

Experimental Evaluation of Nitrate Reduction from Water Using Synthesis Nanoscale Zero-Valent Iron (NZVI) under Aerobic Conditions

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Abstract: The aim of this research was to study the potential of synthesized nanoscale zero-valent iron for nitrate reduction in aqueous solution. Batch technique was used to determine the kinetics and effective parameters. The effects of initial pH level, initial nitrate concentration and nanoscale Fe⁰ concentration on nitrate reduction were studied. Nanoscale zero-valent iron was synthesized by chemical reduction method. The TEM image showed that synthesized nano Fe⁰ has a size in the range of 40-120 nm. Experimental results exhibited that reduction efficiency of nitrate decreases with increasing initial pH and increases significantly due to increasing the concentration of zero-valent iron nanoparticles. Also, it was illustrates that initial concentration of nitrate has little effect on the nitrate reduction efficiency. Under acidic and neutral conditions, pH level of the reaction solution increased considerably after 60 min. However, under alkaline conditions, pH level of the reaction solution decreased. The reduction rate of nitrate reached 80% in 60 min with nanoscale Fe⁰ dosage of 1.0 gl⁻¹ and pH_m4. The observed reaction rate constant was determined to be 0.0255 min⁻¹ for nanoscale concentration 1.0 gl⁻¹. The experimental results indicated that the nitrate reduction with zero-valent iron nanoparticles do not comply the first-order reaction model with respect to nitrate concentration.

Key words: Nitrate reduction • Zero-valent iron • Nanoparticles

INTRODUCTION

Contamination of surface water and groundwater to nitrate has become an increasingly serious environmental problem [1, 2]. Nitrogen compounds accumulate in environment from various sources including industrial waste water, nitrogenous fertilizers, animal manure, septic waste and atmospheric deposition from nitrogen oxide emission [3]. Increase in level of nitrate concentration in drinking water can cause serious health problem. In infants NO₃ is reduced to NO₂, which combine with hemoglobin in the blood to form methemoglobin leading to cyanosis in babies under six month old, particularly [3]. Many countries have limited the concentration of nitrate in their drinking water. The US, EPA has recommended a maximum level (MCL) of 10

mg/L NO₃-N for drinking water [4]. Current practice is to use ion exchange, reverse osmosis, biological denitrification and chemical reduction to remove nitrate from water.

Among different water treatment methods, nano zero-valent iron has a good potential to remove nitrate. Researchers have studied the use of zero-valent iron in halogenated organics, azoaromatics, nitro aromatics and the treatment of different types of compounds such as inorganic compounds like heavy metals [5]. Previous researches have indicated that nitrate could be completely reduced by metallic iron under anoxic and aerobic conditions [1, 6, 7].

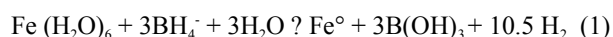
Nano zero-valent iron has high specific surface area, high active surface, easily being scattered which increases denitrification rate of nitrate [1]. In this study

the parameters which contribute to effective nitrate reduction using synthesis iron nanoparticles and the kinetics of reductive denitrification of nitrate have been investigated. These parameters include pH, concentration of both nanoscale Fe⁰ and nitrate. The aim of this research was to study the potential of synthesized Nanoscale zero-valent iron for nitrate reduction in aqueous solution.

MATERIAL AND METHODS

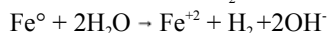
Chemicals: The chemicals were used in this study purchased from Merck Company which include: NaBH₄ (for synthesis), FeSO₄.7H₂O (98%), Methanol (99%), NaOH (99%), H₂SO₄ (98%), KNO₃ (98%). Nitrate reagent (Nitrawer 5) was purchased from Hach Company.

Synthesis of Nanoscale Fe⁰: In a typical synthesis of higher surface Fe⁰ nanoparticles, 4.0 g of FeSO₄.7H₂O was dissolved in 200 mL of 30% methanol and 70% de-ionized water (v/v). The pH was adjusted to about 6.8 by 3.8 M NaOH [8]. Then 1.5 g of NaBH₄ powder was dissolved in 10 mL de-ionized water and the solution was added incrementally to the mixture in ultrasonic shaker at 25°C temperature for about 45 min. After addition of all of the NaBH₄ solution, the mixture was stirred in jar test at a mixing rate 250 rpm for another 45 min and then centrifuged for 15 min at 5000 rpm. The solid particles were washed at least three times with methanol and then dried for 6 hours under vacuum condition. They were then broken up with a spatula and immediately added to the aqueous solution to react with nitrate. The ferrous iron was reduced to zero-valent iron according to the following reaction (Eq. 1) [9]:

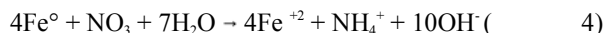


Chemical Reduction of Nitrate by Zero-Valent Iron Nanoparticles: For each set of experiments, 500 cc of aqueous nitrate solution at an arbitrary concentration of nitrate (30, 50 mg/l NO₃-N) and desired initial pH (4, 7, 10) was first put in a glass beakers and freshly prepared zero-valent iron nanoparticles of a selected concentration (e.g 1 g/l, 0.5 g/l or 0.2 g/l) were added. The solution was then simultaneously mixed using a jar test apparatus at a mixing rate of 300 rpm. The glass beakers were removed one by one from the jar test apparatus at intervals of 10, 20, 30 and 60 min. Periodically 20 ml of the aqueous solution passed through a 0.45 μm membrane filter to separate iron nanoparticles. The concentrations of residual nitrate in aqueous solution (NO₃⁻) were detected by Spectrophotometer (VIS DR2800, Hach).

Mechanism of Denitrification by Fe⁰: In aqueous systems, zero-valent iron (Fe⁰) is oxidized to ferrous ion (Fe⁺²) by nitrate and many substances [3]. Under anaerobic condition, H⁺ is the only electron acceptor that will be involved in the reaction. Therefore, the overall process of corrosion in anaerobic Fe⁰-H₂O system is described by Eq. 2 [6]. But under aerobic conditions dissolved oxygen would play a role of the electron acceptor in the cathodic half-reaction. In this case, the primary reaction yields only OH⁻ and not H₂ as shown by Eq. 3 [3, 10, 11].



The reaction and its mechanism between nitrate and ZVI is a true redox reaction [3]. Several studies have indicated the final products of denitrification by zero-valent iron nanoparticles could be N₂ or NH₃ depending on the experimental conditions [6, 7, 11]. But certainly, the main product of this reaction is ammonium as shown in Eq. 4 [7].



RESULTS AND DISCUSSION

Characterization of Iron Nanoparticles: The size of iron nanoparticle were determined using transmission electron microscopy (TEM), manufactured by PHILIPS (EM208 S), with an acceleration voltage of 100 kV. Fig. 1 shows TEM image of the synthesized nanoscale Fe⁰. The particles were ranging from 40 to 120 nm.

Effect of NO₃⁻ Concentration on Nitrate Reduction by Nano Zero-valent Iron: To study the kinetics of denitrification by zero-valent iron nanoparticles, two different initial nitrate concentrations 30 mg/l and 50 mg/l NO₃-N were tested. Fig. 2(a) shows the effect of nitrate concentration on nitrate reduction by nanoscale Fe⁰ when the initial pH was in acidic range. The nitrate reduction (in percentage) for 30 mg/l and 50 mg/l NO₃-N increased to 66.5% and 65.7%, respectively, after 10 min. After this, nitrate reduction increased slightly such that after 60 min the reduction reached to 78.3% (6.5 mg/l NO₃-N) and 79.98% (10.01 mg/l NO₃-N), respectively, for 30 mg/l and 50 mg/l NO₃-N.

From experimental data, kinetic constant rate, K_{obs}, was estimated from Eq. 5 [7], which would be the slope of the regression lines when data are plotted in natural log (Fig. 2b):

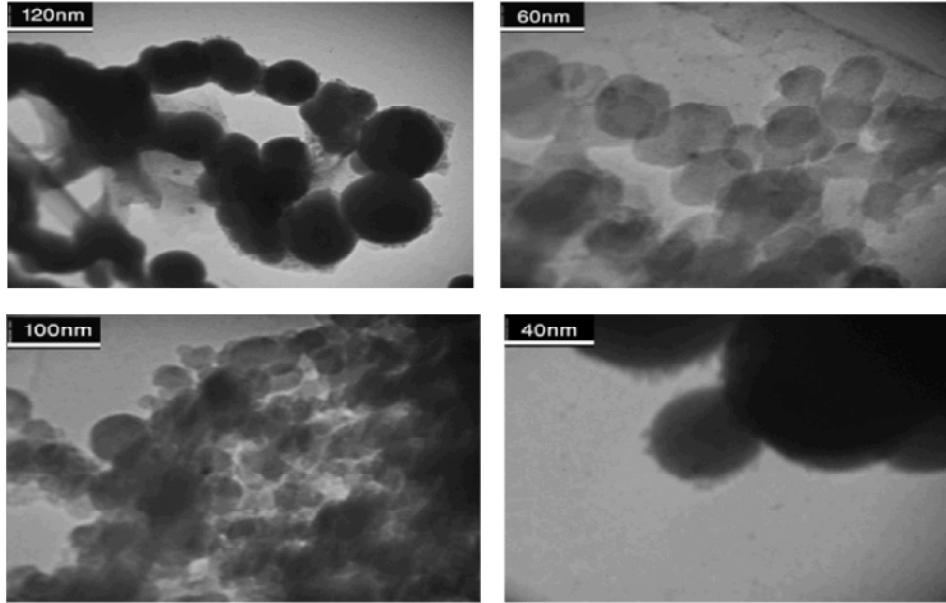


Fig. 1: TEM images of synthesized nanoscale Fe° particles.

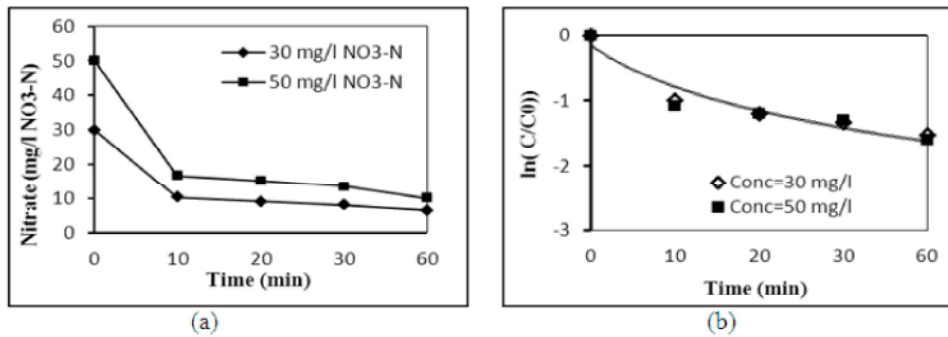


Fig. 2: Effect of NO₃⁻ concentration on nitrate reduction by nanoscale Fe°, T=20°C, Fe°= 1g/L, pH=4.

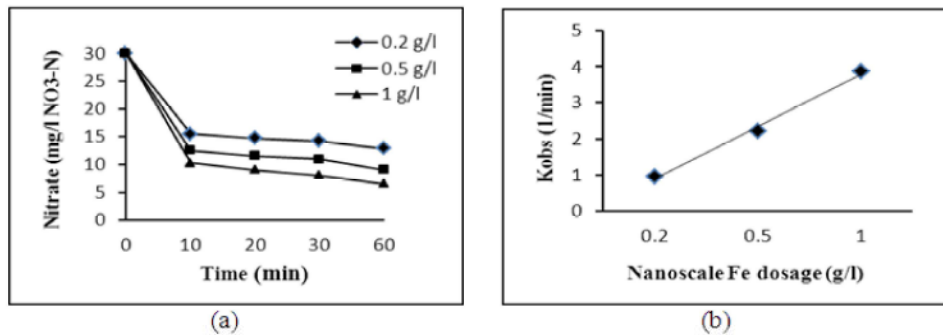


Fig. 3: Effect of Fe° dosage on nitrate reduction by nanoscale Fe°, T=20°C, pH_{in}= 4, C₀=30 mg/l NO₃-N, at 300 rpm.

$$R = -d[\text{NO}_3^-]/dt = K_{\text{obs}} [\text{NO}_3^-] \quad (5)$$

The estimated values of K_{obs} in spite of different initial nitrate concentrations, were ranging from 0.025 min⁻¹ to 0.026 min⁻¹. This implies that initial concentration

of nitrate has little effect on K_{obs}. Fig. 2(b) shows that the data are not well fit to the first order model and a second order model is needed to describe kinetic of the reaction. Similar results were founded by Liou *et al.* [12] and Chen *et al.* [13].

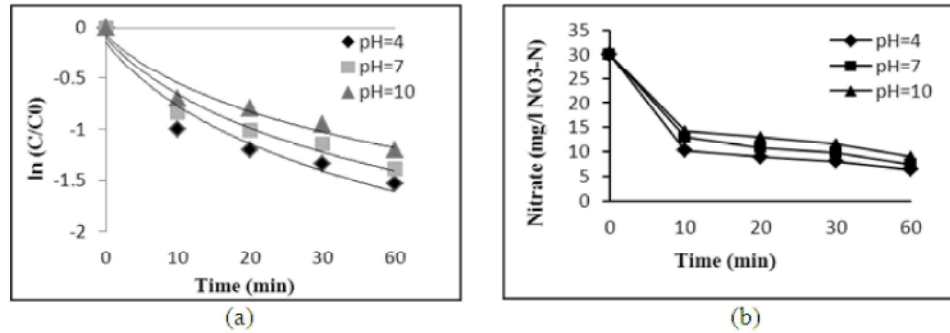


Fig. 4: Effect of initial pH on nitrate reduction by nanoscale Fe⁰, T=20°C, Fe⁰= 1g/L, C₀=30mg/l NO₃-N, stirring at 300 rpm.

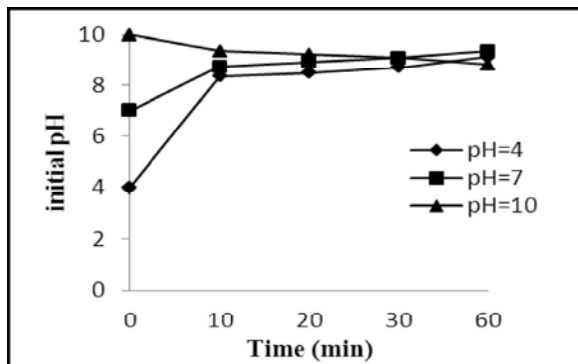


Fig. 5: pH variation during reaction of nitrate by nanoscale Fe, T=20°C, Fe⁰= 1 g/L, C₀=30 mg/l NO₃-N, stirring at 300 rpm.

Effect of Fe⁰ Dosage on Nitrate Reduction by Nano Zero-Valent Iron: Fe⁰ concentration is a significant variable in nitrate reduction by nanoscale Fe⁰. Since denitrification of nitrate by Fe⁰ nanoparticles engages reaction at the metal surface, it was anticipated that the quantity of metal surface area should considerably affect the efficiency of nitrate reduction [12]. In this study three different dosage 0.2 g/l, 0.5 g/l and 1 g/l of nanoscale Fe⁰ was used. As shown in Fig.3 (a), when the concentration of nanoparticles increases, the reduction efficiency of nitrate is increased too. For 0.2 g/l Fe⁰, after 60 min nitrate reduction efficiency reaches 57% and further increase of nanoparticles Fe⁰ to 0.5 mg/l and 1 mg/l, increase the reduction efficiency to 70% and 80%, respectively. Fig. 3(b) also shows a first-order dependence of nitrate reduction on Fe⁰ concentration. It is shown that K_{obs} increases from 0.9 min⁻¹ to 3.87 min⁻¹ when Fe⁰ increases from 0.2 g/l to 1 g/l, presumably because the reaction Fe⁰ site concentration increases with increasing Fe⁰ concentration. Therefore, the relationship between nanoscale Fe⁰ and K_{obs} could be described by a first order kinetic model. A similar behavior

was also reported by Zhang *et al.* [1], Yang and Lee [3] and Choe *et al.* [7].

Effect of Initial Ph Level on Nitrate Reduction by Nanoscale Fe⁰:

Three different pH levels viz., 4, 7, 10 were tested to investigate the effects of pH on nitrate reduction efficiency using nanoscale Fe⁰. Fig. 4(a) shows that initial pH level has a negative impact on the reduction of nitrate. It also illustrates that with rising initial pH from 4 to 10, the reduction efficiencies became lower and lower. When the initial pH was 4, about 80% of nitrate was reduced in 60 min, while the reduction efficiencies dropped to 70 and 64% for initial pH levels 7 and 10, respectively. This suggests that acidic condition could be favorable in the reaction of nitrate using zero-valent iron nanoparticles. Fig. 4(b) shows that relationship between initial pH levels and $\ln(C/C_0)$ could not be explained by the first order reaction model and the data well fit to second-order reaction model. It could be seen that K_{obs} values declines as pH increases. In fact, at lower pH, ferrous hydroxide and other protective layers that deposited on the iron nanoparticles during reaction would dissolve away at the surface of Fe⁰ nanoparticles which causes more fresh reactive sites for chemical reduction of nitrate. Therefore, according to the experimental results, in general, the efficiency of nitrate reduction by zero-valent iron nanoparticles increases as pH decreases. This is also in agreement with those reported by Choe *et al.* [1], Yang and Lee [3], Hu *et al.* [14], Chen *et al.* [13] and Zhang *et al.* [5].

pH Variation During Reaction of Nitrate by Nanoscale Fe⁰:

Fig. 5 shows pH variation during the reaction time. It shows when initial pH adjusted to 4 and 7, pH level of the reaction solution after 60 min reaches to 9.1 and 9.4, respectively. This is due to OH⁻ release during the chemical reaction. However, when initial pH adjusted to

10, pH level of the reaction solution after 60 min reaches to 8.8. Presumably, this is due to formation of hydroxide immediately after addition of OH⁻ which has led to decrease the OH⁻ in the reaction solution and drops secondary pH.

CONCLUSIONS

The results of this study showed that the synthesized zero-valent iron nanoparticles had a good potential to remove nitrate under acidic conditions. Low pH level during the reaction hastened the reduction rate of nitrate and the lower the pH the better the reduction efficiency. The dose of zero-valent iron nanoparticles is one of the most crucial factors to reduce nitrate. For 1 g/L Fe⁰, after 60 min the reaction rate and efficiency reached their maximum level and this follow a first order kinetic model. For similar concentration of nanoparticles, the reaction rate would increase slightly with an increase in initial nitrate concentration. Under acidic and neutral conditions, pH level of the reaction solution increased during the course of the experiments, but under alkaline conditions pH level of the reaction solution fell. Excluding the effect of nano zero-valent iron concentration the kinetic model of reaction in batch studies can be described by second order reaction model.

REFERENCES

1. Zhang, J., Z. Hao, Z. Zhang, Y. Yang and X. Xu, 2010. Kinetics of nitrate reductive denitrification by nanoscale zero-valent iron, *Process Saf and Environ Prot.*, 88(6): 439-445.
2. Su, C. and R.W. Puls, 2004. Nitrate reduction by zerovalent iron: Effects of formate, oxalate, citrate, chloride, sulfate, borate and phosphate, *Environ. Sci. Technol.*, 38(9): 2715-2720.
3. G.C.C. Yang and H.L. Lee, 2005. Chemical reduction of nitrate by nanosized iron: kinetics and pathways, *Water res.*, 39(5): 884-894.
4. G.C.C. Yang, C.H. Hung and H.C. Tu, 2008. Electrokinetically enhanced removal and degradation of nitrate in the subsurface using nanosized Pd/Fe slurry, *J Environ Sci Health a.*, 43(8): 945-951.
5. Zhang, X., S. Lin, X.Q. Lu and Z. Chen, 2010. Removal of Pb (II) from water using synthesized kaolin supported nanoscale zero-valent iron, *Chem Eng Journal.*, 163(3): 243-248.
6. Agrawal, A. and P.G. Tratnyek, 1995. Reduction of nitro aromatic compounds by zero-valent iron metal, *Environ. Sci. Technology*, 30(1): 153-160.
7. Choe, S., Y.Y. Chang, K.Y. Hwang and J. Khim, 2000. Kinetics of reductive denitrification by nanoscale zero-valent iron, *Chemosphere*, 41(8): 1307-1311.
8. Kassae, M., E. Motamedi, A. Mikhak and R. Rahnemaie, 2011. Nitrate removal from water using iron nanoparticles produced by arc discharge vs. reduction, *Chem Eng Journal.*, 166: 490-495.
9. Huang, Y., K. Tan, Q. Tang, F. Liu and D. Liu, 2010. Removal of As (III) and As (V) from drinking water by nanoscale zero-valent iron, *International Conference on Challenges in Environmental Science and Computer Engineering*, 20: 111-114.
10. Lu., M., J. Anotai, C. Liao and W. Ting, 2004. Dechlorination of hexachlorobenzene by zero-valent iron, *Pract. Period. Hazard. Toxic Radioact. Waste Manage.*, 8(2): 136-140.
11. Li, C.W., Y.M. Chen and W.S. Yen, 2007. Pressurized CO₂/zero valent iron system for nitrate removal, *Chemosphere*, 68(2): 310-316.
12. Liou, Y.H., S.L. Lo, C.J. Lin, W.H. Kuan and S.C. Weng, 2005. Chemical reduction of an unbuffered nitrate solution using catalyzed and uncatalyzed nanoscale iron particles, *J Hazard Mater.*, 127(1): 102-110.
13. Chen, Y.M., C.W. Li and S.S. Chen, 2005. Fluidized zero valent iron bed reactor for nitrate removal, *Chemosphere*, 59(6): 753-759.
14. Hu, H.Y., N. Goto and K. Fujie, 2001. Effect of pH on the reduction of nitrite in water by metallic iron, *Water Res.*, 35(11): 2789-2793.