

## Chemical reduction of nitrate by metallic iron

Jie Chi, Shu-Ting Zhang, Xin Lu, Li-Hua Dong and Sui-Liang Yao

### ABSTRACT

The reduction reaction of nitrate by metallic iron under aerobic conditions was investigated in the pH range of 2.0–8.5. The concentration of nitrate, nitrite, ammonia/ammonium and total nitrogen in the reduction solution were monitored. The reduction products of nitrate were ammonia/ammonium remaining in the reduction solution and gaseous nitrogen emitted from the reduction solution. Nitrate predominantly reduced to gaseous nitrogen at the beginning of the reduction reaction, and ammonia/ammonium at the end of the reduction reaction. pH value was an important parameter affecting the reduction of nitrate by metallic iron. At a low pH values, ammonium was the main reduction product, while gaseous nitrogen was the dominant reduction product at high pH values. In the reduction products, gaseous nitrogen was 40.1, 56.0, 68.0, 77.8 and 81.0% after 150-min reduction at pH=2.0, 3.5, 5.0, 7.0 and 8.5, respectively.

**Key words** | ammonia, chemical reduction, contaminated water, denitrification, metallic iron, nitrate

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### INTRODUCTION

Nitrate contamination of groundwater and surface water systems by, for example, nitrogen fertilizers, animal wastes and septic systems causes serious eutrophication problems and health threats to humans. Current technologies to remove nitrate from water include biological denitrification, ion exchange, reverse osmosis (Shrimali & Singh 2001) and chemical reduction (Fanning 2000). Reverse osmosis and ion exchange are not specific to nitrate, and the re-treatment of collected or concentrated nitrate water solution is needed. Biological denitrification is unfavourable because of its relatively low removal rate of nitrate and extra addition of organic substrates required for the treatment of inorganic wastewater.

Studies on nitrate reduction have found that chemical reduction has a higher removal rate of nitrate than biological denitrification processes and a relatively higher selectivity for nitrate than both reverse osmosis and ion exchange methods (Hecke *et al.* 1990; Okazaki & Asakura 1994; Ottley *et al.* 1997; Daum & Vorlop 1999). Currently metallic iron as a powerful and

environmentally friendly reductant is being given much attention. Siantar *et al.* (1996) reported that iron powder treated with 10% H<sub>2</sub> can reduce nitrate and nitrite within minutes at pH 7 under anoxic conditions (N<sub>2</sub>: H<sub>2</sub> = 90%: 10%). The conversion of nitrate by iron to ammonia occurs nearly completely in atmospheric nitrogen at pH 2.5 (Huang *et al.* 1998), and in air in the pH range of 5–7 under buffered conditions (Cheng *et al.* 1997). Hu *et al.* (2001) studied the reduction of nitrate in oxygen atmosphere in the pH range of 2–5. However, production of ammonium ions, which is the only or major product in the reduction reaction, is one of the main disadvantages of this method.

In this study, reduction of nitrate solution in air at room temperature and pressure was investigated by metallic iron under both acidic and alkaline conditions. The aims were to investigate the reduction characteristics of nitrate and the effect of pH on products of nitrate reduction under this experimental condition, and therefore to search for conditions of limited ammonium ions formed.

**Table 1** | Molar absorptivity of nitrate and nitrite ( $M^{-1} cm^{-1}$ )

Wavelength (nm)	Nitrate	Nitrite
301	53.2	105
353	0	43.4

## METHODS

Sodium nitrate was of analytical grade and purchased from Tianjin Third Reagent Manufactory and was used as received.

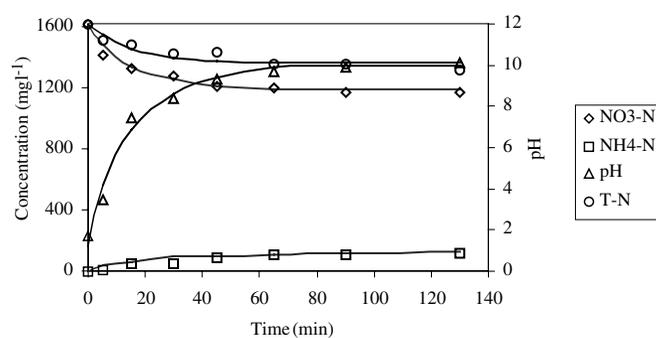
500 ml of sodium nitrate solution ( $1.62 \times 10^5$  mg-N  $l^{-1}$ ) were added to a batch reactor with total volume of 1 l. The pH value of the nitrate solution was adjusted to a desired level using sulfuric acid before reaction. The nitrate solution was exposed to the atmosphere to maintain aerobic conditions throughout the experimental period. The reduction was initiated by adding 560 g iron (94%, 30–40 mesh) to the nitrate solution ( $164$  mol-Fe mol-N $^{-1}$ ) at room temperature. Before use, the iron was treated with 6 M hydrogen chloride for 5 min to activate the surface of the metallic iron. The concentrations of nitrate, nitrite, ammonia/ammonium and total nitrogen in the reduction solution were measured at various reduction times.

The concentrations of nitrate and nitrite were measured by UV-Vis spectroscopy at characteristic wavelengths of 301 and 353 nm, respectively. The molar absorptivities for nitrate and nitrite at these wavelengths are shown in Table 1. Ammonia/ammonium was analysed by the Nessler method (National Environmental Protection Bureau 1997). Total nitrogen was measured by the potassium persulfate method (National Environmental Protection Bureau 1997).

## RESULTS AND DISCUSSION

### Nitrate reduction by metallic iron without pH control

To establish the nitrogen mass balance, the concentration of nitrate, nitrite, ammonia/ammonium and total nitrogen

**Figure 1** | Nitrate reduction vs. time without pH control.

in the reduction solution were monitored. The nitrate reduction profiles without pH control are shown in Figure 1. The initial pH in Figure 1 was 2.0. Nitrate concentration decreased from  $1.62 \times 10^5$  mg-N  $l^{-1}$  to  $1.20 \times 10^5$  mg-N  $l^{-1}$  within 1 h. The concentration of nitrite in the reduction solution was lower than  $6$  mg-N  $l^{-1}$ . According to the nitrogen mass balance calculation, the total concentration of nitrate and ammonia was basically equal to that of the total nitrogen in the reduction solution. Clearly, under our experimental conditions, the decrease in the total concentration of nitrate is due to the reduction of nitrate to ammonia/ammonium remaining in the reduction solution and gaseous nitrogen emitted from the reduction solution.

As shown in Figure 1, the pH value of the reduction solution increased rapidly from 2 to 7 within the first 15 min reduction, to 10 in about 50 min and remained constant thereafter. Coincidentally, the concentration changes of nitrate, ammonia/ammonium and total nitrogen were consistent with the change of pH in the reaction solution. The reduction of nitrate almost stopped after the reaction solution pH reached 9, at which point iron remained in the reduction solution. These facts suggested that the reduction rate of nitrate by iron was sensitive to the solution pH.

Cheng *et al.* (1997) found that the principal reduction product of nitrate by metallic iron under aerobic conditions is ammonia and no  $N_2O$ ,  $NO_2$  or  $N_2H_4$  was identified. Hu *et al.* (2001) reported that the reduction products of nitrate under an oxygen atmosphere were ammonia and nitrogen gases. The following reactions are considered to

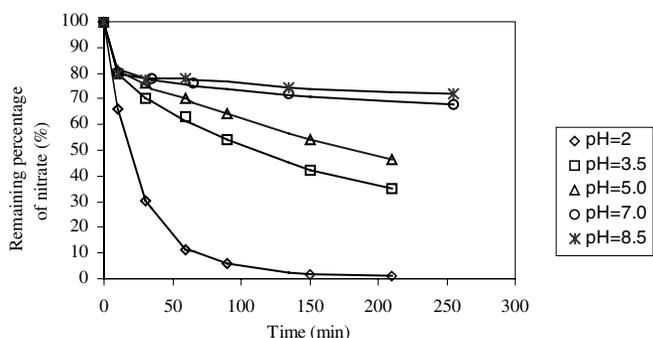
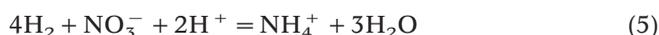
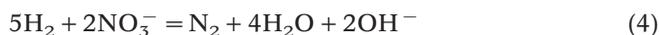
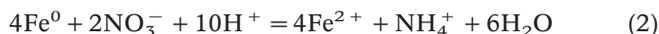
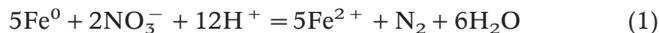


Figure 2 | Nitrate reduction vs. time at various pH values.

relate to the pH increase in the reaction solution under this experimental condition.



### Nitrate reduction by metallic iron with pH control

The time courses of nitrate reduction by iron at pH values of 2.0, 3.5, 5.0, 7.0 and 8.5 are shown in Figure 2. The pH of the reduction solution was maintained at the desired level using sulfuric acid. Rapid reduction of nitrate was observed at pH 2.0, and nitrate was almost completely reduced after 150 min reduction. At  $\text{pH} \geq 3.5$ , concentrations of nitrate dropped down rapidly in the first 10 min, and then decreased gradually at pH 3.5 and 5.0, while at pH 7.0 and 8.5, the nitrate concentrations decreased slightly thereafter.

Figure 3 shows the time courses of the product ratio of gaseous nitrogen and ammonia/ammonium during the reduction reaction by iron at various pH values. As the reduction reaction proceeded, the ratio dropped rapidly. Nitrate predominantly reduced to gaseous nitrogen at the

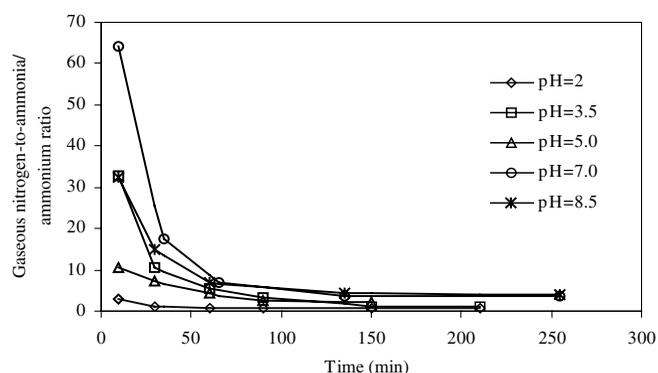


Figure 3 | Product ratio of gaseous nitrogen and ammonia/ammonium vs. time at various pH values.

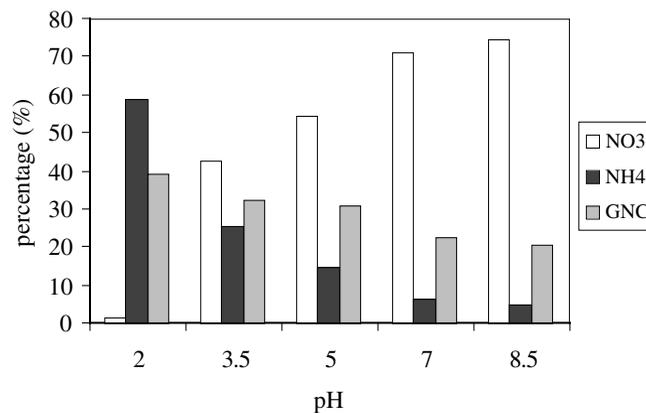


Figure 4 | Effect of pH on the composition of reduction products of nitrate by metallic iron after 150 min reduction. GNC, gaseous nitrogen compound.

beginning of the reduction reaction, and ammonia/ammonium at the end of the reduction reaction.

The effect of pH on the composition of the reduction products is shown in Figure 4. Formation percentage of ammonia/ammonium in the reduction solution greatly decreased with increasing reaction solution pH, and percentage of total nitrogen in the reduction solution decreased gradually with increasing reaction solution pH. In the reduction products, gaseous nitrogen was 40.1, 56.0, 68.0, 77.8 and 81.0% after 150 min reduction at pH 2.0, 3.5, 5.0, 7.0 and 8.5, respectively.

The data from Figure 2 were further analysed to obtain a reaction order with respect to nitrate concentration. For the reduction reaction of nitrate, the rates follow pseudo-first-order kinetics:

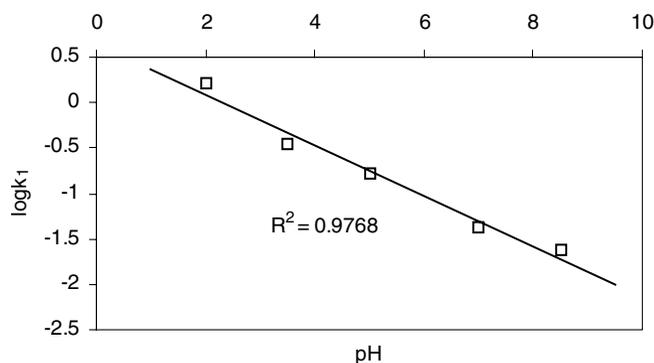


Figure 5 | Relation between the pH value and the logarithm of  $k_1$  value.

$$-d[\text{NO}_3^-]/dt = k_1[\text{NO}_3^-] \quad (6)$$

where  $[\text{NO}_3^-]$  is the concentration of nitrate in the reaction solution at time  $t$ , and  $k_1$  is the pseudo-first-order constant of nitrate. By regression analysis,  $k_1$  values at pH 2.0, 3.5, 5.0, 7.0 and 8.5 were 1.66, 0.246, 0.168, 0.042 and  $0.024 \text{ h}^{-1}$  ( $R^2 = 0.9329\text{--}0.9997$ ), respectively. The reaction constants of nitrate in our experiments are lower than those reported by Cheng *et al.* (1997) and higher than those by Hu *et al.* (2001), because the specific surface area of metallic iron powder used in Cheng's work (325 mesh; 30–40 mesh, in this work) was higher, and the dosage of metallic iron used in Hu's work ( $12 \text{ mol-Fe mol-N}^{-1}$ ;  $164 \text{ mol-Fe mol-N}^{-1}$ , in this work) was lower.

There was a linear relation between the pH value and the logarithm of  $k_1$  value, as indicated in Figure 5. Therefore, the reduction rate of nitrate can be rewritten as:

$$-d[\text{NO}_3^-]/dt = 0.0611[\text{NO}_3^-][\text{H}^+]^{0.27} \quad (7)$$

The observed 0.27th order for  $[\text{H}^+]$  is most likely an artefact caused by the following two facts: (1) the decrease in the dissolution rate of iron and removal rate of precipitates of  $\text{Fe}(\text{OH})_2$  and/or  $\text{Fe}(\text{OH})_3$  with increasing pH values, which may slow down the reduction rate of nitrate; (2) inhibition of nitrate reduction by sulfate added continuously as  $\text{H}_2\text{SO}_4$  during the course of the reaction to maintain constant pH (Huang *et al.* 1998). These results indicated that the reduction rate of nitrate was related to

both the pH value and the nitrate concentration under pH 2.0–8.5 conditions.

## CONCLUSIONS

In this study the reduction reaction of nitrate by metallic iron under aerobic conditions was investigated in the pH range 2.0–8.5. The reduction products of nitrate were ammonia/ammonium remaining in the reduction solution and gaseous nitrogen emitted from the reduction solution, which led to a decrease in total nitrogen in the reduction solution. Most of the nitrate was reduced to gaseous nitrogen at the beginning of the reaction and to ammonia/ammonium at the end. pH was an important parameter affecting the reduction of nitrate by metallic iron. At a low pH, ammonia is the main final reduction product, while gaseous nitrogen is the dominant reduction product at a high pH. The yields of ammonia/ammonium were significantly decreased with increasing pH value of the reduction solution. In the reduction products, gaseous nitrogen was 40.1, 56.0, 68.0, 77.8 and 81.0% after 150 min reduction at pH 2.0, 3.5, 5.0, 7.0 and 8.5, respectively.

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