

Fate of nitrogen species in nitrate reduction by nanoscale zero valent iron and characterization of the reaction kinetics

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ABSTRACT

This study investigates the fate of nitrogen species during nitrate reduction by nanoscale zero valent iron (NZVI) as well as the related kinetics. The NZVI used for the experiments was prepared by chemical reduction without a stabilizing agent. The pseudo first order kinetic constant of nitrate reduction at 30°C with an NZVI/nitrate ratio of 1.25:1, which were the reference conditions of this study, was 4.08 h^{-1} ($R^2 = 0.955$). A nitrogen mass balance was established by quantitative analysis of aqueous-phase and gas-phase nitrogen species. The results confirm that the nitrate was converted to ammonium ion, that ammonia stripping subsequently occurred under a strong alkaline condition, and that the total amount of aqueous nitrogen was consequently reduced. The nitrate reduction rate also increased with a lower pH and a higher temperature when microscale ZVI was used. However, in contrast to the reaction by microscale ZVI, the nitrate reduction rate by NZVI was higher for an unbuffered condition, possibly due to the abundance of surface atoms and the smaller size.

Key words | nanoscale zero valent iron, nitrate reduction, nitrogen balance, reaction kinetic

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INTRODUCTION

Nitrogen is an essential element for living creatures. However, an excessive release of nitrogen from various sources, such as fertilizers, nitrogen pesticides, animal waste, the explosives industry, and septic systems, can cause environmental problems, such as eutrophication. Furthermore, when nitrogen compounds enter a water environment in the form of nitrate, they contaminate drinking water sources (Follett 2001).

Nitrogen is removed through various technologies, including ion exchange, reverse osmosis, biological denitrification, and chemical reduction (Bohdziewicz *et al.* 1999; Soares 2000; Bae *et al.* 2002; Zhang & Huang 2005). However, ion exchange and reverse osmosis require frequent regeneration of the media and generate secondary brine waste. Biological denitrification, the most widely used method, requires intensive maintenance and a constant supply of organic substrates. Moreover, the microbial

processes are generally slower and sometimes more incomplete than chemical reduction. Of the various chemical reduction methods proposed for the effective removal of nitrate, zero valent iron (ZVI) has attracted the most interest. Furthermore, the use of nanoscale zero valent iron (NZVI) has several advantages over microscale ZVI, particularly in terms of its low dosage and high level of stable reactivity (Choe *et al.* 2000).

However, the reaction mechanism and fate of nitrogen are not yet clear. Most studies state that nitrite, nitrogen gas, and ammonia could be possible products of nitrate reduction by ZVI. They also state that the final product is mostly ammonia, which is undesirable (Huang & Zhang 2004). Recently, NZVI has been tested for nitrate reduction to show different profiles of nitrogen species in relation to the reaction time. One profile shows a decrease in the total amount of nitrogen in the aqueous phase after the nitrate is

eliminated. Hence, some researchers (Choe *et al.* 2000) suggested that the final reaction product would be nitrogen gas, which is an ideal product of nitrate reduction. However, no clear pathway has been determined yet. Therefore, the fate of nitrogen should be studied to gain a better understanding of the behavior of nitrogen during nitrate reduction by NZVI. In this study, gas-phase nitrogen species analysis and nitrogen mass balance are used for detailed elucidation of nitrate reduction mechanisms. The way different reaction conditions affect the reaction kinetics is also evaluated for the purpose of characterizing the reaction kinetics.

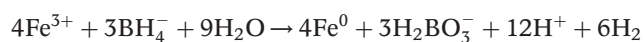
METHODS

Chemicals

Ferric chloride (Junsei Chemical Co., Japan) and sodium borohydride (Samchun Pure Chemical Co., Korea) were used for the NZVI synthesis. Potassium nitrate (Duksan Pure Chemical Co., Korea) was used to prepare a nitrate stock solution, and HEPES (Sigma-Aldrich Inc., USA), sodium hydroxide (Jin Chemical Pharmaceutical Co., Korea), and hydrochloric acid (Jin Chemical Pharmaceutical Co., Korea) were used for the pH adjustment. All solutions were prepared with deionized water after deoxygenation by purging with argon gas for 4 h.

Synthesis and characterization of NZVI

In this research, the mild chemical reduction of metal salts in a solution phase, which had chemical homogeneity as a key advantage, was used to prepare NZVI (Wang & Zhang 1997). The NZVI was synthesized in a 500 mL flask reactor with four open necks. One of the necks was housed with a tunable mechanical stirrer at 60 to 500 rpm. For the reduction of ferric ion to NZVI, a dropping funnel was used (at a rate of 1 drop/s) to introduce 250 mL of borohydride solution (358.4 mM) into 250 mL of ferric ion (Fe^{3+}) solution (71.7 mM). The reduction reaction is expressed as follows (Zhang & Huang 2005):



The NZVI was collected by centrifugation of the solution after 20 min of aging. The collected particles were then washed three times with a large amount of degassed deionized water. The prepared NZVI was immediately used for a batch experiment. The NZVI was characterized with the help of a transmission electron microscope (TEM, Tecnai F20, Philips Electronics Co., Eindhoven, Netherlands), a particle size analyzer (ELS-8000, Otsuka Electronics Co., Osaka, Japan) and a Brunauer Emmett Teller (BET) surface area analyzer (Sorptomatic 1990 Surface Area Analyzer, Thermo Fisher Scientific Inc., Waltham, MA, USA).

Nitrate reduction by NZVI

Batch tests for nitrate reduction were conducted in 1 L Schlenk flasks (Figure 1). The reactor was filled with 700 mL of nitrate solution, and the solution was purged with argon gas before the injection of NZVI. Then, 100 mL of an NZVI slurry containing 1 g of NZVI was added to the reactor, which contained 100 mg/L of nitrate. The solution was continuously stirred with a mechanical stirrer. Samples were taken periodically; they were filtered with 0.45 μm syringe filters; and they were then analyzed immediately. Argon gas was blown continually into the reactor to maintain an anoxic condition during the reaction. The off-gas from the reactor throughout the entire reaction period was absorbed in 200 mL of acidic solution so that gas-phase nitrogen species, such as ammonia and gaseous nitrogen (N_2), could be analyzed. The reaction rate of the

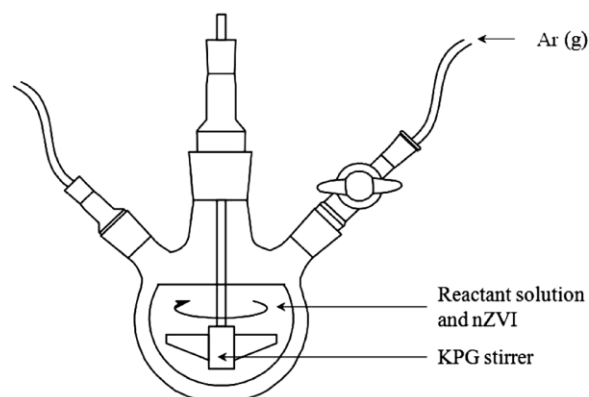


Figure 1 | Schematic of a batch reactor.

nitrate reduction was interpreted by the following pseudo first order rate equation:

$$\frac{dC}{dt} = -k_{\text{obs}}C = -k_{\text{SA}}\alpha_s\rho_m C,$$

where C is the reactant concentration, k_{obs} is the observed pseudo first order rate constant (1 h^{-1}), k_{SA} is the rate constant normalized with the surface area ($\text{L}/\text{m}^2/\text{min}$), α_s is the surface area of NZVI (m^2/g), and ρ_m is the amount of catalyst in the solution (g/L). For investigation of the reaction kinetics, experiments with various reaction conditions (temperature, initial pH, and use of buffer) were conducted under the same NZVI dose and initial nitrate concentration.

Nitrate and nitrite concentrations were analyzed by means of ion chromatography (DX-120, Dionex Co., Sunnyvale, CA, USA). Ammonium and total nitrogen were analyzed by using a standard method (ASTM D1426-03) and a spectrophotometer (HACH Model DR-2010) in accordance with the guidelines of the 20th edition standard method (APHA 1998). In addition, gas chromatography (GowMac 580, Gow-Mac Instrument Co., Bethlehem, PA, USA) was used to analyze gas-phase nitrogen.

RESULTS AND DISCUSSION

Property of NZVI

The TEM morphologies of the prepared NZVI in this study are shown in Figure 2 with different magnifications. Laser scattering particle size analysis shows that the average diameter of the prepared NZVI was 16.7 nm. The BET surface area was $79.06\text{ m}^2/\text{g}$.

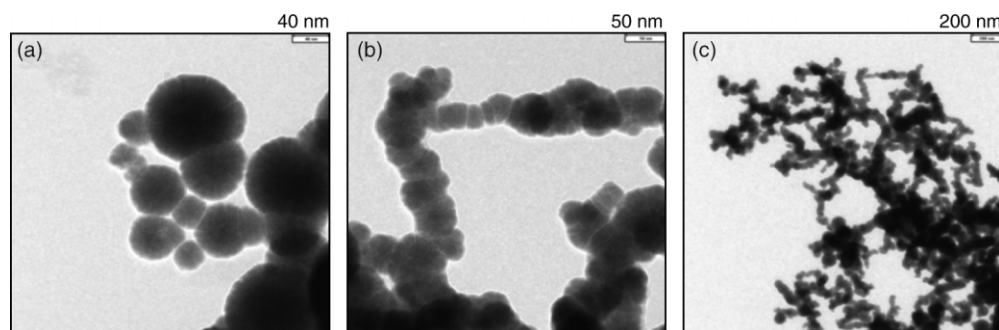


Figure 2 | TEM images of the prepared NZVI.

As shown in Figure 2(c), NZVI is spherical with a chain network structure. The spherical shape and chain net morphology are similar to those observed in other studies (Wang *et al.* 2006). The aggregation of NZVI in aqueous solution without a surfactant is a common behavior but the accessibility of reactants to NZVI is good because the total surface area is unaffected due to the high porosity of the aggregates (Wu *et al.* 2005; Yang & Lee 2005). Therefore, the expected high reaction rate was confirmed by the high nitrate reduction rate of the subsequent experiments.

Fate of nitrogen during nitrate reduction by NZVI

Figure 3(a) shows the profile of aqueous nitrogen species in relation to the reaction time during nitrate reduction by NZVI; the reference conditions were a temperature of 30°C , an initial pH of 7, and an unbuffered status. Figure 3(b) shows the pH in relation to the reaction time. More than 97% of the nitrate was removed within 1 h and complete removal was obtained within 1.5 h. Ammonia was produced as the main by-product, and its concentration decreased after 1 h of reaction. The total amount of nitrogen species in the aqueous phase decreased to 52% of the initial concentration in 3 h as a consequence of the reduced ammonia concentration. Hence, about half of the total nitrogen was converted from an aqueous phase to a gas phase. This phenomenon is in agreement with the results of Choe *et al.* (2000). They suggested that the decrease in the total nitrogen concentration is due to the formation of nitrogen gas during the reaction; however, that suggestion contrasted with the results of previous research involving the use of microscale ZVI, where the end product was ammonia (Huang & Zhang 2004; Wang *et al.* 2006).

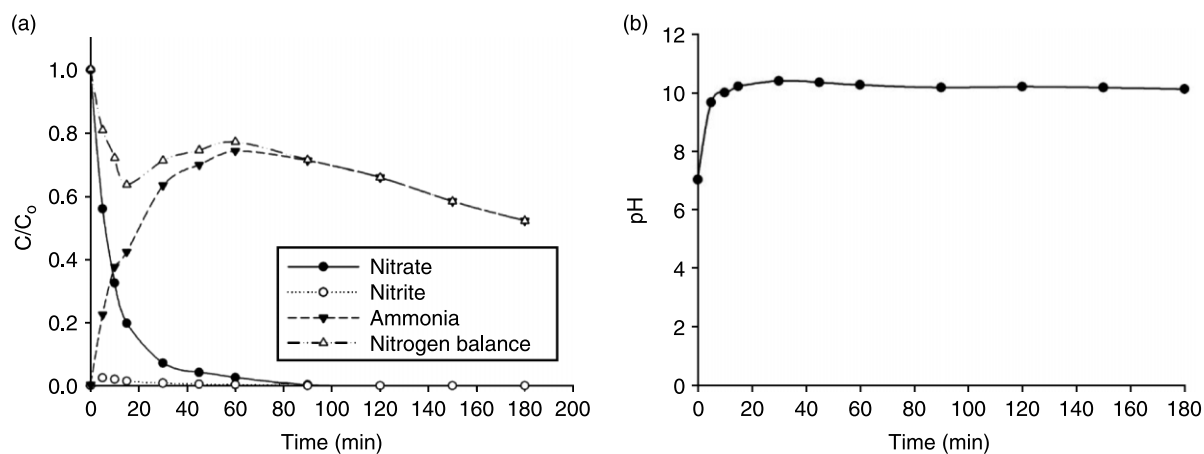


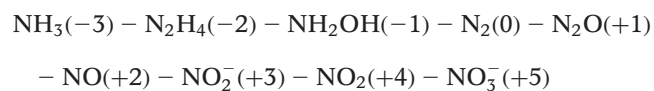
Figure 3 | (a) Concentration of nitrogen species and (b) the pH variation during nitrate reduction by NZVI.

However, the pathways and end products have not yet been clearly determined.

A series of experiments was conducted in the following three steps to determine the fate of nitrogen species: Firstly, the head space gas of an air-tight reactor in which the reaction of NZVI and nitrate occurs was analyzed for nitrogen gas. Secondly, an aqueous solution of ammonia was put into the reactor with NZVI to investigate the conversion of ammonia to nitrogen gas. Finally, the off-gas from the reactor operated under the reference conditions was collected in an acidic solution during the reaction period and analyzed for absorbed ammonia so that the nitrogen in the aqueous phase and gas phase could be completely balanced.

The nitrogen gas generation was investigated with a series of 100 mL air-tight serum bottles under the reference conditions, and the head space air was analyzed by means of gas chromatography. The nitrate was reduced in a short time, and the total nitrogen concentration in the aqueous phase decreased as shown in the previous experiment. However, no nitrogen gas was detected in the head space of any samples. Clearly, nitrogen gas was not a final end product of the nitrate reduction by NZVI under the reference conditions. For further verification of the decrease in the ammonia concentration, an investigation was made of the transformation of ammonia nitrogen during the reaction with NZVI under initial conditions of 100 mg/L of N and 1,250 mg/L of NZVI. As shown in Figure 4(a), the ammonia concentration was unchanged and the pH of the solution was maintained near the initial value during

the reaction. This result suggests that neither the ammonia nor the proton in the aqueous phase reacts with NZVI to form any product such as nitrogen gas. This result is in agreement with the oxidation state of nitrogen in various forms. Nitrogen can have an oxidation state ranging from -3 to $+5$, as shown below. The oxidation state of ammonia and ammonium ions is -3 , which is the most reductive form of nitrogen. Thus, the ammonium ions cannot be reduced further by NZVI; they may be the end product of the following reaction:



The result also indicates that the decrease in the ammonia concentration in the liquid phase of the reaction is a consequence of the stripping in the high pH region. For analysis of the gas-phase ammonia and as the last verification step, the off-gas of the reactor, which operated under reference conditions, was collected and absorbed into an acidic solution during the reaction period. The ammonia concentration of the stripped solution was 132.7 mg/L, which corresponds to the ammonia nitrogen amount of 26.54 mg.

The final mass balance of this experiment is presented in Figure 4(b). Almost half (46.39%) of the nitrogen disappeared in the liquid phase. Moreover, 71% of the TN loss in the aqueous phase was collected in an absorption solution, and most of the total nitrogen mass was conserved. Ammonia was clearly an end product of the nitrate

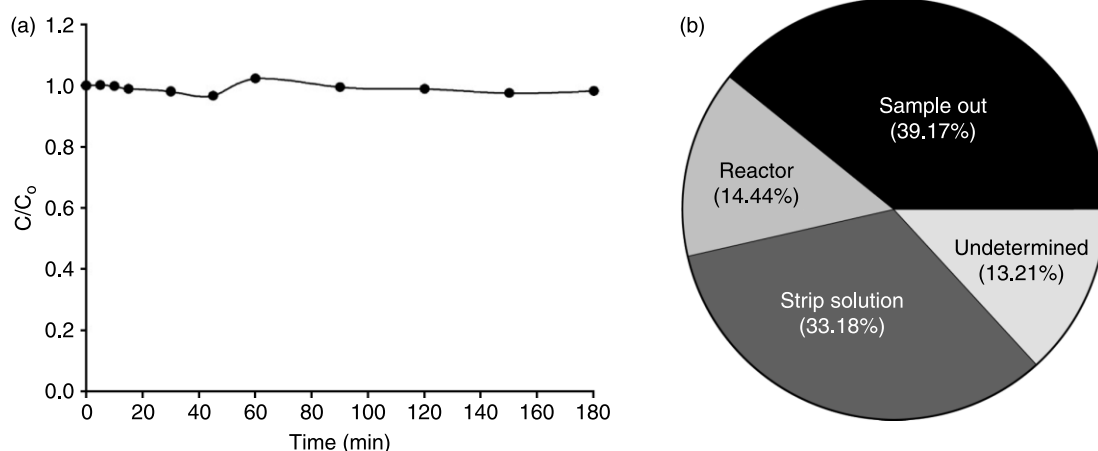
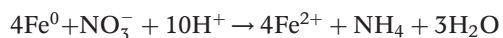


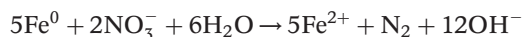
Figure 4 | (a) Ammonium concentration during the reaction with NZVI and (b) the nitrogen mass balance after the reaction.

reduction reaction by NZVI, and the TN loss in the aqueous solution was due to the ammonia stripping at a high pH level.

The two major mechanisms of nitrate reduction with different end products are expressed in the chemical equations below. The Gibbs free energy was calculated for each reaction to determine the major end products of the nitrate reduction and the direction of the reaction. Both reactions have a negative Gibbs free energy value, which indicates a spontaneous reaction. The ammonium ion and the nitrogen gas could therefore be a product of the nitrate reduction. However, the reaction to the ammonium ion has a higher equilibrium constant because the negative Gibbs free energy value is higher than that of the reaction to nitrogen gas. Moreover, the ammonium ion is more thermodynamically favorable end-product of the reaction.



$$\Delta G^\circ = -997.71 \text{ kJ (Alowitz \& Scherer 2002)}$$



$$\Delta G^\circ = -423.34 \text{ kJ. (Choe et al. 2000).}$$

The results show that the fate of the nitrogen species during the nitrate reduction by NZVI was clearly determined. That is, the nitrate was converted to nitrite and ammonium by NZVI; and ammonia, the reaction product, was stripped from the aqueous phase to the gas phase under the high pH condition that resulted from the reaction. The nitrate

reduction by NZVI has a similar pathway to the ammonium ions with assimilatory nitrate reduction by enzymes in most plants, algae, yeast and bacteria (Martinez-Espinosa *et al.* 2007).

Effects of operating conditions on nitrate reduction by NZVI

NZVI shows much higher reaction rates than those of the microscale ZVI in the literature (Ahn *et al.* 2008) mainly due to its smaller size and higher specific surface area. In addition, some of catalytic effects that are specific to nanoscale chemistry can contribute to the reactivity. Some reports have highlighted new features of metals in the nano range. For example, opaque substances become transparent (copper); inert materials become catalysts (platinum); stable materials turn combustible (aluminum); and solids turn into liquids at room temperature (gold) (Uskokovic 2007). The high reactivity of NZVI might

Table 1 | The pseudo first order kinetic constants under various reaction conditions

Temperature (C)	Initial pH	NZVI (g/L)	BET (m ² /g)	k _{obs} (1/hr)	k _{SA} (L/hr-m ²)	R ²
30	3	1.25	79.06	7.98	0.0808	0.979
30	5	1.25	79.06	6.47	0.0655	0.965
30	7	1.25	79.06	4.08	0.0413	0.955
30	7 (buffered)	1.25	79.06	0.65	0.0066	0.905
50	7	1.25	79.06	18.9	0.1913	0.986

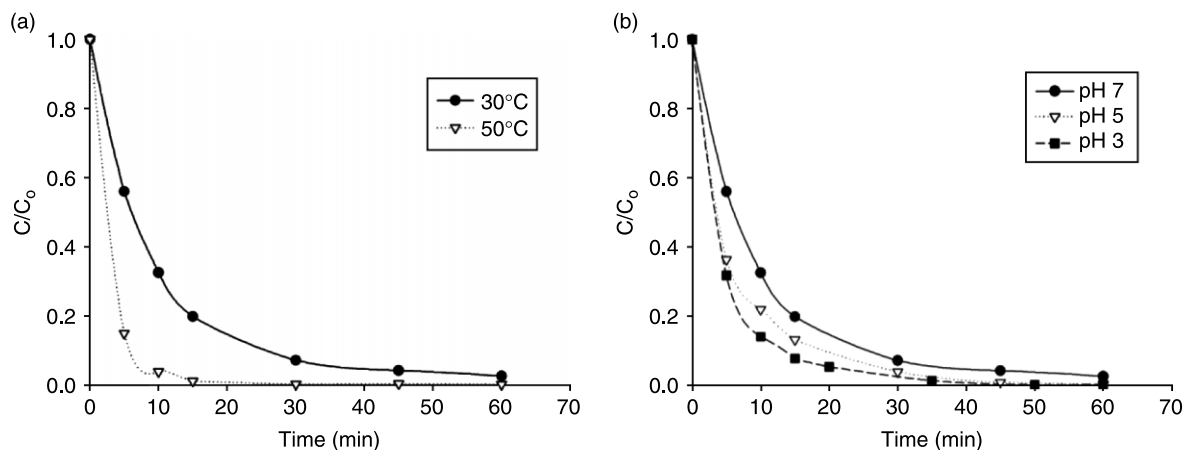


Figure 5 | Nitrate reduction by NZVI under (a) different temperatures and (b) different initial pH values.

therefore be an effect of catalytic behavior. The catalytic behavior of NZVI was determined by studying the effects of specific operating conditions, namely the temperature, initial pH, and use of a buffer. The results, which are presented in Table 1, were compared with the results of microscale ZVI.

Under operating temperatures of 30°C, the nitrate removal was 67.6% after 10 min, the pseudo first order rate constant was 4.08 h^{-1} ($R^2 = 0.9551$), and the surface area-normalized rate constant was $0.0413 \text{ L h}^{-1} \text{ m}^{-2}$. However, when the reaction temperature was 50°C, the nitrate removal by NZVI was significantly enhanced to 96.2% after 10 min. The pseudo first order rate constant was 18.9 h^{-1} ($R^2 = 0.9862$) and the surface area-normalized rate constant was $0.1912 \text{ L h}^{-1} \text{ m}^{-2}$. The rate of nitrate

reduction by NZVI underwent a 4.6-fold increase when the temperature increased due to a supply of excessive energy, which was needed to overcome the activation energy barrier (Ahn *et al.* 2008) (Figure 5(a)).

Figure 5(b) shows the effects of the initial pH value on nitrate reduction by NZVI. Initial pH values of 3, 5, and 7 were selected for this study. The pH value increased gradually as H^+ was consumed in the reaction, and the final pH was in the range of 10.0 to 10.5. The pseudo first order rate constant was 7.99 h^{-1} ($R^2 = 0.9654$) for a pH of 3, 6.47 h^{-1} ($R^2 = 0.9792$) for a pH of 5, and 4.08 h^{-1} ($R^2 = 0.9551$) for a pH of 7. The experimental results confirm that the nitrate removal by NZVI generally increases as the pH is decreased. A lower pH gives rise to a more extensive acid washing of the metallic iron.

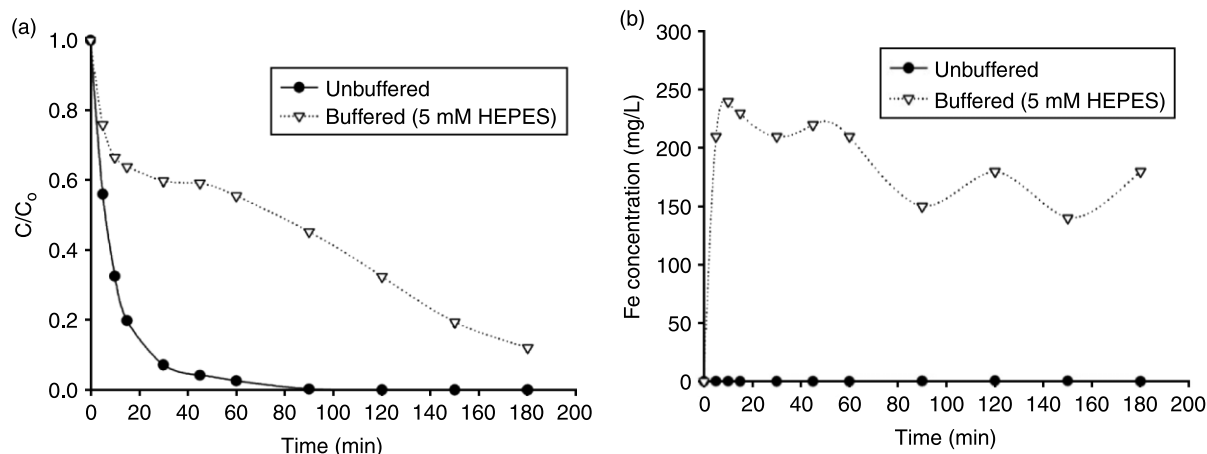


Figure 6 | (a) Nitrate concentrations and (b) total iron concentrations during nitrate reduction by NZVI under different buffer conditions.

That is, a low pH dissolves away the ferrous hydroxide and other protective layers on the surface of the ZVI, yielding fresh reactive sites for chemical reduction (Zhang & Huang 2006). Furthermore, a greater amount of H^+ is supplied under a low pH condition, promoting a faster reaction. The way the temperature and pH value affect the reaction rates is similar to the behavior of the microscale ZVI.

On the other hand, the effect of the buffer on nitrate reduction by NZVI is different from the results of study on microscale ZVI. That study shows better reactivity under a buffered solution (Zhang & Huang 2005). The reaction rate was dramatically decreased when a buffer was added to the reactant solution, and iron ions erupted in a 250 mg/L solution due to the lower pH condition (Figure 6). This outcome is in good agreement with the results of the equilibrium model presented in Table 2. That model indicates that most of the iron exists as aqueous-phase ion in a buffered condition.

The differences between NZVI and microscale ZVI under a buffered condition and a basic condition during nitrate reduction cannot be explained solely on the basis of the high surface area of NZVI. A core-shell structure model was suggested as a means of explaining the special features of NZVI (Figure 7). Table 2 shows that iron hydroxide is the dominant species in an unbuffered condition. Accordingly, the iron/iron hydroxide core-shell structure appears to have been obtained under an unbuffered condition. The core consists of metallic iron, whereas the outer shell consists of iron oxides and hydroxides. An iron oxide coating acts as a barrier for the transfer of electrons and hinders the reaction of microscale ZVI due to the long distance of the electron transfer between the core and the shell.

However, for NZVI, the shell structure acts as a sorbent of reactants on the surface of the NZVI, and further reactions subsequently occur in the shell structure. This theory was originally based on the small size of the NZVI, especially from the distribution of atoms at catalyst surfaces and in bulk phase according to particle size. Due to

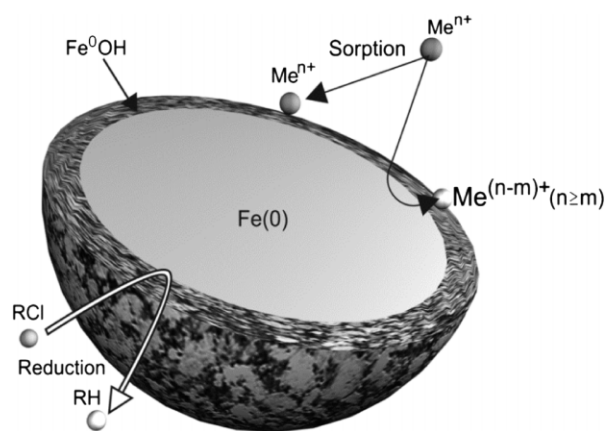


Figure 7 | Core-shell model of NZVI (Theron *et al.* 2008).

their lower coordination, the surface atoms differ from the bulk atoms in terms of their electrical and thermophysical properties. When the ratio of surface atoms to bulk atoms becomes significant, the bulk material can exhibit the properties of the surface atoms (Yetter *et al.* 2009). This outcome means that most of the iron atoms act as surface atoms, which implies that they participate in reactions with contaminants. For NZVI synthesized by the addition of borohydride, the presence of boron may also play a role in the electronic properties of the oxide shell (Lowry & Johnson 2004). Therefore, a reduction reaction is not hindered by the electron transfer through an iron oxide shell structure. Liu *et al.* (2005) reported that the shell structure never grows thick enough to hinder the electron transport across the shell and it apparently dissolves within a reaction period of 2.5 days. Accordingly, the reaction mechanism of NZVI is very different to that of microscale ZVI because of the size of the NZVI and its unique size-induced features.

CONCLUSION

The fate of nitrogen species during nitrate reduction by NZVI was investigated by quantitative analyses of nitrogen species in an aqueous phase and gas phase of off-gas from a reactor. Ammonia is the major product of the nitrate reduction by NZVI, and it is stripped to a gas phase at a high pH value as a result of the consumption of H^+ during the reaction. The final mass balance of nitrogen in an

Table 2 | Chemical species under different buffer conditions

Condition	Fe^{2+} (%)	$Fe(OH)^+$ (%)	$Fe(OH)_2$ (%)	$Fe(OH)_3$ (%)
pH 7 (buffered)	99.237	0.732	0	0
pH 10.1 (unbuffered)	16.03	70.357	9.067	4.543

aqueous phase and a gas phase has an initial value of 86.49%. This percentage strongly supports the proposed fate of nitrogen. In addition, the nitrate reduction is faster with NZVI than with microscale ZVI, and the reaction rate increases as the temperature increases and as the value of the pH decreases. However, when a buffered condition is used to maintain a neutral pH, the reaction rate decreases in a manner that is contrary to the phenomena observed with microscale ZVI. This behavior can be explained by the distribution of atoms in the core-shell structure that is specific to NZVI.

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