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Enhanced reduction of nitrate by zero-valent iron at elevated temperatures

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Abstract

Kinetics of nitrate reduction by zero-valent iron at elevated temperatures was studied through batch and column experiments. It was hypothesized that under increased solution temperatures, the zero-valent iron may accelerate the reduction of nitrate by overcoming the activation energy barrier to nitrate reduction. The results of the batch experiment showed the synergistic effects of elevated temperature (75 °C) and a buffered condition (pH 7.4 with 0.1 M HEPES) to enhance the rate of nitrate reduction by zero-valent iron from $0.072 \pm 0.006\,h^{-1}$ ($(0.35 \pm 0.03) \times 10^{-4}\,L\,m^{-2}\,h^{-1}$) at room temperature to $1.39 \pm 0.23\,h^{-1}$ ($(1.03 \pm 0.07) \times 10^{-3}\,L\,m^{-2}\,h^{-1}$). Complete nitrate removal was obtained in a Fe(0) column after 30 min under both buffered and unbuffered conditions at 75 °C. These results indicate that a temperature increase could overcome the energy barrier. We suggest that an iron reduction process at moderately elevated temperature (50–75 °C) may be a suitable method for removing nitrate from industrial discharges.

Keywords: Nitrate; Elemental iron; Temperature; Buffer; pH

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1. Introduction

Nitrate (NO_3^-) contamination in groundwater and surface water has become an increasingly serious problem in the United States [1,2]. It was reported that 11% of 1242 domestic drinking water wells surveyed between 1992 and 1999, contained NO_3^- levels exceeding 10 mg/L NO_3^--N [2]. Approximately 4.5 million people in the U.S. who rely on well water are exposed to nitrate exceeding 10 mg/L NO_3^--N [3]. The sources of NO_3^- include agricultural runoff, animal wastes, septic systems, atmospheric deposition from nitrogen oxide emission, and industrial processes [1,4–9]. Once nitrate is reduced to nitrite (NO_2^-), it can cause health effects including liver damage, cancers, and methemoglobinemia [1,5–8]. Nitrate can also increase eutrophication levels in rivers and lakes [10]. Because of its toxic effects, the U.S. Environmental Protection Agency has set a maximum contaminant level (MCL) of 10 mg/L NO_3^--N (0.71 mM) in drinking water [1,5,6]. Numerous treatment processes including ion exchange, reverse osmosis, biological denitrification, and chemical reduction processes have been developed for the treatment of water with exceedingly high concentrations of dissolved NO_3^- [1,5,6,8–10]. However, these conventional processes have the defects of being prohibitively expensive, difficult to maintain, and likely to generate concentrated wastes [5,6,9,10].

In recent years, zero-valent iron (Fe(0)) has been intensively studied for its ability to reduce NO_3^- in water and groundwater [4–20]. Fe(0) has received much attention for treating toxic oxidants because it is abundant, inexpensive and readily available, and its reduction process requires little maintenance [21]. Its corrosion products are relatively innocuous [22]. Zero-valent iron was initially proposed as a permeable reactive barrier material for groundwater remediation [23], and later its application has been broadened to include wastewater treatment processes [22,24]. Many researchers reported that it took several hours to several days to completely remove NO_3^- by Fe(0) in batch experiments under ambient conditions [4–6,11]. Su and Puls [4] reported that, when reduced by Fe(0), the half-life of NO_3^- ranged from 7.59 ± 0.23 h at pH 2.89 to 313 ± 30 h at pH 6.5. Alowitz and Scherer [11] reported half-lives ranging from 25.7 ± 0.7 h at pH 5.5 to 247.6 ± 7.6 h at pH 9.0. Acidic and

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highly buffered conditions were shown to be required to obtain a significant extent of NO_3^- reduction by Fe(0) [4–8,11,13]. Huang et al. [6] reported that under pH-controlled conditions, the reduction of NO_3^- by Fe(0) occurred more rapidly at pH 2 than 3 or 4 and that the reduction was negligible at $pH > 4$. They also showed NH_4^+ to be a reduction product in the iron batch experiments. Su and Puls [4] also showed the reduction rate of NO_3^- to be 10 times higher at pH 2.89 than at pH 8.00 and that a reduction product was NH_4^+ at both pHs. Once the solution pH was increased above 5, the reduction rate of NO_3^- was shown to be insignificant unless the iron–water system included Fe^{2+}, Cu^{2+} or Al^{3+} [14–17], or organic buffers, such as HEPES [18,19]. Zawaideh and Zhang [19] reported that at pH 6–8, NO_3^- removal by Fe(0) powder generally did not exceed 50% without buffer treatment. Huang and Zhang [16] showed Good's buffers to increase the rate of NO_3^- reduction by Fe(0) by releasing a significant amount of aqueous Fe^{2+}. They suggested that maghemite (γ-Fe_2O_3) at near neutral pH could inhibit electron transfer from the Fe(0) core whereas at low pH, Fe(0) would maintain a fresh surface. Effort was also made to increase the rate of NO_3^- reduction by using nanoscale Fe(0) [8,9]. Yang and Lee [8] showed the reduction rate of nitrate to be significantly increased to $1.89\ \mathrm{min}^{-1}$ in the nanoscale iron–water system. Choe et al. [9] also showed that nitrate was rapidly reduced at a rate of $0.147 \pm 0.004\ \mathrm{min}^{-1}$ by nanoscale iron to a final product of N_2.

According to previous results [4–7,10–20], the kinetics of NO_3^- reduction by Fe(0) was too slow for practical application. Obviously, this slow reduction is due to a kinetic hindrance to NO_3^- reduction by Fe(0) under the ambient condition because the reduction of NO_3^- to NH_4^+ by Fe(0) is thermodynamically favorable (standard reduction potential $E^0 = 1.32$ V). An attempt was made to enhance the reduction rate of nitrate in the iron–water system by increasing temperature of the solution and the iron, which can supply the excessive energy necessary to overcome the activation energy barrier [25]. Currently, our group showed that 98% of aqueous perchlorate (ClO_4^-), one of the most recalcitrant contaminants, to be removed by Fe(0) in 1 h at 200 °C in a microwave digester [26]. The enhancement in the extent and rate of perchlorate removal by Fe(0) was shown to be mostly due to the heat energy available at such a high temperature. Similarly, it may be possible to enhance the reduction of NO_3^- by Fe(0) by increasing the temperature of the iron–water system. However, to date, little research has been conducted to evaluate the feasibility of using elevated temperature to enhance NO_3^- reduction by Fe(0).

This study was conducted to evaluate the enhancement effect of increased temperature on the extent and rate of NO_3^- reduction by Fe(0). We hypothesized that increasing the temperature of the solution and Fe(0) may help the reaction overcome the activation barrier and that NO_3^- will be more rapidly reduced by Fe(0). Both batch and column experiments with Fe(0) were conducted under buffered and unbuffered conditions at elevated temperatures to determine the effect of temperature and buffered conditions on NO_3^- reduction by Fe(0). The reduction rates were estimated from batch and column experiments through kinetic modeling.

2. Materials and methods

2.1. Chemicals

This study employed Peerless (Detroit, MI) cast iron sieved with a 10–20 mesh as the zero-valent iron. The specific surface area of the Peerless iron was $1.67\ \mathrm{m^2/g}$, measured using a Brunauer–Emmett–Teller (BET) gas adsorption isotherm with N_2 gas. Sodium nitrate ($NaNO_3$, 99%) and HEPES [*N*-(2-hydroxyethyl)piperazine-*N*′-(ethanesulfonic acid)] were obtained from Sigma (St. Louis, MO).

2.2. Batch reduction experiments

Batch reduction experiments were performed in a shaker water bath (Lab-Line Instruments, Melrose Park, IL) whose temperatures were controlled at 20 and 75 °C, respectively. All experimental reactors were prepared in an anaerobic glove box filled with N_2 (Bell-Art Products, Pequannock, NJ). Duplicate Pyrex® vials (12 mL) containing 8 mL of aqueous solution and 1 g of iron were set up for each experiment. The initial concentration of the NO_3^- solution was 0.5 mM (initial pH 6.7). For the buffered solution, 0.1 M HEPES buffer was used to maintain pH at 7.4 throughout the experiments. The solutions were deoxygenated by purging with N_2 for 30 min. After iron was added, the vials were shaken in a horizontal position in the shaker bath at 100 rpm. For the 75 °C experiment, the solution was preheated for 20 min in the shaker bath to reach the desired temperature prior to shaking. Chemical analysis showed that there was no reduction for this non-shaking preheating period. At selected time intervals, duplicate vials were sacrificed and the supernatant was immediately filtered through a 0.22 μm membrane filter (Millipore, MA) for NO_3^- and NH_4^+ determination.

2.3. Column experiments

Column experiments were conducted using a glass column (2.5 cm i.d. × 30 cm *L*; Ace Glass, Vineland, NJ) with Teflon end fittings. The column was packed with Peerless iron and 5 cm at each end of the column was packed with Ottawa sand. The iron column had a porosity of 0.72. To ensure anaerobic conditions, nitrate feed solutions were purged with N_2 for at least 20 min prior to introduction into the column. Nitrate solutions, prepared in either deionized water (initial pH 6.7) or 0.1 M HEPES buffer (pH 7.4) were pumped into the iron column in a horizontal direction at flow rates of 2.5, 4.9, 14.8, and 24.5 mL/min, corresponding to retention times of 30, 15, 5, and 3 min, respectively. The water batch was used to maintain the temperature at 20, 50, and 75 °C, respectively. The solutions were preheated using another water bath (Precision Scientific, Winchester, VA) prior to their introduction into the column to maintain a constant temperature throughout the experiments. After the column retention periods passed, column effluents were sampled and filtered through a 0.22 μm membrane filter (Millipore, MA) for analysis of NO_3^- and NH_4^+.

2.4. Analytical methods

Nitrate was analyzed by Dionex ICS-1000 ion chromatography equipped with a Dionex Ionpac AS 16 column (Dionex, Sunnyvale, CA). Ten millimolars of NaOH solution was used as the eluent and the injection volume was 25 μL. Ammonium ion was analyzed with the Hach spectrophotometer using the salicylate method (Hach, Loveland, CO).

3. Results and discussion

3.1. Results of batch experiments

As shown by previous researchers [4–6,11], nitrate reduction by Fe(0) under an unbuffered condition was slow at room temperature. Only 24.1% of NO_3^- was reduced from solution in the Fe(0) system after 4 h as pH was changed from 6.7 to 7.2–7.7 (Fig. 1a). The pseudo-first-order rate constant and surface area-normalized rate constant were calculated to be $0.072 \pm 0.006\,h^{-1}$ ($R^2 = 0.983$), and $(0.035 \pm 0.028) \times 10^{-3}\,L\,m^{-2}\,h^{-1}$, respectively, by least-square fitting using Sigma Plot (Systat Software, Point Richmond, CA). On the other hand, when the solution was buffered with 0.1 M HEPES, the reduction of NO_3^- by Fe(0) was significantly enhanced, showing about 60% of removal in 4 h (Fig. 1b). The pseudo-first-order rate constant and surface area-normalized rate constant were calculated to be $0.214 \pm 0.015\,h^{-1}$ ($R^2 = 0.990$), and $(1.03 \pm 0.07) \times 10^{-3}\,L\,m^{-2}\,h^{-1}$, respectively, which is consistent with previous results ($(1.0 \pm 0.1) \times 10^{-3}\,L\,m^{-2}\,h^{-1}$) reported by Su and Puls [4]. The rate of NO_3^- reduction by Fe(0) was increased markedly under increasing temperatures. After 4 h, nitrate was reduced by 81% and 95.7% under the unbuffered and buffered conditions, respectively (Fig. 1). Pseudo-first-order rate constants under the unbuffered and buffered conditions at 75 °C were 0.36 ± 0.03 and $1.39 \pm 0.23\,h^{-1}$, respectively, which exceed by 5 and 19 times the rate constant achieved at 20 °C under the unbuffered condition ($0.072 \pm 0.006\,h^{-1}$). These results showed buffering capacity and temperature to be important factors contributing to the rate and extent of NO_3^- reduction by Fe(0) and that the synergistic effect of temperature and buffer could effectively enhance NO_3^- removal in the iron–water system.

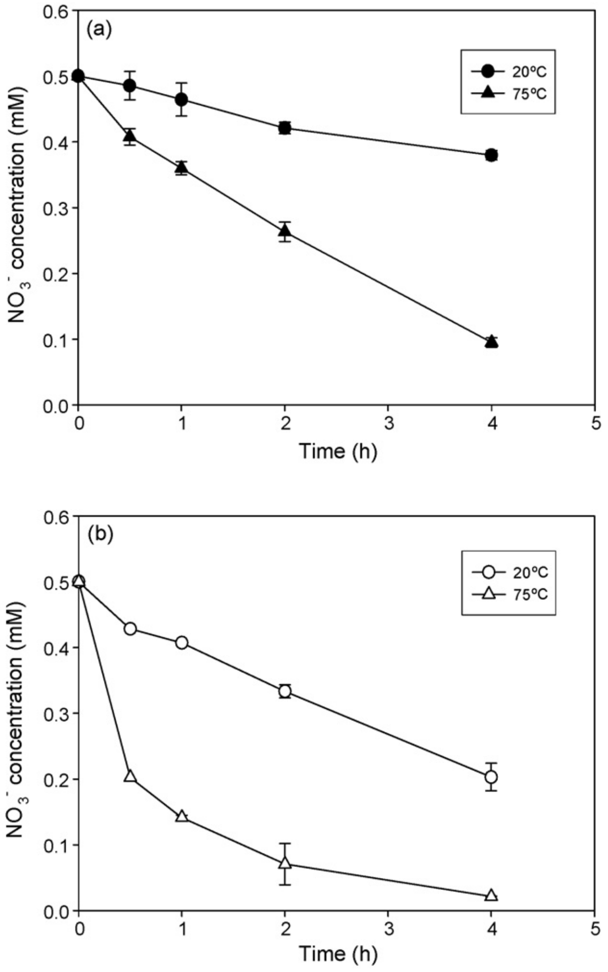

Fig. 1. Nitrate reduction by Fe(0) in batch reactors at 20 and 75 °C (a) under the unbuffered condition (initial pH 6.7) and (b) at pH 7.4 with 0.1 M HEPES. The error bars in the figure indicate the standard deviations which were calculated by replicate data.

3.2. Results of column experiments

Fig. 2 shows the effects of temperature and buffering capacity on NO_3^- reduction in the Fe(0) column. Similar to results from the batch experiments, the extent of NO_3^- reduction by Fe(0) at 20 °C was slow and incomplete in unbuffered solution (Fig. 2a). Only 40.3% of NO_3^- was removed in unbuffered solution after 30 min of retention time at 20 °C. In contrast, the extent of NO_3^- reduction was markedly increased to 91.4% after 30 min at pH 7.4 with 0.1 M HEPES under identical conditions (Fig. 2b), which may be due to constant pH through the experiments resulting from buffering capacity of the solution. The extent and rate of NO_3^- reduction was remarkably enhanced in the iron column with increasing temperature. The extent of NO_3^- reduction by Fe(0) under the unbuffered condition was enhanced to 88% after 30 min of retention time at 50 °C (Fig. 2a). At 75 °C, complete removal of NO_3^- was achieved with 30 min of retention time. Even with only 3 min of retention time, 61% of NO_3^- was removed in the iron column at 75 °C (Fig. 2a). More significant enhancement of NO_3^- reduction was obtained at pH 7.4 with 0.1 M HEPES by elevating temperatures. Nitrate was completely removed after 30 min in the iron column at 50 °C (Fig. 2b). At 75 °C, about 88% of NO_3^- was removed in the iron column after only 5 min of retention time.

Similar to results from the batch experiments, both buffering capacity of solution and temperature appear to affect the rate of NO_3^- reduction by Fe(0) in the iron column. However, the importance of buffering capacity was diminished as the retention time at the elevated temperatures exceeded 15 min. At the short retention time (3 and 5 min), the extent of NO_3^- removal at pH 7.4 with 0.1 M HEPES was 42% and 23% larger than that under the unbuffered condition at 50 and 75 °C, respectively (Fig. 2). At 15 min of retention time, compared to unbuffered conditions, only 8% of additional removal of NO_3^- was achieved at 75 °C

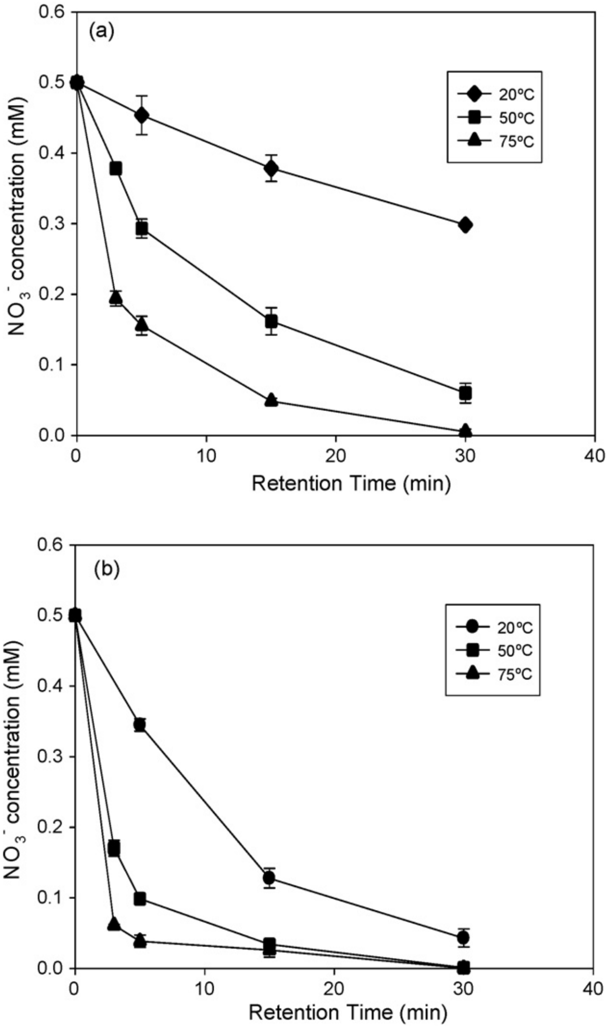

Fig. 2. Nitrate reduction in a Fe(0) column at 20, 50, and 75 °C (a) under the unbuffered condition (initial pH 6.7) and (b) at pH 7.4 with 0.1 M HEPES. The error bars in the figure indicate the standard deviations which were calculated by replicate data.

under the buffered condition. Finally, after 30 min, regardless of buffering capacity, NO_3^- was completely removed in the iron column. These results indicate that the effect of buffering capacity on the reduction of NO_3^- was minimal at retention times greater than 15 min at 75 °C in the iron column, suggesting that NO_3^- may be effectively removed in the Fe(0) column at moderately elevated temperatures without control of pH by buffers.

In order to determine reaction kinetics at elevated temperatures in the iron column, the pseudo-first-order rate constant (k) in the iron column system was estimated using the one-dimensional advection–dispersion-reaction equation under the assumption of a steady-state condition [29]:

$$k = \frac{(v - (2D/x)\ln(C/C_0))^2 - v^2}{4D} \tag{1}$$

where x is effective column length (cm), v is the average linear velocity (cm/s), D is the hydrodynamic dispersion coefficient (cm^2/s), and $D = av + D^*$ (a = dispersivity (cm) and D^* = diffusion coefficient (cm^2/s)). Dispersivity was calculated to be 0.117 cm based on a chloride tracer test using the methods of Brigham [30]. Using an alternate method, by using surface area concentration in the iron column (3781.7 m^2/L), the pseudo-first-order rate constants were also estimated by surface area-normalized rate constants obtained from the batch experiments. At 20 °C, considering standard errors, the calculated rate constants were close to those estimated from batch experiments (Table 1), suggesting that both methods may be useful to predict the reduction kinetics in the iron–water system unless the adsorption of reactant is significant. However, at 75 °C, the predicted reduction rates were somewhat different. The rate calculated from kinetic modeling exceeded the rate estimated from batch experiments by 20% and 117% for buffered and unbuffered conditions, respectively (Table 1). This underestimated rate constant through surface area normalization might be explained by the effect of mass transfer at high temperature. In order to determine the importance of mass transfer in the iron column, we calculated the external mass transfer rate constant estimated using the method described by Arnold et al. [31]. Using an assumed average iron particle diameter of 1 mm, a particle density of 6000 kg/m^3, and an estimated diffusion coefficient of 1.9×10^{-9} m^2/s for NO_3^- in water [32], the external mass transfer rate constant was calculated to be 3.05 min^{-1}, two orders of magnitude greater than the pseudo-first-order degradation rate constant of nitrate in the iron column at 20 °C (Table 1). This suggests that external mass transfer was not the rate-limiting step in the iron column system and that a surface process, such as adsorption or chemical reaction, probably controlled the overall rate of nitrate reduction. In contrast, at 75 °C, the mass transfer rate is about 6–27 times greater than the reduction rates in the iron column, suggesting that mass transfer might affect the overall reaction rate in the iron column. Obviously, increases in temperature will enhance the mass transfer rate, which will then enhance the reduction rate in the iron column.

Table 1
Estimated pseudo-first-order rate constant (k) for NO_3^- reduction in the Fe(0) column at 20 and 75 °C

Temperature (°C)	pH	k (min^{-1})	
		Calculated by Eq. (1)	Estimated from batch experiments
20	Buffered	0.083 ± 0.008	0.065 ± 0.005
	Unbuffered	0.018 ± 0.001	0.022 ± 0.002
75	Buffered	0.505 ± 0.214	0.418 ± 0.070
	Unbuffered	0.237 ± 0.080	0.109 ± 0.010

Activation energy (E_a) for the NO_3^- reduction by Fe(0) was calculated by applying the Arrhenius equation [25]. The calculated E_a value was 28.2 ± 0.3 kJ/mol ($R^2 = 0.986$) at pH 7.4 with 0.1 M HEPES, and 39.5 ± 0.1 kJ/mol ($R^2 = 0.999$) under the unbuffered condition, respectively. These values were smaller than the activation energy for the NO_3^- reduction by FeO (47.18 ± 6.43 kJ/mol) [27] and by sulfate green rust (83.9 ± 7.6 kJ/mol) [28], indicating that Fe(0) may be more effective in reducing NO_3^- in wastewater at elevated temperatures than FeO and green rust.

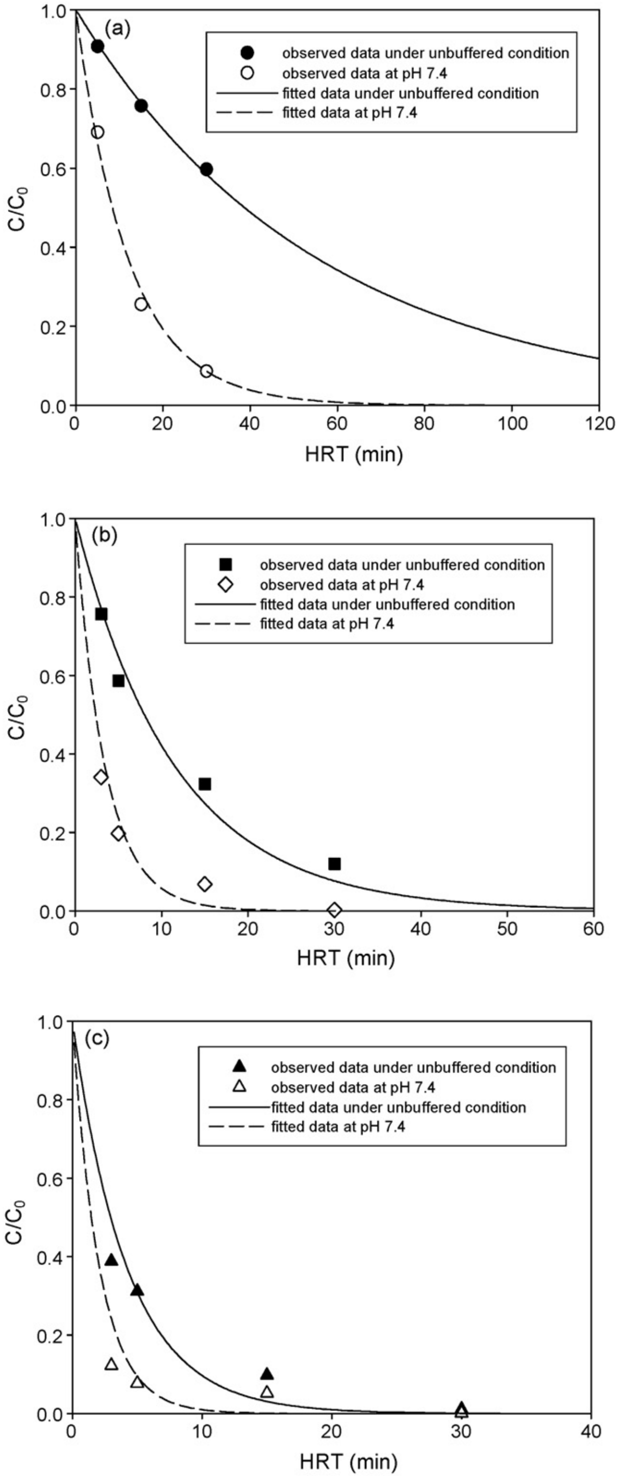

Fig. 3. Observed and predicted NO_3^- concentrations over hydraulic retention time during reduction in a Fe(0) column at (a) 20 °C, (b) 50 °C, and (c) 75 °C.

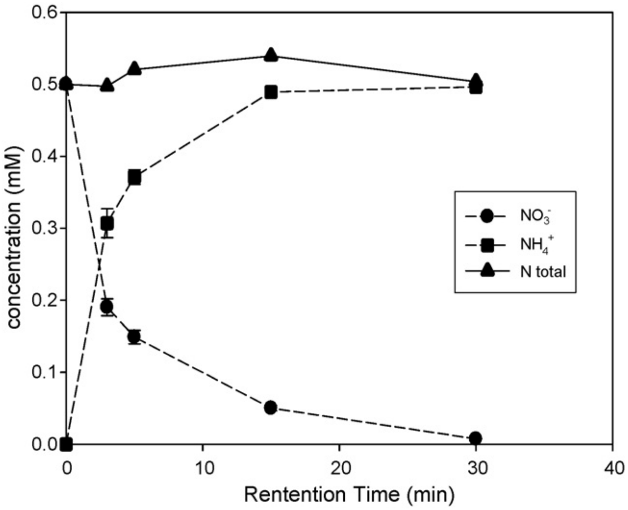

Fig. 4. Concentrations of NO_3^- and NH_4^+ over hydraulic retention time during reduction in a Fe(0) column at 75 °C under the unbuffered condition (initial pH 6.7). The error bars in the figure indicate the standard deviations which were calculated by replicate data.

By using the calculated k values, concentration profiles of NO_3^- over hydraulic residence time (HRT $= x/v$) were estimated at various temperatures (Fig. 3). The fitted curves were well-matched with observed data from the column experiments. According to the fitted curves, more than 99% removal of NO_3^- could be obtained after 4.5 h of retention time in the iron column under the unbuffered condition at 20 °C, whereas the same extent of reduction required only 56 min of retention time at pH 7.4 (Fig. 3). The results predicted that under the unbuffered condition, 54 and 20 min of retention time would be required to remove more than 99% of NO_3^- in the iron column at 50 and 75 °C, respectively. At pH 7.4 with 0.1 M HEPES, retention times of 16 and 9 min were shown to be necessary to obtain NO_3^- removal of 99% at 50 and 75 °C, respectively (Fig. 3). Attempts were made to establish nitrogen balance by measuring NH_4^+ and NO_3^- concentrations in the effluent at 75 °C under the unbuffered condition (Fig. 4). Nitrate was transformed to NH_4^+ by Fe(0) while showing complete mass recovery, which is consistent with previously reported results [4–7,11,12].

In summary, our results showed the synergistic effect of moderately elevated temperature (75 °C) and the buffered condition to significantly enhance the extent and rate of NO_3^- reduction by Fe(0). Complete removal of NO_3^- was obtained within 30 min retention time under both buffered and unbuffered conditions at 75 °C in the Fe(0)-packed column. We suggest that the iron reduction process at moderately elevated temperature may be a promising method for NO_3^- treatment in industrial wastewaters. Since increased reaction rates at moderately elevated temperatures were achieved, applying this technology to treat other low-iron reactive compounds may be possible. On the other hand, the life of zero-valent iron granules may be shortened due to enhanced iron corrosion at elevated temperatures. However, the longevity of iron granules can be compromised to obtain high enough NO_3^- reduction rates that are applicable for wastewater treatment processes. Moreover, unlike permeable reactive barriers, replacing iron granules more frequently may not be difficult, or impractical in wastewater applications.

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