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**Chromium and nickel mobilization from a contaminated soil
using chelants**

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1 **Abstract**

2 The mobilization of chromium and nickel from an industrial soil was investigated using
3 two biodegradable chelants (citric acid and histidine), compared with a persistent one
4 (ethylenediaminetetraacetic acid). Successive metal mobilizations were carried out in batch
5 experiments. The main reactions involved were estimated by modelling the system with MINEQL+.
6 For a single mobilization, citric acid was the most effective for Cr mobilization and EDTA for Ni.
7 Their effectiveness could be explained by their ability to solubilize the mineral matrix and by the
8 competition for the surfaces sites to desorb Cr(VI). Before and after the mobilizations, the
9 distribution of metals was determined by a sequential extraction procedure. Only slight
10 modifications were observed due to the low percentage of solubilized metal. A concentration of
11 0.05 mol.L^{-1} (citric acid and EDTA) allows a good compromise between metal mobilization and
12 preservation of the soil mineral integrity.

13
14 **Keywords:** contaminated soil, chromium, nickel, chelant, mobilization

15

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

1 **1. Introduction**

2

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

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

15 Many studies have been carried out on metal extraction with chelants such as
16 ethylenediaminetetraacetic acid - EDTA, citric acid, nitrilotriacetic acid - NTA, [S,S]-
17 ethylenediaminedisuccinic acid - EDDS (Wasay et al., 2001; Kim et al., 2003; Tandy et al., 2004;
18 Luo et al., 2005; Di Palma and Ferrantelli, 2005; Leštan and Kos, 2005). These chelants have a high
19 affinity for many metals. Several parameters must be taken into account, the choice of the ratio of
20 chelant to metals being important. Consequently, chelant concentration must be higher than trace
21 metal concentration to obtain maximum extraction. But in the soil, there are also major elements
22 such as Fe, Al, Mn, Mg and Ca which can be simultaneously solubilized by the chelants (Kim et al.,
23 2003; Tandy et al., 2004).

24 Whereas many papers have been published about metal extraction with chelants, only few
25 studies have been carried out about Ni and especially Cr extraction. Extractions of Cr and/or Ni
26 using chelants were mainly studied with the purpose of phytoextraction (Turgut et al., 2004; Meers
27 et al., 2005; do Nascimento et al., 2006). Indeed, chelating agents increase the solubility of heavy
28 metals for plant uptake during phytoremediation (Brooks, 1998; Salt et al., 1998). It is of course
29 important to know the degree of biodegradability of the chelants. EDTA is persistent in the
30 environment (Bucheli-Witschel and Egli, 2001) and its presence in soil can lead to uncontrolled
31 leaching of metals (Bordas and Bourg, 1998b), thus limiting its use for phytoextraction (Alkorta et
32 al., 2004). Citric acid and histidine are natural organic molecules that are easily biodegradable, their
33 half-lives, in a soil suspension, being a few days (Brynhildsen and Rosswald, 1997; Römken et al.,
34 2002).

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

4 5 **2. Materials and methods**

6
7 All reagents used to prepare the solutions were with an analytical grade. High purity de-
8 ionized water (Milli-Q system: resistivity 18.2 M Ω .cm, TOC < 10 μ g.L⁻¹) was used for all
9 experiments.

10 11 2.1. Soil sampling and characterization

12
13 The studied soil came from a metallurgical site where special steels, superalloys,
14 aluminium and titanium alloys are produced. The pollution was due to long time refuse storage on
15 the bare ground. Before sampling, a superficial layer of soil (0-5 cm) containing refuse and the main
16 part of the litter was discarded. The 5-10 cm layer of the soil was then sampled manually near the
17 storage zone. This thickness was selected due to its contamination rate. The soil was air-dried and
18 sieved (< 2 mm) (AFNOR, 1994). Soil properties: pH_{H2O} (6.3 \pm 0.1), pH_{KCl} (5.3 \pm 0.1), organic
19 carbon (2.90 \pm 0.08 g.kg⁻¹), cation exchange capacity (12.3 \pm 0.1 meq/100 g) were determined by
20 standard methods (AFNOR, 2004). The granulometry was determined by the standard method, NF
21 X 31-107 (AFNOR, 2004). Bulk powder X-ray diffraction (XRD) was used for mineralogical
22 characterization of the soil sample (INEL CPS 120° Curved Position Sensitive Detector, CuK α 1).

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

26 The chemical distribution of metals in the soil was quantified by the BCR sequential
27 extractions procedure (Ure et al., 1993) accelerated by ultrasound (Pérez-Cid et al., 1998) (**Table**
28 **1**). The sonication was done with a 60W probe (Bandelin, model HD 70). After centrifugation
29 (3000 g), the supernatant was filtered through 0.45 μ m cellulose nitrate filter (Sartorius).
30 The fractionation of Fe was determined by oxalate (Schwertmann, 1964) and pyrophosphate
31 extraction (McKeague, 1967). Oxalate extracts the poorly crystalline Fe oxides and the organically
32 bound Fe and pyrophosphate extracts organically bound Fe.

33 To determine the speciation of Cr, an alkaline digestion was applied (0.5 mol.L⁻¹ NaOH + 0.28
34 mol.L⁻¹ Na₂CO₃) and the quantification of Cr(VI) was carried out using the colorimetric method

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

3 4 2.2. Batch mobilization with chelating agent

5
6 Metal mobilizations were carried out in batch experiments at room temperature ($20 \pm 2^\circ\text{C}$).
7 The solid:solution ratio was 1:10 with 50 mL of EDTA, citric acid or histidine solutions. Na_2 -
8 EDTA salt, citric acid and L-histidine were used. Three replicates were made.

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

15 The effect of chelating agent concentration was studied in the range 10^{-3} to 1 mol.L^{-1}
16 during 140 h. The initial pH of the solutions was adjusted with HNO_3 or NaOH to the soil $\text{pH}_{\text{H}_2\text{O}}$
17 value (6.3). During these experiments, no adjustment of pH was made; the variations were: 6.3-7.7,
18 6.3-6.3, 6.3-7.3 respectively for citric acid, EDTA and histidine. At the end of the experiment, after
19 centrifugation and filtration, the soil was recovered, rinsed with 50 mL of de-ionized water and then
20 air-dried at room temperature. This technique limits modifications in the metals' distribution
21 (Bordas and Bourg, 1998a). The distribution of residual metals was determined by the sequential
22 extractions procedure.

23 24 2.3. Respirometric tests

25
26 A respirometric BOD OxiTop® (WTW, Germany) method was used to monitor the
27 biodegradation of citric acid. Respirometric tests were carried out in the designated measuring
28 bottles: four replicates with citric acid solution at 0.05 mol.L^{-1} and two controls with de-ionized
29 water. A ratio of 9.7 g of soil in 97 mL of solution was used. No inoculums or inhibitors were
30 added. The suspensions of soil were stirred at $20 \pm 1^\circ\text{C}$, in a thermostated room (WTW, Germany),
31 in the dark for 15 days.

32 33 2.4. Chemical analysis and modeling

34

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

5
6 To estimate the main reactions involved in the extracting solutions, the system was modelled with
7 MINEQL+, considering:

- 8 • the main solubilized elements: Al, Fe, Mg, Ca, Mn, Zn, Cu, Pb, Co, Cr(III) and Ni;
- 9 • the constants used come from MINEQL and other databases: Schecher and McAvoy (2001), Pettit
10 and Powell (2001);
- 11 • the calculation was done at 20°C, the ionic strength and the pH were calculated by MINEQL+.

12 13 **3. Results and discussion**

14 15 3.1. Metals speciation in the soil

16
17 The studied soil was a sandy, acid soil, with a low organic carbon content and with
18 moderate levels in Cu, Co, Pb (**Table 2**). In this study, we focused mainly on Cr and Ni because
19 they were present in relatively large proportions, have an environmental impact and are rarely
20 studied (especially Cr) under such conditions. **Table 3** shows the distribution of Cr and Ni in
21 different soil fractions ("control"): $105 \pm 34\%$ of total Cr and $87 \pm 12\%$ of total Ni were recovered.
22 Cr and Ni were present mainly in the "residual" fraction, $101 \pm 34\%$ for Cr and $75 \pm 5\%$ for Ni.
23 Only minor amounts of Cr and Ni were found in the "acid extractable" fraction. Although such a
24 distribution and recovery have been observed in industrial soils (McGrath, 1996; Davidson et al.,
25 1998), it is possible that the R2 fraction ("reducible" fraction) was under-estimated. In our studied
26 soil, crystalline Fe ($\text{Fe}_T - \text{F}_{\text{oxa}}$) is $81 \pm 2\%$; XRD diagrams (data not shown) showed the presence of
27 maghémite ($\gamma\text{-Fe}_2\text{O}_3$). According to the literature, crystalline Fe is known to be only slightly
28 solubilised by hydroxylammonium chloride (Xiao-Quan and Bin, 1993; La Force and Fendorf,
29 2000; Davidson et al., 2004; Neaman et al., 2004).

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

33 34 3.2. Kinetics of metal mobilization in the presence of chelants

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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

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

11 The effectiveness of the chelants ability to solubilize Cr and Ni, observed during our
12 experiments, is not directly related to their complexation constants (**Table 4**). For example, Cr was
13 better solubilized by citrate than by EDTA whereas $\log K(\text{Cr}(\text{EDTA}^-))$ is greater than \log
14 $K(\text{Cr}(\text{citrate})^0)$. This order cannot be justified by the differences in pH conditions. For all
15 experiments, chelants were in large excess compared to total Cr and Ni. Ca, Fe, Mn, Al, and Mg,
16 were simultaneously solubilized by chelants (**Table 5**) corresponding to a partial dissolution of the
17 mineral matrix. According to our modeling, the totality of the solubilized metals was complexed
18 with chelants; however because of their excess, 70 to 80% of the chelants were always present as
19 uncomplexed species. Consequently, the differences in the order of efficiency can not be explained
20 totally by the chelant speciation.

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

1 1998; Hu et al., 2001). Then, citric acid could be more potent in desorbing Cr(VI) than EDTA or
2 histidine, in complement of the mobilization of Cr(III) by complexation.
3 Moreover, the mineral fraction of the soil was more solubilized with citric acid than with EDTA or
4 histidine (**Table 5**) which could explain also the greater mobilization of Cr. Then, it is possible that
5 Ni is included in different minerals that citric acid does not solubilize, or only slightly. The
6 effectiveness of chelants in mobilizing Cr and Ni could result of these two phenomena.

7 8 3.4. Successive extractions with the selected concentration

9
10 For the two most effective chelants (citric acid and EDTA), a concentration of 0.05 mol.L^{-1}
11 seems to be a good compromise between the mobilization of Cr and Ni and the solubilization of the
12 mineral matrix of the soil. Different authors have shown the importance of the mineral matrix.
13 Papassiopi et al. (1999) worked on a calcareous contaminated soil (Pb, Zn and Cd) from past
14 mining and smelting activities. They showed that a limited percentage (less than 10%) of the
15 available EDTA was used for the removal of metals while 90% was consumed by the dissolution of
16 calcite. This was also noted by Lim et al. (2005) who examined EDTA in the removal of metals
17 from a laboratory-contaminated soil (Pb, Cd, Ni). As suggested by these authors, a low
18 concentration of chelants was favourable to the mobilization of metal while preserving the original
19 soil mineral composition.

20 A concentration of citric acid 0.05 mol.L^{-1} , extracted, respectively, $20.9 \pm 0.3 \%$ Co, $2.0 \pm 0.1 \%$
21 Cu, $7.7 \pm 0.2 \%$ Zn, $2.4 \pm 0.1 \%$ Pb. At the same concentration EDTA extracted $22.0 \pm 0.4 \%$, $30 \pm$
22 3% , $6.20 \pm 0.02 \%$, $27.9 \pm 0.2 \%$ of these metals. Only Zn is in the same proportion as Cr and Ni.
23 Zn was better extracted than Cr, by citric acid and EDTA, and was solubilized in the same
24 proportion as Ni. Taking into account their amounts in the soil, Co was better extracted than Cu, Pb
25 with citric acid; and with EDTA, they were mobilized in the same proportion.

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

11 12 3.5. Distribution of metals in soil after treatment with chelating agents

13
14 **Table 3** shows the distribution of chromium and nickel in the soil fractions before and
15 after the mobilization with 0.05 mol.L^{-1} of chelants. After the first treatment, Cr and Ni remained
16 mainly in the "residual" fraction (R4). The amount of Ni in the first three fractions (R1 + R2 + R3)
17 decreased from $10 \pm 1\%$ (before treatment) to $5.1 \pm 0.8\%$, whatever the chelant. Ni was extracted
18 mainly from the "acid extractable" fraction (R1), as it is easily accessible to the chelating agents,
19 but it was also extracted from the fractions R2 and R3.

20 In the case of Cr, the results show that the sum of metal contained in the first three fractions
21 (R1 + R2 + R3) decreased slightly from $3.7 \pm 0.1\%$ (before treatment) to $3.2 \pm 0.3\%$, whatever the
22 chelant. The amount of Cr decreased in the fraction R3, but increased in the fractions R1 and R2
23 after the treatment. It seems that Cr was extracted from the fractions R3 and R4 and was
24 redistributed in both fractions, R1 and R2. In sequential extractions, the reagents used are rarely
25 totally phase-specific. Even if the use of hydroxylammonium chloride is more generally applicable,
26 this reagent does not bring about a complete dissolution of the iron-oxides (Xiao-Quan and Bin,
27 1993; La Force and Fendorf, 2000; Davidson et al., 2004; Neaman et al., 2004). During the
28 sequential extractions, Cr bound to the iron oxides might not be extracted effectively from the

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

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

8

9 **4. Conclusions**

10

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

- 14 • EDTA and citric acid appear to offer the greatest potential as chelating agents, histidine was
15 ineffective in mobilizing Cr and Ni from the soil.
- 16 • Effectiveness of the chelants for Cr extraction can be classified as: citric acid > EDTA >>
17 histidine.
- 18 • For Ni, the effectiveness order was: EDTA > citric acid > histidine.
- 19 • The effectiveness of the chelants, to solubilize Cr and Ni, observed during our experiments is not
20 directly related to their complexation constants. It could be explained by: (i) their ability to
21 solubilize the mineral matrix containing the metals (Al, Ca, Mn, Mg and Fe were removed
22 simultaneously with Cr and Ni by the chelants); (ii) by the competition of the chelating agents with
23 Cr(VI) on the surface sites.
- 24 • In the studied case, a concentration of 0.05 mol.L^{-1} allows having a good compromise between
25 metals mobilization and preservation the soil mineral integrity.
- 26 • After a single extraction with 0.05 mol.L^{-1} of chelant, a potentially remobilizable store of metals
27 could remain available. The percentage of Cr extracted during the first and the second mobilizations
28 was similar but decreased for the third. For Ni, the decrease was observed from the second
29 mobilization on.
- 30 • A sequential extraction procedure, carried out before and after the metal extractions showed only
31 slight modifications due to the low percentage of solubilized metals.

32

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4

5 **References**

6
7 AFNOR, 1994. Qualité des sols, AFNOR Edition, Paris.
8

9 AFNOR, 2004. Evaluation de la qualité des sols, Volume 1. AFNOR Edition, Paris.
10

11 Alkorta, I., Hernández-Allica, J., Becerril, J.M., Amezaga, I., Albizu, I., Onaindia, M., Garbisu, C.,
12 2004. Chelate-enhanced phytoremediation of soils polluted with heavy metals. Reviews in
13 Environmental Science and Biotechnology 3, 55-70.
14

15 Bermond, A., Varrault, G., Sappin-Didier, V., Mench, M., 2005. A kinetic approach to predict soil
16 trace metal bioavailability: preliminary results. Plant and Soil 275, 21-29.
17

18 Bordas, F., Bourg, A.C.M., 1998a. A critical evaluation of sample pretreatment for storage of
19 contaminated sediments to be investigated for the potential mobility of their heavy metal load.
20 Water, Air and Soil Pollution 103, 137-149.
21

22 Bordas, F., Bourg, A.C.M., 1998b. Effect of complexing agents (EDTA and ATMP) on the
23 remobilization of heavy metals from a polluted river sediment. Aquatic Geochemistry 4, 201-214.
24

25 Bourg, A.C.M., Loch, J.P.G., 1995. Mobilization of heavy metals as affected by pH and by redox
26 conditions. In: Salomons W., Stigliani W.M., Biogeochemistry of pollutants in soils and sediment.
27 Springer, Berlin pp. 87-102.
28

29 Brooks, R.R., 1998. Plants that hyperaccumulate heavy metals, CAB International, Wallingford.
30

31 Brynhildsen, L., Rosswall, T., 1997. Effects of metals on the microbial mineralization of organic
32 acids. Water, Air and Soil Pollution 94, 45-57.
33

34 Bucheli-Witschel, M., Egli, T., 2001. Environmental fate and microbial degradation of
35 aminopolycarboxylic acids. FEMS Microbiology Reviews 25, 69-106.

1
2 Centre d'expertise en analyse environnementale du Québec, 2003. Détermination du Chrome
3 hexavalent : méthode colorimétrique. MA. 200-CrHex 1.0. Ministère de l'Environnement du
4 Québec.
5
6 Davidson, C.M., Duncan, A.L., Littlejohn, D., Ure, A.M., Garden, L.M., 1998. A critical evaluation
7 of the three-stage BCR sequential extraction procedure to assess the potential mobility and toxicity
8 of heavy metals in industrially-contaminated land. *Analytica Chimica Acta* 363, 45-55.
9
10 Davidson, C.M., Hursthouse, A.S., Tognarelli, D.M., Ure, A.M., Urquhart, G.J., 2004. Should acid
11 ammonium oxalate replace hydroxylammonium chloride in step 2 of the revised BCR sequential
12 extraction protocol for soil and sediment? *Analytica Chimica Acta* 508, 193-199.
13
14 Di Palma, L., Ferrantelli, P., 2005. Copper leaching from a sandy soil: mechanism and parameters
15 affecting EDTA extraction. *Journal of Hazardous Materials B122*, 85-90.
16
17 do Nascimento, C.W.A., Amarasiriwardena, D., Xing B., 2006. Comparison of natural organic
18 acids and synthetic chelates at enhancing phytoextraction of metals from a multi-metal
19 contaminated soil. *Environmental Pollution* 140, 114-123.
20
21 Dubbin, W.E., 2004. Influence of organic ligands on Cr desorption from hydroxy-Cr intercalated
22 montmorillonite. *Chemosphere* 54, 1071-1077.
23
24 Fanguerio, D., Bermond, A., Santos, E., Carapuça, H., Duarte A., 2002. Heavy metal mobility
25 assessment in sediments based on a kinetic approach of the EDTA extraction: search for optimal
26 experimental conditions. *Analytica Chimica Acta* 459, 245-256.
27
28 Francis, A.J., Dodge, C.J., Gillow, J.B., 1992. Biodegradation of metal citrate complexes and
29 implications for toxic-metal mobility. *Nature* 356, 140-142.
30
31 Geelhoed, J.S., Hiemstra, T., Van Riemsdijk, W.H., 1998. Competitive interaction between
32 phosphate and citrate on goethite. *Environmental Science and Technology* 32, 2119-2123.
33

1 Hamada, Y.Z., Carlson, B.L., Shank, J.T., 2003. Potentiometric and UV-Vis spectroscopy studies of
2 citrate with the hexaquo Fe^{3+} and Cr^{3+} metal ions. *Synthesis and Reactivity in Inorganic and Metal-*
3 *Organic Chemistry* 33, 1425-1440.
4
5 Hu, H.Q., He, J.Z., Li, X.Y., Liu, F., 2001. Effect of several organic acids on phosphate adsorption
6 by variable charge soils of central China. *Environment International*. 26, 353-358.
7
8 Kim, C., Lee, Y., Ong, S.K., 2003. Factors affecting EDTA extraction of lead from lead-
9 contaminated soils. *Chemosphere* 51, 845-853.
10
11 La Force, M.J., Fendorf, S., 2000. Solid-phase iron characterization during common selective
12 sequential extractions. *Soil Science Society of America Journal* 64, 1608-1615.
13
14 Larner, B.L., Seen, A.J., Townsend, A.T., 2006. Comparative study of optimized BCR sequential
15 extraction scheme and acid leaching of elements in the Certified Reference Material NIST 2711.
16 *Analytica Chimica Acta* 556, 444-449.
17
18 Leštan, D., Kos, B., 2005. Soil washing using a biodegradable chelator, in: Nowack B., VanBriesen
19 J.M., ACS Symposium Series 910, Biogeochemistry of chelating agents, Oxford Uni. Press,
20 Oxford, pp. 383-397.
21
22 Lim, T.-T., Chui, P.-C., Goh, K.-H., 2005. Process evaluation for optimization of EDTA use and
23 recovery for heavy metal removal from a contaminated soil. *Chemosphere* 58, 1031-1040.
24
25 Luo, C., Shen, Z., Li, X., 2005. Enhanced phytoextraction of Cu, Pb, Zn and Cd with EDTA and
26 EDDS. *Chemosphere* 59, 1-11.
27
28 McGrath, D., 1996. Application of single and sequential extraction procedures to polluted and
29 unpolluted soils. *The Science of the Total Environment* 178, 37-44.
30
31 McKeague, J.A., 1967. An evaluation of 0.1 M pyrophosphate and pyrophosphate-dithionite in
32 comparison to oxalate as extractants of the accumulation products in podzols and some other soils.
33 *Canadian Journal of Soil Science*. 47, 95-99.
34

1 Meers, E., Ruttens, A., Hopgood, M.J., Samson D., Tack F.M.G., 2005. Comparison of EDTA and
2 EDDS as potential soil amendments for enhanced phytoextraction of heavy metals. *Chemosphere*
3 58, 1011-1022.
4

5 Mulligan, C.N., Yong, R.N., Gibbs, B.F., 2001. Remediation technologies for metal-contaminated
6 soils and groundwater: an evaluation. *Engineering Geology* 60, 193-207.
7

8 Neaman, A., Waller, B., Mouele, F., Trolard, F., Bourrie, G., 2004. Improved methods for selective
9 dissolution of manganese oxides from soils and rocks. *European Journal of Soil Science* 55, 47-54.
10

11 Nowack, B., 2002. Environmental chemistry of aminopolycarboxylate chelating agents.
12 *Environmental Science and Technology* 36, 4009-4016.
13

14 Nowack, B., Sigg, L., 1996. Adsorption of EDTA and metal-EDTA complexes onto goethite.
15 *Journal of Colloid and Interface Science* 177, 106-121.
16

17 Papassiopi, N., Tambouris, S., Kontopoulos, A., 1999. Removal of heavy metals from calcareous
18 contaminated soils by EDTA leaching. *Water, Air and Soil Pollution* 109, 1-15.
19

20 Pérez-Cid, B., Lavilla, I., Bendicho, C., 1998. Speeding up of a three-stage sequential extraction
21 method for metal speciation using focused ultrasound. *Analytica Chimica Acta* 360, 35-41.
22

23 Peters, R.W., 1999. Chelant extraction of heavy metals from contaminated soils. *Journal of*
24 *Hazardous Materials* 66, 151-210.
25

26 Pettit, L.D., Powell, H.K.J., 2001. IUPAC stability constants database, Version 5.3. Academic
27 Software, Otley.
28

29 Quiros, M., Goodgame, D.M.L., Williams, D.J., 1992. Crystal structure and EPR spectrum of
30 bispyridinium bis(citrato)chromium(III) tetrahydrate. *Polyhedron* 11, 1343-1348.
31

32 Römken, P., Bouwman, L., Japenga, J., Draaisma, C., 2002. Potentials and drawbacks of chelate-
33 enhanced phytoremediation of soils. *Environmental Pollution* 116, 109-121.
34

1 Salt, D.E., Smith, R.D., Raskin, I., 1998. Phytoremediation. Annual Review of Plant Physiology
2 and Plant Molecular Biology 49, 643-668.
3

4 Schecher, W.D., McAvoy, D.C., 2001. MINEQL+: A Chemical Equilibrium Modeling System,
5 Version 4.5 for Windows. Environmental Research Software, Hallowell.
6

7 Schwertmann, U., 1964. Differenzierung der Eisenoxide des Bodens durch Extraktion mit
8 Ammoniumoxalat-Lösung. Zeitschrift für Pflanzenernährung und Bodenkunde 105, 194-202.
9

10 Smith, R.M., Martell, A.E., 1974. Critical Stability Constants, Volume 1. Plenum Press, New-York
11 and London.
12

13 Smith, R.M., Martell, A.E., 1982. Critical Stability Constants, Volume 5. Plenum Press, New-York.
14

15 Stumm, W., Sulzberger, B., 1992. The cycling of iron in natural environments: considerations based
16 on laboratory studies of heterogeneous redox processes. Geochimica et Cosmochimica Acta 56,
17 3233-3257.
18

19 Tandy, S., Bossart K.,, Mueller, R., Ritschel, J., Hauser L., Schulin R., Nowack B., 2004.
20 Extraction of heavy metals from soils using biodegradable chelating agents. Environmental Science
21 and Technology 38, 937-944.
22

23 Turgut, C., Pepe, M.K., Cutright, T.J., 2004. The effect of EDTA and citric acid on
24 phytoremediation of Cd, Cr and Ni from soil using Helianthus annuus. Environmental Pollution
25 131, 147-154.
26

27 Ure, A., Quevauviller, P., Muntau, H., Griepink, B., 1993. Improvements in the determination of
28 extractable contents of trace metals in soil and sediment prior to certification. Commission of the
29 European Communities, Community Bureau of Reference - BCR information, EUR 14763 EN,
30 Brussels.
31

32 Wasay, S.A., Barrington, S., Tokunaga, S., 2001. Organic acids for the in situ remediation of soils
33 polluted by heavy metals: soil flushing in columns. Water, Air and Soil Pollution 127, 301-314.
34

- 1 Xiao-Quan, S., Bin, C., 1993. Evaluation of sequential extraction for speciation of trace metals in
- 2 model soil containing natural minerals and humic acid. *Analytical Chemistry* 65, 802-807.

Table captions

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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 Cr³⁺ and Ni²⁺

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.

1 **Table 1**

2 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 ₂ OH-HCl 0.1mol.L ⁻¹ , reagent adjusted to pH=2 with HNO ₃	7 min-20W
R3	"oxidizable"	10 mL H ₂ O 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

3

1 **Table 2**

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

3

1 Table 3

2 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

3

1 **Table 4**

2 Chelant acidity constants (pKa) and complexation constants (LogK_{ML}^a) with Cr³⁺ and Ni²⁺

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

14 nd: no data

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

18 ^b from Smith and Martell, 1974, 1982;

19 ^c from Pettit and Powell, 2001;

20 ^d from Schecher and McAvoy, 2001

1 **Table 5**

2 Elements solubilized by the chelants after a single mobilization (140h) (chelant concentration 0.05
3 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

4 ND: not detected

1 **Table 6**

2 Speciation of solubilized Cr after a single extraction (140 h) by the chelants (chelant concentration

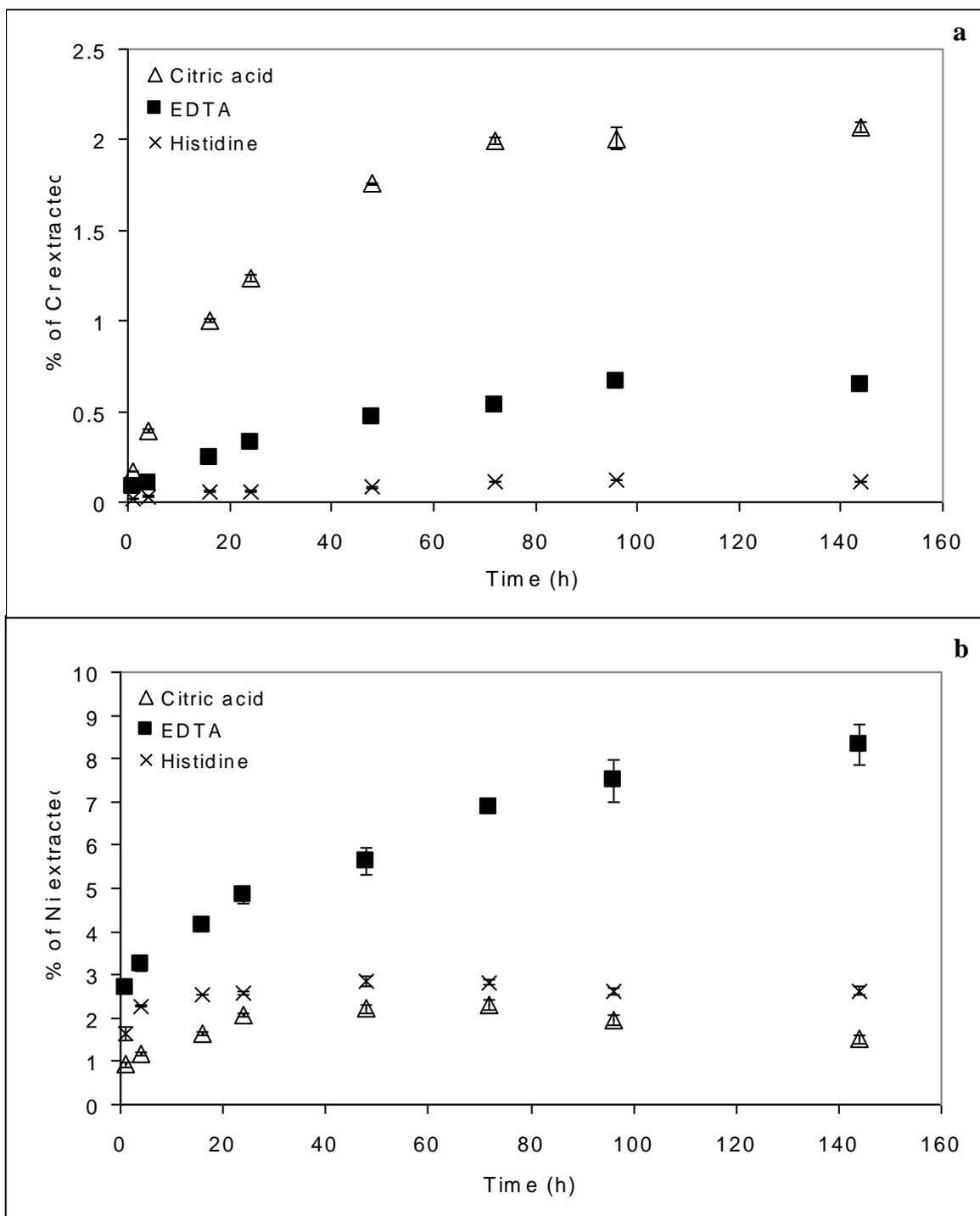
3 0.05 mol.L⁻¹)

Chelant	Cr _T after 140 h (μg.L ⁻¹)	Cr(VI) after 140 h (μg.L ⁻¹)	%/Cr ^a	Cr(III) (μg.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	-	-	-

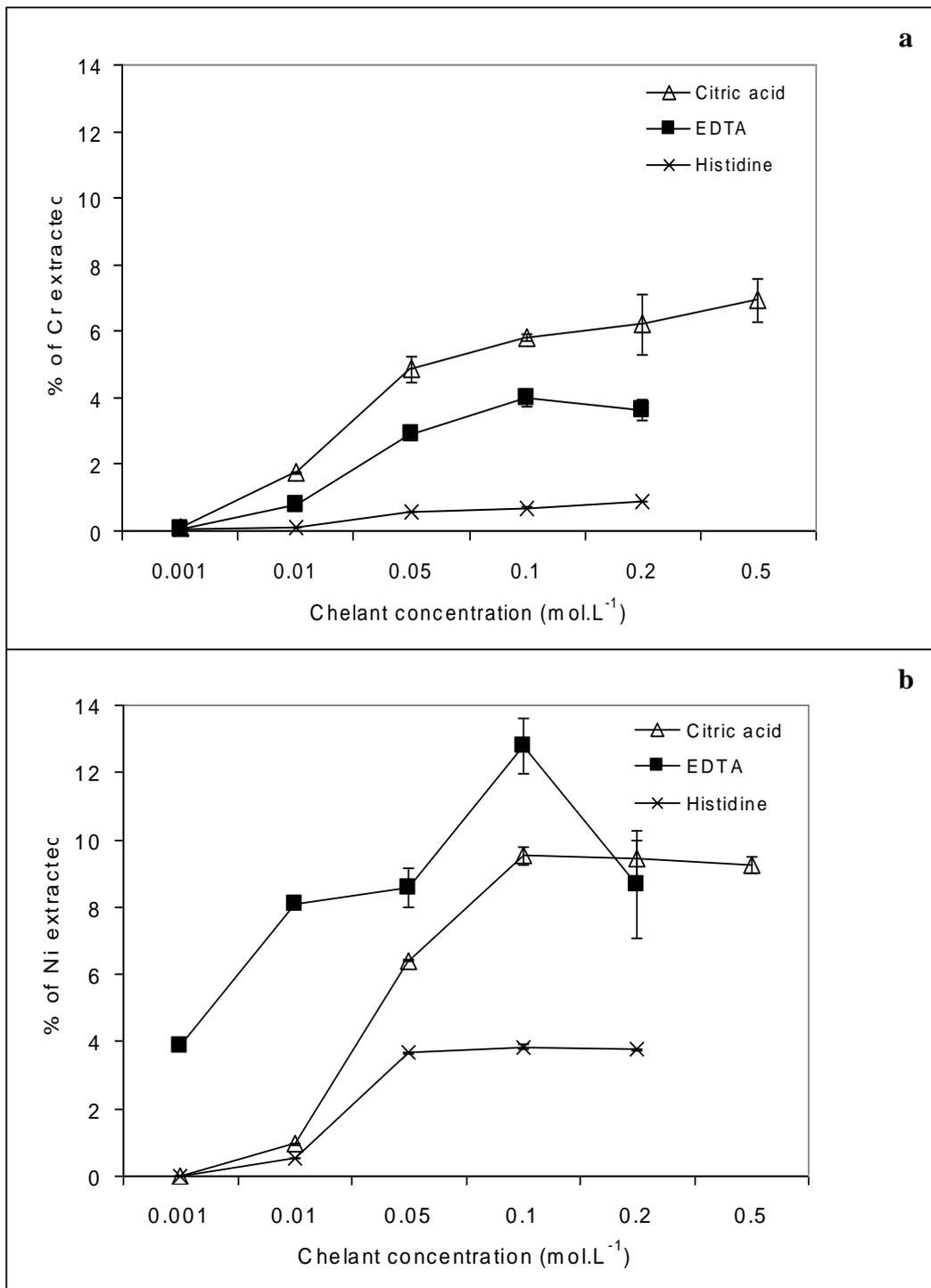
4 **a:** % Cr was based on total Cr content in soil

5 **b:** not detected

6



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



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

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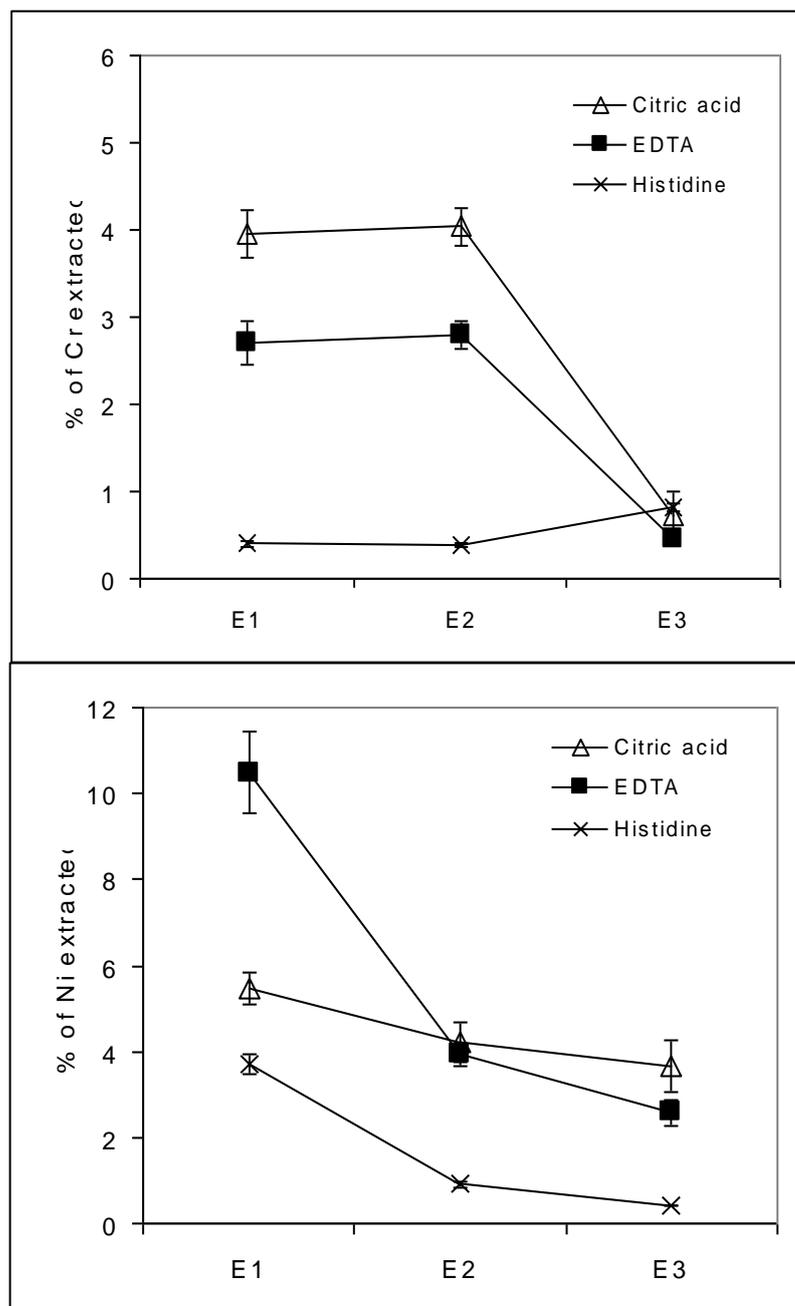


Fig. 3. Successive extractions of Cr and Ni (E1: first extraction, E2: second extraction, E3: third extraction); % Cr was based on total Cr content; chelant concentrations 0.05 mol.L⁻¹. Error bars represent the standard deviation of three samples.