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Reductive denitrification of nitrate by scrap iron filings*

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Abstract: Reduction of nitrate by zero-valent iron is a highly exergonic reaction that has long been known to occur. Use of scrap iron filings (SIF) as the PRB (Permeable Reactive Barrier) material can be used to recycle certain by-products, and identify cheaper replacements for expensive conventional PRB materials, especially pure metallic iron. The feasibility of reductive denitrification of nitrate by SIF was studied by batch experiments. Operational parameters such as pH value, SIF dosage and initial concentration of nitrate were investigated. The removal efficiency of nitrate reached 80% under the conditions of pH of 2.5, nitrate initial concentration of 45 mg/L and SIF dosage of 100 g/L within 4 h. Results indicated that nitrate removal is inversely related to pH. Low pH value condition favors for the nitrate transformation. Different from the results of others who studied nitrate reduction using iron powder, we found that there was a lag time before nitrate reduction occurs, even at low pH. Finally, the possible mechanism of nitrate reduction by Fe^0 is discussed.

Key words: Denitrification, Scrap iron filings (SIF), Zero-valent iron, Nitrate, Mechanism
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INTRODUCTION

Nitrate contamination in groundwater and surface water has become an increasingly serious environmental problem. Anthropogenic sources such as nitrogen fertilizers, animal wastes, and septic systems account for most nitrate contamination of groundwater. Nitrate itself is relatively non-toxic. However, it can be microbially reduced to nitrite, which poses several health threats to humans including methemoglo-binemia, liver damage and cancers. Nitrate outflow onto shallow continental shelves can also promote nearshore algal bloom.

Permeable reactive barrier (PRB) technology is an emerging alternative method to traditional pump and treatment systems for groundwater remediation. Over the past decades, permeable reactive barriers have been developed and used to remove both negatively and positively charged inorganic species from groundwater (Ahn *et al*., 2002; David *et al*., 2000). Metallic iron is being evaluated as a very potential PRB material for preventing the transport of a wide array of highly mobile contaminants into groundwater. Scrap iron filings (SIF), which are primary composed of metallic iron with little oil and grease content, are by-products of mechanical process (such as lathing, drilling or milling processes). SIF as PRB material for in situ remediation of nitrate contaminated water can recycle certain by-products and are relatively cheap replacements for expensive conventional PRB materials, especially pure metallic iron.

Reduction of nitrate by zero-valent iron is a highly exergonic reaction and has long been known to occur. Previous studies (Cheng *et al*., 1997; Fanning, 2000; Hu *et al*., 2001; Huang *et al*., 1998) demonstrated that nitrate can be completely reduced by metallic iron under anoxic and aerobic conditions, with the major product being ammonia.

In this study, the feasibility of reductive denitrification of nitrate by SIF was evaluated in a batch reactor. The objective of this study was to determine

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the capability and rate of nitrate removal from aqueous solution by SIF, and to gain insight into the mechanism of reduction of nitrate by zero-valent iron. Particular attention was paid to the relation between the pH value and the rate of nitrate removal by SIF.

EXPERIMENTS AND METHODS

Chemicals

All chemical reagents, such as sodium nitrate, sodium nitrite, sulfuric acid (H_2SO_4) and acetone were used as received without further purification. Before each experiment, SIF were first pre-treated by diluted H_2SO_4 (pH=2), acetone, and then were rinsed by deionized water several times. After these operations, impurities and organic compounds on the surface of the SIF were removed, which ensured a fresh surface where the nitrate reduction reaction occurred.

Batch experiment procedures

Batch experiments for reduction of nitrate were conducted in 1 L three-necked flask (shown in Fig.1) with total volume of 500 ml solution in a water bath, which maintains the reaction temperature at 25 °C. The reactant solution was stirred by a mixer at 500 rpm. Initial solution pH was adjusted to desired value by diluted H_2SO_4. To ensure anoxic conditions, deionized water for nitrate solution was seethed to remove aqueous oxygen before the reaction, and the reactor was purged with nitrogen gas to replace the head volume during the reaction.

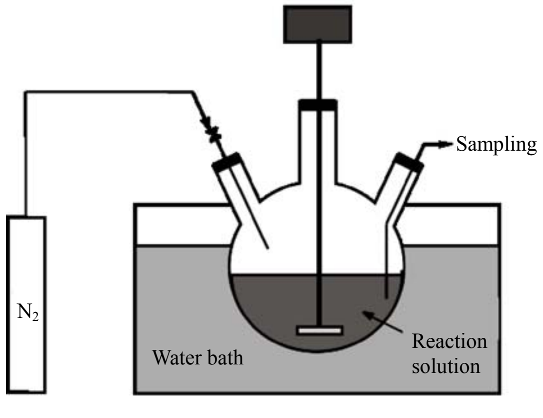

Fig.1 Experimental apparatus for the experiments on denitrificatioin by SIF

Analytic methods

Five ml samples were withdrawn by glass syringes at different reaction time, filtered twice through 0.22 μm membrane filters and then analyzed for nitrate and nitrite using Metrohm 792 Basic Ion Chromatograph (IC) equipped with a Metrosep A Supp 4 column (250 mm×4.0 mm), a Metrosep A Supp 4/5 guard column, and a conductivity detector. The eluent (flowrate=1.0 ml/s) was a standard Metrohm mixture of 2.0 mmol/L sodium carbonate and 1.0 mmol/L sodium bicarbonate. pH value was measured with PHS-25C pH meter.

RESULTS AND DISCUSSION

Denitrification of nitrate

As shown in Fig.2, interestingly, nitrate reduction did not take place immediately upon addition of SIF. Nitrate was removed rapidly after a short lag time. Huang *et al.*(1998) observed that there was a lag time of a few minutes before nitrate reduction took place, but that the lag time was observed only at pH 4, not at pH 2.5.

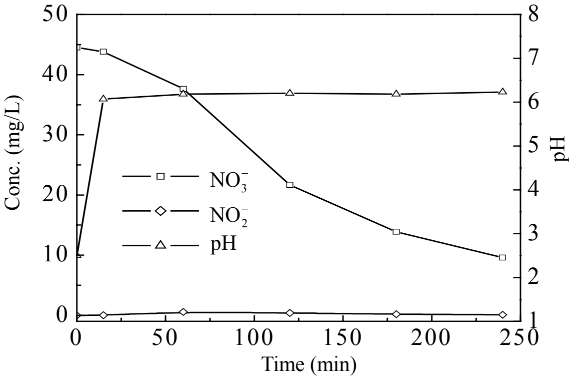

Fig.2 Reductive denitrification of nitrate by SIF (T=25 °C, pH_i=2.5, C_0=45 mg/L, C_{SIF}=100 g/L)

The pH value jumped from 2.5 to 6 in the first few minutes, because the corrosion reaction of Fe took place immediately after the addition of SIF, and then the pH value rose slowly before reaching 6.2 finally. This phenomenon showed that the Fe-H_2O system reaction is very important for the reduction of nitrate.

The removal efficiency of nitrate was 80% after 240 min reaction, and the residual concentration was

9.596 mg/L. Ammonia species are generally considered to be the principal and final products of nitrate reduction, although nitrate is not reduced to ammonia directly. It is theoretically possible that it forms other products including all nitrogen species with lower valence than the +5 of nitrate-N.

IC detected a little quantity of nitrite during our experiments. From the beginning of the reaction, the concentration of nitrite increased to a maximum value, 0.558 mg/L. As the reaction went on, the concentration of nitrite almost fell to zero finally. It was obvious that nitrite is an intermediate reduced product of nitrate. Fig.2 shows that the more nitrite was produced, the faster nitrate was removed from the solution. Ahn *et al.*(2001) also conducted that nitrite was an intermediate product of nitrate reduction by Fe^0.

Effect of initial pH

Fig.3 shows different initial pH values adjusted by diluted sulfuric acid (H_2SO_4). While initial pH was 2.5, the efficiency of nitrate removal reached nearly 80% in 240 min reaction; while initial pH was 4, the efficiency of nitrate removal was lower than 10%. It was obvious that the presence of H^+ greatly enhanced the nitrate reduction. Ahn *et al.*(2001) suggested that both the initial pH of the solution and the change of pH during reactions played very important roles in the reduction. The solutions pH must be maintained below pH 7 for complete reduction of nitrate. They suppressed the rise of pH effectively by using $HgCl_2$.

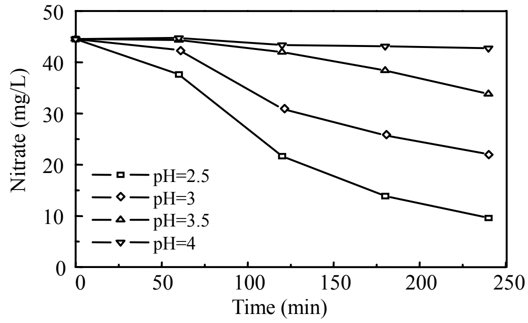

Fig.3 Effects of initial pH on nitrate reduction (T=25 °C, C_0=45 mg/L, C_{SIF}=100 g/L)

Based on the chemical reaction equations (Eqs.(1)–(5), see mechanism) of reduction, a large amount of ferrous and ammonium ions must be formed. To ensure electro-neutrality of the aqueous-phase, an equal-electric charge amount of hydrogen ions was consumed, at the same time that an equal-electric charge amount of hydroxide ions was produced. This is the reason why solution pH rapidly rose to 6 during the first few minutes of the reaction (Fig.2). Another reason for this phenomenon was that Fe corrosion reaction took place easier or faster than the nitrate reduction reaction. Cheng *et al.*(1997) suggested that Fe corrosion was a necessary factor for nitrate reduction.

Effect of SIF dosage

Since the reductive denitrification by Fe^0 takes place on the surface of SIF, the SIF dosage is also a significant variable parameter. Different SIF dosages of 20 g/L, 50 g/L and 100 g/L were evaluated as shown in Fig.4. The reaction of 50 g/L SIF dosage was obviously blocked after one hour reaction, and the removal efficiency of nitrate reached just 50% after 4 h. However, the removal efficiency reached 80% when SIF dosage was 100 g/L.

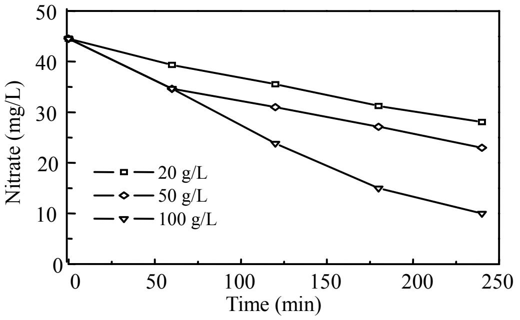

Fig.4 Effects of SIF dosage on nitrate reduction (T=25 °C, pH_i=2.5, C_0=45 mg/L)

The chemical reaction and/or the mass transfer, which includes the reactants transport from the bulk to the iron's surface and the products diffuse from the surface back to the bulk, may control the rate of the overall process of nitrate removal. Because stoichiometric excess of SIF was added in all experiments and the stirring of the reaction solution increased the efficiency of mass transfer by constantly providing new contact surface area of SIF to nitrate, the mass transfer was not the limiting step for reductive denitrification of nitrate by SIF under our experimental conditions. The total rate of mass transfer was also promoted by increasing the surface area because of higher SIF dosage. Choe *et al.*(2000) concluded that in lower stoichiometric excess of Fe^0 particles, the reaction rate linearly increased with increasing amounts of iron to 200 mg/L nitrate solution, and at higher dosage (>50 g/L), its change became very small.

Effect of nitrate initial concentration

The nitrate reduction profiles with different initial nitrate concentration and fixed other parameters are shown in Fig.5. The highest rate of reaction was obtained with the highest initial concentration of nitrate. The removal efficiency of 100 mg/L nitrate dosage was higher than that of 50 mg/L and 25 mg/L. Especially for 25 mg/L nitrate dosage, the nitrate removal was very slow after an hour, and the final removal efficiency was below 60% after 4 h.

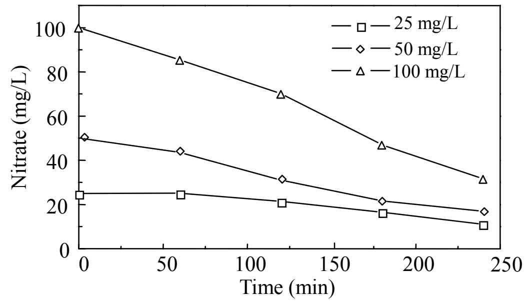

Fig.5 Effects of nitrate initial concentration on nitrate reduction (*T*=25 °C, pH$_i$=2.5, *C*$_{SIF}$=100 g/L)

Mechanism

The electrons required to reduce nitrate must come from Fe^0 either directly or indirectly through the corrosion products, Fe^{2+} and hydrogen. We believe that the mechanism responsible for the rapid reduction of nitrate observed at low pH involves either hydrogen or Fe^0. Fig.6 shows the relationship between pH and pe for Fe-N-H_2O redox system at 25 °C. Fe^{2+} and NH_4^+ have large areas under our experiments condition (anoxic and pH lower than 7). So we could deduce that a large amount of ferrous and ammonium ions must be formed, ammonium ions are the principal and final product of nitrate reduction. Nitrite has a very small area, which indicates that it is an intermediate and can be further reduced to ammonium ions by Fe.

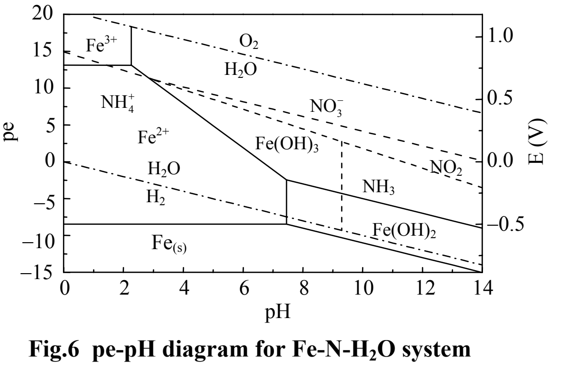

Fig.6 pe-pH diagram for Fe-N-H_2O system

Solid lines are the boundaries for Fe species and dashed lines for N species; assuming $C_{T,Fe}$=0.01 mol/L

So the mechanism of denitrification (as Eqs.(1)–(5) show) includes the direct reduction by metallic iron and indirect reduction by the iron corrosion product, hydrogen. Nitrite is an important intermediate reduced product. Nitrate is reduced to ammonium and nitrite simultaneously, then nitrite is further reduced to the final product, ammonium.

$$2H^+ + Fe^0 \rightarrow H_2(g) + Fe^{2+} \tag{1}$$

$$NO_3^- + Fe^0 + 2H^+ \rightarrow Fe^{2+} + NO_2^- + H_2O \tag{2}$$

$$NO_3^- + 4Fe^0 + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O \tag{3}$$

$$NO_3^- + 4H_2 + 2H^+ \rightarrow NH_4^+ + 3H_2O \tag{4}$$

$$NO_2^- + 3Fe^0 + 8H^+ \rightarrow 3Fe^{2+} + NH_4^+ + 2H_2O \tag{5}$$

At low pH, Fe^{2+} formed as a result of the corrosion on the SIF surface in the first few minutes, meanwhile, the pH jumped to 6 rapidly. And it is possible the aqueous protons are reduced by Fe^0 and form hydrogen species, such as hydrogen atoms (H), which react with nitrate or evolve as H_2. Iron can activate adsorbed H_2 similar to catalytic metals such as palladium (Grittini *et al.*, 1995; Schreier and Reinhard, 1995). Reardon (1995) noted that H_2 molecules split on the iron surface and enter the iron as individual atoms rather than as diatomic molecules. Huang *et al.*(1998) considered that nitrate reduction by Fe^0 is an acid-driven process and that the proton either directly participates in the reaction or indirectly facilitates it. Cheng *et al.*(1997) detected that pH jumped immediately to 8.8 once reductive reaction took place in an unbuffered solution, and that solution pH also rose to 8.8 within a relatively longer time in the presence of buffers, after which, the reaction almost ceased. In contrast to their findings, when the pH rose to 6.2, although the rate slowed down greatly, the reactions were still going on under our studied conditions. So the reduction of nitrate by zero-valent iron may be also considered as an acid-induced process.

There are three reasons for the lag time after the addition of SIF. The first reason is the impurities of the SIF. The second one is that the Fe corrosive reaction took place on SIF surface before the reductions occur, so a passivation layer may cover the SIF surface. The formation of passivation layer ($Fe(OH)_2$ and/or $Fe(OH)_3$) on SIF slowed down the reduction rate of nitrate. However, Cheng *et al.*(1997) suggested that iron corrosion was a necessary factor for nitrate reduction to occur and that the corrosion product of Fe^0 was responsible for nitrate reduction instead of Fe^0 itself. We think that Fe corrosion plays two different roles in nitrate reduction. Fe corrosion triggers nitrate reduction; on the other hand, the corrosion products block nitrate reduction. The third explanation for the lag time is that produced hydrogen would tend to accumulate on the surface of SIF until the sorption capacity for hydrogen gas molecules is saturated. In addition, accumulating bubbles of hydrogen would remain adhered to the surface of SIF until their sizes are large enough to overcome surface tensional forces to enable their release to the water phase.

CONCLUSION

Our results demonstrated that reductive denitrification of nitrate by scrap iron filings (SIF) is an effective and economic method. It can recycle certain by-products if SIF are used as the PRB material for in situ remediation for nitrate contaminated water. On the other hand, SIF are relatively cheap replacements for expensive conventional PRB materials, especially pure metallic iron. Nitrate removal is inversely related to pH of solution. Low pH value condition is favorable for nitrate reduction. The SIF dosage is another factor affecting the removal of nitrate. The removal efficiency of nitrate reached 80% under the conditions of pH of 2.5, nitrate initial concentration of 45 mg/L and SIF dosage of 100 g/L within 4 h. The nitrate reduction reaction by Fe^0 may be considered as an acid-driven and acid-induced process. Fe corrosion could trigger nitrate reduction, although the corrosion products would form a passivation layer on the SIF surface which could slow down the reduction rate of nitrate. Nitrite is an intermediate product of nitrate reduction, and will be further reduced to ammonium finally. Different from the results of others who studied nitrate reduction using iron powder, we found there was a lag time before nitrate reductions occur, even at low pH. More researches are required to determine possible inhibitory effects on treatment systems involving Fe^0 and how to put this method into practice.

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