



## Recovery of EDTA and metal precipitation from soil flushing solutions

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### Abstract

This work studies the effectiveness of a process proposed for the recovery of ethylenediaminetetraacetic acid (EDTA) and metal precipitation from soil flushing solutions. Two series of experimental tests were carried out on two samples of a soil artificially contaminated with copper or lead. The metals were extracted from the soil by flushing with a 0.05 M aqueous solution of EDTA sodium salt (E-Na<sub>2</sub>). Cu or Pb extraction efficiencies of about 95 and 98% were observed, respectively. The two extracted solutions were then treated to obtain EDTA recovery and metal precipitation from the aqueous solution. EDTA recovery was achieved in two steps. An initial evaporation treatment lead to reduce the solution volume by about 75%. This was followed by the acidification of the residue solution, which precipitated more than 93% of the used EDTA. The precipitated EDTA was removed by filtration, and was suitable for reuse after adding an alkaline agent. Metal precipitation from the filtered solution was performed using two different methods: an almost total (99.5%) Pb precipitation in alkaline conditions was achieved after complex destabilization through the sequential addition of ferric ions and sodium phosphate, while 93.6% copper precipitation was achieved with ferrous sulfate as a destabilization agent.

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### 1. Introduction

Heavy metals have long been known to be toxic to human and aquatic life: their persistent bioconcentration and extensiveness have stimulated research efforts to develop appropriate technologies for the treatment of metal-contaminated soils and sediments.

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Heavy metals are often found in soil at high concentrations as a result of agricultural (fertilizers, pesticides, and insecticides applications), industrial emissions and activities (including battery breaking and recycling, oil refining, paint manufacturing, metal moulding, plating, and smelting), past environmental disposal practices, or vehicle emissions [1].

Factors affecting heavy metal retention by soils include: pH, soil type (e.g. particle size), cation exchange capacity (CEC), natural organic matter, age of contamination, and the presence of other inorganic contaminants. For cases in which the heavy metal contamination is very high (thousands of  $\text{mg kg}^{-1}$ ), the metal sorption capacity of most soils is exceeded, and any additional contamination occurs as a discrete metal–mineral phase. Such metal ions can be immobilized in the soil by the formation of insoluble precipitates, incorporation into the crystalline structure of clay particles and metals oxides, and/or by physical entrapment in the immobile water surrounding the soil micro and macropores [2].

The exposure to these pollutants is likely to persist for a long time: metals adsorbed in soils can runoff into rivers or lakes or leach into the groundwater leading to an accumulation in animals, plants, and humans.

Several methods have been proposed for the remediation of heavy metal-contaminated soils. These methods are based on two principles: the immobilization of the metal (by increasing the soil's retention of the metal or by decreasing the metal's rate of mass transfer) and the removal of metals from the soil matrix [3].

Soil washing and in situ soil flushing are techniques which transfer the contaminants to a liquid phase by desorption and solubilization. Generally, in situ technologies are more economical and safer because excavation is not required [4,5].

In the in situ soil flushing application, extracting solutions are infiltrated into the soil. The flushing fluid is typically water and may contain additives to improve contaminant removal, such as a chelating agent [1]. In the remediation of copper (Cu) contaminated soil, the effectiveness of EDTA (ethylenediaminetetraacetic acid,  $\text{E-H}_2$ ) has been widely demonstrated as a chelating agent in flushing treatment [6–9].

In comparison with other chelating agents, EDTA presents the following advantages: a low degree of biodegradability in groundwater [6] and soil [2] and moreover a high level of complexing capacity with respect to heavy metals [6].

The present study deals with an experimentation performed to achieve the recovery of EDTA and the precipitation of metals from soil flushing solutions. Copper and lead (Pb) were chosen to test the effectiveness of the process. Two series of samples of a soil were separately contaminated with either Cu or Pb: the metals were then extracted by flushing using an aqueous solution of EDTA.

The extracted solution was then subjected to treatment with the aim of obtaining the total separation of metals from the solution and the recovery of the chelant agent (EDTA) to allow its reuse in the process. The high cost of EDTA has in fact often precluded its use in the remediation of metal-contaminated soils [10,11]. Furthermore, flushing effluents are characterized by a large excess of free EDTA in solution, or combined with other competitive ions in soil. So the need exists to develop a process that allows the recovery and recycling of EDTA. Electrochemical processes have already been developed for washing effluents [12,13], but they are affected by several operating problems (membrane fouling and degradation) [11]. Therefore, alkaline precipitation is the simplest way to separate metals. A number of studies were performed to set up the precipitation process of metals from

complexes with EDTA or other chelating agents and most of them pertained to equimolar solutions of metal and EDTA [10,11,14], but this differs from the case of solutions extracted from contaminated soils. These solutions are in fact characterized by a large excess of EDTA, while the metal concentration is very low. The effectiveness of the main precipitation methods applied needs to be verified for these particular solutions. In this study two different precipitation processes were chosen and tested using the extracted solutions, for their Cu or Pb precipitation. An optimization of reagent addition was also performed, to reduce the consumption in the process and thus increase the economic feasibility of the whole process.

## 2. Materials and methods

### 2.1. Soil preparation

The composition of the soil used in the experiment is given in Table 1. The soil was mixed for 24 h in a Hobart-type mixer at 120 rpm.

After chemically and physically characterizing the soil, two 1 kg samples were placed in plastic containers prior to artificial contamination.

Table 2 shows the characteristics of the soil used, determined according to Italian regulation [15,16]. pH was measured after mixing 10 g of soil samples with 25 ml of a 0.01 M solution of CaCl<sub>2</sub>.

The total porosity was determined using 100 g of air-dried soil [17]. The sample was weighed: then a known amount of water was added until saturation was obtained. The total porosity ( $f$ ) was determined from:

$$f = \frac{V}{V + V_s} \quad (1)$$

Table 1  
Composition of the soil used in the experiment

Components	Particle size (mm)	(wt.%)
Gravel	>2	7
Sand	0.0625–2	39
Silt	0.002–0.0625	35
Clay	<0.002	19

Table 2  
Characteristics of the soil used

pH	8.1
Organic carbon (%)	2.5
Permeability (cm s <sup>-1</sup> )	3.21 × 10 <sup>-3</sup>
Total porosity (%)	46
Moisture content (g kg <sup>-1</sup> )	24.5
Bulk density (g ml <sup>-1</sup> )	1.25
Particle density (g ml <sup>-1</sup> )	2.3
Cation exchange capacity (meq per 100 g)	15.2

where  $V$  is the volume of water added and  $V_s$  the volume of the dried soil particles [17], calculated as:

$$V_s = \frac{M}{\rho_s} \quad (2)$$

where  $M$  is the mass of the dry soil (g) and  $\rho_s$  ( $\text{g ml}^{-1}$ ) was the density of soil particles.

The pore volume of the soil (PV) was calculated using:

$$\text{PV} = \frac{f}{100} V_c \quad (3)$$

where  $V_c$  is the column volume.

## 2.2. Soil contamination

Soil contamination by Cu was carried out by mixing for 48 h at 120 rpm in a Hobart-type mixer 1 kg of soil and 0.5 l of a saturated aqueous solution of dihydrate copper chloride,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , while soil contamination by Pb was carried out in the same way by using a saturated aqueous solution of lead chloride,  $\text{PbCl}_2$ . After mixing, the samples were air dried and stored in plastic containers for 30 days.

The contamination was carried out so as to obtain a Cu or Pb concentration of at least twice the Italian regulation limit for an industrial site. The maximum concentrations permitted under Italian law [18] are 600 mg of Cu per kg and 1000 mg of Pb per kg.

Subsequent to preliminary acid digestion, a Philips PU 9200 atomic absorption spectrophotometer was used to determine the metal content of six 1 g samples of each contaminated soil. The average Cu and Pb concentration was 1730 mg of Cu per kg and 850 mg of Pb per kg with a standard deviation of  $\pm 8$  and  $\pm 5\%$ , respectively.

The pH of all the contaminated samples was about 7.3. This measured value is lower than that of the uncontaminated soil, shown in Table 2, showing that most of the introduced metal was immobilized into the soil matrix and therefore not precipitated in hydroxide form [19].

Ten 100 g samples were prepared from each contaminated soil: those samples were then dried by exposure to ambient air for 30 days and stored in plastic containers.

## 2.3. Extractant solution

The extractant solution was prepared by dissolving crystals of EDTA sodium salt ( $\text{E-Na}_2$ ) in tap water, so as to obtain a 0.05 M solution of  $\text{E-Na}_2$ . Other studies of extraction of heavy metals from soil, generally used a concentration of 0.01–0.1 M [20–22].

## 2.4. Experimental methodology

The experimental apparatus consisted of a parallel series of Plexiglas columns with an internal diameter of 5 cm and a height of 10 cm.

The 100 g samples of contaminated soil were placed in each column on a base of glass wool so as to grant uniform distribution of the liquid. The flushing solution was introduced

into the column from the top by means of a peristaltic pump (Velp Scientific) and recovered from the bottom. A 2 cm layer of porous media was placed at the top of the column to ensure a uniform distribution of the flushing solution. Before the percolation of the flushing solution, the saturation of the soil porosity was achieved by percolating pure water.

The metal level in the extracted solution was determined by means of a Philips PU 9200 atomic absorption spectrophotometer after filtration through Whatman filter paper (0.45  $\mu\text{m}$ ).

Three different speeds of percolation were adopted:  $9.5 \times 10^{-2}$ ,  $1.9 \times 10^{-1}$ , and  $2.8 \times 10^{-1}$   $\text{m day}^{-1}$ .

The concentration of EDTA was indirectly determined using a Total Organic Carbon (TOC) furnace (Shimadzu TOC Analyzer 5000 A). Preliminary tests performed using pure water as flushing solution showed in fact that the organic content in the extracted solution due to natural organic matter is negligible (an average of less than  $100 \text{ mg l}^{-1}$  was observed).

### 2.5. EDTA recovery

EDTA recovery was performed in two steps. A preliminary evaporation step was carried out to reduce the volume of the solutions extracted from the soil samples; following this, acidification precipitated the protonated EDTA from the evaporator residue.

Each extracted solution was first concentrated by means of a batch vacuum evaporation system consisting of a rotating evaporator (Rotavapor R-1144 Büchi). In each test, 100 ml of solution was placed in a 500 ml evaporation flask with a thermostatically controlled temperature. The operating pressure and temperature were 40 mbar and  $45^\circ\text{C}$ , respectively. Each evaporation run was stopped when a distillate volume equaled 75% of the initial solution volume.

The residue collected in the evaporation treatment was then acidified to pH of 3 using sulfuric acid which precipitated EDTA. After filtrating out the EDTA, the metals were precipitated.

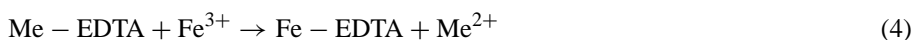
### 2.6. Metal precipitation

Based on the conditional stability constant of Pb-EDTA and Cu-EDTA complexes, for low pH conditions (less than five) the tendency for metal complexes to form may be assumed to follow the sequence:  $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Pb}^{2+}$ . At these pH conditions, both Cu and Pb complexes with EDTA are less stable than ferric complexes.

Therefore, two different precipitation methods were tested in this paper, namely Methods I and II.

#### 2.6.1. Method I

The first method [11] is illustrated in Fig. 1. Ferric ions were added as ferric chloride: this salt depressed the solution of pH, and pH adjustment was not necessary. The solution was shaken for 2 h to ensure the complete reaction.



where  $\text{Me}^{2+}$  is the extracted cation (Cu or Pb).

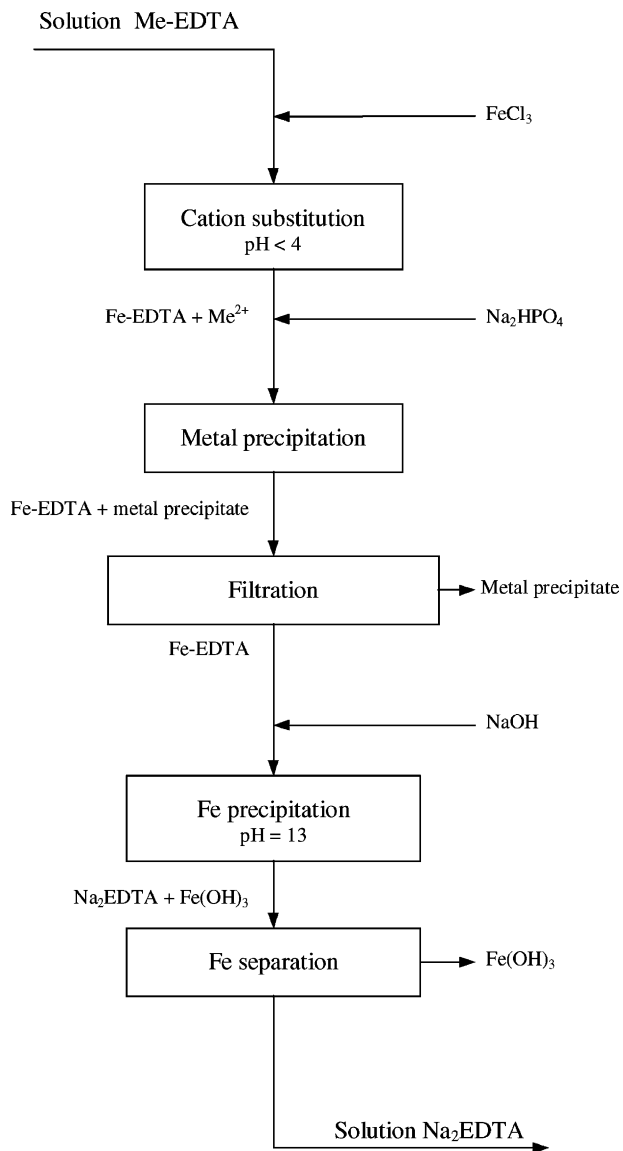
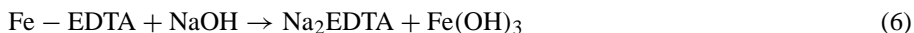


Fig. 1. Precipitation scheme: Method 1 (according to [11]).

The metal was then precipitated, at a pH between 4 and 5 as Cu or Pb phosphate, by adding sodium phosphate ( $\text{Na}_2\text{HPO}_4$ ).



After the addition of sodium hydroxide up to a pH of 13, the precipitation of ferric hydroxide was finally achieved, through the reaction.



Experimental tests of metal precipitation were performed at different Fe/EDTA and  $\text{Na}_2\text{HPO}_4/\text{Me}$  ratios, to determine the optimum conditions for metal removal from the solution. To evaluate the optimum amount of ferric ions needed for the substitution of lead in the Pb-EDTA complexes, Fe/EDTA ratios of 1.5, 3, and 4.5 were tested, and for each stated Fe/EDTA ratio, two series of tests were carried out at  $\text{Na}_2\text{HPO}_4/\text{Me}$  ratios of 3 and 5, respectively.

The ratio between ferric ions and EDTA concentration was used, instead of the ratio between ferric ions and metal, considering that a certain reagent consumption would be expected by free EDTA in solution.

The experimental tests were performed using a 50 ml sample, and shaken for 5 h to allow phosphate formation. Metal precipitate was then separated by centrifugation (at a rotational speed of 7000 rpm for 10 min).

Following this step, the addition of sodium hydroxide brought the pH up to 13, allowing ferric hydroxide to precipitate. The solution was then filtered through a 0.45 mm Whatman filter for the precipitate separation.

Based on the results obtained on equimolar solutions, two series of tests were carried out on each solution. In the first series of tests a Fe/EDTA ratio of 1.5 and a  $\text{Na}_2\text{HPO}_4/\text{Pb}$  ratio of 1 were adopted, while in the second series of tests the two ratios were, respectively, 3 and 5.

### 2.6.2. Method II

The second precipitation method [14] is illustrated in Figs. 2 and 3. A preliminary addition of sulfuric acid was necessary to lower the pH to the range of complex destabilization ( $\text{pH} < 3$ ). Iron ions were added as ferrous sulfate: the solution was shaken for 2 h to ensure complete reaction and the Fe/Me ratio was 3. The metal was then precipitated under alkaline conditions after the addition of sodium hydroxide. Pb precipitation was achieved at a pH of 10 (to avoid the formation of the soluble species  $\text{Pb}(\text{OH})_2^{4-}$ , while Cu precipitation occurred at a pH of 12.

All reagents were supplied by Carlo Erba Reagents, Milano (the EDTA purity grade was 99%).

In each test a small amount of anionic polyelectrolyte was added to enhance flocculation (Floxan 424, Misan Chimica, Milano).

Since most of the data reported in literature about metal precipitation from soil flushing solutions refer to simulated equimolar solutions of metal and EDTA, two series of tests were carried out at room temperature for each precipitation method, in order to allow an easier comparison of results.

Preliminary tests were performed on two simulated solutions: the first one (named solution A\*) was prepared by dissolving EDTA disodium dihydrate ( $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ ) and Pb chloride in tap water, the second one (named solution B\*) was prepared by dissolving the same EDTA salt and Cu chloride in tap water, in amounts which obtained equimolar solutions. Metal concentration in these solutions was the same as previously measured in the solutions extracted from the contaminated soil samples. Furthermore, to evaluate the influence of metal concentration in the precipitation process, two other solutions were

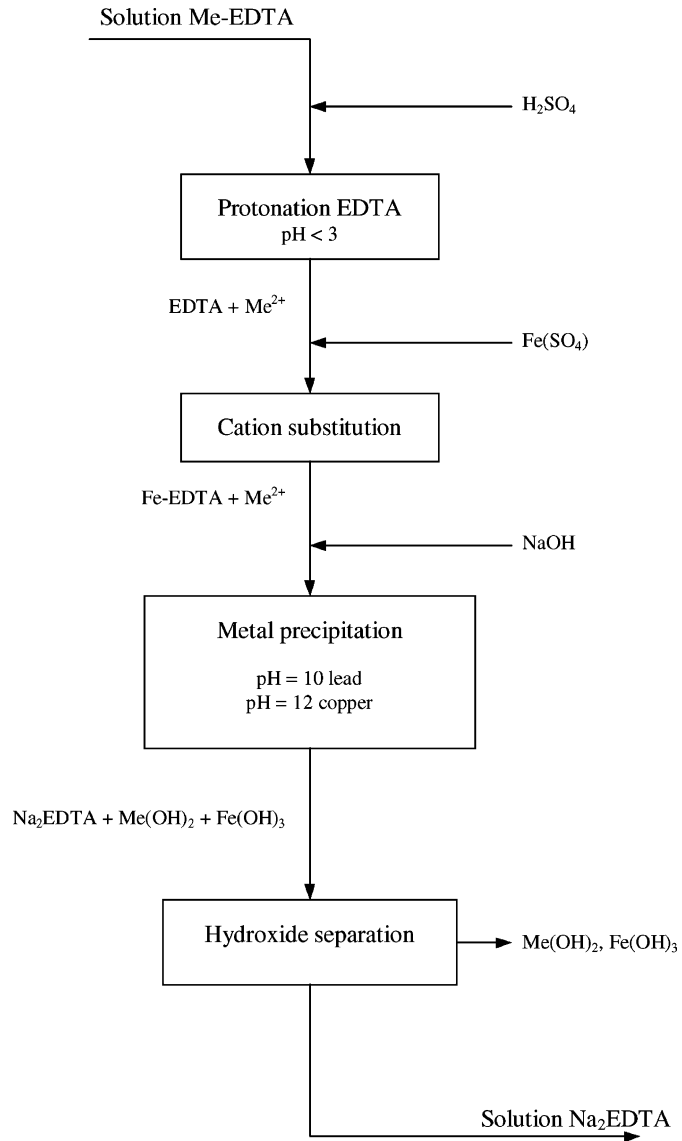


Fig. 2. Precipitation scheme: Method 2 (according to [14]).

prepared, named A75\* and B75\*, that simulated the residue of the evaporation treatment of the extracted solutions. The characteristics of the four simulated solutions are now reported in Table 3.

A second series of tests was then carried out just on the solutions extracted from the contaminated samples. In these tests, Method I was used for Pb precipitation from the solutions extracted from Pb contaminated soil (solution A) and from the residue of their



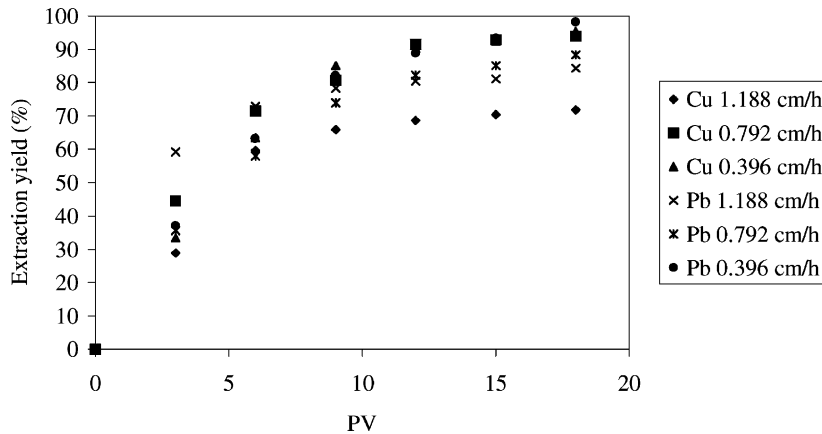


Fig. 3. Experimental results: Cu or Pb extraction yield (0.05 M EDTA).

Table 3  
Characteristics of the simulated equimolar solutions subjected to the precipitation treatment

Solution	Metal concentration ( $\text{mg l}^{-1}$ )	EDTA concentration ( $\text{mol l}^{-1}$ )
A*	350	$1.69 \times 10^{-3}$
A75*	1408.3	$6.8 \times 10^{-3}$
B*	200	$3.14 \times 10^{-3}$
B75*	483.1	$1.3 \times 10^{-2}$

A\*, equimolar solution of Pb and EDTA; A75\*, residue of the evaporation of solution A; B\*, equimolar solution of Cu and EDTA; B75\*, residue of the evaporation of solution B.

evaporation (solution A75), while Method II was used for Cu precipitation from the solutions extracted from Cu contaminated soil (solution B), and from the residue (solution B75) of their evaporation.

### 3. Results and discussion

#### 3.1. Soil flushing

Fig. 3 shows the results of soil flushing tests. An increase in the amount of flushing solution corresponded to an increase in Cu or Pb extraction yield. Between 12 and 15 PV only a slight increase in both metal extraction yield was observed. Soil remediation was considered complete when Cu or Pb concentration reached a value lower than the limits mentioned above. This corresponded to an extraction yield of 95% for each metal: this high value can be explained considering the artificial contamination of the soil carried out.

The results of the present study showed that a Cu or Pb extraction yield higher than 95% can be achieved only at the lowest speed of percolation ( $0.396 \text{ cm h}^{-1}$ ), and when at least 15 PV of extraction solution was used.

Following this, the percolation of 100 ml (about 3 PV) of pure water was necessary to obtain the complete removal of the EDTA entrapped into the soil during the percolation pathway. The total amount of flushing solution percolated was 18 PV (about 600 ml). The last 3 PV only provided slightly more metal extraction from the soil.

The TOC content determination in the extracted solution (about  $6 \text{ g l}^{-1}$ ) shows that in practice all the EDTA was recovered. Only a negligible contribute to the organic content of the extracted solution can be attributed to the natural organic matter of the soil. This was also confirmed by preliminary experiments showing that, by using only pure water as extracting fluid (without any EDTA addition) in practice no metal (Cu or Pb in the two different contaminated soils) was extracted and an organic content of less than  $100 \text{ mg l}^{-1}$  TOC was generally measured in the extracted solution.

Furthermore, since the average Pb concentration in the extracted solutions from Pb-contaminated samples was  $350 \text{ mg l}^{-1}$ , most of the EDTA present was free or complexed with other competitive cations extracted from the soil (i.e. ferric ions). However, this last contribute appeared secondary: the average measured iron concentration in the extracted solutions was in fact  $11 \text{ mg l}^{-1}$ . The same consideration can be made for the solution extracted from the Cu contaminated samples. The average Cu concentration in these solutions was  $200 \text{ mg l}^{-1}$ .

Other studies performed under similar conditions have already shown that, in general, the extraction of heavy metal from soil by EDTA is highly efficient. Numerous works have been developed to verify the application of a chelant extraction to soil washing treatment, while only a few works investigated its application to soil flushing treatment. Soil flushing tests performed [9] on a sandy loam showed that complete Pb removal can be achieved by using 4 PV of a solution containing 0.01 M EDTA. The present study showed that a higher concentration of EDTA and more PV were necessary because of the high organic content of the soil used in the experimentation: heavy metal retention by soils is, in fact, strongly affected by its natural organic matter concentration [2].

### 3.2. EDTA recovery

A preliminary stage of vacuum evaporation was carried out to concentrate the extracted solutions and so reduce the volume for subsequent treatment.

In the solutions extracted from the soil contaminated samples, a large excess of EDTA was in fact observed (Table 3). Most of the EDTA was not combined with Pb or Cu: assuming that all the metal in solution is present in the complexed form, Table 3 shows that only 4% of the total EDTA resulted in the Pb-EDTA complex, and 7% of EDTA resulted in the Cu-EDTA complex.

During the evaporation step, TOC analyses performed on the collected distillate and residue showed a progressive linear concentration of the residue solution, up to a distillate/initial solution ratio of 0.75. A further evaporation of the solution caused the precipitation of EDTA over the vessel walls, due to local excess. A maximum recovery ratio of 0.75 was so considered for the development of the process. This value is close to the maximum recovery ratio allowable to avoid  $\text{Na}_2\text{EDTA}$  precipitation during evaporation. In fact, according to the water solubility of  $\text{Na}_2\text{EDTA}$  ( $105 \text{ mg l}^{-1}$  at  $20^\circ\text{C}$ ), and neglecting the complexes formed between EDTA and other competitive cations, a maximum distillate/residue ratio

Table 4  
EDTA recovery yield after the acidification treatment

Solution	[EDTA] <sub>i</sub> (mol l <sup>-1</sup> )	[Metal] <sub>i</sub> (mol l <sup>-1</sup> )	[EDTA] <sub>f</sub> (mol l <sup>-1</sup> )	[Metal] <sub>f</sub> (mol l <sup>-1</sup> )	EDTA precipitated (%)	EDTA/metal molar ratio
A	0.05	$1.69 \times 10^{-3}$	$9.0 \times 10^{-3}$	$6.65 \times 10^{-3}$	95.5	1.35
A75	0.2	$6.82 \times 10^{-3}$	$1.33 \times 10^{-2}$	$6.82 \times 10^{-3}$	93.4	1.95
B	0.05	$3.14 \times 10^{-3}$	$1.7 \times 10^{-2}$	$1.16 \times 10^{-2}$	91.6	1.4
B75	0.2	$1.3 \times 10^{-2}$	$1.6 \times 10^{-2}$	$1.26 \times 10^{-2}$	94.9	1.3

A, solution from Pb contaminated soil flushing; A75, residue of the evaporation of solution A; B, solution from Cu contaminated soil flushing; B75, residue of the evaporation of solution B.

of 82.8% for the solutions containing the complex Pb-EDTA and 83.4% for the solution containing Cu-EDTA, can be calculated.

The composition of the residue solutions obtained in the evaporation treatment is shown in Table 4: the mass balances performed showed that the metal and the EDTA concentration in the distillate solution were negligible.

The residues from the evaporation treatment were then acidified up to pH of 3 by using sulfuric acid: a substantial precipitation of EDTA occurred, as shown in Table 4. As a consequence of the whole recovery process, EDTA/metal molar ratio was lowered from about 30 to 1.35 in solution A, and from about 16 to 1.4 in solution B.

### 3.3. Metal precipitation from equimolar solutions

#### 3.3.1. Method I

Figs. 4 and 5 show the results obtained in the tests performed on the simulated solutions according to precipitation Method I.

Previous studies have already shown that in the substitution reactions (2) and (3), only a large excess of reagents provided a complete reaction development [11].

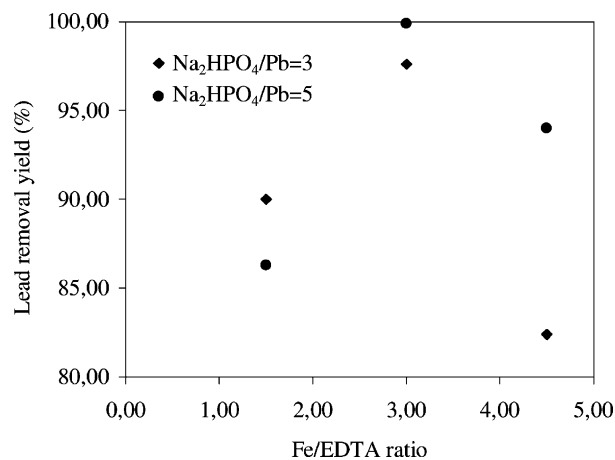


Fig. 4. Experimental results: Pb removal from equimolar EDTA solutions.

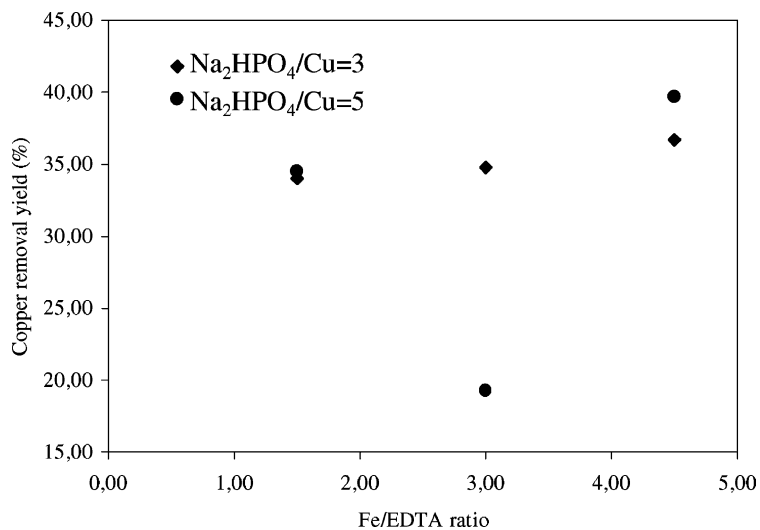


Fig. 5. Experimental results: Cu removal from equimolar EDTA solutions.

These results show that this precipitation method could not be considered suitable for copper precipitation. Conversely, in the case of solutions containing Pb-EDTA complex, high yields were generally achieved. In particular, an almost total lead precipitation occurred at ratios of Fe/Pb = 3 and Na<sub>2</sub>HPO<sub>4</sub>/Pb = 5 ratio. An increase in Fe/EDTA ratio did not provide any further lead removal. Due to the high iron concentration, in fact, the precipitation of iron phosphate occurred, thus subtracting phosphate from the solution.

A second series of tests was then performed only on the solutions containing Pb-EDTA complex, in order to better define the operative conditions. In this second series agitation times of 2, 3.5, and 5 h were tested.

Table 5 and Fig. 6 report the experimental results of the series of tests. Data show that an almost total lead precipitation can be achieved when a Fe/EDTA ratio of 3 is used. A further increase in this ratio in the investigated range, did not provide an increase in lead removal.

While the optimal ratio between Fe to EDTA found in this study is in the range focused in other studies [11], the Na<sub>2</sub>HPO<sub>4</sub>/Pb ratio appears quite low. For Pb precipitation from Pb contaminated EDTA wastewater, Kim and Ong [11], found that an Na<sub>2</sub>HPO<sub>4</sub>/Pb ratio of about 30 was necessary. Considering that the feasibility of the precipitation treatment over a large amount of solution is highly affected by reagents consumption and cost, these results could represent an enhancement to the effective process application in the remediation of metal-contaminated soil.

### 3.3.2. Method II

The tests performed on Cu contaminated solutions according to Method II showed a Cu removal yield of 96.3% from copper contaminated solutions. This result confirms the effectiveness of this simple method in copper precipitation, as already assessed by Chang

Table 5  
Experimental results: Pb precipitation from solution A\*; according to Method I

Fe/EDTA molar ratio	Na <sub>2</sub> HPO <sub>4</sub> /Pb molar ratio	Percent of Pb precipitated at different agitation time (h)		
		2	3.5	5
1.5	1	82.0	86.0	93.1
	2	70.1	80.7	89.6
	3	75.0	81.7	90.0
	4	77.0	80.0	80.8
	5	75.8	81.1	86.3
3	1	35.5	43.0	51.3
	2	78.0	77.8	89.7
	3	80.1	85.8	90.4
	4	94.3	94.1	93.2
	5	99.7	99.8	99.9
4.5	1	5.0	25.2	42.3
	2	13.0	40.0	52.5
	3	68.6	77.3	82.4
	4	76.4	79.9	81.6
	5	93.1	94.0	94.0

[14]. At the same time, this method did not show good efficiency in lead precipitation from lead contaminated solutions. For solutions A, in fact, a lead removal yield of only 28% was observed at experimental conditions. In the above-cited work, bench scale treatability tests performed on plating wastewater showed that very low lead concentration can be achieved with this precipitation method. Moreover, in this study, the wastewater subjected to the precipitation treatment was characterized by quite low Pb concentration, while 25 times greater values occur in the solutions obtained in flushing treatment.

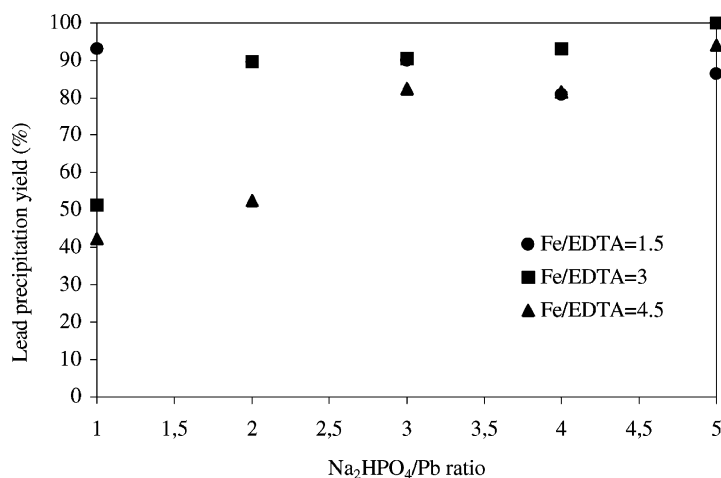


Fig. 6. Reagents optimization in Pb precipitation from EDTA equimolar solutions.

Table 6

Experimental results: metal precipitation from the solutions extracted from Pb contaminated samples

Solution	Fe/EDTA = 1.5, Na <sub>2</sub> HPO <sub>4</sub> /Me = 1		Fe/EDTA = 3, Na <sub>2</sub> HPO <sub>4</sub> /Me = 5	
	[Me] (mg l <sup>-1</sup> )	Me precipitated (%)	[Me] (mg l <sup>-1</sup> )	Me precipitated (%)
A	53.7	96.1	5.5	99.6
A75	38.5	97.2	7.0	99.5

A, solution from Pb contaminated soil flushing; A75, residue of the evaporation of solution A.

### 3.4. Metal precipitation from the solutions extracted from contaminated samples

By lowering the pH of the residue solution, the precipitation of the protonated form of EDTA (H<sub>4</sub>EDTA) occurred. Due to its low water solubility (0.1 g l<sup>-1</sup> at 20 °C), most of the EDTA was recovered, while the filtered solutions were sent to the precipitation treatment for metal separation. The characteristics of these solutions have already been summarized in Table 4.

Based on the results reported in the above section the precipitation of Pb-EDTA was performed according to Method I, while the precipitation of Cu-EDTA was performed according to Method II. The experimental results are shown in Tables 6 and 7 for both the considered metals.

The obtained metal concentration in the treated solution was low enough to allow the reuse of the treated solution for soil remediation, after the addition of the EDTA recovered according to the process reported in the previous section: this ensures a further dilution and the metals level can be consequently lowered.

Finally, Fig. 7 shows the proposed overall process diagram. The process consists of the operations in sequence: soil flushing, evaporation, acidification, filtration, and metal precipitation. For lead precipitation a high efficiency with precipitation Method I was achieved: a metal precipitation of more than 99% was in fact observed. For copper treatment, conversely, a precipitation yield of 93.6% was achieved with precipitation Method II.

The results showed that the process allows a recovery of at least 93% of EDTA from the extracted solution in the acidification treatment. As a consequence of metal precipitation, the filtered solution is an aqueous solution of almost pure EDTA (containing about 7% of the EDTA in the flushing solution). After a suitable addition of NaOH, E-Na<sub>2</sub> can be obtained and reused from both these solutions. The consumption of EDTA in the process is negligible, and no EDTA contamination of soil occurred.

Table 7

Experimental results: metal precipitation from the solutions extracted from Cu contaminated samples

Solution	[Cu] (mg l <sup>-1</sup> )	Cu precipitated (%)
B	8.1	98.9
B75	3.9	99.5

B, solution from Cu contaminated soil flushing; B75, residue of the evaporation of solution B.

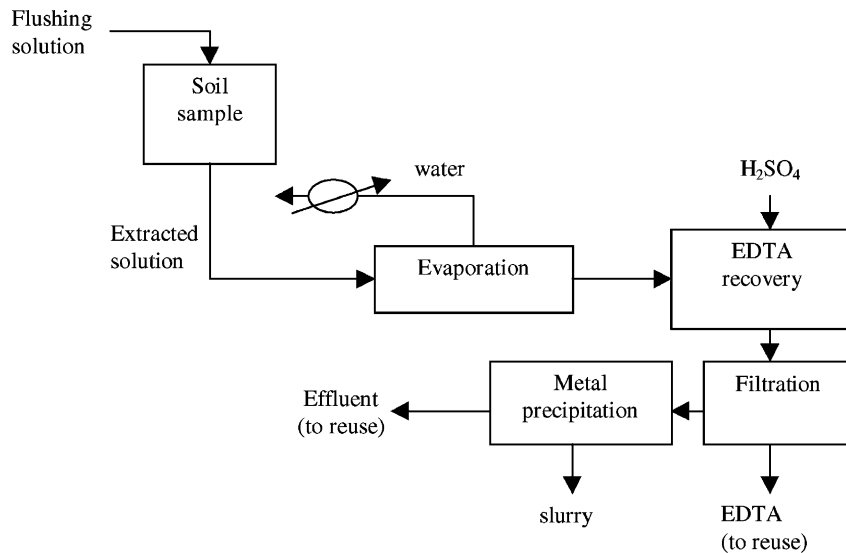


Fig. 7. Scheme of the proposed treatment pathway.

#### 4. Conclusions

The purpose of the present study was to propose and verify a process for the recovery of EDTA from soil flushing process solutions. The experimental tests of soil flushing showed the high EDTA effectiveness in the extraction of copper and lead from contaminated soils. By using a flushing solution at a concentration of 0.05 M of EDTA, extraction yields of 98.2% for Pb and 95.4% for Cu were obtained, with a percolation speed of  $9.5 \times 10^{-2} \text{ m day}^{-1}$  and a total amount of flushing solution of 18 PV.

EDTA recovery from the extracted solution was then achieved in two steps. An initial evaporation to reduce the volume by about 75%, followed by acidification of the evaporation residue solution and filtration, to recover more than 93% of used EDTA. This EDTA was suitable for reuse in the process after its transformation into sodium salt by adding an alkaline agent.

Metal precipitation from the filtered solution was finally performed using two different methods: an almost total (99.5%) Pb precipitation in alkaline conditions was achieved after complex destabilization through the sequential addition of ferric ions and sodium phosphate, while 93.6% copper precipitation was achieved with ferrous sulfate as a destabilization agent.

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