Research Article

Reductive dissolution of goethite and the subsequent transformation of 4-cyanonitrobenzene: Role of ascorbic acid and pH

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Abstract. There is a widespread interest in understanding the reactivity of organic pollutants in reducing systems. The reductive transformation of 4-cyanonitrobenzene (4-CNB) was examined in batch suspensions of goethite (α-FeOOH) and ascorbic acid from pH 6–8. Experimental results demonstrate that ascorbic acid promotes the reductive dissolution of goethite, which in turn, facilitates the reductive transformation of 4-CNB at all pH values examined. 4-CNB transformation rates are dependent on ascorbic acid concentration, oxide loading, and pH. In goethite suspensions, both ferric oxide dissolution and ferrous iron adsorption occur simultaneously. Generally, reductive transformation of 4-CNB by ferrous iron in suspensions of geothite and ascorbic acid would be unlikely at neutral pH because this condition is less favorable for the reductive dissolution of ferric oxides, although favorable for Fe(II) adsorption. However, we find that neutral pH values provide suitable conditions for the reductive dissolution of goethite and the subsequent transformation of 4-CNB by adsorbed Fe(II). Goethite suspensions in which the pH was pre-equilibrated at pH 4, and then increased to pH 6, 7, or 8, were more effective at producing increased Fe(II) concentrations and resulted in faster transformations of 4-CNB. The results of this study provide evidence that naturally occurring organic acids play an indirect role in the transformation of reducible organic pollutants.

Key words. Reduction; ascorbic acid; substituted nitroaromatics; goethite; dissolution; ferrous iron.

Introduction

Many organic compounds that are introduced either purposely or inadvertently into aqueous environments contain functional groups that are susceptible to reductive transformation in oxygen-free waters and sediments. Because reducing environments can occur in subsurface waters and soils, there is interest in understanding the reduction of organic compounds in such environments and in identifying the natural reducing agents responsible for the degradation of anthropogenic pollutants (Smolen et

al., 1999). An important question is whether naturally occurring organic acids contribute to the chemical reduction of organic pollutants through the generation of ferrous iron from ferric oxide dissolution. Sites associated with munitions, textile dyes, and chlorinated solvents are found to be contaminated with pollutants that are resistant to many types of chemical transformation, but are susceptible to reductive transformation. These pollutants include nitroaromatic compounds, which are relatively simple to study and make ideal model compounds to probe the reduction capacity of reduced ferric oxide systems. 4-cyanonitrobenzene (4-CNB) was chosen as a probe compound for this study due to its reactivity and ease of product quantification (Simon et al., 2000 and references therein).

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This research effort draws from studies that have examined the reductive transformation of ferric oxides by ascorbate and other complexing ligands (Banwart et al., 1989; Sulzberger et al., 1989; dos Santos Afonso et al., 1990; Suter et al., 1991; Holmen and Casey, 1996; Deng, 1997; Larsen and Postma, 2001), and another body of work that has examined the effect of adsorbed ferrous iron as a reductant of substituted nitroaromatic compounds (Heijman et al., 1993; Heijman et al., 1995; Klausen et al., 1995; Haderlein and Pecher, 1999; Schultz and Grundl, 2000; Hofstetter et al., 2003) and other reducible organic molecules (Pecher et al., 2002). At first glance, it would seem that these two chemically reactive systems are mutually exclusive: pH near neutral is required in order for ferrous iron to adsorb onto ferric oxide surfaces and serve as an effective reductant (Haderlein and Pecher, 1999), whereas an acidic pH is required for sufficient reductive dissolution of ferric oxides by ascorbic acid (Banwart et al., 1989; dos Santos et al., 1990; Suter et al., 1991; Deng, 1997; Larsen and Postma, 2001).

There has been a thorough examination of the effect of ascorbic acid concentration and pH on the reductive dissolution of ferric oxides. Most studies except for a few (Deng, 1997) have ignored reactions at pH values greater than 6, due to decreased or absent dissolution rates with increasing pH (Suter et al., 1991). This work and earlier studies (LaKind and Stone, 1989), which focused on the kinetics and mechanisms of oxide dissolution, proposed that adsorbed Fe(II) might inhibit dissolution at high pH.

A number of studies have examined the reductive transformation of nitroaromatic compounds in batch systems and column studies containing microbially formed magnetite and Fe(II) (Heijman et al., 1993; Heijman et al., 1995) or Fe(II) added to ferric oxide suspensions (Klausen et al., 1995), but not Fe(II) generated by chemical reductants. Ferrous iron can also be generated in situ through dissimilatory iron reduction (Holmen et al., 1999; Roden and Urrutia, 1999; Zachara et al., 2001; Royer et al., 2002; Doong and Schink, 2002). Many studies have examined the effect of solution composition on the reductive transformation of nitroaromatic and chlorinated organic compounds (Schwarzenbach et al., 1990; Perlinger et al., 1996; Glod et al., 1997; Butler and Hayes, 1998), but these experimental systems also did not include the complexing factor of the reductive dissolution of ferric oxides.

To date, no studies have examined the role of naturally occurring organic compounds, that reductively dissolve ferric oxides, in facilitating the reduction of organic pollutants. The objective of this research was to evaluate whether ascorbic acid (a model of naturally occurring organic acids) can indirectly facilitate the reductive transformation of 4-cyanonitrobenzene through the reductive dissolution of goethite under natural environmental pH (pH: 4–8). Experiments examined the dependence of 4-CNB reduction kinetics on ascorbic acid concentration, oxide loading, pH, and Fe(II) concentrations (adsorbed and aqueous). Ongoing and future studies will extend these findings to naturally occurring soils and other environmentally relevant organic reductants.

Materials and methods

Iron oxides and reagents
Goethite (α-FeOOH), was acquired from Bayer AG and used as received. The surface area of goethite was determined in triplicate using a Gemini 2360 Multipoint N_2 BET surface area analyzer: 15.476 (+/– 0.370) m^2/g.

4-cyanonitrobenzene (97%), 4-cyanoaniline (98%), MES (2-(N-Morpholino) ethanesulfonic acid) (99%), MOPS (3-(N-Morpholino) propanesulfonic acid) (99%), HEPES (2-[4-(2-Hydroxyethyl)-1-piperazine] ethanesulfonic acid) (99%), L-ascorbic acid (ACS certified), ferrous chloride tetrahydrate (99%+), and FerroZine® iron reagent (3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4′,4″-disulfonic acid) (98%) were acquired from Acros and used as received. Ferrous sulfate heptahydrate (ACS certified), hydrochloric acid (trace-metal free), and sodium hydroxide were acquired from Fisher and used as received.

Reduction experiments
Experiments were conducted in order to evaluate the role of goethite and ascorbic acid on the reductive transformation of 4-CNB. All batch oxide suspensions were prepared in 50-mL amber glass bottles using filtered, deoxygenated 18 MΩ water, inside of an anaerobic chamber (5% H_2/95% N_2). Typically, experiments examined the transformation of 4-CNB as a function of time (monitored for up to 20 days and sampled at 12–24 hour intervals) in suspensions of goethite containing ascorbic acid and buffer, set to a specific pH. The default setup of these reactors was: 2 g/L oxide, 1.0 mM ascorbic acid, 1.0 mM buffer, pH 7.0.

0.1 g of goethite was used in each 50.0 mL of aqueous suspension. MOPS and MES buffers were added from aqueous stock solutions of 0.025 M to result in final concentrations of 1.0 mM. Small volumes of 0.1 M HCl and NaOH were added to fix the pH to the desired value. pH was determined using an Orion semi-micro combination electrode (3 M KCl filling solution) and a Fisher pH meter. The electrode was calibrated with a three-point calibration at pH 4.0, 7.0 and 10.0 (+/– 0.02 at 25°C) with standard Fisher buffers. In all cases, 1.0 mL of a stock solution of 4-cyanonitrobenzene (3.89 mM, prepared in

acetonitrile) was added to the oxide suspensions at prede-termined points in time, resulting in an initial concentra-tion of 7.78×10^{-5} M. Amber bottles were sealed with Teflon-coated rubber septa, crimp-sealed and removed from the anaerobic chamber. In between sampling events, bottles containing oxide suspensions were kept on a tem-perature-controlled orbital shaker (New Brunswick) at 25 °C and 225 rpm.

Each reactor suspension was repeatedly sampled: the suspension was centrifuged/filtered and the supernatant was analyzed for 4-cyanonitrobenzene and 4-cyanoani-line (transformation product) using a Waters LC Module 1 HPLC equipped with a UV detector (270 nm) and All-tech Econosil C18 (250 × 4.6 mm) column. Acetonitrile (Fisher Optima) and 5.0 mM sodium acetate (Acros) were used as the mobile phase at 1.0 mL/min. Iron con-centrations (total, adsorbed, and aqueous) in the slurry were determined as detailed in the Iron Determination section. Experimental conditions that were varied in sub-sequent experiments included ascorbic acid concentra-tion (0.5, 1.0, and 5.0 mM), oxide loading (1–4 g/L), and pH (initial and final, as detailed below). Control studies were conducted in which 4-CNB was added to suspen-sions of only goethite and buffer (no ascorbic acid), to solutions containing only $FeCl_2 \cdot 4H_2O$ and ascorbic acid, and to goethite suspensions to which $FeCl_2 \cdot 4H_2O$ was added.

Experiments examining effect of pH

Batch experiments examining the effect of pH on goethite dissolution, Fe(II) adsorption, and 4-CNB transformation varied in their initial conditions. A number of experi-ments were conducted in which the pH of the oxide sus-pensions was immediately set to the target pH (6.0, 7.0, or 8.0 +/–0.1) after the addition of the appropriate buffer and ascorbic acid, and before the addition of 4-CNB. Ad-ditional experiments were conducted in which the pH was pre-equilibrated at a lower value (pH 3.5–4) after the ad-dition of buffer and ascorbic acid, and allowed to equili-brate at this pH for up to one week before adjusting to the target pH of 6.0, 7.0, or 8.0. Suspensions were then al-lowed to equilibrate at this higher pH for one week before spiking with 4-CNB and/or making Fe(II) measurements. In all batch experiments, the pH was monitored through-out each experiment. A drift of +/–0.2 pH units was not uncommon.

Iron determination

5 M HCl extraction is effective for measuring total Fe(II) concentrations (Heron et al., 1994). However, in our batch experiments containing ascorbic acid, it was neces-sary to sample for $Fe(II)_{total}$ and $Fe(II)_{aqueous}$ using an ex-tracting agent different from hydrochloric acid. The addi-

tion of strong acid to batch samples will accelerate ferric oxide dissolution to Fe(II) and result in false concentra-tions of $Fe(II)_{total}$ at near neutral pH values.

Fe(II) analysis and extractions were conducted using a modified FerroZine method (Stookey, 1970; Kostka and Luther, 1994) which does not affect ferric oxide dissolu-tion. 2.0 mL of FerroZine (2.0 mM) prepared in 0.05 M HEPES buffer and set to pH 7.0, was added to 2.0 mL aliquots of the batch suspensions inside of the anaerobic chamber. After 24 hours, these aliquots were filtered. $Fe(II)_{total}$ concentrations were then quantified on a Hitachi UV/Visible Spectrophotometer at 562 nm. Standards were prepared from $FeSO_4 \cdot 7H_2O$, and standard curves were linear up to 0.1 mM. Ferric iron concentrations were not measured in any of the batch systems.

In order to determine $Fe(II)_{aqueous}$, 2.0 mL of the oxide suspension was filtered through a 0.2 µm filter inside of the anaerobic chamber. FerroZine reagent was added to this filtrate and Fe(II) was measured on the spectropho-tometer. The adsorbed fraction of Fe(II) was determined by difference of the total and aqueous values: $Fe(II)_{total} = Fe(II)_{aqueous} + Fe(II)_{adsorbed}$. In most cases, Fe(II) concen-trations were measured at the end of each 4-CNB trans-formation experiment.

### Validation of FerroZine method

To ensure complete extraction of $Fe(II)_{adsorbed}$ and repro-ducibility of the measurements, the FerroZine extraction method was compared with control batch studies in which Fe(II) was added as $FeCl_2 \cdot 4H_2O$ to 2 g/L goethite suspensions. Following 24-hour extractions with 1.0 M HCl, Fe(II) concentrations were determined by the Fer-roZine reagent and compared with Fe(II) concentrations determined by the FerroZine extraction method. There was good agreement between iron concentrations deter-mined from both extraction methods. When FerroZine was added to suspensions containing only goethite, no absorbance was observed after these aliquots were fil-tered, indicating the lack of complex formation between ferric iron and FerroZine. Therefore, all observed ab-sorbance values are due completely to Fe(II)-FerroZine complex concentrations.

Results and discussion

Reduction of 4-cyanonitrobenzene
Kinetic Studies. This research demonstrates that ascorbic acid brings about the reductive dissolution of goethite, which in turn, facilitates the reductive transformation of 4-cyanonitrobenzene by adsorbed Fe(II). The direct re-duction of 4-CNB by either goethite, ascorbic acid, or fer-rous iron alone can be ruled out because control experi-ments with aqueous solutions containing ferrous iron and

ascorbic acid showed no transformation of 4-CNB. Furthermore, 4-CNB is also stable in suspensions containing only pure goethite. Scheme 1 illustrates the transformation of 4-cyanonitrobenzene to 4-cyanoaniline after a gain of 6 electrons and 2 protons. Mass balance is achieved during each batch experiment (Fig. 1a). 4-cyanoaniline is produced in proportion to the amount of 4-CNB reacted.
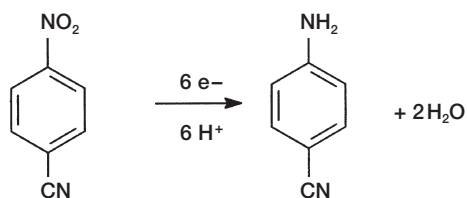
Scheme 1

4-CNB concentration vs. time data in all subsequent experiments were fit to first order kinetics and results are compared with respect to k_{obs}.

$$\text{Rate} = \frac{-d\,[4-\text{CNB}]}{dt} k_{obs}\,[4\text{-CNB}]_t \qquad (1)$$

$$\ln\left(C_t / C_o\right) = -k_{obs}\,t \qquad (2)$$

C_o is the initial concentration of 4-CNB at the beginning of each batch experiment; C_t is the concentration of 4-CNB at time, t; k_{obs} is the pseudo first-order rate constant determined for each batch experiment. Natural log concentration vs. time plots were linear for the first two half-lives (Fig. 1b). In all subsequent figures (except Fig. 6), data points are connected with lines and do not represent model fits. Control experiments were also conducted in which Fe(II) was added to batch suspensions of goethite as $FeCl_2 \cdot 4H_2O$. Pseudo first-order rate constants of 4-CNB transformation were comparable to those in systems containing ascorbic acid.

Effect of ascorbic acid concentration on k_{obs} and Fe(II) concentrations

We have examined the effect of ascorbic acid concentration on the pseudo first-order rate constants of 4-CNB transformation in goethite suspensions. The concentration of ascorbic acid in goethite suspensions was varied from 0.5 mM to 5.0 mM using an oxide loading of 2 g/L at pH 7.0. First-order rate constants of 4-CNB transformation increase as a function of ascorbic acid concentration (Fig. 2a). Error bars are +/– the standard deviation of the mantissa values. As revealed in experiments evaluating the effect of ascorbic acid concentration on the reductive dissolution of ferric oxides to ferrous iron, Fe(II) concentrations (total, adsorbed and aqueous) also in-
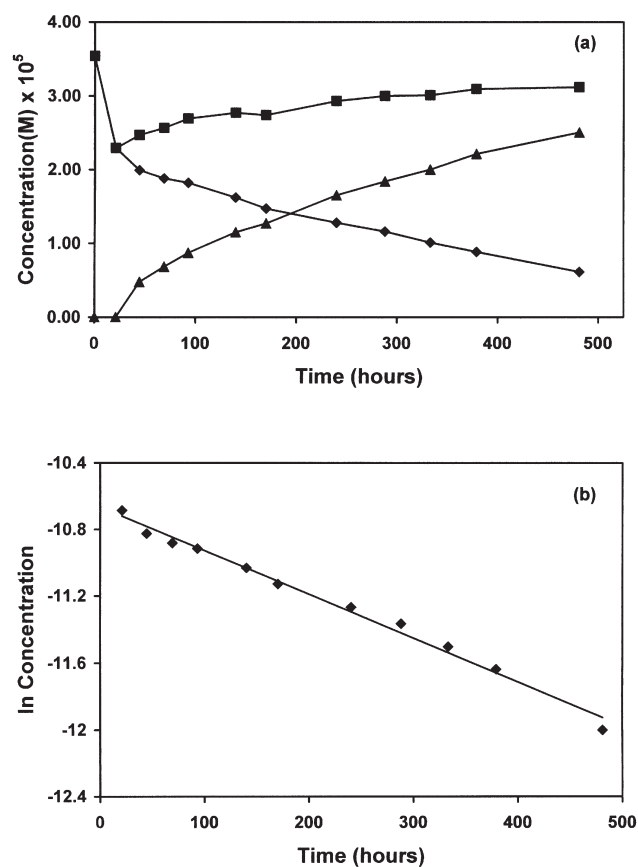

Figure 1. (a) Transformation of 4-CNB (♦) and formation of 4-cyanoaniline (▲) in 2 g/L α-FeOOH, 1.0 mM MOPS, 1.0 mM ascorbic acid at pH 7.0. Mass balance (■) is achieved throughout the experiment. (b) the natural log of 4-CNB concentration plotted as a function of time is linear for all experimental data.

crease with increasing ascorbic acid concentration (Fig. 2b). The concentration of Fe(II)$_{aqueous}$ following 14 days of equilibration remains negligible except for suspensions containing the highest concentration of ascorbic acid. Concentrations of Fe(II)$_{total}$ and Fe(II)$_{adsorbed}$ increase with ascorbic acid concentration. The decreased percentage of Fe(II)$_{adsorbed}$ compared to Fe(II)$_{total}$ at higher concentrations of ascorbic acid is likely due to decreased solid oxide remaining in suspension due to the extensive dissolution of goethite. The observed dependence of ferric iron dissolution on ascorbic acid concentration agrees with other studies conducted at lower pH values (dos Santos Afonso et al., 1990; Suter et al., 1991; Deng, 1997). Only a few studies have examined ferric oxide dissolution near pH 7 because of the slow kinetics, but our efforts demonstrate that significant ferrous iron concentrations (up to 5.9×10^{-5} M) can result from goethite dissolution by ascorbic acid near neutral pH over a period of 400 hours.
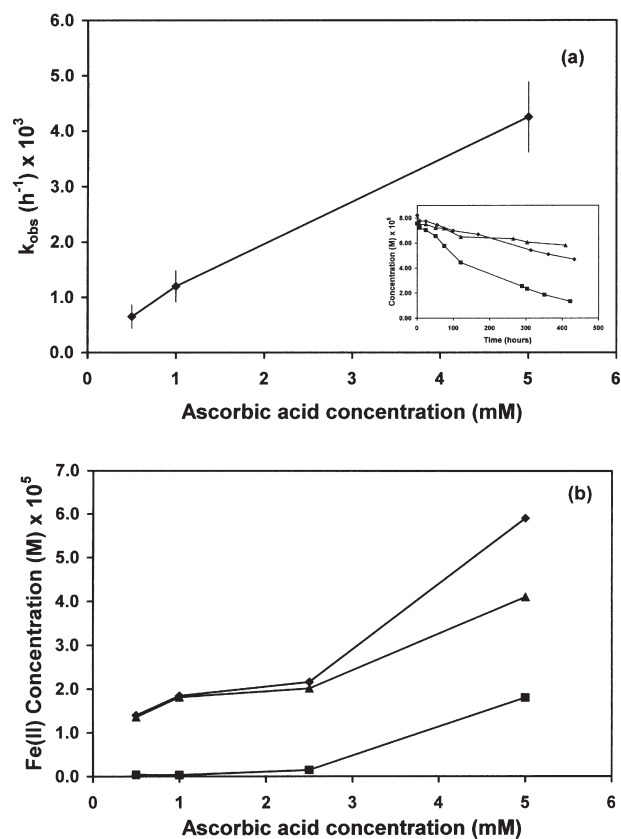
Figure 2. The effect of ascorbic acid concentration on (a) the pseudo first-order rate constants of 4-CNB transformation and (b) ferrous iron concentrations: $Fe(II)_{total}$ (♦), $Fe(II)_{adsorbed}$ (▲), and $Fe(II)_{aqueous}$ (■). Reaction conditions: 2 g/L α-FeOOH, 1.0 mM MOPS, pH 7.0. Inset: Transformation of 4-CNB as a function of time in the presence of 0.5 mM (▲), 1.0 mM (♦), and 5.0 mM (■) ascorbic acid.

Figure 3. The effect of oxide loading on (a) the pseudo first-order rate constants of 4-CNB transformation and (b) ferrous iron concentrations: $Fe(II)_{total}$ (♦), $Fe(II)_{adsorbed}$ (▲), and $Fe(II)_{aqueous}$ (■). Reaction conditions: 1.0 mM ascorbic acid, 1.0 mM MOPS, pH 7.0. Inset: Transformation of 4-CNB as a function of time in the presence of 1 g/L (■), 2 g/L (♦), and 4 g/L (▲) α-FeOOH.

Effect of oxide loading

Experiments were conducted in which the oxide loading of the goethite suspensions was varied from 1 g/L to 4 g/L in order to compare the results to the default conditions of 2 g/L. All experiments were conducted at pH 7.0 with an ascorbic acid concentration of 1.0 mM. Pseudo first-order rate constants of 4-CNB transformation increased as the goethite loading was increased from 1 to 4 g/L (Fig. 3 a). Fe(II) concentrations also increased as a function of oxide loading (Fig. 3 b). The effect of oxide loading on k_{obs} can be explained by the effect of oxide loading on Fe(II) concentrations. This is explained in greater detail in the discussion of the effect of $Fe(II)_{adsorbed}$ on k_{obs}. However, the dependence of k_{obs} and Fe(II) concentration on oxide loading does provide further evidence that goethite suspensions containing ascorbic acid at neutral pH can effectively facilitate 4-CNB transformation.
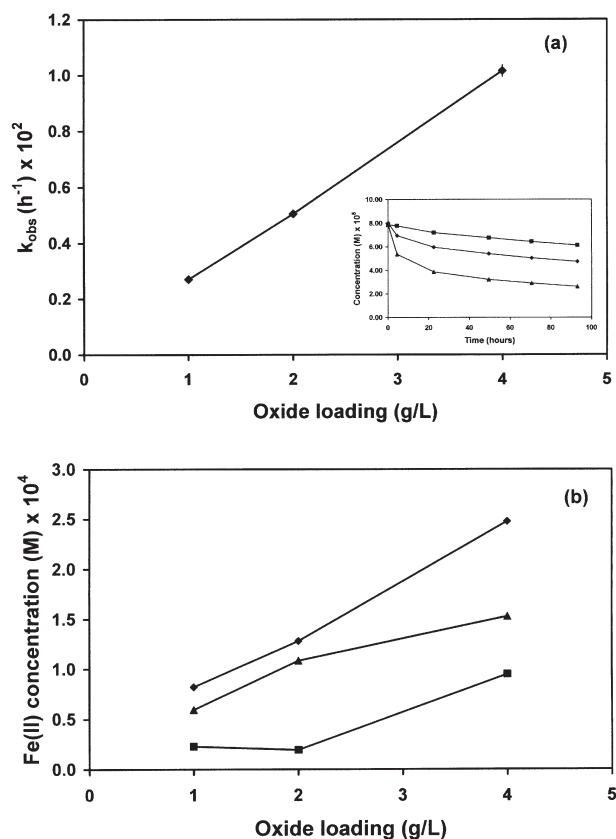
Effect of pH

The main goal of this work was to evaluate whether the reductive dissolution of goethite by ascorbic acid at or around pH 7 can generate sufficient ferrous iron that can adsorb onto the goethite surface and effectively cause the reductive transformation of reducible organic compounds, specifically 4-cyanonitrobenzene. Although the kinetics of ferric iron dissolution are typically slower at higher pH, over a period of time sufficient concentrations of Fe(II) may be produced in order to facilitate reduction of the model organic compound.

It would appear at the outset that the low pH necessary to generate Fe(II) would be mutually exclusive from the high pH needed to adsorb Fe(II) and render it an effective reductant. A goethite suspension at a pH of 6 would produce sufficient Fe(II) through reductive dissolution, but the pH would not be basic enough for maximum adsorption of Fe(II) onto the goethite. A pH of 8 could preclude sufficient Fe(II) formation from the reductive dissolution of goethite, even though this pH is suitable for strong Fe(II) adsorption. Here we evaluate the effect of pH on

the reductive dissolution of goethite and the subsequent reductive transformation of 4-CNB.

Effect of initial pH. In addition to experiments in which the pH was immediately set to 6, 7, or 8, a number of batch experiments were conducted in which the goethite suspension was pre-equilibrated at a lower pH (between 3.5 and 4) for up to 7 days before setting the pH of the goethite suspension to more basic values (pH: 6–8). This exercise of pH-modification was conducted with the intention of generating higher concentrations of Fe(II) from ferric oxide dissolution before the addition of 4-CNB. Figure 4 summarizes the results of all experiments that examined pH as a variable.

Figure 4a illustrates the effect of pH on the pseudo first-order rate constants of 4-CNB transformation in sus-
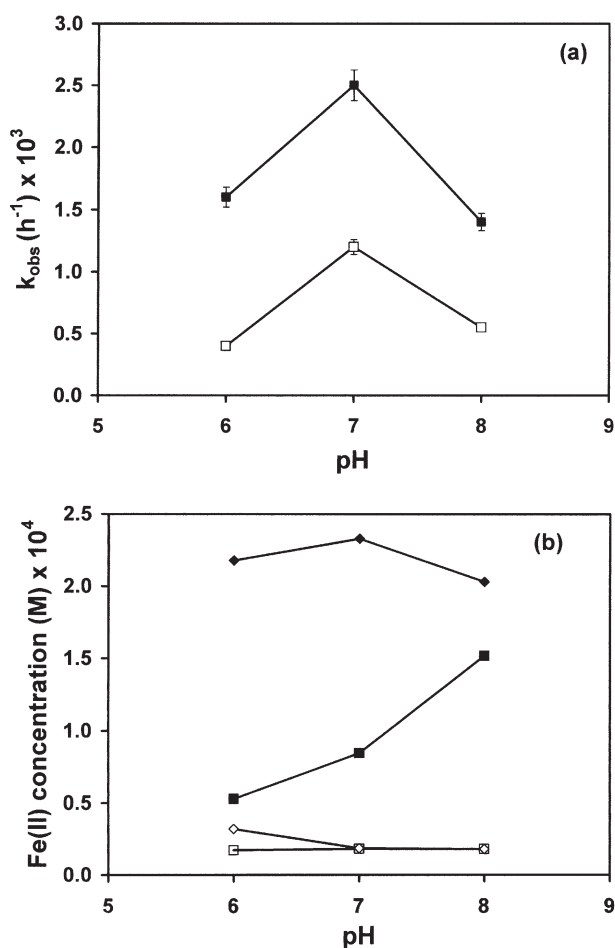

pensions containing 2 g/L goethite and 1.0 mM ascorbic acid. The maximum k_{obs} that was observed occurs at pH 7.0, with observable rate constants 2 to 3 times lower at pH 6.0 and 8.0. These result differ from a study that observed increasing first-order rate constants with increasing pH from 6 to 8 (Klausen et al., 1995). However, these cited experimental systems did not contain the competing effect of an adsorbing species such as ascorbic acid. In all cases, when the pH is pre-equilibrated at pH 3.5–4 for one week before it set to the target pH of 6.0, 7.0, or 8.0, the k_{obs} of 4-CNB transformation is 2 to 4 times greater than in the cases in which the pH was immediately set to the target pH before spiking with 4-CNB. The rate constants at pH 7.0 were also greater than those at pH 6.0 and 8.0 for the batch systems in which the goethite was pre-equilibrated at pH 4. An examination of Fe(II) behavior as a function of pH is warranted in order to elucidate the pH-dependence of k_{obs}.

Figure 4b shows the effect of pH on Fe(II) concentration (total and adsorbed) in batch systems of goethite (2 g/L) and ascorbic acid (1.0 mM). It is apparent that pre-equilibration of the suspensions at a pH 4 increases the overall concentrations of Fe(II) produced (solid symbols), resulting from the increased reductive dissolution of goethite in acidic pH. $Fe(II)_{total}$ concentrations in the pre-equilibrated suspensions are up to 12 times greater than in the batch systems in which the oxide suspension was immediately equilibrated at pH 6, 7, or 8. In the pre-equilibrated suspensions, the total ferrous iron concentrations do not vary significantly as a function of pH, but the $Fe(II)_{total}$ is lower by 15–30 µM at pH 8.0. $Fe(II)_{total}$ also decreases by a factor of 1.8 as the pH is increased from 6.0 to 8.0 in the suspensions without the pre-equilibration step. These observations are expected due to slower ferric iron dissolution kinetics and lower overall Fe(II) production with increasing pH.

The percentage of $Fe(II)_{total}$ that is adsorbed onto the goethite also varies as a function of pH. In suspensions that were pre-equilibrated at pH 4, less Fe(II) is adsorbed at pH 6, and the most Fe(II) is adsorbed at pH 8. As a result, relative concentrations of $Fe(II)_{aqueous}$ decrease as pH is increased, which is due to a greater fraction of Fe(II) being adsorbed with increasing pH. In suspensions that were immediately set to pH 6, 7, or 8, concentrations of $Fe(II)_{adsorbed}$ do not follow any positive or negative trend relative to pH, but remain relatively constant. The pH independence of Fe(II) adsorption here is similar to what was observed in another study that examined the adsorption of Fe(II) to in the presence of ascorbic acid from pH 4 to 10 (Deng, 1997). The adsorbed ascorbic acid is likely to block sites on the goethite surface that would normally be available for Fe(II) adsorption. This is demonstrated more clearly in Figure 5.

Typically, the extent of divalent metal ion adsorption onto goethite increases with increasing pH (Coughlin and
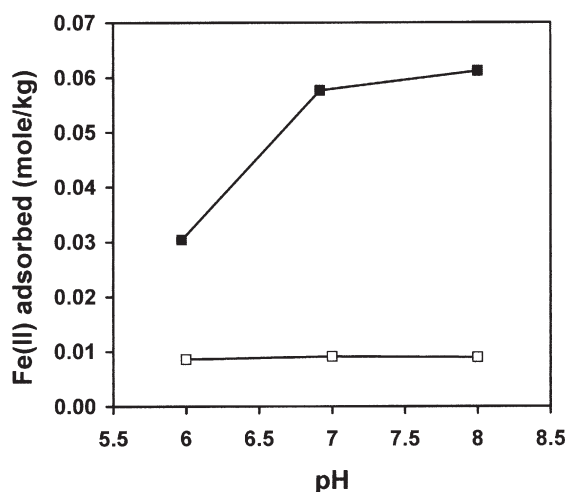
Figure 4. The effect of pH on (a) the pseudo first-order rate constant of 4-CNB transformation and (b) ferrous iron concentrations. Reaction conditions: 2 g/L α-FeOOH, 1.0 mM MOPS, 1.0 mM ascorbic acid. In both (a) and (b), open symbols represent data points in which oxide suspensions were immediately equilibrated at the target pH. Closed symbols represent data points in which goethite suspensions were pre-equilibrated at pH 4.0 for 7 days before being equilibrated at the target pH. Also shown in this figure is $Fe(II)_{total}$ (♦, ◊) and $Fe(II)_{adsorbed}$ (■, □).

Figure 5. Ferrous iron adsorption as a function of pH in the absence (■) and presence (□) of 1.0 mM ascorbic acid. Reaction conditions: 2 g/L α-FeOOH, 1.0 mM buffer.

Figure 6. Pseudo first-order rate constants of 4-CNB transformation (k_{obs}) as a function of Fe(II)$_{adsorbed}$. Data is compiled from all experiments examining the effect of ascorbic acid, oxide loading, and pH on 4-CNB transformation.

Stone, 1995). In an experiment in which Fe(II) was added as $FeCl_2 \cdot 4H_2O$ to goethite suspensions, Fe(II)$_{adsorbed}$ increased with increasing pH (Fig. 5). This adsorption trend compared to the adsorption behavior of Fe(II) observed in goethite suspensions containing ascorbic acid illustrates the competing effect that an additional adsorbing species can have on cation adsorption.

Effect of Fe(II)$_{adsorbed}$ on k_{obs}

Data from all batch experiments were compiled and k_{obs} was plotted as a function of the molar concentration of Fe(II)$_{adsorbed}$ (Fig. 6). As shown, k_{obs} increases with increasing concentrations of Fe(II)$_{adsorbed}$, and the resulting correlation is linear. From this analysis, we propose a second-order rate law:

$$\frac{-d\,[4-CNB]}{dt} = k^*[C]_t\,[Fe(II)_{adsorbed}] \qquad (3)$$

where the bimolecular rate constant, k*, calculated from the slope of the line in Figure 6, has a value of 61.33 (+/− 7.48) $M^{-1}\,h^{-1}$ at 25 °C.

$$k_{obs} = k^*[\,Fe(II)_{adsorbed}] \qquad (4)$$

The dependence of the pseudo first-order rate constant, k_{obs}, on ascorbic acid concentration, oxide loading, and pH can be summarized by its dependence on Fe(II)$_{adsorbed}$. These experimental variables also affect Fe(II) formation from goethite dissolution and subsequent Fe(II) adsorption (Figs. 2−4).

This study has demonstrated that chemical reductants, such as ascorbic acid, can play a role in the reductive
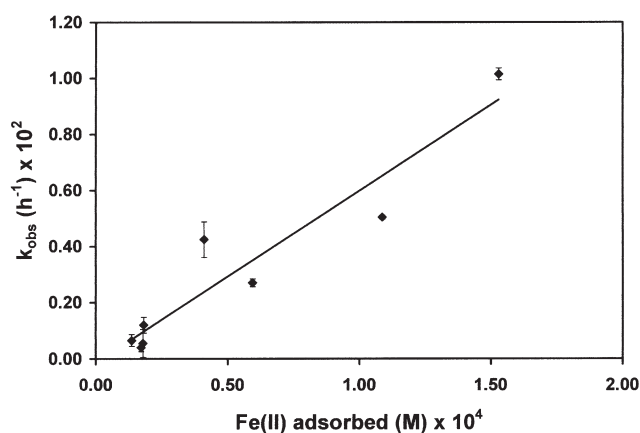
transformation of reducible organic compounds in natural environments containing ferric oxides. These results provide a perspective on how the variability of natural systems can have a significant effect on chemical reactivity. Clearly, there may be a range of reactivity among ferric oxides and among oxide surfaces. In addition, many other small organic acids may also affect reactivity through surface complexation, but the redox characteristics of all present compounds must be evaluated.

The kinetics of the reductive transformation of 4-cyanonitrobenzene depend primarily on the amount of Fe(II)$_{adsorbed}$. As we have shown, the kinetics are also indirectly affected by ascorbic acid concentration, oxide loading, and pH. The results evaluated here are directly applicable to environments that may experience fluctuations in pH, i.e., stratified water bodies. While other biologically active systems that generate Fe(II) are equally important, chemical reductants that generate Fe(II) in soils and sediments cannot be overlooked. Ongoing studies are examining other environmentally relevant organic reductants and iron-containing soils.

Acknowledgments

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