Hexavalent chromium reduction in manganese-rich soils by ZVI nanoparticles: the influence of natural organic matter and manganese oxides

Di Palma L.[1*], Verdone N.[1] and Vilardi G[1].

[1]Sapienza University of Rome, Dept. of Chemical Engineering Materials Environment, Via Eudossiana 18, 00184, Rome

*corresponding author: luca.dipalma@uniroma1.it

e-mail: luca.dipalma@uniroma1.it

Abstract

Hexavalent chromium reduction by nano Zero-Valent Iron (nZVI) has been proved fast and efficient, mainly due to nanoparticles large specific surface area and high chemical reactivity. In this work the influence of natural organic matter and manganese oxide was investigated, through a set of experimental tests carried out on a real polluted soils naturally rich in manganese. Soil samples were characterized in terms of initial concentration of Cr, Cr(VI), Mn, pH, and TOC and three different nZVI solutions were used (120, 360 and 600 mg nZVI L^{-1}) for the treatment. At selected interval times (0, 5, 10, 15, 30, 60, 120 min) a slurry sample was filtered and Cr(VI) residual concentration and pH were measured. The same procedure was carried out on an artificial spiked soil, characterized by a similar TOC and poor of Mn. Furthermore the two soils were mixed with different amounts of leonardite, to evaluate the influence of NOM on treatment efficiency.

Keywords: nZVI, Cr(VI), NOM, Manganese Oxide.

1. Introduction

Heavy metals belong to the priority pollutant class due to their physico-chemical characteristics which hinder their biodegradability by soil microrganisms and which cause their accumulation in the environment (Wuana and Okieimen, 2011). The toxicity of these elements strongly depends on the metal speciation, on its concentration, on the target organism and on the assumption pathway (Broos *et al*., 2005). Chromium (Cr) is considered as a priority pollutant and it is released into the environment by several industrial activities including tanning and metallurgical processes (Kotas and Stasicka, 2000). Naturally occurring chromium amount ranges from 10 to 50 mg kg^{-1} dry soil depending on the parent material (Gorny *et al*., 2016). Chromium exists in oxidation states ranging from +6 to −2 but only the +6 and +3 oxidation states are stable under most natural environments (Richard and Bourg, 1991). Hexavalent chromium Cr(VI), is more soluble and toxic with respect to the trivalent form (Gueye *et al*., 2015), which easily precipitates as chromium hydroxide or to co-precipitates adsorbed onto the surface of other minerals (Davis and Olsen, 1995). Therefore, the reduction of Cr(VI) to Cr(III) is nowadays considered as one of the most suitable remediation process for the remediation of a Cr contaninated soil (Di Palma *et al*., 2015). Among the several reducing agents (Fe(II), H_2S, S^{2-} etc.) successfully tested in literature (Buerge and Hug, 1999), nano zero valent iron, nZVI, appears to be one of the most promising, mainly due to large specific surface area, high superficial activity and the capacity to remain in suspension for long time when injected as colloidal suspension into contaminated zones (Vilardi and Di Palma, 2016). The reduction of Cr(VI) by nZVI is a cyclic, multiplestep electrochemical corrosion process (Powell *et al*., 1995) and it strongly depends on the contact time, the concentration of nZVI and the chemical composition (heavy metals, organic matter, ionic species, etc.) of the surrounding medium. In particular the influence of reactive manganese species and natural organic matter have been often highlighted in literature. In this study the influence of both manganese oxides and NOM on Cr(VI) reduction by nZVI in polluted soils was investigated, focusing on their effect on process efficiency and reduction rate. Manganese dioxide, $\square$-MnO_2 (pyrolusite), effect on Cr(III) oxidation to Cr(VI) was deeply first proposed by Bartlett and James, 1979. They stated that Cr(III) is not oxidized by manganese oxides in dry soils but only in moist soils. The rate and amount of Cr(III) oxidation is influenced by ratio of surface area to solution volume and by the pH of soil solution (Trebien *et al*., 2011). As regards the influence of natural organic matter (NOM) on nZVI mediated reduction processes, several studies reported that NOM, depending on the target pollutant and on the medium characteristics, could both enhance the reduction rate, or hinder the reduction of the target pollutant (Chen *et al*, 2011). The decrease of the contaminant reduction rate was attributed to the competition by adsorbed NOM for reactive surface sites, whilst the increase of the contaminant reduction was generally due to improved electron-transfer (Tratnyek *et al*., 2001). On the other hand, several authors (Bartlett and Kimble, 1976; Lv *et al*., 2016) have clearly demonstrated that humic and fulvic acids are able to reduce Cr(VI) to Cr(III) and to decrease the passivation rate of the nZVI surface (Rivero-Huguet and Marshall, 2009). In this study, a natural Mn and Cr rich soil and an artificially contaminated soil were treated by nZVI, and the influence of both manganese oxides and NOM on Cr(VI) reduction

was investigated, focusing on their effect on process efficiency.

2. Materials and Methods

2.1 Synthesis of nanoparticles

nZVI-particles were synthesized by reduction of iron sulfate heptahydrate ($FeSO_4*7H_2O$) with sodium borohydride ($NaBH_4$). Carboxy methyl cellulose was used as dispersing agent in the ratio $CMC/Fe^{2+}=0.005$ (mol/mol) according to previous studies (He *et al.*, 2007). The synthesis was carried out in a 500-mL flask where nitrogen (N_2) was purged during the entire preparation. The procedure consisted of the preparation of 120 mL of a 0.04 M Fe^{2+}-CMC solution to which 120 mL of a solution 0.08 M of BH_4^- were added drop wise. No buffer systems were used during the preparation or during the experiments. Reaction mixture was shaken vigorously for an hour, up to the gas evolution (hydrogen) ceased. All the reagents were used without any purification and all the solutions were prepared in deionized water (DI).

2.2 Experimental procedure

The natural Mn/Cr-rich soil was collected at an industrial site in Northern Italy (plating and steel industries), whereas the other Mn/Cr-poor soil was collected in a near area. Both soils were mainly composed of silt and clay. As regards the preparation of the BS soil, 8 mL of Cr(VI) stock solution were spiked to 100 g of soil (80 mg Cr(VI)·kg^{-1}). The soil was then dried under mixing conditions for 30 days and then used for the experiments. In Table 1 the main characteristics of natural soils A and B are reported. The characteristics of the spiked soil (BS) are also reported, as well as the limit for civil and industrial reuse according to the Italian regulation (Italian Environmental Regulation, 2006). Leaching tests were first carried out using deionized water and at a liquid/solid ratio equal to 10, to investigate Cr(VI) mobility from the soil to the liquid phase. In brief the experimental procedure for reduction tests on both soils consisted of preparing nZVI-soil slurries, using three different nZVI (120, 360 and 600 mg nZVI·L^{-1}) solutions, added in to 20 g of soil, in order to obtain a Fe(0)/Cr(VI) molar ratio equal to 1.5, 4.5 and 7.5, that corresponded to the stoichiometric ratio, and to an excess of 3 and 5 times with respect to the stoichiometric ratio, respectively, according to the following equation:

$$3Fe^0 + Cr_2O_7^{2-} + 7H_2O \rightarrow 3Fe^{2+} + 2Cr(OH)_3 + 8OH^-$$
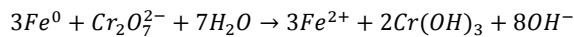
A liquid/solid ratio of 10 was adopted, as optimized in previous studies (Gueye *et al.*, 2016). At selected times interval (0, 5, 10, 15, 30, 60, 120 min) the slurry was filtered (0.45 ☐m) and Cr(VI) and pH were measured on both liquid and solid fractions. Metals concentration was determined after acid digestion according to the EPA 3050B method followed by atomic absorption spectrophotometry (FAAS) analysis, using a Agilent AA DUO 240 Fs instrument. Cr(VI) concentration was determined by colorimetric method with diphenylcarbazide after alkaline digestion according to the EPA 3060A method using a UV-visible spectrophotometry (T80+, PG Instruments, Ltd.). Total Organic Carbon was determined using a Shimadzu TOC Analyzer.

Table 1. Soil characteristics.

Parameter (mg·kg^{-1})	A	B	BS	Limit for civil reuse (mg·kg^{-1})	Limit for industrial reuse (mg·kg^{-1})
pH	7.6	7.77	7.58	-	-
TOC	400	330	310	-	-
Cr	125.2	4.3	83.4	150	800
Cr	73.5	0.71	80.2	2	15
Mn	700	52	52	-	-
Fe	3894	4034	4034	-	-

In a second series of tests, both soils A and BS were mixed with a certain amount of leonardite, a natural occurring organic matter rich in humic substances, as reported in Table 2, in order to increase the TOC to 1.5 and 2 g·kg^{-1}, respectively, and the same experiments performed in the first series of tests where carried out, at a Fe(0)/Cr(VI) = 1.5 (stoichiometric amount).

Table 2. Characteristics of leonardite.

Parameter	Value
TOC (% on d.m.)	60
Humic substances (% on d.m.)	36
Organic N (% on d.m.)	0.8
P_2O_5 (% on d.m.)	0.8
K_2O (% on d.m.)	0.8
MgO (% on d.m.)	<0.14
Microelements (% on d.m.)	<0.14

3. Results and Discussion

3.1 Preliminary leaching tests

Table 3 reports the characteristics of the elutriates from soil A and BS.

Table 3. Characteristics of elutriates.

Parameters	A	BS
pH	7.3	7.2
Cr (mg L^{-1})	7.32	7.95
Cr(VI)(mg L^{-1})	7.02	7.9

As expected almost all the hexavalent chromium was released to the liquid phase from both the tested soils, due to its high solubility and mobility.

3.2 Influence of Mn on Cr(VI) reduction process

The results of the reduction tests are reported in Table 1 (solid phase) and Figure 2 (liquid phase), in terms of Cr(VI) residual concentration.

Table 4. Cr(VI) reduction in soil.

Time (min)	Soil A			Soil BS		
	Fe(0) amount respect to the stoichiometric value					
	x1	x3	x5	x1	x3	x5
	Cr(VI) mg kg^{-1}					
0	73.5	73.5	73.5	80.2	80.2	80.2
5	2.4	2.2	2	1.5	1.3	1.1
10	2.4	2.2	2	1.5	1.3	1.1
15	2	1.9	1.9	1	1	1
30	1.7	1	1	1	1	1
45	1.2	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.
60	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.
120	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.

Results show that the reaction occurred both at the solid/liquid interface, and in the liquid phase. Table 4 shows, in fact, that when both the tested soil were mixed with the nZVI solution, hexavalent chromium was immediately released to the liquid phase, due to its high solubility, as expected basing on the results of the leaching tests. Such dissolution was not dependant on the amount of nZVI in the leaching solution. Following such quick dissolution into the liquid phase, the low residual amount of Cr(VI) in the solid phase slowly decreased during time.

Figure 1 shows that Cr(VI) reduction in the solution in contact with soil BS, quickly occurred and the residual Cr(VI) concentration decreased with the increase of nZVI concentration. An almost constant Cr(VI) concentration in the liquid phase was achieved after 60 minutes of treatment. In particular, the calculated removal efficiencies at the end of the tests (after 120 minutes) were 82, 83.5 and 84 % for the tests performed at equimolar and at a molar excess x3 and x5 between nZVI and Cr(VI), respectively. A different behaviour was observed in the liquid phase in contact with soil A. An initial quick reduction was, in fact, observed in all the tests, until a minimum value of Cr(VI) residual amount in the contact solution was reached after 15 minutes. This first step, was followed by an increase of Cr(VI) concentration in the contact solution, starting from 15 minutes of treatment the Cr(VI) concentration starts to increase, until an apparent asymptotic value at 120 minutes was attained. This trend can be explained considering the re-oxidation effect towards Cr(III) by manganese dioxide, MnO$_2$. The soluble Cr(III) is susceptible of oxidation to Cr(VI) on the surface of MnO$_2$, according to a three-steps mechanism in aqueous solution, involving first soluble Cr(III) sorption to the mineral surface of Mn dioxide, its oxidation to Cr(VI) by Mn(IV) on the surface sites and, finally, Mn(II) and Cr(VI) desorption and release into the

liquid phase (Eary and Rai, 1987). The overall oxidation process strongly depends on the pH of the medium since it seems to be catalyzed by acids (Fendorf and Zasoski, 1992). The pH of the contact solution was then measured in all tests, and the values are reported in Figure 2.
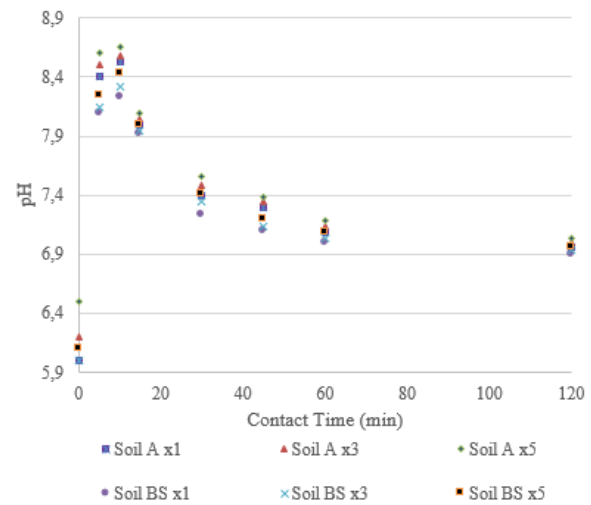

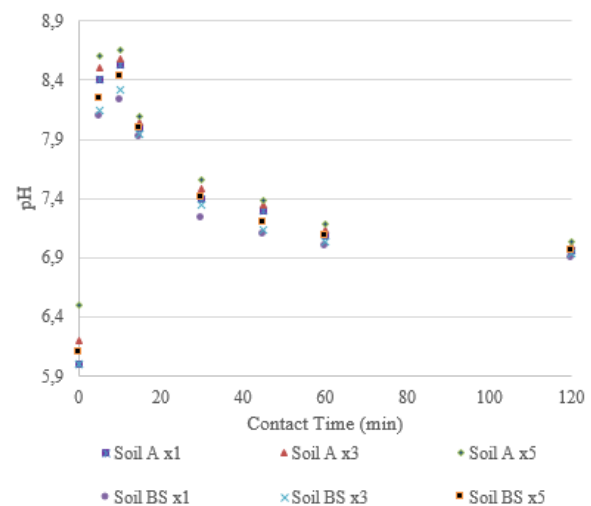**Figure 1.** Cr(VI) reduction in the liquid phase.

Figure 2. pH of the slurry as a function of contact time.

Figure 2 shows that, during the reduction test, starting from initial slight acidic conditions, the pH of the contact solution quickly increased until values larger than 8 were achieved in all the tests. After 10 minutes of treatment, a pH decrease was observed, until a pH around 7 was achieved. Since Cr(III) solubility strongly increases at decreasing pH below 7.9 (Richard and Bourg, 1991), as a result of such pH trend in the contact solution, and the simultaneous reduction of Cr(VI) to Cr(III) by nZVI, Cr(III) became available to oxidation to Cr(VI) by MnO$_2$ in soil A. Conversely, in soil BS, in the absence of Mn, Cr(VI) concentration progressively reduced over time, until an almost constant concentration was attained between 60 and 120 hours of treatment.

3.3 Influence of NOM on Cr(VI) reduction process

In Figure 3 the results of the second series of experiments are reported, as Cr(VI) residual concentration in the

contact solution. Results show that, in the case of soil BS, the presence of humic substances strongly improved Cr(VI) reduction by nZVI, mainly due to the oxidation of humic substances which enhanced the reduction of Cr(VI) to Cr(III) by nZVI (Chen *et al.*, 2011). The calculated removal efficiency increased from 82% (values obtained without any NOM addition) to 90% and 92.2% for TOC=1.5 g kg^{-1} and TOC=2 g kg^{-1}, respectively. In the case of soil A, due to the simultaneous presence of Mn-oxides the same trend previously shown in Figure 1 was observed. The added organic acids favoured the re-oxidation of Cr(III), that resulted enhanced due to the higher decrease of the pH of the soil-solution slurry during time in the contact solution is reported.
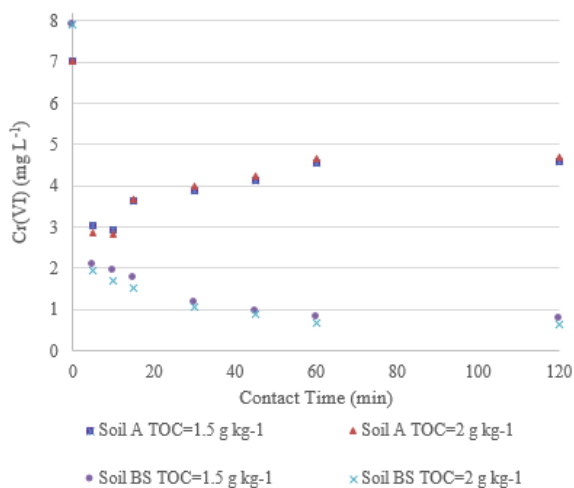

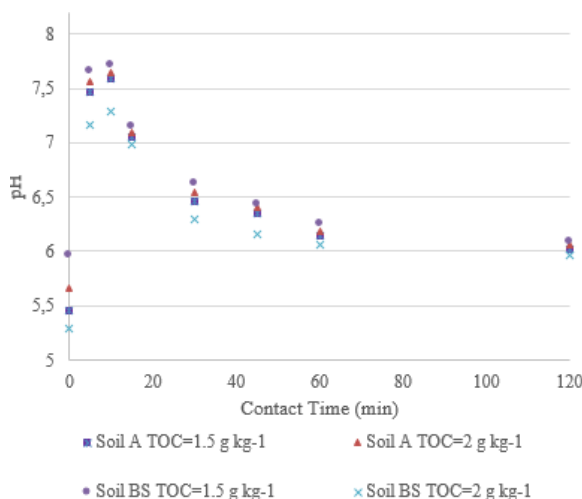**Figure 3.** Cr(VI) concentration in the contact solution over time.

Figure 4. pH of the slurry as a function of contact time.

The trends reported in the figure above are similar to those reported in Figure 2, but the pH values are generally lower than those measured in the previous experiments (without addition of leonardite).

4. Conclusions

In this study, a natural Mn and Cr rich soil and an artificially contaminated soil were treated by nZVI, and the

influence of both manganese oxides and NOM on Cr(VI) reduction was investigated, focusing on their effect on process efficiency. Results show that hexavalent chromium was immediately released to the liquid phase, and the low residual amount of Cr(VI) in the solid phase further slowly decreased during time. Cr(VI) reduction in the liquid phase quickly occurred and the residual Cr(VI) concentration only slightly decreased with the increase of nZVI concentration. The progressive acidification of the liquid phase, due to the development of the oxidation-reduction reaction between Cr(VI) and nZVI favoured the re-oxidation of Cr(III) by MnO$_2$. In the Mn rich soil, in fact, the establishment of pH values below 7.9, determined, after 10 minutes of reaction, the re-oxidation by MnO$_2$ of the solubilized Cr(III) to Cr(VI): after 120 min of treatment, about 50% of the Cr(III) formed by Cr(VI) reduction by nZVI was converted again in the oxidated form. The presence of a high amount of organic matter strongly improved Cr(VI) reduction by nZVI, due to the simultaneous oxidation of humic substances. Cr(III) re-oxidation was also favoured, due to the establishment of more acidic conditions during the treatment.

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