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類神經網路模式輔助之元素鐵/二氧化碳及空氣曝氣兩段式新穎技術處理硝酸鹽污染地下水(2/3)

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計畫主持人：廖志祥
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Innovative Technology of Artificial Neural Network Model aided dual process of Fe^0/CO_2 reduction and Air stripping for nitrate-contaminated Groundwater Treatment

NSC94-2211-E-041-024

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I. 計畫目標

第一年(2004.8.1-2005.7.31): 批次式反應槽研究
第二年(2005.8.1-2006.7.31): 連續式反應槽研究
第三年(2006.8.1-2007.7.31): 連續式現地模型廠研究

II. 第一、二年計畫累積論文發表成果摘要表

Book Chapter

1. Chih-Hsiang Liao, Shyh-Fang Kang, Jin Anotai, Chalermchai Ruangchainikom (2006). 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*", *Chapter 6*, 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 (2006). Characteristics of Nitrate reduction by zero-valent iron powder in the recirculated and CO_2-bubbled system. *Water Research* 40(2), 195-204.
2. Chalermchai Ruangchainikom, **Chih-Hsiang Liao**, Jin Anotai, Ming-Tang Lee (2006). Effects of water characteristics on nitrate reduction by the Fe^0/CO_2 process. *Chemosphere*, 63(2), 335-343.
3. C. Ruangchainikom, C.H. Liao, J. Anotai and M.T. Lee (2005). Innovative process using Fe^0/CO_2 for the removal of nitrate from groundwater. *Water Science and Technology: Water Supply* 5(5), 49-56.

Confernce Papers

1. Chalermchai Ruangchanikom, Jin Anotai, and Chih-Hsiang Liao (2006). Innovative reactor design for treating nitrate-contaminated groundwater by Fe^0/CO_2. International Conference Hazardous Waste Management for a Sustainable Future, January 10-12, 2006, Bangkok, Thailand. (Oral presentation).
2. Setawat Homanee, Chien-Jung Lin, Chalermchai Raungchainikom, Chih-Hsiang Liao, Jin Anotai (2006). Reclamation of iron oxide from Fe^0/CO_2 by Fenton pretreated fluidized bed reactor. International Conference Hazardous Waste Management for a Sustainable Future, January 10-12, 2006, Bangkok, Thailand. (Oral presentation).
3. Chalermchai Ruangchainikom, Chih-Hsiang Liao, Chien-Jung Lin, Jin Anotai, Setawat Homanee (2005). Innovative Chemical Process of Fe^0/CO_2 for the Treatment of Nitrate-

contaminated Groundwater. Regional Symposium on Chemical Engineering (RSCE) 2005 “New Trends in Technology Towards Sustainable Development”, November 30 – December 2, 2005, Hanoi, Vietnam. (Oral presentation)

4. Chalermchai Ruangchanikom, Jin Anotai, and Chih-Hsiang Liao (2005). Innovative Purification Technology of Fe^0/CO_2 for Removing Highly Nitrate-Contaminated Saline Groundwater in Northeastern Thailand. International Conference on Geology, Geotechnology and Mineral Resoureces of INDOCHINA, November 28-30, 2005, Khon Kaen University, Thailand. (Oral presentation).
5. 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).
6. 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).
7. 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)
8. 蕭振文、殷堂凱、廖志祥。運用類神經網路預測廢水廠處理效能，環工學會第二屆環境資訊研討會，台南市成功大學，2004 年 11 月 26-27 日。(口頭報告)

III. 第二年計畫精簡報告 (註: 本精簡報告口頭發表於 2006 年在泰國曼谷之研討會: "*International Conference Hazardous Waste Management for a Sustainable Future*"

Abstract - Nitrate contamination in groundwater and surface water has become an environmental issue of concern in the past decade, including eutrophication and health-related threats to human. To apply this innovative technology in the *in situ* groundwater treatment or drinking water treatment unit, the compact reactor is favorable for easy installation and transportation. In this research, attempt was made to combine the mixing tank of nitrate/Fe^0 and the Fe^0 settling tank into one unique reactor among a series of continuous treatment units. Such reactor consists of a recirculated pump used for complete mixing of reaction mixture in the first compartment and Fe^0 recycling in the second compartment. On top of this, CO_2 gas is introduced into the first compartment through the venturi tube valve. The results indicated that nitrate concentration of 23 mg-N/L decreased to 2.93 mg-N/L within 2.5 hrs under the conditions of influent feeding rate of 3 L/hr, Fe^0 dose of 60 g, and CO_2 gas inflow of 200 mL/min. The supplement of Fe^0 was designed at every operating time of 27 hrs to meet the requirement of nitrate drinking water standard. As a result, 40 g of Fe^0 was supplemented periodically for better practice of controlling nitrate removal efficiency and ferrous accumulation.

Keywords - Carbon dioxide, groundwater contamination, nitrate, reduction, zero-valent iron

INTRODUCTION

In recent years, nitrate contamination in groundwater has become a serious problem because of public health concern. The health effect of nitrate in drinking water is in fact related to nitrite because nitrate can be microbially reduced to nitrite, which causes methemoglobinemia in newborn infant by oxidizing the heme Fe^{2+} of hemoglobin or known as "blue baby syndrome" (Walton, 1951). Additionally, cancers and damages to liver and other organs by nitrite are convinced to be due to formation of nitrosoamines, group of carcinogens produced from reaction of nitrate with amines, amides, and other nitrogenous compounds (Menzer, 1993). Therefore, the U.S. regulatory health limit of nitrate 44 mg/L (~10 mg-N/L) is applied as a safe drinking water quality standard in most of developed countries (Waterhoff et al., 2003). Zero-valent iron (Fe^0), serving as an electron donor to nitrate reduction, represents the most common metallic reducing agent. This process receives widespread attention from many researchers to treat nitrate (Cheng et al., 1997; Huang et al., 1998; Huang et al., 2002 and 2004; Waterhoff et al., 2003; Liao et al., 2003; Choe et al., 2000 and 2004). The reductive removal of nitrate can be seen as a result of metallic iron corrosion, especially significant in acidic solution (Piron, 1991). Generally, the application of acids such as H_2SO_4 (Huang et al., 1998), HCl and acetic acid (Cheng et al., 1997) was used to speed up the rate of nitrate removal. However, the presence of these alien species of sulfate, chloride and acetate will risk the drinking water quality of treated water. To avoid such disadvantage, 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 as carbonation and re-carbonation. In view of process operation, both mixing tank and Fe^0 settling tank are needed for Fe^0 process, as shown in Figure 1. As a result, it takes up more space for two tanks and costs more on construction. However, to apply this innovative technology in groundwater treatment units, a compact reactor is favorable for easy installation and transportation.

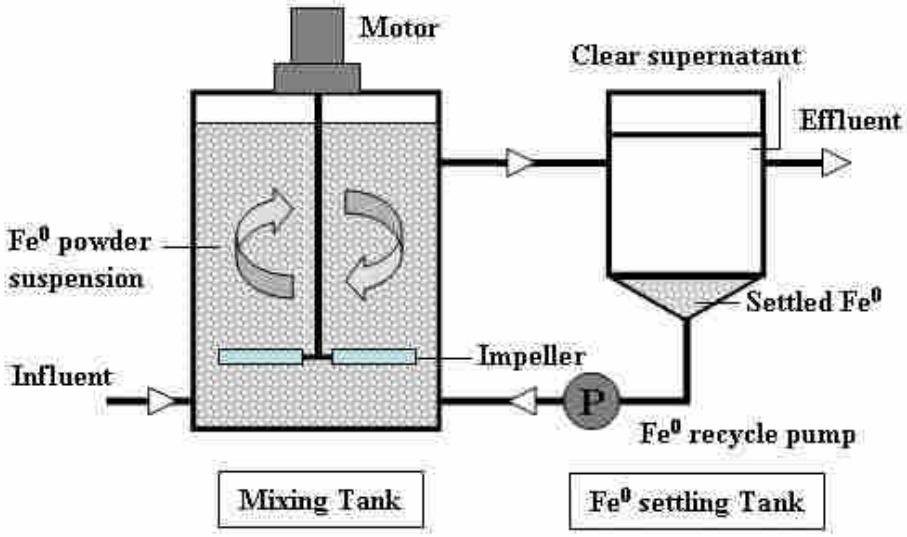

Figure 1. Traditional reactor for Fe^0 process

In this research, attempt was made to combine the mixing tank of nitrate/Fe^0 and the Fe^0 settling tank into one unique reactor among a series of continuous treatment units, as shown in Figure 2. Such reactor consists of a recirculated pump used for complete mixing of reaction mixture in the first compartment and Fe^0 recycling in the second compartment. On top of this, CO_2 gas is introduced into the first compartment through the venturi tube valve. The application of innovative reactor was investigated for removing nitrate from aqueous solution, in terms of process efficiency and process operation.

MATERIALS AND METHODS

Reagents and Materials

Zero-valent iron (Fe^0) of 10 μm size purchased from Merck was used without any pretreatment. The nitrate solution was prepared by dissolving KNO_3 (Merck) in the deionized water. CO_2 gas with purity greater than 99.5% was purchased from a local supplier.

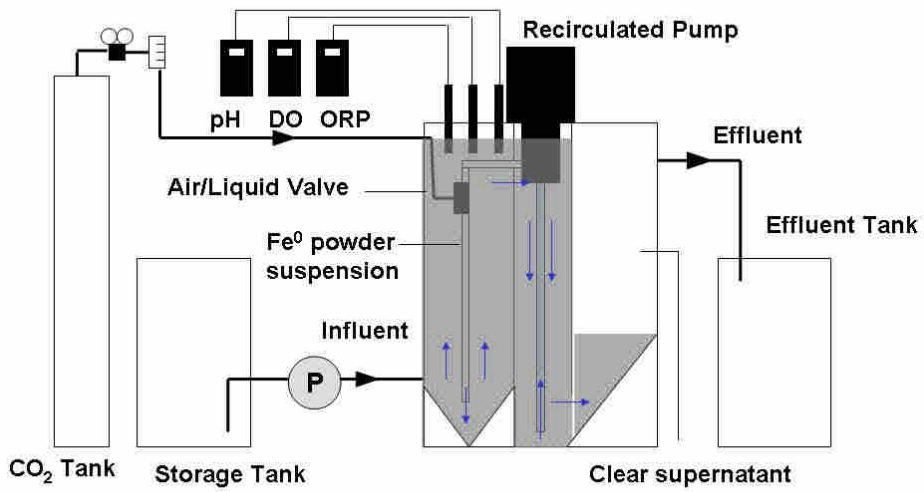

Figure 2. Innovative reactor for nitrate reduction by the Fe^0/CO_2 process.

Innovative reactor

Innovative reactor for nitrate reduction by Fe^0/CO_2 process was presented in Figure 2. The reactor volume reactor was 12 L. Regarding the first compartment, the bottom slope was 75 degree in cone shape to avoid dead-zone settling of Fe^0. With such design, the discharge of recirulated flow at the cone-shape bottom can cause complete mixing of Fe^0 powder and CO_2 bubbles. Then, the discharge moves upward and passes through a weir toward the second compartment. The second compartment is divided into recirculated and settling zones. The Fe^0 powder from the first compartment is sucked into a perpendicular tube by the recirculated pump and discharged back to the first compartment again. This settling zone separates upward supernatant from the Fe^0 powder, which is recycled back to the reaction system through a cone-shape bottom design.

Process Operation

The liquid solution feeding rate was 3 L/hr by using a peristaltic pump. The recirculated flow of 90 L/min was used for complete mixing of reaction solution. The CO_2 gas is introduced into the first compartment through the venturi tube valve with gas pressure controlled at 3 atm. As the reaction of all the experiments was carried on, water samples were taken from the reactor at different time intervals for subsequent analyses of water quality parameters.

Water Analyses

After pre-filtration of treated sample, the solution was analyzed for various water quality parameters. Ferrous ion was able to form a colored complex with 1,10-phenanthroline; therefore, its concentration was determined through the spectrophotometric reading of light absorption of solution at 510 nm, which corresponds to a certain ferrous quantity (Standard Methods, 1995). The residual nitrate, nitrite, and the end product ammonium were analyzed by using Ion Chromatography (IC). Prior to analyses of nitrate, nitrite, and ammonium, 4 drops of 15,000 mg/L H_2O_2 were applied for converting Fe^{2+} to ferric precipitate (Fenton's reaction) and then the sample was filtered by using a 0.45 μm membrane filter to remove the iron precipitate from solution.

RESULTS AND DISCUSSION

Effect of Fe^0 dosage

To determine the optimal Fe^0 dosage on nitrate reduction, 40, 60 and 80 g of Fe^0 were used in the presence of CO_2 bubbling with a constant flow rate of 200 mL/min and an initial nitrate concentration of 23 mg N/L. The effect of Fe^0 on the system parameters including pH, DO, ORP, nitrate residual, ammonium, and ferrous accumulation was shown in Figure 3. In Figure 3a, the pH profiles of different Fe^0 dosage at 40, 60 and 80 g were observed to drop rapidly from the neutral value to 5.41, 5.74, and 5.48, respectively, within 10 min; however, the pH's increased to 5.9, 5.90, and 5.96 in the next 20 min, respectively. Furthermore, the pH profile with 40 g Fe^0 decreased gradually after 20 min. In contrast, the pH profiles with 60 g and 80 g Fe^0 went up to 6.01 and 6.07, respectively. Then, both profiles became decreasing gradually. The decreasing profile of pH in the initial phase may be due to the dominating acidification reaction of CO_2 bubbling since zero-valent iron surface has not yet been activated. However, the reason for the pH rebounding is the consumption of hydrogen ions due to nitrate reduction (Reactions (1)-(3)) as well as the generation of hydroxide ions due to reduction of oxygen and water molecule (Reactions (4)-(5)).

$$4Fe^0 + NO_3^- + 10H^+ = 4Fe^{2+} + NH_4^+ + 3H_2O \quad (1)$$
$$5Fe^0 + 2NO_3^- + 12H^+ = 5Fe^{2+} + N_2 + 6H_2O \quad (2)$$
$$Fe^0 + NO_3^- + 2H^+ = Fe^{2+} + NO_2^- + H_2O \quad (3)$$
$$2Fe^0 + 2H_2O + O_2 = 2Fe^{2+} + 4OH^- \quad (4)$$
$$Fe^0 + 2H_2O = Fe^{2+} + H_2 + 2OH^- \quad (5)$$

The cause of gradually decreasing in pH after Fe^0 being activated was the loss of Fe^0 mass through its corrosion reaction in the system, leading to less consumption of H^+. As presented in Figure 3b, the initial DO ranging from 7.0 to 7.5 mg/L dropped nearly zero within 5 min regardless of Fe^0 dosages. Dissolved oxygen in the solution may be either stripped out of the system through CO_2 bubbling and/or reductively consumed by Fe^0 (see Reaction (4)). As has been well understood, oxygen can act as a role of electron acceptor similar to the nitrate in the Fe^0 system (Reaction (4)). In regard to ORP, Figure 3c shows that the initial values of about 300 mV, indicating an oxidative environment, dropped considerably to –644, –623, and -665 mV in the presence of 40, 60 and 80 g Fe^0, respectively, at time of 10 min. The ORP profiles of different Fe^0 dosages remained rather constant after 1 hr, which were -702, -700, -712 mV, respectively. Such negative ORP values indicate that the reducing environment has occurred in the Fe^0/CO_2 system. However, the ORP value increased gradually as the reaction proceeded further. Theoretically, the more reductive environment created, the more rapid nitrate removal would occur. This is to say that ORP value can serve as an indicator for nitrate removal performance. In Figure 3d, it appears that nitrate concentration remained unchanged within the initial period of 1 hr. This may be due to the lapsed time for the treated nitrate solution transported from the first compartment, passing through the second compartment, to the effluent outlet. In addition, it also takes time to remove impurities from the Fe^0 surface since it was used without any pretreatment (Ruangchainikom et al., 2005). Following the lag phase, the nitrate residue dropped rapidly. The lowest residual NO_3^- concentration occurred at 2 hrs for all Fe^0 dosages. With the Fe^0 dosage of 40 g, the nitrate was removed by 83% at 2 hrs. As the initial Fe^0 increased up to 60 and 80 g, the nitrate was removed by 87% and 90%, respectively, at 2 hrs. Such a result implies that the higher the Fe^0 dosage, the lower the NO_3^- residue in the reaction solution. With 40 g of Fe^0, the nitrate concentration at 21 hrs was beyond the drinking water standard of 10 mg/L NO_3^--N. Therefore, the Fe^0 of 60 g was selected as the optimum dosage to remove 23 mg N/L of nitrate. Concerning the reaction by-product, nitrite (NO_2^-) was not detected in the treated solution, whereas ammonium was the predominant nitrogen-containing species as shown in Figure 3e. Cheng et al. (1997) and Huang et al. (1998) reported that ammonium dominates the reaction products in the Fe^0 process under their studied conditions. The ammonium was produced rapidly when the nitrate reduction began, and its formation rate became reduced as the nitrate reduction rate was slowing down. The ammonium yield agrees very well with the nitrate disappearance on the basis of nitrogen mass balance between accumulated nitrate removal and ammonium formation, the difference of which is within ±5%. In Figure 3f, the ferrous accumulation increased with increasing Fe^0 dosages. It is interesting to point out that the initial lag phase for ferrous accumulation was observed for all Fe^0 dosages. It might be due to the time required for ferrous ion to transfer from the first compartment, passing through the second compartment, to the effluent outlet. Moreover, the activation time of Fe^0 surface is needed as well for removing impurities from the surface of Fe^0. The ferrous accumulation rate in Figure 3f appears to be in consistence with the rate of nitrate removal in Figure 3d. In other words, the nitrate removal is highly correlated with the ferrous concentration in the bulk solution. Therefore, monitoring of ferrous ion can provide a good prediction of the degree of nitrate being removed in the reaction system.

Effect of process operation

In the process operation, as shown in Figure 4, the operating mode was divided into 2 steps, i.e., Step 1: the initial Fe^0 of 60 g Fe^0 was tested for 23 mg N/L of nitrate until its exhaustion without any supplement of Fe^0 in order to determine an appropriate supplementing time point; Step 2: the supplement of 40 g Fe^0 was introduced into the system when the effluent nitrate concentration was higher than 10 mg/L NO_3^--N. This step was designed to control the effluent nitrate so that it can comply with the standard. In Step 1, pH dropped at the beginning and increased after 10 min.

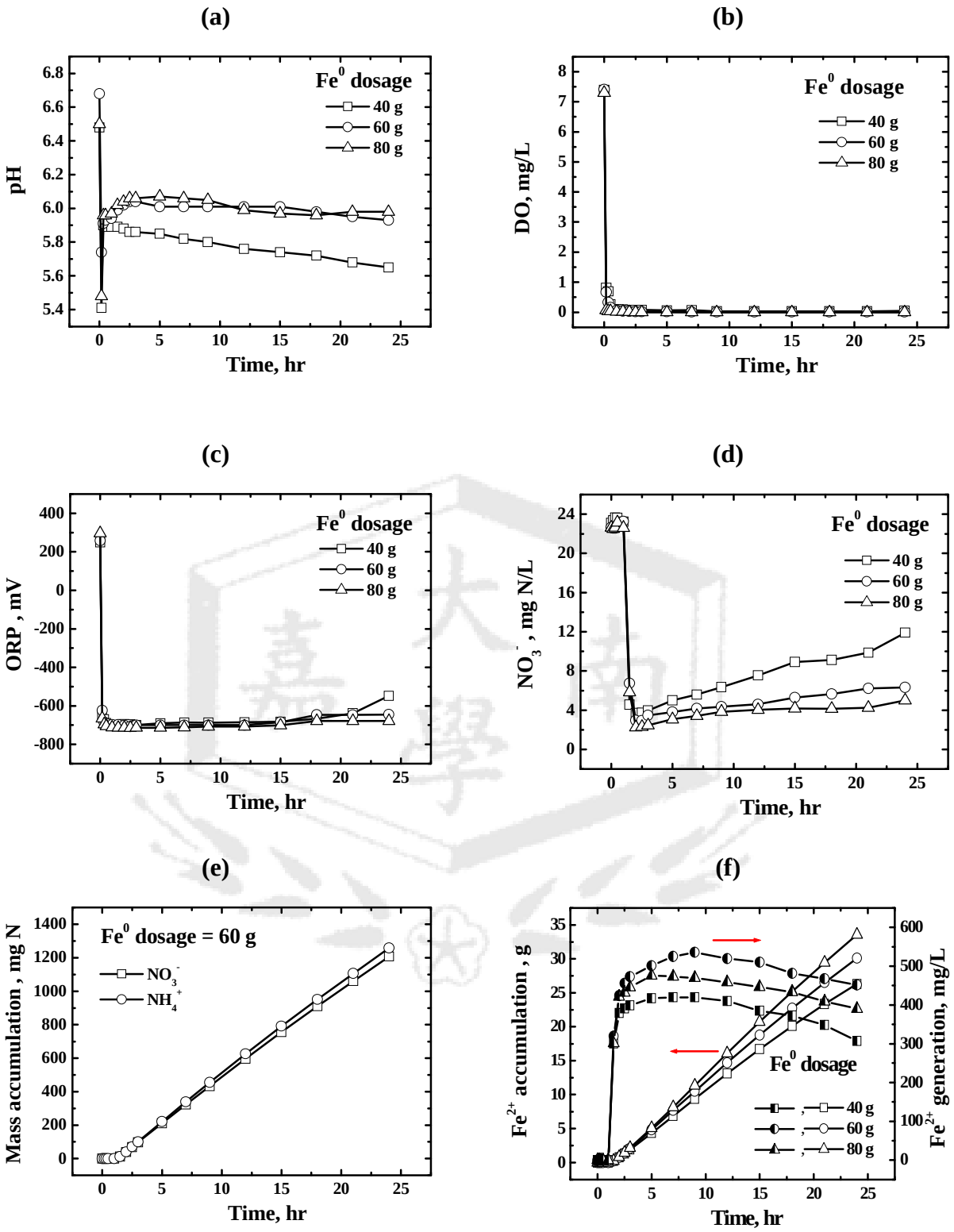

Figure 3 Effect of Fe^0 on (a) pH, (b) DO, (c) ORP, (d) nitrate reduction, (e) mass balance at 60 g Fe^0, (f) ferrous accumulation. The initial NO_3^- concentration was 23 mg N/L. The experiment was conducted by using various dosages of Fe^0 (40-80 g), CO_2 bubbling at an inflow rate of 200 mL/min, and a recirculated flow of 90 L/min.

Then, it gradually decreased, similar to previous scenario. Moreover, it can be seen that pH significantly decreased after 33 hrs because of the decreasing Fe^0 mass in the system. The H^+

consumption for nitrate removal by Fe^0, as illustrated in reaction 1, decreased as Fe^0 mass in the system decreased; on the other hand, since the CO_2 was continuously bubbled into the solution, the H^+ began to build up in the system, resulting in the decrease of the pH. Not only can the pH indicate the reaction extent of the Fe^0, the DO, ORP and ferrous accumulation also relate to nitrate removal. As shown in Figure 4b, the increasing of DO value occurred when Fe^0 in the system diminished. As mentioned earlier, the decreasing of DO in the solution was either stripped out of the system due to continuous CO_2 purging or consumed reductively by Fe^0 (see Reaction (4)). Therefore, the DO in the system rised up in the later time period as the Fe^0 was used up completely.. According to ORP profile in Figure 4c, it is shown that the ORP value changed from the negative to the positive, implying that the reductive environment was diminishing in the system. As seen from Figure 4d, the nitrate removal rate decreased as the reaction proceeded to a longer time period, particularly after 30 min. This indicated that the residual mass of Fe^0 was not sufficient for removing 23 mg N/L of nitrate to the desired drinking water quality standard. In contrast, while nitrate removal decreased, the formations of ammonium and ferrous were decreasing as well, as illustrated in Figures 4e and 4f, respectively. At 48 hrs, the measured ferrous concentration was 22 mg/L, which accounts for the accumulated mass of 43 g, as compared to 60 g at the beginning stage. The unbalance of iron mass might be due to the formation of some iron complex species in the reactor and also the Fe^0 residue in the recirculated pump. By visual observation, it can be seen that the color of solution changed from dark grey to light grey and to light yellow brown as the operation proceeded for 40 hrs. This depicts that the Fe^0 in the reactor has been utilized completely in the reaction system. Prior to the occurrence of breakthrough, the effluent solution was not colorless because $FeCO_3$ (siderite) or $Fe(OH)_3$ (ferric hydroxide) can be also formed in the system. To ensure the compliance with effluent standard, it was found that extra Fe^0 should have supplemented at every 27 hrs rather than every 30 hrs for safety factor consideration. As seen in Figure 4d, the supplement of 40 g fresh Fe^0 at every 27 hrs can consistently control nitrate to less than 10 mg N/L. Correspondingly, the ammonium formation was observed as the nitrate was reduced by Fe^0. In addition, the pH, DO and ORP as expressed in Figures 4a, 4b, and 4c were surprisingly steady after the Fe^0 supplement. Therefore, the supplement of Fe^0 can be successful for maintaining the effectiveness of nitrate removal. However, the optimal Fe^0 supplement in the system should be carefully investigated in view of the best marginal benefit and ferrous ion formation control. To accomplish this goal, 40 g of Fe^0 supplement can be the optimum scenario for both achieving the desired nitrate removal efficiency and controlling ferrous formation.

CONCLUSIONS

Innovative reactor was designed and investigated for removing nitrate from aqueous solution**.** The 23.5 mg-N/L of nitrate can be reduced to 2.93 mg-N/L within 2.5 hrs by using the condition as follows: 3 L/hr of the influent feeding rate, 60 g of Fe^0 dosage, and 200 mL/min of CO_2 gas inflow rate. In view of operation, measure of the optimum Fe^0 supplement needs to be taken to guarantee satisfactory nitrate removal in batch operation using the Fe^0/CO_2 process. In this study, the supplement of 40 g of Fe^0 at every 27 hrs was found to be sufficient to consistently maintain the residual nitrate at a level that complies with the drinking water quality standard.

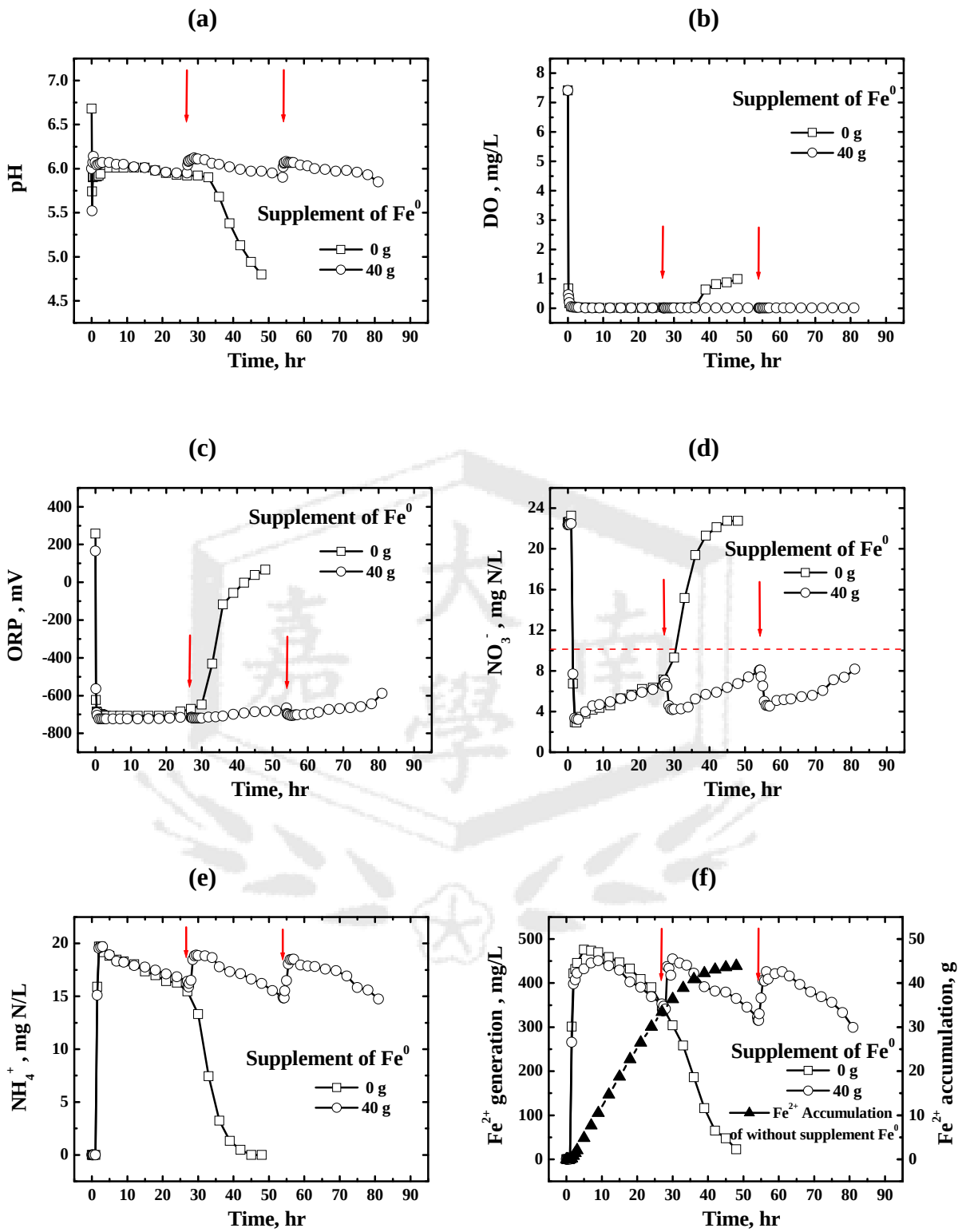

Figure 4 Effect of Fe^0 supplement on (a) pH, (b) DO, (c) ORP, (d) nitrate removal, (e) ammonium formation, (f) ferrous accumulation. The experiment was conducted under the conditions of CO_2 bubbling rate of 200 mL/min and a recirculated flow of 90 L/min. The influent nitrate concentration was 23 mg N/L. The operating mode was divided into 2 steps. Step 1: the initial Fe^0 of 60 g was tested until exhaustion, without any supplement of Fe^0. Step 2: The supplement of 40 g Fe^0 was introduced in the system at times of 27 hrs and 54 hrs, respectively.

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