嘉南藥理科技大學專題研究計畫成果報告

以元素鐵配合二氧化碳曝氣處理地下水中硝酸根離子

計畫類別：☑個別型計畫　　□整合型計畫
計畫編號：CNEV-92-11
執行期間：92年1月1日至92年12月31日

計畫主持人：廖志祥
共同主持人：
計畫參與人員：許瓊元、李明堂

執行單位：嘉南藥理科技大學環工系

中華民國93年02月28日

以元素鐵配合二氧化碳曝氣處理地下水中硝酸根離子

REMOVAL OF NITRATE ION CONTAMINATED GROUND WATER BY ELEMENTAL IRON POWDER COUPLED WITH THE BUBBLING OF CARBON DIOXIDE

Chiung-Yuan Hsu[*], Chih-Hsiang Liao[**], and Ming-Chun Lu**

*Department of Industrial Safely and Hygiene, Chia Nan University of Pharmacy and Science, Tainan, Taiwan
** Department of Environmental Engineering and Science, Chia Nan University of Pharmacy and Science, Tainan, Taiwan

ABSTRACT

This paper presents an innovative technology for the removal of nitrate from groundwater by combination of Fe^0 and CO_2 bubbling. The bubbling of CO_2 created effectively an acidic environment favorable to Fe^0 corrosion, which results in nitrate reduction. In 10 min, the solution pH dropped to 3.2 with CO_2 inflow rate of 500 mL/min. In the presence of Fe^0 (2 g/L), the CO_2 bubbling (500 mL/min) induced conversion of nitrate-N (~7 mg/L) by 85% in 40 min. In addition, the end product in the reaction mixture was ammonium, which accounts for 90-104% of nitrate conversion with the presence of various iron dosages (0.5-2.0 g/L). Though the formation of ammonium is a drawback, the ammonium was eliminated from aqueous phase by a follow-up treatment of settling (30 min) and air-aeration (50 min). What was achieved in this study demonstrates that the Fe^0/CO_2 method can be applied with success for the total removal of nitrate-contaminated waters.

KEYWORDS

Ammonium, carbon dioxide, nitrate, reduction, zero-valent iron.

INTRODUCTION

The health concern of nitrate contaminated groundwater motivated the conducting of this study. As reported, high levels of nitrate, once reduced into nitrite, can cause methemoglobinemia in newborn infants (Walton, 1951). Furthermore, the nitrite may also result in the formation of N-nitrosamines, which is a possible carcinogen in stomach (Mirvish, 1985). Hence, a maximum nitrate concentration of 44 mg/L (10 mg N/L) was applied as a safe drinking water quality standard in most of developed countries.

Among the treatment methods available for nitrate removal, a chemical reduction process of using zero-valent iron powder has received widespread attention from different researchers (Cheng et al., 1997; Huang et al., 1998; Choe et al., 2000). The reductive removal of nitrate can be seen as a result of metallic iron corrosion, especially significant in acidic solution (Piron, 1991). The mechanism of electron releasing from iron metal is presented in Reactions (1)-(5), according to Kelly (1965). Reactions (3) and (4) indicate that the electrons were released from iron metal in two consecutive stages, with Reaction (4) as a rate determining step. In addition, the ejection of Fe^{2+} from the iron metal surface is strongly dependent on pH (Reaction (5)). In other words, lowering the pH accelerates the forward reaction in Reaction (5), and this in turn enhances the rate of electron releasing, as shown in Reaction (4). Another important role the hydrogen ions play is its function in the breakdown of protective films formed on the metal surface through anodic passivation process

(Cohen, 1979).

$$Fe^0 + H_2O \leftrightarrow Fe(H_2O)_{ads} \tag{1}$$
$$Fe(H_2O)_{ads} \leftrightarrow Fe(OH^-)_{ads} + H^+ \tag{2}$$
$$Fe(OH^-)_{ads} \leftrightarrow (FeOH)_{ads} + e^- \tag{3}$$
$$(FeOH)_{ads} \rightarrow (FeOH)^+ + e^- \quad \text{(rate-determining)} \tag{4}$$
$$(FeOH)^+ + H^+ \rightarrow Fe^{2+} + H_2O \tag{5}$$

With above scenario in mind, it is the focus of this study to *in situ* generate sufficient amount of hydrogen ion in the reaction system. Oftentimes, the application of acids such as H_2SO_4 (Huang et al., 1998), HCl and acetic acid (Cheng et al., 1997) might be considered to speed up the rate of nitrate removal. However, in doing so, this will risk the drinking quality of treated water, due to the presence of these alien species of sulfate, chloride and acetate. To avoid such disadvantage, the idea of bubbling CO_2 into water sample was attempted as a major source of supplying hydrogen ions. So far, there was no paper describing the use of CO_2 as a measure to create an acidic environment of solution for nitrate removal purpose. The use of CO_2, which is a clear, colorless, odorless gas species, imposes no adverse effect on treated water quality. In addition, as the hydrogen ions are consumed in the reaction system, the resulted bicarbonate alkalinity can help remove background hardness and ferrous species through the formation of precipitates such as $CaCO_3$ and $FeCO_3$. In water purification processes, the CO_2 is commonly used for stabilizing lime-softened water. In terms of CO_2 supply, the gas can be produced by burning a fuel, such as coal, coke, oil or gas. The ratio of fuel to air is carefully regulated in a CO_2 generator to provide complete combustion (Hammer and Hammer, 2001).

As described above, the goal of this study was to investigate the capability of removing nitrate from contaminated waters by using the Fe^0/CO_2 method. In addition, evaluation was also performed to see whether the presented method is a clean technology for drinking water treatment purpose. Parameters of CO_2 inflow, mixing and iron dosage were explored for their effects on the performance of reaction system.

MATERIALS AND METHODS

Zero-valent iron (Fe^o) of 10 µm size purchased from Merck was used without any pretreatment. A nitrate concentration of 30 mg/L (6.8 mg N/L) was used in this study. The nitrate solution was prepared in the laboratory by dissolving predetermined amount of $NaNO_3$ (Merck) in the deionized water. The standard ammonium (1000 mg/L) used for instrumental analysis was purchased from Merck. CO_2 gas with purity greater than 99.5% was purchased from a local supplier.

In this study, the experiments were conducted in a cylindrical reactor of 5 L, as shown in Figure 1. The liquid volume prepared was 4 L. The solutions to be treated were mixed vigorously by a motor-

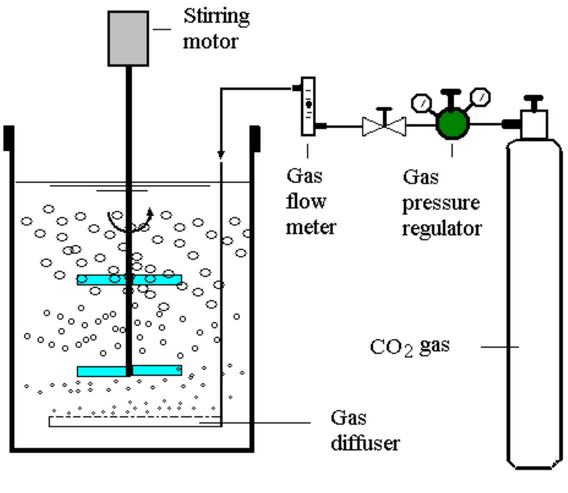

Figure 1. Experimental setup of CO_2 bubbling reactor

driven stirrer (10, 15, 20×10^2 rpm). Depending on desired conditions, the CO_2 inflow rate was controlled within the range of 100-500 mL/min through a gas flow meter. The CO_2 bubbles were created through a simple diffuser of silicate material. The dosage of Fe^0 used in the reaction system was in the range of 0.5-2 g/L. As the reaction was carried on, water samples were taken from the reactor at different time intervals for subsequent analyses of water quality parameters.

After pre-filtration of treated sample, the solution was used for the analyses of nitrate, nitrite, ammonium, and ferrous ion. The residual nitrate and nitrite were analyzed directly by using Ion Chromatography (Dionex). The product of ammonium in reaction mixture was measured by a spectrophotometer (Shimadzu UV-1201) with absorption wavelength set at 550 nm after addition of color-forming reagent (potassium tetra iodomercurate (II) sodium hydroxide, Merck) into pre-filtered water samples. Since ferrous ion is able to form a colored complex with 1,10-phenanthroline, its concentration was determined through the measurement of light absorption at 510 nm, which is equivalent to a certain ferrous quantity (Standard Method, 1995). In addition, the pH was monitored by using a pH meter (Suntex, TS-2) and the oxidation and reduction potential (ORP) by ORP meter (Suntex, TS-2).

RESULTS AND DISCUSSION

Fundamental of CO_2 bubbling

As mentioned earlier, hydrogen ion accelerates the rate of iron corrosion, leading to a higher efficiency of reduction reaction. In this study, the source of hydrogen ion in the reaction system was provided not from the addition of strong acids such as H_2SO_4 and HCl but from the bubbling of CO_2 into aqueous solution. Depending on pH, the solution might be present with the species of H^+, HCO_3^- and $CO_3^=$ as a result of CO_2 bubbling. Therefore, as the consumption rate of hydrogen ions is promoted, solutions will absorb CO_2 continuously, if the gaseous species CO_2 is supplied sufficiently.

Figure 2 presents the effect of CO_2 bubbling on the two profiles of pH as well as ORP along with bubbling time period of 40 min. After only 10 min of CO_2 bubbling (500 mL/min), the solution pH was seen to drop significantly from 6.6 to 3.2, while the ORP increased from +380 to +470 mV. The ORP was highly correlated with the pH, the decrease of which results in the increase of ORP value. As for the rest of reaction period, there's a slight increase in pH, which corresponds to a slight decrease in ORP. Such a result demonstrates that the bubbling of CO_2 is an efficient way of introducing an acidic environment of reaction system.

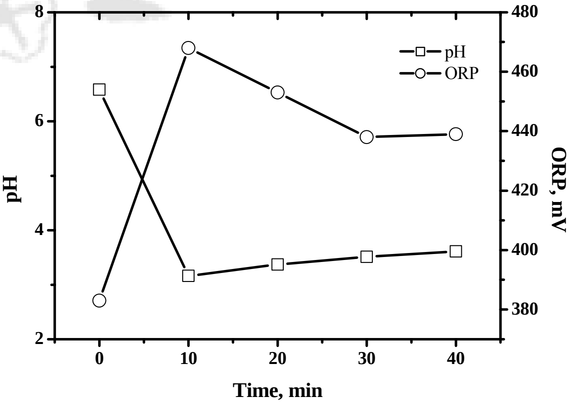

Figure 2. Effect of CO_2 on solution pH and ORP. CO_2 inflow = 500 mL/min; stirring reading = 10; temperature = 31.3°C.

To reveal the effects of stirring power and CO_2 inflow on pH, experiments of three different stirring readings and three different CO_2 inflow rates were performed. The stirring might impose dual effects on the reaction system. One is the holdup of CO_2 bubbles to promote its transfer into liquid phase, while another is the stripping of dissolved CO_2 oversaturated in liquid phase. Consequently, Figure 3 shows insignificant difference of pH under the three different stirring readings of 10, 15, and 20, given the CO_2 inflow of 500 mL/min. On the other hand, as the stirring reading was controlled at 10, the resulted pH profiles indicate that, though the difference of pH is only slight at time of 10 min, the higher the CO_2 inflow, the lower the solution pH profile (Figure 4). Note that all the final solution pH's in Figures 2-4 were seen to be slightly higher than that at time of 10 min. Such a phenomenon might be due to the stripping of CO_2 in excess, as described above.

Conversion of nitrate reduction

As illustrated from the fundamental of CO_2 bubbling, the action of CO_2 bubbling in this study is capable of bringing down the pH from a neutral one to an acidic range of 3-4. Such a result assures one thing that the target contaminant of nitrate should be removed effectively, as evidenced in Figure 5. Without CO_2 bubbling, though the iron dosage was as high as 2 g/L, the removal of nitrate was negligible. However, with the presence of CO_2 bubbling (500 mL/min), the residual nitrate was seen to increase remarkably with decreasing iron dosages (2-0.5 mg/L). For example, at time of 40 min, the residual nitrate-N was 1.1 mg/L with the use of 2 g iron/L. The residues were 1.9 and 4.3 mg NO_3^--N/L, respectively, given iron dosages of 1.0 and 0.5 g/L. In terms of removal efficiency, the efficiencies were 85%, 72%, and 38%, respectively, for the descending iron dosages.

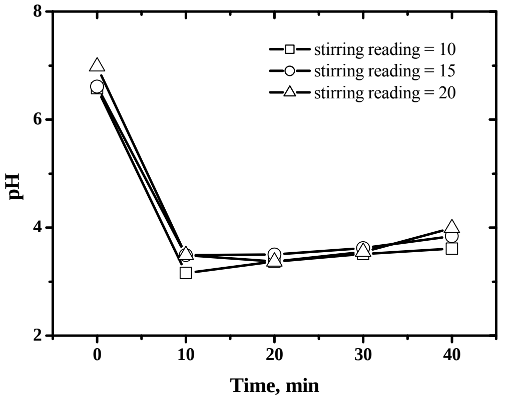

Figure 3. Effect of stirring power on solution pH. CO_2 inflow = 500 mL/min; temperature = 29.5-31.3°C.

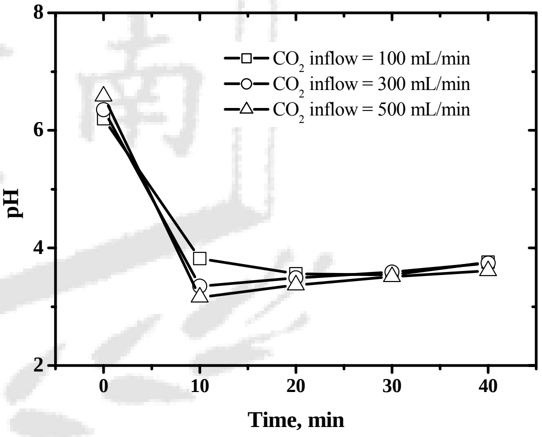

Figure 4. Effect of CO_2 inflow on solution pH. Stirring reading = 10; temperature = 31.7-32.2°C

As shown in Figure 5, the end reduction product was accounted mostly by the species of ammonium. Note that the species of nitrite was not detected in this study. At time of 40 min, the amount of nitrate-N disappearance corresponded to the amount of ammonium-N appearance by 98% when iron dosage was 2 g/L, while the recovery percentages were 104% and 90%, respectively, for the iron dosages of 1 and 0.5 g/L. Thus it is concluded that the nitrate was converted nearly completely into ammonium in the studied reaction system, as is consistent with the literature reports (Cheng et al., 1997; Huang et al., 1998).

Figure 6 further illustrates the variation of solution ORP and pH with identical conditions listed in Figure 5. Without CO_2 bubbling, the pH hangs around a neutral value even with the presence of 2 g iron/L, and the solution ORP ranges from +400 to +330 mV. Since the solution pH is nearly neutral, it is anticipated that the iron corrosion becomes a slow reaction, which leads to insignificant removal of nitrate, as presented in Figure 5. On the other hand, with the CO_2 bubbling, the pH was maintained within the acidic range for different iron dosages, and this assures efficient conversion of nitrate. Note that the increase of pH within the final reaction period might result from the consumption of hydrogen ions as nitrate became reduced due to iron corrosion, as depicted in Table 1. Due to more hydrogen ions being consumed, the iron dosage of 2 g/L led to a pH profile much higher than the two ones with iron dosages of 1 and 0.5 g/L. Further highlighting one important thing, when 2 g iron/L was used, the highest efficiency of nitrate reduction accounts for the lowest ORP value, which hangs around –500 mV during the reaction period of 20-40 min. Based on what was described above, it is summarized that a more reduced environment of solution is favorable to initiate nitrate reduction to occur.

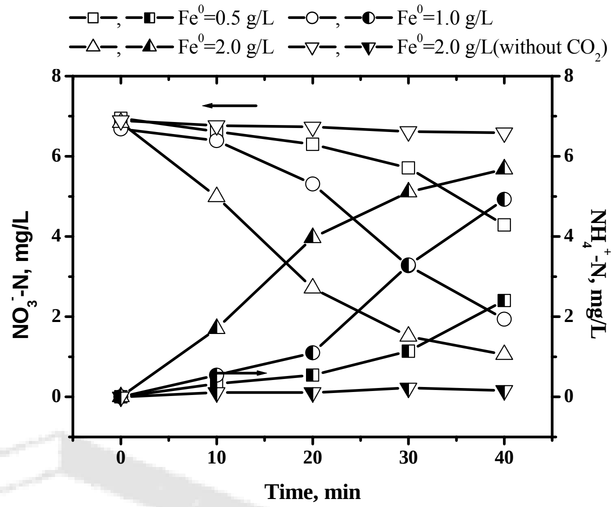

Figure 5. Conversion of nitrate at various Fe^0 dosages. CO_2 inflow = 500 mL/min; stirring reading = 10; initial nitrate = 6.68-6.95 mg/L; temperature = 21.5-23.7°C

Post treatment of ammonium

The advantage of the presented method is the provision of hydrogen ions through CO_2 bubbling, which is a common practice for stabilizing water quality in water purification process, namely carbonation or recarbonation. This method creates no obnoxious species, which might risk the treated water quality. However, there's still a drawback of this method, which is the formation of undesirable end product ammonium in the reaction system. This is to say that the presented method needs to be followed by a post treatment of ammonium to assure a safe drinking water quality. According to the following reaction (Benjamin, 2002), ammonium can be easily stripped out of aqueous phase under alkaline solution, especially at a pH level higher than 9.3.

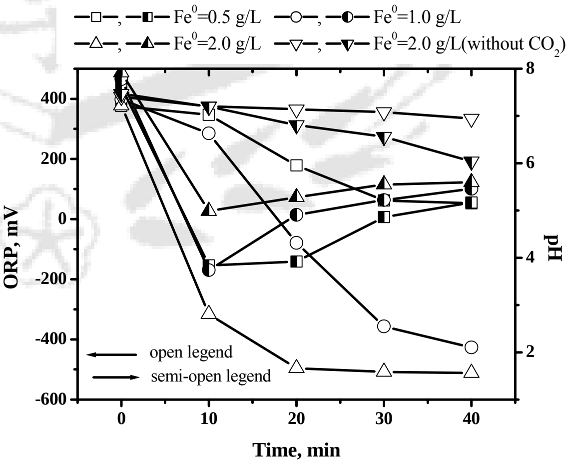

Figure 6. Profiles of solution ORP and pH at various Fe^0 dosages. CO_2 inflow = 500 mL/min; stirring reading = 10; initial nitrate = 6.68-6.95 mg/L; temperature = 21.5-23.7°C

$$NH_4^+ \leftrightarrow NH_3 + H^+ \qquad pK_a = 9.3 \tag{6}$$

With such concept in mind, a follow-up experiment was designed and conducted to trace the residual ammonium previously formed in the reaction mixture by the Fe^0/CO_2 method. The experimental procedure includes (i) phase I (0-40 min): Fe^0/CO_2 reduction of nitrate; (ii) phase II (40-70 min): settling of iron powder and iron corrosion products; and (iii) phase III (70-120 min):

air aeration of supernatant taken from phase II. The action of phase III was conducted purposely to strip the NH_4^+ and to precipitate iron species of dissolving type out of the aqueous system.

Figure 7 shows that 3.9 mg N/L (58%) of NO_3^--N was removed in phase I after a reaction period of 40 min, where 3.8 mg N/L of ammonium was resulted. As the reaction solution was put to standstill for 30 min and the supernatant was aerated with air for 50 min, the nitrate concentration remained rather unchanged. On the other hand, the ammonium converted from nitrate reached to a maximum of 4.4 mg N/L at times of 50-70 min, and then dropped down to a value of around 2.2 mg N/L at time of 120 min, due to air stripping effect. As observed from the two trends of total nitrogen (NO_3^--N and NH_4^+-N) and NH_4^+-N, both seem to parallel to each other. This indicates that the loss of nitrogen-contained species during the aeration period of phase III is all due to the disappearance of ammonium, which was stripped out of the system completely. As for the variation of solution pH over the entire time period, the pH was seen to arise from the lowest point of 4.3 (at 10 min) to 5.6 (at 40 min); in phase II, the pH remained rather unchanged; and in phase III, the final pH pointed to the largest value of 6.3. The arising trend of pH resulted in the enhancement of the ammonium stripping according to Reaction (6). In addition, as shown in Figure 8, the Fe^{2+} accumulated to a maximum of 100 mg/L at time of 40 min. This provides an evidence of reduction of nitrate being undergoing in phase I. After standstill (phase II) and aeration (phase III) treatment, the ferrous was obviously oxidized into iron oxide in the presence of oxygen, leading to a final residue close to zero concentration at time of 120 min. As was observed in the experiment, considerable amount of iron sludge was settled at the bottom layer of reactor. On the other hand, the variation of ORP appears to follow the opposite trend of ferrous change; the higher the ferrous concentration, the lower the ORP value.

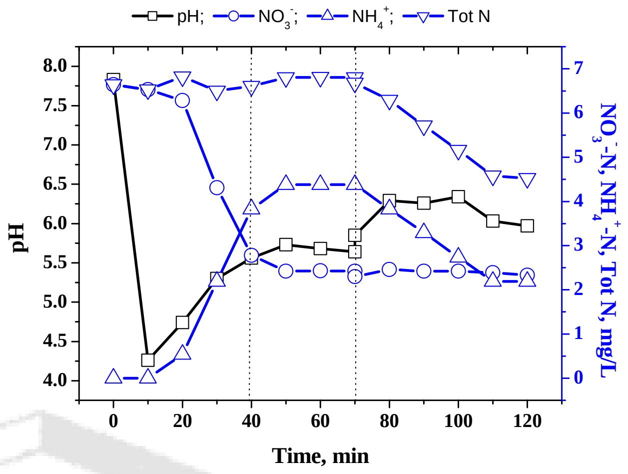

Figure 7. Profiles of NO_3^--N, NH_4^+-N and solution pH within phases I, II and III. The experiment in phase I (0-40 min) was conducted by using 1 g Fe^0/L as well as bubbling CO_2 at an inflow rate of 500 mL/min. In phase II (40-70 min), the reaction solution was put to a standstill state for 30 min, allowing the reaction precipitates and iron powder to settle down. In phase III (70-120 min), the supernatant taken from phase II was bubbled with air at a rate of 500 mL/min.

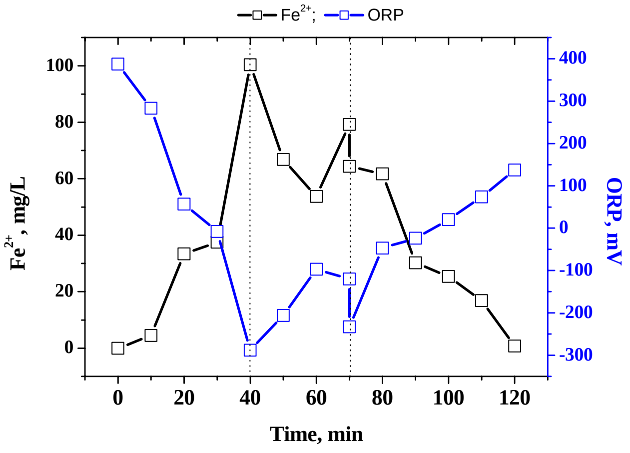

Figure 8. Profiles of Fe^{2+} and ORP within phases I (0-40 min), II (40-70 min) and III (70-120 min).

To sum up, the drawback of the presented Fe^0/CO_2 method for total removal of nitrate can be overcome by a simple post treatment of settling and air aeration.

CONCLUSIONS

Several important aspects of this study were found for nitrate removal using Fe^0 and CO_2 bubbling. Without introducing any obnoxious species into treated water, the use of CO_2 was proven to be effective and efficient in creating acidic environment of solution, which is favorable to nitrate reduction in the presence of Fe^0. The solution pH was seen to drop down to around 3 in 10 min as the CO_2 (500 mL/min) was bubbled into solution. If the facility for CO_2 diffusion is well designed, the bubbling efficiency will be even better. In addition, the efficiency of nitrate-N conversion can reach to 85% during a reaction period of 40 min by using the Fe^0/CO_2 method, and the nitrate was converted into ammonium, which accounts for 90-104% of nitrate conversion with the presence of various iron dosages (0.5-2 g/L). More importantly, the undesirable formation of ammonium in the reaction system can be eliminated from aqueous phase simply by a post treatment of settling (30 min) and air aeration (50 min). Based on what was achieved in this study, there's a great potential of applying the Fe^0/CO_2 method for the total removal of nitrate from contaminated waters.

ACKNOWLEDGEMENT

This research was sponsored by the National Science Council (NSC) of Republic of China under project No. NSC89-2211-E-041-013.

REFERENCES

Benjamin M.M. Water chemistry (1st ed.) (2002) McGraw-Hill Companies, Inc., New York, NY.

Cheng I.F., Muftikian R., Fernando Q., Korte N. 1997. Reduction of nitrate to ammonia by zero-valent iron. *Chemosphere* **35**(11), 2689-2695.

Choe S., Chang Y.Y., Hwang K.Y., Khim J. (2000) Kinetics of reductive denitrification by nanoscale zero-valent iron. *Chemosphere* **41**, 1307-1311.

Coehn, M. 1979. Dissolution of Iron. In G.R.. Brubaker, P. Beverly and P. Phipps, Eds. *Corrosion Chemistry*, Washington, D.C.: ACS.

Hammer M.J. and Hammer M.J., Jr. (4th ed.) (2001) Water and wastewater technology. Prentice Hall, Inc., Upper Saddle River, New Jersey.

Huang C.P., Wang H.W., Chiu P.C. (1998) Nitrate reduction by metallic iron. *Wat. Res.* **32**(8), 2257-2264.

Kelly E.J. (1965) The active iron electrode: iron dissolution and hydrogen evolution reactions in acidic sulfate solutions. *J. Electrochem. Soc.***112**(2)**,** 124-131.

Mirvish S. S. (1985) Gastric cancer and salivary nitrate and nitrite. *Nature* **315**, 461-462.

Piron, D.L. (1991) Prediction of corrosion tendencies. In *the electrochemistry of corrosion*, Houston, TX.: NACE, pp. 37-61.

Standard Methods for the Examination of Water and Wastewater, 19 th ed., American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC. 1995.

Walton G.. (1951) Survey of literature relating to infant methemoglobinemia due to nitrate-contaminated water. *Am. J. Public Health* **41**, 986-995.