

Nitrates Removal by Bimetallic Nanoparticles in Water

Gunay G. Muradova^{a*}, Sevinj R. Gadjeva^a, Luca Di Palma^b, Giorgio Vilardi^b

^aDepartment of Ecology and Soil Science, Baku State University, Zahid Khalilov 23, AZ1148, Baku, Azerbaijan.

^bDepartment of Chemical Engineering Materials Environment (DICMA), Sapienza University of Rome, Via Eudossiana 18, 00184, Rome, Italy.
gunay111@hotmail.com

Nitrate contamination of groundwater has become a major environmental concern since nitrates are easily transferred from unsaturated zone to the saturated one, due to their solubility and low sorptivity on soil particles caused by their negative charge. The effectiveness and rapidity of the reduction of NO_3^- is strongly dependent on the contact time, the concentration of the reductive agent, the properties and composition of the surrounding medium (pH, dissolved oxygen concentration, heavy metals and organic matter concentration). The aim of this work was to investigate the effectiveness of nZVI and bimetallic nanoparticles of Fe/Cu in the remediation of nitrate-polluted groundwaters. nZVI and Fe/Cu nanoparticles were prepared by sodium borohydride reduction method at room temperature and ambient pressure. Results confirm that the decontamination of nitrate in groundwater via the in-situ remediation by Fe/Cu nanoparticles is environmentally attractive. Batch experiments were conducted on water samples contaminated in laboratory using NaNO_3 to fix the initial nitrate concentration to 57.5 mg/L. The Cu/ Fe^0 ratio was fixed to 0.05 (w/w) and the parameter investigated was the $\text{Fe}^0/\text{NO}_3^-$ weight ratio (5,10 and 15 w/w). During the tests the aqueous solution was analyzed to measure the evolution of NO_3^- and pH at 0, 30, 60, 90, 120 and 150 min. The results showed the increasing rate of reduction of nitrate by adding copper to ZVI particles; in fact fixing the $\text{Fe}^0/\text{NO}_3^-$ to 15 the tests without copper resulted in a complete removal within 150 min against the 60 min required by the tests with copper.

1. Introduction

The use of nano Zero-Valent Iron (nZVI) has been considered as a promising alternative for in situ remediation of contaminated sites, due to the small particle size, large specific surface area, and high surface reactivity (Lee et al., 2003; Lien et al., 2007). Therefore, innovative applications of the nZVI for in-situ groundwater remediation or for the treatment of industrial wastewater streams contaminated with toxic material have been already successfully implemented such as TCE (Liu et al., 2005) and Cr(VI) (Zhou et al., 2008).

Research conducted using ZVI in nitrates solution indicated that nitrite, nitrogen gas, and, mostly, ammonia are the products of nitrates reduction. The reaction mechanism of nitrate removals is significantly dependent on pH, both in buffered and unbuffered solutions (Alowitz and Scherer, 2002).

However, nano-scale Fe^0 can lose its reactivity due to oxidation by oxygen in air and, thus limiting its application in site remediation (Guo et al., 2015). The introduction on the nano-scale Fe^0 surface of a second noble metal, such as Pd, Pt, Ni, Ag or Cu, can increase iron stability, thus enhancing redox performances by a catalytic action.

Several studies have already assessed the effectiveness of coating of iron nanoparticles for treating a number of contaminants in water (Zin et al, 2013), such as nitrates (Kang et al., 2012). Among the metals commonly tested in water reemdiation, metallic Cu appears to be one the more promising. It was in fact reported that coating of nZVI by copper decreases the aggregation and agglomeration of nZVI and enhances the rate of nitrate reduction in aqueous solution (Vodyanitskii and Mineev, 2015).

In the present study, the effect of various parameters, including the copper content in nano-Fe/Cu particles and initial concentration, on nitrate reduction was investigated.

2. Materials and method

2.1 Materials

Nitrate solution samples were prepared using distilled water and sodium nitrate (NaNO₃) as a model contaminant. Chemicals used for nZVI and nano-Fe/Cu particles synthesis included iron(II) sulphate, copper (II) chloride, sodium borohydride and carboxymethyl cellulose (CMC). Nitrate measurements were performed by ion chromatography (Dionex ICS - 1100). The pH of the solutions was measured with a Crison 421 pH meter.

2.2 Experimental procedure

Nano zero valent iron particles were prepared from a 1g/L Fe²⁺ aqueous solution, by reacting with sodium borohydride (NaBH₄) at room temperature and in a free oxygen atmosphere. As dispersing agent sodium Carboxy Methyl Cellulose (CMC) was used, at a CMC/Fe²⁺=0.005 molar ratio (He et al., 2007). The reaction of formation of zerovalent iron is as follows:



A 0.86 g/L solution of nZVI was obtained, and use for the reduction tests.

Bimetallic particles were prepared by adding 0.01 g of CuCl₂ (0.05 Cu/Fe according to Sparis et al, 2013) to the prepared colloidal solution of nZVI particles at room temperature and in a free oxygen atmosphere. After 20 min of redox reaction (1), Fe/Cu particles were used for the treatment. The final iron concentration in the solution was 0.86 g/L while copper concentration was below the detection limit (<0.1 mg/L). The obtained nanoparticles were analysed by means of a nanosizer (NANOTRAC, measurement range 0.8 nm-6.5 μm, supplied by Microtrac Inc.) in order to determine the overall particle size distributions; the average size of the obtained nanoparticles was 13.3 nm, with a standard deviation of 5 nm, very close to the size obtained in similar experiments (Di Palma et al., 2015). The redox reaction describing the coating of nZVI with Cu was as follows:



The particles have an nZVI core with a discontinuous Cu shell. The percentage of Cu content can be changed during synthesis. The amount of copper coupling to NZVI is depending on the desired weight ratio of copper to iron.

Nitrate reduction batch experiments were conducted in 250 mL bottles with three-neckedcap. All reactors and solutions were deoxygenated for 30 min by bubbling nitrogen. Deoxygenated sodium nitrate solution (100mL, 57.25 mg/L) was transferred into a reactor under the pressure of nitrogen gas. Freshly prepared Fe/Cu bimetallic nanoparticles were added. Uncoated nZVI was also tested for its effectiveness on nitrate reduction. The nitrate solution was used without any acidification. Samples were collected at time of reaction following: 30min, 60 min, 90 min, 120 min and 150 min. The four Fe⁰/NO₃⁻ weight ratio investigated were 1:1, 5:1, 10:1 and 15:1. All experiments were repeated at least three times to ensure their reproducibility.

3. Results and discussion

3.1 Effect of bimetallic nanoparticles concentration on NO₃⁻ reduction

Four bimetallic nanoparticle concentrations were employed to determine the amount of Fe/Cu required to remove nitrates. In Figure 1 the comparison between nitrate removal by nZVI and Fe/Cu nano-particles is reported. It is possible to observe the remarkable increase in rate removal due to the coating of Cu on nZVI nano-particles. While Figure 2 shows that increasing concentration of Fe/Cu nano-particles greatly enhanced the NO₃⁻ removal efficiency. The four Fe⁰/NO₃⁻ weight ratio investigated were 1:1, 5:1, 10:1 and 15:1. Figure 1 shows the concentration of nitrate during the reduction of 100 mL nitrate solution with 100 mL nano-Fe/Cu particles solution at different weight ratio.

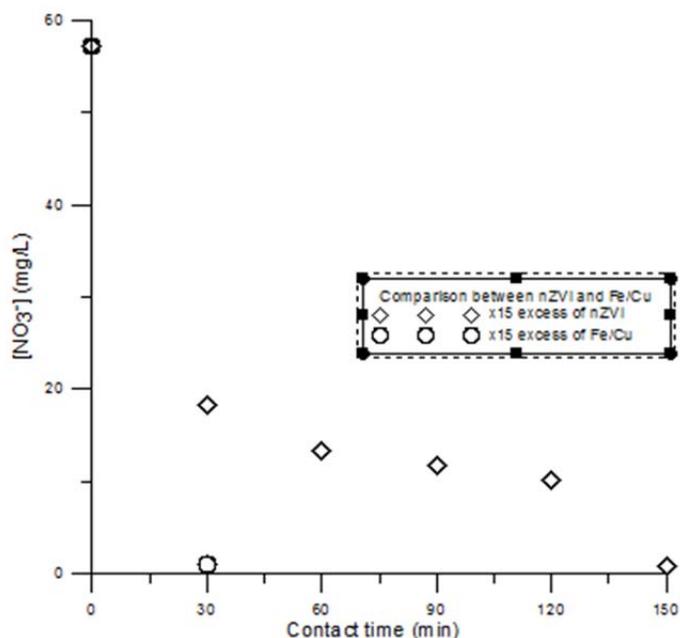


Figure 1: Comparison between nitrate removal by nZVI and nZVI particles coated by Cu (initial nitrate concentration 57,25 mg/L; pH – 4,97)

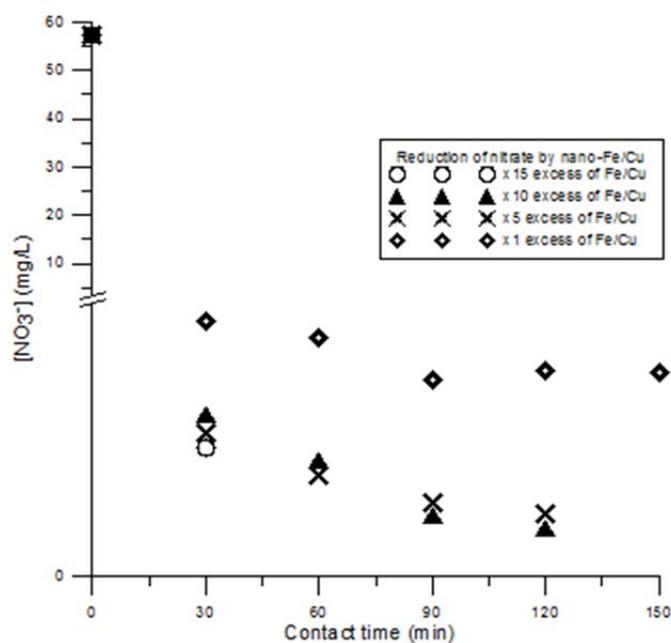


Figure 2: Concentration of residual NO_3^- in the aqueous solution of NaNO_3 at different $\text{Fe}^0/\text{NO}_3^-$ weight ratio (initial nitrate concentration 57,25 mg/L; pH – 4,97)

For comparison, nZVI without Cu was also analyzed. In the presence of copper the total (100%) removal was observed after 1 hour of reaction. Without copper, nitrates were not completely removed after 150 minutes, though a removal of 98% was ensured. Nitrite was initially produced as the main by-product, but their concentration rapidly decreased once the nitrate reduction was almost complete. At the same time, ammonia and ammonium production were observed by several authors (Hwang et al., 2010; Sparis et al., 2013). The highest reduction rate was achieved using x15 excess of Fe/Cu particles with 5% copper, and the lowest using pure (uncoated) nZVI. The main nitrogen species remaining in solution is ammonium, corresponding to

74% of the total nitrogen introduced according to Sparis et al., 2013. Ammonia concentration was 15,73 mg/L corresponding to 12% of the total nitrogen. Total aqueous nitrogen concentration at 2 h contact time corresponds to 87% of the initial nitrogen concentration (Sparis et al., 2013).

The mass balance difference of 13% may be attributed to the potential production of gaseous nitrogen or ammonia and subsequent emission to the air, sorption of nitrate/ammonium ion by nanoparticles. Subsequently other tests were conducted using the x15 excess Fe/Cu solution to treat the same NaNO_3 solution (57.25 mg/L) and the concentration of nitrates was reduced below the EU drinking water limit of 50 mg/L after 5 min (the residual concentration was roughly 2 mg/L).

3.2 Effect of the pH values on nitrates removal

The last parameter investigated was the pH of the treated solution. Extensive studies have reported that pH is an important parameter influencing nitrate reduction by Fe^0 . Although different conclusions were drawn on nitrate reduction by micro- Fe^0 at different pH conditions, most studies indicated clearly that the nitrate removal rate was inversely related to solution pH. It was reported that the Fe^0 surface remains fresh at low pH, thus nitrate can be removed rapidly and completely. However, when the pH is higher than 6.5, negligible nitrate reduction is noticed in unbuffered systems, compared to significant removal in buffered systems. Similarly, strong acidic conditions are also more favourable for nano-scale Fe^0 nitrate reduction.

Solution pH increased rapidly to 8-9 in all of the reactions (3-6). According to the experimental results (Kang et al., 2012), near neutrality conditions are more favourable for nitrate reduction by Fe/Cu nanoparticles. In an acid medium H^+ makes faster the corrosion of Fe^0 and the generation of hydrogen. Thus the rate of nitrate removal by nZVI is strongly increased. About Fe/Cu nanoparticles, the nitrate reduction rate is also promoted in the first 10 min, which might be due to the presence of the Cu catalyst and H^+ . The contact between iron, copper and nitrate could be hindered by the quick production of Fe^{2+} and Fe^{3+} , which is indicated by the grey-green flocks (mixture of $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$) after 5 min (not found in the Fe^0 system). Subsequently at low pH value the rapid generation of flocks can reduce the reactivity of Fe/Cu nanoparticles making the neutral pH the favourable condition, which improve the feasibility of using these bimetallic nanoparticles at real contaminated site. The pH change with time for the various concentration of nano-Fe/Cu are presented in Figure 3.

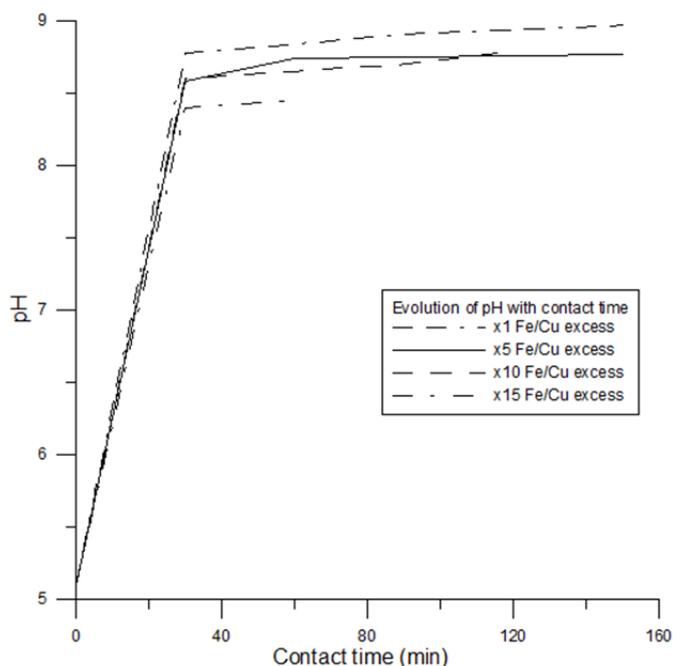


Figure 3: Evolution of pH during the nitrate reduction at different $\text{Fe}^0/\text{NO}_3^-$ weight ratio

As seen in Figure 3, the pH of the solution increased from roughly 5 to higher than 8 in the first 10 min of reaction. The final pH at 150 min reaction time was around 8.6 - 9 in all the tests.

3.3 Kinetic study of nitrate reduction

Figure 4 and 5 show the kinetic profiles accounting for NO_3^- reduction utilizing nano-Fe/Cu. The kinetic study reported shows two correlation coefficients not close to the unit, both for the first-order correlation and the second-order correlation. It is possible to say that initially the reaction mechanism follows a second-order kinetic profile, thanks to the large excess of reducing agent and that during this time (less than 30 minutes), due to the acidic condition (as showed in Figure 3), the following corrosive reaction is promoted (Xu and Zhao 2007; Ponder et al. 2000):



The reaction (7) reduces the reactivity of nanoparticles until basic condition established by the reduction of NO_3^- (3-6) and the catalytic mechanism of Cu (2) stabilize the reduction capacity of nanoparticles and the kinetic reaction mechanism to a first-order mechanism.

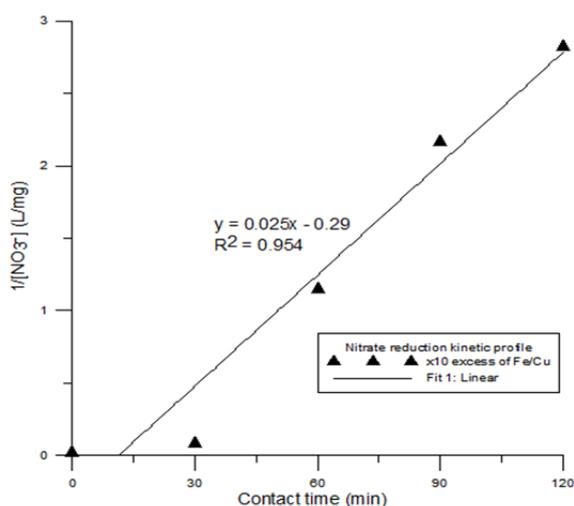


Figure 4: Kinetics of the second-order reaction

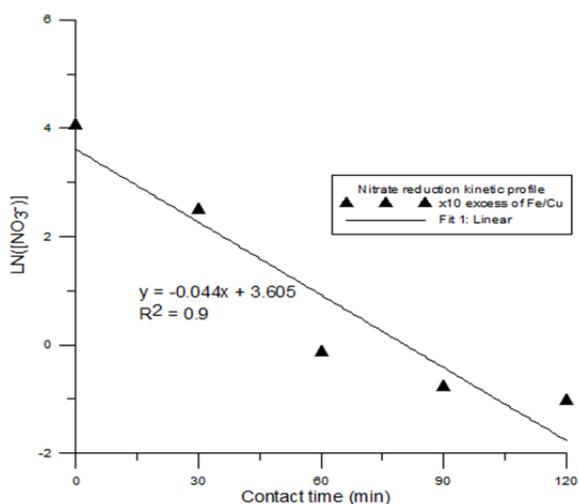


Figure 5: Kinetics of the first-order reaction

4. Conclusions

Bimetallic nano-Fe/Cu particles (in various concentration x15, x10, x5, x1) with 5% w/w Cu content were synthesized and used to reduce nitrates in aquatic solution. More than 80% of the nitrate was reduced within 20 min and complete nitrate reduction was attained within 1 h. The main reduction products are dissolved ammonium and ammonia. Based on nitrogen mass balance calculations, 13%w/w of the initial nitrogen was either emitted to the air in the form of ammonia or nitrogen gas, or sorbed by nano-Fe/Cu nanoparticles. Results showed that the total (100%) removal was observed after 1 hour of reaction. Without copper, nitrates were not completely removed after 150 minutes, though a removal of 98% was ensured. The pH of the treated solution increased from 4.9 to higher than 8 in the first 10 min of reaction. The final pH at 150 min reaction time was around 8.6 - 9 in almost all the systems. The deposition of catalytic Cu on Fe⁰ nanoparticles promoted the nitrate reduction rate significantly. Fe/Cu particles showed a much higher nitrate reduction rate, better properties of air stability and an optimum reduction rate at near-neutral pH, which could have important implications for nitrate in situ remediation.

References

- Alowitz M.J., Scherer M.M., 2002. Kinetics of nitrate, nitrite, and Cr(VI) reduction by iron metal. *Environ. Sci. Technol.* 36, 299-306.
- Di Palma L., Gueye M.T., E. Petrucci E., 2015. Hexavalent chromium reduction in contaminated soil: a comparison between ferrous sulphate and nanoscale zero-valent iron, *J.Haz. Mater.*, 281, 70-76.
- Guo X., Yang Z., Liu H., Lv X., Tu Q., Ren Q., Xia X., Jing C. 2015. Common oxidants activate the reactivity of zero-valent iron (ZVI) and hence remarkably enhance nitrate reduction from water, *Separation and Purification Technology* 146, 227-234.
- He F., Zhao D., Liu J., Roberts C. B. 2007. Stabilization of Fe-Pd Nanoparticles with Sodium Carboxymethyl Cellulose for Enhanced Transport and Dechlorination of Trichloroethylene in Soil and Groundwater, *Ind. Eng. Chem. Res.* 46, 29-34.
- Hwang Y.H., Kim D.G., Ahn Y. T., Moon C.M., Shin H., 2010. Fate of nitrogen species in nitrate reduction by nanoscale zero valent iron and characterization of the reaction kinetics. *Water Sci. Technol.* 61, 705-712.
- Kang H., Xiu Z., Chen J., Cao W., Guo Y., Li T., Jin Z., 2012. Reduction of nitrate by bimetallic Fe/Ni nanoparticles, *Environmental Technology*, 33, 2185-2192.
- Lee T., Lim H., Lee Y. and Park J., 2003. Use of Waste Iron Metal for Removal of Cr (VI) from Aater. *Chemosphere*, 53:479-485.
- Lien H.L., Jhuo Y.S., Chen L.H., 2007. Effect of heavy metals on dechlorination of carbon tetrachloride by iron nanoparticles. *Environ Eng Sci.* 24:21-30.
- Liu Y., Majetich S.A., Tilton R.D., Sholl D.S. and Lowry G.V., 2005. TCE Dechlorination Rates, Pathways, and Efficiency of Nano-scale Iron Particles with Different Properties. *Environ. Sci. Technol.*, 39:1338-1345.
- Ponder S. M., Darab J. G., & Mallouk T. E. 2000. Remediation of Cr(VI) e Pb(II) aqueous solutions using supported, nanoscale zero-valent iron. *Environmental Science & Technology*, 34(12), 2564-2569.
- Sparis D., Mystrioti C., Xenidis A., Papassiopi N. 2013. Reduction of nitrate by copper-coated ZVI nanoparticles, *Desalination and Water Treatment*, 51, 2926-2933.
- Vodyanitskii Yu. N. and Mineev V. G. 2015. Degradation of Nitrates with the Participation of Fe(II) and Fe(0) in Groundwater: A Review, *Eurasian Soil Science*, 2015, 48, 139-147.
- Xu Y., Zhao D., 2007. Reductive immobilization of chromate in water and soil using stabilized iron nanoparticles. *Water Res.*, 41: 2101-2108.
- Zhou H., He Y., Lan Y., Mao J., Chen S., 2008. Influence of complex reagents on removal of chromium(VI) by zero-valent iron. *Chemosphere* 72, 870-874.
- Zin M. T., Borja J., Hinode H., Kurniawan W. 2013. Synthesis of Bimetallic Fe/Cu Nanoparticles with Different Copper Loading Ratios, *International Journal of Chemical, Nuclear, Materials and Metallurgical Engineering*, 7, 12, 687-690.