Nitrate reduction by zero-valent iron under different pH regimes

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Abstract

Nitrate in drinking water can pose a threat to human health. A study of the reduction of NO\textsubscript{3}\textsuperscript{-}, by Fe\textsuperscript{0} is reported here. The anaerobic reduction of NO\textsubscript{3}\textsuperscript{-} was carried out using Fe\textsuperscript{0} powder in unbuffered solutions from pH 2 to greater than 10. The initial pH of the solution was adjusted to 2, 3, or 4 by addition of HCl, H\textsubscript{2}SO\textsubscript{4}, or CH\textsubscript{3}COOH, because the Fe oxidation and NO\textsubscript{3}\textsuperscript{-} reduction reactions consume acidity. Under the conditions of this study, NH\textsubscript{3}/NH\textsubscript{4}\textsuperscript{+} were the only N products. The formation of green rusts divided the NO\textsubscript{3}\textsuperscript{-} reduction process into two phases. Green rusts formed around a pH of 6.5 and contributed to the stabilization of pH. With H\textsubscript{2}SO\textsubscript{4}, the available Fe surface area was limited, initially by the excessive accumulation of H\textsubscript{2} gas at the interface, which inhibited NO\textsubscript{3}\textsuperscript{-} reduction. The surface area normalized pseudo-first order reaction rates for NO\textsubscript{3}\textsuperscript{-} reduction at pH > 6.5 or after the formation of green rusts are consistent with those reported for buffered solutions.

1. Introduction

Nitrate in groundwater is derived from many sources such as agricultural runoff, animal wastes, septic systems and industrial processes, and has become a serious environmental problem. Although the NO\textsubscript{3} itself is relatively non-toxic, NO\textsubscript{2}, derived by reduction of NO\textsubscript{3}, can cause human health problems such as methemoglobinemia, liver damage, and even cancers (Huang et al., 1998; Gabel et al., 1982). Therefore, the NO\textsubscript{3} concentration in the drinking water needs to be limited.

Chemical reduction by Fe\textsuperscript{0} has been used in the treatment of chlorinated organics (Siantar et al., 1995; Gillham and O’Hannesin, 1994; Orth and Gillham, 1996; Roberts et al., 1996; Tratnyek et al., 1997) and nitroaromatic compounds (Agrawal and Tratnyek, 1996; Devlin et al., 1998). Nitrate reduction by Fe\textsuperscript{0} has long been known to occur (Young et al., 1964; Buresh and Moraghan, 1976), but its application to a component of groundwater treatment processes has emerged only recently, as laboratory experiments have shown it to be effective (Rahman and Agrawal, 1997; Cheng et al., 1997a; Siantar et al., 1995; Huang et al., 1998; Choe et al., 2000).

In the reduction process by Fe\textsuperscript{0}, the solution pH is an important parameter influencing the kinetics (Huang et al., 1998; Lavine et al., 2001; Huang and Zhang, 2002, Alowitz and Scherer, 2002). Alkalinity is produced from the reduction of NO\textsubscript{3} by Fe\textsuperscript{0} as well as the corrosion of Fe, as shown in Eqs. (1) and (2).

\begin{align*}
4 \text{Fe}^0 + \text{NO}_3^- + 7 \text{H}_2\text{O} & \leftrightarrow 4 \text{Fe}^{2+} + \text{NH}_4^+ + 10\text{OH}^- \quad (1) \\
\text{Fe}^0 + 2\text{H}_2\text{O} & \leftrightarrow \text{Fe}^{3+} + \text{H}_2 + 2\text{OH}^- \quad (2)
\end{align*}

Thus, the continuous addition of acid or buffering by weak acids is needed to maintain favorable reducing conditions.
conditions and reaction rate. In addition, the reaction rates depend on not only the pH but also the acids used for pH control. Various buffering agents (Matheson and Tratnyek, 1994a; Lipczyska-Kochany et al., 1994) and variation of pH with the same phosphate buffer system have been tested (Chen et al., 2001, Lavine et al., 2001) in the reduction process by Fe\(^0\). Nevertheless, the effect of different acids and pH has not been well characterized (Agrawal and Tratnyek, 1996).

Several types of acids have been used in investigations of NO\(_3^-\) reduction at varied pH. The rate and extent of reaction changed with initial NO\(_3^-\) concentration when the pH was adjusted to neutral with HEPES, 4-(2-hydroxyethyl)-1-piperazineethane-sulfonic acid, in the treatment of NO\(_3^-\) and 1,2-dibromo-3-chloropropane contaminated ground water (Siantar et al., 1996). The rate of reduction of NO\(_3^-\) by Fe\(^0\) was characterized by Alowitz and Scherer (2002) in systems at pH values fixed from 5.5 to 9.0 by multiple organic buffers. The change in reaction rate has been investigated when pH was controlled by constant addition of various buffering agents (Matheson and Tratnyek, 1994a; Lipczyska-Kochany et al., 1994) and for pH control. Various buffering agents (Matheson and Tratnyek, 1994a; Lipczyska-Kochany et al., 1994) and variation of pH with the same phosphate buffer system have been tested (Chen et al., 2001, Lavine et al., 2001) in the reduction process by Fe\(^0\). Nevertheless, the effect of different acids and pH has not been well characterized (Agrawal and Tratnyek, 1996).

To investigate the effects of the initial pH and acid type on NO\(_3^-\) reduction by Fe\(^0\), batch experiments were conducted. Two grams of 100 mesh Fe powder with a BET surface area of 1.19 m\(^2\)/g was placed in a 60-ml glass vial. The test solution with an initial NO\(_3^-\) concentration of 100 mg NO\(_3^-\)-N/L, was acidified using CH\(_3\)COOH, HCl, or H\(_2\)SO\(_4\). Under these experimental conditions, Fe was provided in excess of the amount required to completely reduce NO\(_3^-\) to NH\(_4^+\) and NH\(_3\). The bottle was filled with the solution and capped with a crimpstyle Mininert\textsuperscript{TM} valve. The solution was mixed at ambient conditions (22 \(^\circ\)C) by a rotary shaker (Glas-Col) at 60 rpm. Samples (1 ml) were withdrawn periodically using a glass syringe and filtered with a 0.45-\(\mu\)m membrane filter to remove the Fe particles and any solid products. The filtrate was used to determine aqueous concentrations. With every test, a bottle with no Fe\(^0\) was run as a control. All analyses were conducted in triplicate for reproducibility of data.

3. Results and discussion

3.1. Effect of pH on nitrate reduction

The initial pH was adjusted to 2 or 3 with HCl or H\(_2\)SO\(_4\) or to 3 or 4 with CH\(_3\)COOH, and the changes in the NO\(_3^-\) concentration and pH were followed, as presented in Fig. 1 together with the results of no pH adjustment. In the experiment without acidification [Fig. 1 (a)], the pH rose rapidly from an initial value of 6.2 to greater than 9.3 as the NO\(_3^-\) concentration decreased to 91 mg N/L. Similar to that in all test solutions that reached basic conditions, the reaction rates slowed at higher pH. In contrast in the solutions adjusted to an initial pH of 3 using CH\(_3\)COOH or 2 using HCl in which the pH remained below 7, no NO\(_3^-\) was detected after 15 h [Fig. 1 (b)] or after 8 h [Fig. 1 (c)], respectively. The test solutions adjusted to an initial pH of 4 using CH\(_3\)COOH or 3 using HCl showed incomplete removal of NO\(_3^-\); 65 and 81 mg N/L remaining, respectively, and pH > 10 after 24 h, [Fig. 1 (b) and (c), respectively]. For the solutions acidified with H\(_2\)SO\(_4\), however, the reduction of NO\(_3^-\) was incomplete after 24 h, with 88 mg N/L remaining in the case with an initial pH of 2 and ending at 6.2 and 78 mg N/L remaining in the case with initial pH of 3 ending at 10.62 [Fig. 1 (d)].

The rise in pH, which occurred, was as expected from Eqs. (1) and (2). As a result of differences in pK\(_a\), the total acid concentration varied among test solutions of the same initial pH. The base neutralizing capacity was
higher in the pH 3 CH₃COOH solution than either pH 2 strong acid solution. The more dilute, higher initial pH test solution for each acid had insufficient acidity to maintain an acidic pH during the complete reduction of NO₃⁻ to NH₄⁺ and NH₃, allowing high final pH values.

To examine the relationship between solution pH and the reaction rate, the data shown in Fig. 1 were divided into two groups, one with pH lower than 6.5 and the other higher. The pH of 6.5 was chosen because greenish suspended particles began to appear around this pH. The reaction was assumed to be a pseudo first order. The reaction rate constant was evaluated at each time interval and the corresponding pH was calculated from the average concentration of H⁺ in that time interval. Then the relationship between the obtained pseudo first order reaction rate constant and pH was analyzed. For reaction rates measured above pH 6.5 with 39.8 m²/l Junsei Fe⁰, the obtained relation was log $k_{observed} = -0.4599(pH - 5.48)$ with $r^2 = 0.818$ for $n = 36$ as shown in Fig. 2. Though the rates of NO₃⁻ reduction differed among the 3 acids, the general trend was observed for all acids in Fig. 2. Alowitz and Scherer (2002) reported similar relationships in solutions well buffered by weak organic acids. They reported pseudo first order rates of removal for NO₃⁻ decreasing with pH over the range 5.5–9. For a reactor with 96 m²/l Fisher Fe⁰, they found the relationship of log $k_{observed} = -(0.49 ± 0.04)(pH – 5.5)$ with $r^2 = 0.83$ for $n = 35$. The pH dependence is in agreement, and surface area normalized rate coefficients agree within the variability of types of Fe⁰. However, NO₃⁻ reduction rates in solutions with pH < 6.5 tended to increase with pH or HCl and CH₃COOH, with higher rates observed for the HCl solutions.

Only H₂ and Ar were detected in the analysis of headspace gases, and the only forms of N observed in the aqueous phase were NO₃⁻ and NH₄⁺/NH₃. The thermodynamically stable forms of N as a function of pH and pE have been described by Pankow (1991) both
with and without considering N$_2$ as a species that is kinetically limited in its formation and oxidation-reduction. Under the anaerobic conditions in the presence of Fe$^0$ or greenish suspended particles and pH conditions of this study, NH$_4^+$/NH$_3$ species are the predominant forms at equilibrium. The N mass recovered as NH$_4^+$/NH$_3$ was 91–107% of NO$_3^-$ lost in each of the test solutions.

Fe$^0$ is not thermodynamically stable in water and Fe$^{2+}$ is a predominant species in the p$_E$-pH conditions of this study (Pankow, 1991). The addition of acids can result in the formation of complexes of Fe$^{2+}$ and anions of acids.

Complexes of ligands L$^n$– with Fe$^{2+}$ of the form shown in Eq. (3),

$$\text{Fe}^{2+} + L^{n}{}^- \leftrightarrow \text{FeL}^{2-n}$$  \hspace{1cm} (3)

equation increase the solubility of Fe, change the distribution of Fe species and thus can affect the kinetics of NO$_3^-$ reduction. To demonstrate how the various acids influenced the form of Fe precipitates in the reaction, MINEQL+ was used. The MINEQL+ log formation constants for monocomplexes with Cl$^-$, CH$_3$COO$^-$, SO$_4^{2-}$, and OH$^-$ are $-0.2$, $1.4$, $2.39$, and $4.59$. The Cl$^-$ complexes are negligible, less than 1% of the soluble Fe$^{2+}$ concentrations, in the solutions acidified with HCl. In the test solution acidified to pH 2 with H$_2$SO$_4$, FeSO$_4^{(aq)}$ is initially more important than Fe$^{2+}$ but becomes less important as the total Fe$^{2+}$ in solution exceeds the total SO$_4^{2-}$. Similarly for the solution acidified with CH$_3$COOH to pH 3, FeAc$^+$ becomes more important than Fe$^{2+}$ as the pH rises above the p$K_a$ for CH$_3$COOH, 4.76, and ultimately less important as the total aqueous Fe exceeds the total CH$_3$COO$^-$. In both cases, [FeL$^{2-n}$]/[Fe$^{2+}$] $<$ 2 for CH$_3$COO$^-$ and SO$_4^{2-}$ complexes under all pH conditions of the tests. Thus while these ligands may influence the kinetics of the Fe$^0$ corrosion, they are not expected to have a large impact on the complexation equilibrium composition of the test solutions.

The OH$^-$ precipitate and complexes control the Fe$^{2+}$ solubility at the higher pH values. Iron hydroxide precipitate has been reported to form under anaerobic conditions at a pH of 8.5–10.0 depending on other solution characteristics (Cheng et al., 1997b; Appelo and Postma, 1993; Matheson and Tratnyek, 1994b). MINEQL+ modeling indicates Fe(OH)$_2(s)$ can precipitate at pH 8.1 as the Fe concentration and pH rise for the initially more acidic test solutions and at pH 9.7 for the control with lower soluble Fe concentrations. Fe(II)–Fe(III) mixed hydroxide precipitates, or green rusts, form in anaerobic solutions at even lower pH values (Genin et al., 1998). The slow rates of NO$_3^-$ reduction at higher pH, as evident in all solutions with pH $> 10$ in Fig. 1, might result from the formation of Fe hydroxide precipitates (Cheng et al., 1997a) on the Fe$^0$ surface, thereby limiting the surface concentration of Fe$^0$ and the NO$_3^-$ reduction rates.

Fig. 2. Pseudo-first order rates under different pH regimes.
3.2. pH changes

The formation of Fe hydroxides contributes to the stabilization of pH by consuming hydroxyl ion as well as influencing the available surface area thereby limiting the rate of redox reactions. The pH changes shown in Fig. 1 (b)–(d) can be viewed as being in two phases. The formation of hydroxyl ion in solution from the reductions of NO$_3^-$ and H$^+/\text{H}_2\text{O}$, as in Eqs. (1) and (2), results in a rapid pH rise initially. The oxidation of Fe$^0$ by water proceeds through reaction with H$^+$ as in Eq. (2), such that the corrosion of Fe$^0$ by water is slow at neutral pH (Johnson and Tranyek, 1995) but is greatly enhanced at pH < 4 (Huang et al., 1998; Uhlig and Revie, 1985). The change in alkalinity can be determined from the change in pH and solution composition and compared with that resulting from the measured change in NO$_3^-$ concentration [Eq. (1)]. In the first time steps for the acidified test solutions, the change in alkalinity from corrosion of Fe$^0$ by H$^+/\text{H}_2\text{O}$ [Eq. (2)] is 4–10× that of NO$_3^-$ reduction [Eq. (1)], but once the solutions reached pH > 4.5, NO$_3^-$ reduction was more important. Thus the initial rapid increase in pH is mainly due to the reduction of H$^+/\text{H}_2\text{O}$ to form H$_2$ in these closed systems.

The pH stabilized with the appearance of greenish suspended particles after the initial rapid increase. These appeared after 4 h with CH$_3$COOH and 1 h with HCl and H$_2$SO$_4$. The results of XRD and SEM analyses of the greenish precipitate obtained from the solution with HCl are shown in Figs. 3 and 4, respectively.

The XRD trace shown in Fig. 3 matches that of green rusts (Arden, 1950) and the SEM picture shown in Fig. 4 is typical of surface morphology of the sjogrenite–pyraaurite class (Hansen et al., 1994). Green rusts are known to form at a pH around 7 at ambient temperature (Refait and Genin, 1993; Hansen et al., 1996; Taylor, 1980), as observed in this study. The consumption of the OH$^-$ occurs during the formation (Cheng et al., 1997a; Hansen and Koch, 1998, Summer and Chang, 1993; Tamura et al., 1976; Hansen et al., 1994) as shown in Eq. (4) and buffers the rise in pH, even while the concentration of NO$_3^-$ is reduced sharply.

\[
3\text{Cl}^- + 6\text{Fe}^{2+} + 3/8\text{NO}_3^- + 66/8\text{OH}^- + (21/8 + n)\text{H}_2\text{O} \leftrightarrow \text{Fe(II)}_3\text{Fe(III)}_3(\text{OH})_{12}\text{Cl}_3 \cdot n\text{H}_2\text{O} + 3/8\text{NH}_4^+ \quad (4)
\]

3.3. Green rusts in nitrate reduction

In Fig. 1 (b)–(d), the points of green rusts appearance are shown. After green rusts appeared in the systems, the concentrations of NO$_3^-$ decreased continuously. The continuous NO$_3^-$ reduction was possible due to the stabilized pH by the formation of green rusts. However, the green rusts could have acted as an additional reducing agent (Cheng et al., 1997a; Hansen and Koch, 1998; Summer and Chang, 1993; Hansen et al., 1994).

The appearance of green rusts with CH$_3$COOH came more slowly than with HCl and H$_2$SO$_4$, either due to the additional weak acid buffering or as a result of acetate in the interlayers of the green rusts. Further study on the

![Fig. 3. (a) The XRD traces of green rusts and (b) of greenish suspended particles observed in the experiment.](image-url)
role of the green rusts and different anions in them in the reduction process is needed. In the case of SO$_4^{2-}$ with an initial pH of 2 [Fig. 1(d)], the removal of NO$_3^-$ slowed even though green rusts were present at near neutral pH.

3.4. Hydrogen gas in nitrate reduction

The slow reduction of NO$_3^-$ in the H$_2$SO$_4$ system [Fig. 1(d)] at pH 6–7 with green rusts was coincident with an excessive production of gas bubbles. The gas should be either H$_2$ or H$_2$S, because the reduction of SO$_4^{2-}$ to H$_2$S is thermodynamically favored at these pH conditions (Stumm and Morgan, 1996). However, no H$_2$S was detected in the headspace or in the aqueous phase, and the SO$_4^{2-}$ concentration in the aqueous phase was found to be constant. Moreover, reduction of SO$_4^{2-}$ to H$_2$S has not been reported in other studies of Fe$^0$ using H$_2$SO$_4$ (Huang et al., 1998; Hu et al., 1999). The H$_2$ gas produced in this case occupied 92% of the bottle headspace, as compared with 31% and 14% when HCl [Fig. 1(c)] and CH$_3$COOH [Fig. 1(b)] were used, respectively.

The H$_2$ gas could function as an inhibitor (Kumnick and Johnson, 1975; Ballapragada et al., 1997; Cheng and Wu, 2000) or a reductant (Rylander, 1979, Bruzzoni et al., 2000) depending on the surface condition of Fe. With H$_2$SO$_4$, the H$_2$ accumulated on the Fe$^0$ and inhibited the corrosion of Fe and NO$_3^-$ reduction. The NO$_3^-$ reduction was more rapid and complete with HCl when compared with H$_2$SO$_4$. The difference in NO$_3^-$ reduction with H$_2$SO$_4$ and HCl is not clear but the anions of the acids may be a reason. Chloride ion in solution induces pitting corrosion of the Fe$^0$ surface (Klausen et al., 2001; Gotpagar et al., 1999; Kim and Pyun, 1996), which could enhance reactivity or surface area of the Fe$^0$ for NO$_3^-$ reduction. The H$_2$ could act as a reductant of the reactive surface (Siantar et al., 1996) and result in completion of NO$_3^-$ reduction with less H$_2$ in the headspace.

4. Summary and conclusions

Nitrate reduction with Fe$^0$ was investigated under anaerobic and various pH conditions. The initial pH was set and no further buffering by continuous addition of acid was provided. The initial pH values of 2 and 3 with HCl and CH$_3$COOH, respectively provided sufficient acidity to preserve the activity of the Fe powder throughout the reaction. The NO$_3^-$ can be reduced completely with initial pH setting with acids. The rise of pH was stabilized and the NO$_3^-$ reduction was carried out continuously and completely with the appearance of green rusts at pH 6.5. The pH was buffered by the consumption of hydroxyl ions through the formation of green rusts. The trends in pseudo-first order reaction rates after the formation of green rusts were similar to those reported by Alowitz and Scherer (2002) for systems well buffered by organic acids. When H$_2$SO$_4$ was used for initial pH adjustment, the NO$_3^-$ reduction was stopped even with favorable reducing conditions. The accumulation of H$_2$ gas on the surface of Fe and thus the decrease of available reactive surface area were thought to inhibit the reaction.

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References


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