



Experimental Assessment of Chromium Mobilization from Polluted Soil by Washing

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Chromium contamination in soils mainly results from the discharge of chromium-containing wastes from several industrial activities. Chromium remediation in soils may involve extraction from the soil matrix by washing with an aqueous solution containing a chelating agent. Since any extraction treatment strongly affect soil chemical and physical properties, and the metals distribution into the different soil fractions, one of the major risks of applying this remediation approach may be the increase in the oxidation potential of the soil and, as a consequence, the enhancing of trivalent chromium conversion into the soluble and more toxic hexavalent form. This oxidation potential, in fact, will strongly depends upon several soil characteristics, mainly organics amount and manganese oxide content.

The objectives of this paper were therefore to investigate the effectiveness of selected unspecific chelating agents (Ethylenediaminetetraacetic acid, EDTA, Ethylenediamine-N,N'-disuccinic acid, EDDS, and Nitrilotriacetic acid, NTA) towards total chromium removal and to investigate the effect of the extraction treatment on the potential chromium oxidation capacity of the soil. Experimental batch tests of chromium extraction from soil slurries were performed at different pH and at a 1:10 liquid vs. solid ratio: chromium concentration was determined on the extracted solutions, and mass balances were performed. Results show that using EDTA and EDDS, the calculated maximum chromium extraction efficiencies were 25 % and 27.5 % respectively, depending upon the pH of the extracting solution, while a lower removal rate was observed by using NTA. According to the results of oxidation tests performed after the extractions, as a consequence of soil characteristics modifications induced by the extraction process, the soil showed a different potential of Cr(III) oxidation, depending on the operating conditions of the washing treatment.

1. Introduction

Chromium in galvanic industry contaminated soil is mainly present in two stable forms: trivalent, Cr(III), and hexavalent, Cr(VI). Cr(III) is a low toxicity nutrient for plant growth, instead the hexavalent form is more dangerous and human carcinogen (Kozuh et al., 2000; Molokwane and Chirwa, 2009). Bartlett (1991) showed that Cr(VI) is capable of moving towards groundwater due to its extreme mobility, and it is in thermodynamic equilibrium with the atmosphere. Cr(VI) is the product of oxidation of Cr(III) with atmospheric oxygen and its presence is greater into the earth crust. Since the natural oxidation of Cr(III) is extremely low, most of the Cr(VI) found in soil and groundwater results from pollution. Usually, an high concentration of Cr(VI) in areas close to galvanic industries and steel mill is found. The Cr(III) reactivity increase when the inert crystals and amorphous mineral are transformed in organic and hydroxide forms, smaller and more mobile. The equilibrium between the two chromium forms in soil

depends upon soil physical and chemical characteristics. The oxidation process is only controlled by the reaction kinetics, due to Cr(III) species immobility and insolubility (Bartlett, 1991). Cr(III) tends to be strongly bound by soil humic acid polymers, and this affinity restricts the availability of Cr(III) to be oxidized and reduce the organic matter decomposition. Bartlett and James (1979) have reported that the presence of manganese oxide in soils favors trivalent chromium oxidation, thus increasing the hazards connected to hexavalent chromium contamination of groundwater. The various oxide surface characteristics and the amount of mobile Cr(III) in contact with the surface are the controlling parameters of the Cr(III) oxidation reaction. MnO₂ works, in fact, as an electron link between Cr(III) and the atmospheric oxygen, and it was found that the amount of oxidized Mn in soil is proportional to the amount of oxidized Cr(III) (Bartlett, 1991). As a result, soil Cr(III) oxidation capacity is strongly increased under acidic conditions in the presence of manganese dioxide (MnO₂).

Several studies performed during the past two decades have already assessed that metal extraction could represent an alternative to immobilization technologies for metal contaminated soil remediation (Peters, 1999; Mulligan et al., 2001; Dermatas and Meng, 2003; Dermatas and Moon, 2006), though the potential application of such technique is limited by the potential toxicity of the most common chelating agents and the high overall costs of the treatment (Evangelou et al., 2007). Metal extraction can be performed by the *in-situ* (Finzgar and Lestan, 2007; Tsang et al., 2007) or *ex-situ* (Di Palma et al., 2005) complexation by a chelating agent. The effectiveness of the extraction is strongly dependant upon the presence in the soil matrix of easy exchangeable ions able to form stable complexes with low selective chelating agent (Di Palma, 2009). As a consequence of the extraction process, a strong modification of soil chemical and physical characteristics has been generally observed (Voegelin et al., 2003; Di Palma and Ferrantelli, 2005; Manouchehri et al., 2006; Moutsatsou et al., 2006) and this could affect the equilibrium between the two chromium species. In addition, solubilization of Cr(III) by organic chelant complexation, was found to increase its availability for oxidation to the hexavalent form (Bartlett, 1991). The aim of the present work was therefore to evaluate the effectiveness of selected unspecific chelating agents towards chromium removal from a contaminated soil, and to investigate the effect of the extraction treatment onto the potential chromium oxidation capacity of the soil. The tests was conducted at different pH, using three chelating agents, EDTA, EDDS and NTA, among the most widely used in soil remediation to compare their effectiveness towards chromium extraction.

The treated soil was then subjected to chromium oxidation tests to investigate the effect of the extraction treatment onto the potential chromium oxidation capacity of the soil.

2. Materials and methods

2.1 Soil characterization

The soil was a sandy-loamy soil, collected at an industrial site in Italy. Soil acid digestion was performed to determine the initial chromium content in soil, using hydrogen peroxide (30 % v/v), concentrated hydrochloric acid and nitric acid (50 % v/v) (all provided by Sigma Aldrich), according to EPA Method 3050b (Liu and Evett, 2002). 1 g of soil was dried at 110 °C and placed in a test glass tube with a reflux system. After adding 10 mL of concentrated HCl, the sample was heated to 95 °C and kept in agitation for 15 min. The test glass tube was cooled down to 25 °C and 15 mL of HNO₃ were then added to the solution. The mix was then kept to 95 °C for 2 hours and subsequently cooled down to 25 °C. After the addition of 2 mL of H₂O and 10 mL of H₂O₂, the solution was heated at 95 °C for 2 h and then sampled to determine metal content, after filtration through a 0.45 µm Whatman membrane filter, by atomic absorption spectrophotometry, using an Agilent AA DUO 240 Fs instrument. The initial Cr(III) and Cr(VI) concentration were 155 ± 10 mg/kg, and 0.06 ± 0.005 mg/kg respectively. The amount of MnO₂ into the investigated soil, determined according to the procedure described by Liu and Evett (2002) was 140 ± 10 mg/kg.

2.2 Batch extraction

Batch extraction with chelating agents were carried out to remove Cr(III) and Cr(VI) from contaminated soil 10 g samples. The initial concentration of chromium in samples was 155 mg/kg. The experiments were conducted at different pH to optimize the extraction conditions. EDTA, EDDS and NTA 0.1 M solutions were used, at a 5:1 liquid-solid ratio. The pH of the extractant solution was adjusted by

adding HCl and NaOH. In the tests performed at controlled pH, acetate buffer solutions for pH 5 and phosphate buffer solutions for pH 7 and 9 was used.

The extraction tests were performed in pyrex glass batch vessels in an orbital shaker (120 rpm). In each test the liquid-solid weight ratio was fixed at 10:1 and the temperature was kept at 20 ± 1 °C. The extraction tests were stopped after 1, 2, 3, 4, 6, 15, 24, 48, 72, 120, 168 and 240 h of contact time. At the end of each experiment, the extracted solution was filtered and analyzed by atomic absorption spectrophotometry for metal content according to the above described procedure.

2.3 Standard chromium oxidation tests

The standard chromium oxidation tests was carried out using CCl_3 to provide the Cr (III) oxidation, according to the procedure described by Bartlett (1991). 2.5 g of dried soil were shaken with 25 mL of a 1 M solution of CCl_3 for 15 min and then centrifuged. 0.25 mL of a 1 M buffer phosphate solution at pH = 7.2 were then added. After the oxidation treatment, the analytical determination of hexavalent chromium in the supernatant was carried out by the diphenylcarbazide (DPC) spectrophotometric method (Bartlett and James, 1979). 1 mL of sulfuric acid and 2 mL of diphenylcarbazide were added in 100 mL of acid digested sample, according the procedure previously described. After a 10 min reaction, Cr (VI) was determined at 540 nm using a PG Instruments Ltd T80+ UV spectrophotometer.

3. Results and discussion

3.1 Influence of pH in soil washing

Figures 1 - 3 show the results of the extraction tests: Cr percentage removal along time is reported.

The extraction efficiency was strongly affected by pH: at high concentration, in fact, hydrogen ions could compete with other cation metal, thus decreasing the amount of free chelant in the solution. Alkaline conditions, conversely, favor metal precipitation as hydroxide.

In the extraction tests performed with EDTA and EDDS, the maximum chromium removal efficiency at the end of the experiments was observed at pH = 5, while, at pH 7 and 9 the performances were found to be quite similar and not dependant on the chelant used. In the tests performed with NTA, the difference of extraction efficiency at pH 5 and 7 after 240 h of contact time was negligible, while at pH=9 a significant reduction was observed.

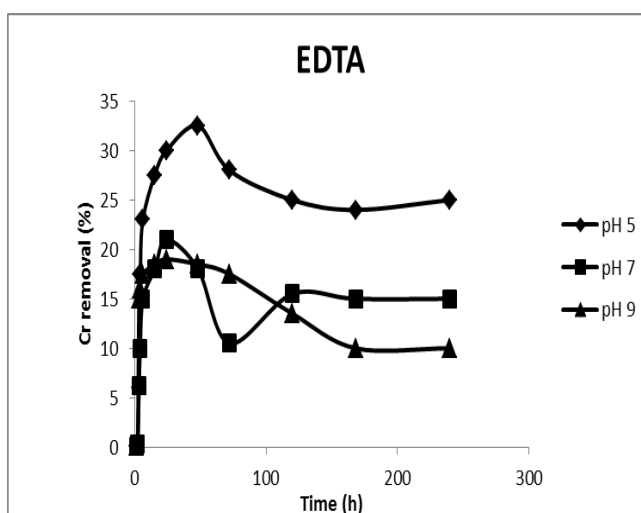


Figure 1: Results of the extraction tests with EDTA

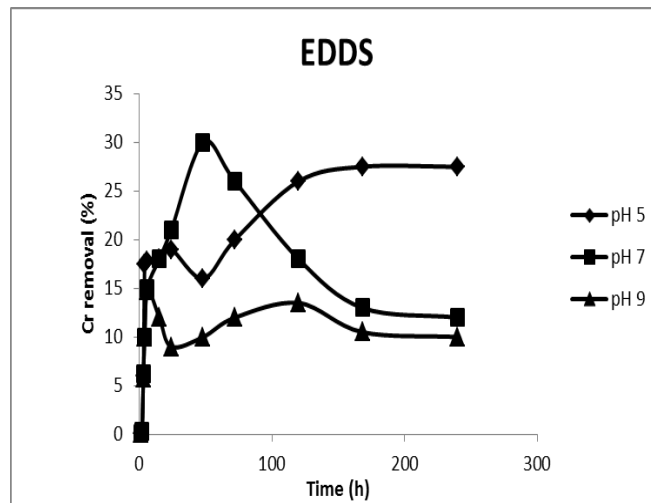


Figure 2: Results of the extraction tests with EDDS

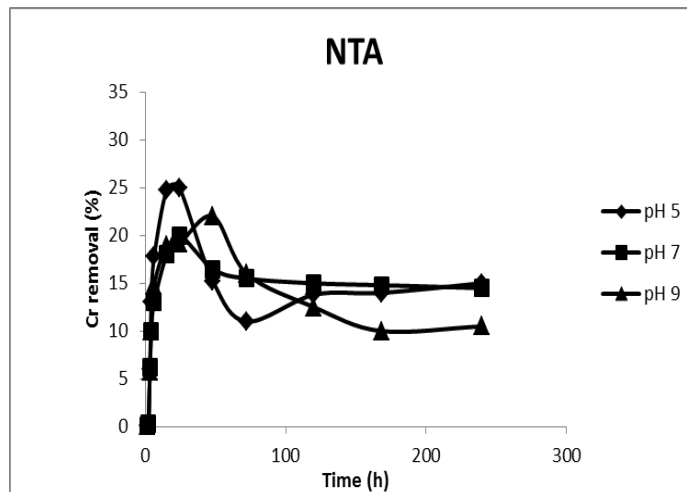


Figure 3: Results of the extraction tests with NTA

This results is in accordance to the results obtained in similar experiments: Bartlett (1991) shown that Cr(III) mobility increased when the pH soil was lower than 5, thus favoring the extraction by washing. Cr(III) is in fact a strong Lewis acid, and could form several inorganic and organic complexes which limit its mobility in the soil matrix.

All the extraction tests showed a typical trend: after an initial sharp increase of chromium in solution to a maximum value generally reached within 24 - 48 h of contact time, a progressive reduction was observed, until steady state conditions (chromium concentration constant along time) were almost achieved. This behavior can be attributed to both the chromium oxide post precipitation (mainly occurring at alkaline or neutral pH) and the exchange reaction between chromium chelates and other cations solubilized (mainly under acidic conditions), according to the mechanisms reported in previous studies (Di Palma and Ferrantelli, 2005).

When comparing the three chelating agent, after 240 h of contact time at pH = 5, the calculated chromium removal efficiencies (27.5 % for EDDS, 25 % for EDTA and 10 % for NTA) were quite low with respect to the extraction efficiency observed in similar studies for other metals (Di Palma et al., 2003; Zhang and Lo, 2006).

3.1 Chromium oxidation potential

The results obtained show that the amount of total chromium after the extractions were easily reduced below the threshold imposed by national standards (150 mg/kg for a civil reuse of the soil, Italian Environmental Regulation, 2006). However, the possibility of Cr(III) moving to Cr(VI) could increase as a consequence of the modification of soil characteristics induced by washing treatment.

After extractions by soil washing, oxidation tests were performed to establish the effective possibility of oxidizing residual Cr(III). The samples were first dissolved by acid digestion and then Cr(III) was oxidized using the standard chromium oxidation test previously described. The initial value of Cr(VI) after oxidation was 5.27 mg/kg: the amount of Cr(VI) resulting from oxidation of Cr(III) after 240 h extractions is shown in Table 1.

Table 1: Results of Cr(III) potential oxidation tests

| Extracting solution | pH | Extraction time (h) | Cr(VI) (mg/kg) |
|---------------------|----|---------------------|----------------|
| EDTA 0,1 M | 5 | 240 | 0,31 |
| EDTA 0,1 M | 7 | 240 | 0,10 |
| EDTA 0,1 M | 9 | 240 | 0,21 |
| EDDS 0,1 M | 5 | 240 | 0,27 |
| EDDS 0,1 M | 7 | 240 | 0,14 |
| EDDS 0,1 M | 9 | 240 | 0,18 |
| NTA 0,1 M | 5 | 240 | 0,16 |
| NTA 0,1 M | 7 | 240 | 0,13 |
| NTA 0,1 M | 9 | 240 | 0,12 |

The amount of oxidizable Cr(III) to Cr(VI) was found to be generally lower after the soil washing process than the initial amount: the observed decrease, up to about 98 %, can be attributed to a decrease of availability of Cr(III) and mobility, and, mainly to the reduction of its mobility. The easily exchangeable chromium, potentially available for oxidation, is in fact the main fraction extracted in washing tests (Lei et al., 2008), while the remaining fraction, strongly bound to the soil matrix, is not available to react onto the immobile manganese oxides surface (Bartlett, 1991).

Results also show that the soil samples treated at pH=5 presented a higher Cr(III) oxidation potential, according to the positive effect on MnO₂ reduction under acidic conditions. In addition, under acidic conditions, humic and fulvic acid solubilization increases and Cr(III) oxidation is consequently favoured, since the bounds between chromium and soil organic matter strongly reduce the soil organic matter decomposition and the availability of Cr(III) for oxidation to Cr(VI) (Kozuh et al., 2000).

It can be mentioned that a stronger extraction treatment (i.e. by increasing the extractant solution acidity, or chelant amount) could also solubilize the chromium presents in less labile forms, thus resulting in an increase of Cr(III) availability for oxidation.

4. Conclusion

In this paper the effectiveness of selected chelating agents (EDTA, EDDS and NTA), commonly used in remediation processes, towards total chromium removal was investigated. The experiments were conducted to evaluate the parameter affecting the extraction process, and to assess the effect of the extraction process conditions on the soil potential oxidation of Cr(III).

Experimental batch tests of chromium extraction from soil contaminated slurries were performed at different pH and at a 1:10 liquid vs. solid ratio. Results show that the extraction efficiencies were strongly dependant upon the pH of the extraction and the contact time: by increasing the pH from 5 to 9, chromium removal by EDDS was reduced by about 64 %. Using EDTA and EDDS, the calculated chromium maximum extraction efficiencies were 25 % and 27.5 % respectively, while a lower removal rate was always observed by using NTA. The maximum extraction efficiencies were obtained within 24-48 h of treatments, while the chromium oxide post precipitation and the exchange reaction between chromium and other cations solubilized, reduced chromium removal at increasing contact times.

According to the results of oxidation tests performed after the extractions, as a consequence of soil characteristics modifications induced by the extraction process, the soil showed a reduce potential of

Cr(III) oxidation (up to 98 % with respect to the initial value), depending on the operating conditions of the washing treatment, mainly due to the extraction of exchangeable chromium from the soil.

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