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Original Research

Soil Washing Technology for Removing Heavy Metals from a Contaminated Soil: A Case Study

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Abstract

Although EDTA solution is considered an efficient soil washing liquid for extraction of heavy metals from soils, its low biodegradability may alter soil properties and suppress plant growth. Alternatively, chlorides are safer and cheaper washing liquids than EDTA. To investigate the efficiency of chlorides versus EDTA in extracting heavy metals from contaminated soils, soil samples (pH 6.14±0.11) were collected from a local agriculture soil in Australia, artificially contaminated with either Pb, Cd or Cr at three different levels of 200, 400 and 600 mg kg^{-1}, and then packed in capped plastic flasks. Batch washing techniques were followed with either EDTA or $FeCl_3$ solutions (prepared at 4 different concentrations of 0.05, 0.1, 0.25 and 0.5 M), and soil suspensions were agitated for different time periods (from 5.0 min. to 60.0 min); afterward, the extraction efficiencies of the investigated metals were considered. The removal efficiency of Pb from the contaminated soil (200 mg Pb kg^{-1}) after 5 minutes of EDTA application seemed to be relatively high (≈75%). Afterward this efficiency decreased gradually with time. The efficiencies of the extracted Cd and Cr by soil washing with EDTA increased significantly with increases in the agitating period. Generally, the extraction efficiencies by EDTA decreased noticeably with increasing levels of soil contamination. On the other hand, the efficiencies of Pb, Cd and Cr extractions were high – especially when increasing both the concentrations of applied $FeCl_3$ solution and the time of agitation. The results also highlighted that soil washing with $FeCl_3$ seemed to be more favourable over EDTA for rapid extraction of heavy metals from contaminated soils. The efficiencies of extracting heavy metals by soil washing with 0.5M $FeCl_3$ for only one hour were 93.79±2.35%, 97.4±2.45% and 81.75±7.86% for Pb, Cd and Cr, respectively.

Keywords: heavy metals, soil, EDTA, $FeCl_3$, soil washing

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Introduction

Soil pollution is an important issue worldwide [1] – especially when related to heavy metals [2]. These metals are not biodegradable and can persist in soils for years [3]. Soil is considered the main sink of these metals [4] and the presence of heavy metals can impose serious health hazards for human life, animals and aquatic biota with prolonged exposure [5-7]. Thus, soil remediation is necessary to attain more acceptable environmental conditions [8]. In this concern, ethylene di amine tetra acetic acid (EDTA) forms water-soluble complexes with heavy metals in soil [9, 10] and therefore is considered an efficient soil-washing liquid for extracting these metals from soils [11, 12]. This amendment can also be used for inducing phytoextraction of heavy metals [13] and probably metalloids from polluted soils by grown plants [14]. However, EDTA is of low biodegradability in soil [12] and persists under natural conditions [15]. Up to 64% of applied EDTA can be retained in an acidic soil after remediation [16]. Such conditions may alter soil properties and suppress plant growth [17].

Alternatively, chlorides are safer and cheaper washing liquids than EDTA [18]. These chlorides are used successfully in extracting heavy metals from soil [19, 20]. It is worth mentioning that the complexation process of EDTA with heavy metals is endothermic and spontaneous [21], inducing 2-step processes (i.e., fast desorption within the first hour followed by steady release within subsequent hours) [22]. Thus, there is a need to investigate the efficiency of chlorides versus EDTA to extract heavy metals from contaminated soils – especially within the first 60-minute time period after application. To attain this aim, soil samples (pH 6.14±0.06) were collected and artificially contaminated with the following metals of Pb, Cd and Cr at three different levels (i.e., 200, 400 and 600 mg kg^{-1}). These samples were packed in capped plastic flasks. Batch washing experiments were followed using either EDTA or $FeCl_3$ solutions (prepared at 4 different concentrations). The soil suspensions were agitated for different time periods (from 5.0 min. to 60.0 min); afterward, heavy metal concentrations were measured in the supernatants and the extraction efficiencies of heavy metals were considered, and the major changes (pH, EC and organic matter contents) that might occurred in soil were also a matter of concern.

Materials and Methods

Soil Sampling and Preparation

Surface soil samples (0-30 cm depth) were collected from Burnley Campus Garden at Melbourne University, Australia. The collected soil samples were air dried, ground and passed through a 2 mm sieve to remove debris and stones. The prepared soil samples were analysed for their physical and chemical properties (Table 1).

Table 1. Physical and chemical properties of the studied soil.

Parameter	Unit	Value
pH	--	6.14±0.11
EC	dS m^{-1}	0.27±0.02
O.M.	%	10.23±0.74
Total Pb	mg kg^{-1}	26.3±3.8
Total Cd	mg kg^{-1}	1.11±0.32
Total Cr	mg kg^{-1}	9.47±032
Particle size distribution		
Sand	%	81.00
Silt	%	12.80
Clay	%	6.20
Textural class	Loamy sand	

Preparing Pb-, Cd- and Cr-Contaminated Soil

A clean soil (1000 g) was placed in a 5000 mL high-density polyethylene container, and then the very fine salts of PbO, $CdCO_3$ and Cr_2O_3 were mixed with the soil to bring the concentrations of studied metals to 200, 400 and 600 mg kg^{-1} for each. In this study we aimed to use less soluble salts to investigate the efficiency of selected washing solutions to remove Pb, Cd and Cr from contaminated soils. For 200 mg kg^{-1} artificially contaminated soil, 0.22 g of PbO, 0.31 g of $CdCO_3$, and 0.29 g of Cr_2O_3 was mixed with the soil. In addition, 0.43 g of PbO, 0.63 g of $CdCO_3$, 2.92 g of Cr_2O_3 and 0.59 g of Cr_2O_3 was added to 1 kg of soil to get the soil to 400 mg kg^{-1} of each element. For the 600 mg kg^{-1} artificially contaminated soil, 0.65 g of PbO, 0.94 g of $CdCO_3$, and 0.88 g of Cr_2O_3 was mixed with 1 kg of soil. The prepared soils were irrigated to field capacity and incubated for one month to ensure that the added metal ions were distributed homogeneously throughout the soil. After the incubation period, the soil samples were air dried and subjected to further experimental procedures.

Preparation of Washing Solutions

Washing solutions of iron chloride ($FeCl_3$, 97%) and ethylene di amine tetra acetic acid- di potassium (purity 98%) salts with different concentrations of 0.0, 0.05, 0.10, 0.25 and 0.5 M were prepared by dissolving 0.0, 8.36, 16.72, 43.10 and 88.90 g of $FeCl_3$ in a litter of deionized water to attain the above-mentioned concentrations, respectively. In addition, 20.64, 41.27, 105.28 and 210.56 g of EDTA-di potassium salt were dissolved in 1 L in order to attain the concentrations of 0.0, 0.05, 0.10, 0.25 and 0.5 M, respectively.

Batch Washing Studies

Batch washing experiments were conducted using a series of capped plastic flasks of 100 mL capacity on a mechanical shaker. The effects of initial soil concentration and shaking time on the removal of heavy metals were investigated. The concentrations of Pb, Cd and Cr were 0.0, 200, 400 and 600 mg kg^{-1} soil. Time course experiments were carried out by shaking the sorption mixture at various agitation times from 5.0 min. to 60.0 min. (5.0, 15, 30 and 60 min.). All experiments were carried out at an agitation rate of 180 rpm. At the end of the agitation time, the supernatant was separated from soil particles by centrifuging at 5000 rpm for 10 min. and analysed for their contents of Pb, Cd and Crby using inductively coupled plasma (ICP; Jobin Yvon Horiba – ULTIMA 2, France) supplemented with a hydride generator system.

Soil Analysis

The collected soil samples were subjected to several analyses prior to and after soil washing procedures. Soil reaction (pH) and electrical conductivity (EC) were determined in 1:1 soil-to-water suspensions and supernatant, respectively [23]. Organic matter was determined using loss on ignition method [24]. In addition, total contents of Pb, Cd and Cr were measured in the soil samples following digestion by aqua regia [25].

Statistical Analysis

All results were statistically analyzed using the SAS package (ver. 9.1). Means of three replicates for all chemicals and physical analyses were subjected to one-way ANOVA. Tukey's honestly significant difference (HSD) studentized range test was applied for significant differences among means ($P<0.05$). The graphs were plotted using the Sigma Plot 10 program. Extraction efficiency of studied metals was calculated as follows:

$$\text{Extraction efficiency (\%)} = \frac{Amount\ \ of\ heavy\ metals\ \ in\ supernatuant}{amounts\ \ of\ initial\ \ heavy\ metal\ +total\ \ added\ \ of\ heavy\ metals} * 100 \quad (1)$$

Results and Discussion

Extraction of Pb from the Contaminated Soil

Fig. 1 shows the extraction efficiency of Pb from soil using distilled water, EDTA and $FeCl_3$ solutions. Clearly

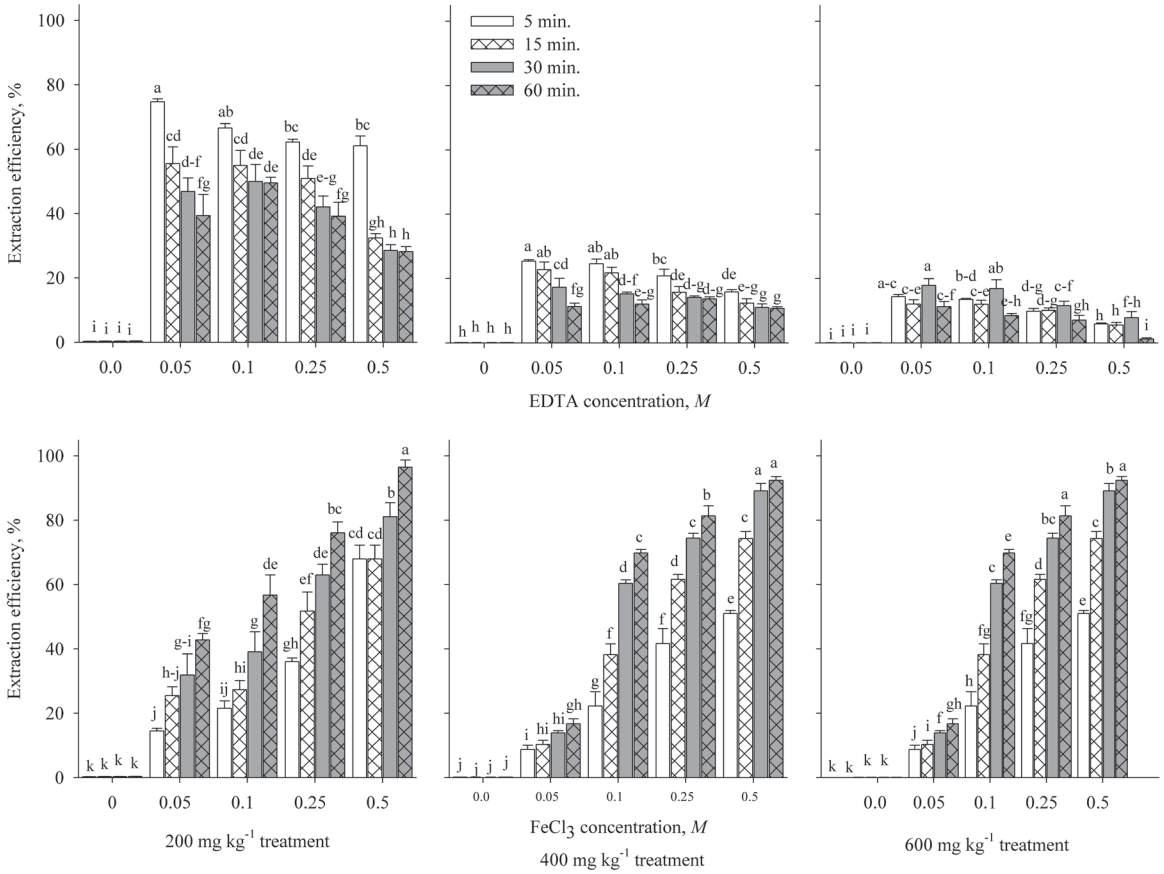

Fig. 1. Extraction of Pb from soil (200, 400 and 600 mg kg^{-1}) with different concentrations of EDTA and $FeCl_3$ extracts (0.05, 0.1, 0.25 and 0.5 M) at different shaking time (5.0, 15, 30 and 60 min.). Means with the same letter within columns are not significantly different.

either EDTA or $FeCl_3$ solutions have the ability to extract Pb compared to distilled water. The removal efficiency of Pb from the contaminated soil (200 mg Pb kg^{-1}) after 5 minutes of EDTA application seemed to be relatively high (≈75%); afterward, this efficiency decreased gradually with time (Fig. 1). On the other hand, the Pb-extraction efficiency decreased noticeably with the increasing level of soil contamination with Pb (added in the form of PbO), in spite of that, no significant effect was detected for increasing the concentrations of EDTA solution on the calculated Pb-extraction efficiencies. Generally, the solubility of PbO in soil depends on its pH value [26] and can be considered according to the reaction suggested by Lindsay [27] as follows:

$$PbO + 2H^+ \leftrightarrow Pb^{2+} + H_2O \quad (2)$$

This reaction probably increased soil pH and this might, in turn, increase Pb sorption by dimer silicate and/or aluminum groups [28]. Accordingly, the mobility and bioavailability of Pb in soils decreased [29]. Although the application of EDTA to soil is thought to form soluble Pb-complexes [12, 30], under such alkaline conditions, the efficiency of heavy metal extraction with EDTA seemed to be relatively low [22] and probably formed Pb-EDTA complexes of relatively low mobility [31].

Alternatively, the application of $FeCl_3$ to the investigated soil might be an appropriate solution to increase the efficiency of Pb extracted from soils. Results obtained herein reveal that the efficiency of Pb removal increased significantly with increasing concentrations of applied $FeCl_3$ solution. Such increases seemed to be more pronounced with increasing contact time up to 60 min (Fig. 1). It seems that the efficiency of Pb extraction from the contaminated soils by $FeCl_3$ did not vary significantly when increasing the level of Pb contamination in soil. This might take place because of the acidic action of $FeCl_3$ in soil as illustrated from the equations adapted from Lindsay [27]. The soil pH gradually decreased from 6.14 in the control treatment to reach 1.96 when the soil was treated with 0.5 M of $FeCl_3$ (Table 2)

$$FeCl_3 \leftrightarrow Fe^{3+} + 3Cl^- \quad (3)$$

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3^0 + 3H^+ \quad (4)$$

Thus, the solubility and bio-availability of heavy metals (i.e., Pb) in such acidic conditions increased [32]. It is worth mentioning that the superiority of $FeCl_3$ solution over EDTA in extracting Pb from soil was also noticed by Guo et al. [20].

Extraction of Cd from Artificially Contaminated Soils

Fig. 2 reveals that washing the contaminated soil with either EDTA or $FeCl_3$ solution significantly improved the efficiency of the extracted Cd from soil. Moreover, increasing the concentrations of the washing solution resulted in further significant increases in the Cd-extraction efficiency. However, distilled water recorded the lowest extraction efficiency of Cd compared to EDTA and $FeCl_3$ solutions. The reaction time was an additional significant factor affecting the Cd extraction efficiencies. This might be attributed to the effectiveness of the metal binding organic ligand (EDTA) in chelating Cd [33] to form soluble [34] and bioavailable complexes [35]. Accordingly, EDTA is an effective means for remediating soils contaminated with Cd [36, 37].

On the other hand, soils that were washed with $FeCl_3$ extracts might form soluble metal (Cd)-chloride complexes [38] and these soluble complexes probably increased the removal percentage of Cd from soil [39] – especially at low soil pH. Generally, these two

Table 2. Changes of soil properties as affected by EDTA and $FeCl_3$ washing solutions.

Washing solution	Concentration, M	pH	EC, ds m^{-1}	O.M., %
EDTA	Control	6.14±0.06 a	0.27±0.013 d	10.23±0.74 c
	0.05	6.15±0.03 a	0.83±0.05 d	11.05±0.07 bc
	0.1	6.16 ±0.03 a	1.62±0.22 c	11.47±0.06 b
	0.25	6.10 ±0.1 a	4.22±0.41 b	12.82±0.11 a
	0.5	6.2 ±0.06 a	7.34±0.14 a	13.37±0.13 a
$FeCl_3$	Control	6.14 ±0.06 a	0.27±0.013 e	10.23±0.74 a
	0.05	4.19±0.08 b	0.53±0.1 d	10.24±0.16 a
	0.1	3.28 ±0.08 c	0.89±0.02 c	10.45±0.32 a
	0.25	2.8±0.1 d	1.94±0.07 b	10.42±0.08 a
	0.5	1.96 ±0.13 e	3.89±0.05 a	10.39±0.13 a

Means with the same letter within column are not significantly different.

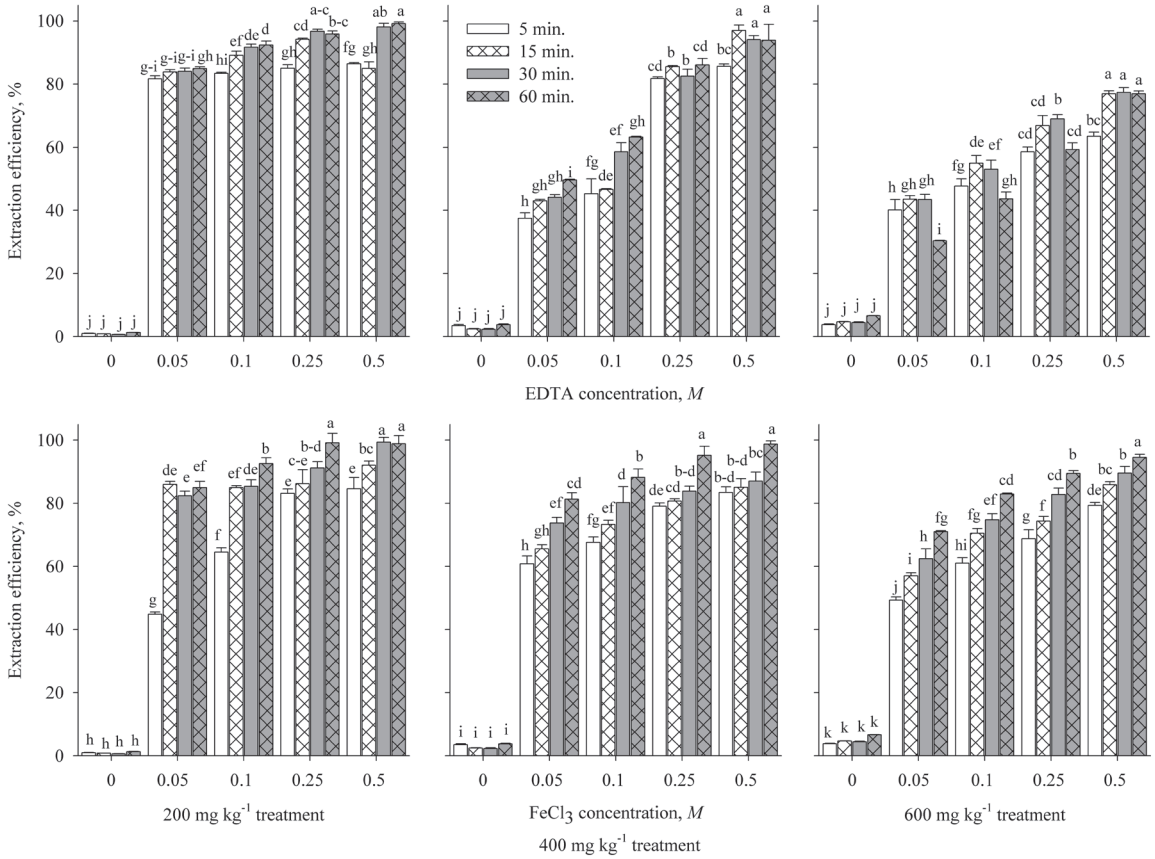

Fig. 2. Extraction of Cd from soil (200, 400 and 600 mg kg^{-1}) with different concentrations of EDTA and $FeCl_3$ extracts (0.05, 0.1, 0.25 and 0.5 M) at different shaking time (5.0, 15, 30 and 60 min.). Means with the same letter within columns are not significantly different.

amendments seemed to have comparable effects on increasing the extraction efficiency of Cd from lower contaminated soil, i.e., 200 mg Cd kg^{-1}. However, $FeCl_3$ seemed to be more favorable over EDTA for washing Cd-contaminated soil when the level of soil contamination is 400 mg Cd kg^{-1} or higher.

Extraction of Cr from Artificially Contaminated Soils

Results reveal that soil washing with either EDTA or $FeCl_3$ solution resulted in significant increases in the extraction efficiency of Cr from the soil compared to distilled water (Fig. 3). The concentration of either of these extracts was of further significant effect on the extraction process of Cr from contaminated soil. In this concern, $FeCl_3$ seemed to be more efficient than EDTA in the extraction process of Cr from soil throughout the investigated reaction time periods. Generally, information available on extraction of Cr from soils with EDTA is limited. This information refers to the potentiality of EDTA in decontaminating soils polluted with Cr [40, 41]. However, the removal efficiency of Cr from soils seems to be low compared with the other metals because Cr exists mainly in the form of bichromate ($HCrO_4^-$) anion [42]. The results obtained herein also reveal that the time of contact was of significant effect on Cr-extraction efficiency by EDTA. It seems that the 60-minute time period was probably enough to attain successful extraction of Cr (extraction efficiency ≈90%) from the contaminated soil (i.e., 200 mg Cr kg^{-1}) after being washed with 0.5 M EDTA extract. The corresponding efficiencies decreased in soils of higher contamination levels (i.e., 400 and 600 mg Cr kg^{-1}). It is worth mentioning that only a 30-minute time period was enough to attain successful soil washing with EDTA in soil contaminated with 600 mg Cr kg^{-1}. Concerning the soil washing with $FeCl_3$, results show that increasing the concentration of $FeCl_3$ solution resulted in corresponding significant increases in Cr-extraction efficiency. The strong acidic conditions that were provided during the hydrolysis of $FeCl_3$ [18] might enhance the reduction of Cr(IV) to form soluble Cr(III) [43].

Changes in Soil properties Caused by Soil Washing

Data presented in Table 2 show the major changes occurring in the treated soil neither by EDTA nor $FeCl_3$ extracts. The obtained results showed that EDTA has no significant effect on soil pH. The value of soil pH varied from 6.10 to 6.16. However, using $FeCl_3$ extract led to a significant reduction in soil pH in order to reach

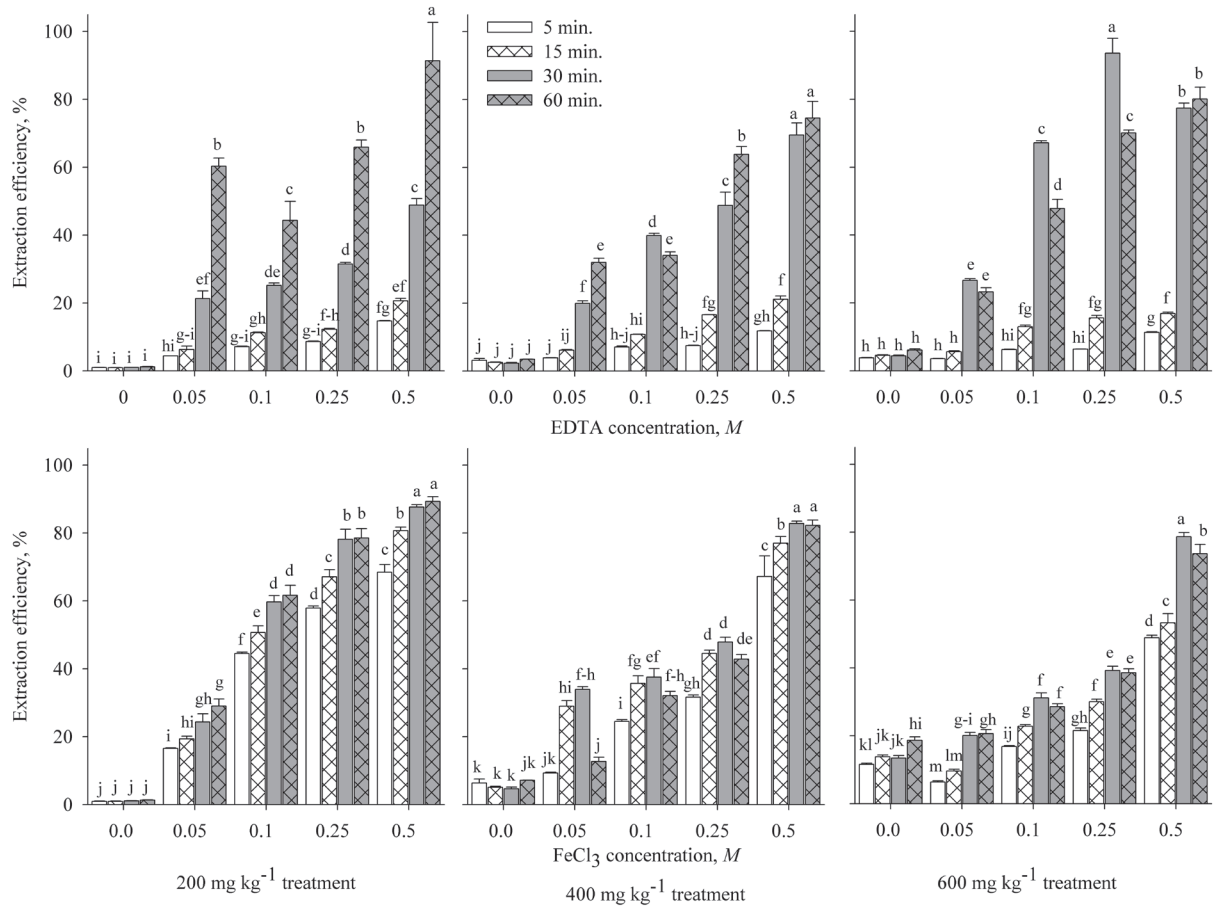

Fig. 3. Extraction of Cr from soil (200, 400 and 600 mg kg^{-1}) with different concentrations of EDTA and $FeCl_3$ extracts (0.05, 0.1, 0.25 and 0.5 M) at different shaking time (5.0, 15, 30 and 60 min). Means with the same letter within columns are not significantly different.

the lowest value of 1.96 when the soil was treated with 0.5 M of $FeCl_3$ extract. It is clear that increasing the concentration of $FeCl_3$ gradually decreased the soil pH due to the hydrolysis of $FeCl_3$.

On the other hand, EDTA has no significant effect on soil pH. However, increasing the concentration of EDTA washing solution gradually increased soil EC value compared to $FeCl_3$ washing solution. The EC value of the treated soil with EDTA was almost two times those of $FeCl_3$ treatments. The highest EC value was recorded for EDTA treatment with an average value of 7.34 dS m^{-1} when the soil was treated with 0.5 M of EDTA. A positive action was observed for EDTA washing solution, by increasing the concentration of EDTA treatment organic matter contents of the treated soils was increased. The values of organic matter contents were 10.23, 11.05, 11.47, 12.82 and 13.37% when the soil was washed by EDTA washing solution of 0.0, 0.05, 0.1, 0.25 and 0.5 M solutions, respectively. The increase of soil organic matter could be attributed to the presence of organic carbon in EDTA compound [14]. $FeCl_3$ has no significant effect on soil organic matter contents. From the above-mentioned information, attention should be paid when using soil washing technology for treating heavy metal-contaminated soils to avoid the leachability of macro nutrients (i.e., N, P and K). In addition, the increased soil salinity might hinder the agricultural productivity of the treated soil. Therefore, additional treatments might be required to leach the soil to overcome the salinization problem.

Conclusions

In conclusion, soil washing with $FeCl_3$ seemed to be more favourable over EDTA for rapid extraction of heavy metals from contaminated soils. The efficiencies of extracting heavy metals by soil washing with 0.5M $FeCl_3$ for only one hour were 93.79±2.35% for Pb, 97.4±2.45% for Cd and 81.75±7.86% for Cr. Attention should be paid regarding the use of EDTA and $FeCl_3$ washing solutions regarding the potential leachability of soil macro nutrients (i.e., N, P and K), and the potential salinization of soil when treated with washing solutions – especially EDTA.

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Conflict of Interest

The authors declare no conflicts of interest.

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