Nitrate reduction and its effects on trichloroethylene degradation by granular iron

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ABSTRACT

Laboratory column experiments and reactive transport modeling were performed to evaluate the reduction of nitrate and its effects on trichloroethylene (TCE) degradation by granular iron. In addition to determining degradation kinetics of TCE in the presence of nitrate, the columns used in this study were equipped with electrodes which allowed for in situ measurements of corrosion potentials of the iron material. Together with Raman spectroscopic measurements the mechanisms of decline in iron reactivity were examined. The experimental results showed that the presence of nitrate resulted in an increase in corrosion potential and the formation of thermodynamically stable passive films on the iron surface which impaired iron reactivity. The extent of the decline in iron reactivity was proportional to the nitrate concentration. Consequently, significant decreases in TCE and nitrate degradation rates and migration of degradation profiles for both compounds occurred. Furthermore, the TCE degradation kinetics deviated from the pseudo-first-order model. The results of reactive transport modeling, which related the amount of a passivating iron oxide, hematite (α-Fe$_2$O$_3$), to the reactivity of iron, were generally consistent with the patterns of migration of TCE and nitrate profiles observed in the column experiments. More encouragingly, the simulations successfully demonstrated the differences in performances of three columns without changing model parameters other than concentrations of nitrate in the influent. This study could be valuable in the design of iron permeable reactive barriers (PRBs) or in the development of effective maintenance procedures for PRBs treating TCE-contaminated groundwater with elevated nitrate concentrations.

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1. Introduction

Granular iron permeable reactive barriers (PRBs) have been successful for treatment of various contaminants in groundwater, but most commonly chlorinated hydrocarbons (Phillips et al., 2010; Guan et al., 2015). They are now regarded as one of the proven and cost-effective groundwater remediation technologies (Warner et al., 2005; Obiri-Nyarko et al., 2014). While the technology is well established, remaining issues include effects of constituents in groundwater for the treatment (Lo et al., 2005) and long-term performance with regard to reactivity and permeability (Obiri-Nyarko et al., 2014; Ansaf et al., 2016). In particular, it has been suggested that effects of co-existing oxidants, such as nitrate and chromate, must be taken into account in order to evaluate the long-term performance of PRBs (Farrell et al., 2000; Schlicker et al., 2000; Ritter et al., 2003).

Nitrate is widely used as a nitrogen fertilizer and a major component in animal wastes and septic tank effluent. It is highly mobile in the soil and thus, frequently detected in groundwater. Its occurrence in groundwater contaminated with chlorinated hydrocarbons is not uncommon (Yabusaki et al., 2001; Bastiaens et al., 2002). While early studies have shown that nitrate can be reduced to ammonia by granular iron (Cheng et al., 1997; Huang et al., 1998; Alowitz and Scherer, 2002; Westerhoff and James, 2003), there is evidence that nitrate can have a negative effect on the ability of granular iron to degrade chlorinated hydrocarbons (Siantar et al., 1996; Ritter et al., 2003; Mishra and Farrell, 2005). Kinetics and mechanisms for nitrate reduction by iron has been

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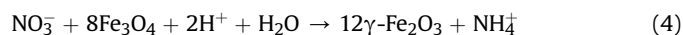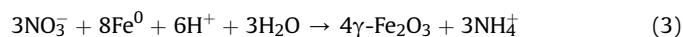[1] Present address: SNC-Lavalin, Inc., Saskatoon, S7K 1K3, SK, Canada.

extensively studied (Choe et al., 2004; Rodríguez-Maroto et al., 2009; Li et al., 2010; Hwang et al., 2011).

Granular iron is generally covered with a double layer of oxides: an inner layer of magnetite and an outer layer of higher valence iron oxides (i.e., hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3)) (Ritter et al., 2002; Odziemkowski and Simpraga, 2004). Since the reactivity of granular iron depends on the electron transfer rate from the inner iron core to the oxidant, the electrical conductivity of the surface films is an important factor in maintaining the reactivity of granular iron materials (Schlicker et al., 2000; Huang and Zhang, 2005). Three-valent iron oxides differ from iron(II) or mixed valent Fe(II)/Fe(III) oxides, such as magnetite, in that they form passive films that are not conductive. Thus, the removal of the outer passive layer is necessary in order for the iron to be effective in degrading chlorinated hydrocarbons and other contaminants.

As shown by Ritter et al. (2002), when placed in water, the outer oxide layer is removed by autoreduction processes:

$$Fe_2O_3 + Fe^0 + 6H^+ \rightarrow 3Fe^{2+} + 3H_2O \tag{1}$$

$$3Fe_2O_3 + 2H^+ + 2e^- \rightarrow 2Fe_3O_4 + H_2O \tag{2}$$
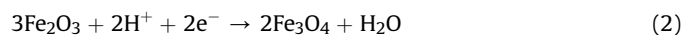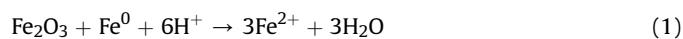
The presence of nitrate, however, appears to hinder the autoreduction processes, resulting in incomplete removal of hematite from the iron surface (Ritter et al., 2003). As an oxidant itself, nitrate might also cause the formation of passive iron oxide film (Schlicker et al., 2000):

$$3NO_3^- + 8Fe^0 + 6H^+ + 3H_2O \rightarrow 4\gamma\text{-}Fe_2O_3 + 3NH_4^+ \tag{3}$$

$$NO_3^- + 8Fe_3O_4 + 2H^+ + H_2O \rightarrow 12\gamma\text{-}Fe_2O_3 + NH_4^+ \tag{4}$$

However, it is not certain which reaction mechanism is the main cause of decline in iron reactivity. For example, the iron used in the study of Ritter et al. (2003) was not pre-autoreduced by contact with water, so it is not clear whether the reduced trichloroethylene (TCE) degradation rate was caused by the formation of trivalent iron oxide or by the pre-existing oxides. In addition, the significantly higher concentration of nitrate than TCE (the molar ratio of nitrate to TCE was 9:1) could result in a competitive advantage for nitrate, reducing the TCE degradation rate.

It has been shown that TCE degradation rates deviate from typical first-order kinetics in the presence of nitrate. To quantitatively describe the kinetic behavior, Farrell et al. (2000) introduced a concept of effective half-life ($t_{1/2} = 0.693\theta/\ln(C_0/C_e)$) to represent the integrated reaction rates along the length of the column, where θ is the hydraulic residence time, C_0 is the influent concentration and C_e is the effluent concentration. Schlicker et al. (2000) proposed a general formula for the breakthrough time of nitrate, which was derived from the migration rate of the nitrate, the influent nitrate concentration, and pore water velocity in their column experiments. While those approaches can be useful to estimate longevity of iron materials under particular experimental conditions, a more generalized method is required to accurately delineate the temporal and spatial changes in iron reactivity when passivated as a result of reaction with nitrate.

Modeling complex reactive transport systems has been advanced significantly in recent years (Mayer et al., 2001, 2002; Weber et al., 2013), and inclusion of evolving iron reactivity into a multi-component reactive transport framework has been suggested to be the key component to predict long-term performance of iron PRBs (Jeen et al., 2007; Bilardi et al., 2013). Jeen et al. (2007), in particular, proposed an empirical relationship between the amounts of secondary precipitates and iron reactivity and successfully simulated the geochemical patterns observed in column

experiments. Furthermore, Jeen et al. (2013) considered the effects of chromate, as a co-existing oxidant, on the degradation of TCE where Fe(OH)$_3$ was included as a passivating reaction product of chromate reduction. Considering that both chromate and nitrate can cause the accumulation of passivating reaction products on iron surfaces (Schlicker et al., 2000), the approach used in Jeen et al. (2013) could also be applied to the conditions where nitrate affects the degradation of TCE.

The objectives of this study were 1) to determine the processes that contribute to the decline in iron reactivity toward TCE degradation in the presence of nitrate, 2) to evaluate the relationship between the nitrate concentration and the extent of iron passivation, and 3) to simulate the geochemical changes in iron columns in the presence of nitrate for the purpose of designing PRBs. Column experiments were conducted using pre-conditioned iron material and three different concentration ratios of nitrate and TCE (molar ratios of 1:1, 1:10, and 21:1) to examine the causes of declining TCE degradation rate in the presence of nitrate. The corrosion potential shifts and the surface film formation were examined by continuous in situ measurements and periodic measurements of the composition of the surface films. Finally, reactive transport modeling was conducted to evaluate the dominant geochemical processes observed in the column experiments.

2. Experimental methods

2.1. Column setup

Granular iron was obtained from Connelly-GPM, Ltd. (Chicago, IL). As-received iron grains are irregularly shaped, and the grain size varies over a wide range from −8 to 50 mesh (0.30−2.38 mm). Surface area of the iron, determined by the Brunauer−Emmett−Teller (BET) method (Brunauer et al., 1938) using a Micrometrics Gemini III 2375 surface area analyzer, was 1.23 m^2 g^{-1}. Three Plexiglas columns (0.2 m long, 38 mm I.D.), each having 5 sampling ports located at 0.025, 0.05, 0.1, 0.15 and 0.175 m from the influent end, were setup for this study (Table 1; Fig. S1 of Supporting Information). Samples were also collected from the influent and effluent lines. Two additional ports were fitted with Swagelok® reducing fittings, located in the wall of each column at a 90° angle to the row of sampling ports. These ports (ports L and H, located at 0.05 and 0.15 m from the inlet, respectively) were used to hold the reference electrodes (Ag/AgCl/Cl$^-$$_{sat}$) for the measurement of corrosion potential. Serving as the electrical connector, a pure iron rod (70 mm long, 2 mm O.D.) was fitted to a Swagelok® reducing unit on the opposite side from the reference electrode of port L.

After the columns were packed with iron, nitrogen gas was passed through the columns to remove oxygen from the pore space. Initially, to saturate the columns, deoxygenated Millipore water was introduced to all columns at a flow rate of 0.05 mL min^{-1} using an Ismatec™ multi-channel peristaltic pump. Then, the flow rate was increased to an average of 0.14 mL min^{-1}, resulting in residence times of approximately 13.75 h. Once the corrosion potential reached a quasi-steady state, the influent was switched to a 10 mg L^{-1} TCE solution. Corrosion potential measured at columns A and B reached a quasi-steady state shortly after Millipore water was added to the columns. Thus, as soon as the corrosion potential for column C reached the equilibrium value that was observed in columns A and B, TCE was added to the column C influent solution (at 45 PV as compared to 200 PV for columns A and B; Table 1). Finally, nitrate with different concentrations (4.7, 47, and 100 mg L^{-1} for columns A, B, and C, respectively) was added to each column (Table 1). It should be noted that the second cycle for column C experiment used nitrate concentration of 20 mg L^{-1} to further evaluate the effect of nitrate concentration on TCE degradation. For