NSC93-2211-E-041-001-
93　08　01　　94　07　31

94　5　23

Innovative Technology of Artificial Neural Network Model aided dual process of Fe^0/CO_2 reduction and Air stripping for nitrate-contaminated Groundwater Treatment

NSC93-2211-E-041-001

：

：

：

I.

Book Chapter
1. Chih-Hsiang Liao, Shyh-Fang Kang, Jin Anotai, Chalermchai Ruangchainikom (2005). Aqueous Nitrate Reduction by Zero-valent Iron Powder. To be published in the Book of *"Engineering Application of Zero-valent Iron for Water and Groundwater Pollution Control"*, American Society of Civil Engineers (ASCE), Rao Surampalli, Irene M. C. Lo, Keith C. K. Lai (Eds).

Jounal Papers
1. Chalermchai Ruangchainikom, Chih-Hsiang Liao, Jin Anotai, Ming-Tang Lee (2005). Effects of water characteristics on nitrate reduction by the Fe^0/CO_2 process. Submitted to *Chemosphere*. In revision.
2. Chalermchai Ruangchainikom, Chih-Hsiang Liao, Jin Anotai, Ming-Tang Lee (2005). Characteristics of Nitrate reduction by zero-valent iron powder in the recirculated and CO_2-bubbled system. Submitted to *Water Research*.

Confernce Papers
1. C. Ruangchainikom, C.H. Liao, J. Anotai and M.T. Lee (2005). Nitrate Removal by Fe^0/CO_2 Process with Various Water Qualities. 1st IWA-ASPIRE Conference, 10-15 July 2005, Singapore. (Oral presentation).
2. Chalermchai Ruangchainikom, Chih-Hsiang Liao, Jin Anotai, Ming-Tang Lee (2005). Innovated Process of Fe^0/CO_2 for the Removal of Nitrate from Groundwater. IWA Leading-Edge Conference on Water and Wastewater Treatment Technologies (LET 2005), 6-8 June 2005, Sapporo, Japan. (Oral Presentation).
3. Chalermchai Ruangchainikom, Chih-Hsiang Liao, Jin Anotai, Ming-Tang Lee (2004). Zero-valent iron reduction of nitrate-contaminated water in the Presence of CO_2 Bubbling. The 29th Wastewater Treatment Technology Conference of the Chinese Institute of Environmental Engineering, National Cheng-Kung University, Tainan, Taiwan, November 26-27, 2004. (Oral presentation)
4.

2004　11　26-27　（　　　）

II.

Abstract In this study, Fe^0/CO_2 process was investigated for removing nitrate from aqueous solution, in terms of process efficiency, process operation mode, and post treatment of the end product ammonium. The results show that the nitrate of 30 mg/L could be removed from solution within 30 min under the conditions of 2 g/L Fe^0 and 200 mL/min CO_2 flow rate. Additionally, nitrite was not detected in treated solution, whereas ammonium is the predominant nitrogen-containing species. The normalized residual nitrate concentration decreased with increasing nitrate concentration (2.18-24.19 mg N/L). Nitrate removal was inhibited significantly in the presence of humic acid. In comparison of operation modes, NO_3^- reduction efficiency with increasing number of batch operation in Mode 2 (treated solution was emptied and refilled with freshly prepared solution for the next batch treatment, containing the same level of nitrate as the previous batch.) is better than that with Mode1 (treated solution was retained in the reactor and spiked with concentrated nitrate solution to raise nitrate concentration to a level close to the one in the previous batch.). However, to guarantee satisfactory nitrate removal in batch operation mode, zero-valent iron supplement needs to be taken into consideration. For example, the nitrate removal efficiency without Fe^0 supplement is decreasing in the third batch, compared to those with supplements of 0.25 and 1 g/L. According to a preliminary study, the undesired end-product ammonium can be removed from solution by about 95% within 22.5 hr with the air flow rate of 500 mL/min and the solution pH around 12; the ammonium concentration decreased from 6.4 to 0.3 mg 12N/L. Note that stripping time can be further shortened by increasing air flow rate and using efficient air diffuser.

**Keywords** nitrate; groundwater; zero-valent iron; carbon dioxide

Introduction

Nitrate contamination in groundwater and surface water has become an environmental issue of concern in the past decade in view of eutrophication and health-related threats to human. Hence, the regulatory criteria of nitrate 44 mg/L (~10 mg-N/L) is applied as a safe drinking water quality standard in most developed countries (Westerhoff et al., 2003). Actions need to be taken for numerous sites locating at governmental and private facilities, where the nitrate concentration in groundwater is beyond 10 mg N/L. In recent years, the chemical reduction of nitrate has received widespread attention from many researchers (Cheng et al., 1997; Huang et al., 1998; Choe et al., 2000; Huang and Zheng, 2002; Alowitz and Scherer, 2002; Westerhoff and James, 2003; Liao et al, 2003; Choe et al., 2004; Huang and Zheng, 2004). Of the chemical reduction processes, zero-valent iron (Fe^0), serving as an electron donor to nitrate reduction, represents the most common metallic reducing agent since zero-valent iron is readily available at low cost and non-toxic. Nitrate reduction by Fe^0 is a fast reaction under acidic condition. The use of CO_2 to supply hydrogen ions in the solution is promising in view of its non-negative effect on treated water quality as well as a very common practice in water purification processes such carbonation and re-carbonation. In this study, Fe^0/CO_2 process was investigated for removing nitrate from aqueous solution, in terms of process efficiency, process operation mode, and post treatment of the end product ammonium.

Materials and methods

Material and reagents

Zero-valent iron (Fe^0) of 10 μm size (specific surface area ≈ 1 m^2/g) purchased from Merck KGaA, Germany was used without any pretreatment. The CO_2 gas with purity greater than 99.5% was purchased from a local supplier. A nitrate concentration of 2.25.-23 mg N/L, prepared from sodium nitrate (Merck KGar Germany), was used in this study. Solutions were prepared using water generated by a Millipore-Q system (Millipore Simplicity, France).
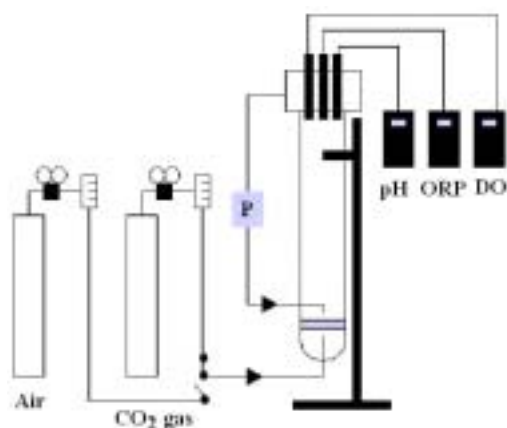
Figure 1. Configuration of reactor for the Fe^0/CO_2 system.

Experimental methods

As shown in Figure 1, the experiments were conducted in a cylindrical reactor of 1.3 L. The liquid volume was 1 L. Internal recirculated flow was used to achieve homogeneous mixing of solution using a peristaltic pump. The CO_2 gas was introduced by passing through a disk diffuser of silicate material installed at the bottom of reactor. As the experiments were carried on, water samples were taken from the reactor at different time intervals for subsequent analyses.
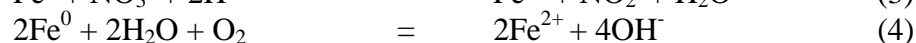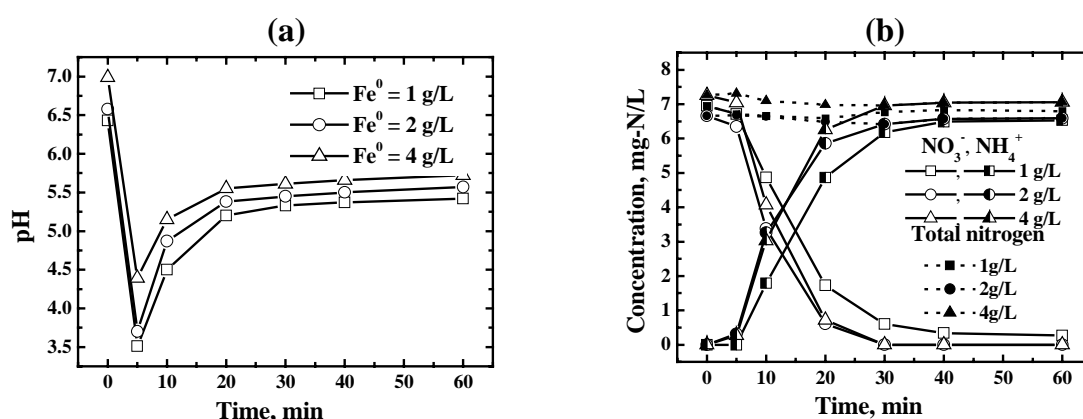
Analytical methods

After pre-filtration of treated sample, the filtrate was used for the analysis of ferrous ion. Ferrous ion was able to form a colored complex with 1,10-phenanthroline; therefore, its concentration was determined through the spectrophotometric reading (SHIMADZU, UV-1201, Japan) of light absorption of solution at 510 nm, which corresponds to a certain ferrous quantity (Standard method, 1995). The residual nitrate, nitrite, and ammonium were analyzed by using Ion Chromatography (IC; DIONEX-120, USA). In IC analyses, 4 drops of 15,000 mg/L H_2O_2 was spiked into the above filtrate to convert Fe^{2+} to ferric precipitate (Fenton's reaction) and then the water sample was furthered filtered using a 0.45 μm membrane filter to remove the iron precipitate from solution. In addition, the pH, DO, ORP were monitored continuously by using a pH meter (Suntex, TS-1, Taiwan), DO meter (WTW, Oxi 340, Germany), and ORP meter (Suntex, TS-2, Taiwan), respectively.

Result and discussion

Effect of Fe^0 dosages

The nitrate reduction profiles with different initial iron dosages were presented in Figure 2. The initial NO_3^- concentration was 6.95 mg N/L. As can be seen from Figure 2 (a), the pH trends for all Fe^0 dosages dropped sharply to an acidic value of around 3.5-4.5. Then, the pH increased gradually and became steady around pH 5.0-5.5. The rebounding pH is due to the hydroxyl ion produced from the reduction of NO_3^- by Fe^0 (Reactions (1) – (3)) as well as that of H_2O by Fe^0 (Reactions (4) and (5)).

$$4Fe^0 + NO_3^- + 10H^+ \quad = \quad 4Fe^{2+} + NH_4^+ + 3H_2O \quad\quad (1)$$
$$5Fe^0 + 2NO_3^- + 12H^+ \quad = \quad 5Fe^{2+} + N_2 + 6H_2O \quad\quad (2)$$
$$Fe^0 + NO_3^- + 2H^+ \quad = \quad Fe^{2+} + NO_2^- + H_2O \quad\quad (3)$$
$$2Fe^0 + 2H_2O + O_2 \quad = \quad 2Fe^{2+} + 4OH^- \quad\quad (4)$$

$$Fe^0 + 2H_2O \qquad = \qquad Fe^{2+} + H_2 + 2OH^- \qquad (5)$$

Figure 2. Effect of Fe^0 dosage on (a) pH and (b) nitrate residue, ammonium formation and total nitrogen mass balance. The initial NO_3^- concentration was 6.95 mg N/L. The experiment was conducted by using various Fe^0 dosages as well as bubbling CO_2 at an inflow rate of 200 mL/min and a recirculated flow of 1000 mL/min.

In regard to nitrate removal in Figure 2(b), nitrate was removed slightly in the initial stage and then dropped down swiftly after 5 min for all Fe^0 dosages. The initial lag phase for nitrate removal might be due to the time required for the hydrogen ions to transport onto the iron metal surface. The nitrate reduction was seen to increase remarkably with increasing iron dosages (1-4 g/L). The nitrate removal with dosage of 1 g Fe^0/L was 91% at 30 min, and 96% at 60 min. On the other hand, as the dosages were 2 and 4 g/L, respectively, the nitrate was completely removed at time of 30 min in either case. In addition, the residual profiles of NO_3^- show no difference for the two dosages of 2 and 4 g/L, but the difference becomes quite significant as the dosage was reduced from 2 to 1 g/L. In view of marginal benefit in nitrate removal, the optimum Fe^0 dosage of 2 g/L is recommended in the case of initial nitrate of 6.95 mg N/L. In addition, nitrite (NO_2^-) was not detected in treated solution, whereas ammonium is the predominant nitrogen-containing species. The ammonium occurred rapidly when the nitrate reduction began, and its formation rate was reduced as the nitrate reduction rate became slowing down. Cheng et al. (1997) and Huang et al. (1998) reported ammonium as dominating reaction products in the Fe^0 process. As for the mass balance, ammonium accounts for 95-105% of the total nitrogen.

Effect of initial nitrate concentration

To investigate the effect of initial nitrate concentration on Fe^0/CO_2 process, the initial nitrate concentration was varied from 2.2 to 24.2 mg N/L. The experiment was carried out with 2 g/L Fe^0, 200 mL/min CO_2 inflow rates, and a recirculated flow of 1000 mL/min. The results show that the curves of all initial concentrations exist a lag phase over the initial period of 5 min, where nitrate was removed only slightly. Nitrate was transformed almost completely within 30 min for the initial NO_3^- of 2.2 mg N/L and 6.8 mg N/L. In contrast, the initial nitrate of 10.4 mg N/L and 24.2 mg N/L reduced to 3.4 mg N/L (93% removed) and 4 mg N/L (81% removed), respectively at time of 60 min. It appears that the normalized residual nitrate concentration decreases with increasing nitrate concentration.
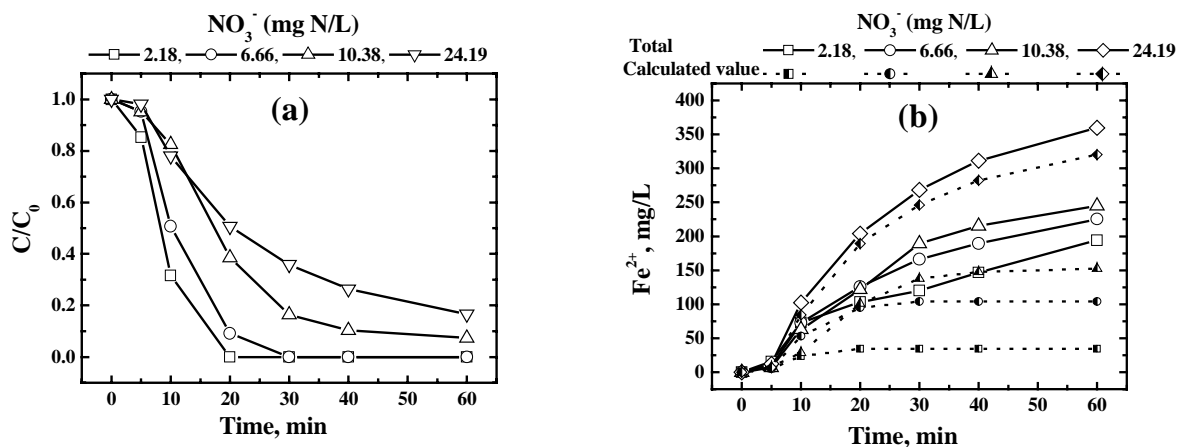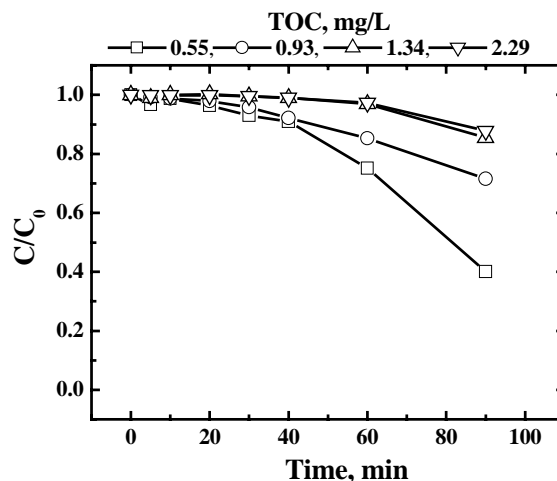
Figure 3. Effect of initial nitrate concentration on (a) nitrate reduction and (b) ferrous accumulation. Nitrate concentration was in the range of 2.18-24.19 mg N/L. The experiment was conducted by using 2 g/L Fe^0 as well as bubbling CO_2 at an inflow rate of 200 mL/min and a recirculated flow of 1000 mL/min.

According to Reactions (1) and (5), both water and nitrate molecules will compete with each other for Fe^0-releasing electrons, leading to the formation of ferrous ions. As shown in Figure 2(b), ferrous accumulation exhibited an exponential trend after the first 5-min lag phase. The rate of ferrous accumulation increased with increasing nitrate concentration. To differentiate the competition reactions with Fe^0 between water and nitrate, ferrous concentration based on the dominating stoichiometric Reaction (1) was calculated and plotted in Figure 2(b). The differences between the measured and calculated profiles indicate those ferrous ions deriving from reduction reaction of H_2O with Fe^0 (Reaction 5). By visual comparison between the measured and the calculated ferrous ion, significant differences of ferrous profiles are observed for the initial nitrate of 2.18, 6.66 and 10.38 mg N/L. It demonstrates that ferrous ion generated in the system occurs from nitrate reduction when nitrate still remain in the solution. However, ferrous ion generated after 20 min or 30 min should be primarily due to water reduction since the corresponding nitrate residues were very low or near to zero. In addition, it was observed that the calculated ferrous concentration for the case of initial nitrate at 24.19 mg N/L is close to the measured one during the later reaction period. This implies that Reaction (1) occurs much faster than reaction (5) when the initial nitrate concentration is sufficiently high. This also implies that zero-valent iron corrosion rate is accelerated, depending on the level of nitrate in the solution.

*Effect of humic acid on nitrate reduction*

Humic substances of natural organic matter (NOM) are commonly found in diverse water and soil environments. Its effect on nitrate reduction is presented in Figure 4. It is interesting to find that nitrate removal decreased remarkably with increasing humic acid content. This implies that humic acid was an important factor adversely affecting nitrate removal in the Fe^0/CO_2 process. Retardation on nitrate reduction might derive from the strong competition of humic acid with nitrate for the available reactive surface sites of Fe^0. The presence of humic acid results in the inactivation of surface of Fe^0. According to the study of Tratnyek et al. (2001), who reported that carbon tetrachloride reduction rate by zero-valent iron decreased in the presence of three aquatic and soil humic acids. Of these, the soil humic acids appear to have the greatest impact, possibly due to stronger adsorption of soil humic acid onto Fe^0. Based on such result, pretreatment of NOM is recommended to achieve a better performance of this process.

Figure 4. Effect of humic acid on nitrate reduction. The experiment was conducted by using various humic acid concentrations (0.55-2.29 mg/L) with CO_2 bubbling at an inflow rate of 200 mL/min, 2g Fe^0/L and a recirculated flow of 1000 mL/min. The initial nitrate concentration was 30 mg/L. The Na_2CO_3 and $CaCl_2.2H_2O$ used as background species were 94 mg/L as $CaCO_3$ and 150 mg/L as $CaCO_3$, respectively.

Effect of operating mode

In view of process operation, two modes were designed and conducted, including Mode 1; the treated solution was retained in the reactor and spiked with concentrated nitrate solution to raise nitrate concentration to a level close to the one in the previous batch; and Mode2: the treated solution was emptied and refilled with freshly prepared solution for the next batch treatment, containing the same level of nitrate as the previous batch. The profiles of pH and nitrate were almost the same in the first batch treatment because the experiments were conducted under identical conditions. Note that nitrate in the first batch could be removed completely from solution within 30 min in both operation modes. According to the 2nd and 3rd batches, significant differences between the two modes began to appear. With Mode 1, the efficiency of nitrate reduction decreased with increasing number of batch. For example, the efficiency of nitrate reduction was 100% at 60 min, 86.4% at 120 min, and 65.2% at 180 min. The decreasing of nitrate reduction efficiency was due to the rising of pH. As shown in Figure 4(a), the pH level in Mode 2 was lower than that in Mode 1. This seems to justify why the residual nitrate has a value lower in Mode 2 than in Mode 1 since lower pH is favorable to Fe^0 corrosion. On the other hand, the continuous accumulation of NH_4^+ and Fe^{2+} in Mode 1 might be the reason of deterioration of nitrate reduction. These cations tend to suppress Fe^{2+} dissolution from Fe^0 surface, leading to lesser electrons available to nitrate reduction. In addition to this, the rising of pH in Mode 1 is also one of the key reasons behind such phenomenon. As the pH continues to increase, precipitation of iron corrosion product is accelerated and may occupy and coat on the reactive sites of Fe^0 available to nitrate reduction. It is important to notice that the pH governs the process performance in a significant way and needs to be monitored continuously in operating this process.
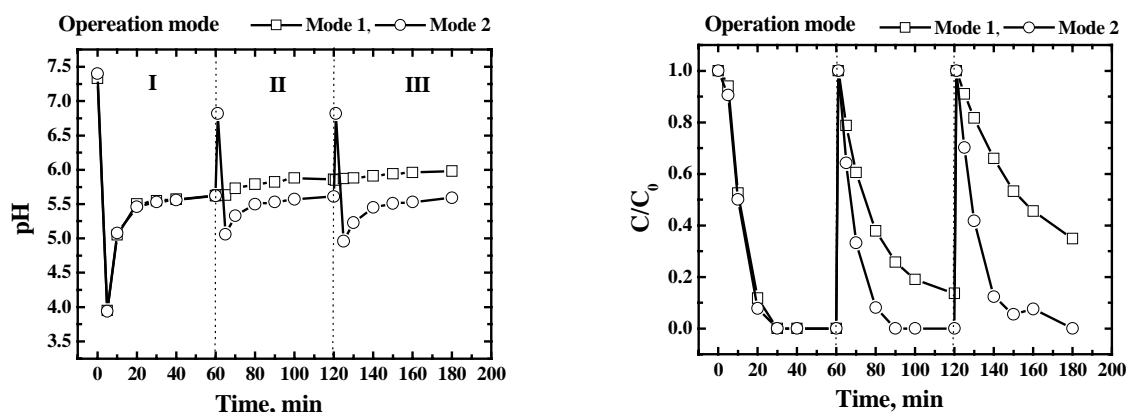
Figure 5. Effect of different operation modes on (a) pH and (b) nitrate reduction. The experiment was conducted under the conditions of CO_2 bubbling rate of 200 mL/min and a recirculated flow of 1000 mL/min. The first phase (0-60 min) was conducted by using 2 g Fe^0/L and initial NO_3^- of 6.8 mg N/L. In the second (60- 120 min) and third phases (120-180 min), 3 mL of 10,000 mg/L nitrate solution was spiked into the reactor at 60 min and 120 min, respectively (the operating Mode 1). In the operating Mode 2, the treated solutions from the first phase were emptied and refilled with fresh nitrate-contained solution of the same concentration level as the previous batch at times of 60 and 120 min, respectively.

Supplement of fresh Fe^0

As understood from the above operating mode, the reduction efficiency of nitrate by zero-valent iron decreases with increasing number of batch treatment, and the process operation using Mode 2 outperforms Mode 1 on nitrate removal. With such understanding in mind, it appears that supplement of fresh zero-valent iron is required to maintain a satisfactory efficiency of nitrate reduction when the process is operated in a longer time period. Hence, the experiment of Mode 2 was further tested by stepwise supplement of fresh Fe^0 during each batch operation. As shown in Figure 6(a), nitrate can be removed by 100% in all cases, and supplement of 1 g Fe^0 imposes the most rapid removal of nitrate in the third batch. Without Fe^0 supplement, the nitrate can be removed completely from solution in 60 min for the third batch, which is compared to the required times of 30 and 20 min, respectively, with Fe^0 supplements of 0.25 and 1.0 g. As mentioned earlier, Figure 6 (b) shows that, without Fe^0 supplement, ferrous accumulations were 222, 183, and 159 mg/L, respectively, in the order of batch treatment. The accumulation values indicate that the activity of Fe^0 was decreasing with increasing number of batch operation. With Fe^0 supplement of 0.25 g, ferrous accumulations were 213, 206, and 197 mg/L, respectively. As the Fe^0 supplement was 1 g, ferrous accumulations were 211, 232 and 248 mg/L, respectively. Based on these ferrous accumulation data, it was demonstrated that appropriate amount of the Fe^0 supplement applied is necessary to meet the requirement of nitrate removal efficiency in the studied batch operation.

## *Post treatment of ammonium*

As mentioned earlier, ammonium is the dominating end product in the nitrate reduction by Fe^0/CO_2 process. Unfortunately, ammonium is an undesirable species. Therefore, a post treatment of separating ammonium from treated water is needed to assure a safe drinking water quality if the reduction process of Fe^0 is employed for the treatment of nitrate-contaminated waters. According to the following reaction (6), ammonium can be stripped out of aqueous phase under alkaline solution, especially at a pH level higher than 9.3.

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

With the above concept in mind, a follow-up experiment was designed and conducted to guarantee ammonium removal in solution. As can be seen from Figure 7, the ammonium can be removed from solution by about 95 % within 22.5 hr with the air flow rate of 500 mL/min, when alkaline solution as sodium hydroxide was applied to increase the solution pH up to around 12; the ammonium concentration was reduced from 6.4 to 0.3 mg N/L. Hence, it is feasible that the end product ammonium in the reaction system of Fe^0/CO_2 can be removed by air stripping under the condition of adjusted solution pH value higher than its pKa 9.3. When further applied to field operation, ammonium can be removed by improving stripping facilities to shorten the stripping time.
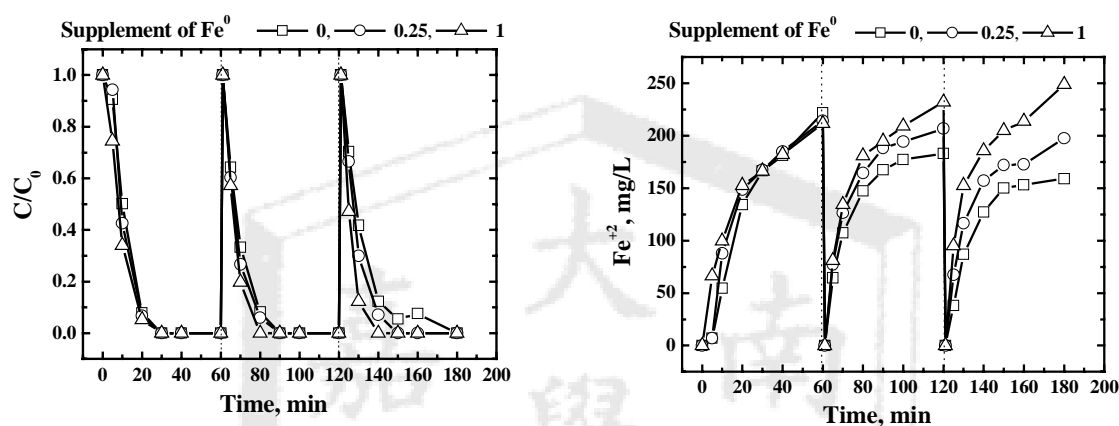
Figure 6. Effect of Fe⁰ supplement. Three batches were conducted under the conditions of CO_2 bubbling rate of 200 mL/min and a recirculated flow of 1000 mL/min. The time for each batch was 60 min. The first batch was conducted by using 2 g Fe^0/L and 6.8 mg NO_3^--N/L. In the second batch (60- 120 min) and third batch (120- 180 min), the treated solution of previous batch was removed from reactor, the iron residue from previous batch was reclaimed and then Fe^0 was supplemented at various dosages. In the meantime, fresh solution of 6.8 mg NO_3^--N/L was refilled into reactor for the next batch operation.
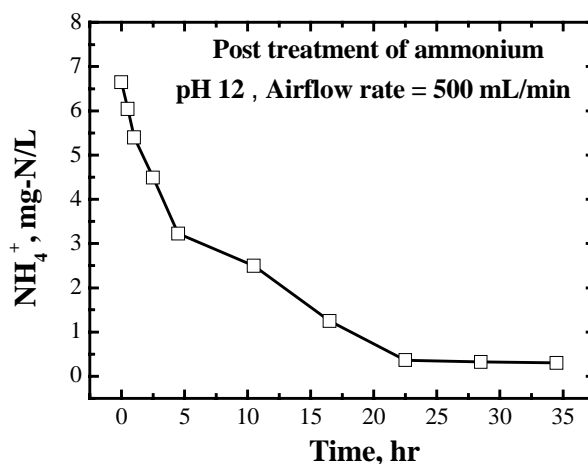
Figure 7. Post treatment of ammonium with air bubbling and the pH adjusted at 12.

Conclusions

As a result, the Fe^0/CO_2 process is capable of removing nitrate of 30 mg/L within 30 min under the conditions of 2 g/L Fe^0 and 200 mL/min CO_2 flow rate. The normalized residual nitrate concentration decreased with increasing nitrate concentration (2.18-24.19 mg N/L). Humic acid plays a role of inactivating nitrate reduction because of its adsorption onto zero-valent iron surface. In view of different process operation modes, it was interesting to find that batch operation mode (Mode 2) outperformed the spiked nitrate mode (Mode 1) in nitrate removal when these were compared on the same basis. The key reason behind such difference is the rising of pH in Mode 2, which is not favorable to Fe^0 corrosion. In addition, the measure of zero-valent iron supplement needs to be taken to guarantee satisfactory nitrate removal in the batch operation mode. The appropriate amount of the Fe^0 supplement applied can meet the requirement of nitrate removal efficiency in the studied batch operation. Moreover, ammonium as a dominating product in the studied reaction system can be stripped out of the aqueous by adjusting the solution pH at 12 and by air bubbling. According to the test run, when alkaline species NaOH was applied for pH adjustment and the air flow rate was controlled at 500 mL/min, ammonium was stripped out of solution from 6.4 to 0.3 mg N/L within 22.5 hr, 95% being removed. To shorten the ammonium stripping time, future research should be focused on improving the system of ammonium stripper.

References

Alowitz, M.J. and Scherer, M.M. (2002) Kinetics of nitrate, nitrite, and Cr(VI) reduction by iron metal. Environmental Science and Technology **36**, 299-306.

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

Choe, S., Liljestrand, H.M. and Khim, J. (2004) Nitrate reduction by zero-valent iron under different pH regimes. Applied Geochemistry **19**, 335-342.

Huang, C.P., Wang, H.W. and Chiu, P.C. (1998) Nitrate reduction by metallic iron. Water Research **32**, 2257-2264.

Huang, Y.H. and Zheng, T.C. (2004) Effects of low pH on nitrate reduction by iron powder. Water Research **38**, 2631-2642.

Huang, Y.H. and Zheng, T.C. (2002) Kinetics of nitrate reduction by iron at near neutral pH. Journal of Environmental Engineering **128**, 604-611.

Liao, C.H., Kang, S.F. and Hsu, Y.W. (2003) Zero-valent iron reduction of nitrate in the presence of ultraviolet light, organic matter and hydrogen peroxide. Water Research **37**, 4109-4118.

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

Tratnyek PG., Scherer M.M., Deng B., Hu S. (2001) Effect of natural organic matter, anthropogenic surfactants, and model quinines on the reduction of contaminants by zero-valentiron. Water Research **35** (18), 4435-4443.

Westerhoff, P. and James, J. (2003) Nitrate removal in zero-valent iron packed columns. Water Research **37**, 1818-1830.