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Prevention of iron passivation and enhancement of nitrate reduction by electron supplementation

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ABSTRACT

Zero-valent iron (ZVI) permeable reactive barriers (PRB) are susceptible to passivation due to both surface oxidation and the potential accumulation of oxidized mineral species. In this study, we investigated electrically induced reduction (EIR) as a supplemental electron source to rejuvenate passivated ZVI material and aid in resumption of nitrate reduction. In bench reactors, ZVI granules were added to the groundwater containing elevated concentration of nitrate (approximately 5000 mg/L). Nitrate reduction proceeded actively (an average rate of 6.9 mg/L/h) for approximately 48 h then decreased sharply until reaching a complete halt, suggesting severe ZVI passivation. In reactors supplemented with low voltage of direct current (DC), nitrate reduction resumed at a rate of 10.2 mg/L/h within 408 h, which was 47.8% faster than in the ZVI reactor without supplemented current. This robust activity was sustained for more than 1000 h. X-ray diffraction (XRD) analysis indicates there are, as hypothesized, different mineral phases formed on the ZVI depending on whether or not current is applied, suggesting that ZVI passivation may be both avoided and/or reversed by EIR, which also enhances the efficiency of ZVI for reducing nitrate and other reducible constituents. The results suggest that EIR can enhance the removal rate of reducible compounds and positive influence on the long-term performance of PRB.

1. Introduction

Nitrate is often classified as a priority pollutant in groundwater because of its toxicity and widespread occurrence [1]. The main sources of nitrate pollution are from the use of nitrogen-containing fertilizers [2,3] and irrigation with domestic wastewater [4]. Possible health consequences of nitrate ingestion include methemoglobinemia, the blue-baby syndrome in infants under 6 months of age [5]. Biological and physical–chemical treatment processes are able to remove nitrate, but may be expensive or difficult to operate [6]. Zero-valent iron (ZVI) is a treatment process that can operate *in situ* to remediate groundwater in permeable reactive barriers or *ex situ* in packed-bed reactors [7–10].

Despite its potential for treating a variety of environmental contaminants, ZVI is not without its problems. For example, nitrate reduction by ZVI is a corrosive process, as described in Eq. (1) [11], in which high valence oxide species form and remain stable at the ZVI surface. This process forms a film that acts as a barrier to further reactions at the ZVI surface [12].

$$NO_3^- + 10H^+ + 4Fe \rightarrow NH_4^+ + 3H_2O + 4Fe^{2+} \quad (1)$$

Farrell et al. [13] investigated the performance of ZVI for trichloroethene (TCE) reduction in packed columns fed with different ionic solutions. Trichloroethene removal in the presence of calcium sulfate or calcium chloride was unaffected over a 2-year period, but TCE reduction rates decreased in the presence of calcium nitrate. They concluded that nitrate contributed to increased iron surface passivity. Phillips et al. [14] also reported the negative effects of mineral precipitates and corrosion on an *in situ* reactive barrier after 15 months of operation. It has been suggested by several groups that the presence of nitrate, in particular, results in the formation of a surface film of oxidized minerals on the iron that interferes with TCE reduction [15–17]. This layer, which is composed mainly of hematite (Fe_2O_3) and iron oxyhydroxides like goethite (FeOOH), may inhibit the mechanisms responsible for contaminant treatment, including direct electron transfer and catalytic hydrogenation [17]. Reduction in permeability and formation of passivating layers that limit mass transport of nitrate to the reactive surface are the two primary concerns in the long-term sustainability of *in situ* ZVI systems.

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Table 1
Constituents of batch reactors.

	Components				
	Nitrate (mg/L)	Fe^0 (g)	Electric field (V/m)	Inoculum[a] (mL)	Sterilized
Fe^0 only	0	5.8	0	200	Yes
$NO_3^- + e^-$[b]	5000	0	6	200	Yes
$NO_3^- + Fe^0$	5000	5.8	0	200	Yes
$NO_3^- + Fe^0 + e^-$	5000	5.8	6	200	Yes
$NO_3^- + Fe^0 + e^-$ (unsterilized)	5000	5.8	6	200	No

[a] Natural groundwater was used as inoculum.
[b] The 'e^-' corresponds to application of current (EIR).

In recent work by our group, we used electrically induced reduction (EIR) based on low-voltage direct current (DC) supplementation as a stand-alone technology for reductive dechlorination of TCE [18]. In this study, we investigated EIR as a supplemental electron source to rejuvenate passivated ZVI material and aid in resumption of nitrate reduction. We hypothesized that the reduction process involves electrons from the DC source, which reduces the hematite (Fe_2O_3) layer and releasing Fe^{2+} upon contact at the iron surface. This would then allow both electron transfer and catalytic hydrogenation to occur.

2. Methods and materials

2.1. Batch experiments

Cast iron aggregate (purity > 99.0%, Peerless Metal Powders & Abrasives, Cleveland, OH) was chosen for use in this study. All batch tests employed 580-mL wide-mouth Nalgene bottles with septa lids. Initial treatment conditions are listed in Table 1.

In order to ensure the consistent composition of the treatments, all the reactors were inoculated with 200 mL natural groundwater, which is known to contain a diversity of bacteria. In addition to inoculated natural groundwater, artificial groundwater was used as the medium, which consisted of: Na_2SO_4 0.31 mM, $NaHCO_3$ 1.6 mM, NaCl 0.85 mM, KCl 0.85 mM, trace metals solution 12.5 mL, and vitamin solution 12.5 mL, dissolved in deionized water [19]. In order to buffer for the expected pH increase during iron corrosion, 60 mM HEPES acid (Sigma–Aldrich, St. Louis, MO, USA) and 30 mM HEPES salt ($NaC_8H_{17}N_2O_4S$; Sigma–Aldrich, St. Louis, MO, USA) were added to the medium, to maintain the pH at 7.0. All equipment and reagents were autoclaved at 120 °C for 20 min before use, and the reactors were incubated at room temperature (~25 °C).

Each reactor contained two solid, rod-shaped graphite electrodes (#14751, Alfa Aesar, MA, USA), measuring 6.15 mm in diameter and 38.10 mm in long, installed 10 cm apart at the two ends of each reactor. The electrodes were connected to an electrical source for active treatment, while electrodes were installed but disconnected for a control reactor. Electrical current was applied to the electrodes by an adjustable AC–DC adaptor. The potential output of the adapter was adjusted to apply an electric field of 6 V/m. In each test, multiple reactors were prepared in an anaerobic chamber with N_2 as the ambient gas.

2.2. Analytical methods

Nitrate and nitrite were analyzed using a Dionex DX 500 ion chromatograph (IC) (Dionex, Sunnyvale, CA) equipped with a Dionex ASRS ULTRA II suppressor. Separation was achieved with a Dionex AS16 column maintained at 30 °C using an eluent of 10 mM sodium hydroxide. Samples from batch experiments were collected with a 10-mL disposable syringe and passed through a 0.22 μm syringe filter (Fisher Scientific, Pittsburgh, PA) before analysis. Ammonium concentrations were analyzed by the salicylate method (Hach, Loveland, CO).

Loss in ZVI reactivity to effect NO_3^- reduction has been most often attributed to the formation of passivating metal oxides [13,17,20]. To better understand the role of electron supplementation on the formation of such metal oxides, we conducted X-ray diffraction (XRD) analysis on representative precipitated particles obtained from each artificial groundwater reactor at the end of the experiment. Samples were dried in a nitrogen atmosphere in an anaerobic chamber to prevent any additional oxidation. X-ray diffraction analyses of the fresh, reacted, and regenerated samples were performed using a Bruker AXS D8 advanced X-ray diffractometer ($\lambda = 1.5418$ Å). Samples for XRD analysis were dried in an anaerobic chamber with a nitrogen atmosphere.

3. Results and discussion

3.1. Nitrate reduction in batch reactors

Nitrate removal in the various batch reactors is summarized in Fig. 1. In all cases, high initial concentrations of nitrate (5000 mg/L) insured for rapid passivation of the ZVI. The results indicate that in the control reactors (0 V/m), nitrate decreased from 5000 to 4669 mg/L within 48 h at an average rate of 6.9 mg/L/h; however, nitrate reduction slowed considerably after 48 h, likely due to passivation of the ZVI by nitrate. Nitrate reduction in the control reactor containing sterilized groundwater is attributed to ZVI only, as there was no possibility for bacterial nitrate reduction to occur.

In contrast, rapid removal of nitrate was observed over 1300 h in reactors that were connected to the DC source. In the reactor amended with 5000 mg/L nitrate and with an applied current ($NO_3^- + e^-$ in Fig. 1), a mean nitrate removal rate of 3.0 mg/L/h was obtained. In the reactor containing nitrate, and iron and with current applied ($NO_3^- + Fe^0 + e^-$ in Fig. 1), either abiotic or biotic treatments, mean reduction rate of 5.7 mg/L/h was achieved. These results are 90% greater than what was achieved with current

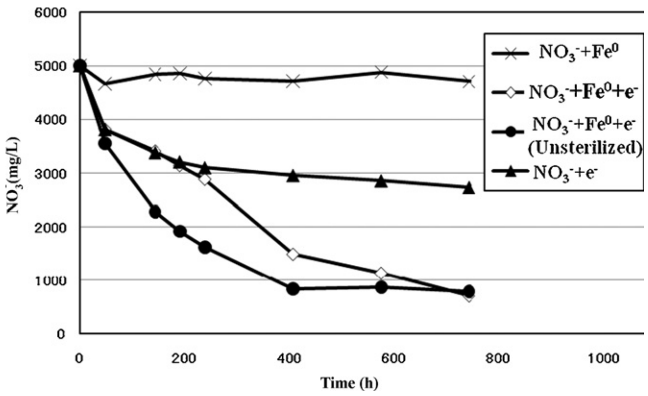

Fig. 1. Nitrate removal as a function of time for various conditions. ZVI = 5.8 g. Initial nitrate concentration of 5000 mg/L/h.

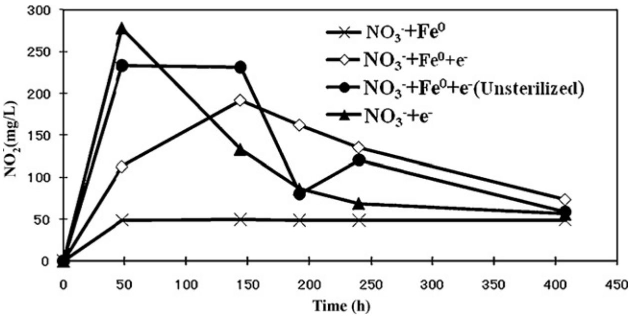

Fig. 2. Nitrite concentration as function of the time for various conditions.

alone (no Fe^0 present). Besides, in the biotic reactor amended with 5000 mg/L nitrate and with current applied ($NO_3^- + Fe^0 + e^-$ (unsterilized) in Fig. 1), mean reduction rate of 10.2 mg/L/h was observed in the period between 0 and 408 h, which was 18.6% faster than that of the treatment using artificial groundwater. Together, these results suggest that ZVI passivation may be avoided and/or reversed by supplementation of external DC current, which also enhances the overall efficiency of the ZVI for nitrate removal.

In the abiotic reactor, nitrate reduction was consistently less than in the unsterilized reactor which contained bacteria. We assume that two kinds of bacteria might have contributed to nitrate reduction in these experiments: (1) autotrophic denitrifying bacteria which can use hydrogen released by ZVI (or water electrolysis) as an electron donor and reduce nitrate to nitrogen gas rather than to ammonium; (2) dissimilatory iron-reducing bacteria (DRB) which use Fe(III) oxides as terminal electron acceptors and convert Fe^{3+} to Fe^{2+} resulting in more nitrate reduction. In this study, an additional carbon source was not provided to the natural groundwater, so if Fe(III) reduction occurred, the HEPES buffer would have served as the carbon source, which has been observed by Coyne [21].

3.2. Nitrite and ammonium production

Fig. 2 documents the concentrations of nitrite (NO_2^-) observed in all reactors during nitrate reduction, while Fig. 3 details the ammonium concentrations. The results show relatively uniform conversions of nitrate to ammonium with nitrite as an intermediate product. The combined use of Fe^0 and electrical current attained the highest level of ammonium production (exceeding 1100 mg/L). In contrast, in the reactor without applied current, the concentration of ammonium was never greater than 50 mg/L. This result suggests that supplementation of external DC current may enhance the efficiency of ZVI for nitrate reduction. Similar results to these have been obtained in other ZVI studies of reductive conversion of nitrate to ammonium [11,13,22–26]. This result was likely caused by the reaction conditions of the treatments especially the specific surface area of ZVI. As reported by Choe et al. [27], iron particles at the nanoscale and the resulting large surface area had a marked effect on the degradation mechanism of nitrate. They reported nitrate being converted to ammonia when using micro-scale iron particles; in contrast, nitrate was reduced to nitrogen gas when using nanoscale iron. In terms of practical applications, heterotrophic bacteria would be able to use ammonium as an alternative nitrogen source in the groundwater system [28,29], and therefore we consider the generated ammonium to be readily assimilated during microbial metabolism and growth in most natural matrices. In addition, a number of indigenous bacteria (e.g., anammox bacteria) can oxidize ammonium under anaerobic conditions and produce N_2 gas [27,30–32]. It is also worth noting that nitrate reduction by ZVI may produce nitrogen gas, which was not quantified in the experiment.

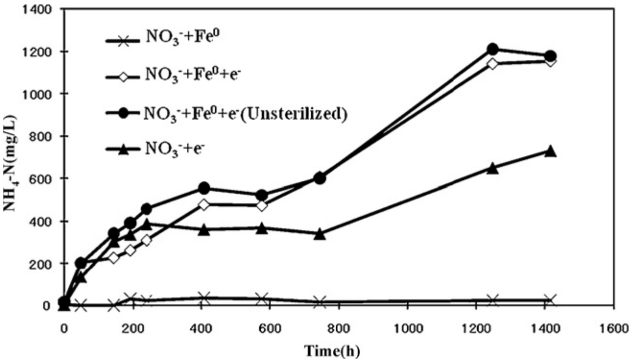

Fig. 3. Ammonium concentration as function of the time for various conditions.

3.3. Characterization of ZVI surface passivation

The XRD patterns obtained from analysis of the Fe only reactor (panel A of Fig. 4) closely matched that of magnetite (Fe_3O_4) with common peaks at 18, 30, 35.5, 37, 43.53, 57, 62.5, and 74 degree

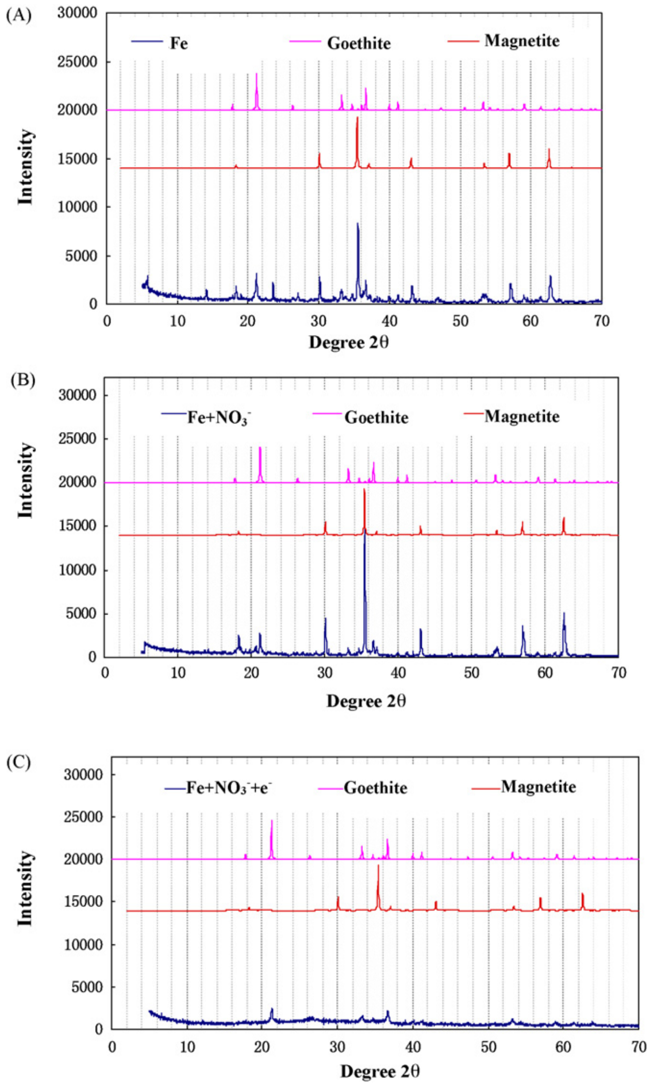

Fig. 4. X-ray diffraction patterns obtained from precipitated iron particles for reactors containing sterile groundwater with the following components: (A) Fe^0 only, (B) $NO_3^- + Fe^0$, and (C) $NO_3^- + Fe^0 + e^-$.

in 2θ, Cu source. A few additional peaks of lower intensity corresponded to goethite (α-FeOOH) (peaks at 21.23, 26.33, 33.26, 34.7, 36.65, 39.98, 41.18, 47.3, 50.63, 53.24, 54.23, 59.06, 61.4 and 63.98 degree in 2θ, Cu source).

The XRD analysis indicated the amount of Fe_3O_4 substantially increased on the surface of the ZVI granules from the $NO_3^- + Fe^0$ reactor that was disconnected from the DC source (Fig. 4B). This indicates that nitrate was causing passivation of the ZVI surface; however, the amount of α-FeOOH as indicated by the relative intensity remained stable. As a main corrosion product, Fe_3O_4 may be formed by oxidation of $Fe(OH)_2$ and may be argued not to be a passivating oxide as observed in a study conducted by Cornell and Schwertmann [33]; however, Farrell et al. [13] indicated that adherence of Fe_3O_4 to the ZVI surface might hinder both the solubilization of Fe^{2+} and the release of electrons at anodic sites, thus limiting the rate of iron corrosion and decreasing reduction rates. In this study, the increase in Fe_3O_4 layer on the ZVI surface in $NO_3^- + Fe^0$ reactor disconnected from the DC source is likely to have hindered the reduction of nitrate as indicated in Figs. 1–3. These results are consistent with other studies that have reported nitrate-accelerated iron oxidation [17,34,35].

On the other hand, only two peaks of very low intensity consistent with α-FeOOH were evident in the XRD profile of material obtained from the $NO_3^- + Fe^0 + e^-$ reactor that received current (panel C in Fig. 4). In addition, Fe_3O_4 was not observed in XRD diffractogram for this reactor. These results are consistent with our expectation that EIR can reverse passivation by preventing formation and/or promoting elimination of iron oxide mineral phases. α-FeOOH is the major constituent of passive films on iron formed by dissolution and precipitation reactions [17,36], which corresponded to active reduction of nitrate. The small amount of goethite detected may have formed during sample preparation because during this time, current was not provided and the concentration of nitrate was still very high (~500 mg/L). The study conducted by Liu et al. [37] proposed a mechanism for restoration of the ZVI surface; however, this was conducted cathodically. Our study involved a column of ZVI granules in between two electrodes; therefore, the material was not associated with a single electrode. Though the exact mechanism was not determined in this study, it is surmised that the continuous feed of electrons to the ZVI media increases the release of electrons and reduces oxidized Fe at the ZVI surface.

In summary, results of the XRD analysis suggest that DC electron supplementation may reduce surface passivation of ZVI by preventing formation of iron oxide mineral phases. This corresponded to the absence of Fe_3O_4 in the XRD analysis in treatments where electrical current was applied to the ZVI. This also resulted in enhancing the reduction of nitrate to ammonium as indicated by a higher rate of in the decrease of nitrate concentration relative to treatment with no ZVI. Hence, this technique can increase the life-span PRB or be applied to other activities where minimal iron corrosion is desired. For better understanding of the mechanisms involved in using this technique to prevent ZVI passivation, further research is to be conducted. Results from this bench-scale study shed lights on using low-voltage electricity in enhancing PRB for its reduction of nitrate and potentially preventing PRB from being passivated. Findings from this study may carry applicable significance that can be used for field test.

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