

## 단 신

### 금속철을 이용한 수용액내 질산염의 환원기작

安三暎\* · 吳眞花 · 孫京希  
순천대학교 환경교육과  
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## Mechanistic Aspects of Nitrate Reduction by Fe(0) in Water

Samyoung Ahn\*, Jinhwa Oh, and Kyounghee Sohn

Department of Environmental Education, Sunchon National University, Sunchon 540-742, Korea  
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Removal of nitrate ion from wastewater has been an important theme in environmental science. High nitrate concentration in drinking water can cause serious health risk such as methemoglobinemia in newborn infant and gastric cancer related to reduction of nitrate to nitrite.<sup>1</sup> Nitrate is an important nutrient for plant growth, causing abnormal algae blooming in lake and reservoir on high concentration of nitrate.

Physicochemical methods to remove nitrate such as ion exchanges and reverse osmosis have been limited in small facilities<sup>2</sup> due to the relatively expensive operation cost and disposal problem of high level of treated waste streams.<sup>3</sup> Biological denitrification has been applied in combination of activated sludge treatment. None of them, however, can be an exclusive method, diverse and adequate methods for nitrate removal are needed depending on different feature and condition of water. Chemical process to convert nitrate to ammonia can be alternative ways, especially for nitrate containing wastewater which is inadequate for biological treatment because of coexisting toxic materials such as heavy metals or high levels of hazardous chemicals. The process can be connected to ammonia removal facilities such as air stripping or liquid fertilizer for the best effectiveness.

In the last few years, new interest in the reactions of reducing metals has been created by researchers to treat contaminated water containing halogenated organic solvents<sup>4</sup> or Cr(VI).<sup>5</sup> Another approach to the use of iron metal in environmental remediation is abiotic nitrate

reduction.

Nitrate reduction in water by zerovalent metal, for example Fe(0) or Al(0) was mentioned in several studies, however reports were as a part of biological denitrification where the metals are electron donor to form H<sub>2</sub>, which is then taken by microorganism,<sup>6,7</sup> or as a part of catalytic reduction by hydrogen/palladium.<sup>8</sup> Here we report results of abiotic nitrate reduction using Fe(0) and the various factors to influence the reduction.

## MATERIALS AND METHODS

**Experimental design.** The reactions should be strictly anaerobic, hence all handling was carried out in nitrogen atmosphere and the aqueous solution was saturated with N<sub>2</sub> before use (5 h bubbling). NaNO<sub>3</sub> and NaNO<sub>2</sub> were purchased from Junsei Chemical, KH<sub>2</sub>PO<sub>4</sub> and K<sub>2</sub>HPO<sub>4</sub> from Aldrich and used without further purification, and iron metal powder from Samchun pure chemical and washed with dilute HCl and distilled water for further purification. Iron was stored under N<sub>2</sub> atmosphere.

In a typical experiment, a 1 L three neck round bottom flask was filled with 800 mL degassed and deionized water (Milli-Q), 73 mg/L, NO<sub>3</sub><sup>-</sup> and iron powder. HgCl<sub>2</sub>, HCl, NaOH, or phosphate buffer solution was used for initial pH adjustment.

Conditions for reaction 1 (pH 4.71): 5 g iron powder, 73 mg/L NO<sub>3</sub><sup>-</sup>, 7.37×10<sup>-4</sup> mol HgCl<sub>2</sub>.

Conditions for reaction 2 (pH 4.0): 5 g iron powder,

73 mg/L  $\text{NO}_3^-$ , pH was adjusted with HCl.

Conditions for reaction 3 (pH 7.0): 5 g iron powder, 73 mg/L  $\text{NO}_3^-$ , pH was adjusted with NaOH.

Conditions for reaction 4 (pH 4.71): 1 g iron powder, 73 mg/L  $\text{NO}_3^-$ ,  $7.37 \times 10^{-4}$  mol  $\text{HgCl}_2$ .

Conditions for reaction 5 (pH 4.93): 5 g iron powder, 73 mg/L  $\text{NO}_2^-$ ,  $7.37 \times 10^{-4}$  mol  $\text{HgCl}_2$ .

Conditions for reaction 6 (pH 5.45): 5 g iron powder, 73 mg/L  $\text{NO}_3^-$ , Buffer solution with pH 5.45 was prepared using  $\text{KH}_2\text{PO}_4$  and  $\text{K}_2\text{HPO}_4$ .

Initial pH of each reaction was measured before addition of iron. Samples for nitrate and nitrite analysis and pH measurement were taken with 25 mL disposable syringes and filtered through 0.2 RC-membrane filters (Sartorius) prior to storage and analysis. Samples for ammonia analysis were acidified with dilute HCl prior to storage.

**Analytical methods.** Nitrate and nitrite were analyzed with a Dionex DX-120 ion chromatograph. Ammonia was analyzed by either spectrophotometer (Standard Method 4500-NH<sub>3</sub> F) or titration (Standard Method 4500-NH<sub>3</sub> C).<sup>9</sup> pH was measured with Hanna 8520 pH meter.

## RESULTS AND DISCUSSION

### The effect of pH of solution on nitrate reduction

It is known that the reduction of nitrate to ammonia by iron under standard conditions and pH 7 proceeds via equation 1.<sup>10</sup>



As indicated in eq. 1, the reduction of nitrate accompanies increase in the pH of a solution, referring that this reaction will be affected by pH of the solution. To test the influence of pH on reduction, the pH of solution were tuned with  $\text{HgCl}_2$ , NaOH, or HCl.  $\text{HgCl}_2$  was initially added as an antibiotic to exclude the possible biological influence caused by microorganism during reaction, but later it turned out that it also effectively reduced the pH change of solution. The small change of pH of solution resulted in profound differences in reduction. Fig. 1 shows the change of nitrate concentration and pH vs reaction time of three different reactions. The reaction 1 (solid line with a black circle) was completed within 5 h while the pH of solution changed from pH 4.71 to pH

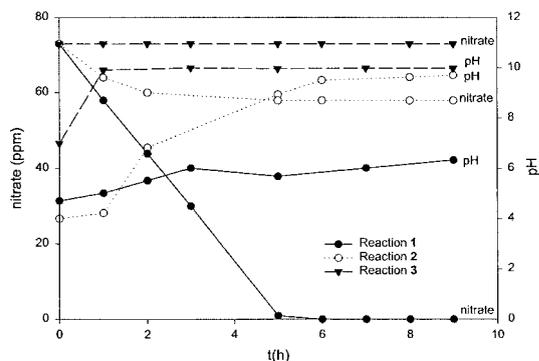


Fig. 1. Nitrate reduction and pH change (reaction 1, 2, and 3).

6.34. In contrast, by the reduction at pH 7 (reaction 3: long dashed line with a black triangle down) no reduction took place within 24 h (graph shows until 10 h). As this reduction favors the low acidity, reaction was carried out at pH 4 with a HCl solution (reaction 2: dotted line with a white circle). Only 27% (73 ppm to 53 ppm) of nitrate was reduced in 8 h, pH value of solution reached about 9, and after that no reduction occurred. It clearly shows that not only the initial pH of the solution but also the change of pH during reactions play a very important role for the reduction and that the pH of solutions needs to be maintained below pH 7 for complete reduction of nitrate. In case of HCl solution (reaction 2), the failure of complete reduction is attributed to the fast increased pH during the reaction, although the initial pH is even lower than that of the reaction 1.  $\text{HgCl}_2$  in reaction 1 suppresses the rise of pH effectively. The reason for the successful suppress of pH change by  $\text{HgCl}_2$  may be explained partly with the formation of insoluble  $\text{Hg}(\text{OH})_2$  ( $K_{sp} = 3.6 \times 10^{-26}$ ) reducing the  $[\text{OH}^-]$  concentration. However, further investigation on the role of  $\text{HgCl}_2$  and the reduction in other buffer solution are in process.

In all experiments the amount of nitrate consumed equaled the amount of ammonia produced, supporting the observation that there were no formation of gaseous products.

### Influence of amount of iron on the reduction

Fig. 2 shows that 1 g of iron also reduced the 95% of nitrate (from 73 ppm to 3.96 ppm) within 24 h and the pH of solution rises to 9 in the end. It is a very encouraging result, because the wastewater containing a high

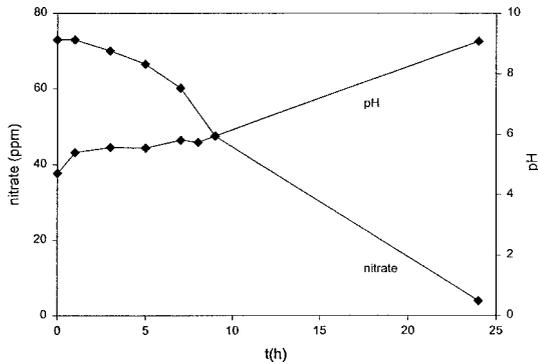


Fig. 2. Nitrate reduction and pH change (reaction 4).

concentration of nitrate can be preliminarily treated with a small amount of iron to reduce the concentration to the level adequate for the following treatments.

#### Reduction of nitrite with iron

On the nitrate reduction experiment, small concentration of nitrite was detected in some samples. In case of reaction 1, it appeared after 1.5 h (0.59 ppm), increased to 1.26 ppm after 3 h and disappeared in the end; in other reactions, the nitrite concentrations were between 0~0.5 ppm depending on the reaction conditions and reaction time. To clarify this observation, we carried out the nitrite reduction under the same conditions applied for the nitrate reduction (reaction 5). Nitrite was completely reduced to ammonia by Fe(0) within 7 h (Fig. 3), verifying that the nitrate reduction takes place via nitrite as an intermediate. Formation (even 1.26 ppm) of a little more amount of nitrite in reaction 1 compared to other reactions can be attributed to the most effective nitrate reduction on this conditions.

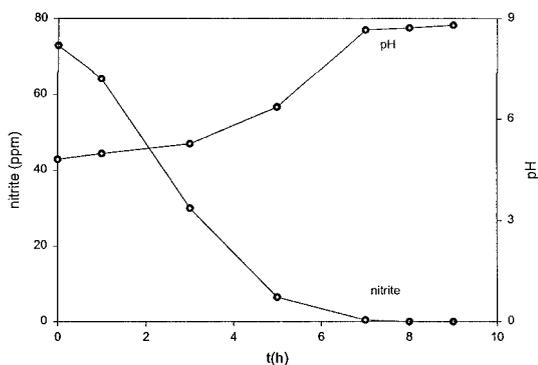


Fig. 3. Nitrite reduction and pH change (reaction 5).

#### Influence of phosphate on the nitrate reduction

As this reduction proceeds best under pH 7 and the pH value of natural water ranges 6~8 in general, we conducted the reaction in a phosphate buffer solution with an initial pH 5.45 (reaction 6). In addition, often the high levels of nitrate coincides with high levels of phosphate, so the behavior of phosphate ion during nitrate reduction by iron is worthy of investigating. In the phosphate-buffer solution, we found that iron did not reduce nitrate at all and phosphate concentration decreased in ion chromatography. It seems that phosphate forms an insoluble solid with Fe<sup>2+</sup> to form Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> which is deposited on the iron metal and deactivated the clean iron surface for the nitrate reduction.

#### CONCLUSION

Under investigated reaction conditions, the nitrate reduction by Fe(0) is favored in a pH range of 4 to 7. In these pH conditions, 73 ppm NO<sub>3</sub><sup>-</sup> can be completely reduced by 5 g Fe(0) in 5 h and 1 g Fe(0) in 24 h (95% reduction). Nitrite is an intermediate on the nitrate reduction to ammonia. Reduction of nitrite to ammonia proceeds at a little slower rate than the reduction of nitrate to nitrite, because small amount of nitrite (0~1.26 ppm depending on the reaction conditions and reaction time) was detected in our experiments and the reduction of nitrite to ammonia itself requires 7 h, longer than 5 h for the nitrate reduction. Phosphate forms insoluble salt with Fe(II), deposits on the surface of iron metal deactivating the oxidation of iron.

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