Chromium and nickel mobilization from a contaminated soil using chelants

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Abstract

The mobilization of chromium and nickel from an industrial soil was investigated using two biodegradable chelants (citric acid and histidine), compared with a persistent one (ethylenediaminetetraacetic acid). Successive metal mobilizations were carried out in batch experiments. The main reactions involved were estimated by modelling the system with MINEQL+. For a single mobilization, citric acid was the most effective for Cr mobilization and EDTA for Ni. Their effectiveness could be explained by their ability to solubilize the mineral matrix and by the competition for the surfaces sites to desorb Cr(VI). Before and after the mobilizations, the distribution of metals was determined by a sequential extraction procedure. Only slight modifications were observed due to the low percentage of solubilized metal. A concentration of 0.05 $mol.L^{-1}$ (citric acid and EDTA) allows a good compromise between metal mobilization and preservation of the soil mineral integrity.

Keywords: contaminated soil, chromium, nickel, chelant, mobilization

Capsule: Chelant-induced dissolution of soil mineral matrix which controls metal solubilization

1. Introduction

Metal contaminated soils are a serious environmental problem with implications for human health. The presence of metals in soil has two main origins: the alteration of the bedrock and human activities, the latter being the major cause of high levels of metals in soils (metallurgical industries, surface treatment industries, sewage sludge amendment...). The risks are related to the mobility and the bioavailability of the metals and consequently to their speciation in soil. Even when immobilized in the less mobile fractions, metals remain harmful and constitute pollutant stores, which can be removed if environmental conditions such as pH and Eh change (Stumm and Sulzberger, 1992; Bourg and Loch, 1995).

Various remediation methods, in-situ or ex-situ, are available. The conventional methods are solidification/stabilization, biochemical processes, phytoremediation, soil washing (Mulligan et al., 2001). Among ex-situ techniques, soil washing using chelating agents is an effective technique (Peters, 1999).

Many studies have been carried out on metal extraction with chelants such as ethylenediaminetetraacetic acid - EDTA, citric acid, nitrilotriacetic acid - NTA, [S,S]-ethylenediaminedisuccinic acid - EDDS (Wasay et al., 2001; Kim et al., 2003; Tandy et al., 2004; Luo et al., 2005; Di Palma and Ferrantelli, 2005; Leštan and Kos, 2005). These chelants have a high affinity for many metals. Several parameters must be taken into account, the choice of the ratio of chelant to metals being important. Consequently, chelant concentration must be higher than trace metal concentration to obtain maximum extraction. But in the soil, there are also major elements such as Fe, Al, Mn, Mg and Ca which can be simultaneously solubilized by the chelants (Kim et al., 2003; Tandy et al., 2004).

Whereas many papers have been published about metal extraction with chelants, only few studies have been carried out about Ni and especially Cr extraction. Extractions of Cr and/or Ni using chelants were mainly studied with the purpose of phytoextraction (Turgut et al., 2004; Meers et al., 2005; do Nascimento et al., 2006). Indeed, chelating agents increase the solubility of heavy metals for plant uptake during phytoremediation (Brooks, 1998; Salt et al., 1998). It is of course important to know the degree of biodegradability of the chelants. EDTA is persistent in the environment (Bucheli-Witschel and Egli, 2001) and its presence in soil can lead to uncontrolled leaching of metals (Bordas and Bourg, 1998b), thus limiting its use for phytoextraction (Alkorta et al., 2004). Citric acid and histidine are natural organic molecules that are easily biodegradable, their half-lives, in a soil suspension, being a few days (Brynhildsen and Rosswald, 1997; Römkens et al., 2002).

The aim of this study is to compare the ability of two natural and biodegradable chelants (citric acid and histidine) with a persistent one (EDTA) to solubilise metals from an industrial soil contaminated mainly by nickel and chromium.

2. Materials and methods

All reagents used to prepare the solutions were with an analytical grade. High purity de-ionized water (Milli-Q system: resistivity 18.2 MΩ.cm, TOC < 10 µg.L^{-1}) was used for all experiments.

2.1. Soil sampling and characterization

The studied soil came from a metallurgical site where special steels, superalloys, aluminium and titanium alloys are produced. The pollution was due to long time refuse storage on the bare ground. Before sampling, a superficial layer of soil (0-5 cm) containing refuse and the main part of the litter was discarded. The 5-10 cm layer of the soil was then sampled manually near the storage zone. This thickness was selected due to its contamination rate. The soil was air-dried and sieved (< 2 mm) (AFNOR, 1994). Soil properties: pH_{H2O} (6.3 ± 0.1), pH_{KCl} (5.3 ± 0.1), organic carbon (2.90 ± 0.08 g.kg^{-1}), cation exchange capacity (12.3 ± 0.1 meq/100 g) were determined by standard methods (AFNOR, 2004). The granulometry was determined by the standard method, NF X 31-107 (AFNOR, 2004). Bulk powder X-ray diffraction (XRD) was used for mineralogical characterization of the soil sample (INEL CPS 120° Curved Position Sensitive Detector, Cu*K*α1).

The total metal content was determined in the sample after a microwave-assisted digestion with *aqua regia* (microwave oven: MARCH 5, CEM). A recent study (Larner et al., 2006) proved the correctness of this method by comparison with HF digestion.

The chemical distribution of metals in the soil was quantified by the BCR sequential extractions procedure (Ure et al., 1993) accelerated by ultrasound (Pérez-Cid et al., 1998) (**Table 1**). The sonication was done with a 60W probe (Bandelin, model HD 70). After centrifugation (3000 *g*), the supernatant was filtered through 0.45 µm cellulose nitrate filter (Sartorius).

The fractionation of Fe was determined by oxalate (Schwertmann, 1964) and pyrophosphate extraction (McKeague, 1967). Oxalate extracts the poorly crystalline Fe oxides and the organically bound Fe and pyrophosphate extracts organically bound Fe.

To determine the speciation of Cr, an alkaline digestion was applied (0.5 mol.L^{-1} NaOH + 0.28 mol.L^{-1} Na_2CO_3) and the quantification of Cr(VI) was carried out using the colorimetric method

with diphenylcarbazide (Centre d'expertise en analyse environnementale du Québec, 2003). Cr(III) is calculated by subtracting Cr(VI) from total Cr.

2.2. Batch mobilization with chelating agent

Metal mobilizations were carried out in batch experiments at room temperature (20 ± 2°C). The solid:solution ratio was 1:10 with 50 mL of EDTA, citric acid or histidine solutions. Na_2-EDTA salt, citric acid and L-histidine were used. Three replicates were made.

An optimum contact time was determined by a preliminary experiment. For this, each chelating agent was applied at 0.01 $mol.L^{-1}$ and the suspension pH was established with no adjustment (variation of pH were 3.2-5.2, 4.7-5.7, 7.2-7.9 respectively for citric acid, EDTA and histidine). The suspensions were shaken on an orbital shaker (IKA Labortechnik KS501 digital model - 150 rpm). At various time intervals (1, 4, 16, 24, 48, 72, 96, 144 h), sacrificial samples were analyzed for metal content.

The effect of chelating agent concentration was studied in the range 10^{-3} to 1 $mol.L^{-1}$ during 140 h. The initial pH of the solutions was adjusted with HNO_3 or NaOH to the soil pH_{H2O} value (6.3). During these experiments, no adjustment of pH was made; the variations were: 6.3-7.7, 6.3-6.3, 6.3-7.3 respectively for citric acid, EDTA and histidine. At the end of the experiment, after centrifugation and filtration, the soil was recovered, rinsed with 50 mL of de-ionized water and then air-dried at room temperature. This technique limits modifications in the metals' distribution (Bordas and Bourg, 1998a). The distribution of residual metals was determined by the sequential extractions procedure.

2.3. Respirometric tests

A respirometric BOD OxiTop® (WTW, Germany) method was used to monitor the biodegradation of citric acid. Respirometric tests were carried out in the designated measuring bottles: four replicates with citric acid solution at 0.05 $mol.L^{-1}$ and two controls with de-ionized water. A ratio of 9.7 g of soil in 97 mL of solution was used. No inoculums or inhibitors were added. The suspensions of soil were stirred at 20 ± 1°C, in a thermostated room (WTW, Germany), in the dark for 15 days.

2.4. Chemical analysis and modeling

For all experiments, the metals were analyzed after sample centrifugation (3000 *g* - Bioblock Scientific, Sigma 2-15) and filtration (0.45 µm cellulose nitrate filter-Sartorius). Depending on the concentration, flame atomic absorption spectrometer (Varian SpectrAA 220) or graphite furnace atomic absorption spectrometer (Varian SpectrAA 800) was used.

To estimate the main reactions involved in the extracting solutions, the system was modelled with MINEQL+, considering:

• the main solubilized elements: Al, Fe, Mg, Ca, Mn, Zn, Cu, Pb, Co, Cr(III) and Ni;

• the constants used come from MINEQL and other databases: Schecher and McAvoy (2001), Pettit and Powell (2001);

• the calculation was done at 20°C, the ionic strength and the pH were calculated by MINEQL+.

3. Results and discussion

3.1. Metals speciation in the soil

The studied soil was a sandy, acid soil, with a low organic carbon content and with moderate levels in Cu, Co, Pb (**Table 2**). In this study, we focused mainly on Cr and Ni because they were present in relatively large proportions, have an environmental impact and are rarely studied (especially Cr) under such conditions. **Table 3** shows the distribution of Cr and Ni in different soil fractions ("control"): 105 ± 34% of total Cr and 87 ± 12% of total Ni were recovered. Cr and Ni were present mainly in the "residual" fraction, 101 ± 34% for Cr and 75 ± 5% for Ni. Only minor amounts of Cr and Ni were found in the "acid extractable" fraction. Although such a distribution and recovery have been observed in industrial soils (McGrath, 1996; Davidson et al., 1998), it is possible that the R2 fraction ("reducible" fraction) was under-estimated. In our studied soil, crystalline Fe (Fe_T - F_{oxa}) is 81 ± 2 %; XRD diagrams (data not shown) showed the presence of maghémite (γ-Fe_2O_3). According to the literature, crystalline Fe is known to be only slightly solubilised by hydroxylammonium chloride (Xiao-Quan and Bin, 1993; La Force and Fendorf, 2000; Davidson et al., 2004; Neaman et al., 2004).

In the environment, chromium is present in two stable forms Cr(VI) and Cr(III). The chromium speciation experiment allows to estimate the content in Cr(VI) (28 ± 3 $mg.kg^{-1}$) representing 25 ± 3% of the total Cr.

3.2. Kinetics of metal mobilization in the presence of chelants

Figure 1 indicates two steps in metal mobilization: a fast step (<1 h) followed by a slower one. This has already been observed by many authors (Bordas and Bourg, 1998b; Bermond et al., 2005). The fast step corresponds to the solubilization of accessible metals (exchangeable and slightly adsorbed). During this fast step, the mobilization is greater for Ni than for Cr. This result is consistent with the fractionation of the metals in the soil (**Table 3**) which showed more Ni in the R1 fraction (acid extractable) than Cr. The slower step may correspond to the solubilization of less mobile and less accessible metals, those bound to oxides, which requires a partial dissolution of the matrix. This step is important for the Ni extraction with EDTA, which can be explained by the amount of Ni in the "reducible fraction" fraction compared to Cr (**Table 3**) (Nowack, 2002; Dubbin, 2004).

As over a contact time of 140 h, the major part of the mobilizable metals is extracted; this was considered to be appropriate for the present study. "True equilibrium" would be reached after longer extraction times; it depends on the chelants and the mineral matrix considered (Bordas and Bourg, 1998b; Fangueiro et al., 2002).

The respirometric test (BOD OxiTop® method), showed an increase in microbial activity in the presence of citric acid after 168 h (data not shown), thus only a slight degradation of citric acid by microbial activity would be expected for a contact time of 140 h. A limited and slow biodegradation of the nickel-citrate complex in the presence of a selected citrate-metabolizing bacterium has indeed been evidenced by Francis et al. (1992).

3.3. Effect of the chelating agents on metals mobilization

For these experiments, the initial pH of the chelating agent solutions was adjusted to the soil pH and monitored throughout the experiment. At the end of the experiments the pHs were respectively 7.7, 6.3 and 7.3 with citric acid, EDTA and histidine. The percentage of Cr extracted was calculated from total Cr content. The main reactions involved in the metals' complexation by chelants were estimated by modelling the system for the pH range 5-8 using MINEQL+ (Schecher and McAvoy, 2001).

The percentage of Cr and Ni extracted increased with the chelating agent concentration up to a maximal value (**Figure 2**). Effectiveness of the reagents for Cr mobilization can be classified as: citric acid > EDTA >> histidine. For 0.1 mol.L^{-1} citric acid, 7.7 ± 0.1% of Cr was extracted, beyond 0.1 mol.L^{-1} the effectiveness of citric acid was similar. Within pH range of the experiments, Cr was

totally complexed with EDTA and citrate, as $Cr(EDTA)^-$ and $Cr(citrate)^0$ respectively. Quiros et al. (1992) and Hamada et al. (2003) described only discrete $Cr(citrate)_2^{3-}$ units; these authors did not quote formation constants. Thus, in the absence of data, the $Cr(citrate)_2^{3-}$ complex was not taken into account. In the absence of data on complexation constants, the $Cr(histidine)^{2+}$ complexes were not taken into account. For Ni, a maximum of 12.8 ± 0.8 % was extracted with 0.1 $mol.L^{-1}$ EDTA. The effectiveness of the reagents for Ni mobilization can be classified as: EDTA > citric acid > histidine. Within pH range of our experiments, Ni was totally complexed with chelants. $Ni(EDTA)^{2-}$ and $Ni(histidine)^+$ were the only complexes formed with these two chelants whereas for citrate, there was a mixture of three Ni complexes: $Ni(citrate)^-$ (10 %), $NiH(citrate)_2^{3-}$ (35 %) and $Ni(citrate)_2^{4-}$ (55 %).

The effectiveness of the chelants ability to solubilize Cr and Ni, observed during our experiments, is not directly related to their complexation constants (**Table 4**). For example, Cr was better solubilized by citrate than by EDTA whereas $logK(Cr(EDTA^-))$ is greater than $log\ K(Cr(citrate)^0)$. This order cannot be justified by the differences in pH conditions. For all experiments, chelants were in large excess compared to total Cr and Ni. Ca, Fe, Mn, Al, and Mg, were simultaneously solubilized by chelants (**Table 5**) corresponding to a partial dissolution of the mineral matrix. According to our modeling, the totality of the solubilized metals was complexed with chelants; however because of their excess, 70 to 80% of the chelants were always present as uncomplexed species. Consequently, the differences in the order of efficiency can not be explained totally by the chelant speciation.

For a chelant concentration of 0.05 $mol.L^{-1}$, the amounts of Cr(III) and Cr(VI), present in the extraction solution after 140 h, were determined (**Table 6**). Cr(VI) is more mobilized in presence of citric acid (1.6 ± 0.3 %) than with EDTA (0.6 ± 0.1 %) or histidine (0.1 ± 0.3 %). The chelating agents do not bind Cr(VI) but could desorb it by competition for surface sites as well known for phosphates with ascorbate, citrate and EDTA (Nowack and Sigg, 1996; Geelhoed et al.,

1998; Hu et al., 2001). Then, citric acid could be more potent in desorbing Cr(VI) than EDTA or histidine, in complement of the mobilization of Cr(III) by complexation.

Moreover, the mineral fraction of the soil was more solubilized with citric acid than with EDTA or histidine (**Table 5**) which could explain also the greater mobilization of Cr. Then, it is possible that Ni is included in different minerals that citric acid does not solubilize, or only slightly. The effectiveness of chelants in mobilizing Cr and Ni could result of these two phenomena.

3.4. Successive extractions with the selected concentration

For the two most effective chelants (citric acid and EDTA), a concentration of 0.05 $mol.L^{-1}$ seems to be a good compromise between the mobilization of Cr and Ni and the solubilization of the mineral matrix of the soil. Different authors have shown the importance of the mineral matrix. Papassiopi et al. (1999) worked on a calcareous contaminated soil (Pb, Zn and Cd) from past mining and smelting activities. They showed that a limited percentage (less than 10%) of the available EDTA was used for the removal of metals while 90% was consumed by the dissolution of calcite. This was also noted by Lim et al. (2005) who examined EDTA in the removal of metals from a laboratory-contaminated soil (Pb, Cd, Ni). As suggested by these authors, a low concentration of chelants was favourable to the mobilization of metal while preserving the original soil mineral composition.

A concentration of citric acid 0.05 $mol.L^{-1}$, extracted, respectively, 20.9 ± 0.3 % Co, 2.0 ± 0.1 % Cu, 7.7 ± 0.2 % Zn, 2.4 ± 0.1 % Pb. At the same concentration EDTA extracted 22.0 ± 0.4 %, 30 ± 3 %, 6.20 ± 0.02 %, 27.9 ± 0.2 % of these metals. Only Zn is in the same proportion as Cr and Ni. Zn was better extracted than Cr, by citric acid and EDTA, and was solubilized in the same proportion as Ni. Taking into account their amounts in the soil, Co was better extracted than Cu, Pb with citric acid; and with EDTA, they were mobilized in the same proportion.

Successive mobilizations were carried out, during 140 h, to check if the metals potentially mobilizable could be solubilized, under our experimental conditions (**Figure 3**). Whatever the chelant considered, the percentage of Cr extracted during the first and the second mobilization was similar and decreased for the third. For Ni, the decrease was observed from the second mobilization on. EDTA and citrate mobilized a large amount of the major elements, hence the great mobilization of Cr and Ni in the first mobilization (**Table 5**). In the second and the third mobilization, major elements were mobilized at low concentrations (data not shown), which led to the decrease after these mobilizations. In the presence of chelants, the metals were extracted from a store of mobilizable metals operationally defined by the experimental conditions used. For Cr, this store is exhausted after the second extraction and for Ni it was exhausted after the first one.

3.5. Distribution of metals in soil after treatment with chelating agents

Table 3 shows the distribution of chromium and nickel in the soil fractions before and after the mobilization with 0.05 mol.L^{-1} of chelants. After the first treatment, Cr and Ni remained mainly in the "residual" fraction (R4). The amount of Ni in the first three fractions (R1 + R2 + R3) decreased from 10 ± 1% (before treatment) to 5.1 ± 0.8%, whatever the chelant. Ni was extracted mainly from the "acid extractable" fraction (R1), as it is easily accessible to the chelating agents, but it was also extracted from the fractions R2 and R3.

In the case of Cr, the results show that the sum of metal contained in the first three fractions (R1 + R2 + R3) decreased slightly from 3.7 ± 0.1% (before treatment) to 3.2 ± 0.3%, whatever the chelant. The amount of Cr decreased in the fraction R3, but increased in the fractions R1 and R2 after the treatment. It seems that Cr was extracted from the fractions R3 and R4 and was redistributed in both fractions, R1 and R2. In sequential extractions, the reagents used are rarely totally phase-specific. Even if the use of hydroxylammonium chloride is more generally applicable, this reagent does not bring about a complete dissolution of the iron-oxides (Xiao-Quan and Bin, 1993; La Force and Fendorf, 2000; Davidson et al., 2004; Neaman et al., 2004). During the sequential extractions, Cr bound to the iron oxides might not be extracted effectively from the

fraction R2, and thus it can be extracted with the last fraction R4, but also in fraction R3. This part of Cr can thus be redistributed in the fractions R1 and R2, during the mobilization with chelants.

In the studied case, the modifications in metal speciation from the second and the third extraction could not be evaluated because of: (i) the low quantities of extracted metals, (ii) the changes in soil composition during the extractions in presence of chelants (partial dissolution of the mineral phases), (iii) the lack of selectivity of reagents used in the sequential extractions procedure and (iv) the possible of readsorption during the protocol.

4. Conclusions

The results of this study, as regards the comparison between the ability of two natural and biodegradable chelants with a persistent one to solubilize chromium and nickel from a contaminated soil, can be summarized as follows:

• EDTA and citric acid appear to offer the greatest potential as chelating agents, histidine was ineffective in mobilizing Cr and Ni from the soil.

• Effectiveness of the chelants for Cr extraction can be classified as: citric acid > EDTA >> histidine.

• For Ni, the effectiveness order was: EDTA > citric acid > histidine.

• The effectiveness of the chelants, to solubilize Cr and Ni, observed during our experiments is not directly related to their complexation constants. It could be explained by: (i) their ability to solubilize the mineral matrix containing the metals (Al, Ca, Mn, Mg and Fe were removed simultaneously with Cr and Ni by the chelants); (ii) by the competition of the chelating agents with Cr(VI) on the surface sites.

• In the studied case, a concentration of 0.05 $mol.L^{-1}$ allows having a good compromise between metals mobilization and preservation the soil mineral integrity.

• After a single extraction with 0.05 $mol.L^{-1}$ of chelant, a potentially remobilizable store of metals could remain available. The percentage of Cr extracted during the first and the second mobilizations was similar but decreased for the third. For Ni, the decrease was observed from the second mobilization on.

• A sequential extraction procedure, carried out before and after the metal extractions showed only slight modifications due to the low percentage of solubilized metals.

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Table captions

Table1: Sequential extractions procedure for 0.5 g of air-dried soil

Table2: Main physical and chemical properties of the soil

Table 3: Cr in the soil fractions before and after treatments with chelants

Table 4: Ni in the soil fractions before and after treatments with chelants

Table 5: Chelant acidity constants (pKa) and complexation constants ($LogK_{ML}$) with Cr^{3+} and Ni^{2+}

Table 6: Speciation of solubilized Cr after a single extraction (140 h) by the chelants (chelant concentration 0.05 $mol.L^{-1}$); % Cr was based on total Cr content in soil

Figure captions

Figure 1: Extraction of Cr (a) and Ni (b) vs. contact time (chelant concentration 0.01 $mol.L^{-1}$; 5 g of soil in 50 mL); % Cr was based on total Cr content. Error bars represent the standard deviation of three samples.

Figure 2: Cr and Ni extracted vs. chelating agent concentration after a single extraction (% Cr was based on total Cr content). Error bars represent the standard deviation of three samples.

Figure 3: Successive extractions of Cr and Ni (E1: first extraction, E2: second extraction, E3: third extraction); % Cr was based on total Cr content; chelant concentrations 0.05 $mol.L^{-1}$. Error bars represent the standard deviation of three samples.

Table 1

Sequential extractions procedure for 0.5 g of air-dried soil

	Operationally defined fractions	Reagents	Time and sonication power
R1	"acid extractable"	20 mL AcOH 0.11 $mol.L^{-1}$	7 min-20W
R2	"reducible"	20 mL NH_2OH-HCl 0.1$mol.L^{-1}$, reagent adjusted to pH=2 with HNO_3	7 min-20W
R3	"oxidizable"	10 mL H_2O_2 30% 25 mL $AcONH_4$ 1 $mol.L^{-1}$, reagent adjusted to pH=2 with HNO_3	2 min-20W 6 min-20W
R4	"residual"	7.5 mL HNO_3 69% + 2.5 mL HCl 37%	microwave-assisted digestion

Table 2

Main physical and chemical properties of the soil

Parameters		Values
Clay (< 2 µm)		177
Fine silt (2/20 µm)		161
Coarse silt (20/50 µm)		63
Fine sand (50/200µm)		119
Coarse sand (200/2000 µm)	$g.kg^{-1}$	480
Al		43.1 ± 0.9
Fe		33.6 ± 0.8
Mg		2.6 ± 0.1
Ca		2.2 ± 0.1
Mn		921 ± 36
Zn		138 ± 4
Cu		29 ± 2
Pb	$mg.kg^{-1}$	87 ± 3
Co		40 ± 2
Cr		113 ± 10
Ni		280 ± 20

Table 3

Cr and Ni in the soil fractions ($mg.kg^{-1}$) before and after treatments with chelants

	Treatment extraction	Fractions			
		R1	R2	R3	R4
Cr	Control	0.081 ± 0.003	0.68 ± 0.02	3.44 ± 0.09	114 ± 39
	EDTA	0.12 ± 0.02	1.33 ± 0.09	2.01 ± 0.32	88.13 ± 0.01
	Citric acid	0.15 ± 0.01	1.13 ± 0.04	2.04 ± 0.33	106 ± 12
	Histidine	0.18 ± 0.02	1.24 ± 0.10	2.5 ± 0.2	96 ± 2
Ni	Control	4.1 ± 0.3	12.6 ± 0.4	12 ± 2	201 ± 20
	EDTA	0.8 ± 0.2	6.6 ± 0.5	8 ± 1	177 ± 12
	Citric acid	0.78 ± 0.01	5.4 ± 0.7	5.8 ± 0.1	148 ± 51
	Histidine	0.58 ± 0.07	4.1 ± 0.7	9 ± 4	155 ± 64

Table 4

Chelant acidity constants (pKa) and complexation constants ($LogK_{ML}$ [a]) with Cr^{3+} and Ni^{2+}

Chelant	pKa [b] (T=25°C, I=0.1 M)	$LogK_{ML}$ (T = 25°C, I = 0.1 M)	
		Cr^{3+}	Ni^{2+}
EDTA	10.17, 6.11, 2.68, 1.5	23.4 [c]	20.1 [c]
Citric acid	5.66, 4.34, 2.90	8.7 [c,d]	6.6 [c]
Histidine	9.08, 6.02, 1.7	nd	16.6 [c]

nd: no data

[a] K_{ML} = [ML]/[M].[L] with L = fully deprotonated ligand and M = metal cation (charges omitted for simplification)

[b] from Smith and Martell, 1974, 1982;

[c] from Pettit and Powell, 2001;

[d] from Schecher and McAvoy, 2001

Table 5

Elements solubilized by the chelants after a single mobilization (140h) (chelant concentration 0.05 mol.L^{-1})

Soluble metals	Concentration (µmol.L^{-1})		
	EDTA	Citric acid	Histidine
Al	7360 ± 82	10579 ± 39	82 ± 4
Fe	4570 ± 76	5850 ± 44	29 ± 2
Mg	564 ± 7	1150 ± 13	218 ± 2
Ca	4360 ± 150	3550 ± 79	788 ± 4
Mn	877 ± 17	909 ± 12	49 ± 2
Co	14.8 ± 0.3	14.1 ± 0.2	4.7 ± 0.2
Cu	14 ± 1	0.94 ± 0.06	4.9 ± 0.9
Zn	13.09 ± 0.05	16.8 ± 0.8	3.6 ± 0.2
Pb	11.8 ± 0.1	1.01 ± 0.05	ND
Cr	8.5 ± 0.3	14 ± 1	1.35 ± 0.02
Ni	26 ± 6	40 ± 5	17.8 ± 0.8

ND: not detected

Table 6

Speciation of solubilized Cr after a single extraction (140 h) by the chelants (chelant concentration 0.05 mol.L^{-1})

Chelant	Cr_T after 140 h ($\mu g.L^{-1}$)	Cr(VI) after 140 h ($\mu g.L^{-1}$)	%/Cr[a]	Cr(III) ($\mu g.L^{-1}$)	%/Cr[a]
Citric acid	738 ± 67	186 ± 40	1.6 ± 0.3	552	4.9 ± 0.3
EDTA	442 ± 16	64 ± 10	0.56 ± 0.09	378	3.34 ± 0.09
Histidine	70.4± 0,9	15 ± 3	0.1 ± 0.03	55	0.49 ± 0.03
Water	17 ± 1	ND[b]	-	-	-

a: % Cr was based on total Cr content in soil

b: not detected

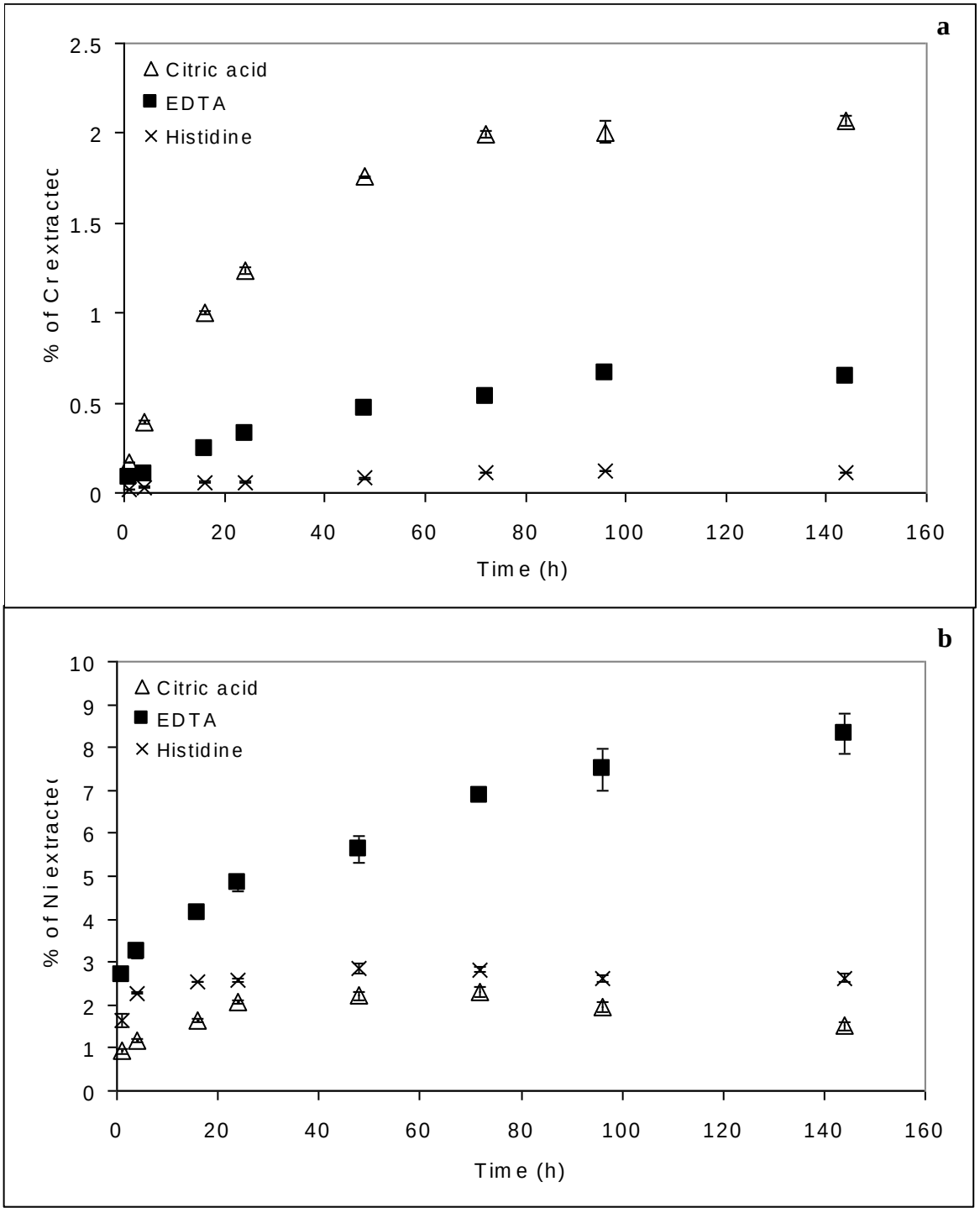


Fig. 1. Extraction of Cr (a) and Ni (b) vs. contact time (chelant concentration 0.01 mol.L^{-1}; 5 g of soil in 50 mL); % Cr was based on total Cr content. Error bars represent the standard deviation of three samples.

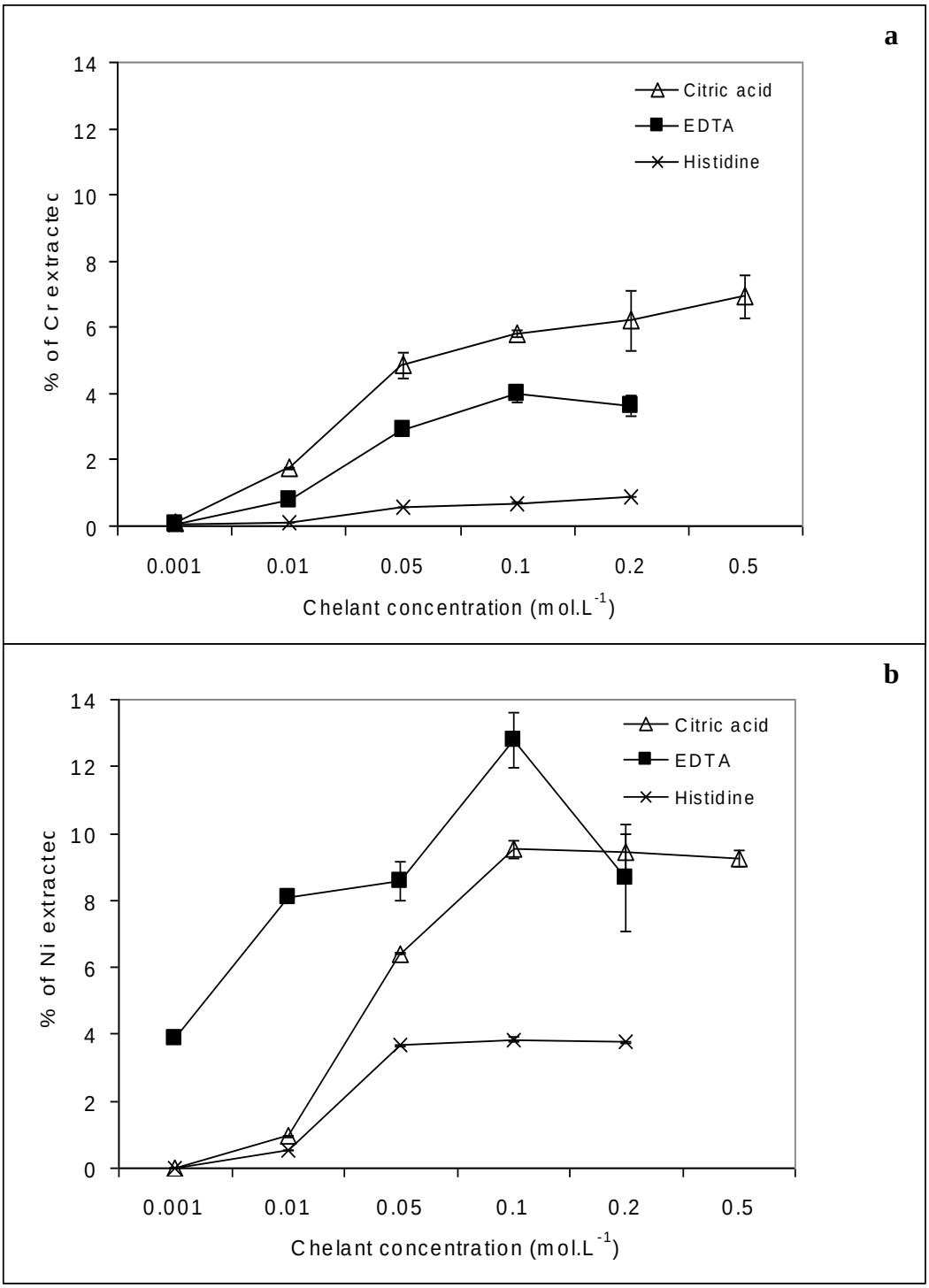


Fig. 2. Cr (a) and Ni (b) extracted vs. chelating agent concentration after a single extraction (% Cr was based on total Cr content). Error bars represent the standard deviation of three samples.

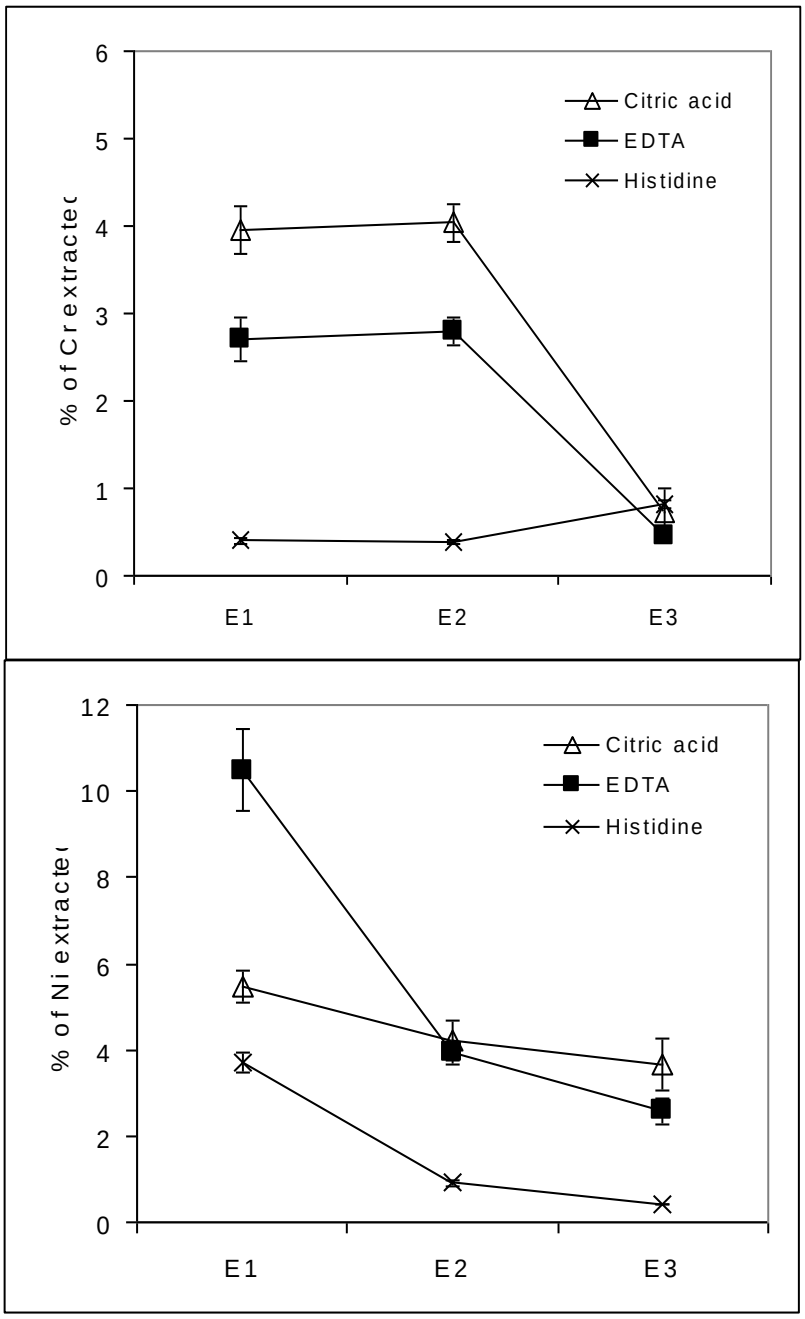


Fig. 3. Successive extractions of Cr and Ni (E1: first extraction, E2: second extraction, E3: third extraction); % Cr was based on total Cr content; chelant concentrations 0.05 mol.L^{-1}. Error bars represent the standard deviation of three samples.