

The Influence of Heavy Metals and Organic Matter on Hexavalent Chromium Reduction by Nano Zero Valent Iron in Soil

Mouhamadou Thierno Gueye^a, Luca Di Palma^b, Gunel Allahverdiyeva^c, Irene Bavasso^b, Elisabetta Petrucci^b, Marco Stoller^b, Giorgio Vilardi^b

^a Université Cheikh Anta Diop de Dakar (UCAD), Dakar Fann, Senegal

^b Sapienza Università di Roma, Dipartimento di Ingegneria Chimica Materiali Ambiente, via Eudossiana 18, 00184 Roma

^c Baku State University, 23 Khalilov St., Baku, Azerbaijan

During the last decades great attention has been paid at evaluating the feasibility of Cr(VI) reduction in soil by nano zero valent iron (nZVI). An inhibitory effect on the Cr(VI) reduction by Fe⁰ nanoparticles is generally shown in the presence of high level of heavy metals and natural organic matter in soil. Heavy metals in the environment can react with nZVI by redox reactions, precipitation/dissolution reactions, and adsorption/desorption phenomena. As a result of the presence of metals as Ni, Pb, a decrease in the rate of Cr(VI) reduction was observed. Hence, in the present study, experimental tests of Cr(VI) reduction by nZVI in the presence of selected heavy metals, such as nickel and lead, and in the presence of high level of organic matter, are presented and discussed. Results showed a decrease in the rate of Cr(VI) reduction in soil by nZVI (at a x25 stoichiometric excess) from 91% to 78%, 71% and 74% in the presence of Ni, Pb and both metals respectively. As regards the results of Cr(VI) reduction in the presence of organic matter, by using a reducing solution of nZVI (x25 stoichiometric excess) a decrease of Cr(VI) reduction yield from 91% to 12% was observed after 2 hours of treatment in a soil containing 35.71 g/kg of organic matter. Such low efficiency was attributed to the adsorption of organic matter onto Fe⁰ nanoparticles surface, thus saturating the active reaction sites of Fe⁰ nanoparticles. In addition, a significant reduction of the organic carbon in the treated soil was observed (up to 77.5%) caused by the degradation of organic matter and its dissolution in the liquid phase. A slight decrease of the total metal concentration in treated soil was also observed. Finally, kinetic tests show that Cr(VI) reduction using nZVI in the presence of a high concentration of organic compound obeyed a pseudo-zero-order kinetic model.

1. Introduction

Hexavalent chromium is a priority pollutant in many countries (Di Palma et al., 2012). Its wide distribution in the environment is the result of the extensive exploitation of chromium to produce stainless steel, wood treatment products, tanning of leather or pigments (Xu et al., 2004). Reduction of Cr(VI) to Cr(III) is desirable as the latter species is an essential nutrient for maintaining normal physiological function and also has a low mobility and bioavailability (Di Palma et al., 2015). Given the strong dependence of Cr mobility and toxicity on its redox state, remediation technologies that reduce Cr(VI) such as a reduction by zero-valent iron (ZVI), are of significant interest (Jacobs et al., 2005). Over the last several years several studies demonstrated that nZVI is an efficient (Alowitz and Scherer, 2002) and inexpensive reductant for Cr(VI) (Oh et al., 2007).

In particular, a special attention has been devoted at evaluating the effect of naturally occurring heavy metals (Kabir-ud-Din and Khan, 2002), organic compounds (Wittbrodt and Palmer, 1995), and/or co-ordinating reagents (Tandy et al., 2004) on the reduction rate of Cr(VI) mediated with ZVI (Zhou et al., 2008).

Natural occurring metals in soil, or heavy metals resulting from industrial pollution, can interfere with the reaction/precipitation typical mechanism of Cr(VI) reduction (Di Palma, 2009).

The specific removal mechanisms involved in the treatment of heavy metal contamination with ZVI, depend on the standard redox potential (E^0) of metal contaminant. Metals with a E^0 more negative or equal than Fe (e.g., Cd and Zn) are simply removed by adsorption onto the iron (hydr)oxide shell. Metals with higher E^0 than Fe (e.g., Cr, As, Cu, U, and Se) are removed by reduction and precipitation (Li and Zhang, 2007) or by both reduction and ads (e.g., Pb and Ni).

Soil organic matter strongly affects the effectiveness of soil remediation processes. Simple aliphatic organic acids with one to three carboxylic acid groups such as acetic, citric, formic, fumaric, lactic, oxalic, malonic, valeric, succinic, tartaric, and p-hydroxybenzoic acid occur frequently in soil and subsurface environments. Such compounds are released by organisms or are produced during the decomposition of larger biopolymers and can alter chemical processes in soils through complexation with metal ions in solution and ligand exchange reactions at soil surfaces (Gonzini et al., 2010). In particular, they play a crucial role in chromate reduction by nZVI via adsorption and complexation with the surface sites of nZVI and/or with the iron corrosion products.

In this paper, experimental tests of Cr(VI) reduction by nZVI were reported and discussed: the effects on Cr(VI) reduction rate in the presence of selected other heavy metals, and on a soil characterized by high level of organic matter were investigated.

2. Materials and Methods

2.1 Materials

Soil samples S1 were collected at an industrial site in Northern Italy (plating and steel industries). The samples were artificially contaminated by applying solutions of $\text{Ni}(\text{NO}_3)_2$, $\text{Pb}(\text{CH}_3\text{COO})_2$ or both simultaneously. The slurry was shaken daily for one week, and then air dried and cured at room temperature ($20 \pm 2^\circ\text{C}$) for additional four weeks.

Soil samples S2 were collected at an agricultural site close to the chromium contaminated site: they showed a high TOC value, as shown in Table 1, where the main characteristics of the soils used in the experiments are reported.

The initial soil characterization was carried out through commonly used protocols (Liu and Evett, 2002). Metals concentration was determined after acid digestion technique according to the EPA 3050B method followed by atomic absorption spectrophotometry (FAAS) analysis, using a Agilent AA DUO 240 Fs instrument. The concentration of Cr(VI) was determined by the colorimetric method of diphenylcarbazide (Bartlett, 1991) after alkaline digestion according to the EPA 3060A method (US EPA, 1996) using a UV-visible spectrophotometry (T80+, PG Instruments, Ltd.). The organic compound content is given by the Shimadzu Total Organic Carbon Analyzer instrument (TOC-L model).

Table 1 reports the mean concentration of heavy metals in the soils, as well as the limits for a civil reuse (mg/kg), or industrial reuse (mg/kg) according to Italian regulation (Italian Environmental Regulation, 2006).

Table 1: Selected characteristics of the soil used in the experiments.

Parameters	S1	S2	Limit for civil reuse (mg/kg)	Limit for industrial reuse (mg/kg)
pH	6.85	7.54	-	-
C.E.C. (meq 100 g ⁻¹)	9.6	12.43	-	-
T.O.C. (g kg ⁻¹)	1.38	35.71	-	-
Cr (mg kg ⁻¹)	155.2	104.7	150	800
Cr (VI) (mg kg ⁻¹)	55.48	51.48	2	15
Ni (mg kg ⁻¹)	156.16	126	120	500
Mn (mg kg ⁻¹)	817.63	710	-	-
Fe (mg kg ⁻¹)	36267	41000	-	-
Pb (mg kg ⁻¹)	18	26	100	1000

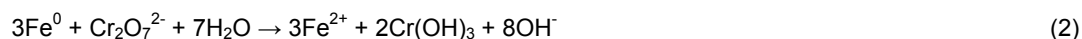
2.2 Experimental procedure

Nano zero valent iron particles were prepared from a 1 g·L⁻¹ 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 and Zhao, 2007). The reaction of formation of zero valent iron is as follows:



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

The reduction tests with nZVI were performed in batch mode, by mixing 5 g of soil in an orbital shaker at 120 rpm with 50 mL of the reducing solution. The stoichiometric amount of nZVI was calculated according to the following equation:



As regards the effect of organics in soil, the experiments were performed at room temperature (20 ± 1 °C), and at the end of each test, the reaction was stopped by washing the soil with distilled water and the soil sample was filtered through a 0.45 μm Whatman membrane filter. The concentration of total Cr and metals in the liquid phase was determined by atomic absorption spectroscopy, according to the procedure described in the previous section.

3. Results and discussion

3.1 Effect of metals

Figure 1 shows that, in the presence of Ni, Pb and both metals, a decrease in the rate of Cr(VI) reduction during the treatment of S1 with a reducing solution of nZVI 25 times in excess with respect to stoichiometric Fe/Cr(VI) ratio, from 91% to 78%, 71% and 74% respectively occurred. These results suggest that Ni^{2+} and Pb^{2+} , whose redox potential is slightly higher than Fe, were initially adsorbed on the surface of nZVI and then reduced, thus determining a nZVI consumption and consequently preventing Cr(VI) reduction. However, the effect of metals presence on Cr(VI) reduction effectiveness was not additive. When only lead was present, in fact, the reduction of Cr(VI) was lower than in the presence of both lead and nickel: conversely, when only nickel was present, the effect of the single metals resulted higher than in the tests where both metals were present.

This specific behaviour was strictly related to the redox potential of the two selected metals. Lead, in fact, whose redox potential is higher than iron, quickly reacted with nZVI: the simultaneous presence of Ni, did not affect significantly this behaviour. Conversely, since nickel has got a redox potential greater than iron, it can be reduced by nZVI to form bimetallic nanoparticle iron Fe/Ni, thus increasing the reduction rate (Hu et al., 2010). On the other hand, oxidation and co-precipitation by iron oxides are the other possible reaction mechanisms depending upon the geochemical conditions such as pH, Eh and initial concentration and speciation of contaminant metals (Lien et al., 2007). In addition, during each tests, pH slightly decreased, starting from an initial alkaline value (7.99). Such initial alkalinity is probably due to the reaction of Fe^0 with water producing hydroxyl ion according to the reaction (Liu et al., 2005, Orth W.S. and Gillham R.W., 1996):



The final pH of the reducing solutions in contaminated soil (soil+Ni, soil+Pb and soil+Ni+Pb), after 120 min reaction, were 7.65, 7.46 and 7.45 respectively for initial pH 7.99. Such a slight pH decrease was attributed to the consumption of hydroxyl ions by trivalent chromium and iron oxy-hydroxides formation, despite of the release of 8 mol ions hydroxide for each mole of Cr(VI) according to the stoichiometric reaction 2) (Powell et al., 1995).

The formation of oxy-hydroxides of Cr and Fe on the surface of the nanoparticles during the reaction also determined the progressive passivation of reactive surface (Lee et al., 2003).

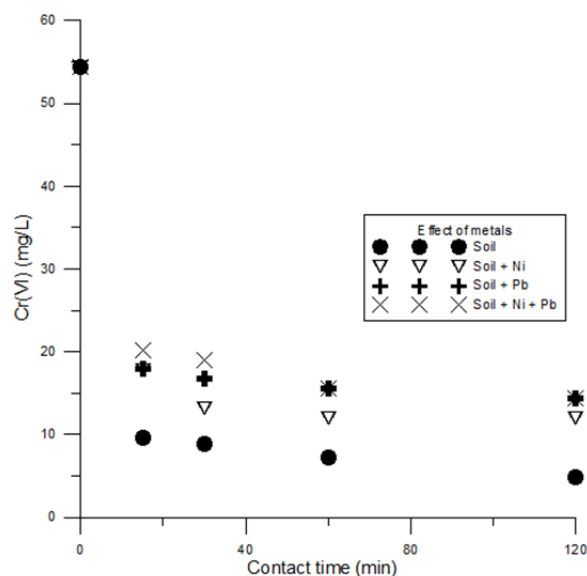


Figure 1: Cr(VI) residue as a function of time in artificially contaminated soils.

3.2 Effect of soil organic matter on Cr(VI) reduction

It was observed that only a slight decrease (about 12%) in the amount of Cr(VI) in the soils S2 occurred after 2 hours of treatment by the nZVI (x25) reducing solution. These results suggest that an elevated organic matter concentration had an inhibitory effect on the Cr(VI) removal by ZVI nanoparticles. Even prolonging the reaction time up to 16 h, only a constant value of 36% reduction of Cr(VI) was calculated, thus indicating that steady conditions were attained.

Regarding the reaction mechanism, it has been proposed that ZVI nanoparticles first reduce Cr(VI) to Cr(III), then Cr(III) also precipitates as Fe(III)–Cr(III) hydroxides on the ZVI nanoparticles surfaces. Steady conditions were therefore due to the passivation of the surface of nanoparticles, with the consequent loss of reactivity (Wu et al., 2009).

The inhibitory effect of organic, is only in apparent contrast with the results of other experiments in literature (Rivero-Huguet and Marshall, 2009): in fact, the nature of organic matter strongly influence the reaction mechanisms. Acidic or chelating compounds, such as humic and fulvic substances in soil, generally increase the reduction effectiveness, by forming complexes with reaction products as Fe(III) and Cr(III) thus preventing their precipitation and the passivation of iron nanoparticles. Conversely, in the presence of non humic organic matter, such as organic wastes, the reduction inhibition was attributed to the solubilization of the organic matter of soil and its adsorption of organic compounds onto the surface of iron nanoparticles, thus reducing the availability of free active reaction sites.

Furthermore, Table 2 reports the mean parameters in the natural and treated soil. A significant reduction of the organic carbon in soil occurred during the treatment, due to organics dissolution in the liquid phase. A slight decrease of the total metal concentration in treated soil due to the dissolution in the extract was also observed. At the same time, the TOC of the liquid phase in the reactor correspondingly increased. Furthermore, during treatment alkaline conditions were always kept: the final pH of the slurry was 7.39, starting from and initial value of 7.42.

Table 2: Characteristics of the soil.

	Natural soil		After treatment
	S1	S2	S1
T.O.C. (g kg ⁻¹)	1.38	35.71	1.14
Cr (mg kg ⁻¹)	155.2	104.7	154
Cr (VI) (mg kg ⁻¹)	55.48	51.48	4.82
Ni (mg kg ⁻¹)	156.16	126	155.2
Mn (mg kg ⁻¹)	817.63	710	800
Fe (mg kg ⁻¹)	36267	41000	34000
Pb (mg kg ⁻¹)	18	26	18

3.3 Kinetics

Figure 2 shows the kinetic profiles of Cr(VI) reduction using nZVI in the slurry reactor under agitation (120 rpm). Good correlation coefficient was obtained (0.92), thus revealing that Cr(VI) reduction using nZVI and in the presence of a high concentration of organic compound obeys a pseudo-zero-order kinetic model; this mechanism was previously observed by several authors (Reisner and Pradeep, 2014) in TCE degradation by nZVI and it was caused by the overloaded substrate which occupied the surface-active-sites. Considering that the redox process obeys a pseudo-zero-order kinetic model, the reduction of Cr(VI) taking place in the slurry reactor can be described by the following relation:

$$[\text{Cr(VI)}] = [\text{Cr(VI)}]_0 - k_{\text{obs}} * t \quad (4)$$

where $[\text{Cr(VI)}]$ is the actual concentration of Cr(VI) (mg/kg), $[\text{Cr(VI)}]_0$ is the initial concentration of Cr(VI), t is the treatment time (min) and k_{obs} is the overall kinetic rate constant for the heterogeneous redox process (min^{-1}).

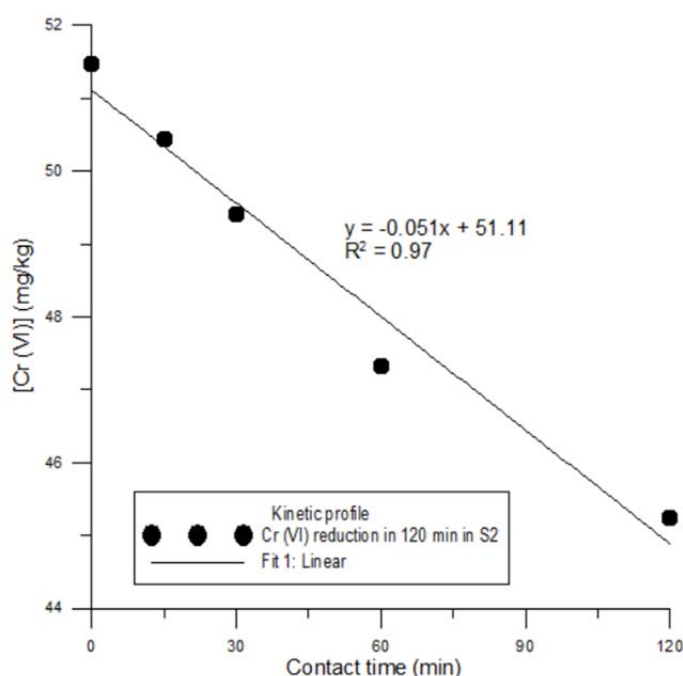


Figure 2: Kinetics of pseudo-zero order of the Cr(VI) reduction.

4. Conclusion

The reduction of hexavalent chromium performed using nanoparticle zero valent iron proved to be fast and efficient: the effectiveness of the process depended on the contact time, the concentration of nZVI and the chemical composition (namely, heavy metals and organic matter content) of the soil. In this study, the effect of the presence of nickel and lead, and of a huge amount of organic matter, on the removal of Cr(VI) by CMC stabilized ZVI nanoparticle was investigated on artificially contaminated soils. A decrease in the rate of Cr(VI) reduction from 91 % to 78 %, 71% and 74 % was observed in the presence of Ni, Pb and both metals respectively, using a nZVI solution in a large excess (x25) with respect to the Cr(VI) content in soil. As regards the residual heavy metal content after the treatment, the results show a negligible reduction of the total concentration of metals in the treated soil. These results suggested that Ni^{2+} and Pb^{2+} , with redox potentials slightly higher than that of Cr(VI), were initially adsorbed on the surface of nZVI and then reduced, thus decreasing the Cr(VI) reduction rate. Regarding the effect of the presence of organic compounds on the removal of Cr(VI) by nZVI a significant decrease in the rate of Cr(VI) reduction was observed in the presence of high level of organic matter in the soil, as well as a significant reduction of the organic carbon in the treated

soil. This behavior has been attributed to the dissolution of organic matter into the liquid phase, and its adsorption onto nanoparticles. Finally, Cr(VI) reduction using nZVI and in the presence of a high concentration of organic compound obeyed a pseudo-zero-order kinetic model.

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.
- Bartlett R.J., 1991, Chromium cycling in soils and water: links, gaps, and methods, *Environ. Health Perspectives*, 92, 17-24.
- Di Palma, L., 2009. Influence of indigenous and added iron on copper extraction from soil, *J. Haz. Mater.*, 170, 96-102.
- 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.
- Di Palma, L., Mancini, D., Petrucci E., 2012. Experimental Assessment of Chromium Mobilization from Polluted Soil by Washing, *Chemical Engineering Transactions*, 28, 145-150, 2012. DOI: 10.3303/CET1228025.
- Gonzini, O., Plaza, A., Di Palma, L., Lobo M.C., 2010. Electrokinetic remediation of gasoil contaminated soil enhanced by rhamnolipid, *Journal of Applied Electrochemistry*, 40, 1239-1248.
- He, F., Zhao, D., 2007, Manipulating the Size and Dispersibility of Zerovalent Iron Nanoparticles by Use of Carboxymethyl Cellulose Stabilizers, *Environ. Sci. Technol.* 41, 6216-6221.
- Hu CY, Lo SL, Liou YH, Hsu YW, Shih K, Lin CJ, 2010. Hexavalent chromium removal from near natural water by copper-iron bimetallic particles. *Water Res.* 44:3101–3108.
- Italian Environmental Regulation, 2006, Environmental standards assessment, G.U. n. 88 of April 14th 2006.
- Jacobs J.A., Testa S.M., 2005. Overview of chromium(VI) in the environment: background and history. In: Guertin J., Jacobs J.A., Avakian C.P., editors. *Chromium(VI) handbook*. New York: CRC Press; p. 1–21.
- Kabir-ud-Din K.H., Khan Z., 2002. One-step three-electron oxidation of tartaric and glyoxylic acids by chromium(VI) in the absence and presence of manganese(II). *Transit. Metal Chem.* 27, 617–624.
- 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 H.L. metals on dechlorination of carbon tetrachloride by iron nanoparticles. *Environ Eng Sci.* 24:21–30.
- Liu C., Evett J.B., 2002, *Soil properties, Testing, Measurement, and Evaluation*, 5th ed., Prentice-Hall, New York, USA.
- 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.
- Oh, Y.J., Song, H., Shin, W.S., Choi, S.J., Kim, Y.H., 2007. Effect of amorphous silica and silica sand on removal of chromium(VI) by zero-valent iron. *Chemosphere* 66, 858–865.
- Orth W.S. and Gillham R.W., 1996. Dechlorination of Trichloroethene in Aqueous Solution Using Fe–O. *Environ. Sci. Technol.*, 30:66–71.
- Reisner D. E., Pradeep T., 2014. *Aquananotechnology: Global Prospects*, 1st ed., CRC Press,
- Rivero-Huguet, M., Marshall, W.D., 2009. Influence of various organic molecules on the reduction of hexavalent chromium mediated by zero-valent iron. *Chemosphere* 76, 1240–1248.
- Tandy, S., Bossart, K., Mueller, R., Ritschel, J., Hauser, L., Schulin, R., Nowack, B., 2004. Extraction of heavy metals from soils using biodegradable chelating agents. *Environ. Sci. Technol.* 38, 937–944.
- Wittbrodt, P.R., Palmer, C.D., 1995. Reduction of Cr(VI) in the presence of excess soil fulvic acid. *Environ. Sci. Technol.* 29, 255–263.
- Wu, Y.J., Zhang, J.H., Tong, Y.F., Xu, X.H., 2009. Chromium (VI) reduction in aqueous solutions by Fe₃O₄-stabilized Fe⁰ nanoparticles. *J. Hazard. Mater.* 172, 1640–1645.
- 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.