Influence of indigenous and added iron on copper extraction from soil

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ABSTRACT

Experimental tests of copper leaching from a low permeability soil are presented and discussed. The objective of the experiments was to investigate the influence of indigenous and added iron in the soil towards copper mobilization. Metals' leaching was performed by flushing (column tests) or washing (batch tests) the soil with an aqueous solution of ethylenediaminetetraacetic acid, EDTA. An excess of EDTA was used in flushing tests (up to a EDTA:Cu molar ratio of about 26.2:1), while, in washing tests, the investigated EDTA vs. copper molar ratios were in the range between 1 (equimolar tests) and 8.

Copper extraction yield in flushing tests (up to about 85%) was found to depend upon contact time between the soil and the leaching solution and the characteristics of the conditioning solution. The saturation of the soil with a $NaNO_3$ solution before the treatment, favoured the flushing process reducing the time of percolation, but resulted in a lower metal extraction during the following percolation of EDTA.

The indigenous iron was competitive with copper to form EDTA complexes only when it was present in the organic and oxides–hydroxides fractions. Artificial iron addition to the soil resulted in an increase of both the exchangeable iron and the iron bonded to the organic fraction of the soil, thus increasing the overall amount of iron available to extraction.

In both batch and continuous tests, the mechanism of copper extraction was found to involve the former dissolution of metal salts, that lead to an initial high concentration of both copper and selected competitive cations (essentially Ca^{2+}), and the following EDTA exchange reaction between calcium and copper complexes. The initial metal salts dissolution was found to be pH-dependant.

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1. Introduction

Contamination of soils with heavy metals, due to the uncontrolled disposal of hazardous wastes, is a widespread environmental problem and requires appropriate remedial techniques. Several studies performed during the past two decades [1] have already assessed that heavy metals extraction from contaminated soil can be successfully performed by the in situ soil flushing technology [2,3] or the ex situ soil washing technology [4–8]. Both technologies involve the leaching of metals and other cations from the contaminated soil, through their complexation with a chelating agent or the dissolution of metal compounds (oxides, hydroxides, carbonates) under acidic conditions. The chelating effectiveness of ethylenediaminetetraacetic acid (EDTA) has been widely demonstrated in both washing and flushing treatments [2,9]. In comparison to other chelating agents, EDTA presents the following advantages: a low degree of biodegradability in groundwater [5] and soil [1,4] and moreover a high level of complexing capacity with respect to heavy metals [10,11].

The leaching solution is generally an aqueous solution of the chelating agent, and the leaching treatment can be realized in batch conditions (soil washing) or by continuous percolation in the soil (soil flushing).

During the continuous percolation of the leaching solution, a dramatic decrease in hydraulic conductivity is generally observed in low permeability soil. This behaviour is mainly due to the binding of EDTA to soil organic matter and the cation exchange between the leaching solution and the soil [12]. As a consequence soil packing often occurs. However, due to the need of excavation and transportation of the contaminated soil, soil washing is generally more expensive and risky than soil flushing.

In addition, both the techniques often determine a stronger modification of soil properties and characteristics together with a huge EDTA consumption, due to the potential chelation of all the exchangeable cations present in soil able to form stable complexes with EDTA [13].

This can be attributed to both the low selectivity of EDTA, and the abundance of easy extractable ions (such as calcium iron, aluminium) in the most common soils [14,15].

In addition, a strong dissolution of carbonates under acidic conditions, such that induced by the percolation into the soil of aqueous solutions of EDTA may occur. In many soils, in fact, the carbonate–bicarbonate system is the main buffering mechanism.

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In low permeability soils, however, because of the dissolution of clay minerals, the solubilization of iron is expected [16]. An abundance of iron can therefore influence the extraction effectiveness of other metals. In addition, iron forms the most stable complex with EDTA, according to Kim et al. [7].

The objective of this paper was therefore to investigate the influence of iron towards copper extraction from a low permeability soil.

Flushing experiments with an aqueous solution of Na_2–EDTA were performed. Several experimental conditions were investigated, including the effectiveness of a soil preconditioning (before any extraction) with $NaNO_3$ solution [17]. Since the risk associated to the residual EDTA entrapped into the soil is well-known and widely reported [18], to complete the extraction process, flushing tests with EDTA solutions were followed by a further extraction with distilled water.

To compare the behaviour of both indigenous and exhogenic iron (as a result of a contamination), the experimental tests were performed on three samples of a clayey soil, spiked respectively by only Cu or only Fe, or by both Cu and Fe. Sequential extraction tests were performed to assess the source of the iron present in the leachate.

A comparative batch test was then carried out, to assess the extent of metal dissolution under long time contact conditions.

As a consequence of the competition mechanisms between heavy metals and indigenous metals a great excess of EDTA is required in the remediation processes [19] thus increasing the risk of a contamination of the soil by EDTA itself. In addition, since the cost of reagents is the major cost involved in flushing treatment [5], a large excess of EDTA strongly increase the overall costs of the treatment. For these reasons, though the need of field tests validation is required, this paper aims to provide an useful tool in planning remediation program that involve heavy metals extraction from low permeability soils.

2. Materials and methods

2.1. Soil characterization

The soil used in the experiments was a clayey soil collected in a cave near Bracciano, Rome, Italy. It was chosen as representative of a typical clayey soil in central southern Italy.

The soil was initially passed through a 2 mm sieve: the resulting soil composition is given in Table 1. The soil was then mixed for 24 h in a Hobart-type mixer at 120 rpm. Table 2 shows the main chemical and physical characteristics of the soil used.

pH was measured after mixing 10 g of soil samples with 25 ml of a 0.01 M solution of $CaCl_2$ [4].

The total porosity was determined on 100 g of air-dried soil [3].

The soil hydraulic conductivity was determined according to the modified ASTM D2434 standard test (Falling Head Method) [20].

The samples were subjected to acid digestion according to the EPA3050B method: the leachate was analyzed with a Philips PU9200 atomic absorption spectrophotometer to determine total metal content, after filtration through Whatman membrane filter (0.45 μm).

Since metal extraction effectiveness depend upon the leachability of the different metal form, preliminary sequential extraction using the Tessier's method [21] were performed to investigate Fe

Table 1
Composition of the soil used in the experiment (ASTM classification).

Component	Gravel	Coarse sand	Medium and fine sand	Silt and clay
Particle size	>2 mm	0.425–2 mm	0.075–0.425 mm	<0.075 mm
% vol.	–	45	24	31

Table 2
Characteristics of the soil used in the experiments.

Parameter		Value
pH		6.7
Organic carbon (%)		0.8
Hydraulic conductivity (water) (cm/s)		0.00775
Hydraulic conductivity (EDTA 0.05 M) (cm/s)		0.00080
Total porosity (%)		45.6
Moisture content (g/kg)		27.5
Bulk density (g/cm^3)		1.30
Soil particle density (ρ_s) (g/cm^3)		2.31
Pore volume (ml)		42
$CaCO_3$ (g/kg)		83.4
Metals (mg/kg)		
	Fe	Mn
Exchangeable	0.4 ± 0.1	10.8 ± 1.2
Bound to carbonates	20.4 ± 1.4	44.8 ± 2.1
Bound to oxides–hydroxides	33100 ± 210	905.2 ± 85
Bound to organic matter	2380 ± 150	7.8 ± 1.0
Residue	4420 ± 120	515.2 ± 15
Total	39921 ± 490	1484 ± 490
Cu (total)		0.5 ± 0.1
Zn (total)		1.2 ± 0.1
Ni (total)		n.d.
Al (total)		93330 ± 705
Hg (total)		n.d.
Ca (total)		930 ± 65
Mg (total)		280 ± 30
Na (total)		100 ± 20
Cationic exchange capacity (cmol/kg)		15.00

and Mn distribution into five fractions: exchangeable, bound to carbonate, Fe–Mn oxides, bound to organic matter and residual.

Soil mineral composition determined by X-ray analysis, performed using a Siemens type diffractometer, showed a prevalent content of illite, quartz, feldspars, and the presence of lower amounts of calcite and muscovite.

2.2. Soil contamination

Three 1.5 kg samples of the soil was spiked by mixing each of them for 48 h at 120 rpm in a Hobart-type mixer together with 1 L of a saturated aqueous solution of dihydrate copper chloride, $CuCl_2 \cdot 2H_2O$, or hexahydrate iron chloride, $FeCl_3 \cdot 6H_2O$, or both the reagents. After mixing, the three samples were air dried by exposure to ambient air for 90 days before metal analytical determination.

The artificial contamination was carried out so as to obtain a concentration approximately twice than the Italian regulation limit for copper at an industrial site (600 mg Cu/kg of soil) [22].

The metal content of six 1 g samples of each contaminated soil was determined, according to the procedure described in the previous paragraph. The average Cu concentration in the soil contaminated by only copper was 1110 mg Cu/kg with a standard deviation of ±78 mg. The average Fe concentration in the soil contaminated by only iron was 1205 mg Fe/kg with a standard deviation of ±50 mg.

In the sample contaminated by both copper and iron, the actual concentration of the two metals were 1150 mg Cu/kg with a standard deviation of ±48 mg, and 1170 mg Fe/kg with a standard deviation of ±85 mg, respectively.

100 g samples were then prepared from the three contaminated initial samples, and stored in plastic containers.

2.3. Experimental procedure

2.3.1. Column tests (flushing)

The experimental apparatus for flushing tests was a series of Plexiglas columns, with an internal diameter of 5 cm and a height

Table 3
Summary of the experimental conditions (flushing tests).

Test	Spiked metal	Conditioning (M)	EDTA (M)	pH_0
F1a	Fe + Cu	H_2O (pH = 5)	0.05	5.0
F1b	Fe	H_2O (pH = 5)	0.05	5.0
F1c	Cu	H_2O (pH = 5)	0.05	5.0
F2a	Fe + Cu	$NaNO_3$ 0.05	0.05	4.45
F2b	Fe	$NaNO_3$ 0.05	0.05	4.45
F2c	Cu	$NaNO_3$ 0.05	0.05	4.45
F3a	Fe + Cu	$NaNO_3$ 0.025	0.025	4.47
F3b	Fe	$NaNO_3$ 0.025	0.025	4.47
F3c	Cu	$NaNO_3$ 0.025	0.025	4.47
FN	–	$NaNO_3$ 0.05	0.05	4.45

of 10 cm. Samples (50 g) of the contaminated soil were placed in the column, above a layer of glass wool, to ensure uniform distribution of the liquid.

The columns were initially saturated (conditioning phase) with a volume of water or conditioning agent ($NaNO_3$) corresponding to the pore volume [17].

The flushing solution was introduced from the top of the column by means of a peristaltic pump (Velp Scientific mod. Gilson Minipulse 3). The average speed of percolation calculated in the tests was in the range between 0.24 and 1.78 ml/min.

The leaching solutions were prepared by dissolving crystals of ethylenediaminetetraacetic acid disodium salt (EDTA–Na_2) in distilled water, so as to obtain a 0.05 M or a 0.025 M solution of EDTA–Na_2.

The EDTA solution was injected in a plateau mode (constant concentration in the feed solution).

The tests were carried out by percolating 500 ml of the selected EDTA solution, followed by 200 ml of water at the same pH. This final percolation of water was performed to ensure the removal of the residue EDTA entrapped into the soil.

At selected time intervals, each one corresponding to the percolation of 100 ml of the injecting solution (about 2.4 pore volumes—PV), samples of the extracted solution were collected and filtered (Whatman 0.45 μm) for metal determination. To evaluate soil mineral dissolution, Ca, Fe, Al, and Mg content in the leachates were determined, according to the procedure described in the previous section.

The electrical conductivity of the collected samples was measured by an HI 8033 conductimeter (Hanna Instruments).

The experimental conditions of flushing tests are summarized in Table 3.

All the tests were performed in triplicate: the standard deviation calculated in each test was in the range between 0.6 and about 3.5%.

2.3.2. Batch tests (washing)

The washing solution was prepared by dissolving EDTA–Na_2 in distilled water (Table 4).

The liquid vs. solid (L/S) ratio was fixed at 5: in a previous study this L/S ratio was found as optimum for copper extraction by washing from a sandy soil. In addition, this value is often assumed as a lower limit in metal extraction from soil, to ensure a good mixing of the soil slurry [4].

Table 4
Summary of the experimental conditions (washing tests).

Test	EDTA:Cu (molar ratio)	EDTA [M]	EDTA (mol):kg soil (kg)	pH_0
W11	1	0.0035	0.0175	4.80
W00	–	–	–	4.90
W20	–	0.007	0.035	4.90
W21	2	0.007	0.035	4.90
W41	4	0.014	0.070	4.72
W81	8	0.028	0.140	4.62

As regard the EDTA/Cu molar ratio, the tests were performed at equimolar concentration and at selected excesses of EDTA with respect to Cu (2:1, 4:1 and 8:1—using tap water). The excess of EDTA was realized by increasing the EDTA concentration in the washing solution and, as a consequence, obtaining more acidic washing solutions.

The tests on uncontaminated soil samples were performed after acidifying the washing solutions up to pH = 4.9 by adding hydrochloric acid.

All the tests were performed by mixing at 175 rpm in a magnetic stirrer 100 g of soil and the corresponding volume of washing solution according to the L/S ratio adopted. At selected times (every 10 min within the first reaction hour, every 30 min between the first and the third hour, and after 4, 5, 7, 10, 15, 20, 23 and 24 h) the contact solution was sampled (5 ml). A sedimentation time of 2 min was always allowed to the soil slurry, prior the sampling for metal content determination, according to the procedure described in the previous section.

The inorganic carbon content in the contact solution was also determined, using a Shimadzu 5000-A Total Organic Carbon Analyzer.

In any flushing or washing test, the total amount of bound EDTA was also computed, together with the extraction efficiency with respect to the initial amount of any investigated metal. Free EDTA was calculated as the amount of EDTA not combined to the considered metals (Al, Ca, Cu and Fe).

3. Results and discussion

3.1. Soil flushing tests

Table 5 shows the results of the column tests: both the extraction yield for Cu and Fe are shown, together with the amount of Ca, Cu, Fe extracted in each test. The time required to percolate the leaching solution is also reported.

In a first series of experimental tests the initial conditioning of the soil was performed by injecting water (test F1a and F1b). The initial removal of Cu^{2+} and Fe^{2+} by water in the conditioning phase was always negligible. This is in accordance with the results obtained by Voegelin et al. [23], that found that only small amounts of metals are released during the conditioning phase, mainly due to the mobilization of colloidal particles resulting from column packing.

After the conditioning phase, the soil was subjected to the extraction tests with the EDTA solution. The percolation was slow, due to the strong difference in conductivity between the conditioning solution and the leaching one (786 μS for water, 6 mS for the 0.05 M EDTA solution). This behaviour was first observed by Kedziorek and Bourg [17], and was attributed to the dispersion of colloids, thus inducing poor permeability, that is reasonable to expect when the clayey component in the soil is prevalent. Also Arnon et al. [12] found that the swelling of clay minerals during water percolation may induce a decrease in soil hydraulic conductivity, thus resulting in a progressive decrease in the speed of percolation of the leaching solution.

Both the tests were therefore interrupted after 24 h from the beginning of the whole extraction process. In correspondence of this great increase in retention time, at the end of the experiments, a total Cu extraction yield of about 91% and about 95% were calculated for test F1b and F1c respectively.

To prevent soil clogging during the percolation of the leaching solution, a preconditioning phase with a solution of $NaNO_3$ (at the same concentration of the following EDTA solution) was then carried out in all the other tests. Table 5 shows that all the tests where the $NaNO_3$ solution was injected before metal extraction with EDTA were successfully completed in a time interval ranging from 7.5 and 19 h. The leachate could be recovered continuously at each perco-

Table 5
Experimental results of flushing tests.

Test	Test duration (h)	EDTA:metal added (mol/mol)	Metals extracted						Free EDTA[a] (%)
			Fe (mg)	Al (mg)	Cu (mg)	Cu removal (%)	Ca (mg)	Total (mol)	
F1a	–	12.32	56.48	11.50	49.80	90.99	93.55	4.57	81.75
F1b	–	23.27	94.32	13.45	0.00	0.00	158.81	6.16	75.37
F1c	–	26.19	44.60	13.20	57.09	95.15	118.00	5.14	79.44
F2a	3.80	12.32	38.69	9.35	33.47	61.15	39.79	5.60	89.75
F2b	11.25	23.27	51.40	10.20	0.00	0.00	48.10	4.61	90.00
F2c	12.63	26.19	32.60	11.40	50.36	92.02	50.99	4.82	87.69
F3a	6.53	6.16	51.57	12.70	43.71	79.87	29.33	5.18	77.46
F3b	15.63	11.64	60.37	12.45	0.00	0.00	39.22	4.20	79.82
F3c	13.63	18.33	34.43	13.45	51.93	94.89	52.83	4.93	73.95
FN	32.47	–	45.08	16.90	0.00	0.00	79.72	4.22	86.30

[a] As the amount of EDTA in excess with respect to Fe, Al, Ca and Cu amounts.

lation step. No obstacle to the percolation was observed: an almost constant percolation speed was observed during each test. This confirms that no modification occurred in soil matrix.

As in the case of the initial preconditioning with water, the mobilization of Cu^{2+} and Fe^{2+} by the $NaNO_3$ solution was negligible. Conversely, an initial great dissolution of Ca^{2+} was observed (about 2.29 and 1.90 mmol of Ca^{2+} were the average calcium dissolution during the conditioning phase in tests F2 and F3, respectively).

This initial calcium dissolution can be attributed in this case to two main factors. First of all, the dissolution of the calcareous fraction of the soil, that strongly occurs under acidic conditions. In addition, soil conditioning with $NaNO_3$ favoured a cationic exchange between calcium ions in the soil matrix and sodium ions in the percolating solution [17].

It can be noted that the time required to complete the extraction procedure was strictly related to the concentration of EDTA in the leaching solution (increasing the EDTA concentration, the duration of the test decreased) and also strongly depended upon the type of the contamination.

In particular, it can be reasonably assumed that in the presence of both exhogenic Cu and Fe, since the soil was contaminated by using soluble salts, the presence of a higher amount of voids resulted in a high soil permeability to the same leaching solution. The duration of the tests (shown in Table 5), together with the extent of the excess of EDTA in the flushing solution, were the main factors to determine metal extraction yield. The higher percolation speed was the reason to explain how in the test F2, the lowest Cu extraction yield were reached though they involved an higher concentration of EDTA in the leaching solution with respect to the tests F1 and F3.

By comparing the results of the tests F2 and F3, also the extraction of both indigenous and added iron was found to depend mostly on the contact time than on the increase in the EDTA concentration in the leaching solution. In addition, the overall amount of iron extracted was in any case lower in the presence of a contemporary contamination by copper.

The results of sequential extraction performed after the artificial contamination and after the tests F1a and F1b are reported in Table 6. These results show that the iron present in the exchangeable fraction was easily extracted, while no variations

were observed in the carbonate fraction. In addition, as a consequence of the EDTA promoted extraction, the amount of iron bonded to the organic fraction of the soil and the amount present as oxides and hydroxides were reduced.

At the same time, about the effect of iron towards copper extraction, it is useful to compare the results obtained in tests F2c and F3c (shown in Fig. 1) to the results obtained in tests F2a and F3a (shown in Fig. 2). In both the figures, also the amount of Ca extracted at each step is shown. The presence of added iron determined a lower copper extraction at the end of each test, and the extent of copper extraction yield reduction was higher when the excess of EDTA in the leaching solution was higher.

The results reported in the above mentioned Figs. 1 and 2, show that, generally, during the injection of EDTA, both copper and iron were continuously extracted. For both metals the extraction was mainly observed during the first three steps of injection while only small amounts of copper were extracted during the two following injections of EDTA and the last injections of water. The maximum amount extracted was observed for both metals after the passage of 200 ml of leaching solution (about 4.8 PV). At the same time, in all the tests where iron was spiked into the soil, a high iron extraction yield was observed, and this resulted in a lower overall copper extraction.

This behaviour can be explained considering the extraction mechanism. Due to the not selectivity of its chelation mechanism, EDTA can extract from the solution all the available cations. Since calcium carbonate easily undergoes to dissolution under acidic conditions, an initial great mobilization of calcium ions was first observed [14], according to the:

$$CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-} \tag{1}$$

and to the exchange of calcium ions (Ca_{ads}^{2+}) between the leaching solution and the soil matrix:

$$Ca_{ads}^{2+} + Na_2EDTA \Leftrightarrow CaEDTA + 2Na_{ads}^{+} \tag{2}$$
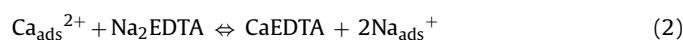
Simultaneously, a lower immediate availability of other metals (mainly copper, iron and only a negligible amount of aluminium and magnesium) was observed, due to the lower solubility of their compounds [24] and also considering the poor exchangeable properties of illite [25].

Table 6
Results of iron sequential extraction tests.

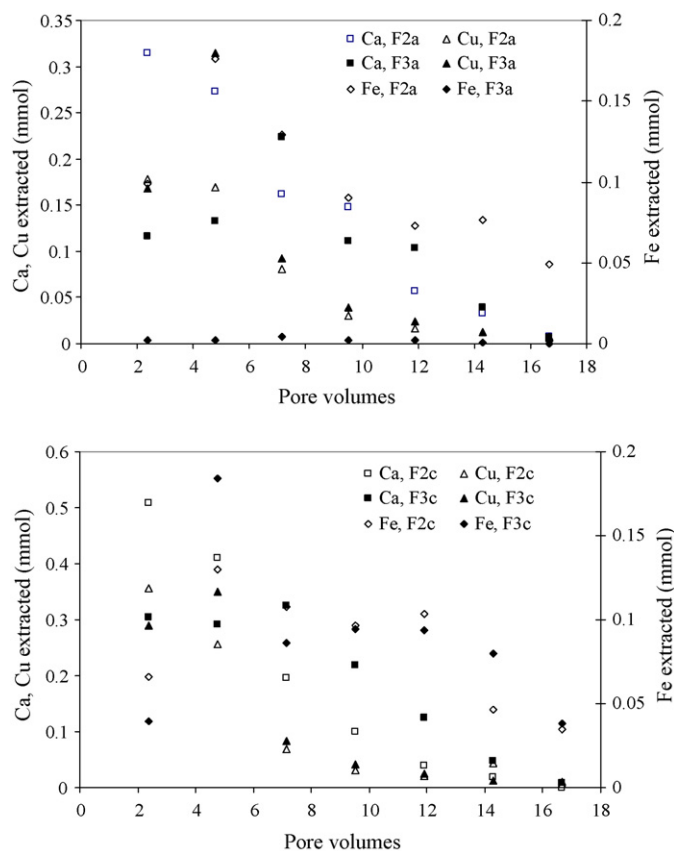| Fraction	After contamination (mg/kg)	After F1a (mg/kg)	After F1b (mg/kg)	After F1c (mg/kg)
Exchangeable	300	nd	nd	nd
Bound to carbonates	nd	nd	nd	nd
Bound to oxides–hydroxides	33,500	33,077	32,900	32,680
Bound to organic matter	2,880	2,580	2,500	2,040
Residue	4,440	4,400	4,440	4,340
Total	41,120	40,057	39,840	39,060

Fig. 1. Metals extraction in tests F2 and F3.

After this initial Ca^{2+} mobilization, the percolation of the leaching solution progressively caused the mobilization of mainly copper, iron and aluminium. Considering the carbonate and exchangeable fraction negligible with respect to the total amount of iron in the soil, as shown in Table 2, the iron available to the extraction process was mainly the amount bounded to organic fraction (mainly trivalent iron, [26]) and the iron present in the oxide–hydroxide fraction, in particular as amorphous hydroxides, according to Kim et al. [7]. This is also confirmed by the results of the soil sequential extractions performed after the percolation of EDTA,

Fig. 2. Experimental results: equimolar test W11.

Table 7
Experimental results of washing tests.

Test	pH_f	Extraction time (h)	$t_{50\%}$ (min)	η_{Cu} (%)	η_{Fe} (%)
W11	6.08	24	>1440	48.54 ± 1.5	0.46 ± 0.01
W00	6.74	24	–	–	n.d.
W20	6.51	24	–	–	n.d.
W21	6.26	24	<10	78.39 ± 2.7	0.61 ± 0.01
W41	5.35	24	<10	99.06 ± 0.5	1.46 ± 0.02
W81	5.25	24	<10	99.97 ± 0.01	3.07 ± 0.02

reported in Table 7, that also show that a negligible extraction of iron from the residue fraction was observed.

When labile iron was present, due to the lower affinity to EDTA for Cu^{2+} with respect to Fe^{3+}, especially at the pH values lower than 6 [7,24], a large amount of iron was then extracted by EDTA.

The results of iron sequential extraction tests are in accordance to the results obtained by Lei et al. [27]. They found that EDTA may induce metal mobilization from the carbonate, iron and manganese oxides, organic matter and residue fractions of a contaminated soil analyzed with the Tessier sequential extraction procedures.

The results reported in Table 5 also show that in each tests the amount of aluminium extracted accounted about one third of the amount of iron extracted. Despite of the huge amount of aluminium in the silicate matrix, the formation of EDTA–Al complexes was less favoured than EDTA–Fe complexes [7]. In addition, the extraction of aluminium appeared to be not dependant upon the nature of the contamination (Cu or Cu and Fe), but only on the contact time between the leaching solution and the soil. Similar results were obtained in another study on soil flushing, where, as a result of the hydraulic conductivity reduction induced by soil packing a larger degree of Fe and Al dissolution occurred [16].

A negligible amount of both magnesium and manganese was also observed in the leachate during all the experiments.

Table 5 also reports the results of mass balance for EDTA. At the pH conditions achieved during the tests, free EDTA can be reasonably assumed to be in the form of $EDTA–Y^{2-}$ [15]. Results show that, in any test, the large excess of EDTA with respect to the actual extractable metal in the soil mainly resulted in a huge amount of not combined EDTA in the leachate.

This result is in accordance to the results obtained in other recent experiments [28,29] where an optimal dosage of EDTA were found to maximize the removal of target contaminants from contaminated soil. An excessive increase in EDTA concentration in the leaching solution did not result in appreciable gain in heavy metals removal, due to the complexation of competitive cations.

In addition, for all the considered metals, a residual metal extraction was observed during the final percolation of pure water. This higher further extraction was generally not negligible (up to about 0.36% for Fe in test F3a and 5.84% for Cu in test F2c).

This further extraction can be attributed to the removal of traces of EDTA–metal complexes entrapped into the soil.

3.2. Soil washing

The mechanism of extraction observed in this study, is consistent with that already verified in another study [30] on a different type of soil.

To evaluate competitive effects between Ca, Cu, and Fe, Fig. 3 reports for the equimolar test W11, the amount of Cu and Fe extracted along time, together with the amount of Ca. After the initial mobilization of Ca^{2+} (as previously observed in the flushing tests), increasing the contact time between the soil and the washing solution, due to the lower EDTA affinity for Ca^{2+} with respect to Cu^{2+} in all the pH range [24], an exchange reaction occurred between
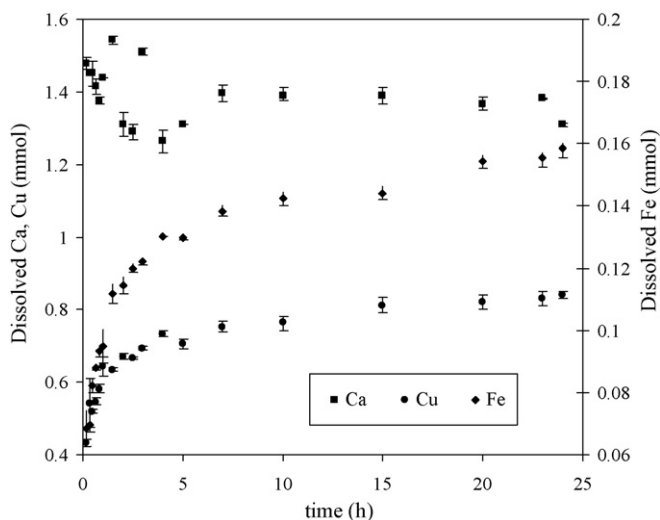
Fig. 3. Results of washing (batch) tests at increasing EDTA:Cu ratio.
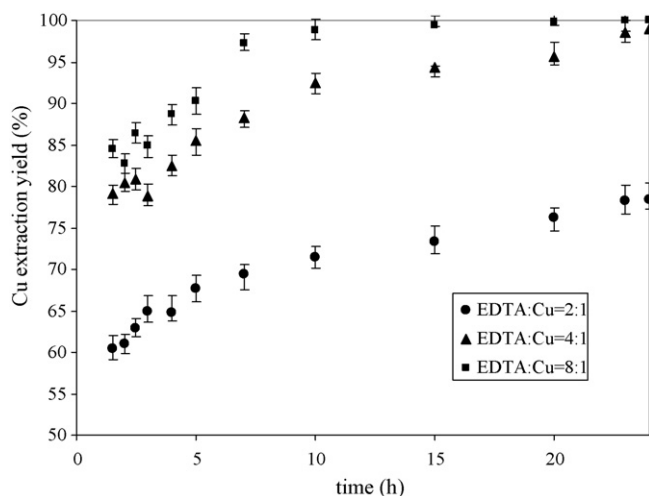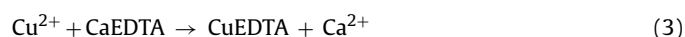
Ca–EDTA and Cu–EDTA, according to the:

$$Cu^{2+} + CaEDTA \rightarrow CuEDTA + Ca^{2+} \qquad (3)$$

that show how an equimolar exchange between Ca^{2+} and Cu^{2+} occurred, as confirmed by the data reported in Fig. 3.

It was also observed that, at the end of the treatment, reaction (3) did not resulted fully developed. A further slight increase in Cu^{2+} was in fact still measured in the contact solution after 24 h, together with the simultaneous reduction in Ca^{2+} availability (Fig. 1). However, the decrease in Ca^{2+} in solution can be mostly addressed to the inversion of reaction (1): during the tests, in fact, pH increased, and, as a consequence, a substantial calcium precipitation as carbonate occurred. This is confirmed by the total inorganic carbon content of the contact solution, that quickly raised up to 4 mg/l (within 5 h of reaction), while, after 24 h was lower than 1 mg/l, thus showing a similar behaviour than Ca^{2+} ions.

The results of the washing tests are summarized in Table 7, where the overall Cu (η_{Cu}) and Fe (η_{Fe}) extraction yield are shown, together with the time required to achieve a reduction of 50% Cu concentration (Cu half-life, $t_{50\%}$) and the pH measured at the end of each test (pH$_f$).

To achieve an higher Cu^{2+} extraction yield, in the test W21, W41 and W81, EDTA concentration in the leaching solution was increased: three EDTA:Cu ratios were tested: 2:1, 4:1 and 8:1. The results in term of copper and indigenous iron extraction yield in these tests are presented in Fig. 3. The same behaviour shown by equimolar tests W11 was observed. With respect to this test, in particular, the initial amount of Ca^{2+} measured in the contact solution was higher, according to the more acidic conditions established in the contact solution (the pH of the extractant solution was 4.9, 4.72 and 4.62 at 2:1, 4:1 and 8:1 EDTA:Cu ratios respectively). The first step of the extraction mechanism was therefore dependant upon the pH of the leaching solution. The same trend was in fact observed in all the washing tests, when a lower or higher initial dissolution of both calcium occurred, depending upon the pH of the leaching solution, determined by EDTA concentration.

Results also show that an increase in Cu^{2+} extraction yield was achieved as a consequence of the increase in EDTA concentration in the washing solution, as expected considering that in all the washing tests the same contact time was adopted.

As regards the comparison between the flushing and washing tests results, a higher extraction yield was calculated for iron in the washing tests performed at a EDTA/Cu ratio of 8:1, with respect to the extraction yield calculated for indigenous iron in flushing test F1c, where, even considering the same contact time of the washing

tests (24 h) a larger excess of EDTA was realized in the leaching solution.

It can be considered, however, that, due to the high iron content in the investigated soil, even the amount extracted in flushing tests corresponded to a significant amount of iron in solution during the extraction process. Considering the high stability of Fe^{3+}–EDTA complexes, this must be taken into account in the evaluation of EDTA consumption during the remediation process.

Finally, in the view of the soil remediation, Cu^{2+} extraction yield in washing tests strongly depend on EDTA:Cu ratio. According to Italian Environmental Regulation [22], soil remediation to allow a civil reuse of the soil was successfully achieved at EDTA:Cu = 4 at a liquid/soil (L/S) ratio of 5.

4. Conclusions

A low permeability clayey soil spiked with copper and/or iron was subjected to column extraction and to 24 h batch extraction with aqueous solution of EDTA.

The results of the tests show that:

- a preliminary conditioning of the soil with $NaNO_3$ solution was necessary to avoid variations in soil conductivity and to allow the percolation of the leaching solution;
- during soil conditioning, as a consequence of cation exchange between Na^+ and Ca^{2+}, an initial huge dissolution of Ca^{2+} was observed;
- the mechanism of metal extraction involved a two-step dissolution–chelation process where, after metal salts dissolution due to the strong acidity of the leaching solution, EDTA chelation occurred, displacing competitive ions (in particular Ca^{2+}) and so favouring the formation of Cu^{2+}–EDTA complexes.
- the final flushing with pure water to remove the residue EDTA entrapped into the soil resulted in a not negligible further metals extraction;
- metals extraction yield mostly depended upon the contact time than an increase in the excess of EDTA;
- the indigenous iron was competitive with copper to form EDTA complexes, only when present in the organic and oxides–hydroxides fractions;
- the iron added resulted in the presence of exchangeable iron and in an increase in the iron amount bonded to the organic fraction of the soil, thus increasing the overall amount of iron available to extraction.

The comparison with the results obtained in the washing tests show that the extraction yield obtained in column tests were lower than those obtained in washing tests, even considering that in flushing tests an higher EDTA:Cu ratio was used and, consequently, a lower pH was measured at the beginning of the test. A higher amount of iron was extracted during washing tests, and a lower amount of EDTA not combined to the investigated metals in the extracted solution was consequently observed. As regards the influence of iron towards copper extraction, at the investigated conditions, the flushing treatment results in a lower copper extraction from the soil, but, at the same time, the displacement of Cu by iron in the complexes with EDTA was better prevented. Since the flushing treatment ensures a higher amount of EDTA not bound to the target metals at the end of the tests, the performance of the treatment can be reasonably increased by recycling the extracted solutions before their treatment.

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