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pH Dependence on Reduction Rate of 4-Cl-Nitrobenzene by Fe(II)/ Montmorillonite Systems

CHRISTOPHER A. SCHULTZ AND
TIMOTHY J. GRUNDL*

Geosciences Department and Great Lakes WATER Institute,
University of Wisconsin−Milwaukee,
Milwaukee, Wisconsin 53211

The pseudo-first-order reduction of 4-Cl-nitrobenzene by Fe(II) in aqueous systems containing montmorillonite clays is investigated over the pH range 6.00−8.00. Silica and alumina is also investigated as simple analogues to aluminosilicate mineral surfaces. At pH 7.25, montmorillonite clays were found to be as much as 1000 times less effective than ferric oxides at mediating the reaction when expressed on a surface area basis. Reaction rates increase dramatically as the pH rises and at pHs above 7.5 approach those previously reported for surface bound Fe(II) on ferric oxides at pH 7.22. This increase in reactivity is attributed to both an increase in concentration of the $FeOH^+$ ion and to the increased sorption of Fe(II) at high pH. Sorption isotherms for Fe(II) to montmorillonite clays at pH 7.00 are reported. Two surface sites are suggested on clay minerals and incorporated into a kinetics model for the pH dependence of the reaction. The overall reaction is modeled as the sum of the reactions between 4-Cl-NB and three reductants; $FeOH^+$ and Fe(II) bound to the two surface sites. $FeOH^+$ is found to be the most effective reductant in our systems. Intrinsic rate constants for both surface sites and $FeOH^+$ are presented. Although the minerals investigated are much less effective at mediating the reaction than ferric oxides, the rates are sufficiently fast to be of importance to environmental processes. At neutral pHs, half-lives are less than a week and decrease to the scale of hours above pH 7.5. This is quite rapid in the context of groundwater systems in which residence times can be months or years.

Introduction

Nitroaromatic (NAC) and polynitroaromatic (PNAC) compounds are of interest to environmental scientists because they are dangerous and widely distributed in the environment (*1, 2*). NACs are used by agriculture as herbicides and insecticides, by industry as chemical feedstock and dyes, and by the military as explosives (*1, 3*). The extensive use of these compounds has resulted in the intentional and accidental introduction into the environment, both due to their mode of use and as a result of improper disposal methods. Concern about the NACs as environmental contaminants has led to extensive and varied approaches to the remediation of these materials.

A considerable body of literature has developed concerning various methods of degrading this class of compounds in the environment. Proposals for the remediation of NACs include phytoremediation, reaction with solid reductants, and reaction with aqueous reducing agents. Schnoor (*4*) has proposed that TNT and other explosives can be remediated by hybrid poplar trees, and other researchers have developed a tobacco plant that degrades TNT (*5*). There are several methods of reducing NACs to their aniline analogues by reaction with zerovalent iron (e.g. ref *6*). A body of work from the Schwarzenbach group (*7*−*10*) has investigated the reaction between NACs and various forms of ferrous iron complexed with both organic ligands and mineral surfaces. This method of (P)NAC degradation has the advantage of using a mobile reductant (aqueous Fe(II)) which can be introduced at a distance from the potentially explosive contamination site.

This body of work has established that Fe(II) can reduce many NACs if complexed to iron oxide minerals at near neutral pH conditions. Reaction rates are largely independent of the iron oxide mineral itself indicating that the reactivity is due to the formation of an inner-sphere complex between the generic iron oxide surface and Fe(II) (*9, 11, 12*). This can be readily understood in terms of electron density being donated to the Fe(II) atom by the adjoining OH^- ligands (*13, 14*). Complexed Fe(II) is thereby provided with extra reducing power.

Aqueous phase complexing with hydroxyl ligands (i.e. hydrolysis of Fe^{2+} to $FeOH^+$) should also provide an increase in reducing power. This can be understood in terms of a solution phase complex between an electron-donating ligand (OH^-) and a metal ion (Fe^{2+}) donating electron density to the complex and stabilizing the oxidized state of the metal (*13, 14*). Both processes make the complex a more powerful reductant than the metal ion alone. In the case of Fe^{2+}, hydroxide donates electron density through both the σ and π orbitals (*14*), and this results in the reduction rate of O_2 by $FeOH^+$ that is 10^6 times faster than O_2 reduction by Fe^{2+} (*15*). The extra reducing power of an Fe(II) = goethite surface complex and $FeOH^+$ is essentially equivalent as indicated by the nearly identical calculated one electron redox potential at pH 7 ($E_h°$) of 0.36 and 0.34 V, respectively (*13, 15*).

A similar effect is observed for Fe(II) in iron-rich silicate minerals. The oxidation by O_2 of structural Fe(II) at the surface of augite and hornblende is faster than the equivalent oxidation of Fe(II) in solution (*16*−*18*). White and Yee (*16*) estimate the $E_h°$ of these minerals to be within the range 0.33−0.52 V. The redox lability of iron contained in smectite clay minerals is also well established. Iron rich montmorillonites are rapidly and reversibly reduced by chemical reductants (*19*) and by bacterial action (*20, 21*). Bacteria are also capable of reducing the ferric iron contained in iron oxide minerals (*22*).

Work by Schwarzenbach (*23*) and Stumm (*13, 24*) determined the single electron reduction potentials for a number of ferrous iron reducing agents and for chlorinated and nitrated pollutants. It has been shown that (P)NACs are reduced by iron porphyrin, ferrous iron complexes of quinone (*7*), and *Streptomyces* sp. exudates under iron reducing conditions (*25*). Ferrous iron has also been shown to reduce NACs in the presence of iron oxides (*8, 9, 26*). The overall reduction reaction consists of a six-electron reduction of the nitroaromatic to the corresponding aminoaromatic through two stable intermediates, the nitroso- and hydroxylamino-analogues (Figure 1a). The reaction of aqueous ferrous iron itself (Fe^{2+}) with NACs is not thermodynamically favorable; the ferrous iron must form an inner-sphere complex that is capable of transferring the first electron. The iron complexed

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* Corresponding author phone: (414)229-4765; fax: (414)229-5452; e-mail: grundl@uwm.edu.

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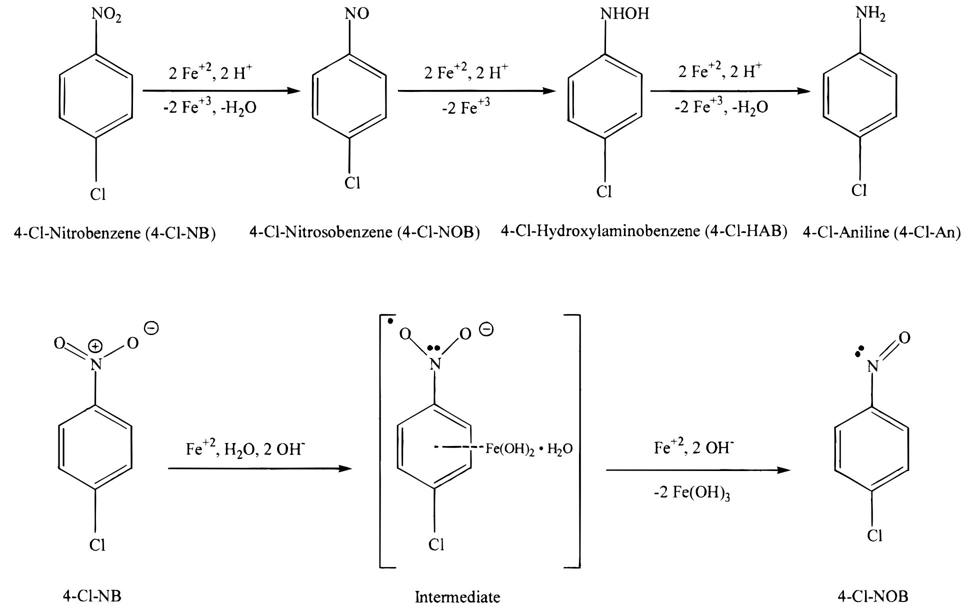


FIGURE 1. (a) Overall reduction reaction of 4-Cl-nitrobenzene to 4-Cl-aniline. (b) Proposed mechanistic pathway for the first reductive step of 4-Cl-nitrobenzene to 4-Cl-nitrosobenzene.

to the radical intermediate may stabilize it, further favoring the reaction (Figure 1b).

The present study is concerned with determining if montmorillonite clay minerals are capable of mediating the reduction of NACs to their aniline analogues by forming similar complexes with ferrous iron. Montmorillonite clays exhibit very large surface areas (approximately 700 m^2/g) and a correspondingly large cation exchange capacity (80−150 mequiv/100 g) (*34*). Montmorillonites are ubiquitous, forming from weathering of primary silicate minerals under neutral to alkaline conditions. Montmorillonites have several attributes that make them desirable mediators for this reaction; they have a strong ability to form surface complexes with metals, and, in addition, iron within the lattice may facilitate and promote the reaction. Silica gel and alumina were also examined, because the surface of a clay consists of individually exposed silicon and aluminum hydroxides, thus these phases are the simplest analogues to the surface of a clay. Silica and alumina can also be considered simple analogues for silicate and aluminosilicate minerals that, in general, form the bulk of the solid phases encountered in the environment. This study has measured the rate of reaction for the reduction of NACs by ferrous iron when mediated by montmorillonite clays and has developed a mechanistic and kinetic model for the reaction.

Experimental Section

Chemicals. 4-Chloronitrobenzene (4-Cl-NB); 4-chloroaniline (4-Cl-An); *N*-2-hydroxyethylpiperazinepropanesulfonic acid (EPPS, pK_a 8.00); ferrous chloride tetrahydrate; and ferrozine were purchased from Aldrich Chemical (Milwaukee, WI). 3-(*N*-morpholino)propanesulfonic acid (MOPS, pK_a 7.20); 2-(*N*-morpholino)ethanesulfonic acid monohydrate (MES, pK_a 6.15); silica gel; alumina; and hydroxylamine hydrochloride were purchased from Fisher Scientific (Pittsburgh, PA). Gas was obtained from Praxair (Oak Brook, IL). All chemicals were analytical grade and were used without further purification. SWa-1 nontronite clay was obtained from the Clay Minerals Society, and Wyoming montmorillonite was obtained commercially. Both clay minerals were Na-saturated prior to use. Ferrous chloride solution (1.0 M) was prepared using a modified procedure of Klausen (*8*), wherein ferrous chloride tetrahydrate solid was transferred to an anaerobic hood, dissolved in deaerated water (10 mL), and filtered through a 0.22 μm filter into concentrated hydrochloric acid (1 mL). This procedure eliminated any trace colloids potentially present in the ferrous chloride tetrahydrate solid. Subsequent dilutions of this acidic stock solution to more basic experimental vials were done in the anaerobic chamber.

Analytical Procedures. 4-Cl-NB and 4-Cl-An were analyzed using the method of Klausen (*8*, *26*). Analysis was performed by HPLC using an Econosphere C-18 3U column (Alltech Associates, Deerfield, IL), Waters model 501 HPLC Pump (Waters Inc., Milford, MA), and Gilson model 112 UV/visible detection at a wavelength of 254 nm (Gilson, Middleton, WI). The mobile phase was 10 mM, pH 6 hydroxylamine hydrochloride in methanol/water, 3/2 v/v. Aqueous ferrous iron concentrations were measured spectrophotometrically using ferrozine (*27*, *28*) at a wavelength of 562 nm on a Beckman model DU 7400 spectrophotometer (Beckman, Fullerton, CA). All experiments were buffered using sulfonic acid buffers. The buffers and pH ranges used are as follows: MES, pH 6.00−6.50; MOPS, pH 6.75−7.50; and EPPS, 7.75−8.00. All procedures were carried out in an anaerobic chamber under an atmosphere of H_2/N_2 (10:90) with a palladium catalyst scrubber. All experiments were carried out in the dark, and the temperature was maintained at 23 ± 2 °C.

Measurement of Ferrous Iron K_d. A 25 mL borosilicate glass vial was loaded with 240 mg of mineral, 22 mL of deoxygenated water, and 2 mL of buffer. Sufficient ferrous chloride (1.0 M stabilized with 0.1 M HCl) was added to obtain a desired initial concentration. The pH was checked and adjusted with sodium hydroxide (0.1 M). The volume added was generally 110% of the volume of $FeCl_2$ added.

Samples were shaken overnight on a shaker table. An aliquot was removed, and ferrous chloride (1.0 M) and sodium hydroxide (0.1 M) were added to obtain a new ferrous iron concentration. The oxide minerals settled out of suspension rapidly, and the supernatant (100 μL) was added directly to ferrozine (1 mL) for analysis. The clays remained in suspension and required centrifugation for 15 min prior to ferrozine analysis.

Preparation of Kinetics Experiments. 4-Cl-NB was chosen as a representative nitroaromatic compound. The kinetics of this reaction were measured using batch experiments for each mineral and the blank (no minerals added) at pHs from 6 to 8. Borosilicate glass serum bottles were loaded with dry mineral (10 g/L), transferred into an anaerobic hood where deaerated water and the buffer were added, sealed with a black butyl-rubber stopper, and shaken overnight to suspend and hydrate the mineral. Sulfonic acid-based buffer (1.0 M), $FeCl_2$ (1.0 M), and NaOH (0.1 M) were used to provide the desired final concentrations (buffer 50 mM and Fe^{2+} 500 μM after sorption to the mineral) and pH. The addition of $FeCl_2$ and NaOH were made in smaller quantities over several days to prevent the precipitation of $Fe(OH)_2$(s). The final solution was shaken overnight to ensure sorptive equilibrium. pH levels remained unchanged throughout the course of the experiment.

To start a kinetics experiment, 4-Cl-NB (0.1 M in methanol) was added by syringe to yield an initial concentration of 50 μM. The experiment was periodically sampled by syringe for measurement of the ferrous iron concentration and analysis of the organics. The reaction was quenched by adding 100 μL of hydroxylamine (2.16 M, pH 6) to 1 mL of solution. At high pH clay experiments, the use of hydroxylamine was ineffectual. In these cases, the experimental solution was sampled, centrifuged, and directly injected into the HPLC. The time assigned to these samples was the time of injection.

Results

Sorption Experiments. In our study, it was discovered that the sorption of ferrous iron to clay minerals was significant. Despite the recognized importance of ferrous iron to environmental redox processes in terms of its ability to transfer electrons and poise the E_h of the system, we have found only two papers which explicitly address the sorption of ferrous iron to mineral surfaces (*12, 29*). Haderlein and Pecher (*12*) report minimal sorption of ferrous iron onto several ferric oxides (K_ds from 0.25 to 2.3 at pH 7.25).

To have a constant aqueous Fe(II) concentration at the start of each kinetics experiment, the sorption of Fe(II) to each mineral over the entire pH range had to be determined. Sorption isotherms for ferrous iron in a background of sulfonic acid buffer (50 mM), sodium, and chloride were determined for each of the minerals over the pH range of 6−8. Sodium originated from the clay as iron was exchanged to the surface, and chloride came from the ferrous chloride solution, which was stabilized using hydrochloric acid (0.1 M). The ionic strength of the various experiments ranged from 9 to 35 mM at the beginning and increased to a range of 12−50 mM at the end of the experiment; the ranges result from differences in the loading of the iron and the extent of ionization of the buffer. These measurements were performed in batch experiments by successive additions of ferrous iron followed by equilibration for 24 h. The additions of Fe(II) were made in increments small enough to prevent precipitation of ferrous hydroxide ($Fe(OH)_2(s) = Fe^{2+} + 2OH^-$, log $K_{sp} = -14.5$ (*30*)). These experiments were performed for the purpose of determining the quantity of ferrous chloride which must be added to obtain a specific concentration of Fe(II) in the water (500 μM); therefore, no competition or reversibility experiments were run. An example isotherm for the sorption of ferrous iron to SWa-1 at pH 7.00 is presented in Figure 2. The data follow a Freundlich isotherm with a distribution coefficient of 21.2 and an exponent of 0.38 (Figure 2). Wyoming montmorillonite behaves in a similar manner with a distribution coefficient of 36.7 and an exponent of 0.33 (data not shown). A more complete study of Fe(II) sorption to clays is currently underway.

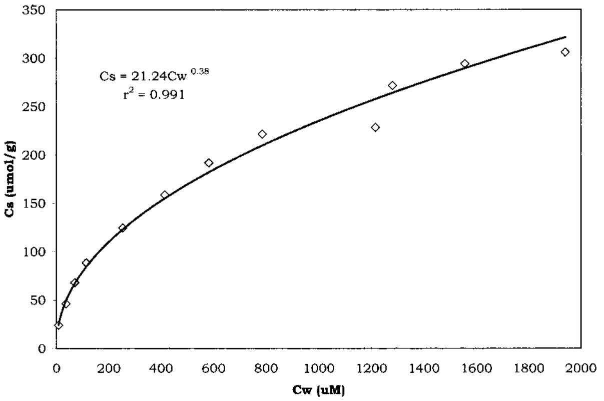


FIGURE 2. Sorption isotherm for ferrous iron to SWa-1montmorillonite at pH 7.00. Solution was 50 mM MOPS buffer and 10 g/L clay.

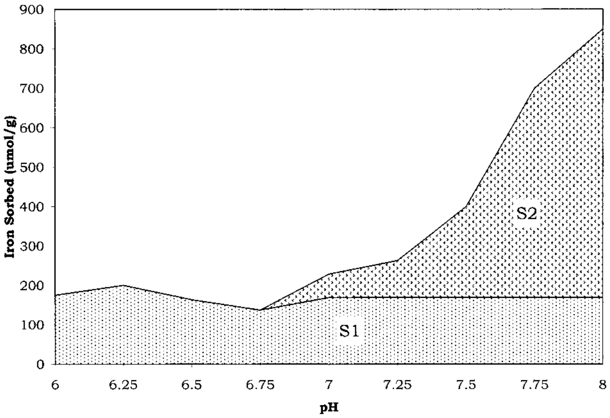


FIGURE 3. Amount of ferrous iron bound to SWa-1montmorillonite when solution contains 500 μM ferrous iron. Amount of iron on surface site 1 (S1) is measured below pH 6.75. Above pH 6.75, S1 is set to the average of the values from 6.00 to 6.75. Amount of iron on surface site 2 (S2) is the difference between the measured value and the value assigned to S1.

From these experiments the amount of Fe(II) needed to obtain an aqueous concentration of 500 μM was determined (Figure 3). Figure 3 indicates that the necessary iron loading was constant up to pH 6.75 and then rose rapidly. It was also noted that the color of the samples changed from tan to green over the pH range from 6 to 7 and to dark green at pH 8 as the samples were loaded. These changes were attributed to a change in the manner in which iron is bound to the surface. It was assumed that the consistent extent of sorption from pH 6.00 to 6.75 was due to a cation exchange type process on the clays and that the concentrations of these exchange sites remained unchanged at all pHs. The increase in sorption at pHs above 6.75 was assumed to be from a second set of sorption sites. The actual nature of these sites has not been determined. Although the concentration of Fe(II) in solution is always well below the nominal solubility of $Fe(OH)_2$ (less than one-quarter of the calculated solubility at pH 8 and well below that at all other pHs measured), precipitation in microenvironments or the formation of mixed valent precipitates cannot be ruled out particularly at high pHs (*12, 31*).

Regardless of the type of surface sites involved, the geochemical implication of this sorption data is that in reduced sediments, especially those containing more than a few percent clay, the pool of sorbed, redox-labile ferrous iron can be vast. Our data indicates that at pHs as low as 6.00, the concentration of ferrous iron sorbed to clays is considerably higher than the concentration of iron in solution. Therefore the poising capacity of similar sediment systems can be large, and the addition of an oxidizing agent may have less effect on the redox potential than would be expected from the redox species that are measurable in the aqueous phase.

For the purposes of kinetics modeling, the sorbed iron on clays was interpreted to exist on two independent sorption sites of surface bound iron, S1 and S2 (Figure 3). The S1 site

TABLE 1. Concentration of Surface Bound Ferrous Iron (μmol/g) for S1 and S2 over the pH Range 6−8

pH	6.00	6.50	7.00	7.50	8.00
			Surface Site 1 (S1)		
SWa-1	175	164	169	169	169
montmorillonite	158	149	156	156	156
silica	4	7	16	31	120
alumina	1	11	20	69	N/A[a]
			Surface Site 2 (S2)		
SWa-1			59	231	681
montmorillonite			112	594	674

[a] N/A means not available.

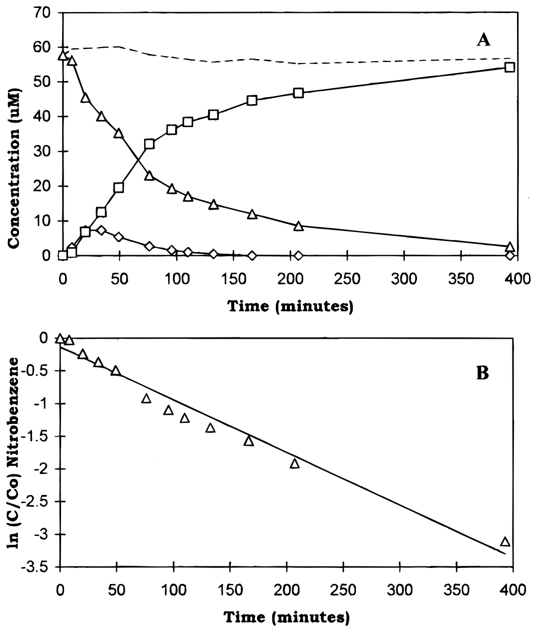


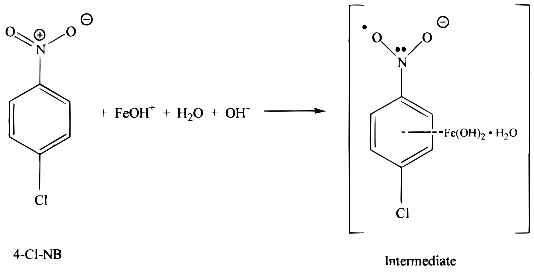
FIGURE 4. (a) Reduction of 50 μM 4-Cl-NB (Δ), in growth of the intermediate 4-Cl-HAB (◊) and the final product, 4-Cl-An (□) as mediated by SWa-1at pH 7.75. Mass balance is indicated by the sum of all three species (- - -). (b) Natural log plot of the 4-Cl-NB data contained in (a). Solid line is the linear regression through the data.

is the pool of iron sorbed predominately on exchange sites which is evident below pH 6.75. These sites are considered to remain active within the larger pool of iron sorbed at pHs above 6.75. The extent of sorption attributed to S2 sites at pHs above 6.75 is the difference between iron sorbed to S1 sites (the average of the loadings from pH 6 to 6.75) and total sorption. Sorption of ferrous iron to the oxide minerals did not exhibit any distinction between sites 1 and 2; therefore, oxide minerals are modeled with only one surface site (listed as S1). The values for the sorption of ferrous iron attributed to S1 and S2 sites (on clays) are listed in Table 1for each mineral from pH 6 to 8.

Kinetics Experiments. The measurement of the kinetics of 4-Cl-NB reduction was performed in batch experiments by reaction of 4-Cl-NB with Fe(II) (500 μM) in the presence of each mineral every quarter pH unit for the blank and the clays (SWa-1 and Wyoming montmorillonite) and every half pH unit for silica gel and alumina from pH 6 to 8. The concentrations of 4-Cl-NB, 4-Cl-An, and one of the intermediates were measured and plotted versus time (Figure 4a). The presence of the intermediate was based on the measurement of an HPLC peak that grew in early in the experiment and subsequently decayed to zero. The compound was not identified but was presumed to be 4-Cl-HAB because 4-Cl-NOB is probably rapidly reduced to 4-Cl-HAB. The pseudo-first-order nature (with respect to NB) of this reaction is evident from the plot of $\ln(C/C_o)$ versus time (Figure 4b). The k_{obs} values for the blank (no added minerals) and for each mineral are listed in Table 2at every half pH unit from 6 to 8.

Mechanistic Model. Previous studies of this reaction have reported that the rate of reaction in the absence of a mediating surface at neutral conditions is slow and not of interest (*8, 9, 26*). The present study is concerned with longer time periods, and as a result the blank was found to have significant reactivity, especially at higher pHs. The reactivity of Fe(II) in the absence of a mediating surface was found to be very low at pHs below 7 but became significant above pH 7 (Figure 5).

The reaction rate for the blank is modeled by attributing the reaction to reduction by $FeOH^+$. The $E_h°$ for this species is 0.34 V SHE, similar to that of surface bound Fe(II) species ($E_h° = 0.36$ V (bidentate) or 0.34 V (monodentate) vs the standard hydrogen electrode (SHE)) (*13, 16*), but it has been ignored in the past because of its low concentration at neutral pH. At pH 7, the concentration of $FeOH^+$ represents only 0.08% of the total concentration of Fe(II) in solution (*32*). The first electron transfer, the rate-limiting step, for the reaction between $FeOH^+$ and 4-Cl-NB is shown in eq 1.



$$\text{rate} = k_{\text{FeOH+}} * [\text{FeOH}^+] * [\text{4-Cl-NB}] * [\text{OH}^-] \qquad (1)$$

The best-fit value for k_{FeOH^+} is $6.3 \times 10^{+13}$ min $^{-1}$ M^{-3} and was obtained from experiments conducted with no minerals present (Figure 5).

Ferric oxyhydroxide precipitates are formed during the course of this reaction, and these precipitates are a source of mediating surfaces that could potentially control the reaction. If ferric precipitates controlled the rate of reaction, the expected kinetic behavior in any given experiment would be an ever-increasing rate over time as the concentration of ferric precipitates increased. In contrast to this, the observed behavior is pseudo-first-order in ferrous iron for many half-lives (Figure 4b) as is expected for a homogeneous reaction with $FeOH^+$ as the reductant. Furthermore, a characteristic pattern of rate increases is observed as the pH moves from 6 to 8 that exactly correlates to the increase in $FeOH^+$. Both of these observations indicate that ferric precipitates do not control the reactivity in the blank experiments.

Aqueous complexes formed between ferrous iron and carbonate ($FeCO_3^0$ (aq)) are also known to be quite reactive in the oxidation of ferrous iron by oxygen (*38*), and a similar reactivity might occur in the oxidation of NB. Our experiments were carbonate free and were carried out under a strict N_2/H_2 atmosphere; therefore, no $FeCO_3^0$(aq) was present to serve as a control on the reactivity of the system.

The observed reaction rates for surface-mediated reactions are the result of three competing reactions using $FeOH^+$ and the two types of surface bound iron, S1 and S2, as discussed previously. The equations for the reactions between the surface species and 4-Cl-NB along with the associated rate laws are given in eqs 2 and 3.

TABLE 2. Observed Pseudo-First-Order Rate Constants (1/min) for Each Mineral at Each pH[a]

pH	6.00	6.50	7.00	7.50	8.00
blank	6.31 (±6.33) E-6	9.87 (±9.19) E-6	6.07 (±0.64) E-4	9.20 (±0.76) E-4	1.24 (±0.12) E-2
Swa-1	1.94 (±2.34) E-6	9.58 (±2.28) E-6	1.06 (±0.17) E-4	4.59 (±0.68) E-3	2.16 (±0.20) E-2
montmorillonite	7.71 (±3.93) E-6	7.63 (±8.61) E-6	2.70 (±0.36) E-4	1.45 (±0.15) E-3	1.35 (±0.22) E-2
silica	3.10 (±0.94) E-6	8.43 (±0.74) E-6	1.86 (±0.22) E-4	6.57 (±0.80) E-3	3.00 (±0.21) E-2
alumina	1.17 (±1.27) E-6	7.19 (±0.62) E-6	2.24 (±0.08) E-4	2.01 (±0.11) E-3	N/A[b]

[a] Errors are ±1 SD. [b] N/A means not available.

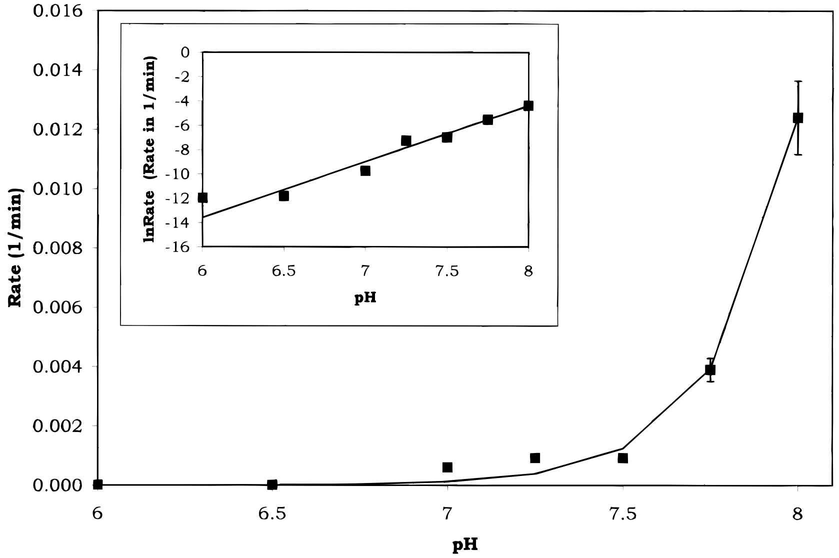


FIGURE 5. pH dependence of observed rate of 4-Cl-NB reduction by ferrous iron in the absence of a mediating mineral. Solid squares are the measured data. Error (±1 SD) is within the size of the data symbol, except where shown. Solid line is the modeled fit to the data. Inset is the natural log plot of the same data.

$$4\text{-Cl-NB} + \mathrm{Fe(S1)}^{2+} + \mathrm{H_2O} + 2\mathrm{OH}^- \rightarrow \text{intermediate}$$

$$\mathrm{rate}_{\mathrm{Fe(S1)}} = k_{\mathrm{Fe(S1)}} * [4\text{-Cl-NB}] * [\mathrm{Fe(S1)}^{2+}] * [\mathrm{OH}^-]^2 \quad (2)$$

$$4\text{-Cl-NB} + \mathrm{Fe(S2)}^{2+} + \mathrm{H_2O} + 2\mathrm{OH}^- \rightarrow \text{intermediate}$$

$$\mathrm{rate}_{\mathrm{Fe(S2)}} = k_{\mathrm{Fe(S2)}} * [4\text{-Cl-NB}] * [\mathrm{Fe(S2)}^{2+}] * [\mathrm{OH}^-]^2 \quad (3)$$

The overall observed rate law for surface-mediated reactions can be written as the sum of the rate laws of the three reductants, FeOH^+, Fe(S1), and Fe(S2):

$$\mathrm{rate} = k_{\mathrm{FeOH}^+} * [\mathrm{FeOH}^+] * [\mathrm{NB}] * [\mathrm{OH}^-] + k_{\mathrm{Fe(S1)}} * [\mathrm{Fe(S1)}] * [\mathrm{NB}] * [\mathrm{OH}^-]^2 + k_{\mathrm{Fe(S2)}} * [\mathrm{Fe(S2)}] * [\mathrm{NB}] * [\mathrm{OH}^-]^2 \quad (4)$$

The intrinsic rate constants $k_{\mathrm{Fe(S1)}}$ and $k_{\mathrm{Fe(S2)}}$ can be determined by fitting eq 4 to the observed reaction rates for each mineral. Note that the model for the overall kinetics is fit to experimental data with only two degrees of freedom, $k_{\mathrm{Fe(S1)}}$ and $k_{\mathrm{Fe(S2)}}$. The resulting values of the intrinsic rate constants are listed in Table 3for both Swa-1 and Wyoming montmorillonite. Figure 6is the graphical representation of eqs 1 through 4 for SWa-1. The logarithmic inset in Figure 6 illustrates that the model fits the data over the entire pH range studied. A comparable plot is obtained for Wyoming montmorillonite (data not shown).

Further insights into this reaction on clay minerals were obtained from kinetic experiments performed on flasks early in the loading process. In these experiments, essentially all of the ferrous iron added to the system was sorbed, and the reaction did not proceed. This condition is unique to clays and cannot be achieved with ferric oxides because they have a very low affinity for ferrous iron (*12*). This lack of reactivity in the presence of surface bound Fe(II) leads to two conclusions: first, the second electron of the first reduction, nitro- to nitroso- (Figure 1b), came from the solution, hence the need for a consistent concentration of aqueous ferrous iron, and second, the organic radical formed in the first electron transfer is not mobile on the mineral surface, otherwise it would be capable of obtaining the second electron from a second surface-bound iron.

TABLE 3. Intrinsic Rate Constants as Obtained from Kinetics Modeling

	k_{FeOH^+}[a]	$k_{\mathrm{Fe(S1)}}$[b]	$k_{\mathrm{Fe(S2)}}$[b]
blank	6.3E+13		
SWa-1	6.3E+13	8.0E+17	8.0E+16
montmorillonite	6.3E+13	2.0E+17	2.0E+16
silica	6.3E+13	3.3E+17	
alumina	6.3E+13	3.4E+17	

[a] 1/(min*M^3). [b] 1/(min*mol/g*M^3).

Discussion

The overall rates of reaction obtained in the present study can be compared to the overall rates obtained on ferric oxides by previous workers. After adjusting to a constant ferrous iron concentration, the overall rate of reduction reported by Hoffstetter (*9*) on goethite at pH 7.22 is equal to the rates seen on our minerals at pH levels between 7.4 and 7.8. At these high pHs, the primary reductant in our systems is FeOH^+. It seems clear that ferrous=ferric oxide sorption

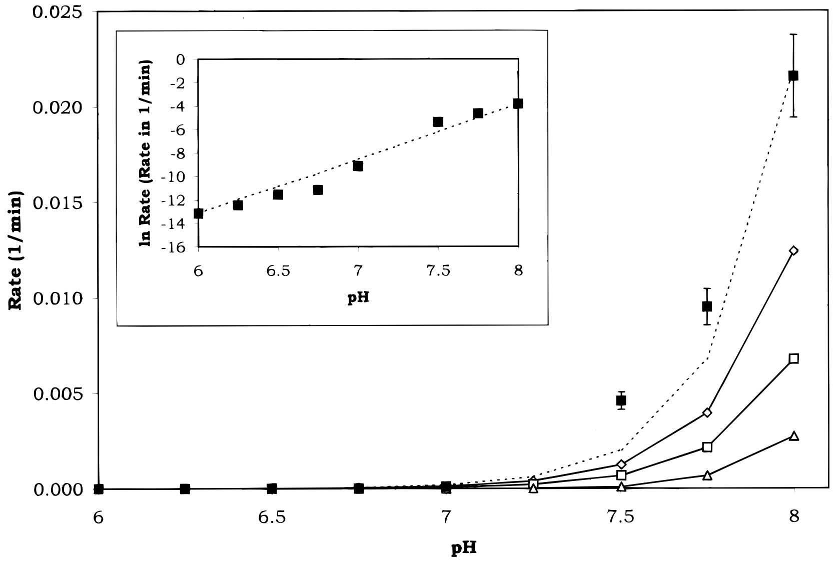


FIGURE 6. pH dependence of observed rate of 4-Cl-NB reduction by ferrous iron mediated by SWa-1montmorillonite. Solid squares are the measured data. Error (±1 SD) is within the size of the data symbol, except where shown. Modeled reaction rates of the three reductants $FeOH^+$ (◇), Fe(S1) (□), and Fe(S2) (Δ) are plotted. The dashed line is the sum of these three rates and represents the modeled fit to the overall reaction. Inset is the natural log plot of the measured data and the modeled fit to the overall reaction.

TABLE 4. Observed Rate Constants at pH 7.25 (k_{obs}), Surface Areas, and Observed Rate Constants Normalized to Mineral Surface Area ($k_{obs}{}^{sa}$)^a

	k_{obs} (1/min)	surface area (m^2/g)	k_{obs}sa (1/min*m^2)
goethite	4.40E-02	17.5	3.93E-04
SWa-1	6.21E-04	35.5	1.75E-06
montmorillonite	4.88E-04	40.0	1.22E-06
silica	9.71E-04	450	2.16E-07
alumina	7.55E-04	155	4.87E-07

[a] Surface areas for clays represent edge areas.

complexes on the surface of ferric oxides are analogous to $FeOH^+$ complexes in the aqueous phase. This idea is supported by the near equivalence in the E_h°s of $FeOH^+$ and ferrous=ferric oxide centers (*13, 15*). Ferrous=alumina oxide or ferrous=silica oxide centers are much less effective at mediating this reaction. A similar phenomenon is seen in the mineral mediation of the reduction of Cr(VI) by aqueous Fe(II). Ferrous=ferric oxide centers (supplied by α- and γ-FeOOH) increase the rate of Cr(VI) reduction by factors of 20−40, respectively, whereas ferrous=silica centers (supplied by SiO_2 and iron deficient montmorillonite) increase the rate by factors of 1.2−4, respectively (*39*). Ferrous=alumina centers (supplied by Al_2O_3) increased the rate by a factor of 2 (*39*).

The difference in the behavior between ferric oxides and the oxides of aluminum and silicon in our system is clearly seen by comparison of the observed overall rates on a surface area basis. Table 4lists the overall rate constants for each mineral at pH 7.25 divided by the respective surface areas. Goethite data were extracted from information contained in Hoffstetter (*9*). Surface areas for alumina and silica were specified by the supplier. Basal plane surfaces, which account for the vast majority of the total surface area, do not have a surface charge sufficient to dehydrate Fe(II) ions. Interlayer ions that remain hydrated occur close to the central plane of the interlayer space and are not inner spherically complexed to the surface (*33*). As a result, edge surfaces are the only place where ferrous ions inner spherically sorb to the surface of a clay and therefore are the active surfaces on a clay mineral. Edge surface areas of smectite clays have been estimated to constitute anywhere from 1% to 10% of the total surface area (*34, 35*). For the present calculations, it was assumed that 5% of the total surface area of the clays consists of edges. The total surface area was set to 720 m^2/g (*36*) and 800 m^2/g (*37*) for SWa-1 and Wyoming montmorillonite, respectively. As can be seen in Table 4, the clay minerals as well as silica and alumina exhibit a reactivity, when expressed on a surface area basis, that is in stark contrast to goethite. Goethite exhibits a reactivity that is as much as 1000 times as large. Ferrous iron that is sorbed to the edges of the clays as well as to silica and alumina forms ferrous=alumina oxide or ferrous=silica oxide centers, and these centers are much less effective at mediating the reduction reaction.

A further observation that supports the conclusion that ferrous=ferric oxide centers are an important surface reactant is that both intrinsic rate constants ($k_{Fe(S1)}$ and $k_{Fe(S2)}$) for the reaction on SWa-1 are four times faster than for the reaction of Wyoming montmorillonite (Table 3). SWa-1 is an iron rich montmorillonite (a nontronite) that has ferric iron in 3 out of 4 octahedral sites, whereas Wyoming montmorillonite contains only one-fifth as much octahedral iron. It is possible that the difference in the intrinsic rate constants is due to the relative paucity of iron centers on the edge sites of Wyoming montmorillonite. It is also possible that the additional structural ferric iron contained in SWa-1 promotes the precipitation of a highly reactive, mixed valent "green rust" at the surface of the clay.

Although the minerals investigated in this study are much less effective at mediating the reduction of 4-Cl-NB than ferric oxides, the rates of reaction are sufficiently fast to be of importance to environmental processes. Extrapolation of our results to other nitro-compounds can be accomplished by reference to previously defined relationships between degradation rate and the E_h° (*8, 9*). Most NACs and (P)NACs react more rapidly than 4-Cl-NB, and no previously measured compound reacts more slowly than 1/4 of the 4-Cl-NB rate. In our systems, at neutral pHs and at environmentally reasonable Fe(II) concentrations (500 μM), measured 4-Cl-NB half-lives are less than a week. This is quite rapid in the context of groundwater systems in which residence times can be months to years. Furthermore, a rise in pH to 7.5 or more will decrease half-lives to the scale of hours. This same rise in pH also increases the relative importance of the aqueous reactant FeOH$^+$ with respect to heterogeneous reductants.

A comparison can be made between the reactivity of Fe(II) and NB and the reactivity with other common oxidants. Kinetic studies exist for the reduction by Fe(II) of Cr(VI) and molecular oxygen (*39, 40−43*). A direct comparison of the intrinsic reaction between all three oxidants can be made by using published intrinsic rate constants (*40, 43*) and setting the pH to 7.2, the concentration of oxidant (NB, Cr(VI), O$_2$) to 50 μM, and the concentration of Fe(II) to 500 μM. Under these conditions, the relative rates of reaction (rate $= -d[\text{oxidant}]/dt$) are 1:8.4:0.1 for NB:Cr(VI):O$_2$, respectively. These rates show that NB is intermediate in reactivity between oxygen and Cr(VI); however, this applies only to the specified conditions and is not directly applicable to natural environments where pH and ionic strength variations, complexing ligands, mineral surfaces, and bacteria are present. Changes in pH, ionic strength, and the presence of Fe(II)−ligand complexes are all known to affect reaction rates (*30, 38, 41, 42, 44−49*). Mineral surfaces also mediate the oxidation of Fe(II) (*2, 12, 39*), and bacterial action can accelerate Fe(II) oxidation by several orders of magnitude (*50*).

The ability to reduce nitrated pollutants without the need for solid-phase reductants may be useful to the design of engineered or in-situ remediation systems. The primary conditions that need to be achieved for Fe^{2+} mediated reduction to proceed are anaerobiosis, the presence of aqueous Fe^{2+}, and either ferrous=ferric oxide centers (heterogeneous reaction) or pH levels of 7.5−8.0 (homogeneous reaction). The use of a soluble, mobile reductant (FeOH$^+$) in the homogeneous case would allow in-situ remediation to proceed even with highly sorbed, immobile contaminants. This may prove to be an advantage over the heterogeneous case in which the contaminant must move to the site of reaction.

The fully reduced (poly)aromatic anilines that result from Fe^{2+} mediated pathways are carcinogenic compounds. These anilines are stable under reducing conditions (*11*); however, under aerobic conditions they are subject to a variety of oxidative, sorptive, and polymerization reactions that either degrade or immobilize the compound (*2*). The need for aerobic conditions to fully degrade or immobilize the aniline forms must be kept in mind when designing any remediation scheme.

Although the data presented here pertains only to a mononitrated aromatic, the complete reduction of di- and trinitrotoluenes (TNT) on ferric oxides has been demonstrated (*9*). Work on the homogeneous reduction of PNACs is progressing in our laboratory. This provides a much simpler pathway for the remediation of polynitrated explosive residues than straight biodegradation that requires microaerobic or alternating anaerobic/aerobic conditions, often requires carbon amendment, and may result in incomplete degradation (*51*).

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