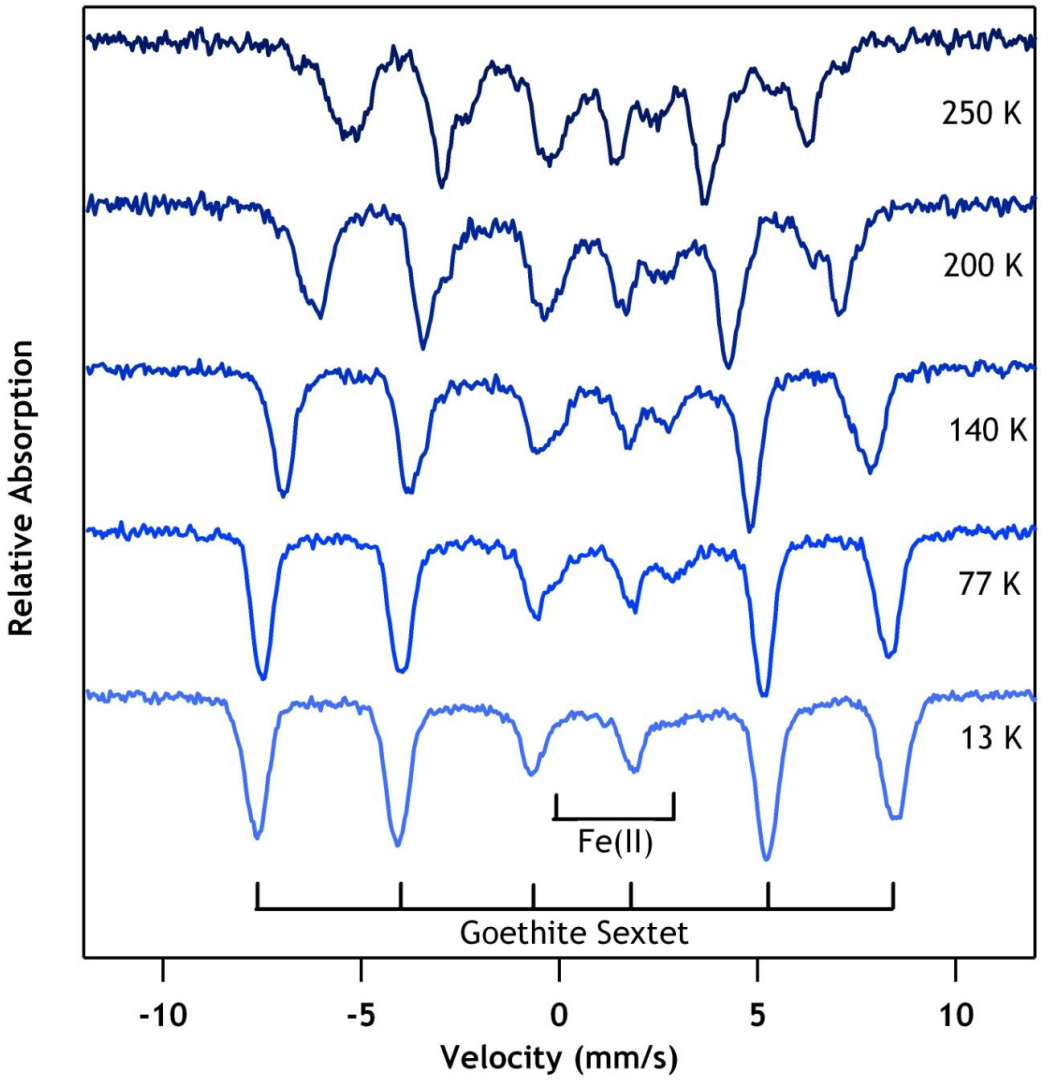

Figure 3.8 Mössbauer spectra of phosphated ^{56}Goethite in an aqueous ^{57}Fe phase. The phosphate was at a concentration of 500 μM PO_4^{3-} with a ^{57}Fe(II) concentration of 100 μM. Results show that electron transfer occurs despite the presence of an adsorbed layer of phosphate. However, there is also a ^{57}Fe(II) doublet seen, which means that not all the Fe(II) was oxidized. Mössbauer analysis was conducted by Drew E. Latta [29].

CHAPTER 4: ENGINEERING AND SCIENTIFIC SIGNIFICANCE

Summary

The sorption experiments conducted in this study showed that phosphate followed characteristic anion sorption the goethite surface. More phosphate sorption is seen at lower pH values and as pH increases, phosphate sorption decreases. In addition, as aqueous phosphate concentrations increase there is increased phosphate sorption. Experimental results showed that phosphate sorption was not significantly affected for reaction times greater than 20 hours or with changes in Fe(II) concentrations.

Fe(II) pH edges showed typical cation sorption, where more Fe(II) sorption occurred at higher pH values. Sorption isotherms were not affected by the presence or absence of phosphate when the Fe(II) concentration was held constant. In addition, with increased aqueous Fe(II) the pH edge shifted to a higher pH. In the Fe(II) sorption isotherm it was seen that with increased aqueous Fe(II) concentrations there is increased Fe(II) sorption in the presence of phosphate when compared to results without phosphate from Cwiertny [28]. The isotherm appeared to be approaching a plateau where goethite surface sites would be saturated; however the goethite surface was still undersaturated at the concentrations tested.

After analyzing the experimental results and comparing the outcomes to the hypothesis, it appears that the initial hypothesis was disproved. At the very least, at the concentrations tested, an adsorbed layer of phosphate does not inhibit electron transfer. Phosphate does not appear to affect Fe(II) sorption onto a goethite surface or electron transfer. It is possible that a higher aqueous concentration of phosphate would result in an adsorbed layer that would affect Fe(II) sorption and effectively shut of electron transfer between the adsorbed Fe(II) phase and the bulk Fe(III) phase, however this remains to be seen, and requires further research.

Recommended for Future Work

It is recommended that sorption experiments be carried out at higher concentrations of both phosphate and Fe(II) to see if any significant changes in the Fe(II) sorption pH occurs. In addition, an Fe(II) sorption isotherm should be conducted in the absence of phosphate to compare to the results obtained in this study. A higher concentration of aqueous phosphate may also lead to an adsorbed layer of phosphate that would inhibit electron transfer.

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