

Chemical Reduction of Hexavalent Chromium (VI) in Soil Slurry by Nano Zero Valent Iron

Mouhamadou Thierno Gueye, Elisabetta Petrucci, Luca Di Palma*

Dipartimento di Ingegneria Chimica Materiali Ambiente, Sapienza Università di Roma, via Eudossiana 18, 00184, Roma, Italy
luca.dipalma@uniroma1.it

The increasing industrial development of recent decades has led to the production of increasing quantities of waste containing heavy metals, elements often harmful to the environment, which in the past were not properly disposed of, thus inducing soil and groundwater pollution.

In particular, chromium (Cr) and its derivatives are largely used in industries such as textiles, electronics, metallurgy, tanneries. Consequently, large quantities of this element were released into the environment due to leakage or incorrect disposal.

Chromium is a transition element present in nature in three stable forms: metallic Cr, trivalent Cr(III) and hexavalent Cr(VI). Metallic Chromium is rarely found in nature, mainly as natural chrome metallic inclusions in diamonds, fragments of as meteorites and metal alloys in fluvial deposits. The trivalent form is characterized by a relatively low toxicity, while the hexavalent chromium present in different compounds of industrial origin, is considered highly toxic towards the respiratory system and carcinogenic.

In the present work, lab experiments of Cr(VI) contaminated soil clean-up by chemical reduction with nanoparticles of zero valent iron (nZVI) are presented and discussed. The aim of the work was to optimize the main operative parameters of the reduction process (pH, nZVI concentration, liquid/solid ratio). Cr(VI) reduction using nZVI was found to obey a pseudo-first-order kinetic: the kinetic constant depended upon the nZVI: Cr(VI) ratio. The use of nZVI in combination with sodium dithionite was also studied, by performing tests in batch conditions at pH = 1.3, in order to assess the optimal ratio between nZVI and Cr(VI), and between dithionite and Cr(VI). The results obtained showed an increase of Cr(VI) reduction rate with respect to the tests carried only with nZVI: for long treatment times, up to 24 hours, an almost total removal of Cr(VI) was achieved when a large excess of reagents was used.

1. Introduction

Heavy metals are common soil pollutants and constitute a threat for the ecosystems since they are not subject to natural degradation (Alunno Rossetti et al., 2006). In particular, in the surrounding areas to galvanic industries, textile and metallurgical high concentrations of hexavalent chromium are often found (Di Palma and Verdone, 2012). Hexavalent chromium is highly toxic and on the basis of epidemiological and experimental evidence has been classified by the IARC (International Agency for Research on Cancer) as a human carcinogen, class I (Di Palma et al., 2005). It also has high water solubility and mobility in the environment (Bartlett, 1991), making it a potential risk for contamination of groundwater and soil (Kozuh et al., 2000). Technologies for Cr(VI) removal from soil include bioremediation (Chai et al., 2009), electrokinetic processes (Gonzini et al., 2010), and oxidation/reduction processes (Singh et al., 2011), even by iron-based particles (Cundy et al., 2008).

The present paper deals with the clean-up of a soil polluted by long term industrial activity. The aim of the experimental work was to achieve the removal of hexavalent chromium through a decontamination treatment based on the chemical reduction in the trivalent form, insoluble and less toxic (Di Palma et al., 2012).

Recently, the chemical reduction of Cr(VI) with zero valent iron nanoparticles (nZVI) has received considerable attention in the field of environmental remediation and is becoming an increasingly used for the treatment of hazardous and toxic waste and cleaning up groundwater and contaminated soils (Li et al., 2006). In addition, a previous study also demonstrated that stabilized ZVI with carboxy-methyl-cellulose (CMC) proved to be a very effective effective reducing agent against the Cr(VI) (Di Palma et al., 2015).

In this paper we have tested the use of the reducing agent in the treatment of polluted industrial soil. To this purpose, as reducing agents, zero valent iron nanoparticles (nZVI) stabilized with (CMC), and a combination of nZVI stabilized and sodium dithionite were studied. The tests were carried out in batch mode, at different ratios between nZVI and dithionite and chromium, as well as varying the pH of the reducing solution.

The objective of this work was to optimize the main parameters (pH, concentration of Fe(0), solid-liquid ratio) to determine the optimum conditions for the reduction of Cr(VI). The experiments were conducted on samples of contaminated soil collected in an area affected by activities of coating and surface finishing of steels, characterized by high concentrations of Cr(VI) and other heavy metals. It was therefore developed a kinetic model with which to correlate the experimental data and obtain an estimate of the kinetic constants of the reaction.

2. Materials and Methods

2.1 Soil characterization

Soil characterization was carried out through commonly used protocols (Liu and Evett, 2002). The main characteristics of the soil are reported in Table 1.

Table 1: Selected characteristics of the soil

Parameter	Value
pH	7.54
C.E.C. (meq/100 g)	9.6
Organic carbon (g/kg)	14.45
Organic matter (g/kg)	24.91

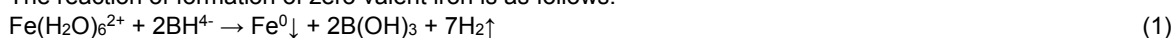
Metals concentration was determined after acid digestion technique according to the EPA 3050B method (Liu and Evett, 2002) followed by atomic absorption spectrophotometry (FAAS) analysis, using a Agilent AA DUO 240 Fs instrument. The concentration of Cr(VI) was determined by the colorimetric method of diphenylcarbazide (Bartlett, 1991) after alkaline digestion according to the EPA 3060A method (US EPA, 1996) using a UV-visible spectrophotometry (T80+, PG Instruments, Ltd.). Table 2 reports the mean concentration of heavy metals in the soil, and the limits for a civil reuse (mg/kg), or industrial reuse (mg/kg) according to Italian regulation (Italian Environmental Regulation, 2006).

Table 2: Metals in soil

Metal	Concentration (mg/L)	Limit for industrial reuse (mg/kg)	Limit for civil reuse (mg/kg)
Cr	155.2	150	800
Cr(VI)	54.4	2	15
Ni	156.2	120	500
Mn	817.6	-	-
Fe	36267	-	-
Pb	18.0	100	1000

2.2 Experimental procedure

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



The size of nZVI and soil particles were measured using a Malvern Instruments Zetasizer 3600 Zen.

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:



The experiments were performed at room temperature (20 ± 1 °C), and at the end of each test, the soil sample was filtered through a 0.45 µm Whatman membrane filter, and the reaction was stopped by washing the soil with distilled water. The pH in the liquid phase was measured using a GLP42+ Hanna Instrument. The residue amount of metals and Cr(VI) in soil after treatment was determined according the above mentioned procedure. In a first series of tests devoted to the reduction process optimization, selected concentration of Fe⁰ were used. With respect to the stoichiometric ratio, excesses of iron equal to 15, 20 and 25 times, corresponding to concentrations of Fe⁰ equal to 0.131, 0.175 and 0.219 g / L, were adopted.

In a second series of tests, carried out at room temperature and pH = 1.3, the combination of Fe⁰ and dithionite was tested. The tests were conducted at molar ratios combined Fe⁰ / Cr (VI) and Na₂S₂O₄ / Cr (VI) equal to 15-15; 20-20, 25-25 (hereafter named as Fe15-D15, Fe20-D20 and Fe25-D25, respectively). All tests were conducted in triplicate.

3. Results and Discussion

3.1 Effect of nZVI concentration and pH

The study reveals that treating polluted soil with a nZVI aqueous solution, the chromium removal was time dependant and increasing with Fe⁰ concentration, as shown in Figure 1. In the test performed at the concentration of 15 times excess, Cr(VI) removal of about 70% was achieved: the residue amount in the soil was 16.1 mg/kg then higher than the limit for both residential and industrial reuse according to Italian Regulation (Italian Environmental Regulation, 2006, see Table 2). Residue level below this threshold was not achieved either increasing the Fe⁰/Cr(VI) ratio up to 25, or prolonging the reaction up to 24 hours of treatment (data not shown). This behaviour can be explained considering that that the Cr(VI) reductive reaction occurred on the Fe⁰ nanoparticles surfaces. As the Fe⁰ nanoparticles mass concentration increased, the reactive sites proportionally increased, thus determining a corresponding increase of Cr(VI) removal efficiency.

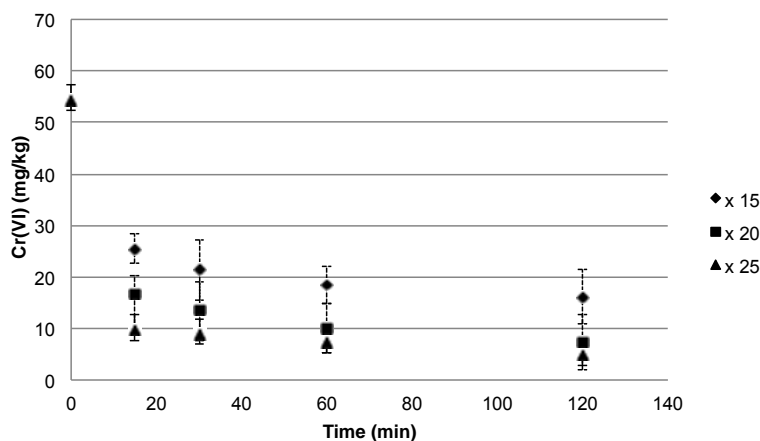


Figure 1: Cr(VI) residue in the soil treated with nZVI

In addition, during treatment alkaline conditions were established, depending on the concentration of Fe⁰, due to the reaction (2) and the side reaction of Fe⁰ with water producing hydroxyl ion according to the (Liu et al., 2005):



However, the final pH of the slurries were 7.64, 7.43 and 7.17 for initial pH 7.76, 7.73 and 7.63 for the tests conducted with x15, x20, and x25 excess, respectively. Such a slight decrease in pH after 120 min of reaction was due to the consumption of hydroxides by trivalent chromium and iron, to form oxy-hydroxides of Cr and Fe on the surface of the nanoparticles (Powell et al., 1995), despite their release according to the above mentioned reactions 2 and 3 (Orth and Gillham, 1996). The formation of oxy-hydroxides of Cr and Fe on the surface of the nanoparticles during the reaction also determined the passivation of reactive surface (Lee et al.,

2003), thus explaining the reduction of reagent efficiency over time, as already observed in other studies (Rivero-Huguet and Marshall, 2009).

3.2 Kinetics

Figure 2 shows representative kinetic profiles accounting for Cr(VI) reduction using nZVI in the slurry reactor under agitation (120 rpm). Good correlation coefficients were obtained from the linear regression analysis, thus revealing that Cr(VI) reduction using nZVI obeys a pseudo-first-order kinetic model, as found in other studies in literature (Franco et al., 2009).

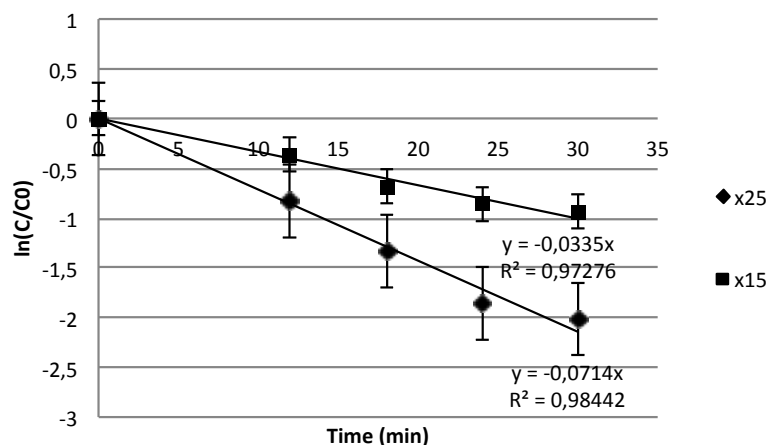


Figure 2: Kinetics of pseudo-first order of the Cr(VI) reduction

Considering that the redox process obeys a pseudo-first-order kinetic model (Wang et al., 2010), the reduction of Cr(VI) taking place in the slurry reactor can be described by the following relation (Xu and Zhao, 2007):

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

where [Cr(VI)] is the instantaneous concentration of Cr(VI) (mg/L), t is the treatment time (min) and k_{obs}^* is the overall kinetic rate constant for the heterogeneous redox process (min^{-1}).

Taking into account the heterogeneous nature of the redox process carried out under constant and intense agitation and the collisions among the suspended soil microparticles (SSM), as well the collisions of these particles with the nZVI, at k_{obs}^* can be represented by the (Franco et al., 2009):

$$k_{obs}^* = k_h \cdot \left\{ [Cr(VI)_0] \cdot [Fe^0]_0 \right\}^y = \left(k_{sa} \cdot a_s \cdot Z_h \cdot \theta \cdot A_{(SSM)} \right) \cdot \left\{ [Cr(VI)_0] \cdot [Fe^0]_0 \right\}^y \quad (5)$$

where [Cr(VI)]₀ and [Fe⁰]₀ are the initial concentrations of Cr(VI) and nZVI, respectively, and k_h and y are empirical constants for the specific redox process.

The parameter k_h is the heterogeneous kinetic rate constant, representing the redox process taking place at the surface of the nZVI under perfect mixing conditions, in contact with SSM, and:

- Z_h is the heterogeneous collision frequency factor;
- k_{sa} is the specific kinetic rate constant related to the active surface area of iron nanoparticles ($\text{l} \cdot \text{min}^{-1} \cdot \text{m}^{-2}$) (He et al., 2007);
- a_s is their average specific surface area ($\text{m}^2 \cdot \text{g}^{-1}$)
- $\theta A_{(SSM)}$, with $0 \leq \theta \leq 1$, is the average active surface area of the SSM where θ is the fraction of the SSM surface containing Cr(VI).

Thus, once obtained k_{obs}^* from the kinetics data (Figure 2), and measured the size of nZVI and SSM, the values of the kinetic parameters were calculated, as shown in Table 3.

3.3 Combination of nZVI and dithionite for Cr(VI) reduction

The method uses the nZVI in combination with dithionite ($\text{Na}_2\text{S}_2\text{O}_4 = \text{D}$) in equimolar ratio, to inhibit oxidation, aggregation and precipitation of ferrous iron, which mitigates the surface passivation of nZVI. The mechanism

of Cr(VI) treatment in Na₂S₂O₄ applications involves the conversion of Fe(III) in soils to Fe(II) by Na₂S₂O₄ and the subsequent reduction of Cr(VI) to Cr(III) by Fe(II) to form the Cr_xFe_{1-x}(OH)₃ solid (Paul et al., 2002).

Sodium dithionite in water undergoes dissociation and disproportionation reactions to form primarily sulfoxyl radicals (SO₂^{•-}), sulfites (SO₃²⁻), and thiosulfates (S₂O₃²⁻) via following equations:

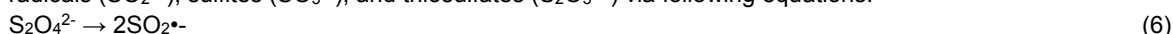
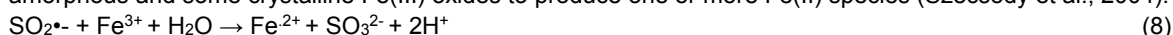


Table 3: Values of kinetic parameters

Fe ⁰ /Cr(VI) (mol/mol)	[Fe ⁰] (g/l)	K [*] _{obs} (min ⁻¹)	k _{sa} (l·m ⁻² ·min ⁻¹)	a _s (m ² ·g ⁻¹)	Θ	A _(SSM) (m ²)	Z _h (l·g ⁻¹ ·m ⁻²)	Y
15/1	0.131	0.0335	4.27·10 ⁻⁸	5.98·10 ⁶	0.31	2.07	287.25	1
25/1	0.175	0.0714	5.45·10 ⁻⁸	5.98·10 ⁶	0.31	2.07	287.25	1

During dissociation reactions, dithionite can reduce structural iron in clays and dissolve and reduce amorphous and some crystalline Fe(III) oxides to produce one or more Fe(II) species (Szecsody et al., 2004):



The oxidation of 1 mol of dithionite by Fe(III) to 2 mol of sulfite ultimately resulted in the production of 4 mol of acid. To limit the precipitation of Fe(OH)₂ which can inhibit the dissemination of Fe(II), the test were performed in a pH range between 2 and 5 by adding H₂SO₄. In such conditions, the reduction of Cr(VI) by the Fe (II) can be written as:



The results of the laboratory tests carried out using combined solutions of nano zero valent iron and dithionite, indicate that treatment is more effective in long term compared to that made with only Fe⁰ (Figure 3). Thus, the combination resulted in both an almost complete elimination of Cr(VI) using the solution Fe25-D25: lowering of the concentration of couple Fe-D, the residual Cr(VI) was below 2 mg/kg after treatment with the Fe20-D20 solution, thus allowing a civil reuse of the soil (Italian Environmental Regulation, 2006), and below the limit for industrial reuse when the Fe15-D15 solution was used.

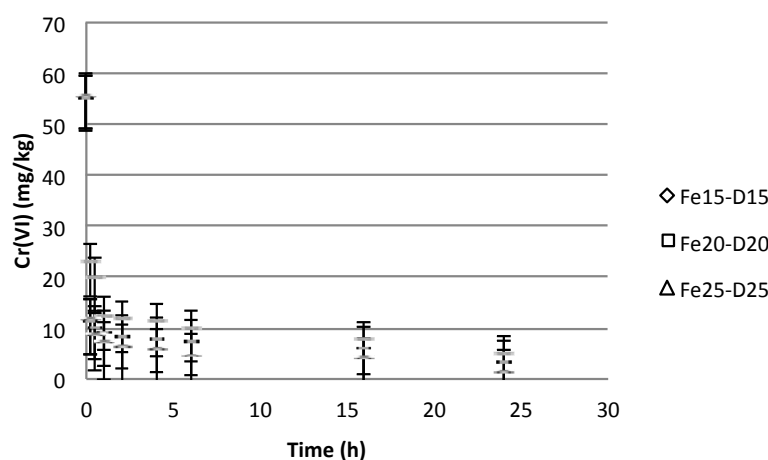


Figure 3: Cr(VI) residue as a function of time by combining solution of nZVI and dithionite

4. Conclusions

In the present work the reduction of hexavalent chromium in contaminated soil, through a decontamination treatment based on chemical reduction was investigated. As reducing agents solutions of stabilized zero valent iron nanoparticles (nZVI) and a combination of nZVI and sodium dithionite were used.

The results showed that increasing the ratio Fe⁰/Cr(VI)₀ the percentage of removal of chromium also increased. After 120 min of treatment, using Fe⁰ excess of 15, 20 and 25 times, respectively, Cr(VI) content in the soil was reduced of to 70.3 %, 86.6 %, 91.1 %. Tests conducted prolonging contact time up to 24 h did not show significant increasing of performances, due to progressive Fe⁰ inactivation. Only when the higher reagent excess was used it was possible to obtain levels of Cr(VI) residues in the soil such as to permit its reuse for commercial or residential purpose in accordance with current legislation in Italy. Cr(VI) reduction

obeyed a pseudo-first-order kinetic, and was correlated, in accordance to literature model, to the collision frequency between SSM and nZVI and the average specific surface area available for the redox process. To investigate the possibility of further reducing Cr(VI) level, in a second series of tests, the reductant solution consisted in a mixture of nZVI and sodium dithionite. Tests were carried out in batch conditions at pH = 1.3, to assess the optimal ratio between $\text{Fe}^0/\text{Cr(VI)}_0$ between and dithionite/ Cr(VI)_0 , showed a similar increase of the reduction rate of Cr(VI) with respect to the tests carried only with nZVI. Furthermore, for long treatment times (up to 24 h) it was possible to obtain in this case an almost total removal of Cr(VI), though using a large excess of reagents (25 times with respect the stoichiometric amount).

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