



Coupled acidification and ultrasound with iron enhances nitrate reduction

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ARTICLE INFO

Article history:

Received 18 March 2008

Received in revised form 7 June 2008

Accepted 4 July 2008

Available online 12 July 2008

Keywords:

Nitrate

Passive oxide film

Zero-valent iron

pH

Ultrasound

ABSTRACT

Contaminated soils, especially when pollutant concentrations are high, pose potentially serious threats to surface and groundwater quality, when there are spills, discharges, or leaking storage tanks. For in situ remediation of nitrate in groundwater, the use of zero-valent iron (Fe^0) is suggested. The formation of passivating scales on Fe^0 over time may limit the long-term reduction potential of Fe^0 . The aim of this study was to investigate the effect of ultrasound and pH on the destruction of passive oxide film. Batch tests were conducted in a specially designed protocol using ultrasound, and changing iron (commercial iron powder of micro-scale grain size) loading and pH. The results showed deactivation of the degradation process by Fe^0 with combined ultrasound/iron system and with ultrasound alone. However, the degradation rate increases with decrease in pH. The degradation rate was 45% for pH 2 and 20% for pH 4. The combination of iron, acidification, and ultrasound showed excellent degradation efficiency, and the degradation rate was 99%. Acidification could destroy passive oxide film and activate iron, thus, hastening the reaction between Fe^0 and nitrate. Ultrasound was helpful in destroying or preventing the formation of passive oxide film under acidification.

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1. Introduction

Zero-valent iron (Fe^0) has been proposed for use for remediation of groundwater for nitrate [1–8]. Mechanisms for electrochemical reduction may involve direct electron exchange between nitrate and Fe^0 . Nitrate reduction by Fe^0 involves corrosion of iron coupled with the process of reducing nitrate. Corrosion of Fe^0 involves oxidation–reduction reactions (where $\text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2e^-$ is a primary anodic half-reaction) and coordination processes (such as hydration and dissolution of Fe^{2+}). As nitrate reduction by Fe^0 is a corrosive process, the formation of passivating scales on Fe^0 over time may limit its long-term reduction potential. Ritter et al. [9] showed that the rate of removal was so rapid that the initial presence of Fe_2O_3 at the iron surface did not affect the performance of an in situ permeable iron wall. However, the passive layer of Fe_2O_3 interferes with contaminant degradation, because it inhibits mechanisms involved in contaminant reduction, including electron transfer and catalytic hydrogenation.

Permeable reactive barriers of iron were developed as a passive, in situ treatment method for the treatment of nitrate contamination [10–12]. A commercial iron product is often used in barriers. This material is impure and is usually covered with a passive oxide film, which forms during the production of the granular iron material.

The film consists of an inner layer of Fe_3O_4 and an outer passive layer of Fe_2O_3 [13]. This passive layer should prevent the onset of mechanisms involved in contaminant treatment, including direct electron transfer and catalytic hydrogenation.

The rates of chemical reactions of Fe^0 powder are dependent on the surface concentrations of the segments such as surface sites. The surface is found to be deactivated over time because of the precipitation of iron oxides/hydroxides on the iron surface and consequent decrease of the porosity of the surface. Acid washing is an important process for removal of iron oxide on the iron surface. The reduction of nitrate by Fe^0 was proved an improvement after acid washing [14]. In addition, the solution pH is an important parameter influencing the kinetics. The NO_3^- can be reduced completely with initial pH setting with acids [4,15]. As acoustic cavitation is known to increase the active surface area of the solids by cracking the passive layer of particles, sonication in the presence of zero-valent iron has been explored for the reduction of carbon tetrachloride and nitrobenzene [16,17].

The passive oxide film on the iron surface interferes with contaminant degradation. The aims of this study were to investigate the effects of ultrasound and pH on the destruction of passive oxide film. Most previous experimental studies in this regard have been performed with relatively pure iron materials that were initially free of thick oxide films, whereas in this study, commercial iron powder of micro-scale grain size was used. This material was exposed to air and was expected to cover with a passive oxide film. Batch tests were conducted with a specially designed protocol,

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changing the iron loading, pH, and ultrasound usage. The results clarify the effect of acidification and ultrasound on the formation or destruction of the passive oxide film of iron.

2. Experimental methods and materials

2.1. Materials and analyses

Potassium nitrate (99%), H₂SO₄ (97%), and Fe powder (99%, 10 μm) were obtained from Merck KGaA (Germany). All the reagents and Fe powder were used without further purification. Solutions were prepared using water of 18.2 MΩ cm quality obtained from a Millipore-Q system. The concentrations of NO₃⁻ in the aqueous solution were measured by standard method using a Genesys 6 UV/visible scanning spectrophotometer, at 200 nm, resulting in detection limits of 0.053 mg/L for nitrate. The pH was measured using a Suntext TS-1 pH meter.

2.2. Batch tests

To investigate the effects of ultrasound and pH on destroying the passive oxide film of iron particle, batch experiments were conducted in capped 40 mL glass vials. Six series of batch tests with different iron loadings and pH values were designed for this study (Table 1).

Iron powder of known weight was placed in a 40 mL glass vial. The test solutions, with an initial NO₃⁻ concentration of 100 mg/L, were acidified to be pH 2 and 4 using H₂SO₄ for acid batch tests. The bottle was filled with the solution, and the vial capped. Vials of each batch, tested with ultrasound, were immediately placed in a D150h ultrasonic tank (150 W, 43 kHz, Delta Instrument Co., Taiwan) at a controlled temperature of 10 °C. Obtaining a clear sample is important for optical analysis by UV/visible spectrophotometer. For this, the glass vial was placed over a square magnet (10 cm long by 10 cm wide by 1 cm high) to rapidly condense the iron powder at the bottom of the vial. Clear samples (5 ml) were withdrawn into centrifuge vials using a glass syringe at the setting times. The centrifuge (Kubota KN-70, Double Eagle Enterprise Co. Ltd., Taiwan)

was used at 3000 rpm for 30 min to remove residual solid products. The solution samples were then analyzed within 6 h.

3. Results and discussion

3.1. Effect of pH on nitrate reduction

Fig. 1 shows the changes in pH over time for the batch tests of initial pH 2 and 4 together with the results of no pH adjustment. In the experiments without acidification, the initial pH values were 6.12 and thereafter maintained at around 6. In the reduction process by Fe⁰, alkalinity can be achieved from reduction of NO₃⁻ by Fe⁰ as well as corrosion of Fe, as shown in the following equations:



Hence, minor changes in pH indicate that the chemical reduction process by Fe⁰ did not progress significantly. The reason for this is that the passive layer prevented the reduction process, including direct electron transfer and catalytic hydrogenation. Fig. 2 also indicates the same phenomenon; the dimensionless concentrations (C/C₀) of nitrate remained around 1.0 during the test time of 4 h for all the batch tests without acidification.

Fig. 1(a), (c), and (e) shows different results when the NO₃⁻ solution was acidified such that the pH 2. BT052-2, BT102-2, and BT202-2 show that the pH rose slowly from an initial value of 2.0–3.77, 3.42, and 3.83 for iron loadings of 0.5 g/40 mL, 1.0 g/40 mL, and 2.0 g/40 mL, respectively. Besides, Fig. 1(b), (d), and (f) shows change in pH when the NO₃⁻ solution was acidified such that the pH 4. BT054-2, BT104-2, and BT204-2 show that the pH rose rapidly from an initial value of 4.0 to greater than 10.0 for iron loadings of 0.5 g/40 mL, 1.0 g/40 mL, and 2.0 g/40 mL. These results were obtained by coupling acidification with Fe⁰ without ultrasound. Accordingly, it was proved that OH⁻ was produced obviously in the chemical reduction of NO₃⁻ by Fe⁰ under low pH conditions. The pH of the solution is an important parameter in the reduction process by Fe⁰ [4].

Table 1
Six series of batch tests for different iron loadings and pH values

Reference ID	Iron	Acid adding	Ultrasound	Reference ID	Iron	Acid adding	Ultrasound
Initial condition: 0.5 g Fe/40 ml solution, pH 2				Initial condition: 0.5 g Fe/40 ml solution, pH 4			
BT052-1	Yes	Yes	Yes	BT054-1	Yes	Yes	Yes
BT052-2	Yes	Yes	No	BT054-2	Yes	Yes	No
BT052-3	Yes	No	Yes	BT054-3	Yes	No	Yes
BT052-4	Yes	No	No	BT054-4	Yes	No	No
BT052-5	No	Yes	Yes	BT054-5	No	Yes	Yes
BT052-6	No	Yes	No	BT054-6	No	Yes	No
BT052-7	No	No	Yes	BT054-7	No	No	Yes
Initial condition: 1.0 g Fe/40 ml solution, pH 2				Initial condition: 1.0 g Fe/40 ml solution, pH 4			
BT102-1	Yes	Yes	Yes	BT104-1	Yes	Yes	Yes
BT102-2	Yes	Yes	No	BT104-2	Yes	Yes	No
BT102-3	Yes	No	Yes	BT104-3	Yes	No	Yes
BT102-4	Yes	No	No	BT104-4	Yes	No	No
BT102-5	No	Yes	Yes	BT104-5	No	Yes	Yes
BT102-6	No	Yes	No	BT104-6	No	Yes	No
BT102-7	No	No	Yes	BT104-7	No	No	Yes
Initial condition: 2.0 g Fe/40 ml solution, pH 2				Initial condition: 2.0 g Fe/40 ml solution, pH 4			
BT202-1	Yes	Yes	Yes	BT204-1	Yes	Yes	Yes
BT202-2	Yes	Yes	No	BT204-2	Yes	Yes	No
BT202-3	Yes	No	Yes	BT204-3	Yes	No	Yes
BT202-4	Yes	No	No	BT204-4	Yes	No	No
BT202-5	No	Yes	Yes	BT204-5	No	Yes	Yes
BT202-6	No	Yes	No	BT204-6	No	Yes	No
BT202-7	No	No	Yes	BT204-7	No	No	Yes

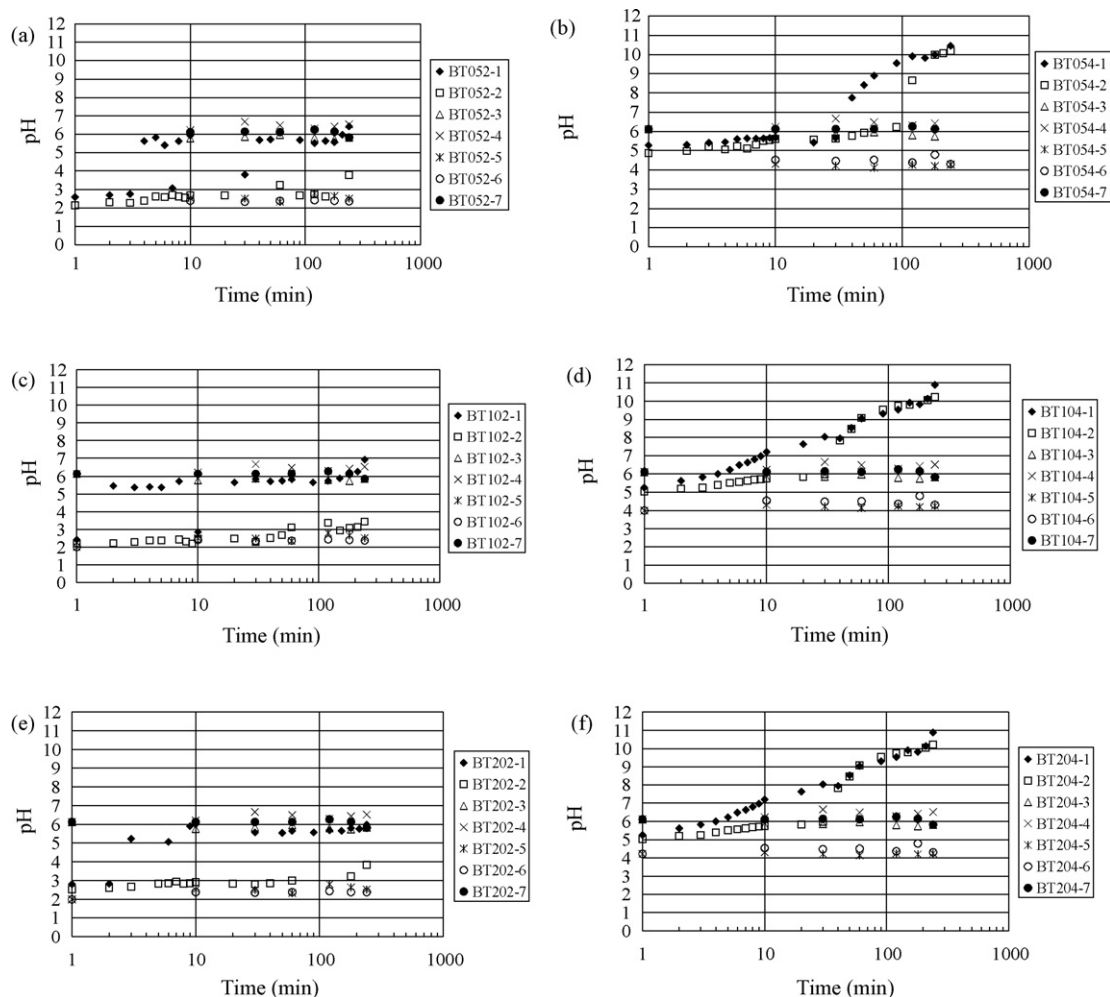


Fig. 1. Change in pH over time for initial condition: (a) 0.5 g Fe/40 ml solution, pH 2.0; (b) 0.5 g Fe/40 ml solution, pH 4.0; (c) 1.0 g Fe/40 ml solution, pH 2.0; (d) 1.0 g Fe/40 ml solution, pH 4.0; (e) 2.0 g Fe/40 ml solution, pH 2.0; (f) 2.0 g Fe/40 ml solution, pH 4.0 (initial nitrate concentration = 100 mg/L for every case).

In Fig. 2(a), (c), and (e), BT052-2, BT102-2, and BT202-2 shows the changes in NO_3^- concentration under pH 2 for the iron loadings of 0.5 g/40 mL, 1.0 g/40 mL, and 2.0 g/40 mL, respectively. For BT052-2, the NO_3^- concentration decreased slowly and the degradation rate was 13% after 4 h. For BT102-2 and BT202-2, the NO_3^- concentrations decreased rapidly and the degradation rates were 45% and 34% after 4 h, respectively. The degradation rate increased significantly when the iron loading was increased. In the tests of pH 4 batch, BT054-2, BT104-2, and BT204-2 show that the degradation rates of nitrate by Fe^0 were 7%, 20%, and 20%, respectively. The degradation rate also increased when the iron loading was increased. From a comparison of the results of degradation rate of the samples of pH 4 batch with those of pH 2 batch, it can be seen that the lower pH condition evidently leads to a greater degradation rate in the reduction process by Fe^0 . Therefore, it is reasonable to expect that the H_2SO_4 added can destroy passive oxide film and activate the iron, thereby hastening the reaction between Fe^0 and nitrate.

3.2. Effect of ultrasound on nitrate reduction

In addition to the tests with acidification, experiments were performed with iron alone, ultrasound alone, and combined ultrasound/iron system, to investigate the effect of sonication on the chemical reduction of NO_3^- by Fe^0 . In Fig. 2(a), BT052-3 and BT052-7 shows changes in NO_3^- concentration after being tested with

combined ultrasound/iron system and ultrasound alone, respectively. For the initial iron loading of 0.5 g/40 mL, the concentration of nitrate remained almost the same during the 4 h of the experiment. Even when the iron loadings were increased to 1.0 g/40 mL and 2.0 g/40 mL, there was no change in the concentration of nitrate (BT102-3, BT102-7, BT202-3, and BT202-7 in Fig. 2(c) and (e)). The maximum degradation rate was 3% both for ultrasound alone and for the combined ultrasound/iron system. The variations in pH for the corresponding tests (Fig. 1) also indicate deactivation of the degradation process by Fe^0 during the experiment. This indicates that ultrasound could not degrade the nitrate. Also, ultrasound could not destroy passive oxide film of iron or help the chemical reduction process by iron. Zhang et al. [18] reported that ultrasound (250 W and 30 kHz in power and frequency) enhanced the reduction of C.I. Acid Orange 7 by Fe^0 and that it caused pitting and cracking of the metal surface, thus, increasing the rate of degradation. However, pitting and cracking were not observed in this study. The power and frequency of ultrasound generator used here was 150 W and 43 kHz. Perhaps, the less power used here rendered ultrasound incapable of cracking the passive film of iron particles.

3.3. Effect of coupling ultrasound and pH on nitrate reduction

In Fig. 2(a), (c), and (e), BT052-1, BT102-1, and BT202-1 present the changes in NO_3^- concentration for tests of batch pH 2 involving

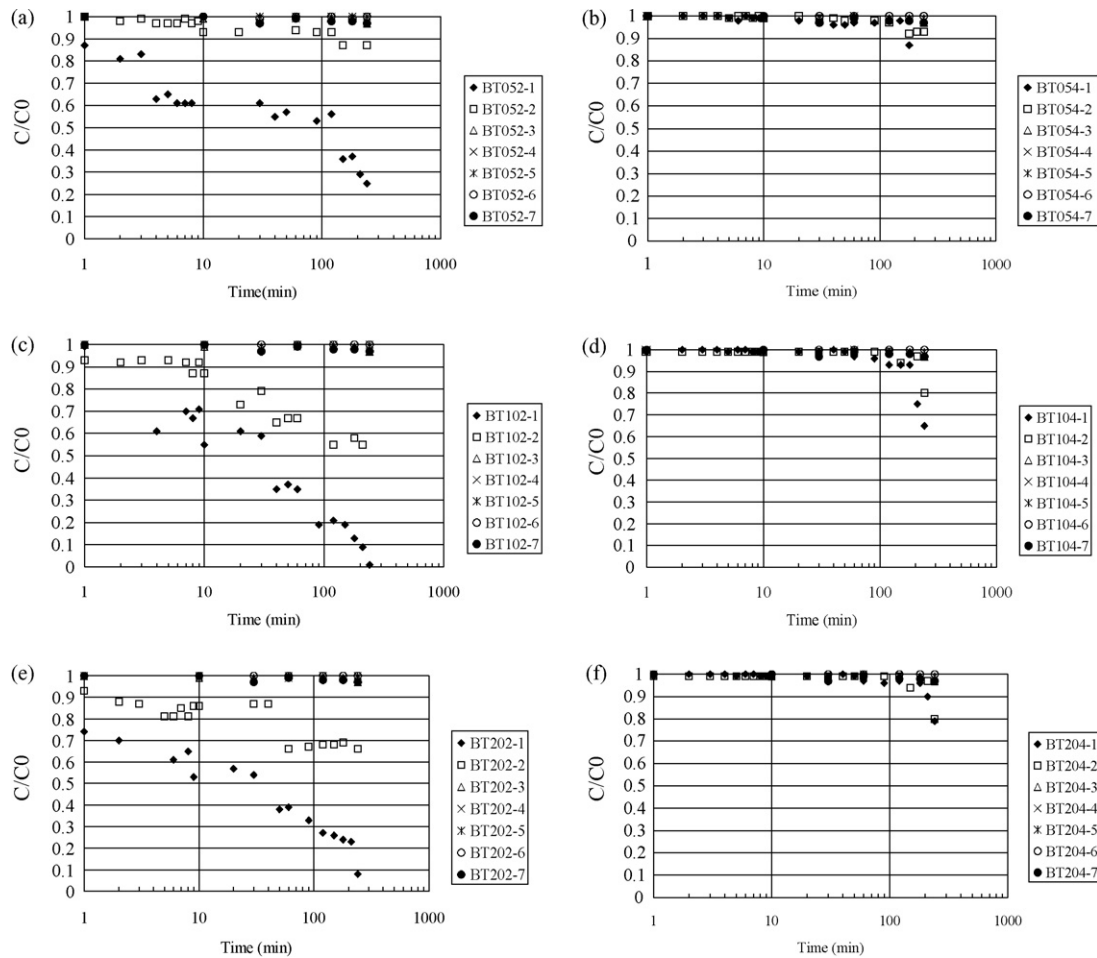


Fig. 2. Change in NO_3^- concentration over time for initial condition: (a) 0.5 g Fe/40 ml solution, pH 2.0; (b) 0.5 g Fe/40 ml solution, pH 4.0; (c) 1.0 g Fe/40 ml solution, pH 2.0; (d) 1.0 g Fe/40 ml solution, pH 4.0; (e) 2.0 g Fe/40 ml solution, pH 2.0; (f) 2.0 g Fe/40 ml solution, pH 4.0 (initial nitrate concentration = 100 mg/L for every case).

a combination of ultrasound and acidification with iron. In these tests, NO_3^- concentration decreased rapidly with time. The degradation rates of nitrate by Fe^0 were 37%, 47%, and 75% at 4 min, 90 min, and 240 min, respectively for BT052-1. However, the corresponding figures without ultrasound were 3%, 7%, and 13%. In Fig. 1(a), BT052-1 and BT052-2 show a higher rise in pH when ultrasound and acidification were combined. This suggests that ultrasound possibly aids acid in destroying passive oxide, although ultrasound by itself cannot destroy passive oxide. Alternatively, the vibrations caused by ultrasound could have prevented the formation of passive oxide films on the iron particles. Both mechanisms are helpful in increasing the degradation efficiency.

On increasing the iron loading to 1.0 g/40 mL, BT102-1 shows a higher degradation rate than that of BT052-1. For BT102-1, the degradation rates of nitrate by Fe^0 were 39%, 81%, and 99% at 4 min, 90 min and 240 min, respectively. The combination of iron, acidification, and ultrasound also showed an excellent degradation rate in comparison to that of the tests conducted with the combination of acidification and iron. The degradation rate rose from 45% to 99% when the ultrasound was used. Moreover, Fig. 1(c) shows that the pH of BT102-1 also rose rapidly from the initial value of 2 to around 7 after 4 h, which is better than that of BT102-2. The tests for iron loading of 2 g/40 mL showed a greater degradation rate after the first few minutes than that shown by the tests for loading of 1 g/40 mL. However, the final degradation rate was only 92%, that is, less than that of 1 g/40 mL. In addition, the tests without ultrasound also showed the same phenomenon. The degradation rates

of 4 h for iron loading of 1 g/40 mL and 2 g/40 mL were 45% and 34%, respectively.

In Fig. 2(b), (d), and (f), BT054-1, BT104-1, and BT204-1 present the changes in NO_3^- concentration for the tests of pH 4 batch by combining ultrasound and acidification with iron. The NO_3^- concentration decreased slowly with time in these tests. The degradation rates of nitrate by Fe^0 for BT054-1 were 1%, 3%, and 13% at 5 min, 90 min, and 240 min, respectively. However, for tests without ultrasound, the corresponding rates were 1%, 2%, and 7%. In Fig. 1(b), BT054-1 and BT054-2 show a rapid rise in pH for both with and without ultrasound.

On increasing the iron loading to 1.0 g/40 mL, BT104-1 shows a higher degradation rate than that of BT054-1. For BT104-1, the degradation rates of nitrate by Fe^0 were 1%, 6%, and 20% at 5 min, 150 min, and 240 min, respectively. The combination of iron, acidification, and ultrasound also showed a higher degradation rate in comparison to the tests conducted with a combination of acidification and iron. The degradation rate rose from 7% to 20% when ultrasound was used. Moreover, in Fig. 1(d), the pH of BT104-1 and BT104-2 also rose rapidly from the initial value of 4 to over 10 after 4 h. The tests of iron loading of 2 g/40 mL showed that the tests without ultrasound also presented a lower NO_3^- degradation rate in reduction process by Fe^0 .

From the results of batch tests conducted with a combination of acidification and ultrasound with iron, it is clear that low pH conditions can increase the degradation rate of nitrate by Fe^0 . This is because H^+ could possibly crack the passive oxide on the

surface of iron particles, thus, increasing the area of reaction surfaces on the iron particles. Besides, in the reduction process of low pH, ultrasound may either enhance the effect of cracking on the surface of iron particles or prevent the formation of passive oxide by high-frequency vibrations.

4. Conclusions

After performing a series of batch tests and comparing the results obtained thereby, the following conclusions are drawn:

- Because of passive oxide films on the surface of iron particles, commercial iron powder did not apparently show any NO_3^- degradation when used alone.
- Ultrasound by itself could not degrade NO_3^- ; similarly, when used with iron, it could not enhance the degradation efficiency.
- H^+ could destroy passive oxide films on the surface of iron particles and thus, increase the area of reaction sites on iron particles. The lower the pH of solution, the higher is the degradation rate.
- The ultrasound could crack passive oxide films on the surface of iron particles, and thus, increase the area of reaction sites on the iron particles. In the reduction process with low pH, ultrasound may either enhance the effect of cracking on the surface of iron particles or prevent the formation of passive oxide films by high-frequency vibrations.
- The optimum method to enhance the degradation efficiency of commercial iron powder in NO_3^- degradation is coupling acidification and ultrasound with iron.

Acknowledgments

The authors thank the Diwan University, Taiwan for financially supporting this research under Contract No. DWU95C31 and DWU96C30.

References

- [1] L.L. Zawaideh, T.C. Zhang, The effects of pH and addition of an organic buffer (HEPES) on nitrate transformation in Fe^0 -water systems, *Water Sci. Technol.* 38 (1998) 107–115.

- [2] A. Rahman, A. Agrawal, Reduction of nitrate and nitrite by iron metal: implications for ground water remediation, in: ACS National Meeting, San Francisco, CA. Extended Abstract–Division of Environmental Chemistry 37, 1997, pp. 157–158.
- [3] F. Cheng, R. Muftikian, Q. Fernando, N. Korte, Reduction of nitrate to ammonia by zero-valent iron, in: ACS National Meeting, San Francisco, CA. Extended Abstract–Division of Environmental Chemistry 37, 1997, pp. 165–166.
- [4] F. Cheng, R. Muftikian, Q. Fernando, N. Korte, Reduction of nitrate to ammonia by zero-valent iron, *Chemosphere* 35 (1997) 2689–2695.
- [5] D.P. Siantar, C.G. Schreier, M. Reinhard, Transformation of the pesticide 1,2-dibromo-3-chloro propane (DBCP) and nitrate by iron powder and by $\text{H}_2/\text{Pd}/\text{Al}_2\text{O}_3$. Preprint extended abstract, Division of Environmental Chemistry, Am. Chem. Soc., Anaheim, CA, 209: 150-ENVR Part 1, April 2–7, 1995. Stumm, W., Morgan.
- [6] C.P. Huang, H.W. Wang, P.C. Chiu, Nitrate reduction by metallic iron, *Water Res.* 32 (1998) 2257–2264.
- [7] S. Choe, Y.Y. Chang, K.Y. Hwang, J. Khim, Kinetics of reductive denitrification by nanoscale zero-valent iron, *Chemosphere* 41 (2000) 1307–1311.
- [8] S. Jin, P.C. Chiu, Nitrate reduction by zero-valent iron, in: Proceedings of the Mid-Atlantic Industrial Waste Conference, 1999, pp. 240–247.
- [9] K. Ritter, M.S. Odziemkowski, R.W. Gillham, An in situ study of the role of surface films on granular iron in the permeable iron wall technology, *J. Contam. Hydrol.* 55 (2002) 87–111.
- [10] P.G. Tratnyek, T.L. Johnson, M.M. Scherer, G.R. Eykholt, Remediating ground water with zero-valent metals: chemical considerations in barrier design, *Groundwater Monit. Remediat.* 17 (1997) 108–114.
- [11] C.F. Chew, T.C. Zhang, In situ remediation of nitrate-contaminated groundwater by electrokinetic/iron wall processes, *Water Sci. Technol.* 38 (1998) 135–142.
- [12] L.A. Schipper, M. Vojvodić-Vuković, Nitrate removal from groundwater and denitrification rates in a porous treatment wall amended with sawdust, *Ecol. Eng.* 12 (2000) 269–278.
- [13] M.S. Odziemkowski, L. Gui, R.W. Gillham, D.E. Irish, The role of oxide films in the reduction of nitrosodimethylamine with reference to the iron groundwater remediation technology, in: K.R. Hebert, R.S. Lillard, B.R. MacDougall (Eds.), *Oxide Films, Proceedings of the International Symposium, The Electrochemical Society, Pennington, NJ, 2000–2004*, pp. 357–368.
- [14] P. Westerhoff, Reduction of nitrate, bromate, and chlorate by zero-valent iron (Fe^0), *J. Environ. Eng.* 129 (2003) 10–16.
- [15] S. Choe, H.M. Liljestrandb, J. Khim, Nitrate reduction by zero-valent iron under different pH regimes, *Appl. Geochem.* 19 (2004) 335–342.
- [16] H.M. Hung, F.H. Ling, M.R. Hoffmann, Kinetics and mechanism of the enhanced reductive degradation of nitrobenzene by elemental iron in the presence of ultrasound, *Environ. Sci. Technol.* 34 (2000) 1758–1763.
- [17] E.J. Weber, Iron-mediated reductive transformation: investigation of reaction mechanism, *Environ. Sci. Technol.* 30 (1996) 716–719.
- [18] H. Zhang, L. Duan, Y. Zhang, F. Wu, The use ultrasound to enhance the decolorization of the C.I. Acid Orange 7 by zero-valent iron, *Dyes Pigments* 65 (2005) 39–43.